Universidade de Aveiro Departamento de Química
Ano 2019

Diana Cristina dos Santos Neto Julião

Materiais híbridos oxometálicos para o processo de dessulfurização oxidativa

Oxometal hybrid materials for oxidative desulfurization technology

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Química Sustentável, realizada sob a orientação científica da Doutora Isabel Maria de Sousa Gonçalves, Professora Associada do Departamento de Química da Universidade de Aveiro, e da Doutora Maria de La Salete da Silva Balula, Investigadora Principal do REQUIMTE da Faculdade de Ciências da Universidade do Porto.

Trabalho desenvolvido no âmbito do projeto REQUIMTE-LAQV (UIF/QUI/50006/2013) e CICECO-Instituto de Materiais de Aveiro, POCI-01-0145-FEDER-007679 (UID/CTM/50011/2013), financiado por fundos nacionais através do FCT/MEC e quando aplicado cofinanciado pelo FEDER sob o acordo PT2020. A autora agradece o apoio financeiro concedido pela FCT através da bolsa PD/BD/102783/2014.

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR
COMPETE 2020
PROGRAMA OPERACIONAL COMPETITIVIDADE E INTERNACIONALIZAÇÃO
PORTUGAL 2020
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To live is to choose. But to choose well you must know who you are and what you stand for, where you want to go and why you want to go there.

Kofi Annan

o júri

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agradecimentos

Curioso como há tanto e tantas pessoas para agradecer por quatros anos que passaram tão rápido, mas que se refletirão num crescimento pessoal e profissional para o resto da vida! Espero que as minhas palavras possam transmitir a real gratidão e amizade que sinto.

As primeiras pessoas a quem tenho de agradecer e dedicar umas linhas neste trabalho, são a Doutora Salete Balula e Professora Isabel Gonçalves. À Doutora Salete a quem o acaso me juntou e o sotaque e o coração nortenho não separaram, agradeço por me incutir o bichinho da investigação desde os meus tempos de ainda "pequenina" nestas andanças e por ter acreditado e apostado em mim durante todos estes anos. À Professora Isabel que me recebeu de braços abertos, agradeço todas as palavras de confiança que sem saber foram de certa forma fulcrais para que também eu acreditasse mais em mim. Foi um convívio curto que espero que se estenda por muitos anos! Obrigada!

À Galp, em especial ao Dr. Jorge Ribeiro e Drª. Rita Valença devo um enorme agradecimento. Sem eles este trabalho não teria sido de todo possível, tendo em conta todo o trabalho envolto em gasóleo real.

Ao Professor Baltazar de Castro e ao REQUIMTE – Laboratório Associado para a Química Verde por receberem esta "forasteira" e permitirem parte da realização do meu trabalho no vosso meio. Nada melhor que tentar dessulfurizar combustíveis sob condições sustentáveis num Laboratório tão "Verde".

Ao CICECO e ao Departamento de Química agradeço as condições cedidas que permitiram realizar este trabalho.

Ao Doutor Martyn Pillinger e Doutora Ana Gomes um enorme agradecimento por toda a ajuda prestada com a preparação e caracterização dos eficientes catalisadores. Agradeço também a todos os elementos do Departamento de Química da Universidade de Aveiro que de alguma forma contribuíram para este trabalho.

Ao Doutor Luís Cunha Silva agradeço a constante simpatia e boa disposição e a ajuda e colaboração na cristalografia de raios-X.

agradecimentos

Ao núcleo duro de Ciências: Fátima Mirante, André Barbosa e Susana Ribeiro agradeço o constante companheirismo e interajuda. Que comida boa nunca nos falte. Agradeço também aos vários elementos dos diferentes grupos, desde orgânicos a inorgânicos, por me fazerem constantemente sentir como parte de uma grande família e tornarem os dias mais brilhantes. Aqui não posso esquecer e deixar de agradecer também a todos os “eletrões” que foram passando e trazendo vivacidade, boa disposição e curiosidade para o ambiente de trabalho. Porque pequenos ou grandes todos contam e de alguma forma fizeram parte desta minha etapa.

Às meninas de Aveiro: Patrícia Neves, Margarida Antunes, Sofia Bruno, Ana Gomes e Ana Luísa Costa agradeço a constante boa receção e amizade. A boa disposição não falha e com certeza contarei convosco para a vida, que comemoremos muitos aniversários juntas.

Aos meus amigos de sempre e àqueles que o doutoramento me trouxe e ficarão para sempre! Um especial obrigado à Maria, Ana Luísa e Ricardo por acreditarem em mim e ouvirem todas as minhas conversas infindáveis e (chatas) de escrita.

Às minhas sete bolas peludas por todo o amor infinito e incondicional que me impediu de entrar num túnel escuro nestes últimos meses.

Aos meus pais.

palavras-chave

molibdénio(VI), óxidos de molibdénio, catálise homogénea, dessulfurização oxidativa, enxofre, combustíveis líquidos, peróxido de hidrogénio, solventes sustentáveis.

resumo

O petróleo contém quatro classes de compostos: aromáticos, cicloalcanos, alcanos e compostos com átomos de enxofre, azoto e/ou oxigénio. A presença de enxofre é prejudicial, para a indústria do petróleo como também para o ambiente, onde é o maior contribuinte para a poluição ambiental. A UE impôs legislações restritas para o conteúdo de enxofre nos combustíveis. No entanto o tratamento destes combustíveis, resulta num processo dispendioso devido às condições severas aplicadas (elevadas temperaturas e pressões de H_2) incompatíveis com outros requisitos necessários para o combustível. O desenvolvimento de tecnologias alternativas que consigam remover o enxofre sob condições sustentáveis e economicamente mais viáveis é por isso bastante importante. A dessulfurização oxidativa (ODS) tem revelado ser um processo eficaz, no qual os compostos de enxofre são oxidados através da combinação de um catalisador e um oxidante, sendo as espécies oxidadas removidas facilmente por extração com solventes polares apropriados. Seguindo esta palavra de ordem, durante o presente trabalho foram desenvolvidos novos sistemas catalíticos, baseados na combinação pouco explorada Mo(VI)-oxo/H_2O_2, para eficientemente dessulfurizar diesel modelo e combustíveis reais. Deu-se especial atenção às condições experimentais, a partir das quais tentou-se substituir solventes orgânicos voláteis por opções mais sustentáveis, como líquidos iónicos (LIs), solventes eutécticos (DES) ou sistemas livres de solvente. Os rácios H_2O_2/S e temperatura reacional foram otimizados de forma a alcançar-se elevada eficiência de dessulfurização e economia do processo. De forma direta ou indireta (quando em solução) todos os catalisadores foram reutilizados e/ou reciclados por vários ciclos de ODS. De uma forma geral a eficiência de dessulfurização foi mantida por pelo menos três ciclos consecutivos. De todos os catalisadores aplicados, o $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ sobressaiu pela sua extraordinária performance de reutilização e estabilidade na dessulfurização de um diesel modelo por dez ciclos consecutivos sob condições sustentáveis (H_2O_2/S = 3,7 na ausência de solvente). O IndMo(CO)$_3$Me revelou ser um catalisador eficaz sob condições similares. Ambos foram tratados como catalisadores heterogéneos e recuperados e reutilizados sem tratamento adicional. Apesar dos valores sensacionais obtidos em meio monofásico, quando aplicados num gasóleo real (2300 ppm S), não exibiram a mesma eficácia. Os melhores resultados obtidos neste trabalho e quando comparados com o descrito na literatura foram alcançados em meio bifásico (gasóleo/[BMIM]PF$_6$): IndMo(CO)$_3$Me (95 ppm), [MoO$_2$Cl$_2$(DEO)] (129 ppm), CpMo(CO)$_3$Me (372 ppm), [MoO$_2$Cl$_2$(DMB)$_2$] (381 ppm), $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (500 ppm), [MoO$_2$Cl$_2$(di-*t*Bu-bipy)] (621 ppm) e dois materiais híbridos à base de molibdénio (740 e 741 ppm). O $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (259 ppm) também revelou elevada eficiência catalítica, mas na presença de MeCN como solvente de extração.

keywords

molybdenum(VI), molybdenum oxides, homogeneous catalysis, oxidative desulfurization, sulfur, liquid fuels, hydrogen peroxide, sustainable solvents.

abstract

Crude oil contains four classes of compounds: aromatics, cycloalkanes, alkanes and compounds with atoms of sulfur, nitrogen and/or oxygen. The presence of sulfur brings a lot of damage, for the petroleum industry itself as well as for the environment, where is a major contributor of air pollution. The EU has imposed strict legislations on the S content in transportation fuels. However, the production of such ultra-low sulfur fuels by conventional hydrodesulfurization technologies is very costly, due to the harsh conditions (high temperatures and high H_2 pressures) needed that are incompatible with other important fuel requirements. The development of alternative technologies that could successfully remove sulfur under sustainable and inexpensive conditions is very important. Oxidative desulfurization (ODS) has proven to be an effective approach for this purpose. In this process the sulfur compounds are oxidized by the combination of a suitable catalyst with an oxidant. The oxidized species are removed by extraction with appropriate polar solvents. Following this strategy, in the present work novel catalytic systems were developed based on the unexplored combination Mo(VI)-oxo/H_2O_2 for efficiently desulfurizing model and real liquid fuels. Special attention was given to the experimental conditions, particularly the substitution of organic volatile solvents by more sustainable options, such as ionic liquids (ILs), deep-eutectic solvents (DES) or solvent-free systems. Also, low H_2O_2/S ratios and low temperatures (50 or 70 °C) were considered to achieve the optimal conditions. Directly or indirectly (when dissolved) all the catalysts were reused and/or recycled for several ODS cycles. In general, the desulfurization efficiency was maintained at least until the third consecutive cycle. Of all the catalysts studied, the species $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ stood out due to its remarkably recyclability and stability performance for desulfurization of a model diesel for ten consecutive cycles under eco-sustainable conditions (H_2O_2/S = 3.7 and solvent-free system), with its immiscibility in the reaction environment being of added value. The complex IndMo(CO)$_3$Me also displayed a remarkable behaviour under similar conditions. Both catalysts were treated as heterogeneous catalysts and recovered and reused without further treatment. Despite these outstanding results, the absence of solvent during the ODS was detrimental to the treatment of real diesel samples (2300 ppm S). The highest and the best ODS results were achieved using biphasic systems (diesel/[BMIM]PF$_6$): IndMo(CO)$_3$Me (95 ppm), [MoO$_2$Cl$_2$(DEO)] (129 ppm), CpMo(CO)$_3$Me (372 ppm), [MoO$_2$Cl$_2$(DMB)$_2$] (381 ppm), $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (500 ppm), [MoO$_2$Cl$_2$(di-*t*Bu-bipy)] (621 ppm) and two hybrid molybdenum compounds (740 and 741 ppm). The species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ also displayed high catalytic efficiency but using MeCN as reaction medium.

articles

From the research line of the presented work the following articles were published:

D. Julião, A.C. Gomes, M. Pillinger, R. Valença, J.C. Ribeiro, I.S. Gonçalves, S.S. Balula, *A recyclable ionic liquid-oxomolybdenum(VI) catalytic system for the oxidative desulfurization of model and real diesel fuel*, Dalton Transactions, 45 (2016) 15242-15248.

D. Julião, A.C. Gomes, M. Pillinger, R. Valença, J.C. Ribeiro, I.S. Gonçalves, S.S. Balula, *Desulfurization of liquid fuels by extraction and sulfoxidation using* H_2O_2 *and* $[CpMo(CO)_3R]$ *as catalysts*, Applied Catalysis B: Environmental, 230 (2018) 177-183.

D. Julião, F. Mirante, S.O. Ribeiro, A.C. Gomes, R. Valença, J.C. Ribeiro, M. Pillinger, B. de Castro, I.S. Gonçalves, S.S. Balula, *Deep oxidative desulfurization of diesel fuels using homogeneous and SBA-15-supported peroxophosphotungstate catalysts*, Fuel, 241 (2019) 616-624.

D. Julião, A.C. Gomes, L. Cunha-Silva, R. Valença, J. C. Ribeiro, M. Pillinger, B. de Castro, I.S. Gonçalves, S.S. Balula, *A sustainable peroxophosphomolybdate/*H_2O_2 *system for the oxidative removal of organosulfur compounds from simulated and real high-sulfur diesels*, Applied Catalysis A: General (in press).

D. Julião, A.C. Gomes, M. Pillinger, R. Valença, J.C. Ribeiro, I.S. Gonçalves, S.S. Balula, *Desulfurization of liquid fuels by extraction and sulfoxidation with* H_2O_2 *and indenylmolybdenum tricarbonyl pre-catalyst*, Applied Catalysis B: Environmental (submitted).

D. Julião, A.C. Gomes, L. Cunha-Silva, M. Pillinger, A.D. Lopes, R. Valença, J.C. Ribeiro, I.S. Gonçalves, S.S. Balula, *Dichlorodioxomolybdenum(VI) complexes bearing oxygen-donor ligands as catalysts for oxidative desulfurization of simulated and real diesel*, Catalysis Communications (in press).

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Abbreviations and acronyms

Ligands

acac	acetylacetonate
bipy	2,2’-bipyridine
Cp	cyclopentadienyl
DEO	*N,N′*-diethyloxamide
DMB	*N,N*-dimethylbenzamide
di-*t*bu-bipy	4,4’-di-*tert*-butyl-2,2’-bipyridine
Ind	Indenyl
HBPT	hexabutylphosphoric triamide
HMPT	hexamethylphosphoric triamide
Mepz	3-methylpyrazole
Phen	1,10-phenantroline
trz	1,2,4-triazole

Solvents and compounds

[BMIM]PF$_6$	1-butyl-3-methylimidazolium hexafluorophosphate
[BMIM]BF$_4$	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM]Cl	1-butyl-3-methylimidazolium chloride
[BMIM][NTf$_2$]	1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
[HMIM]BF$_4$	1-hexyl-3-methylimidazolium tetrafluoroborate
[OMIM]BF$_4$	1-methyl-3-octylimidazolium tetrafluoroborate
[OMIM]PF$_6$	1-methyl-3-octylimidazolium hexafluorophosphate
[MMIM]DMF	1,3-dimethylimidazolium dimethylphosphate
[EMIM]DEP	1-ethyl-3-methylimidazolium diethylphosphate
[BMIM]DBP	1-butyl-3-methylimidazolium dibutylphosphate
4-MDBT	4-methyldibenzothiophene
4,6-DMDBT	4,6-dimethyldibenzothiophene
4,6-DMDBTO$_2$	4,6-dimethyldibenzothiophene sulfone
BT	1-benzothiophene
BTO$_2$	benzothiophene sulfone
ChCl	choline chloride
DBT	dibenzothiophene
DBTO$_2$	dibenzothiophene sulfone
DMF	dimethylformamide
EG	ethylene glycol
GLY	glycerol
HPEOH	1-(2’-hydroxyphenyl) ethanone oxime
MCPBA	meta-chloroperoxybenzoic acid
MeCN	acetonitrile
MeOH	methanol
*n*Bu-Li	*n*-butyllithium
PEG	polyethylene glycol
Ph	phenyl

PPh_4Cl	tetraphenylphosphonium chloride
TBACl	tetrabutylammonium chloride
($n$$Bu_4N$)Cl	
*t*BHP	*tert*-butyl hydroperoxide
THF	tetrahydrofuran
TM	*N,N,N*-trimethylammonium

Instruments

EDX	energy dispersive X-ray analysis
FT-IR	fourier transform infrared spectrosocpy
FT-Raman	fourier transform raman spectroscopy
GC	gas cromatography
ICP	inductively coupled plasma
NMR	nuclear magnetic ressonance
PXRD	powder X-ray diffraction
SEM	scanning electron microscopy
TG	thermogravimetric analysis

Symbols

h	hours
min	minutes
T	temperature
δ	chemical shift
θ	angle of incidence
ν	frequency

Others

DES	deep eutectic solvents
EDS	extractive desulfurization process
ee	enantiomeric excess
HDS	hydrodesulfurization
IL	ionic liquid
m	medium band (FT-IR)
ODN	oxidative denitrogenation
ODS	oxidative desulfurization
POMS	polyoxometalates
ppm	parts per million
r.t.	room temperatue
s	strong band (FT-IR)
vs	very strong band (FT-IR)
w	weak band (FT-IR)

Chapter 1

INTRODUCTION

1. Introduction

“All organisms modify their environment, and humans are no exception”.[1] Over the past 200 years, the human activity resulting from their constant growth and expansion of technology, induced drastic effects in the environment through alterations of carbon, sulfur and nitrogen flows.[1-3]

The sulfur present in the atmosphere comes from two different sources: (i) natural emissions that range from volcanic activity and hot springs to natural decay of vegetation on land, in wetlands and oceans; and (ii) artificial emissions, also known as anthropogenic emissions, which result from industrial processes. The latter have surpassed natural flows ever since the 20’s, where the sulfur emissions rose very rapidly due to the use of fossil fuels which were very rich in sulfur. The anthropogenic sulfur emissions are mainly comprised of SO_2 resulting from the burning of fossil fuels. The presence of this gas in high concentrations exerts harmful effects on human health, vegetation and materials (corrosion). Also, SO_2 is one of the precursors of acidic deposition (acid rain) that affects the planet on a large scale from metropolitan areas to remote regions by decreasing the pH of aquatic environments causing the loss of fish populations and declining the forest growth by acid deposition.[3, 4]

To reduce the nefarious effects caused by the over use of fossil fuels during the last century, some sulfur reduction policies have been imposed on transportation fuels (diesel and gasoline). Since 2009, mandatory environmental directives issued by the European Union (2009/30/EC) limited the sulfur content in diesel and gasoline to 10 ppm.[5] The environmental regulations imposed in the United States of America allow a maximum of sulfur corresponding to 15 ppm for diesel (since 2006) and 10 ppm for gasoline (since 2017).[6] The increase of the environmental concern has been also noticeable for non-road vehicles that use more heavier fuels, such as fuel oils. An example are the container ships, in which the permitted sulfur content up to the present day is exceedingly high comparing to road vehicles (3.50% m/m, since 2012). After 2020 the sulfur content of any fuel oil used on board ships shall not exceed 0.50% (m/m).[7]

1.1. Oxidative desulfurization process

The World is highly dependent on the energy prevenient from crude oil resources, most of which are estimated to comprise heavy crude oil that contains high concentrations of different types of sulfur (Figure 1.1) and other contaminants besides the common hydrocarbons and aromatic compounds.[8]

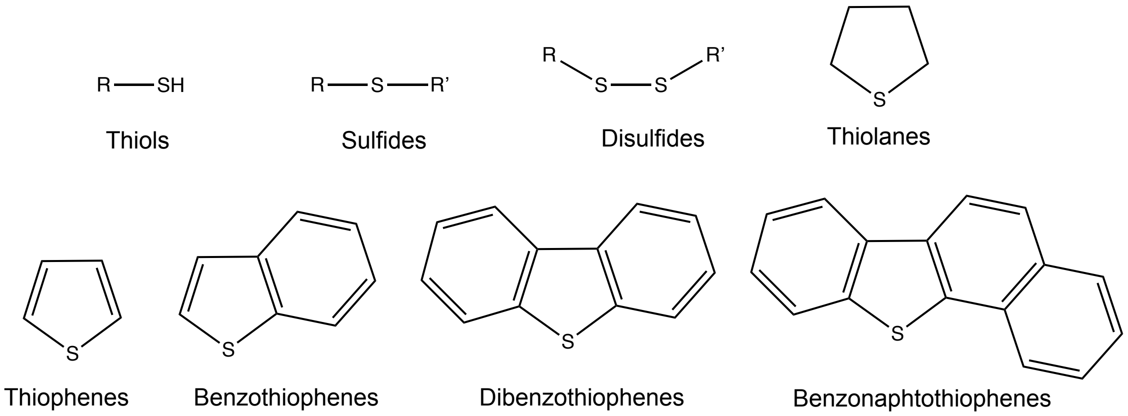


Figure 1.1. Sulfur-compounds present in crude oil. Adapted from reference [9].

The hydrodesulfurization process (HDS) is the principal technology applied by petroleum refining industries to remove the sulfur from lower quality feed stocks, respecting the stringent sulfur values imposed by the different environmental regulations around the world. In HDS, the removal of sulfur from the feed is performed under high H_2 pressure (3.0 to 5.0 MPa) and elevated temperature (300 to 500 °C) in the presence of $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ catalysts in fixed bed or fluidized bed reactor.[10] Depending on the nature of the sulfur compounds, the reaction conditions and the catalyst used, HDS can proceed by different reaction pathways employing different active sites of the catalyst surface. The typical HDS reactions occur via a hydrogenolysis pathway in which H_2 is added to the molecules, occuring a cleavage of C-S bonds and generation of H_2S (Figure 1.2, a). In the case of benzothiophene derivatives (refractory sulfur compounds), the HDS proceeds via two reaction pathways, hydrogenolysis and hydrogenation, which occur in parallel. The hydrogenation pathway is based on successive addition of H atoms to all atoms of the molecules, which leads to the cleavage of the aromatic ring and subsequently removal of sulfur from the ring as H_2S (Figure 1.2, b).[10, 11] This second pathway is responsible for the loss of octane in fuels, due to the olefin saturation.[11] Also, the high temperatures required for the removal of sulfur from refractory sulfur compounds and the S-containing impurities present in oil-derived feedstocks promote the catalyst deactivation.[12] The reactivity of the refractory sulfur compounds, specially those with alkyl substituents on their 4 and/or 6 positions, has a crucial role in the effectiveness of the HDS process limiting their treatment by normal operation conditions making it a very costly option for deep desulfurization (Figure 1.3).[13, 14]

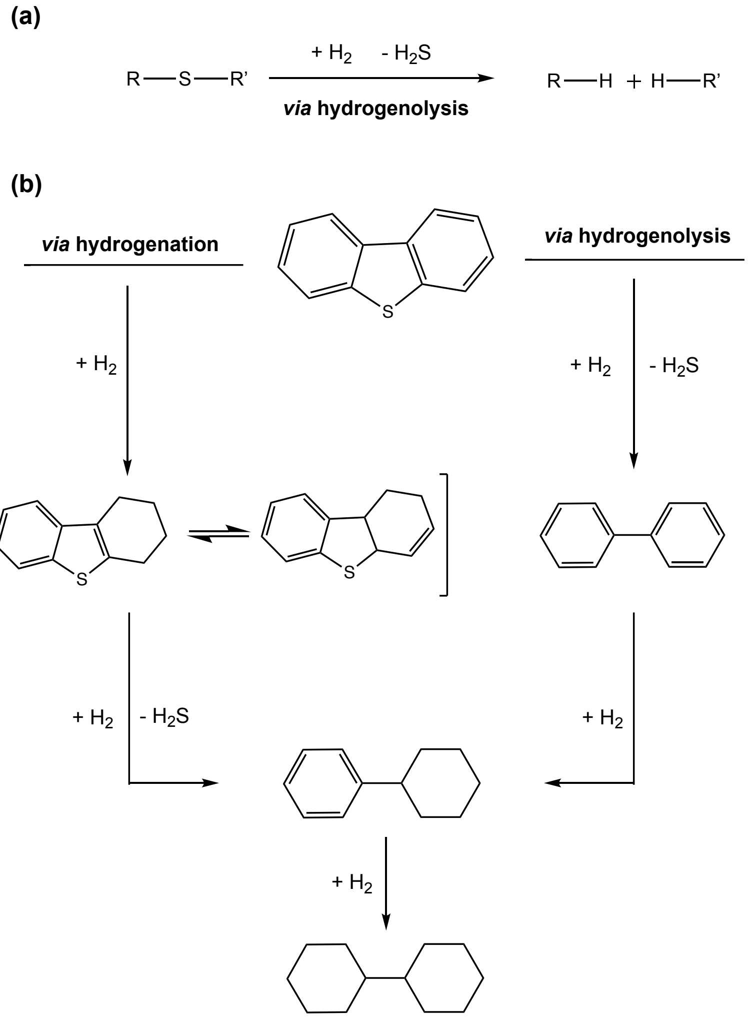


Figure 1.2. Reaction pathway for HDS of an aliphatic sulfur compound and a benzothiophene derivative. Adapted from reference [11].

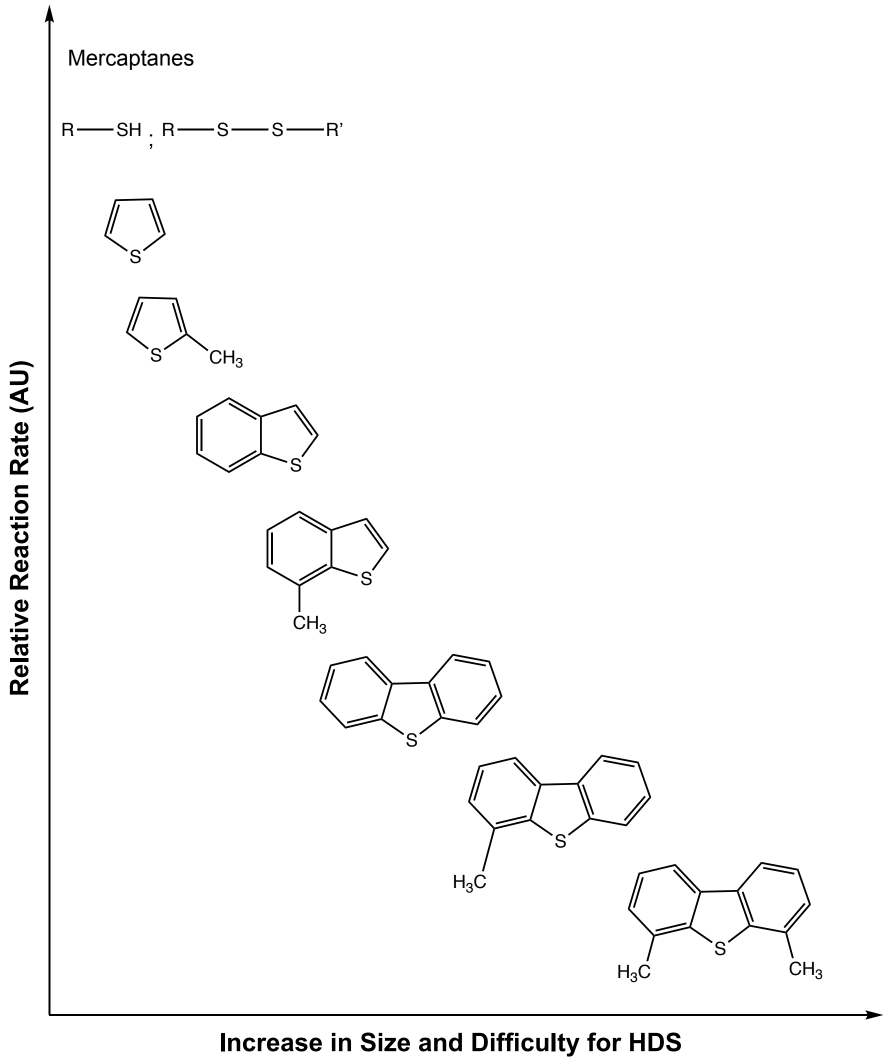


Figure 1.3. Reactivity of various sulfur compounds in HDS versus their ring sizes and positions of alkyl substitutions. Adapted from reference [14].

The development of alternative desulfurization processes, able to operate under milder conditions without consuming H_2 to produce fuels with very low levels of sulfur compounds is required but still a challenge for both academia and industry. Only a few novel desulfurization processes have shown the potential to produce ultra clean fuels, namely adsorptive desulfurization, bio-desulfurization, extractive desulfurization and oxidative desulfurization.[8, 11] During the last years a large number of publications has been dedicated to oxidative desulfurization (ODS) technology, indicating that this is a field of high interest. This technology operates under mild conditions, i.e., low temperature and ambient pressure without requiring expensive H_2, resulting in a more economic process than HDS.[13, 15] ODS involves a chemical reaction, based on a selective oxidation of sulfur compounds present in fuels and the consequent removal of the oxidized sulfur compounds, i.e. sulfones and/or sulfoxides by liquid-liquid extraction with polar solvents or adsorption over solid adsorbents.[10] The sulfones and sulfoxides possess a higher polarity than non-oxidized sulfur compounds, facilitating their extraction from the fuel with non-miscible polar solvents.[16]

Many organic polar solvents, including dimethylformamide, acetonitrile, toluene, methanol, dichloromethane, among others, have been used as extractants in ODS. However, their toxicity, volatility and flammability make them an undesirable choice. In contrast to the conventional solvents, ionic liquids (ILs) seem to be more competitive and environmentally compatible due to their unique physical properties such as non-volatility, solubility for organic and inorganic compounds, good thermal and chemical stability, non-flammability and recyclability.[17] Besides their contribution as extraction solvents, some ILs also appear to have a beneficial effect on the activation of H_2O_2 by providing an environment that results in a higher rate of chemical oxidation.[18-20]

The catalytic oxidation step must be performed using a selective oxidant in the presence of a suitable catalyst, in order to improve the selectivity of oxidant to sulfur atoms, preventing the oxidation of olefins or aromatic compounds present in fuels. The oxidation of these compounds is responsible for reducing the octane rating (if performed on olefin-containing gasoline) and increasing the loss of fuel quality.[21] The oxidants commonly used in ODS are hydrogen peroxide, organic hydroperoxides (e.g. *tert*-butyl-hydroperoxide), and peracids. More unusual are ozone, nitrogen oxides, molecular oxygen and peroxy organic acids (e.g. sulfuric acid and nitric acid). The mechanism is related with the donation of oxygen atoms from the oxidant to the sulfur compounds to form the oxidized species without rupture of C-C and C-S bonds (Figure 1.4).[8, 13] The first oxidant employed in the ODS process was nitrogen dioxide (NO_2), occurring an extraction step with methanol to remove both sulfur and nitrogen compounds from petroleum feedstock. However, this type of oxidant was responsible for non-selective reactions when in the presence of oxygen.[8] Another example of an active oxidant is *tert*-butyl hydroperoxide (*t*BHP), which is the most widely employed organic hydroperoxide due to its miscibility in the oil phase, avoiding mass transfer limitation.[22] The ODS process using this oxidant was patented by Lyondell Chemicals [23-25] and EniChem/UOP [26, 27]. The drawbacks presented by *t*BHP are its high cost, possible transportation problems, low amount of active oxygen (17.8%) and the waste treatment of generated alcohol (*tert*-butanol, *t*BuOH) as coproduct. This alcohol can be applied as a potential octane-boosting compound for gasoline.[13, 28] The age of “environmentality” initiated two decades ago, led to some technical improvements, such as process simplification, milder or more sustainable operation conditions and the use of cheaper or more environmentally friendly oxidants.[29] Under this demand for viable and greener processes, molecular oxygen (O_2) is the most desirable oxidant due to its low cost, large abundance, high active oxygen content (50%) and environmental benignity.[30] One of the limitations of the use of O_2 includes the difficulty in controlling the stoichiometry of added oxidant and safety concerns, particularly at elevated temperatures.[31] In addition to O_2, hydrogen peroxide (H_2O_2) is the most attractive oxidant, being considered the best option to use as an oxidant in an ODS process as a result of a considerable number of advantageous features (Section 1.3.).[13, 32] Like *t*BHP or O_2, H_2O_2 requires to be selectively activated by an appropriate catalyst to be effective as oxidant.[33]

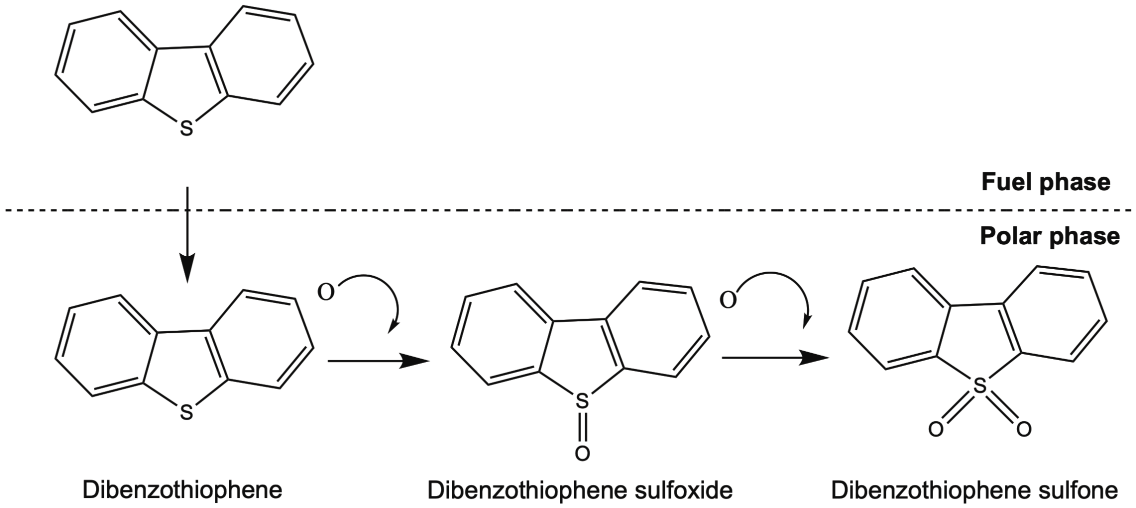


Figure 1.4. Oxidative desulfurization of a refractory sulfur compound in ODS process.

The most investigated catalysts in ODS processes using H_2O_2 as oxidant are the polyoxometalates (POMs) [34-43], some organic and inorganic acids [21, 44], lewis acidic ionic liquids [45, 46], high valent oxo-molybdenum [47, 48], oxo-rhenium (MTO) [49-51] and oxo-vanadium complexes [52]. Heterogeneous catalysts are commonly used in ODS, due to their capacity to be separated from the reaction medium and the possibility to be recycled. Therefore, some of the homogeneous catalysts have been heterogenized using different support materials, such as metal-organic frameworks (MOFs), silica nanoparticles and carbon nanotubes (CNTs). The incorporation of the homogeneous catalysts in these supports results in an attractive way of exploring new catalytic systems, based on simple procedures that produce highly active and robust novel materials.[53]

When compared to HDS, the oxidation step in an ODS process originates a more successful desulfurization of refractory sulfur compounds (benzothiophenes and derivatives) since the reactivity of these compounds towards oxidation is expected to be the reverse of that for HDS. In fact, the sulfur atoms with higher electron density are more easily oxidized. The presence of electron donating groups, such as alkyl substituents, increases the electron density on sulfur compounds, increasing the reactivity towards oxidation. The reactivity decreases with the decrease of alkyl side chains (Figure 1.5).[10, 44] Therefore, the refractory sulfur compounds known to be more difficult to remove by HDS method, can be easily desulfurized by ODS process.

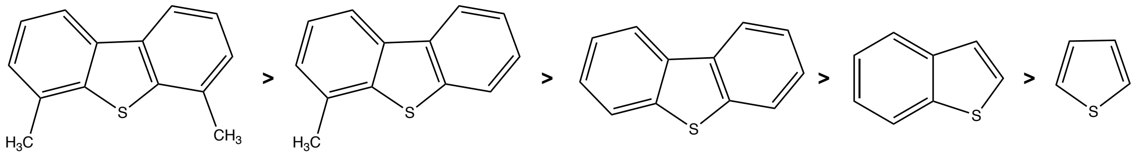


Figure 1.5. The reactivity order for several refractory sulfur compounds in ODS process.

1.2. Ionic Liquids

Various solvents are classified as the most damaging chemicals to the environment mainly due to their volatility which makes them difficult to recover and reuse.[17] An environmentally benign alternative to these solvents are ionic liquids (ILs), first described by Walden [54] in 1914. ILs are defined as molten salts with melting points lower than 100 °C. These salts are typically constituted by cations such as alkylammonium, phosphonium, pyridinium and imidazolium and anions like halides, $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$, $[(CF_3SO_2)_2N]^-$ and $[CF_3CO_2]^-$, possessing ionic-covalent crystalline structures. The possible choices of cation and anion that will result in the formation of ILs are numerous. In fact, more than 10^6 different ILs can be prepared by combining all the known cations and anions, and this number can increase to one trillion (10^{18}) if all the ternary ILs systems are included.[55] By varying the cations and/or anions with specific functions, it is possible to design abundant ILs with required functionalities, being considered tunable and versatile materials.[56, 57] For this reason, ILs have been used for a wide range of applications [55, 58, 59] including drug delivery [60], as active pharmaceutical ingredients [61], as lubricants [62], in membrane technology [63, 64] and catalysis [17, 65], as novel electrolytes for energy application [66, 67] such as batteries, heat storage [68, 69] and solar and fuel cells, in recovery of biofuels [70] and for deep desulfurization of fuels as extraction solvents [48, 71, 72]. Considering the wide-ranging

ILs and applications, it is difficult to make a generalization about their properties, since some of their basic physical properties, such as viscosity or density, are still under evaluation by researchers.[56]

The first ILs, also known as first-generation ILs, are the organo-aluminates that comprise bulky cations such as imidazolium and pyridinium. These ILs were unstable towards water and air, limiting their range of applications.[58, 73] The second-generation of ILs already presented air and water-stability, which originated a high number of publications in various areas of applications.[56] Some examples of these are 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]BF_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]PF_6$). Curiously, more recently, Rogers and co-workers [74] proved that contrary to what was originally reported, the second-generation ILs containing $[BF_4]^-$ and $[PF_6]^-$ anions are hydrolytic unstable, liberating hydrogen fluoride at high temperatures. However, these were exceptions and most of the second-generation ILs are stable in water and organic chemicals.[58] Two factors can be responsible for the miscibility of the IL in water. The first and the most important is the presence of fluorinated anions, such as $[PF_6]^-$, $[OTf]^-$ and $[NTf_2]^-$, which increases the hydrophobicity of the IL. Another property that can increase the hydrophobicity of the IL is the alkyl chain length on the cation. However, this was only evident for a series of ILs, such as $[C_n mim][BF_4]$, where n = 2-5 resulted in ILs completely water-miscible.[58, 75] It is important to refer that most hydrophobic ILs can dissolve up to 1% of water, which can affect their physical properties.[58, 76]

An irregular packaging of the ions caused by the combination of bulky asymmetric organic cations with small inorganic anions explains why ILs remain liquids at room temperature and possess low melting points.[56] Comparing to the conventional solvents, ILs possess extremely low vapor pressures, even at high temperatures, avoiding the problems associated with emissions and classifying them as green solvents. Besides their low pressures, most of the ILs can be distilled at 200-300 °C under low pressure without decomposition, making possible the recovery of significant amounts of pure substance.[77] These results also confirm the thermal stability above 350 °C observed for most ILs.[57] However, in imidazolium-containing ILs, the presence of halide anions dramatically reduces the thermal stability. Generally, the anion stability follows the order: $[PF_6]^- > [NTf_2]^- \approx [BF_4]^- >$ halides.[75]

One of the most important properties for ILs is their high polarity. There seems to be an inversely proportional relation between viscosity and polarity, i.e. shorter alkyl chains on the cation and smaller anion size causes a decrease in viscosity and a polarity increase.[76] Maintaining the cation (1-butyl-3-methylimidazolium) was found that the IL polarity decreased in the order of $[NO_2]^-$ > $[NO_3]^-$ > $[BF_4]^-$ > $[NTf_2]^-$ > $[PF_6]^-$, probably due to the higher charge delocalization.[58, 78] The polarity values of ILs can also be sensitive to temperature and water, suffering an increase with the decrease of the temperature or increase of water-content.[58, 79]

ILs have the capacity to dissolve most materials, such as polymers, organic and inorganic compounds and organometallics. Their solubility is largely dependent on the cation/anion combination and from the material.[80, 81] Furthermore, an increase of the chain length of alkyl substituents on both cations and anions can lead to an increase in the lipophilicity of ILs.[17] The high solubility showed by ILs is an important characteristic to use these solvents in homogeneous catalysis, where it is required that the solvent solubilizes and stabilizes the active catalytic species, remaining unreactive. In fact, the high dissolution capacity of ILs combined with the possibility of catalyst separation from the reaction medium, for further reutilization, is crucial for the use of the homogeneous processes on an industrial scale.[82]

1.2.1. Ionic liquids in ODS

ILs have been widely applied during the last decade in oxidative desulfurization systems (ODS), with the first reference to the use of ILs in ODS being from 2003 by Lo *et al.* [20]. ILs have also been mostly used in extractive desulfurization processes (EDS). In the EDS process, the most used ILs are the Lewis and Brønsted acidic ILs, Fe(III)-containing ILs or redox ILs, such as $[BMIM]Cl/AlCl_3$ and $[BMIM]Cl/FeCl_3$, and also the ILs containing imidazolium and pyridinium cations and anions $[BF_4]^-$, $[PF_6]^-$, alkylsulfates or alkylphosphates.[83, 84] However, as this process is mainly based on the solubility of the sulfur compounds, it usually fails to provide a high degree of sulfur removal.[85, 86] For example, Lu *et al.* [87] studied the extraction capacity of $[HMIM]BF_4$ in the desulfurization of a model diesel containing dibenzothiophene (DBT). Using EDS only 6% of sulfur was removed, but when this process was added to ODS an increase to 93% of desulfurization was achieved. Thus, in order to increase the efficiencies of the sulfur removal, the extraction using ILs must be combined with a chemical oxidation, since the oxidized sulfur compounds, i.e. sulfoxides and/or sulfones, are more easily extracted by ILs than the non-oxidized compounds.[48] Through sulfoxidation studies, it is known that aliphatic sulfur compounds are easily oxidized due to their high reactivity resulting from the nucleophilicity of the sulfur atom and their molecular sizes, allowing their oxidation using an oxidant, such as H_2O_2. However, the aromatic sulfur compounds in fuels are very difficult to oxidize, requiring high amounts of H_2O_2 to reach high sulfur removal levels. This obstacle can be avoided with the use of appropriate catalysts.[13, 88] The published work reporting the oxidation of several sulfides focuses mainly on the use of transition-metal catalysts, in the presence of H_2O_2.[89, 90] Therefore, it is important to guarantee a high catalytic performance of metal complexes (W, Mo, V and Re) in extractive IL media.[83] One of the first reports on the IL-based oxidation of fuel using metal complexes as catalysts was by Zhu *et al.* [91] in 2007. In this work, a dibenzothiophene (DBT)-containing model oil was used and only 16.5% and 22% of desulfurization was achieved using [BMIM]BF_4 and [OMIM]BF_4 as extraction solvents, without the oxidative process. The addition of H_2O_2 to the system caused an increase of sulfur removal to 30% and 33.8%, respectively. However, when the catalysts $[WO(O_2)_2Phen \cdot H_2O]$ and $[MoO(O_2)_2Phen]$ were present in the system, practically complete removal of DBT was obtained after the same reaction time (3 h). Curiously, the same reactions performed in the absence of ILs only reached 50.3% and 41.6% of sulfur removal, for $[WO(O_2)_2Phen \cdot H_2O]$ and $[MoO(O_2)_2Phen]$, respectively. These experiments revealed that an effective removal of DBT is dependent on the combination of oxidative and extractive processes. Also, the water-miscible IL [BMIM]BF_4 was more effective for the ODS process than the corresponding water-immiscible analogues [OMIM]BF_4, [BMIM]PF_6 and [OMIM]PF_6, which contribute to the formation of a triphasic system (IL/H_2O_2/oil). The ILs phase containing the immobilized catalysts could be recycled for several cycles without decrease in activity. More recently, the same authors published a study where an effective removal of different refractory sulfur compounds was achieved in both water-miscible [BMIM]BF_4 and water-immiscible [BMIM]PF_6, [OMIM]BF_4 and [OMIM]PF_6 ILs. In this study it was also observed that the amount of IL strongly influences the desulfurization efficiency, where a larger amount of IL led to a higher desulfurization.[92] Another study revealed that this increase in efficiency caused by the higher amount of IL is not continuous, i.e. after a determined volume of IL the effect on desulfurization efficiency is minimal. Also, the ODS efficiency of three water-immiscible ILs ([MMIM]DMP, [EMIM]DEP and [BMIM]DBP) were compared for the desulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT) and higher desulfurization rates were found for longer carbon chain ILs. The polarity of the ILs generally decreases when the alkyl group chain length extends. Therefore, these types of ILs will have higher extraction capacities for non-polar compounds, such as the non-oxidized 4,6-DMDBT, which will positively affect the oxidative step.[93] Ge *et al.* [94] tested the ODS of a model oil containing DBT, using as catalysts surfactant-type quaternary ammonium salts of the octamolybdate anion with H_2O_2, in the presence of acidic ILs. The effectiveness of acidic ILs in ODS was affected by the cation and anion structure. Maintaining the anion, the removal of the sulfur compounds was positively affected in the order: imidazolium > triethylammonium > pyridinium. In case of the anion, $[BF_4]^-$ possessed a higher effectiveness for ODS, following by $[HSO_4]^-$ and $[H_2PO_4]^-$.

As demonstrated by the work mentioned above, high desulfurization efficiency can be achieved using ILs combined with catalytic oxidation, since these solvents are highly effective to extract aromatic sulfur compounds from model diesels solutions. Most ODS studies are concentrated on the extraction properties presented by imidazolium ILs, which result from the appropriate combination of these cations with bulky anions that leads to high absorptions of the S-containing molecules. Some factors are responsible for decreasing their efficiency, such as strong hydrogen bonds between the ions and the increase of the steric hindrance promoted by the refractory sulfur compounds containing alkyl substituents.[57, 95]

1.3. Hydrogen peroxide as oxidant

For all kinds of oxidation reactions, the choice of the oxidant determines the practicability and efficiency of the respective reactions.[32] To choose the ideal oxidant, some requirements must be considered: price, selectivity, simplicity of handling, nature of the coproduct and percentage of available oxygen (Table 1.1).[96] The active oxygen content is calculated as the ratio between the weight of oxygen that can be transferred to a substrate and the molecular weight of the oxidant.[33] This percentage also represents a way of measuring the atom utilization of the oxidant, which must be maximized in order to avoid the formation of high amounts of wastes. This is one of the twelve principles of Green Chemistry.[97] As it is clear from Table 1.1, both H_2O_2 and O_2 are the most environmentally innocuous, their coproduct is water. However, it is important to mention that some of the coproducts referred in Table 1.1, e.g. *t*BuOH and acetic acid, can be readily recycled and used in some applications.[96]

Table 1.1. List of some oxidants, the resulting coproduct and the corresponding percentage of active oxygen. [96, 98]

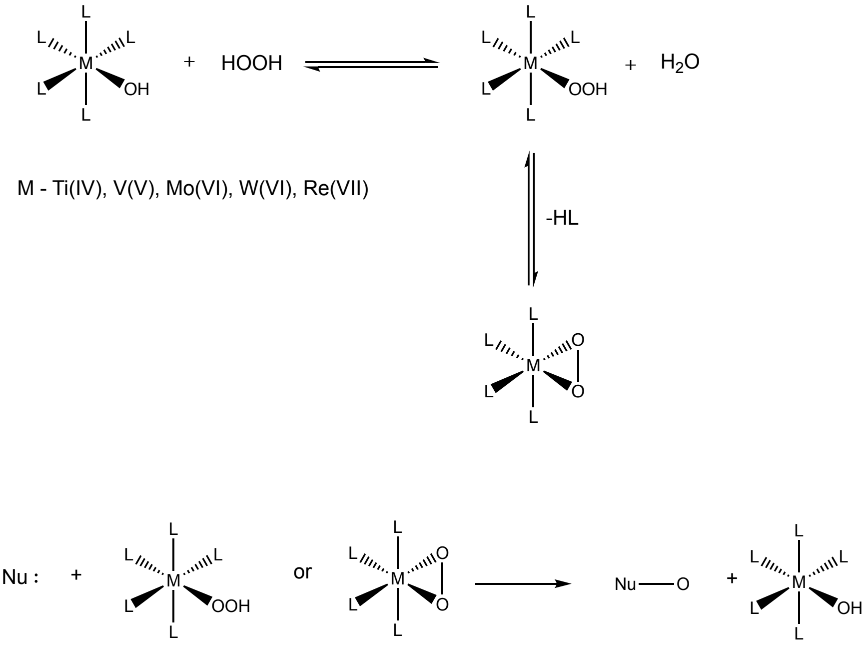
Oxidant	% Active Oxygen	Coproduct
O_2	50 (100)	H_2O (none)
H_2O_2	47	H_2O
O_3	33.3	O_2
CH_3CO_3H	26.6	CH_3CO_2H
NaClO	21.6	NaCl
*t*BHP	17.8	*t*BuOH
$C_5H_{11}NO_2$[*1]	13.7	$C_5H_{11}NO$
$KHSO_5$	10.5	$KHSO_4$
PhIO	7.3	PhI

[*1] *N*-Methylmorpholine-N-oxide

H_2O_2 was discovered in 1818 by Louis Jacques Thénard [99] through the acidification of barium peroxide with nitric acid. Nowadays it is produced on a massive scale by an anthraquinone auto-oxidation process.[100]

The environmental safety of H_2O_2, i.e. waste-avoiding oxidant, and environmental regulations and laws resulting from a major environmental concern, played a fundamental role in the growth of this oxidant over the past few years.[29] An example is the replacement of chlorine compounds with H_2O_2 in industry (textile, paper and pulp) and in environmental remediation. Moreover, the use of large amounts of H_2O_2 for the industrial production of propylene oxide allowed the release of any byproducts to be avoided.[29, 100] Besides, its atom efficiency of 47% and consequent lower amount of waste, other important advantages are its attractive solubility in water and in several organic solvents [33, 101], easy operation, transportation and easy availability.[32] All these arguments make it the ideal oxidant for a variety of catalytic applications, particularly in synthetic organic chemistry, where it can replace less sustainable oxidants.[100]

The low intrinsic reactivity of H_2O_2 allows its selective activation by converting it into more active species. This is essential to increase the selectivity of the oxidative reactions.[102] When considered its activation in the presence of transition metals, the mode of activation has an important influence on the reaction selectivity. The mode of activation is related with the nature of substrate, transition metal complex, e.g. ligand type coordinated to the metal center and free coordination positions and in a lesser extension to the reaction conditions.[33] The interaction of H_2O_2 with first row transition metals, such as Co(II)/Co(III), Mn(II)/Mn(III), Fe(II)/Fe(III) and Cu(I)/Cu(II) generally causes a homolytic cleavage of the O-O and O-H bonds leading to the formation of radicals, which are responsible for a myriad of undesirable products. Thus, for most synthetic applications, radical formation should be limited or inhibited. The activation by the formation of intermediate active species (peroxo, oxo or hydroperoxo) containing active oxygen to be transferred for reactions with appropriate nucleophiles, such as alkenes, sulfides, amines, etc. (Figure 1.6) is an advantageous path that normally originates selective reactions. These active intermediates result from a heterolytic cleavage of O-O bond by early d^0 transition metals, such as Re(VII), Mo(VI), V(V), Ti(IV) or W(VI). This mechanism is the basis for a wide variety of catalytic reactions.[33, 103, 104]



Nu : = sulfide, alkene, etc.

Nu—O = sulfoxide, epoxide, etc.

Figure 1.6. Activation of H_2O_2 by heterolytic cleavage and reaction with nucleophiles.[104]

The formation of active intermediates by the interaction of H_2O_2 with the metal complex is also the basis for the mechanism of the oxidation of sulfur compounds to sulfones and sulfoxides.[48, 105] The fuels contain aliphatic and aromatic sulfur compounds which possess different reactivities and molecular sizes, resulting in distinct oxidation efforts. The selective oxidation of these sulfur atoms in fuels produces oxidized sulfur compounds without the rupture of C-C and C-S bonds, avoiding a reduction of octane rating.[21]. The reaction temperatures should not exceed 80 °C, to avoid inefficient decomposition of H_2O_2 and undesirable oxidation reactions, responsible for degrading the quality of the liquid fuels.[106]

1.4. Molybdenum and tungsten-catalysed oxidation of S-containing compounds

The intense interest from the scientific community in developing effective oxidative desulfurization systems capable of selectively oxidizing organosulfur compounds in fuels, added to the need of sulfoxides production for the synthesis of natural and biologically significant molecules, makes catalytic sulfoxidation a research topic of emergent relevance.[107, 108]

The oxygen transfer reactions have been extensively studied with most of the elements of groups VI to VIII, from which stands out molybdenum with more catalytic systems based on these reactions. Although a parallelism has been observed to the oxygen transfer chemistry of molybdenum and tungsten regarding to their discovery and progress, a lack of an adequate research effort in tungsten chemistry is observable.[109] Both are recognized as selective catalysts for the oxidation of various organic substrates, such as olefins, amines, alcohols and sulfides.[110-113] However, by the amount of reported works it is clear that despite the lack of investigation in detail of tungsten chemistry, this is recognized as a better catalyst for oxygen transfer reactions with H_2O_2 than other transition metals, in which is included molybdenum that is generally used with other hydroperoxide oxidants, such as *t*BHP.[89, 114-118] In these reactions are always involved oxometal species containing a terminal oxo ligand, which can participate as reactants, final products or intermediates. Depending on the d^n configuration of the metal, the presence and nature of *trans* ligands and the coordination stereochemistry, the M=O bonds may diverge, influencing the activity, selectivity and catalyst stability.[96, 109] These oxometal groups are stabilized at highly oxidized metal centers and can present diverse geometries, from linear or bent geometries for MO_2, to pyramidal or planar for MO_3, and a *cis*-octahedral geometry for the MO_4 fragment.[109, 119] The typical catalysts with a terminal oxygen atom, Mo(VI)-oxo and W(VI)-oxo species, have demonstrated to be very active and highly selective catalysts for the oxidation of several sulfides to the corresponding sulfoxides or sulfones.[88] The oxygen atom present in the coordination sphere of the metal center can be replaced by organic ligands. If a metal-carbon interaction occurs, these compounds will be designated as organometallic complexes.[120] The presence of σ and π donor ligands plays an important role in the stabilization of the active center due to its high oxidation state. Thus, catalytic properties of metal complexes are, to a certain extent, dependent on the nature of the ligands around the metal center.[121, 122]

1.4.1. Molybdenum homogeneous catalysts with a terminal oxygen atom

The chemistry of Mo(VI) is largely dominated by complexes containing the *cis*-$[MoO_2]^{2+}$ structural unit. The particular interest in these complexes ascended in the late 60's when ARCO and Halcon [123, 124] patented a process based on homogeneous industrial catalysis to produce propylene oxide using *t*BHP as oxidant, catalysed by Mo(VI) compounds. Besides their versatility as homogeneous [125] and heterogenous [126] catalysts resulting from interesting chemical properties, these complexes are also used as materials precursors [127] and models of molybdoenzymes [128]. There are a great diversity of dioxomolybdenum(VI) complexes, from neutral or ionic to mono or binuclear types. These complexes are generally six-coordinated and present the following general formulas: *neutral mononuclear* $[MoO_2X_mL_n]$ where $m \in \{0,1,2\}$ and $n \in \{1,2,3,4\}$; the related *ionic* complexes $[MoO_2X_mL_n][Y_o]$ where $m \in \{0,1\}$, $n \in \{1,4\}$, $o \in \{1,2\}$ and the *binuclear* species $[MoO_2L]_2$ or $[(MoO_2X_mL_n)_2(\mu\text{-}O)_p]$ where $m \in \{0,1\}$, $n \in \{1,2\}$, $p \in \{1,2\}$.[129, 130] With few exceptions, all of these complexes present a distorted octahedral geometry, with the oxo and the L ligands *cis* to each other and the X ligands in *trans* configuration.[130] The X ligands usually correspond to alkyl, halides (F, Cl, Br), isothiocyanates, siloxanes while the L ligands may involve a ligand with one or two N- (nitrogen) or O- (oxygen) donor atoms bound to the metal.[130] The two different ligand sets X and L can be easily varied in order to fine tune the ligand surrounding of the Mo(VI) center. From the described complexes, the most common are the $[MoO_2X_2L_n]$ where $n \in \{1,2\}$, which result from adduct formation between MoO_2X_2 and Lewis base ligands, and coordinated solvent molecules that occupy the empty positions through the metal center.[126]

The research groups of Modena [131] and Kagan [132] were the pioneers in the selective oxidation of sulfides to sulfoxides catalysed by Mo(VI)-oxo complexes comprising different ligands in the presence of *t*BHP and H_2O_2.[114, 133-135] Although the sulfoxidation studies with Mo(VI)-oxo complexes began almost 30 years ago, molybdenum is still under-explored in this area, being its application mainly focused on epoxidation reactions where Mo complexes have played a fundamental role as catalysts and have been extensively studied for more than 50 years.[123] However, in both molybdenum catalysed oxidative reactions the use of more environmentally friendly oxidants is still scarce.[30, 88] Due to recent environmental constraints, sulfoxidation has assumed a more prominent position, as has the gradual exchange of less sustainable oxidants by H_2O_2, as can be observed in Figure 1.7, which illustrates a search in the database Web of Science using the keywords: *catalysis* and *molybdenum* and *sulfides oxidation* or *desulfurization* and *hydrogen peroxide*.

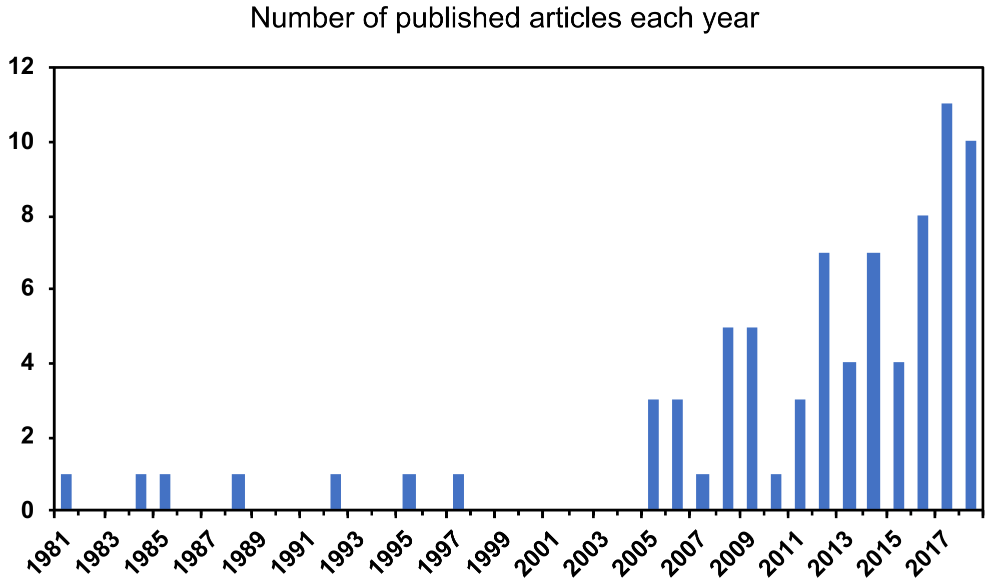


Figure 1.7. Number of reports since 1981 until September 2018 about oxidation of sulfur compounds catalysed by molybdenum complexes using H_2O_2 as oxidant.

From the oldest reports it has been found that several molybdenum complexes are active in the oxidation of sulfides producing sulfoxides with high yields. An example are the complexes $[MoO_2L_2]$ where the L correspond to bidentate or monodentate ligands, such as acac (acac = acetylacetonate) and hexaalkylphosphonic triamides (HMPT and HBPT), respectively which efficiently oxidize aryl methyl sulfides (thioanisole) with H_2O_2 (entries **1**-**2** in Table 1.2).[131, 136] Kinetic studies revealed the absence of considerable effects on the reaction rate by addition of external ligands.[131, 136] These results rule out that the occurrence of the oxygen-transfer process depends on a displacement of the ligand and consequent coordination of the substrate. Therefore, the oxidation of the sulfur compounds proceeds via an external nucleophilic attack of substrates to the O-O bond of molybdenum peroxo specie (Figure 1.6). Additionally, it was also demonstrated that the structure of the sulfur compounds affects the oxidation rates, which increase with the increasing nucleophilicity of sulfur compounds.[131, 136]

Unsubstituted sulfides including dialkyl, cyclic, benzylalkyl and substituted arylalkyl and dialkyl sulfides bearing different functional groups susceptible to oxidation or deprotection such alkenes, alkynes, alcohols, esters, ketones, aldehydes and oximes revealed to be selectively oxidized to the corresponding sulfoxides and sulfones by different families of Mo(VI)-oxo complexes and H_2O_2 without affecting the sensitive functional groups, such as C=C bonds that are known to be easily oxidizable and that are importantly preserved during the desulfurization of fuels to avoid the loss of fuel quality (entries **5**, **6**, **9** and **10** in Table 1.2).[137-140] One of these efficient catalysts is [MoO_2Cl_2], which is the simplest molybdenyl derivative (entry **5** in Table 1.2).[138] Depending on the solvent used, acetonitrile or acetone/water, it can efficiently and selectively oxidize a variety of sulfur compounds to the corresponding sulfones or sulfoxides, respectively, at room temperature. Despite its effectiveness, it can be vulnerable due to its hygroscopicity, moisture sensitivity and by the fact that it is coordinatively unsaturated.[126] Its stabilization can be achieved by adduct formation with oxygen, nitrogen and sulfur donor ligands.

Although the number of reports about molybdenum-catalysed oxidation of sulfur compounds is still marginal, different L ligands have been employed, namely monodentate, bidentate and tridentate, usually based on nitrogen, oxygen and sulfur donor atoms.[113, 131, 136, 141-145] Among them, *N*-donor ligands are usually the most employed due to their robustness for oxygen transfer reactions.[121] Dioxomolybdenum(VI) complexes containing tridentate *O*,*N*,*O* or *O*,*N*,*S* coordinated ligands derived from salicylaldehyde derivatives (entries **11**, **14** and **18** in Table 1.2) were active for sulfoxides production with high yields obtained from different sulfur substrates.[142, 143, 145] An exception was the [MoO_2(ONS-type)] complex, that revealed ineffectiveness for aromatic sulfides, such as thiophene that suffered decomposition during the catalytic reaction.[142] From this type of ligands few studies are known using chiral ligand types, which allow the achievement of enantiopure sulfoxides (entry **11** from Table 1.2).[143] All the chiral complexes selectively oxidized different sulfur compounds with high yields, but in different enantiomeric excess (*ee*). These differences are related with the presence of bulky substituents which may provide a positive or negative effect on the *ee*, depending on their positions. The better *ee* resulted from the presence of bulky *t*-Bu groups in the salicylaldehyde moiety of complex 4 represented in entry **11** in Table 1.2 (41.3%), while poor *ee* were obtained when bulky substituents were present in the amino alcohol, e.g. complex 5 (5.5%).

Like MoO_2Cl_2, other compounds, such as MoO_3, Na_2MoO_4 and polyoxomolybdate anions ranging from $[Mo_2O_7]^{2-}$ to $[Mo_8O_{26}]^{4-}$, have also been applied as catalysts and materials precursors of other Mo(VI)-oxo based on the *cis*-$[MoO_2]^{2+}$ structural unit (entries **6**, **9**, **10** and **20** in Table 1.2).[137, 139, 140, 146] The catalytic efficiency of some of these compounds (MoO_3, $Na_2MoO_4{\cdot}2H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and other prepared from them ($[(n\mathrm{Bu}_4N)(\pi\text{-}C_5H_5N)]_4(\beta\text{-}Mo_8O_{26})$ and $[n\mathrm{Bu}_4N]_4(\alpha\text{-}Mo_8O_{26})$) was compared for the oxidation of thioanisole under the same experimental conditions and reaction time (10 min) (entry **10** in Table 1.2).[140] Amongst all catalysts, tetra-(tetraalkylammonium)octamolybdates (3 and 4) were outstanding in both reactivity and selectivity. Additionally, other sulfur compounds were also oxidized by $[n\mathrm{Bu}_4N]_4(\alpha\text{-}Mo_8O_{26})$ and H_2O_2 in the presence of several solvents, such as water, ethanol, methanol, acetonitrile, hexane, 2-butanone, 1,4-dioxane, benzene, carbon tetrachloride and isopropanol. The results showed that polar solvents are more suitable for these oxygen transfer reactions due to the higher affinity to the catalyst. Organic oxidants (MCPBA and *t*BHP) were also tested and provided worst results than H_2O_2 (94% with MCPBA, 51% with *t*BHP and 97% with H_2O_2).[140] Results reported by other authors (entries **6** and **9** in Table 1.2) under similar conditions presented high conversions for sulfoxide or sulfone obtained using MoO_3 and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ complexes.[137, 139] In these works, thioanisole and various other substituted and unsubstituted sulfur compounds were also studied. As previously mentioned, also here was demonstrated that less nucleophilic sulfur compounds, e.g. dibenzothiophene, require more time to be oxidized to the corresponding sulfoxide and/or sulfone. A hybrid material prepared from MoO_3 and an organic ligand 1,2,4-triazole (trz), was also used in catalytic sulfoxidation with H_2O_2 (entry **17** in Table 1.2).[147] These materials are interesting since these can act as source of soluble active species or as heterogeneous catalysts, depending on their structure, composition and catalytic reaction conditions. The $[MoO_3(trz)_{0.5}]$ was able to oxidize thioanisole (99% at 6 h) and benzothiophene (72% at 24 h). The catalytic activity of the anion $[Mo_7O_{24}]^{6-}$ containing tetrabutylammonium $[n\mathrm{Bu}_4N]^+$ as counter-cation and the parent di-peroxo derivative $[n\mathrm{Bu}_4N]_6[Mo_7O_{22}(O_2)_2]$ (prepared by replacing one of the terminal oxo from Mo3 and Mo5 centers by a peroxo group) was compared for thioanisole oxidation (Figure 1.8) (entry **20** in Table 1.2).[146] The activity of $[nBu_4N]_6[Mo_7O_{24}]$ was significantly higher than its di-peroxo complex, achieving complete oxidation of thioanisole five minutes faster than $[nBu_4N]_6[Mo_7O_{22}(O_2)_2]$ that achieved a total conversion after 10 min of reaction. The identification of intermediates through mass spectrometric (nanoESI-MS) technique indicated that both complexes form the same active intermediate specie $[Mo_2O_{11}]^{2-}$ but with different proportions resulting in different catalytic behaviours.

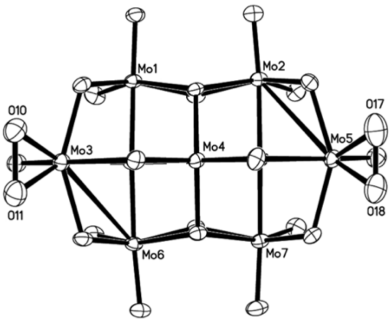


Figure 1.8. Structural plot of di-peroxo $[Mo_7O_{22}(O_2)_2]^{6-}$ anion.[146]

Another important type of molybdenum(VI) complexes extensively employed as stoichiometric reactants or even as catalysts in the presence of peroxidic oxidants such as H_2O_2, organic peroxides or molecular oxygen, are the oxo-diperoxo, also known as Mimoun complexes $[MoO(O_2)_2(L\text{-}L)]$ with seven-fold coordination.[148, 149] These complexes emerged in 1969 after their discovered by Mimoun and co-workers [150].

The use of oxo-diperoxomolybdenum(VI) complexes ligated with 8-quinolinol allowed the epoxidation of a series of various alkenes. The same efficiency was observed for catalytic sulfoxidation of three different sulfides, which were totally oxidized but with low to moderate selectivity for sulfoxide (entry **4** in Table 1.2).[144] An organic bidentate O,N ligand, namely 1-(2'-hydroxyphenyl) ethanone oxime, $HPEOH_2$, was also introduced in the same type of peroxo complexes and its catalytic properties were described for the oxidation of some sulfide compounds (entry **8** in Table 1.2). Total conversion of sulfides was obtained after 1 h of reaction using $PPh_4[MoO(O_2)_2(HPEOH)]$ as catalyst with H_2O_2 and acetonitrile as solvent.[113] Most of the reactions were selective for the sulfone instead of the sulfoxide. The decrease in the amount of H_2O_2 and reaction time would promote an increase in the yield of sulfoxide. Two oxo-peroxomolybdenum(VI) complexes were applied as catalysts in sulfoxidation reactions. The complexes applied were, one similar to the previous complex in entry **8** in Table 1.2

with a different bidentate O,O ligand, i.e. acylpyrazolonate (Q^R) $PPh_4[MoO(O_2)_2(Q^R)]$ and the complex $[MoO(O_2)(Q^R)_2]^-$ (entry **19** in Table 1.2).[141] The $PPh_4[MoO(O_2)_2(Q^R)]$ complex achieved higher conversions when the temperature was increased from 0 °C (31%) to 60 °C (94%), which consequently decreased the sulfoxide selectivity from 100% to 85%. In general, the $[MoO(O_2)(Q^R)_2]^-$ complex showed higher catalytic performance with high conversion and selectivity to sulfoxide at 25 °C and in the presence of different solvents (chloroform and an IL $[BMIM]PF_6$).[141]

The unique properties and the advantages resulting from the utilization of ILs as solvents, as well as their good results obtained for oxidation of sulfides to sulfoxides, sometimes without requiring a catalyst (as shown by Kühn and coworkers [151]) has led to an increase of their application in oxygen transfer reactions.[141, 152] Some authors explored the oxo-diperoxomolybdenum(VI)-catalysed sulfide oxidation using H_2O_2 oxidant and $[BMIM][PF_6]$ solvent.[152] Using the $[MoO(O_2)_2(H_2O)_n]$ complex as catalyst, several solvents were compared, including ILs with different anions, such as $[BMIM][BF_4]$ and $[BMIM][NTf_2]$ and a bulky imidazolium cation $[OMIM][PF_6]$ (entry **15** in Table 1.2).[152] The results showed that the oxidation of the sulfides is strongly dependent on the solvent employed. The oxidized products obtained in conventional solvents media, such as water, DMSO and chloroform, achieved low yields after 18 h, probably caused by the low solubility of the catalyst and substrates. On the other hand, when different ILs were used, high yields were obtained (>97%) at 1 h of reaction, from which occurred 100% selectivity to sulfone.[152] The authors supposed the occurrence of a metal-catalysed mechanism, since no conversion was observed in the absence of Mo(VI) catalyst. Using $[BMIM][PF_6]$ as solvent and H_2O_2 as oxidant, the catalytic activity of two oxo-peroxomolybdenum(VI) complexes was compared, namely the previously mentioned $[MoO(O_2)_2(H_2O)_n]$ (entry **15** in Table 1.2) and $[MoO(O_2)_2(Mepz)_2]$ (Mepz = 3-methylpyrazole), for oxidation of various sulfides.[152] Both oxo-peroxo complexes showed similar yields in the oxidation of alkyl and aryl-substituted sulfides, however $[MoO(O_2)_2(Mepz)_2]$ presented higher selectivity for sulfoxide. As expected, the less nucleophilic sulfur compounds, e.g. dibenzothiophene and benzothiophene, were the most difficult to oxidize in comparison to the alkyl/aryl-substituted sulfides, obtaining 63% and 65% conversion using $[MoO(O_2)_2(Mepz)_2]$, and 67% and 16% with $[MoO(O_2)_2(H_2O)_n]$, respectively. The sulfones were the major product obtained, showing very low values of selectivity to sulfoxide. The application of ILs as solvents allows the recycling of the systems containing homogeneous catalysts. The recycled $[MoO(O_2)_2(H_2O)_n]$ complex kept its catalytic efficiency and selectivity to sulfoxide for ten cycles.[152] In a recent article from the same workgroup, it was described the asymmetric oxidation of prochiral sulfides using $[MoO(O_2)_2(H_2O)_n]$ as catalyst with H_2O_2 in the presence of a L-valine derivative, i.e. (S,S)-HL^{iPr} and $[PPh_4]Br$ (entry **16** in Table 1.2).[153] Also here, $[BMIM][PF_6]$ was tested as solvent, but despite the high conversions, low *ee* was achieved (≤2%) due to the low solubility of (S,S)-HL^{iPr}. Acetonitrile, methanol and dimethylformamide also revealed to be useless, due to a possible coordination to the Mo center, limiting the access of the precursor ligand HL^{iPr} and therefore the formation of the catalyst responsible for the asymmetric process.[153] The better conversion/*ee* combination was achieved in the presence of chloroform (87%/38%) at 1 h and 0 °C. The presence of a counter-cation $[PPh_4]^+$ helped to increase the solubility of the catalyst formed in-situ during the asymmetric reactions, improving its catalytic activity. Most of the sulfides were efficiently oxidized, however with *ee* ranging from 21% to 40%.

Two peroxomolybdates, namely a dinuclear $[nBu_4N][(Ph_2PO_2)\{MoO(O_2)_2\}_2]$ (2) and a trinuclear $[nBu_4N]_2[(PhPO_3)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]$ (1) complex, were employed as catalysts for the oxidation of sulfides to sulfoxides and sulfones by H_2O_2 (Figure 1.9).[154] Both catalysts demonstrated low selectivity for sulfoxide, giving in most of sulfide oxidations higher yields for sulfone product (entry **3** in Table 1.2).

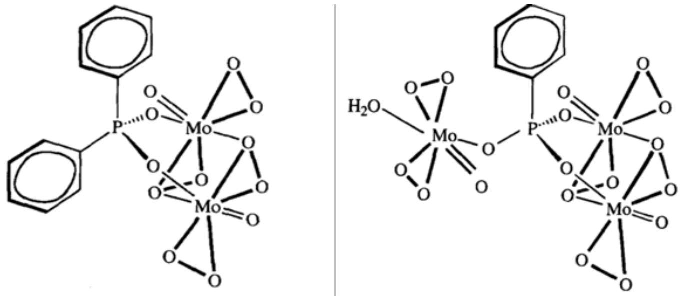


Figure 1.9. Dinuclear $[(Ph_2PO_2)\{MoO(O_2)_2\}_2]^-$ (left) and trinuclear $[(PhPO_3)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]^{2-}$ (right) structures.[154]

Several molybdenum(VI) complexes containing *cis*-$[MoO_2]^{2+}$, $MoO(\eta^2\text{-}O_2)_2$ and MoO_3 oxo units form effective catalysts for oxidation of sulfides to sulfoxides and/or sulfones.[113, 131, 136, 138-145, 147, 152-154] A class of Mo(VI)-oxo complexes that can englobe all these oxo units are the organomolybdenum complexes.[155] The first organometallic dioxomolybdenum(VI) complex, $[Cp'MoO_2Cl]$ (Cp' = cyclopentadienyl, η^5-C_5R_5; R = H), was synthetized by Cousins and Green [156] in 1963. Later, the catalytic activity of $[Cp'MoO_2Cl]$ (substituted cyclopentadienyl ligand, R = CH_3) was described for olefin epoxidation with different peroxidic oxidants.[157] Low yields and unspecific synthetic pathways have postponed their use as oxidative catalysts for years.[158] The development of a general and simple one-step synthesis involving tricarbonyl complexes [Cp'Mo(CO)$_3$Cl] (R = H, CH$_3$, CH$_2$Ph) and *t*BHP was developed by Romão and co-workers [159] (Figure 1.10) and triggered the interest in these complexes as catalyst precursors. During the last 15 years several [Cp'Mo(CO)$_3$R] (Cp = substituted and unsubstituted cyclopentadienyl, R = halide, alkyl, alkylester, N-heterocyclic carbene, ansa bridged alkyl or cycloalkyl group, etc) complexes have been synthesized and applied in oxygen transfer reactions, mainly olefin epoxidations.[155] However, only a few reports are available for the oxidation of sulfides to sulfoxides or sulfones using these complexes (entries **7** and **13** from Table 1.2).[160, 161]

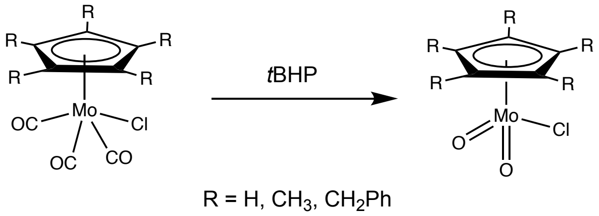


Figure 1.10. One-step synthesis of [Cp'MoO$_2$Cl] (Cp' = η^5-C_5R_5; R = H, CH$_3$, CH$_2$Ph) complexes from their corresponding [Cp'Mo(CO)$_3$Cl] precursors (oxidative decarbonylation).[159]

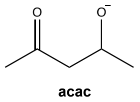
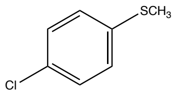
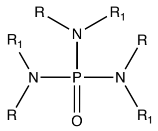
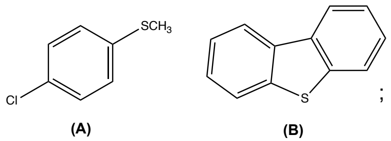
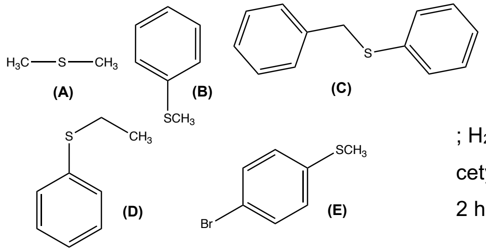
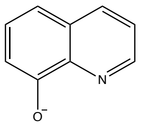
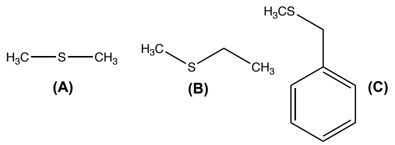
Gamelas *et al.* [160] have reported selective oxidation of dialkyl, aryl-alkyl, benzylic and benzothiophene sulfides to either sulfoxides or sulfones using H_2O_2, in the presence of two tricarbonyl complexes [Cp'Mo(CO)$_3$Cl] (Cp' = η^5-C_5R_5; R = H, CH$_3$) (entry **7** from Table 1.2). In general, all the aryl-alkyl and diaryl substrates were effectively and selectively oxidized at the sulfur atom (without affecting other sensitive functional groups) by both complexes under mild conditions. A different behaviour was observed for benzothiophenic derivatives, e.g. dibenzothiophene that showed to be more difficult to oxidize, resulting in moderate yields (<70%).

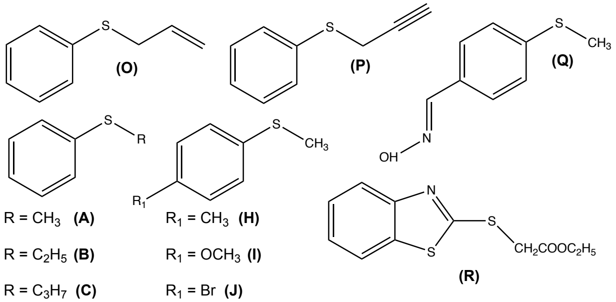
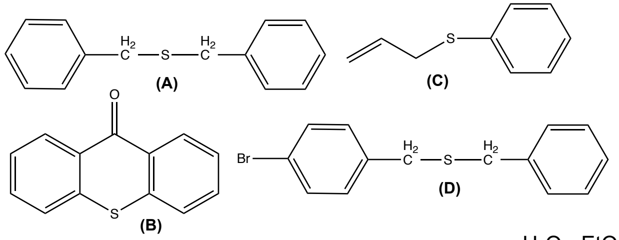
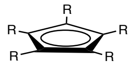
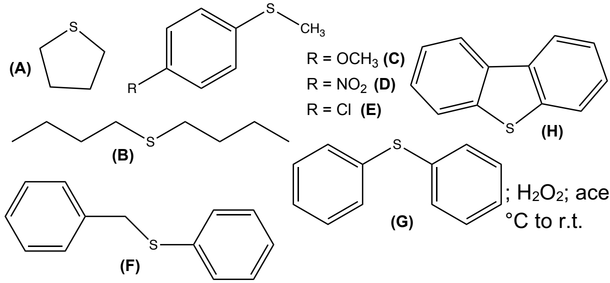
In order to analyse the effect of substituents, three cyclopentadienyl molybdenum complexes [(η^5-C_5H_5)Mo(CO)$_3$(-C≡CR)], R = Ph (1), C$_6$H$_4$-*p*-CF$_3$ (2), C$_6$H$_4$-*p*-CH$_3$ (3) were compared for thioanisole oxidation with H_2O_2 (entry **13** in Table 1.2).[161] The reactivity order of the catalysts was found to be 3 (100%) > 2 (64%) > 1 (56%), while for selectivity towards sulfoxide a reverse performance was achieved, i.e. 1 > 2 > 3**.** The different results obtained can be related with the presence of a substituent on the phenyl ring (complexes 2 and 3), which promotes its activation affecting the catalytic efficiency of the complexes. Using complex 1, various sulfides were oxidized. In most of the cases moderate to high conversions were obtained until 2 h of reaction at room temperature.

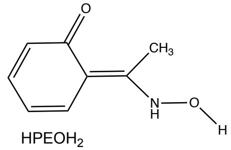
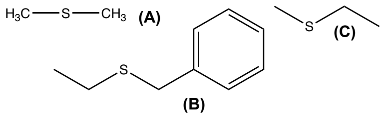
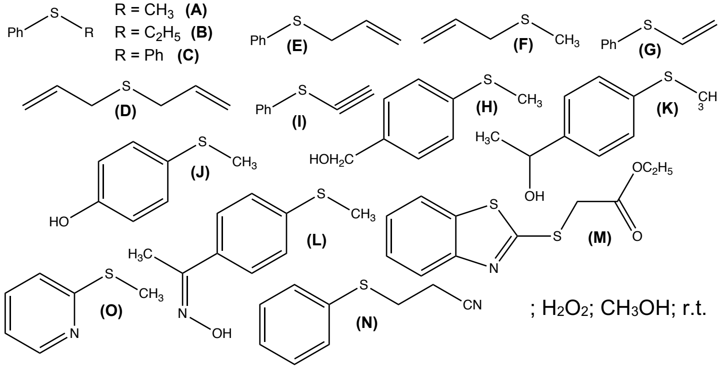
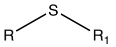
However, for bulky sulfides it was necessary to resort to high temperatures (60 °C or 100 °C), as well as an increase in the reaction time, in order to improve their conversions to the corresponding oxidized species. All complexes were stable for five catalytic cycles.[161]

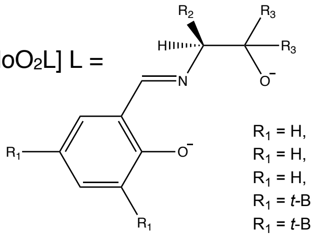
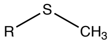
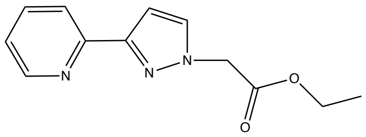
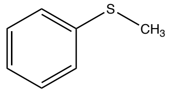
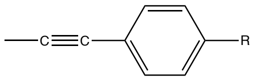
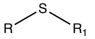
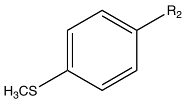
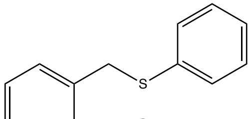
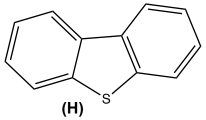
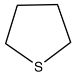
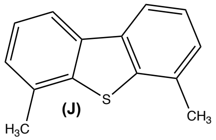
In addition to the sulfoxidation studies with the tricarbonyl complexes, a tetracarbonyl [$Mo(CO)_4L$] (L = ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate) was applied as efficient sulfoxidation catalyst with H_2O_2 (entry **12** in Table 1.2).[162] These organometallic complexes have generally a common precursor, i.e. $Mo(CO)_6$, from which the tetracarbonyl complexes are obtained by efficient and quick synthesis methodologies, such as microwave-assisted synthesis.[162] The authors applied the tetracarbonyl complex (entry **12** in Table 1.2) in the oxidation of thioanisole using a mild temperature (35 °C) and H_2O_2 as oxidant. After 10 min of reaction, a conversion of 87% was observed, after which no considerable progress was observed (only 1%) in the following 6 h of reaction. Without catalyst no reaction took place. Hence, molybdenum species are responsible for the sulfoxidation reaction, possibly via electrophilic attack on the sulfur atom in thioanisole.[162]

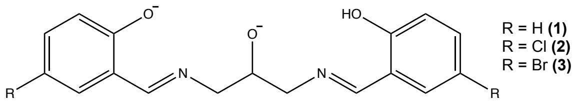
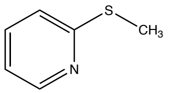
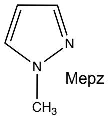
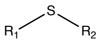
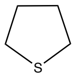
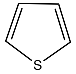
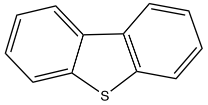
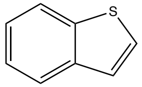
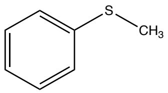
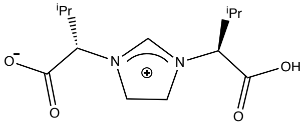
Table 1.2. Application of Mo(VI)-oxo complexes in oxidation of sulfur compounds.

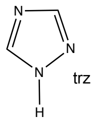
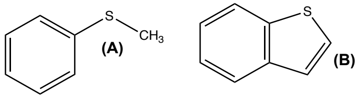
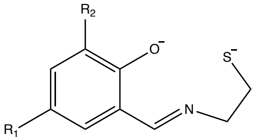
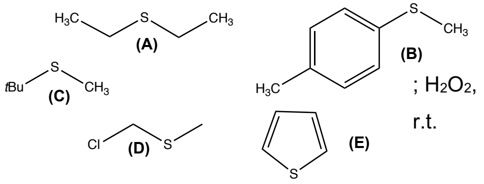
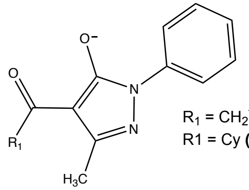
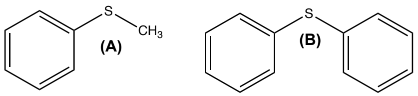
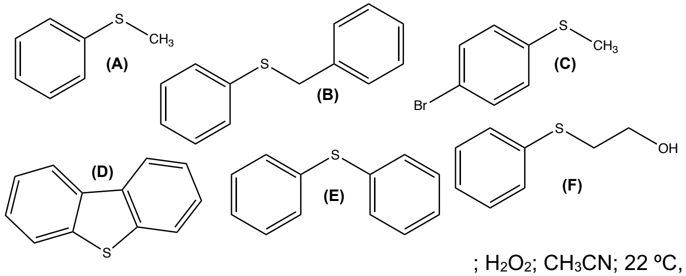
	Molybdenum complexes	Reaction conditions	Observations[a]	Ref.
1	$[MoO_2L_2]$ L=  acac	 ; H_2O_2; EtOH; N_2; 25 °C	**Yield:** 90%	[131]
2	$[MoO_2L_2]$ L =  $R=R_1=CH_3$ HMPT (**1**) $R=R_1=CH_3(CH_2)_3$ HBPT (**2**)	 (A) (B) ; H_2O_2; CH_2Cl_2/H_2O; H_2SO_4; 40 °C	**Yield:** 1/**A** – 72%; 30 min 2/**A** – 72%; 10 min 1/**B** – 52%; 60 min	[136]
3	$[Y]_2[(PhPO_3)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]$ (**1**) $[Y][(Ph_2PO_2)\{MoO(O_2)_2\}_2]$ (**2**) Y = [*n*Bu_4N]	 (A) (B) (C) (D) (E) ; H_2O_2; $CHCl_3$; cetylpyridinium chloride; r.t.; 2 h	**Yield:** 1/2/**A** – 17/16% (81/78% to SO_2) 1/2/**B** – 72/60% (28/40% to SO_2) 1/2/**C** – 23/13% (56/75% to SO_2) 1/2/**D** – 36/12% (29/77% to SO_2) 1/2/**E** – 30/26% (51/59% to SO_2)	[154]
4	$[MoO(O_2)_2L]^-$ L = 	 (A) (B) (C) ; H_2O_2; CH_2Cl_2; PPh_4Cl; 40 °C; 1 h	**Yield:** **A** – 18% **B** – 50% **C** – 54%	[144]

5	$[MoO_2X_2]$ X = Cl	 R = CH_3 **(A)** R = C_2H_5 **(B)** R = C_3H_7 **(C)** R = $CH_2C_6H_5$ **(D)** R = Ph **(E)** R = $(CH_2)_3OH$ **(F)** R = CH_2CHCH_2 **(G)** R_1 = CH_3 **(H)** R_1 = OCH_3 **(I)** R_1 = Br **(J)** R_1 = NO_2 **(K)** R_1 = $CH_2CO_2CH_3$ **(L)** R_1 = CH_2OH **(M)** R_1 = COH **(N)** ; H_2O_2; acetone/H_2O, CH_3CN; r.t.	**Yield:** **F**/CH_3CN – 89%; 60 min **M**/acetone/H_2O – 94%; 10 min **N**/acetone/H_2O – 93%; 10 min **O**/acetone/H_2O – 90%; 25 min	[138]
6	$[MoO_3]$	 ; H_2O_2; EtOH; 50 °C	**Yield:** **A** – 96%; 14 min **B** – 98%; 40 min **C** – 94%; 15 min **D** – 96%; 16 min	[139]
7	Cp' =  $[Cp'Mo(CO)_3X]$ X = Cl; Cp' = η^5-C_5R_5, R = H (**1**), CH_3 (**2**)	 R = OCH_3 **(C)** R = NO_2 **(D)** R = Cl **(E)** ; H_2O_2; acetone/CH_3OH; -20 °C to r.t.	**Yield:** **1**/**C** – 98%; 2 h **1**/**H** – 60%; 6 h **1**/**G** – 95%; 7 h **2**/**D** – 75%; 3.5 h	[160]

8	$[MoO(O_2)_2L][Y]$ Y = PPh_4 L =  HPEOH$_2$	; H_2O_2; CH_3CN; 78 °C; 1 h	**Yield:** **A** – 4% (96% to SO_2) **B** – 4% (96% to SO_2) **C** – 96%	[113]
9	$(NH_4)_6Mo_7O_{24}·4H_2O$	; H_2O_2; CH_3OH; r.t.	**Yield** (sulfone)**:** **C** – 94%; 60 min **G** – 91%; 30 min **J** – 92%; 60 min **M** – 89%; 120 min **Note:** The oxime group (**L**) was not tolerated under the reported experimental conditions.	[137]
10	$(NH_4)_6Mo_7O_{24}·4H_2O$ (**1**) $[MoO_3]$ (**2**) $[(n\text{Bu}_4N)(\pi\text{-}C_5H_5N)]_4[(\beta\text{-}Mo_8O_{26})]$ (**3**) $[(n\text{Bu}_4N)]_4[(\alpha\text{-}Mo_8O_{26})]$ (**4**) $Na_2MoO_4·2H_2O$ (**5**)	 R = CH_3, R_1 = CH_2CH_2OH **(A)** R = CH_3, R_1 = CH_2COCH_3 **(B)** R = CH_3, R_1 = CH_2CN **(C)** R = CH_3, R_1 = $CH_2CH_2COOCH_3$ **(D)** R = CH_2=$CHCH_2$, R_1 = CH_2=$CHCH_2$ **(E)** R = $(CH_2)_4$ **(F)** R = CH_3, R_1 = $CH(CH_3)CH_2CH_3$ **(G)** R = $C_6H_5CH_2$, R_1 = CH_3 **(H)** R = C_6H_5, R_1 = CH_3 **(I)** R = C_6H_5, R_1 = CH_2CH_3 **(J)** R = 2-Cl-C_6H_5, R_1 = CH_3 **(K)** R = 4-Cl-C_6H_5, R_1 = CH_3 **(L)** R = 4-$CH_3OC_6H_4$, R_1 = CH_3 **(M)** R = 4-$NO_2C_6H_4$, R_1 = CH_3 **(N)** R = 4-$CH_3C_6H_4$, R_1 = CH_3 **(O)** ; H_2O_2; *t*BHP; MCPBA; CH_3OH; H_2O; MeOH; EtOH; CH_3CN; isopropanol; 2-butanone; 1,4-dioxane; hexane; C_6H_6; CCl_4 25 ºC	**Yield:** **4**/**I**/H_2O/H_2O_2 – 62%; 10 min **4**/**I**/hexane/H_2O_2 – 35%; 10 min **4**/**I**/CH_3CN/H_2O_2 – 87%; 10 min **4**/**I**/*t*BHP – 51%; 10 min **1**/**2**/**3**/**4**/**5**/**I**/H_2O_2 – 89, 87, 96, 97 and 89%; 10 min **4**/**H**/H_2O_2 – 99%; 10 min **4**/**N**/H_2O_2 – 94%; 150 min **Cat. recyclability**: Four catalytic cycles with cat. 4. At 10 min in 3rd and 4th cycle occurred a slight decrease in the activity. **Cat. stability:** Cat. 4 maintained the characteristic Mo=O and Mo-O-Mo bonds.	[140]

11	[MoO$_2$L] L =  R_1 = H, R_2 = Bn, R_3 = H **(1)** R_1 = H, R_2 = Ph, R_3 = H **(2)** R_1 = H, R_2 = Bn, R_3 = Ph **(3)** R_1 = *t*-Bu, R_2 = Ph, R_3 = H **(4)** R_1 = *t*-Bu, R_2 = Bn, R_3 = Ph **(5)** R_1 = *t*-Bu, R_2 = Ph, R_3 = Ph **(6)**	 R = Ph **(A)** R = *p*-Cl-C_6H_4 **(B)** R = *p*-Br-C_6H_4 **(C)** R = *p*-Me-C_6H_4 **(D)** R = *p*-MeO-C_6H_4 **(E)** R = *p*-NO2-C_6H_4 **(F)** ; H_2O_2; CH_2Cl_2; 0 ºC	**Yield:** **5/A** – 77%; ee – 5.5% (S); 2 days **4/A** – 90%; ee – 39.6% (S); 2 days **4/D** – 90%; ee – 41.3% (S); 10 h **Cat. stability:** Cat. 4 preserved its structure.	[143]
12	[Mo(CO)$_4$L] L =  ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate	 ; H_2O_2; CH_3OH/CH_2Cl_2; 35 ºC	**Yield:** 87%/88% - 10 min/6 h	[162]
13	[Cp’Mo(CO)$_3$X] Cp’ =  X =  R = H **(1)** R = CF_3 **(2)** R = CH_3 **(3)**	 R = Ph, R_1 = CH_3 **(A)** R = R_1 = CH_3 **(B)** R = R_1 = C_2H_6 **(C)** R = R_1 = Ph **(D)**  R_2 = CH_3 **(E)** R_2 = Cl **(F)**  **(G)**  **(H)**  **(I)**  **(J)** ; H_2O_2; CH_3CN; r.t.; 60 ºC; 100 ºC	**Yield: (T.C.)** **1/A** – 56%; 2 h (> selectivity to SO) **2/A** – 64%; 2 h **3/A** – 100%; 1.5 h **1/E** – 100%; 8 h **1/J** – 75% (100% to SO_2); 8 h **1/H** – 100%; 10 h **Cat. recyclability:** The activity of the three catalysts was maintained for five cycles.	[161]

14	$[MoO_2XL_2]$ X = H_2O; L = 	 ; H_2O_2; CH_3CN; r.t.	**Yield:** **1** – 65% (T.C. = 98%) **2** – 66% (T.C. = 97%) **3** – 67% (T.C. = 96%)	[145]
15	$[MoO(O_2)_2L_n]$ n∈{1,2}; $L_n = H_2O$ (**1**) L_2 =  (**2**)	 R_1 = Ph, R_2 = Ph **(A)** R_1 = Ph, $R_2 = CH_3$ **(B)** R_1 = p-CH_3-C_6H_4, $R_2 = CH_3$ **(C)** R_1 = p-Cl-C_6H_4, $R_2 = CH_3$ **(D)** R_1 = p-Br-C_6H_4, $R_2 = CH_3$ **(E)** R_1 = Ph, $R_2 = C_2H_5$ **(F)**  **(G)**  **(H)**  **(I)**  **(J)** ; H_2O_2; H_2O, $CHCl_3$, DMSO, $[BMIM][PF_6]$, $[BMIM][BF_4]$, $[BMIM][NTf_2]$, $[C_8mim][PF_6]$; 20 ºC;	**Yield:** 1/**A**/H_2O – 86% (25%)*; 18 h 1/**A**/$CHCl_3$ – 100% (6%)*; 18 h 1/**A**/$[BMIM][PF_6]$ – 0% (100%)*; 1 h 1/**A**/$[BMIM][NTf_2]$ – 0% (100%)*; 1 h 1/**I**/$[BMIM][PF_6]$ – 1% (67%)*; 1 h 2/**I**/$[BMIM][PF_6]$ – 3% (63%)*; 1 h 2/**H**/$[BMIM][PF_6]$ – 1% (65%)*; 1 h 2/**C**/$[BMIM][PF_6]$ – 87% (85%)*; 1 h 1/**C**/$[BMIM][PF_6]$ – 66% (91%)*; 1 h **Cat. recyclability:** System 1/IL was recycled for ten cycles without significant decrease in its activity. *T.C. (total conversion)	[152]
16	$[MoO(O_2)_2L_n]$ $L_n = H_2O$	 ; H_2O_2; $[BMIM][PF_6]$, toluene, MeOH, DMF, CH_3CN, CH_2Cl_2, 1,2-$C_2H_4Cl_2$, $CHCl_3$, (S,S)-HL^{iPr}; $[PPh_4]Br$; 0 ºC; 1 h  (S,S)-HL^{iPr}	**Yield:** $[BMIM][PF_6]$ – 100%; ee ≤ 2%; $CHCl_3$ – 87%; ee – 38%; MeCN – 95%; ee ≤ 2%; **Cat. stability:** recovery solid = $Na\{[Mo(O)(O_2)_2(H_2O)]_2(\mu\text{-}L^{iPr})\}$	[153]

17	$[MoO_3L_{0.5}]$ L = 	 ; H_2O_2; CH_3CN; 70 ºC;	**Yield:** **A** – 39% (T.C. = 99%); 6 h **B** – 0% (T.C. = 72%); 24 h **Cat. stability:** Formation of intermediate metal species.	[147]
18	$[MoO_2L]$ L =  $R_1 = R_2 = H$ (**1**) $R_1 = Br, R_2 = H$ (**2**) $R_1 = R_2 = Cl$ (**3**)	 ; H_2O_2, *t*BHP; CH_3CN, $CHCl_3$, H_2O; r.t.	**Yield:** **1/A**/H_2O – 94%; 1 h **1/B/E**/H_2O – no reaction. **Cat. recyclability:** 1 was reused for two cycles: activity decrease. **Cat. stability:** Formation of a precipitate catalytically inactive.	[142]
19	$PPh_4[MoO(O_2)_2L]$ (**1**) $[MoO(O_2)L_2]^-$ (**2**)  $R_1 = CH_2{}^tBu$ (**1**) R1 = Cy (**2**)	 ; H_2O_2; Cl_3CH, [BMIM]PF_6; 0 ºC, 25 ºC, 60 ºC	**Yield:** **2/A**/$CHCl_3$ – 90%; 25 ºC; 1 h **2/A/**[BMIM]PF_6 **–** 90%; 25 ºC; 1 h **Cat. stability:** Leaching	[141]
20	$[Mo_7O_{24}]^{6-}[Y]^+$ (**1**) $[Mo_7O_{22}(O_2)_2]^{6-}[Y]^+$ (**2**) $Y = [nBu_4N]$	 ; H_2O_2; CH_3CN; 22 ºC, r.t.	**Yield:** **1/A** – 46%(54% to SO_2); 5 min; r.t. **2/A** – 81%(14% to SO_2); 5 min; r.t. **1/B** – 0%(100% to SO_2); 1 h; 22 °C **2/B** – 0%(100% to SO_2); 3 h; 22 °C **1/D** – 0%(100% to SO_2); 9 h; 22 °C **2/D** – 0%(100% to SO_2); 36 h; 22 °C **Cat. stability:** Formation of intermediate species. The main active: $[Mo_2O_{11}]^{2-}$.	[146]

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[a] The yields given are percentage of sulfoxide formed. The exceptions are described as sulfone. T.C. corresponds to Total Conversions. The yields presented are the most substantial for the organization of the present thesis.

1.4.2. Proposed mechanistic studies for molybdenum catalysed sulfoxidation reactions

The evolution and development of the chemistry of molybdenum results from an extensive investigation that has been performed for a long time, in the context of olefin epoxidation with *t*BHP as oxidant.[158, 163] Thus, as expected almost all mechanistic studies were performed in this context, although some doubts still remain concerning the intermediary species formed and their influence on catalytic reaction, and the causes for possible decompositions of the starting complex (catalyst/catalyst precursor). In the oxidation of organic substrates, such as sulfides or alkenes with H_2O_2 or organic peracids catalysed by molybdenum complexes, the heterolytic mechanism is the most acceptable.[104, 164]

Two contradictory alternative mechanisms were originally proposed and have created a long-standing debate through the years. The pioneer Mimoun [150, 165] proposed a step-wise mechanism that involves the formation of an intermediate resulting from the coordination of the substrate to the metal center (Figure 1.11). This mechanism depends on the presence of a free coordination site on the metal center or the replacement of a ligand in the coordination complex.[166] The other mechanism was reported by Sharpless *et al.* [167] and it is based on a concerted step where a direct attack of nucleophilic substrate on an electrophilic peroxo oxygen center occurs by a spiro structure transition state (Figure 1.11).

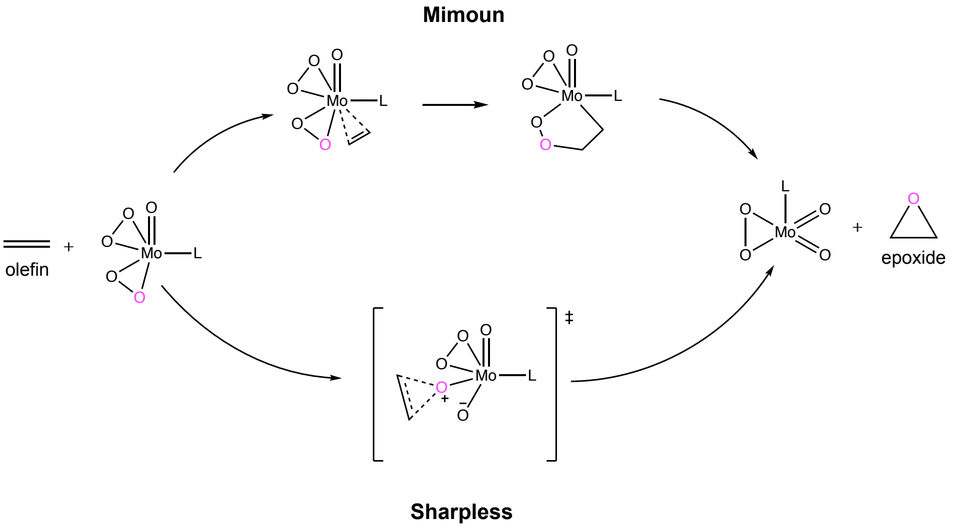

Figure 1.11. Proposed mechanisms for olefin epoxidation by Mimoun [150] and Sharpless [167].

In the light of the mechanistic controversy, Di Furia *et al.* [166] have studied sulfide oxidation by two oxo-diperoxomolybdenum complexes $[MoO(O_2)_2L][Y]$ (Y = (nBu$_4$N); L = $C_5H_4NCO_2^-$ or $C_5H_4NOCO_2^-$) and H_2O_2. Both complexes showed a similar oxidizing ability, indicating that in sulfoxidation reactions, the nature of the coordination sphere of the molybdenum complexes plays an insignificant role, which is a good evidence for a process not involving association of the substrate to the metal center, where such a coordination would require the formation of an unsaturated site on the metal.[166] Also, the addition of external highly nucleophilic ligands, such as HMPT had no effect on the reaction rate, showing to be not able to displace the bidentate $C_5H_4NCO_2^-$ and $C_5H_4NOCO_2^-$ ligands, and thus sustaining the statement of absence of substrate coordination.[136, 166] Very few theoretical studies performed years later have explored the pathways associated with the oxygen atom transfer reaction by the Sharpless mechanism from an oxo-diperoxo $[MoO(O_2)_2(OPH_3)]$ and oxo-monoperoxo $[MoO_2(O_2)(OPh_3)]$ complexes to dimethyl sulfides and sulfoxides.[168, 169] During the theoretical studies (DFT) the oxo-monoperoxo complexes were less reactive than the oxo-diperoxo complexes with regard to sulfoxide oxidation to the corresponding sulfone. Both complexes behaved as stronger electrophilic oxidants toward the sulfide.[169] Thus, only oxo-diperoxo-promoted oxygen atom transfer was considered for the mechanistic study. The calculations revealed that the oxidation of sulfides and sulfoxides is an asynchronous process, occurring first the cleavage of an O-O bond and then the formation of a S-O bond and reduction of the peroxide to an oxo ligand as proposed by the Sharpless mechanism (Figure 1.12).[168]

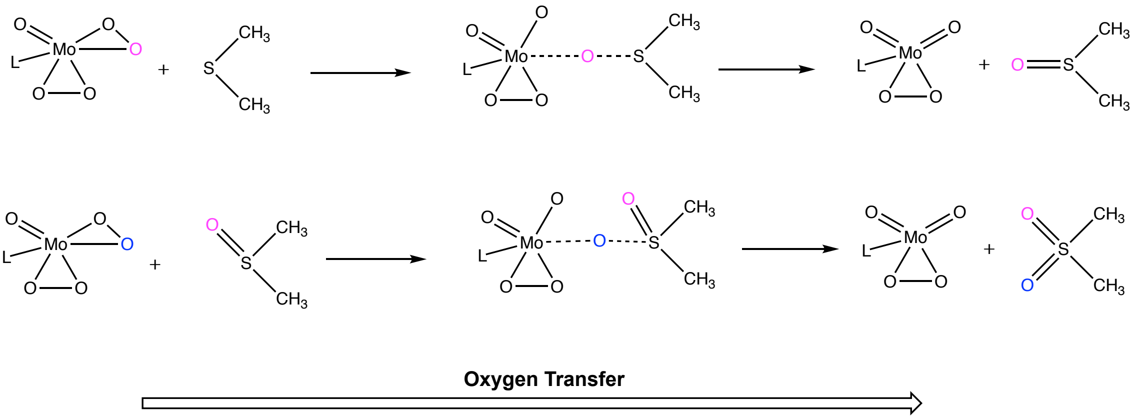

Figure 1.12. Reaction pathway for the oxygen atom transfer process from oxo-diperoxo molybdenum complexes to sulfides and sulfoxides.

Recently, Carrasco *et al*. [152] performed some DFT studies for sulfoxidation mechanism involving oxo-diperoxomolybdenum complexes $[MoO(O_2)_2L]$ where L corresponds to Mepz, dmpz and H_2O, contemplating the presence of H_2O_2 as oxidant, which was not analysed in reports described above by Sensato *et al*. [168, 169]. During the studies the solvent effects were not considered, since these usually do not promote an alteration of energy profiles. The possibility of the substrate entering as a ligand in the vacant position of the oxo-diperoxo complex $[MoO(O_2)_2L]$ (Mimoun mechanism in Figure 1.12) was discarded due to the low enthalpic contribution that would not compensate the unfavourable entropic one.[152] Analysing Figure 1.13, it is possible to understand the importance of H_2O_2 for the sulfoxidation process, since this oxidant allows a continuous catalytic cycle, obtaining again the initial oxo-diperoxomolybdenum active species, allowing to proceed the oxidative process from sulfoxide to sulfone (the sulfoxide product can perform a second nucleophilic attack over one peroxo ligand).[152] As previously mentioned, the homologous oxo-monoperoxo complex $[MoO_2(O_2)L]$ is substantially less active than the oxo-diperoxomolybdenum complex.[169]

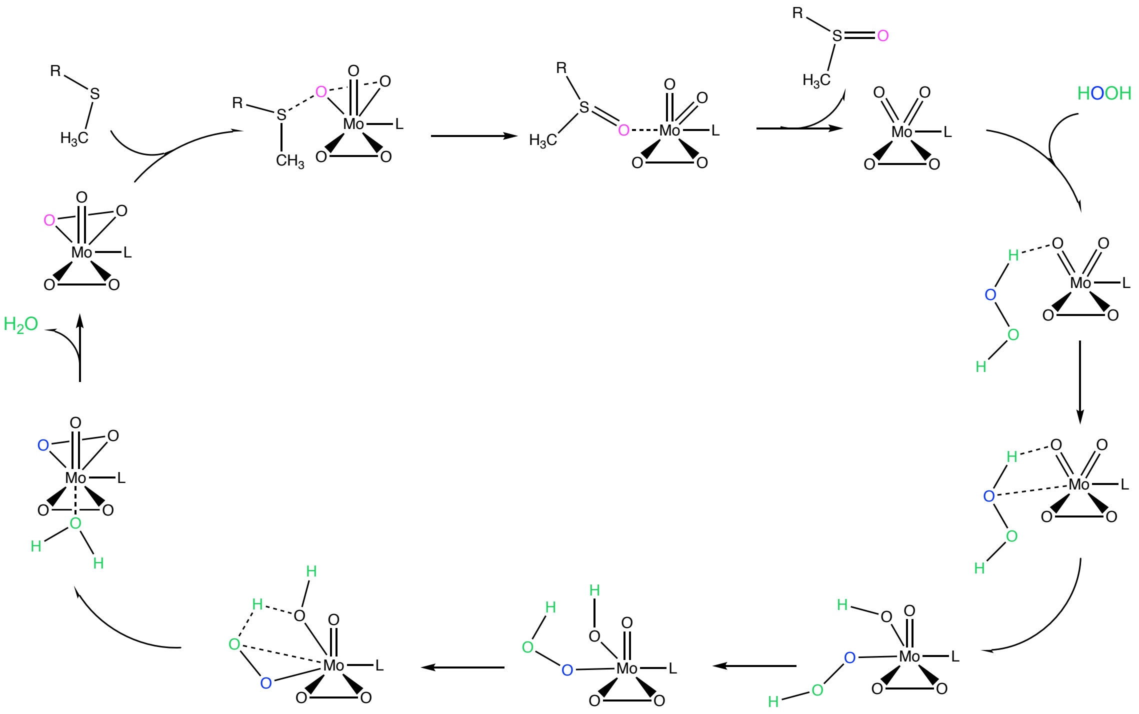

Figure 1.13. Catalytic cycle theoretically investigated for sulfoxidation of CH_3SR (R = CH_3, Ph) with H_2O_2 catalysed by oxo-diperoxo complexes $[MoO(O_2)_2L]$.[152]

Under similar conditions, the authors also tested the viability of the Thiel mechanism [148, 149] proposed for olefin epoxidation catalysed by oxo-diperoxomolybdenum complexes. This mechanism implies that (i) the oxidizing agent coordinates to the Mo(VI) center, (ii) undergoes a proton transfer to one of the peroxo ligands and (iii) is activated for oxygen transfer by η^2-coordination (Figure 1.14).[170] Considerable energetic differences observed between both mechanisms, indicated that the Sharpless mechanism is favoured.

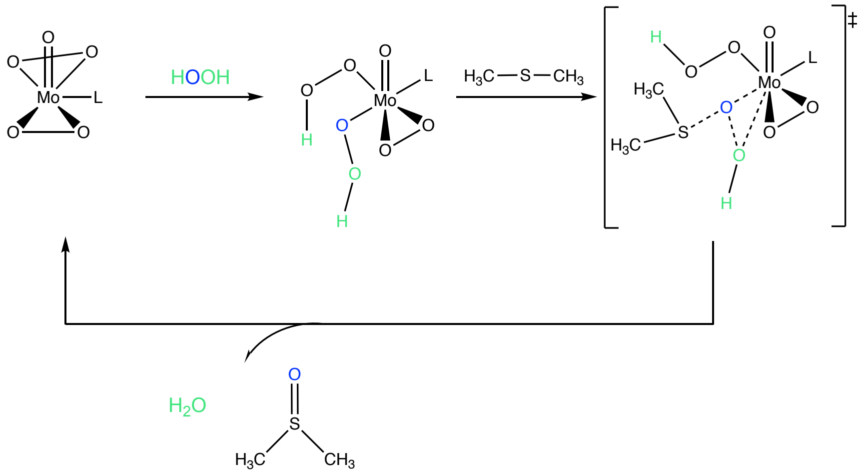

Figure 1.14. Catalytic Thiel-type cycle theoretically investigated for the oxidation of CH_3SCH_3 to sulfoxide with H_2O_2 catalysed by oxo-diperoxo $[MoO(O_2)_2L]$.

Oxo-peroxomolybdenum complexes are important catalysts for oxygen transfer reactions, resulting in more mechanistic and catalytic studies. In contrast, the organometallic oxo complexes have not been so extensively used, as observed by the number of publications described in Table 1.2.[160-162] A similar report to the theoretical DFT studies presented by Carrasco *et al.* [152] was also performed by Calhorda and coworkers [105] for sulfoxidation focusing on cyclopentadienyl dioxomolybdenum complexes $[CpMoO_2Cl]$ (Cp = cyclopentadienyl, η^5-C_5H_5) and H_2O_2 as oxidant. The barriers calculated and showed in Figure 1.15 indicated that the most favourable path involved the oxo-peroxo complex **C** as the better active species for the sulfoxidation reaction than complex [CpMoO(OH)(OOH)Cl] (**D**).[105] Interestingly, this is contrary to the result found for olefin epoxidation, where the active specie **C** is known to be inactive and calculated barriers are much higher.[105] The oxidation of sulfides and sulfoxides from **C** can occur by different pathways. One option is based on an outer-sphere nucleophilic attack of the substrate (sulfide or sulfoxide) on one oxygen atom of the oxidant that is activated through coordination to the Mo center, and subsequent formation of oxidized sulfur species and regeneration of complex **A.** The alternative hypothesis, that is more favoured for olefin epoxidation, is related with another intermediate species, namely $[CpMo(OH)(O_2)(OOH)Cl]$, whose formation results from another portion of H_2O_2 in order to activate the OH bond. The first option is the most thermodynamically favoured (Figure 1.16).[105]

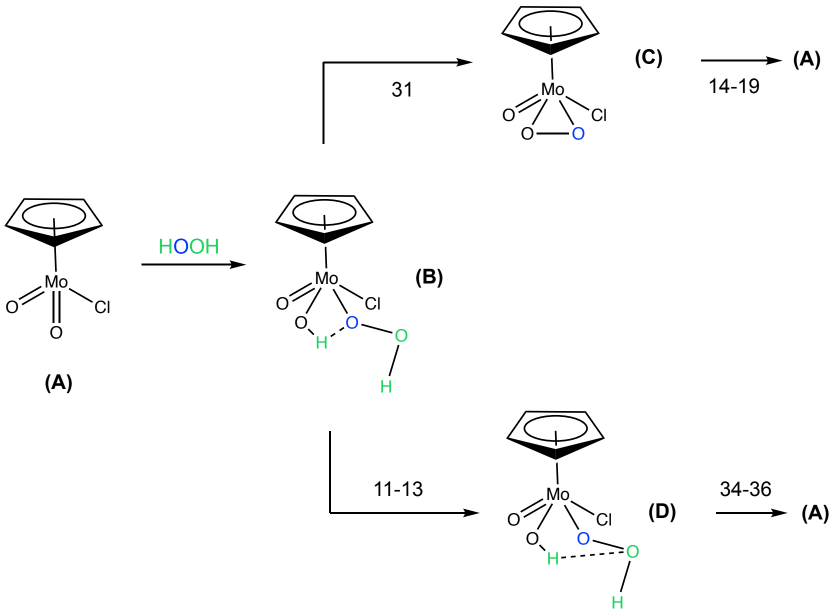

Figure 1.15. Preferred active species for sulfoxidation (energy barriers are presented in kcal.mol^{-1}).

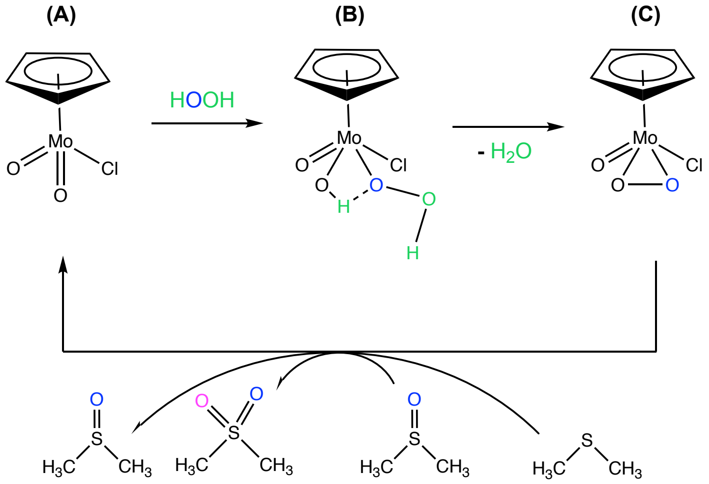

Figure 1.16. Catalytic cycle for sulfoxidation using a cyclopentadienyl molybdenum complex **A** as catalyst and H_2O_2 as oxidant.

During the sulfoxidation theoretical studies, authors also analysed the mechanism proposed with MoO_2Cl_2 as catalyst with H_2O_2, which revealed to be very similar and followed the same Sharpless-type mechanism to that described for the cyclopentadienyl dioxomolybdenum complex [$CpMoO_2Cl$] (**A**).[105] Specifically, in this case the reaction takes place in water, therefore one water molecule and the oxidant coordinated to the Mo center to complete the coordination sphere (Figure 1.17). The α-

hydrogen of H_2O_2 migrates to the water oxygen, while one hydrogen of the same water moves to the Oβ atom of oxidant, making the Oα atom available to suffer an external attack from the substrate and thus producing the corresponding sulfoxide or sulfone.[171, 172] Both systems presented the same outer-sphere mechanism, however in the present case occurs the coordination of the final product to the metal center, as a result from the coordinative unsaturation of the MoO_2Cl_2. Interestingly, by the mechanisms calculated for both substrates (sulfide and sulfoxide) it was noted that the second process (formation of sulfone) is thermodynamically more favourable, i.e. it is not easy to prevent the oxidation of sulfides to sulfones.

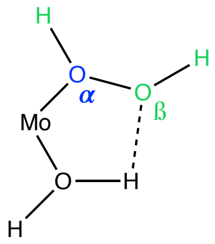

Figure 1.17. Schematic diagram showing the coordination of the water and H_2O_2 and the corresponding designation of α and β oxygen atoms.

1.5. Purpose of the present thesis

The increasing concern about the problems associated with sustainable development and the urgency for “greener” technologies inevitably contributed to the development and dissemination of catalytic processes, mainly those related with oxidative transformations. These are essential in chemistry, industry, for fine chemical and in other several application areas, from petroleum to pharmaceutic and agrochemical industries. Therefore, the main goal of this PhD in Sustainable Chemistry was the development of novel catalytic systems based on sustainable experimental conditions for efficiently desulfurizing model and real liquid fuels (diesel, gasoline and jet fuel). The Mo(VI)-oxo complexes and H_2O_2 were the epicenter of the current work, from which all systems emerged.

The catalytic activity and stability of a wide variety of molybdenum(VI) complexes, from dioxomolybdenum(VI) complexes containing monodentate or bidentate ligands to tricarbonyl and peroxomolybdate derivative compounds, were explored for the first time for the oxidation of refractory sulfur compounds present in fuels, using H_2O_2 as environmentally friendly oxidant. By the discussion performed in Section 1.4.1 and 1.4.2

it was demonstrated the scarce catalytic and mechanistic studies performed in this area. Therefore, the work developed here represents an important contribution for development in this catalytic area, identifying, when possible, the active species involved.

A special attention was also given to the reaction conditions, from which the solvent chosen was considered a crucial parameter, since the application of the wrong solvent may result in the removal of desirable aromatic and olefinic compounds from the fuel, modifying the fuel properties. Due to the harmful consequences resulting from the use of conventional organic solvents, attention was paid to ionic liquids which possess unique physical and “greener” properties. In order to decrease the cost associated to their production and the energy necessary to promote their regeneration, low amounts of these solvents were used wherever possible. In a more radical approach, solvent-free systems (monophasic) were used. All the explored systems were executed using a multicomponent model diesel containing three or more refractory sulfur compounds, e.g. dibenzothiophene, benzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. Once the best conditions were reached, the work proceeded to the treatment of untreated real liquid fuels, i.e. diesel (2300 ppm S) and jet fuel (1100 ppm S) provided by Galp Energia. Besides sulfur compounds which are present in several forms (mercaptans, sulfides, disulfides, thiophenes and their derivatives), the fuels also possess a complex mixture of hydrocarbons, which has a strong impact on the efficiency of the oxidative desulfurization process. This complex fuel composition can promote a competitive oxidation with other compounds besides sulfur, decreasing the efficiency for the oxidation of the sulfur compounds. Therefore, to maximize the catalyst performance (desulfurization efficiency) for the treatment of real fuel samples, optimization studies were performed (solvent, temperature, H_2O_2 and catalyst amounts).

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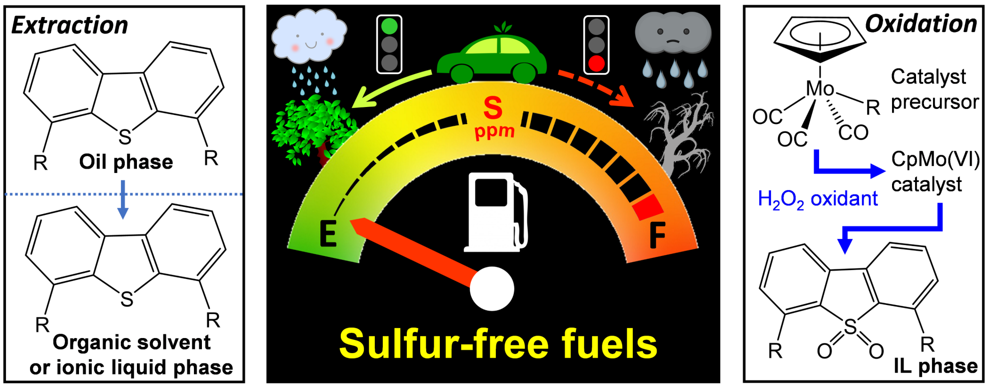
Chapter 2

ORGANOMETALLIC CATALYST PRECURSORS: [CpMo(CO)$_3$R]



2. Organometallic catalyst precursors: [CpMo(CO)$_3$R]

2.1. Introduction

Molybdenum complexes are composed of several classes of compounds, among which stands out the complexes featuring a η^5-coordinated cyclopentadienyl (Cp) ligand, [CpMoO$_2$R] (Cp = η^5-C$_5$H$_5$). The high catalytic efficiency of this class of compounds is well known for oxygen transfer reactions.[1] The first work was published in 1991, when Trost and Bergman [2] tested these complexes as catalysts for olefin epoxidation with *t*BHP oxidant. However, the application of these complexes as active catalysts stagnated for several years, during which time the congeners CpReO$_3$ were preferred due to the ease and efficiency of the synthesis methods.[3]

The possibility to obtain [CpMoO$_2$R] complexes from the parent tricarbonyls, [CpMo(CO)$_3$R], and using the latter as catalyst precursors under catalytic operation conditions [4], increased the investigation of these complexes, originating the synthesis of numerous unsubstituted or substituted cyclopentadienyl complexes comprising a diversity of different ligands, which are known to strongly influence the overall performance of the catalyst.[3, 5] Almost all mechanistic and catalytic studies using these complexes as catalysts were performed using *t*BHP as oxidant.[3] Analytical investigations provided by Poli *et al.* [6] revealed the remarkably stability of CpMo-based complexes in aqueous environments. These results provided significant advances in terms of green chemistry and sustainable development, from which benign processes can be developed attending to stringent environmental criteria.[6] In oxidative catalysis, a greener path passes for the substitution of less sustainable oxidants and volatile solvents for environmentally friendly components. From a waste-avoidance perspective,

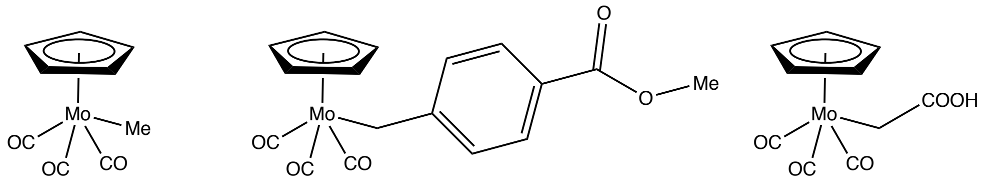
H_2O_2 is the best option; however, there are only a few reports on the use of [$CpMo(CO)_3R$]/H_2O_2 systems in the oxidation of sulfides.[7, 8]

This chapter describes the first investigation of the use of [$CpMo(CO)_3R$] (Cp = η^5-C_5H_5) complexes in oxidative desulfurization (ODS) processes. The application of three different [$CpMo(CO)_3R$] complexes as homogeneous catalysts is presented. The ODS systems studied combined catalytic oxidation and extraction stages, using H_2O_2 oxidant and an ionic liquid (IL) as extraction solvent to desulfurize a multicomponent model and untreated real liquid fuels (diesel and jet fuel). The recyclability of [$CpMo(CO)_3R$]@IL systems was studied for several consecutive cycles.

2.2. Results and Discussion

2.2.1. Organometallic catalyst precursors

Three organometallic molybdenum complexes were used as catalyst precursors for desulfurization of a model diesel and real liquid fuels: [$CpMo(CO)_3Me$] (**1**), [$CpMo(CO)_3CH_2$-*p*C_6H_4-CO_2Me] (**2**) and [$CpMo(CO)_3CH_2COOH$] (**3**) (Figure 2.1). A detailed description of their preparation and corresponding characterization is described in Section 2.4.



1 **2** **3**

Figure 2.1. Catalyst precursors [$CpMo(CO)_3R$] (**1**-**3**).

2.2.2. Desulfurization of a model diesel

A multicomponent model diesel containing 2000 ppm of sulfur was prepared by dissolution of DBT, BT, 4-MDBT and 4,6-DMDBT in *n*-octane. In a typical ODS process, the catalyst precursor of the type [$CpMo(CO)_3R$] was added to the extraction solvent, followed by addition of the model diesel resulting in a biphasic system. This mixture was stirred for 10 min at 50 °C to perform an initial extraction where a certain amount of the sulfur compounds present in the model diesel phase was transferred to the IL phase. After this, aq. H_2O_2 was added to the system to initiate the metal-catalysed oxidation of the extracted sulfur compounds, which promotes ongoing extraction of the diesel phase by decreasing the concentration of non-oxidized sulfur compounds in the extractant phase (Figure 2.2). It is noteworthy that no desulfurization of the model diesel was observed after the initial extraction stage in the presence of H_2O_2 and absence of catalyst.

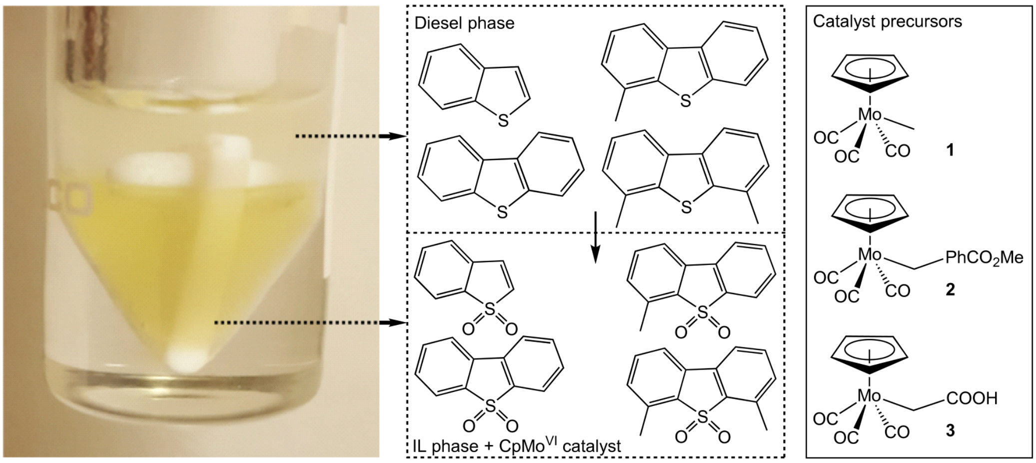


Figure 2.2. Typical ODS reaction mixture and ODS process for the catalyst precursors [CpMo(CO)$_3$R] (**1**-**3**).

2.2.2.1. Optimization studies

With the objective of optimizing the ODS conditions, the influence of some experimental parameters on the removal of sulfur compounds from the multicomponent model diesel was investigated, using complex [CpMo(CO)$_3$Me] (**1**) as catalyst precursor. The evaluated parameters were the type of extraction solvent (MeOH, MeCN and two different imidazolium ILs - [BMIM]PF$_6$ and [BMIM]BF$_4$), the volume ratio model diesel/extraction solvent (1:1, 1:0.5, 1:0.3), the type and amount of oxidant (*t*BHPaq or H_2O_2; 0.60, 0.30, 0.22 and 0.15 mmol of H_2O_2), the amount of catalyst **1** (10-30 μmol) and the reaction medium temperature (25 and 50 °C).

The extraction capacity as reaction medium of four different solvents were analysed for the ODS process using 0.750 mL of extraction solvent and 0.750 mL of the model diesel with a reaction temperature of 50 °C in the presence of 10 μmol of catalyst **1** and 0.60 mmol of H_2O_2. The influence of each solvent (MeOH, MeCN, [BMIM]PF$_6$ and [BMIM]BF$_4$) on desulfurization is illustrated in Figure 2.3. For the initial extraction stage, the desulfurization of each sulfur compound followed the order BT > DBT > 4-MDBT > 4,6-DMDBT. This order is related with the molecular diameter and geometry of each sulfur compound, as well as with their solubility in different polar solvents.[9] Considering all of the sulfur compounds present in the model diesel, the initial extraction performance followed the order MeCN > [BMIM]BF_4 > [BMIM]PF_6 > MeOH. However, in the oxidative catalytic stage, which is initiated by the addition of H_2O_2 to the ODS system, a near complete desulfurization of the model diesel was achieved in the presence of [BMIM]PF_6 after 5 h of reaction at which point only 35 ppm of BT persisted in the model diesel phase. This difficulty in removing BT is usually accounted as an effect of the electron density at the S atom.[10-13] For equal reaction time (5 h), the desulfurization efficiency of each extraction solvent followed the order MeOH (83.1%) < [BMIM]BF_4 (85.3%) < MeCN (90.9%) < [BMIM]PF_6 (98%). Therefore, [BMIM]PF_6 proved to be the preferred extraction solvent and reaction medium for chemical oxidation, despite its low extraction efficiency during the initial extraction stage when compared to MeCN. This behaviour has been noted previously for desulfurization systems and can be associated with the water-immiscibility of [BMIM]PF_6, which results in the formation of a triphasic system (diesel/H_2O_2/IL) in the presence of aqueous H_2O_2 and model diesel.[14, 15]

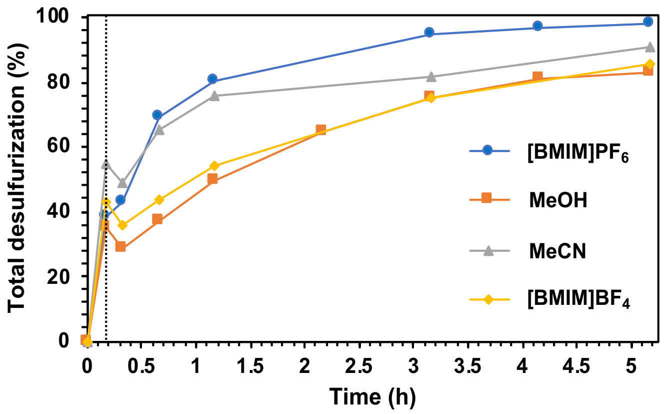


Figure 2.3. Desulfurization of a model diesel (2000 ppm S) using [CpMo(CO)$_3$Me] (**1**) (10 μmol) as catalyst precursor in the presence of different extraction solvents with H_2O_2 (0.60 mmol) oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The diesel/extraction solvent volume ratio is an important parameter in an ODS process mainly due to the high cost of ILs. To minimize these drawbacks and favour application of ILs in ODS processes, it is necessary decrease the dosage of IL. To investigate the effect of the diesel volume/[BMIM]PF_6 ratio, a comparative study was performed in which model diesel/[BMIM]PF_6 volume ratios of 1:1, 1:0.5 and 1:0.3 were tested, using 10 μmol of catalyst **1** in the presence of 0.60 mmol of H_2O_2 at 50 °C. Figure 2.4 displays the desulfurization profiles obtained for different volume ratios of model diesel/[BMIM]PF$_6$. The consequences of a decrease in the volume ratio are mainly evident during the initial extraction stage, where a higher transfer of sulfur compounds from the model diesel to the IL was obtained for the 1:1 ratio. The extraction yield decreased linearly with the decrease in the volume ratio (from 42.7% to 23%). These results were expected since a higher IL volume results in an improvement of the transfer of non-oxidized sulfur compounds from the model diesel to the IL phase. However, during the catalytic stage, the influence of the volume ratio was less perceptible since a complete desulfurization was obtained after 6 h of ODS reaction using all model diesel/[BMIM]PF$_6$ volume ratios. The different effects of model diesel/IL volume ratios observed during the initial extraction and catalytic stages can be related with the sulfur Nernst partition coefficients that are more sensitive to chemical extraction than purely physical extraction.[16, 17] In other words, the similar catalytic efficiency observed for each model diesel/[BMIM]PF$_6$ system must be due to the oxidation of the sulfur compounds, since the oxidized species possess a polarity comparable to the IL, facilitating the desulfurization through the continued transfer of sulfur compounds from the model diesel to the IL phase during the ODS process, independently of the model diesel/[BMIM]PF$_6$ volume ratios.

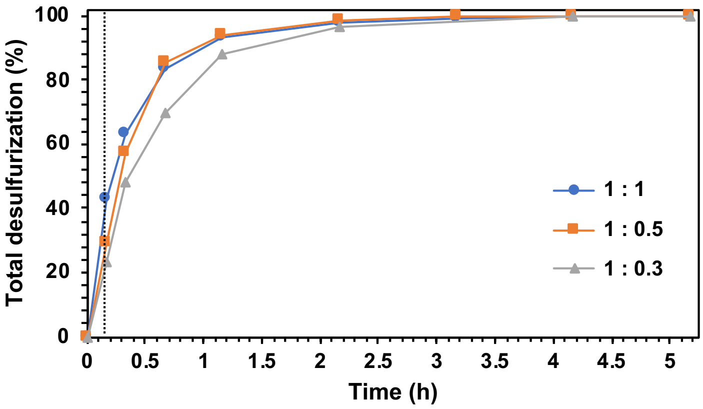


Figure 2.4. Desulfurization of a model diesel (2000 ppm S) using [CpMo(CO)$_3$Me] (**1**) (10 μmol) as catalyst precursor, in the presence of different volume ratios of model diesel/[BMIM]PF$_6$, with H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The influence of different amounts of catalyst **1** (10, 20 and 30 μmol) was investigated in desulfurization of the model diesel, maintaining all the other reaction conditions constant (model diesel/[BMIM]PF_6 volume ratio = 1:0.3, 0.60 mmol of H_2O_2 and 50 °C) (Figure 2.5). The efficiency of the ODS processes was similar using 10 or 20 *μ*mol of the catalyst since these presented similar desulfurization profiles. A slight increase of desulfurization is observed using 30 *μ*mol of catalyst, mainly during the first 2 h of reaction. After 4 h a complete desulfurization was observed in the presence of 30 *μ*mol of catalyst, while 81 and 19 ppm of S were still present in the model diesel using 10 and 20 *μ*mol catalyst, respectively.

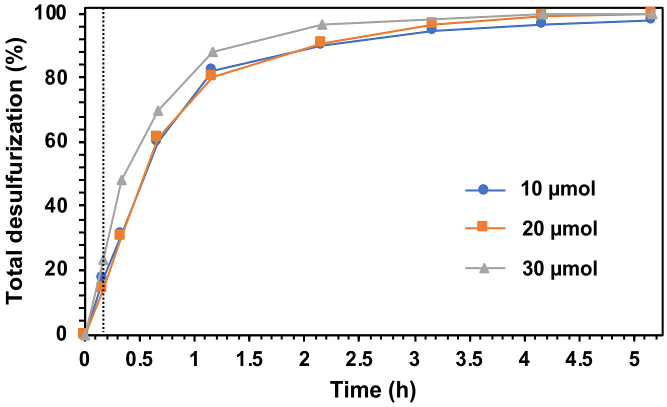


Figure 2.5. Desulfurization of a model diesel (2000 ppm S) using different amounts of [CpMo(CO)$_3$Me] (**1**) as catalyst precursor, [BMIM]PF_6 (0.250 mL) as extraction solvent, H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Using the best experimental conditions observed so far (model diesel/[BMIM]PF_6 volume ratio = 1:0.3, 30 *μ*mol of catalyst **1** and 50 °C), the amount of 30% aq. H_2O_2 was varied in the range 0.15-0.60 mmol. Figure 2.6 displays the desulfurization profiles of the multicomponent model diesel using different amounts of oxidant (0.60, 0.30, 0.22 and 0.15 mmol). The highest desulfurization of the model diesel was obtained using 0.30 mmol of H_2O_2, where a complete desulfurization was achieved after 2 h. It is noteworthy that at 1 h, only 9 ppm of sulfur was present in the model diesel. The slower desulfurization registered with the higher amount of H_2O_2 (0.60 mmol) can be related with a decrease in contact area between the model diesel and the IL phase containing the catalyst since the aqueous H_2O_2 phase is located between these two phases.[14]

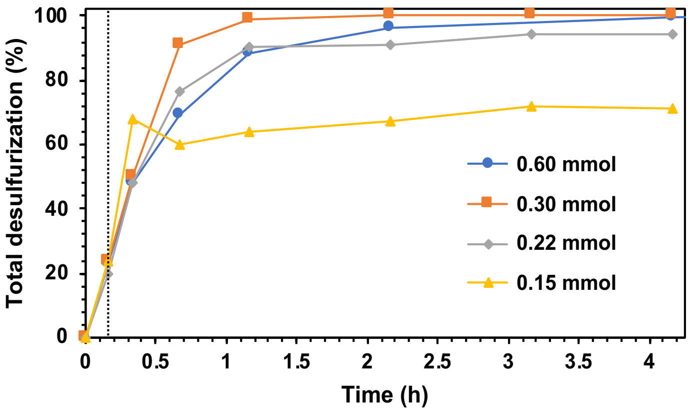


Figure 2.6. Desulfurization of a model diesel (2000 ppm S) using [CpMo(CO)$_3$Me] (**1**) (30 μmol) as catalyst precursor, [BMIM]PF$_6$ as extraction solvent (0.250 mL), and different amounts of H_2O_2 as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

During the desulfurization process of real liquid fuels high temperatures (> 80 °C) must be avoided in order to preserve some of the constituents of these complex mixtures responsible for the quality of the fuel. Therefore, two different temperature values were applied to the reaction medium, namely 25 °C and 50 °C (Figure 2.7). The desulfurization efficiency obtained at room temperature showed to be lower than 50 °C, in which the major difference was observed during the catalytic oxidative step. After 1 h of oxidation only 75% of desulfurization of model diesel was achieved at 25 °C instead of near complete desulfurization at 50 °C.

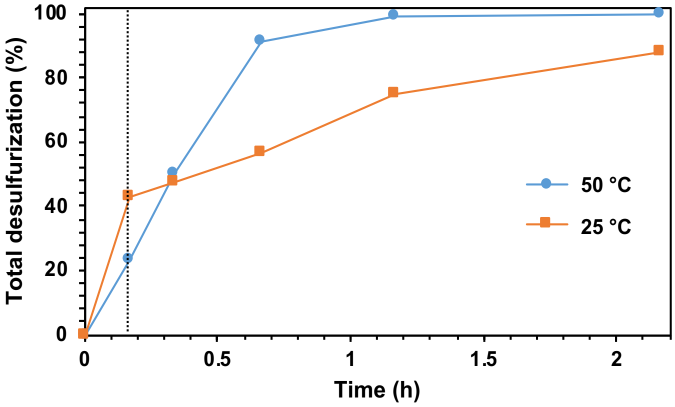


Figure 2.7. Desulfurization of a model diesel (2000 ppm S) using [CpMo(CO)$_3$Me] (**1**) (30 μmol) as catalyst precursor, [BMIM]PF$_6$ (0.250 mL) as extraction solvent, and H_2O_2 (0.30 mmol) as oxidant and different reaction temperatures. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Various reported works present the *tert*-butyl hydroperoxide (*t*BHP) as a success oxidant for the oxidative catalytic systems using molybdenum complexes as catalysts.[3, 18-20] Therefore, the desulfurization efficiency of the optimized catalytic system was investigated using aqueous *t*BHP (*t*BHPaq) instead of H_2O_2, keeping the other parameters constant (reaction temperature of 50 °C, 30 μmol of catalyst precursor **1** and 1:0.3 (*v*/*v*) model diesel/[BMIM]PF_6). Results displayed in Figure 2.8 show a complete desulfurization after 1 h using H_2O_2 oxidant, while in the presence of *t*BHPaq the obtained desulfurization after 2 h was approximately 84%. The different rates observed during the catalytic stage for each oxidant can be related with the possibility of specific catalytic pathways using H_2O_2 and *t*BHPaq. However, both ODS systems presented a yellow coloured phase after addition of H_2O_2 or *t*BHPaq, indicating the formation of active species in both systems, since the yellow colour is generally associated with the presence of active oxo-peroxomolybdenum(VI) species (Figure 2.2).[15, 21]

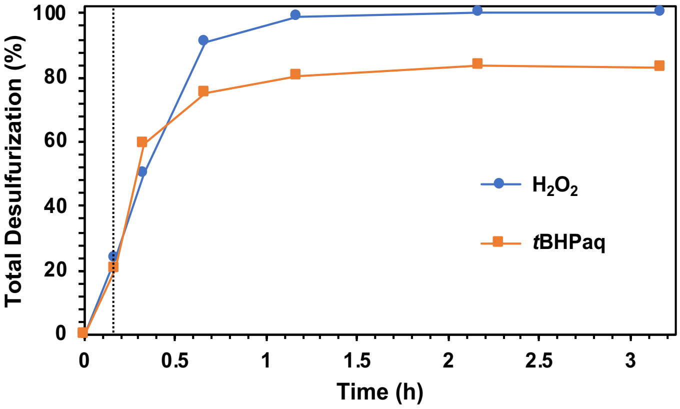


Figure 2.8. Desulfurization of a model diesel (2000 ppm S) using [CpMo(CO)$_3$Me] (**1**) (30 μmol) as catalyst precursor, [BMIM]PF_6 (0.250 mL) as extraction solvent, and H_2O_2 or *t*BHPaq (0.30 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

2.2.2.2. Comparison of [CpMo(CO)$_3$R]@[BMIM]PF_6 efficiency

After optimization of the ODS conditions using [CpMo(CO)$_3$Me] catalyst, the desulfurization performance of other [CpMo(CO)$_3$R] (R = CH_2PhCO_2Me (**2**) and CH_2COOH (**3**)) catalyst precursors was investigated (Figure 2.1). The desulfurization profile was compared for the three catalyst precursors (30 μmol) using the optimized experimental conditions, i.e. 1:0.3 model diesel/[BMIM]PF_6 volume ratio, 0.30 mmol of H_2O_2, and a reaction temperature of 50 °C (Figure 2.9). As expected, the initial extraction obtained in the presence of the various catalysts was similar (around 20%) since the extraction stage is generally only influenced by the extraction solvent efficiency. During the oxidative catalytic stage, which begins after addition of the oxidant, different desulfurization efficiencies were observed for each catalyst. A complete desulfurized model diesel was obtained in the presence of catalyst precursor **1** after 2 h of ODS reaction (at 1 h only 8 ppm of sulfur remained in the model diesel), while at the same reaction time catalyst precursor **2** led to 95% desulfurization and catalyst precursor **3** to 80% desulfurization. Catalyst precursor **3** presented the lowest oxidative desulfurization efficiency, with a reaction time of 4 h being required to obtain sulfur-free model diesel. Thus, the reactivity order of the catalysts was **1** > **2** > **3**. The main reason for the different catalytic activity observed may be caused by distinct steric hindrance effects promoted by the difference of –R size groups present in $[CpMo(CO)_3R]$ catalyst precursors. This effect will promote a different interaction rate between the complex and the oxidant to form active catalytic species, i.e. oxo-peroxomolybdenum(VI) complexes. Comparing the catalytic activity of complexes **2** and **3**, the presence of a substituent on the phenyl ring in its molecular structure may lead to activation of the phenyl ring, which may affect the catalytic efficiency.[7] According to the literature, complexes of the type $[CpMo(CO)_3R]$ can be oxidized into the corresponding dioxo $[CpMoO_2R]$ and oxo-peroxo $[CpMoO(O_2)R]$ derivatives using H_2O_2 or *t*BHPaq oxidants. The $[CpMoO_2R]$ are intermediates in the formation of $[CpMoO(O_2)R]$; both CpMo(VI) species are recognized as being active catalysts for oxidation reactions.[22] The oxo-peroxo complexes present a characteristic yellow colour, as observed in this work (Figure 2.2).

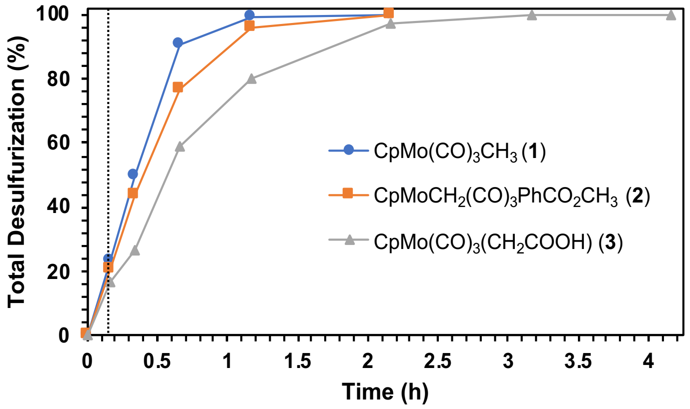


Figure 2.9. Desulfurization profile of a model diesel using different catalyst precursors **1**, **2** and **3** in the presence of $[BMIM]PF_6$ (0.250 mL) as extraction solvent and H_2O_2 (0.30 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

2.2.2.3. [CpMo(CO)$_3$R]@[BMIM]PF$_6$ recyclability and reutilization

Recyclability and reutilization tests were performed for several ODS cycles using the complexes [CpMo(CO)$_3$R] as precursors to homogeneous catalysts. Since the catalysts could not be removed from the reaction medium, the extraction phase containing the catalyst entrapped in [BMIM]PF$_6$ was reused and recycled for at least five consecutive ODS cycles (Figure 2.10, 2.11 and 2.12). After removal of the model diesel phase at the end of each ODS cycle, different procedures were performed for the "reused" and "recycled" series of reactions. In the reused ODS tests, a fresh portion of model diesel was added to the IL phase and, after completing the initial extraction stage, fresh oxidant was added to start the catalytic stage. In the recycled ODS tests, the IL phase was washed with a mixture of ethyl acetate and diethyl ether (1:1 *v*/*v*) to remove the sulfur-containing compounds resulting from the extraction/oxidation processes, and then fresh portions of model diesel and oxidant were added sequentially as carried out for the reused ODS tests. The results showed that for all three catalysts precursors **1**-**3**, both the reused and recycled ODS systems were stable up to and including the third cycle. However, during the fourth and fifth cycles the reused systems generally display a loss in efficiency, especially noticeable for the most active precursor **1**. This fall-off in desulfurization efficiency probably occurs due to the saturation of the extraction phase with the oxidized sulfur compounds along the various consecutive cycles, blocking the extraction of more portions of sulfur compounds from the model diesel, thus promoting a decrease of desulfurization efficiency. Accordingly, the washing treatment prevents the saturation of sulfur compounds in the IL phase, promoting a continuous extraction/oxidation for various ODS cycles as shown in Figure 2.10, in which near-complete desulfurization is maintained for seven cycles.

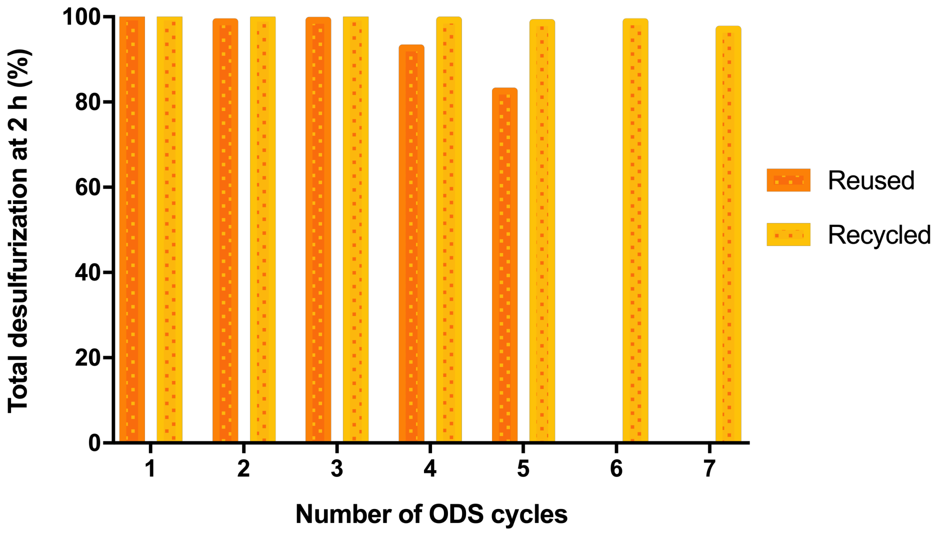


Figure 2.10. Desulfurization data for five and seven consecutive reused and recycled ODS cycles, respectively, using [CpMo(CO)$_3$Me] (**1**) (30 μmol) as catalyst precursor, a model diesel and [BMIM]PF$_6$ with a volume ratio of 1:0.3, at 50 °C with H_2O_2 (0.30 mmol) as oxidant. Results obtained after 2 h of ODS reaction.

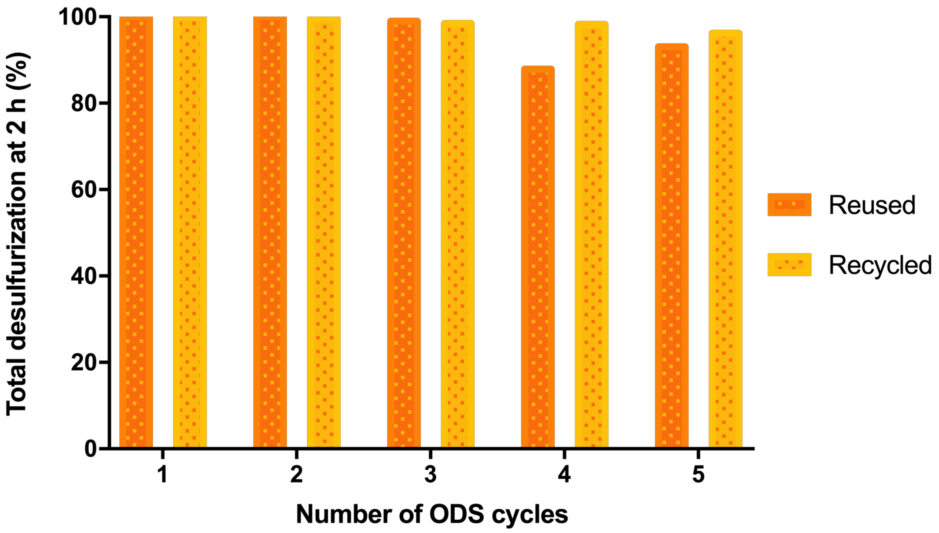


Figure 2.11. Desulfurization data for five consecutive reused and recycled ODS cycles, using [CpMo(CO)$_3$(CH$_2$-*p*C$_6$H$_4$-CO$_2$Me] (**2**) (30 μmol) as catalyst precursor, a model diesel and [BMIM]PF$_6$ with a volume ratio of 1:0.3, at 50 °C with H_2O_2 (0.30 mmol) as oxidant. Results obtained after 2 h of ODS reaction.

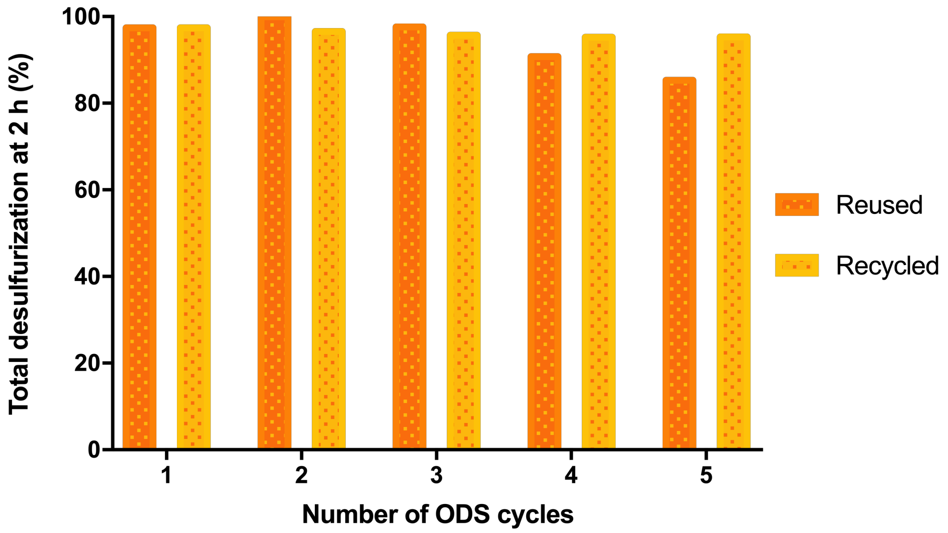


Figure 2.12. Desulfurization data for five consecutive reused and recycled ODS cycles, using $[CpMo(CO)_3CH_2COOH]$ (**3**) (30 μmol) as catalyst precursor, a model diesel and $[BMIM]PF_6$ with a volume ratio of 1:0.3, at 50 °C with H_2O_2 (0.30 mmol) as oxidant. Results obtained after 2 h of ODS reaction.

2.2.3. Desulfurization of real liquid fuels

The catalyst precursor that revealed the highest desulfurization efficiency ($[CpMo(CO)_3Me]$ (**1**)) was used in the oxidative desulfurization of untreated real liquid fuels supplied by Galp Energia (a diesel with ca. 2300 ppm S and a jet fuel sample with ca. 1100 ppm S). The main families of sulfur compounds present in this untreated diesel were benzothiophene and dibenzothiophene derivatives.[23] The desulfurization process of the untreated real diesel and jet fuel was performed using the same conditions applied for the ODS of the model diesel. To verify the effect of the extraction time, extraction tests using equal proportions of untreated diesel and MeCN were performed with durations of 5, 10 and 30 min. According to the results presented in Table 2.1, the extraction efficiency was not time dependent, since the sulfur content present in the real diesel after 5, 10 and 30 min of extraction was practically equal regardless of the time applied. However, maintaining the extraction time and using two different solvents, namely MeCN and DMF, a better desulfurization efficiency was obtained using DMF (34.2%) than MeCN (17.8%). For desulfurization of the jet fuel, the best result was achieved in the presence of MeCN, which can be related with the polarity and the chemical composition of this fuel.

The real diesel and jet fuel were further desulfurized through a catalytic oxidative step involving application of a biphasic fuel/$[BMIM]PF_6$ system in the presence of $[CpMo(CO)_3Me]$ (**1**) and H_2O_2 with a reactional temperature of 50 °C. The oxidative desulfurization of the diesel with an initial extraction of 10 min (1910 ppm S) catalysed by **1** allowed a sulfur removal from 1910 to 372 ppm S. The desulfurization of the real diesel increased when MeCN was used as final extraction solvent. Referring to Table 2.1 it is evident that MeCN possesses higher extraction efficiency than DMF after the oxidation process, which is the opposite of that observed during the initial extractions. This behaviour can be related with a higher affinity of the sulfoxides/sulfones towards MeCN, while the non-oxidized species possess more affinity to DMF. On the other hand, the time of the final extraction stage seemed to have an important influence in the desulfurization efficiency of the process, since a longer final extraction allowed higher desulfurization. Using MeCN as final extraction solvent, the desulfurization efficiency increased from 74.4% to 83.8% upon increasing the final extraction time from 10 to 30 min. In the case of jet fuel, the initial extractions with MeCN and DMF were similar with desulfurization efficiencies of 14.7% and 9.9%, respectively. When the catalytic oxidation using model diesel conditions occurred followed by final extraction with DMF and MeCN, jet fuels with low amounts of sulfur content were obtained (277 and 267 ppm, respectively). These results demonstrate that the oxidation is an important step for desulfurization of fuels, achieving better results when a conciliation of extraction and oxidation is achieved.

The remarkable high oxidation efficiency of the [CpMo(CO)$_3$Me] (**1**) catalyst is clarified when compared with other reported works for the oxidative desulfurization processes of real diesel using various homogeneous and heterogeneous metallic catalysts.[15, 23, 24]

Table 2.1. Experiments performed for desulfurization of untreated real diesel and jet fuel, using the model diesel conditions

Fuel	Catalyst	Extraction process[a]	Extraction time (min)	ODS process[b,c]	S content (ppm)	Desulfurization efficiency (%)
Diesel	----	MeCN	5	----	1920	16.5
		MeCN	10	----	1910	16.9
		MeCN	30	----	1890	17.8
		DMF	30	----	1513	34.2
	1	---	---	DMF[b]	1000	56.5
		---	---	MeCN[b]	1533	33.3
		MeCN	30	MeCN[b]	372	83.8
		MeCN	10	MeCN[c]	588	74.4
		MeCN	10	DMF[c]	521	77.3
		DMF	30	DMF[b]	384	83.3
Jet fuel	----	MeCN	30	----	938	14.7
	----	DMF	30	----	991	9.9
	1	----	30	DMF[b]	277	74.8
		MeCN	30	MeCN[b]	267	75.8

[a] Liquid-liquid fuel/organic solvent extraction of non-oxidized sulfur compounds during 30, 10 or 5 min at 70 °C.

[b] Oxidative desulfurization in a biphasic fuel/[BMIM]PF_6 system during 2 h using the same conditions applied for the model diesel with a final extraction with an organic solvent (MeCN or DMF) during 30 min.

[c] Oxidative desulfurization in a biphasic fuel/[BMIM]PF_6 system during 2 h using the same conditions applied for the model diesel with a final extraction with an organic solvent (MeCN or DMF) during 10 min.

2.3. Conclusions

In summary, complete desulfurization of a multicomponent model diesel was achieved after only 2 h, using 30 μmol of catalyst. A high desulfurization efficiency was also obtained for real diesel (83.8%, 372 ppm S) and jet fuel (75.8%, 267 ppm S), combining liquid-liquid extraction and an oxidative catalytic stage. The optimization of the ODS process was performed employing cyclopentadienyl molybdenum tricarbonyl complexes as catalyst precursors, an ionic liquid ([BMIM]PF_6) as solvent and aqueous H_2O_2 as oxidant, resulting a H_2O_2/S ratio of 6 and a reaction temperature of 50 °C. A key finding is that the net sulfur removal levels are strongly influenced by the catalytic sulfoxidation activity which is not the same for the different catalyst precursors investigated. The results are consistent with previous experimental and theoretical studies, indicating that [CpMo$(CO)_3$R] catalyst precursors react with the oxidant to give oxo-peroxo active species of the type [CpMoO(O_2)R] in which the Mo-bonded R group remains coordinated to the metal center, thereby influencing catalytic performance. This opens up the possibility of ODS optimization through ligand design and indeed such an approach has already been successful in optimizing [CpMo$(CO)_3$R] catalyst precursors for olefin epoxidation.[25, 26] Further work in our laboratories will therefore focus on preparing a wider range of cyclopentadienyl molybdenum complexes and evaluating their performance in catalytic ODS processes.

2.4. Experimental Section

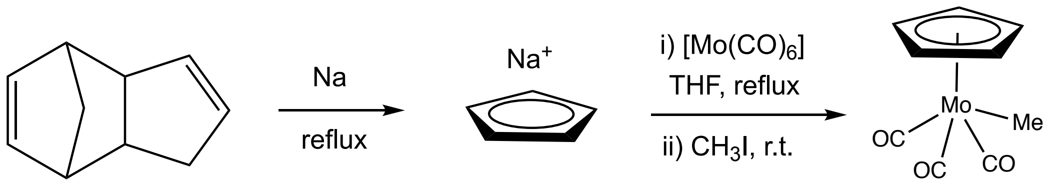
2.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: dibenzothiophene (Sigma-Aldrich, 98%), 1-benzothiophene (Fluka, 95%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), methanol (Sigma-Aldrich), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium tetrafluoroborate (Sigma-Aldrich, ≥98%), ethyl acetate (Fischer Chemical, analytical grade), diethyl ether (Merck), dimethylformamide (Fischer), 70 wt.% *tert*-butylhydroperoxide in water (*t*BHPaq, Sigma-Aldrich) and 30% w/v hydrogen peroxide (H_2O_2, Sigma-Aldrich). Untreated diesel and jet fuel samples containing 2300 and 1100 ppm S, respectively, were supplied by Galp Energia.

The desulfurization of the model diesel was monitored by a Bruker 430-GC-FID gas chromatograph, using a Supelco capillary column SPB-5 (30 m x 250 μm id.; 25 μm film thickness) and hydrogen as carried gas (55 $cm^3\ s^{-1}$). The analysis of sulfur content in the treated liquid fuels was performed by Galp Energia through ultraviolet fluorescence test method (ISO 20846), using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry (ISO 8754), using an OXFORD LAB-X, LZ 3125.

2.4.2. Catalyst precursors synthesis

[CpMo(CO)₃Me] (**1**) was synthetized by the reaction of Na[CpMo(CO)₃] with CH_3I.
Anal. Calcd for $C_9H_8MoO_3$ (260.90). Selected FT-IR (KBr, cm^{-1}): ν = 3435 (br), 3113 (m), 2979 (m), 2900 (m), 2816 (w), 2007 (vs, *ν*(CO)), 1903 (vs, *ν*(CO)), 1421 (m), 1159 (m), 1060 (w), 1006 (m), 912 (w), 822 (vs), 584 (s), 561 (vs), 486 (vs), 449 (vs). ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS): δ = 5.23 (s, 5H, C_5H_5), 0.30 (s, 3H, CH_3) ppm.[27]



1

Figure 2.13. Preparation of catalyst precursor **1**.

[CpMo(CO)₃(CH₂-*p*C₆H₄-CO₂Me] (**2**) was synthetized by addition of methyl 4-(bromomethyl)benzoate to Na[CpMo(CO)₃].

Anal. Calcd for $C_{17}H_{14}MoO_5$ (394.23): C, 51.79; H, 3.58. Found: C, 51.98; H, 3.65%. Selected FT-IR (KBr, cm^{-1}): ν = 2004 (vs, *ν*(CO)), 1936 (vs, *ν*(CO)), 1906 (vs, *ν*(CO)), 1705 (vs, *ν*(C=O), 1598 (vs), 1282 (s). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.79 (d, J = 6.2 Hz, 2H, pC_6H_4), 7.22 (d, J = 6.2 Hz, 2H, pC_6H_4), 5.26 (s, 5H, Cp), 3.84 (s, 3H, O-CH_3), 2.88 (s, 2H, CH_2-pC_6H_4) ppm. $^{13}C\{^1H\}$ (126 MHz, CD_2Cl_2, 298 K): δ = 240.1 (CO *trans* CH_2-pC_6H_4-CO_2CH_3), 228.9 (2 CO *cis* CH_2-pC_6H_4-CO_2CH_3), 167.4 (C^8), 158.5 (C^2), 129.5 ($C^{4,6/3,7}$), 127.6 ($C^{4,6/3,7}$), 125.5 (C^5), 94.4 (Cp), 51.9 (C^9), 4.1 (C^1) ppm. $^{13}C\{^1H\}$ HSQC (126/400 MHz, CD_2Cl_2, 298 K): δ ^{13}C/δ ^1H = 129.5/7.79 ($C^{4,6/3,7}H$), 129.5/7.22

($C^{4,6/3,7}H$), 94.4/5.26 (Cp), 51.9/3.84 (C^9H_3), 4.1/2.88 (C^1H_2-$p$$C_6H_4$) ppm. ^{95}Mo (26 MHz, CD_2Cl_2, 298 K): δ = - 1546 ppm. ^{13}C CP MAS NMR: δ = 240.7 (CO), 229.0 (CO), 166.5 (C^8), 157.9 (C^2), 130.1 ($C^{4,6/3,7}$), 126.8 ($C^{4,6/3,7}$), 122.9 (C^5), 94.4 (Cp), 51.9 (C^9), 4.6 (C^1) ppm.[21]

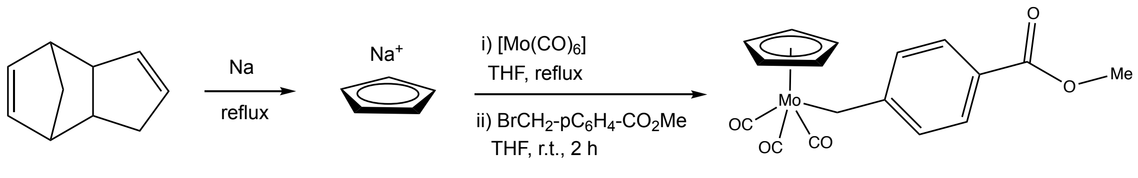


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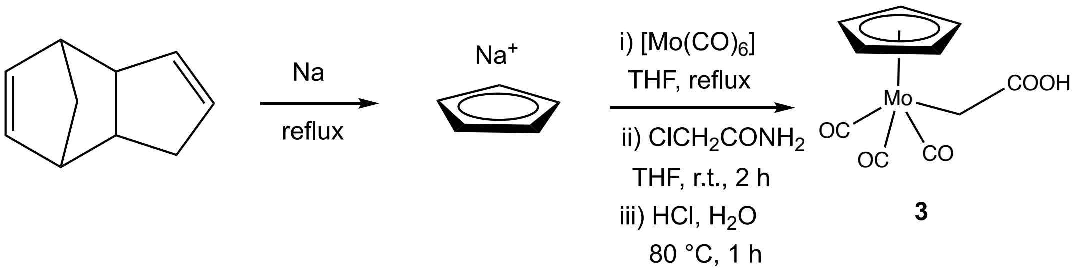
Figure 2.14. Preparation of catalyst precursor **2**.

[CpMo(CO)$_3$CH$_2$COOH] (**3**) To the reaction of NaCp with Mo(CO)$_6$, was added 2-chloroacetamide, resulting the [CpMo(CO)$_3$CH$_2$COONH$_2$] complex, which was posteriorly hydrolysed.

Anal. Calcd for $C_{10}H_8MoO_5$ (304.11): C, 39.50; H, 2.65. Found: C, 39.2; H, 2.65. FT-IR (KBr, cm^{-1}): ν = 3438 (br), 3120 (w), 2935 (w), 2784 (w), 2624 (w), 2524 (w), 2025 (vs, *ν*(CO)), 1949 (vs, *ν*(CO)), 1931 (vs, *ν*(CO)), 1908 (vs, *ν*(CO)), 1647 (vs, *ν*(C=O)), 1427 (m), 1416 (m), 1283 (vs, *ν*(C-O)), 1104 (m), 1043 (m), 1002 (w), 923 (w), 844 (m), 825 (m), 742 (w), 655 (m), 580 (m), 552 (s), 482 (s), 435 (m), 360 (w). FT-Raman (cm^{-1}) ν = 3129 (m), 3109 (w), 3020 (w), 2959 (w), 2013 (s), 1957 (vs), 1935 (w), 1903 (s), 1110 (s), 1058 (w), 1043 (s), 465 (w), 440 (m), 417 (m), 394 (m), 362 (s), 341 (s), 156 (w), 140 (s), 124 (vs), 112 (vs). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 5.43 (s, 5H, Cp), 1.80 (s, 2H, C*H*$_2$COOH). ^{13}C NMR (126 MHz, CDCl$_3$, 298 K): δ = 239.3 (CO), 226.3 (CO), 188.0 (CH$_2$*C*OOH), 93.8 (Cp), -4.5 (*C*H$_2$COOH).[28]



3

Figure 2.15. Preparation of catalyst precursor **3**.

2.4.3. ODS studies

2.4.3.1. Model diesel

The ODS reactions were carried out under atmospheric pressure, using a borosilicate reaction vessel (5 mL) loaded with a magnetic stirring bar and immersed in a thermostated oil bath at 50 °C. A model diesel with a sulfur concentration of 2000 ppm was prepared by the dissolution in equal parts of dibenzothiophene, 1-benzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene in *n*-octane.

The conditions applied during the ODS experiments resulted from the evaluation of several parameters using a biphasic ODS system. The evaluated parameters were: nature of extraction solvent (MeOH, MeCN, [BMIM]PF_6 or [BMIM]BF_4), the volume ratio model diesel/extraction solvent (1:1, 1:0.5, 1:0.3), type of oxidant (*t*BHPaq or H_2O_2), amount of H_2O_2 (0.60, 0.30, 0.22 and 0.15 mmol), amount of catalyst **1** (10, 20 and 30 μmol) and reaction medium temperature (25 and 50 °C).

The ODS reactions composed of a biphasic liquid-liquid system combining extraction and catalytic oxidation. Before addition of H_2O_2, an initial extraction of sulfur compounds present in the model diesel was performed by vigorously stirring the model diesel/extractant mixture for 10 min at 50 °C. After this stage, 30% aq. H_2O_2 (0.30 mmol; H_2O_2/S molar ratio = 6) was added to initiate the catalytic stage.

The periodic quantification of sulfur content by GC analysis was executed by taking aliquots with a microsyringe directly from the model diesel phase during the ODS reactions. In a typical procedure, a standard (tetradecane) was used to dilute the aliquot removed. For the recyclability tests, the model diesel phase was removed at the end of each cycle and the extractant phase was either reused immediately with no further treatment (cycles denoted “reused”) or washed with a mixture of ethyl acetate and diethyl ether (1:1 *v*/*v*) to remove the sulfur-containing compounds (cycles denoted “recycled”). The consecutive cycles were performed under the same experimental conditions through the addition of fresh samples of model diesel and oxidant.

2.4.3.2. Untreated real liquid fuels

The ODS experiments were performed using untreated real diesel and jet fuel samples with sulfur contents of 2300 and 1100 ppm, respectively. These were supplied by Galp Energia. The different fuels were desulfurized maintaining the model diesel reaction proportions (H_2O_2/S/catalyst) at 50 °C for 2 h using [CpMo(CO)$_3$Me] (**1**) as catalyst precursor. Some initial extraction studies were performed with MeCN and DMF at 50 °C in the case of jet fuel, and 70 °C for diesel.

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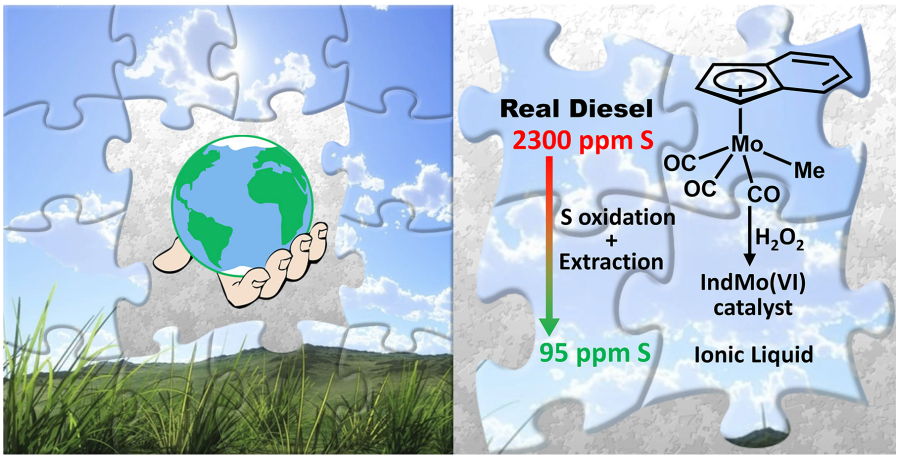
Chapter 3

ORGANOMETALLIC CATALYST PRECURSOR: [IndMo(CO)$_3$Me]



3. Organometallic catalyst precursor: [IndMo(CO)$_3$Me]

3.1. Introduction

The indenyl ligand ($C_9H_7^-$, or Ind) has played a key role in the development of organometallic chemistry and has been shown to be very flexible in terms of its coordination to metals.[1, 2] When compared to their η^5-cyclopentadienyl (C_5H_5, or Cp) counterparts, η^5-indenylmetal complexes frequently display higher reaction rates for fundamental organometallic reactions. This phenomenon was first observed by Hart-Davis and Mawby in migratory insertion reactions involving the complex [η^5-IndMo(CO)$_3$Me].[3] Later on, Basolo and coworkers [4] coined the term "indenyl effect" to describe the remarkable (up to 10^8) rate enhancements observed in substitution reactions for the complexes [η^5-IndRh(CO)$_2$] and [η^5-IndMn(CO)$_3$] over the corresponding Cp compounds. The origin of the indenyl effect has traditionally been attributed to the relative ease with which the ligand can "slip" from a pentahapto (η^5) to a trihapto (η^3) coordination mode. This haptotropic shift facilitates associative reaction mechanisms by opening up an additional coordination site on the metal. Theoretical calculations showed that the increased ability of indenyl to undergo η^5-to-η^3 shifts, when compared to Cp, is a direct consequence of the different bonding of the π ligands to the metal in the two coordination modes, i.e. the (η^5-Cp)–M bond is stronger than the (η^5-Ind)–M bond, while the (η^3-Cp)–M bond is weaker than the (η^3-Ind)–M bond.[5]

The distinctive reactivity of indenylmetal compounds has led to their use as catalysts for some important organic transformations.[6, 7] Increased activity of indenylmetal catalysts has frequently been associated with the traditional explanation of the indenyl effect, i.e. a change in hapticity along the reaction coordinate, which is likely to be operative when substrate coordination to the metal center is a key step of the reaction mechanism.[8] However, a more facile η^5-to-η^3 rearrangement for Ind may not always be at the origin of increased catalytic activity. For example, Chirik and coworkers [9] determined that an indenyl effect for olefin insertion into zirconocene dihydride complexes was more likely due to the increased electrophilicity of the metal center in the indenyl-substituted zirconocenes, rather than a change in hapticity. In catalysis, the indenyl ligand has several other advantages over its Cp counterpart, such as greater options for ligand modification, and a different steric profile that could be beneficial for asymmetric catalysis.[10] The practical importance of indenylmetal complexes is amply illustrated by the use of zirconocene derivatives as single-center catalysts (in combination with methylaluminoxane (MAO)) for the polymerization of olefins in the petrochemical industry.[11-13] For example, unsubstituted bis(indenyl)zirconium dichloride, Ind_2ZrCl_2, yields atactic polypropylene (PP) with high activity [14], the unbridged derivative (2-phenylindenyl)$_2$ZrCl$_2$ produces elastomeric PP with alternating atactic and isotactic blocks [15], and the bridged derivative *rac*-Me$_2$Si(2-methyl-4-phenyl-indenyl)$_2$ZrCl$_2$ produces PP of very high isotacticity (*mmmm* ≥ 99%) and molecular weights with melting points as high as 160 °C.[16]

Besides olefin polymerization, another vitally important catalytic process in the petrochemical industrial is the desulfurization of transportation fuels.[17] Organosulfur compounds in liquid fuels are converted to sulfur oxides (SO_x) during combustion. Both during emission and while in the atmosphere, SO_2 can become oxidized to form sulfate particulate matter. These pollutants are harmful to human health and to the environment. They also prevent the use of more advanced emission control systems in motor vehicles, e.g. for limiting NO_x emissions. The sulfur content of gasoline and diesel fuels has therefore been regulated to meet increasingly strict fuel quality standards. In Europe, ultra-low sulfur fuels containing < 10 ppm became mandatory in 2009.[18] These specifications represent a major operational and technical challenge for the petroleum refining industry. Conventional hydrodesulfurization (HDS) technology is unsuited to deep desulfurization since severe operating conditions are required (such as high hydrogen pressures and temperatures) and even then, the removal of refractory sulfur-containing heterocycles, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), remains a major obstacle. Alternative desulfurization technologies are therefore needed to either supplement or replace HDS.[17-19] One of the most promising is oxidative desulfurization (ODS).[20, 21] A typical ODS process involves the catalytic conversion of sulfides to sulfones with hydrogen peroxide under relatively mild conditions (50-90 °C, atmospheric pressure). The sulfones are then removed from the petroleum stream by distillation, extraction, adsorption, etc. An attractive feature of ODS is that it can be very effective for the removal of benzothiophene derivatives.

Many different types of transition metal catalysts have been explored for ODS.[20, 21] The first organometallic complexes to be reported for ODS were the cyclopentadienyl molybdenum tricarbonyl complexes [η^5-CpMo(CO)$_3$R] (R = Me, CH$_2$-*p*C$_6$H$_4$-CO$_2$Me, CH$_2$COOH).[22] Simultaneous extraction and catalytic ODS was performed with these complexes by immobilizing them in an ionic liquid. The high sulfoxidation activity of the catalyst precursor [η^5-CpMo(CO)$_3$Me] enabled complete desulfurization within 1 h at 50 °C of a model diesel containing benzothiophene and dibenzothiophene derivatives. By sequentially performing extractive desulfurization and ECODS steps, 83–84% sulfur removal was achieved for untreated real diesel and jet fuel samples. These promising results have led us to explore other organomolybdenum compounds as catalysts or catalyst precursors for ODS processes. Herein, we report on the use of the indenyl complex [η^5-IndMo(CO)$_3$Me] for the ODS of model and real liquid fuels. This complex was chosen due to the previous reports of its distinctive reactivity in, for example, CO insertion reactions [3], and catalytic epoxidation of limonene [23]. A comparative study indicates that the η^5-indenyl complex may be a better precursor for ODS than its η^5-cyclopentadienyl counterpart. Indeed, through application of a biphasic system, it has been possible to achieve a desulfurization efficiency of 96% for a real untreated diesel with a high sulfur content.

3.2. Results and Discussion

3.2.1. Organometallic catalyst precursor

An organometallic molybdenum complex based on indenyl (Ind) ligand, IndMo(CO)$_3$Me (**1**) was used as catalyst precursor for the oxidative desulfurization of a model diesel and untreated liquid fuels (diesel and jet fuel). Its structure is presented in Figure 3.1 and the corresponding characterization can be seen in Section 3.4.2.

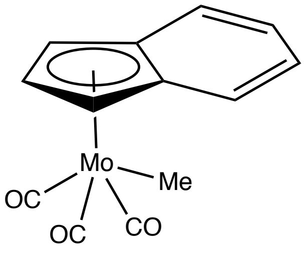


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Figure 3.1. Catalyst precursor IndMo(CO)$_3$Me (**1**).

3.2.2. Desulfurization of a model diesel

A model diesel with a sulfur content of 2000 ppm was prepared by dissolution of various sulfur compounds, namely BT, DBT, 4-MDBT and 4,6-DMDBT, in *n*-octane. The conditions used initially in the ODS studies were based on those optimized previously for the cyclopentadienyl complexes [η^5-CpMo(CO)$_3$R] (R = Me, CH$_2$-*p*C$_6$H$_4$-CO$_2$Me, CH$_2$COOH), presented in Chapter 2.[22] Each ODS procedure was performed using [η^5-IndMo(CO)$_3$Me] (**1**) as catalyst precursor and H$_2$O$_2$ as oxidant.

3.2.2.1. Optimization studies

The first parameter to be analysed was the effect of the presence or absence of an extraction solvent (ionic liquid). In the absence of an extraction solvent, only a catalytic oxidation step takes place in which the sulfur compounds are transformed into the corresponding sulfoxides and/or sulfones (Figure 3.2).

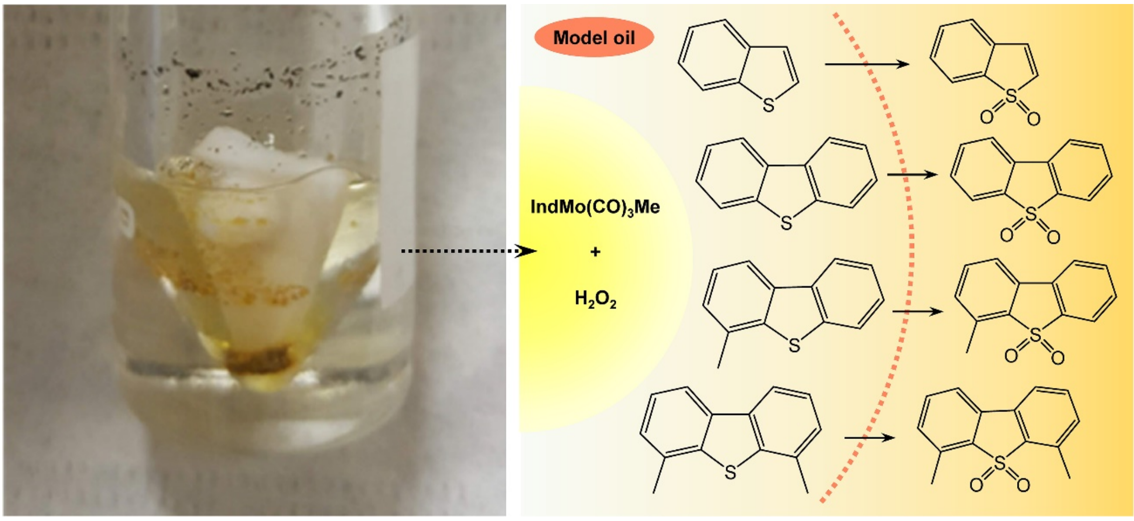

Figure 3.2. Typical ODS reaction mixture and schematic representation of the solvent-free ODS process (no extraction solvent).

Figure 3.3 presents the desulfurization results obtained for the monophasic (i.e. no extraction solvent) and biphasic (equal volumes of model diesel and [BMIM]PF$_6$) systems, using a reaction temperature of 50 °C. Both systems allowed a complete desulfurization of the model diesel, within 2 h for the biphasic system and 3 h for the solvent-free one. From an industrial and environmental point of view it is important to lower the cost of the process by, for example, avoiding the use of unnecessary reactants. For this reason, the solvent-free system was chosen for the succeeding optimization studies. Avoiding the use of the ionic liquid in the process is desirable not only from the economic viewpoint but also because these solvents are not necessarily “green”, since they may release hydrofluoric acid under certain reaction conditions, such as high temperatures.[24]

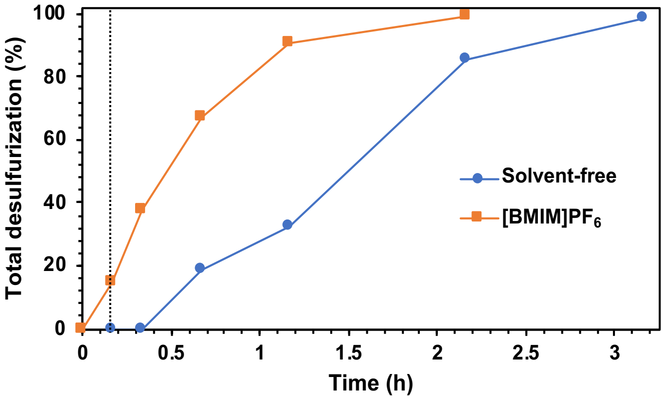

Figure 3.3. Oxidative desulfurization of the model diesel (2000 ppm S) at 50 °C in the presence or absence of an extraction solvent, with complex **1** (30 μmol) as catalyst precursor, and H_2O_2 (0.30 mmol) as oxidant. The vertical dashed line indicates the point at which the oxidant was added.

The next parameter to be evaluated was the amount of oxidant (30% aq. H_2O_2). Three different amounts were tested for the solvent-free system, namely 0.15, 0.30 and 0.60 mmol. The results show that 0.30 mmol is the optimal amount to achieve the best desulfurization profile, obtaining a sulfur-free model diesel after 3 h of ODS reaction (Figure 3.4). The kinetic profile reveals the presence of an induction period of about 10 min prior to the onset of ODS, presumably due to conversion of the Mo(II) tricarbonyl precursor to a catalytically active oxomolybdenum(VI) complex. Induction periods have often been observed for cyclopentadienyl molybdenum(II) tricarbonyl complexes [η^5-CpMo(CO)$_3$R] (R = alkyl, halide) when used as catalysts precursors for the epoxidation of olefins with *tert*-butyl hydroperoxide as oxidant.[25, 26] These complexes are known to undergo oxidative decarbonylation to give catalytically active dioxo [η^5-CpMoO$_2$R] and oxoperoxo [η^5-CpMo(O)(O$_2$)R] complexes.[27, 28] In the case of complex **1** with H_2O_2, oxidative decarbonylation of the complex is indicated by its solubilization together with a change in colour to yellow after the first minute of the reaction (Figure 3.5), which is the usual colour of oxo-peroxomolybdenum(VI) complexes. An induction period is observed due to a low concentration of active species in the reaction mixture at the beginning of the reaction, which restricts substrate conversion to low values. As soon as a critical amount of oxidized species is formed, oxidation of the benzothiophene substrates becomes quite fast, as indicated by the upturn in desulfurization performance observed after 10-30 min in the plots of Figure 3.4. After about 2 h of reaction, a dark blue precipitate appeared and the liquid phase became colourless, which may be indicative of the formation of a less soluble species containing Mo(V) centers. This transformation is presumably due to the decrease in the concentration of oxidant in the mixture as the reaction progresses and conversion of all substrate molecules to the corresponding sulfones. Accordingly, it was verified that the yellow colour was restored upon addition of more oxidant.

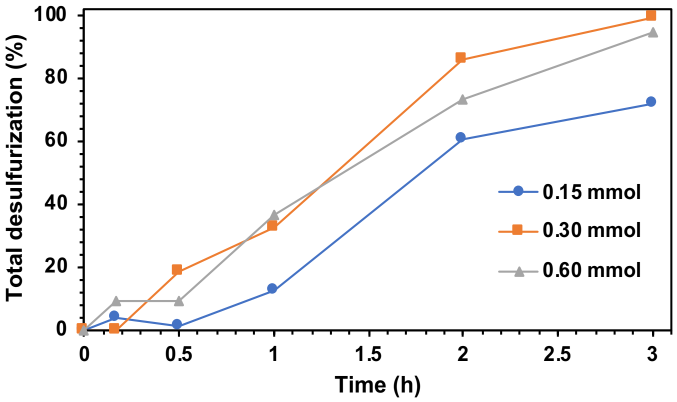

Figure 3.4. Oxidative desulfurization of the model diesel (2000 ppm S) at 50 °C with complex **1** (30 μmol) as catalyst precursor, and different amounts of H_2O_2 oxidant.

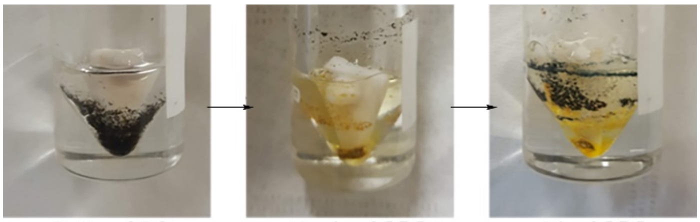
Before ODS
10 min of ODS
2 h of ODS

Figure 3.5. Typical ODS reaction with complex **1**.

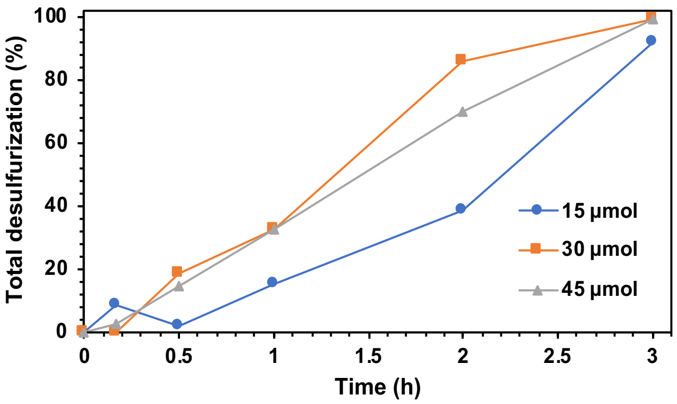

Figure 3.6. Oxidative desulfurization of the model diesel (2000 ppm S) at 50 °C with different amounts of complex **1** as catalyst precursor, and H_2O_2 (0.30 mmol) as oxidant.

The influence of the amount of complex **1** in the ODS process was analysed using the best experimental conditions observed so far (solvent-free system, 0.30 mmol of H_2O_2, at 50 °C). With the higher amounts of catalyst (30 and 45 μmol), the ODS profiles are similar and a completely desulfurized model diesel was obtained after 3 h, while the lower amount of catalyst (15 μmol) led to 92% desulfurization at the same reaction time (Figure 3.6). In the latter case, the amount of non-oxidized sulfur compounds decreased from 160 ppm at 3 h to 31 ppm at 4 h, corresponding to a net desulfurization efficiency of 98.5%. From these results a catalyst amount of 30 μmol was deemed to be optimal for the next set of experiments which were performed to evaluate the effect of the reaction temperature.

Three different temperatures were studied, namely 25, 50 and 70 °C. Temperatures above 80 °C cannot be used for the ODS of real liquid fuels due to the possibility of oxidizing other components, such as olefins and hydrocarbons, which may degrade fuel quality as well as decrease the efficiency of the oxidative desulfurization through the unwanted consumption of the oxidant.[29] As shown in Figure 3.7, higher reaction temperatures promote a faster ODS reaction using complex **1** as catalyst precursor. While complete desulfurization of the model diesel is achieved after 2 h at 70 °C, a reaction time of 3 h is required to reach the same level of desulfurization at 50 °C. At the lower temperature of 25 °C the catalyst dissolved slowly and the formation of active species in the reaction mixture was held back such that a total desulfurization higher than 25% was not reached even after 3 h of reaction.

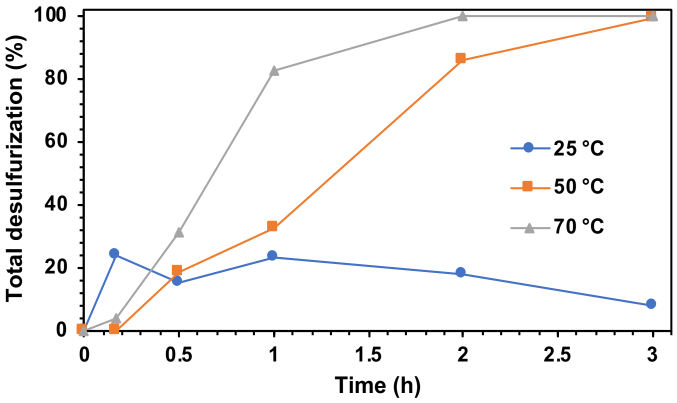

Figure 3.7. Oxidative desulfurization of the model diesel (2000 ppm S) at different temperatures, using complex **1** (30 μmol) as catalyst precursor and H_2O_2 (0.30 mmol) as oxidant.

3.2.2.2. Catalyst reusability

As ascertained above, complex **1** can be used very successfully as a catalyst precursor for ODS of a model diesel under optimized conditions. However, it is important to understand if the catalytic efficiency of the active species formed can be maintained during consecutive ODS cycles. For this purpose, at the end of an ODS cycle when complete desulfurization was reached, the sulfur-free model diesel was removed from the solid catalyst and a new ODS cycle was initiated by adding fresh portions of oxidant and model diesel, without subjecting the used catalyst to any other treatment. Figure 3.8 presents the desulfurization results obtained for five consecutive ODS cycles. The results show that the catalytic activity is maintained for the first four ODS cycles, with complete sulfur oxidation being reached after 2 h reaction. A slight drop in performance was only apparent during the fifth cycle, which led to 98% sulfur oxidation at 2 h. Possible causes of this minor loss of efficiency are the precipitation of sulfones after four consecutive cycles (since no catalyst washing step was performed), and the loss of a residual amount of molybdenum catalyst after the fourth cycle.

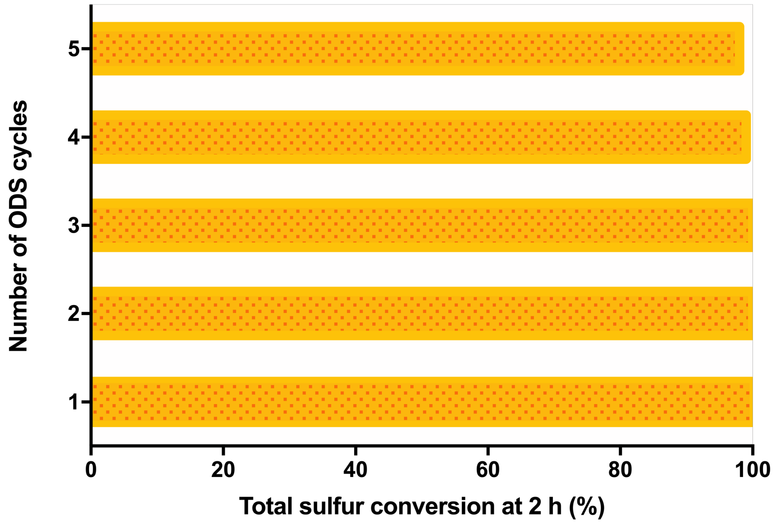

Figure 3.8. Oxidative desulfurization data for the model diesel (2000 ppm S) in five consecutive ODS cycles using complex **1** (30 μmol) as catalyst precursor and H_2O_2 (0.30 mmol) as oxidant, at 70 °C.

3.2.2.3. Ligand influence (Cp vs. Ind)

The catalytic performances of [η^5-IndMo(CO)$_3$Me] (**1**) and [η^5-CpMo(CO)$_3$Me] were compared in the solvent-free ODS process (0.750 mL of model diesel (2000 ppm S), 30 μmol of catalyst and 0.60 mmol of H_2O_2, at 50 °C). The system containing the indenyl complex was the most efficient, with an ODS efficiency of 94% being reached after 3 h, while for the same reaction time an efficiency of only 28% was achieved with the system containing the cyclopentadienyl complex (Figure 3.9). These results point to a significant “indenyl effect” and indicate that indenylmolybdenum complexes may be much better ODS catalyst precursors than their Cp congeners. This may be caused by the higher affinity of the indenylmolybdenum active catalyst for the model diesel, demonstrated by its high dissolution in this phase. The same behaviour was not observed for the Cp complex.

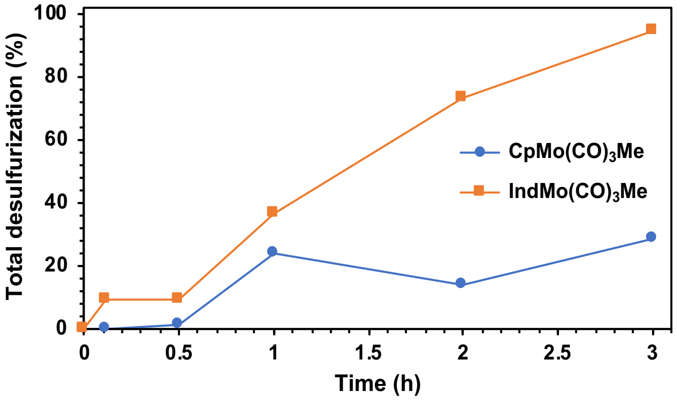

Figure 3.9. Oxidative desulfurization of the model diesel (2000 ppm S) at 50 °C with [η^5-IndMo(CO)$_3$Me] (**1**) or [η^5-CpMo(CO)$_3$Me] (30 μmol) as catalyst precursor, and H_2O_2 (0.60 mmol) as oxidant.

3.2.3. Desulfurization of untreated liquid fuels

Two types of untreated liquid fuels were desulfurized under the optimal conditions found for the multicomponent model diesel. The untreated liquid fuels were diesel and jet fuel samples with sulfur contents of 2300 and 1100 ppm, respectively. In order to maximize the desulfurization of the untreated diesel, different procedures were adopted, such as the application of initial and/or final extractions with MeCN or DMF, and the use of monophasic (solvent-free) or biphasic (diesel/[BMIM]PF_6 during the 2 h oxidative catalytic stage) systems. For solvent-free and biphasic systems, the highest desulfurization efficiencies were reached when an initial extraction was included in the ODS process together with a final extraction (Table 3.1). Extractions with DMF gave the best result for the solvent-free system (70% desulfurization efficiency), while extractions with MeCN gave the best result for the biphasic system (95.9% desulfurization efficiency). The initial extraction was particularly important for the solvent-free ODS system, as shown by the significantly lower sulfur removal obtained when this step was omitted (e.g. 53.8% with a final extraction with DMF). For the biphasic system, the presence of the ionic liquid (IL) solvent [BMIM]PF_6 during the catalytic oxidative stage is advantageous since this solvent possesses a high extractive capacity for the sulfur compounds, increasing the catalytic efficiency. The IL also serves as a barrier to avoid the oxidation of other diesel components that could compete with the oxidation of sulfur compounds and therefore cause a decrease in the desulfurization efficiency. In conclusion, the best desulfurization result for diesel was obtained using the biphasic system, i.e. diesel/[BMIM]PF_6, in the presence of the indenyl complex as catalyst precursor and H_2O_2 as oxidant, and with initial/final extractions with MeCN. Using this process, the sulfur content of the untreated diesel could be lowered from 2300 ppm to 95 ppm. Without the initial extraction with MeCN, the final treated diesel contained 150 ppm of sulfur. These high oxidative desulfurization efficiencies for the treatment of high-sulfur real diesel are unprecedented. In our previous study of the desulfurization of the real diesel sample (2300 ppm S) using the complex [η^5-CpMo(CO)$_3$Me] as catalyst precursor for the ODS step (Chapter 2) [22], the biphasic diesel/[BMIM]PF$_6$ ODS system in combination with initial/final MeCN extractions was also found to give the best desulfurization efficiency. The latter system led to 83.8% desulfurization with an ODS step performed at 50 °C, while the present system with the indenyl complex led to 95.9% desulfurization with an ODS step performed at 70 °C.

Table 3.1. Experiments performed for desulfurization of untreated real diesel and jet fuel, using the model diesel conditions

Fuel	ODS system	Initial extraction[a]	Final extraction[b]	S content (ppm)	Desulfurization efficiency (%)
Diesel	Solvent-free	----	MeCN	1079	53.1
		----	DMF	1063	53.8
		MeCN	MeCN	847	63.2
		DMF	DMF	697	70.0
	Biphasic [BMIM]PF$_6$	MeCN	MeCN	95	95.9
		DMF	DMF	126	94.5
		----	MeCN	150	93.5
		----	DMF	171	92.6
Jet fuel	Solvent-free	----	MeCN	464	57.8
		----	DMF	497	54.8

[a] Liquid-liquid fuel/organic solvent extraction of non-oxidized sulfur compounds during 5 min at 70 °C.

[b] Liquid-liquid fuel/organic solvent extraction of oxidized sulfur compounds during 30 min at 70 °C.

The capacity of the indenyl complex **1** to work as catalyst precursor for ODS of real fuel samples was further confirmed by performing reactions with the jet fuel sample containing 1100 ppm of sulfur. Only the monophasic (solvent-free) system was studied with a final extraction step; no initial extraction was performed since previous work with

η^5-cyclopentadienyl complexes had shown that an initial extraction only had a minor influence on the desulfurization of the jet fuel. Desulfurization efficiencies of 57.8% and 54.8% were obtained with final MeCN and DMF extraction, respectively (Table 3.1).

3.3. Conclusions

In this work an eco-friendly solvent-free ODS reaction (H_2O_2/sulfur ratio = 6, T = 70 °C) employing an indenylmolybdenum catalyst (30 μmol) has been optimized to completely desulfurize a high-sulfur multicomponent model diesel within 2 h. The good recyclability of the catalyst formed was confirmed by performing five consecutive ODS cycles. The ODS reaction using the organometallic catalyst can be successfully applied in a process for the treatment of real diesel and jet fuel. Remarkable results were obtained for diesel treatment, especially when using the diesel/[BMIM]PF_6 oxidative system, [IndMo$(CO)_3$Me] catalyst precursor and H_2O_2 oxidant, in combination with initial and final extraction steps. Under these conditions, a treated diesel with a residual sulfur content of only 95 ppm was obtained, corresponding to a desulfurization efficiency of 95.9%. This is one of the best results yet reported for sulfur removal from an actual commercial diesel using oxidative desulfurization.

3.4. Experimental Section

3.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: indene (Sigma-Aldrich), tetrahydrofuran anhydrous (Sigma-Aldrich, 99%), *n*-butyllithium (1.6 M solution in hexane, Sigma-Aldrich) molybdenum hexacarbonyl (Fluka), iodomethane (Sigma-Aldrich, 99%) hexane (Sigma-Aldrich, 99%) and pentane (Sigma-Aldrich, 98%), dibenzothiophene (Sigma-Aldrich, 98%), 1-benzothiophene (Fluka, 95%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical), dimethylformamide (Fischer) and 30% w/v hydrogen peroxide (H_2O_2, Sigma-Aldrich). An untreated diesel and jet fuel samples containing 2300 and 1100 pm S, respectively were supplied by Galp Energia.

GC-FID was carried out in a Bruker 430-GC-FID gas chromatograph using hydrogen as the carrier gas (55 cm^3 s^{-1}) and fused silica SPB-5 Supelco capillary columns (30 m × 0.25 mm i.d.; 25 μm film thickness). The analysis of sulfur content of the treated diesel and jet fuel were performed by Galp Energia by ultraviolet fluorescence using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

3.4.2. Catalyst synthesis

IndMo(CO)$_3$Me: In a Schlenk tube under inert atmosphere, *n*-BuLi (1.6 M solution in hexane, 5.5 mL, 8.8 mmol) was added to a cooled THF solution (30 mL at 0 °C) of freshly distilled indene (1mL, 1.0 g, 8.62 mmol). The resultant yellow solution of IndLi was stirred for 20 min and allowed to warm slowly to room temperature, followed by the addition of $Mo(CO)_6$ (1.7 g, 6.5 mmol) and the resultant mixture was refluxed for 20 h. A brown solution was obtained, which was cooled to room temperature. CH_3I (1.87 g, 0.84 mL, 13.2 mmol) was added and, after stirring for 5 h, the solvent was removed under reduced pressure to give a yellowish-brown residue. This residue was purified by dry column vacuum chromatography under air using silica gel as stationary phase and hexane as the mobile phase. Combination of all the fractions and removal of solvent by reduced pressure afforded a yellow solid which was further purified by extracting with pentane. Yield: 1.02 g, 51%. $C_{13}H_{10}MoO_3$ (310.06): calcd C 50.34, H 3.25; found C 50.34, H 3.67. FTIR (KBr): v=3093 (w), 2965 (w), 2924 (w), 2891 (w), 2857 (w), 2011 (vs, *v*CO), 1933 (vs, *v*CO), 1907 (vs, *v*CO), 1524 (w), 1479 (w), 1447 (w), 1385 (w), 1338 (w), 1261 (w), 1157 (w), 1126 (w), 1030 (w), 1041 (w), 898 (w), 817 (m), 751 (m), 738 (w), 698 (w), 589 (w), 562 (m), 483 (m), 459 (w) cm^{-1}. FT-Raman: v = 3110 (s), 3091 (s), 3069 (s), 3036 (m), 2985 (w), 2892 (m), 2012 (m), 2009 (s), 1908 (vs), 1524 (m), 1466 (w), 1447 (vs), 1392 (m), 1339 (vs), 1248 (w), 1210 (w), 1155 (w), 1120 (w), 1040 (m), 1030 (m), 993 (m), 860 (m), 733 (vs), 599 (w), 544 (w), 488 (w), 457 (s), 437 (s), 406 (w), 372 (m), 343 (m), 293 (m), 175 (s), 160 (s), 137 (s), 108 (vs) cm^{-1}. ^1H NMR (400MHz, $CDCl_3$, 25 °C): δ=7.37–7.33 (m, 2H, $C^{5-8}H$), 7.27–7.21 (m, 2H, $C^{5-8}H$), 5.84 (d, 2H, $C^{1,3}H$), 5.49 (t, 1H, C^2H), –0.33 (s, 3H, CH_3) ppm $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25°C): δ=240.3 (CO trans to CH_3), 226.4 (2CO *cis* to CH_3), 125.9, 124.3 (C^{5-8}), 112.4 ($C^{4,9}$), 90.7 (C^2), 80.2 ($C^{1,3}$), –8.5 ($\mathit{C}H_3$) ppm.[23]

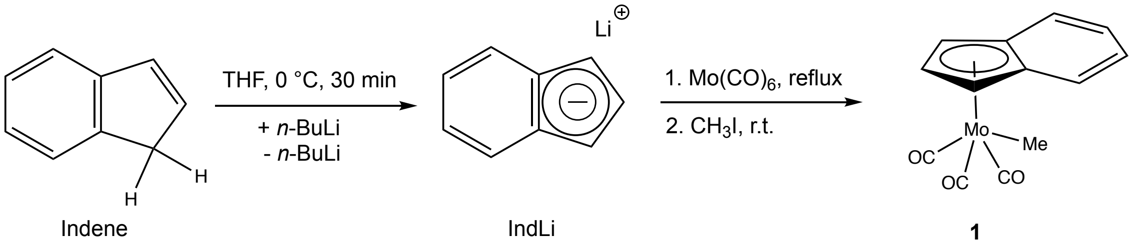

Figure 3.10. Synthesis route used to obtain the IndMo(CO)3Me (**1**).

[CpMo(CO)$_3$Me]: The experimental procedure and corresponding synthesis is presented in Chapter 2.

3.4.3. ODS studies

3.4.3.1. Model diesel

The catalyst precursor **1** was tested for ODS of a model diesel with a sulfur concentration of 2000 ppm resulting from the dissolution of equal parts of dibenzothiophene derivatives (dibenzothiophene, benzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene) in an *n*-octane solution. The reactions were performed under atmospheric pressure, using a borosilicate reaction vessel (5 mL) with magnetic stirring and immersed in a thermostated oil bath. In a typical ODS procedure, the mixture comprising catalyst (30 μmol), model diesel (0.750 mL) and 30% aq. H_2O_2 (0.30 mmol) was heated to 70 °C under stirring. These experimental parameters resulted from previous tests which were performed to optimize the amount of catalyst (15, 30 and 45 μmol) and oxidant (0.15, 0.30 and 0.60 mmol), temperature of reaction medium (25, 50 and 70 °C), and the use of a biphasic ([BMIM]PF_6) or monophasic (solvent-free) system.

The quantification of the sulfur content present in the model diesel during the ODS reactions was carried out by GC. Aliquots were removed periodically from the reaction and diluted with an external standard (tetradecane) prior to injection.

The solid catalyst was reused for several cycles by removing the model diesel after complete desulfurization and by adding fresh model diesel and H_2O_2 samples, maintaining the conditions applied during the first ODS cycle.

3.4.3.2. Untreated liquid fuels

After the successful desulfurization of the model diesel (2000 ppm S), ODS tests were performed with untreated liquid fuels, namely diesel and jet fuel with sulfur contents of 2300 and 1100 ppm, respectively. The tests were performed maintaining the oxidant/S/catalyst proportions at 70 °C with continuous stirring during 2 h. To achieve the best desulfurization results, some diesel samples were treated in advance by a liquid-liquid extraction process using MeCN or DMF. The effect of applying a biphasic system to desulfurize untreated diesel samples was also tested, using an ionic liquid ([BMIM]PF$_6$).

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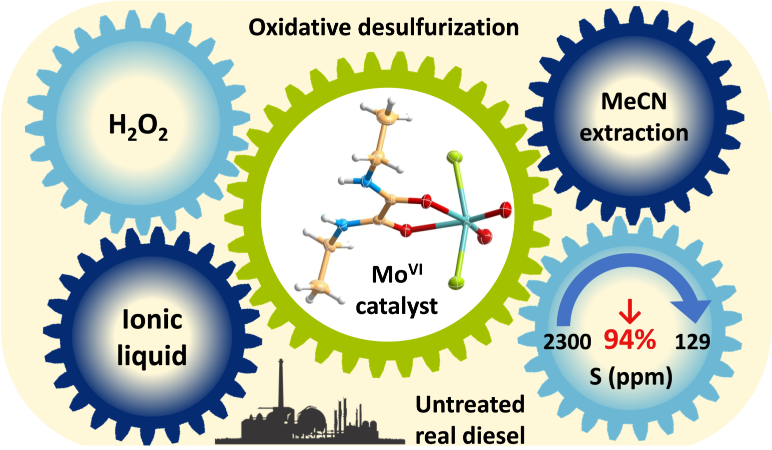
Chapter 4

[$MoO_2Cl_2L_n$] BEARING MONO- AND BIDENTATE *O*-DONOR LIGANDS



4. [$MoO_2Cl_2L_n$] bearing mono- and bidentate *O*-donor ligands

4.1. Introduction

Homogeneous catalysts with oxomolybdenum(VI) active centers have been shown to be effective for a broad range of oxidative organic transformations such as the epoxidation of olefins, oxidation of amines and oxidation of sulfides.[1-4] The ready availability of the simplest molybdenyl derivative, MoO_2Cl_2, has led to its extensive use in many reactions. In the presence of a coordinating solvent, adducts of the type [$MoO_2Cl_2(Solv)_2$] (Solv = DMF, THF, DMSO, MeCN) are formed. However, these complexes tend to be air and moisture sensitive, and can only be handled and stored under an inert gas atmosphere.[5] More stable complexes can be prepared by replacement of the coordinated solvent molecules by organic ligands containing oxygen and/or nitrogen donor atoms, giving complexes of the type [$MoO_2Cl_2(L)_2$] with monodentate ligands and [$MoO_2Cl_2(L)$] with bidentate ligands. Complexes bearing N-donor Lewis base ligands, such as those derived from 2,2′-bipyridine, have received the most attention, and have been optimized for use as catalysts for the epoxidation of olefins using *tert*-butyl hydroperoxide (*t*BHP) as oxidant.[5-7] Less attention has been paid to complexes bearing O-donor ligands. However, we recently showed that complexes containing *N*,*N*-dimethylbenzamide (DMB) as a monodentate ligand and *N*,*N*′-diethyloxamide (DEO) as a bidentate ligand (Figure 4.1) are extremely active catalysts for the epoxidation of olefins with *t*BHP.[8]

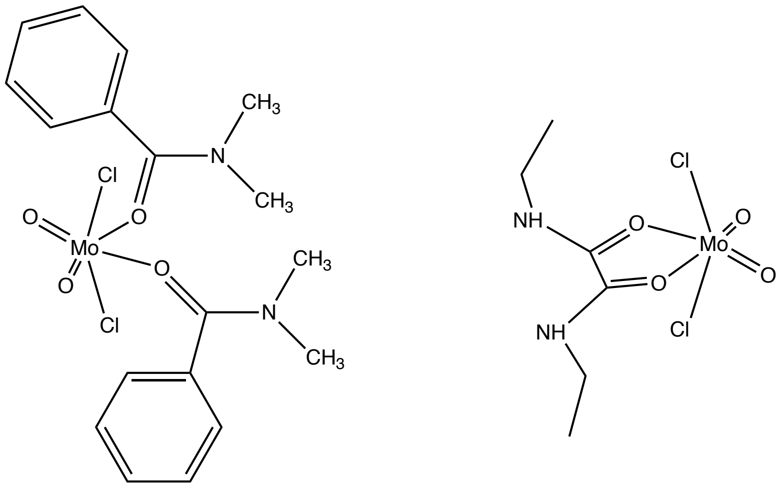
A recent review by Thiruvengetam and Chand highlights the application of oxomolybdenum(VI) complexes for the oxidation of sulfides using aqueous hydrogen peroxide as oxidant.[4] Sulfoxidation is an important reaction not only from the point of view of organic synthesis (for the selective preparation of sulfoxides or sulfones) but also for the oxidative desulfurization (ODS) of transportation fuels. Regulations on the permissible levels of sulfur in fuels are becoming more and more strict, with a global shift towards "zero sulfur" fuels, and the revamp of existing hydrodesulfurization (HDS) facilities to meet these lower caps is cost-prohibitive since elevated temperatures and hydrogen pressures are required, as well as higher catalyst amounts and/or improvements in catalyst performance.[9] Sulfoxidation chemistry is seen as an economically viable alternative route to diesel desulfurization that could complement conventional HDS technology. In ODS, organosulfur compounds are oxidized to the corresponding sulfoxides and/or sulfones which can then be removed by adsorption, distillation, or solvent extraction.[10, 11] An important variant of ODS is extractive-catalytic ODS in which the extraction of sulfur-containing compounds/products and catalytic oxidation take place simultaneously in a one-pot biphasic system. We recently showed that the complex [MoO_2Cl_2(4,4'-di-*tert*-butyl-2,2'-bipyridine)] could be used successfully in an ECODS process for the desulfurization of model and real diesel.[12]

In the present work, ODS systems containing the complexes [$MoO_2Cl_2(DMB)_2$] (**1**) and [MoO_2Cl_2(DEO)] (**2**) have been optimized for the desulfurization of a multicomponent model diesel. The best system, using complex **2** entrapped in the ionic liquid [BMIM]PF_6, could be used for the near-complete removal of sulfur from an untreated real diesel.

4.2. Results and Discussion

4.2.1. Dioxomolybdenum(VI) catalysts

Two dioxomolybdenum(VI) complexes bearing *O*-donor ligands were synthesized, one containing two monodentate ligands *N,N*-dimethylbenzamide (DMB), [$MoO_2Cl_2(DMB)_2$] (**1**), and other containing the bidentate ligand *N,N'*-diethyloxamide (DEO), [MoO_2Cl_2(DEO)] (**2**) (Figure 4.1). The respective syntheses and detailed characterization can be consulted in the Section 4.4.2.



1 **2**

Figure 4.1. Dioxomolybdenum(VI) complexes: [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**).

Crystalline material of the compound [$MoO_2Cl_2(DEO)$]·THF suitable for X-ray diffraction analysis was isolated by controlled recrystallization. The crystal structure revealed the neutral complex [$MoO_2Cl_2(DEO)$] crystallised with a THF molecule (asymmetric unit, asu) in the monoclinic space group $P2_1/c$ (Figure 4.2). The Mo(VI) centre coordinates to two chlorine atoms, two terminal oxygen atoms (two oxo groups) and also two oxygen atoms of the organic ligand (DEO), by an *O,O′*-chelating mode, {$MoCl_2O_4$}. The coordination centre shows distorted octahedral geometry, with the four oxygen atoms constituting the axial plane and the chlorine atoms located in the two remaining apical positions. The distortion from an ideal octahedron can be confirmed by an inspection of the bond lengths and internal bond angles and is notably influenced by the well-known *trans* effect exerted by the terminal oxo groups (detailed information about bond lengths and angles for the Mo1 coordination centre is in Table 4.1). In fact, the $Mo–O_{ligand}$ bond lengths [2.2276(19) and 2.2423(19) Å] are clearly longer than the $Mo=O_{oxo}$ distances [1.688(2) and 1.698(2) Å], while the Mo–Cl bond lengths [2.3809(8) and 2.3690(8) Å] are longer still. Furthermore, the *cis* angles are found between 71.09(7) and 105.29(11)°, while the *trans* angles fall in the range of 160.36(3)–162.99(9)°. The most important crystallographic features of the {$MoCl_2O_4$} core of the complex are analogous with those observed in the previous crystal structures reporting related coordination centres.[8]

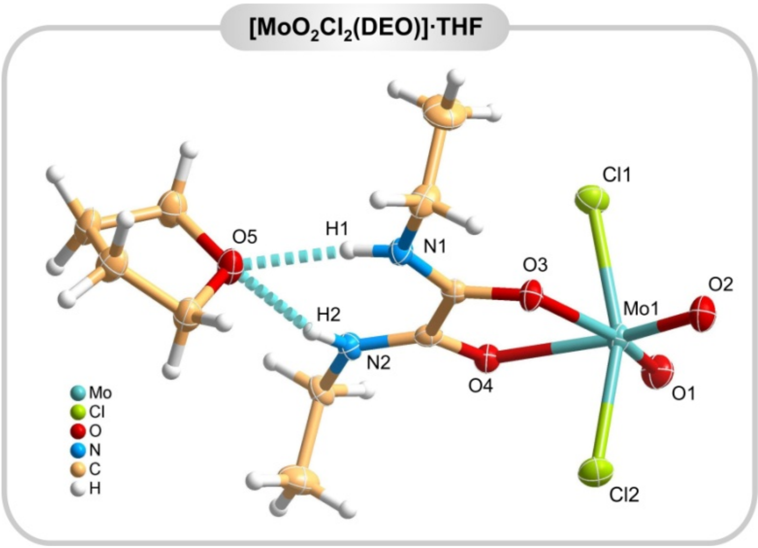


Figure 4.2. Schematic representation of the crystal structure of compound [MoO$_2$Cl$_2$(DEO)]·THF, including the intermolecular hydrogen bonds (light blue dashed lines). Thermal ellipsoids are drawn at 50% probability level, and the labelling scheme is provided for all non-H-atoms of the first coordination sphere as well as for the atoms involved in N–H···O hydrogen bonds. Details concerning the bond distances and angles of the Mo coordination centre are summarized in Table 4.1.

Table 4.1. Selected bond lengths and angles for the Mo(VI) coordination centre of the neutral complex [MoO$_2$Cl$_2$(DEO)]

Bond lengths /Å		Angles /°			
Mo1–O1	1.688(2)	O1–Mo1–O2	105.29(11)	O2–Mo1–Cl2	96.19(8)
Mo1–O2	1.698(2)	O1–Mo1–O3	162.52(9)	O3–Mo1–O4	71.09(7)
Mo1–O3	2.2276(19)	O1–Mo1–O4	91.72(9)	O3–Mo1–Cl1	80.19(6)
Mo1–O4	2.2423(19)	O1–Mo1–Cl1	94.82(8)	O3–Mo1–Cl2	84.19(6)
Mo1–Cl1	2.3809(8)	O1–Mo1–Cl2	96.56(8)	O4–Mo1–Cl1	82.54(6)
Mo1–Cl2	2.3690(8)	O2–Mo1–O3	91.95(9)	O4–Mo1–Cl2	81.17(6)
		O2–Mo1–O4	162.99(9)	Cl1–Mo1–Cl2	160.36(3)
		O2–Mo1–Cl1	96.17(8)		

The neutral complex [MoO$_2$Cl$_2$(DEO)] establishes two strong N–H···O hydrogen bonds with the solvent crystallization molecule THF, involving the two NH groups of the coordinated DEO ligand and the oxygen atom of the furan ring (Figure 4.2 and 4.3 – top; Table 4.2 details geometric information for the main hydrogen bonding interactions found in the crystal structure). Additionally, the extended packing arrangement is driven by numerous C–H···O and C–H···Cl intermolecular interactions (light pink dashed lines in Figure 4.3) involving the adjacent complexes and THF molecules, ultimately leading to a dense three-dimensional supramolecular structure (Figure 4.3 – bottom).

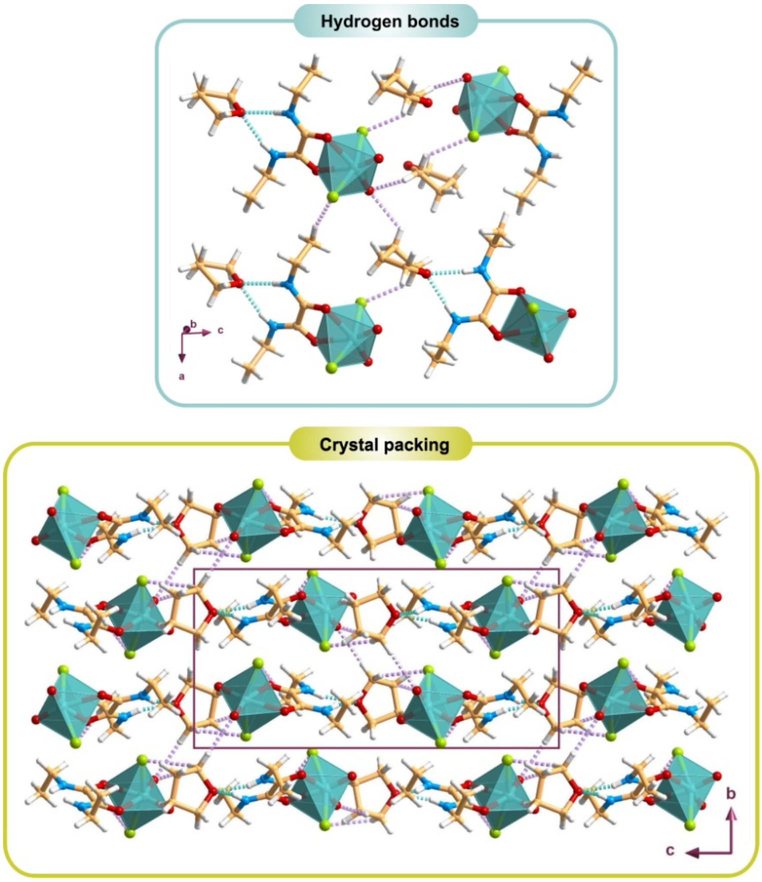


Figure 4.3. Representation of selected features of the extended structure of compound [MoO_2Cl_2(DEO)]·THF: (**a**) hydrogen bonding network involving adjacent complexes and THF molecules; (**b**) crystal packing arrangement viewed along the [1 0 0] direction of the unit cell. Strong (N–H···O) and weak (C–H···O and C–H···Cl) hydrogen bonds are drawn as light blue and pink dashed lines, respectively. The geometric details of these interactions are listed in Table 4.2.

Table 4.2. Geometric information (distances in Å and angles in degrees) for the D–H···A hydrogen bond interactions of the compound [MoO$_2$Cl$_2$(DEO)]·THF.[a]

D–H···A	*d*(H···A)	*d*(D···A)	∠(DHA)
N1−H1···O5	1.950(13)	2.826(3)	165(3)
N2−H2···O5	1.993(15)	2.859(3)	163(4)
C1−H1B···Cl2^{i}	2.85	3.785(4)	160.9
C9−H9A···O1^{ii}	2.62	3.235(4)	120.1
C10−H10A···O1^{iiii}	2.48	3.457(4)	168.2
C10−H10B···Cl1^{iv}	2.84	3.657(4)	140.0

[a] Symmetry transformations used to generate equivalent atoms: (i) *x–, y, z;* (ii) *x–1, –y+1/2, z–1/2;* (iii) –x, y*–1/2*, –z+1/2; (iv) *x, –y+1/2, z–1/2.*

4.2.2. Desulfurization of a model diesel

The catalytic efficiency of each catalyst [MoO$_2$Cl$_2$(DMB)$_2$] (**1**) and [MoO$_2$Cl$_2$(DEO)] (**2**) was tested in the treatment of a model diesel containing 3000 ppm of different sulfur species, namely DBT, 4-MDBT and 4,6-DMDBT. The conditions were optimized for both catalysts by varying different parameters (extraction solvent, temperature, volume of H_2O_2, amount of catalyst and model diesel/solvent volume ratio). In a typical ODS procedure a biphasic liquid-liquid system was used, in which an initial extraction of sulfur compounds from the model diesel phase to the extraction solvent phase occurred. After the addition of H_2O_2 oxidant, the catalytic oxidative stage started, where the sulfur compounds were oxidized to the corresponding sulfoxides and/or sulfones.

4.2.2.1. Optimization studies

To achieve the highest desulfurization efficiency in the presence of a catalyst, it is crucial to investigate the influence of the various experimental parameters in the ODS process. The studied parameters were the extraction solvent ([BMIM]PF$_6$, [BMIM]BF$_4$ and MeCN), the amount of catalyst (5, 10 and 20 μmol) and H_2O_2 (0.13, 0.26 and 0.60 mmol) and finally, the effect of the volume ratio model diesel/extraction solvent (1:1, 1:0.5, 1:0.3) and temperature (50 and 70 °C). This optimization study was performed for both catalysts **1** and **2**.

From an environmental and economic point of view, the choice of solvent is of considerable importance. Most of the organic solvents present high volatility or incapacity to be recycled. They can be replaced by ILs that can combine functionalities of extraction and oxidative reaction medium.[12-14] Therefore, different ionic liquids ([BMIM]PF_6 and [BMIM]BF_4) and a volatile organic solvent MeCN were compared as solvents in a biphasic ODS process with a volume ratio of 1:1 (0.750 mL model diesel). Also, 10 *µ*mol of catalyst **1** and 0.60 mmol of H_2O_2 were used, with a reaction temperature of 50 °C. Figure 4.4 shows the desulfurization results obtained in the presence of the various solvents. The initial extraction capacity of the solvents (before addition of oxidant) followed the order MeCN (52.8%) > [BMIM]PF_6 (41.2%) > [BMIM]BF_4 (28.3%). After the addition of H_2O_2, higher desulfurization efficiency was observed using the IL [BMIM]PF_6. The desulfurization efficiency was faster in water-immiscible [BMIM]PF_6 than in water-miscible MeCN and [BMIM]BF_4. This suggests that any benefit of having the oxidant in the same liquid phase as the catalyst may be offset by catalyst deactivation or alteration caused by the presence of water. The reaction performed in a solvent-free medium only resulted in 68% removal of the sulfur compounds present in the model diesel phase. Therefore, [BMIM]PF_6 was selected as the solvent to proceed with the optimization tests.

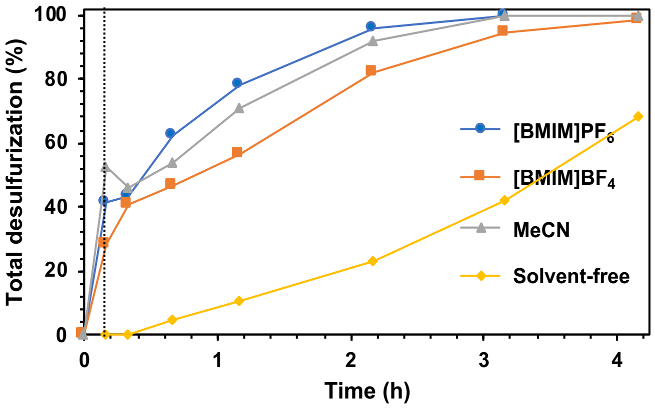


Figure 4.4. Desulfurization of a model diesel (3000 ppm S) using [$MoO_2Cl_2(DMB)_2$] (**1**) (10 *µ*mol) as catalyst, in the absence and presence of different extraction solvents, using H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

A compromise was sought between the desulfurization efficiency (preferably achieving values greater than 99.5% within 1-3 h) and the desire to use the minimum amounts of extraction solvent, oxidant and catalyst. The oxidant/S molar ratio should be as small as possible, to avoid the oxidation of fuel components responsible for the its quality.[15] The results of the optimization experiments with three different amounts of H_2O_2 (0.13, 0.26 and 0.60 mmol) using equal portions of $[BMIM]PF_6$ and model diesel, 10 μmol of catalyst **1** and a temperature at 50 °C are present in Figure 4.5. As can be observed, complete desulfurization was achieved after 2 h using 0.13 and 0.26 mmol of H_2O_2, and after 3 h using 0.60 mmol of this oxidant. The slower kinetic profile obtained for the highest amount of H_2O_2 used can be related with a decrease of contact area between the model diesel and the IL phase, caused by the higher amount of aqueous H_2O_2 located between these two phases, decreasing the transfer of sulfur compounds from the model diesel to the $[BMIM]PF_6$ phase and consequently limiting the number of sulfur species to be oxidized.[14, 16] Using 0.13 and 0.26 mmol of H_2O_2, a similar desulfurization profile was found, so the lower amount of H_2O_2 was chosen to continue the ODS tests.

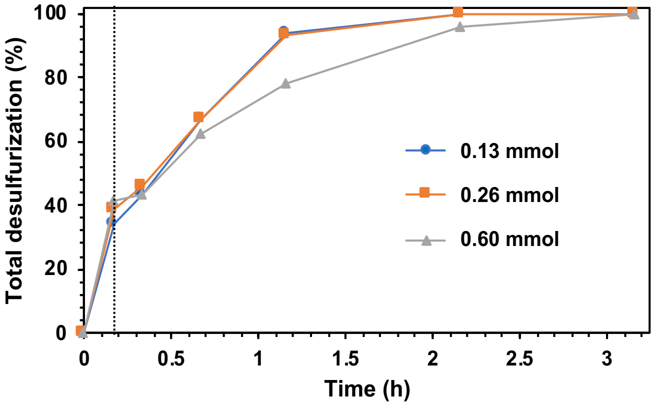


Figure 4.5. Desulfurization of a model diesel (3000 ppm S) using $[MoO_2Cl_2(DMB)_2]$ (**1**) (10 μmol) as catalyst, $[BMIM]PF_6$ as extraction solvent (0.750 mL) and different amounts of H_2O_2 as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Figure 4.6 displays the desulfurization profile obtained in the presence of different amounts of catalyst **1** (5, 10 and 20 μmol). All the other reaction parameters were maintained ($[BMIM]PF_6$ as extraction solvent, 0.13 mmol of H_2O_2, 50 °C). Different desulfurization results were obtained for each amount of catalyst **1**. Nevertheless, after 2 h practically complete desulfurization of the model diesel was achieved for all three catalyst amounts. Taking into account the overall desulfurization profiles, 10 μmol was the amount chosen to continue the optimization studies.

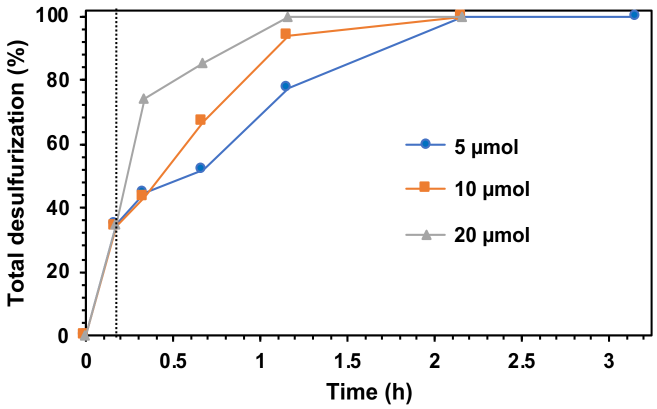


Figure 4.6. Desulfurization of a model diesel (3000 ppm S) using different amounts of [MoO$_2$Cl$_2$(DMB)$_2$] (**1**) as catalyst, [BMIM]PF$_6$ (0.750 mL) as extraction solvent, H_2O_2 (0.13 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

During these optimization studies, three different model diesel/[BMIM]PF$_6$ volume ratios were tested, in which the model diesel amount (0.750 mL) was maintained, and the IL amount was varied: 1:1, 1:0.5 and 1:0.3 (Figure 4.7). The ODS reactions were performed in presence of 10 *µ*mol of catalyst **1**, 0.13 mmol of H_2O_2 and a reaction temperature of 50 °C. Similar results were obtained using 1:1 and 1:0.5 of model diesel/[BMIM]PF$_6$, allowing 100% and 99% of sulfur removal after 2 h, respectively. The 1:0.5 volume ratio (0.375 mL of IL) was the amount chosen to continue the ODS studies.

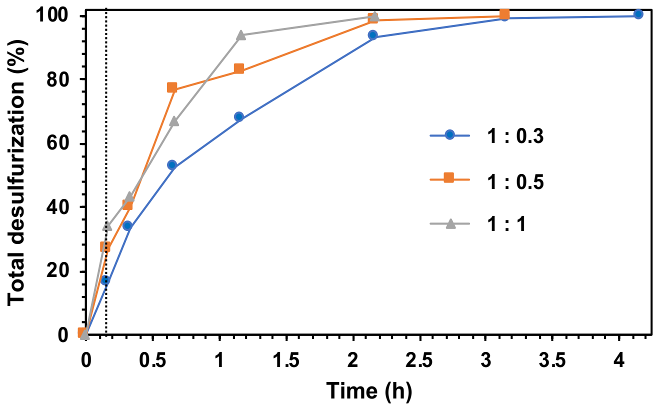


Figure 4.7. Desulfurization of a model diesel (3000 ppm S) using [MoO$_2$Cl$_2$(DMB)$_2$] (**1**) (10 *µ*mol) as catalyst, in the presence of different model diesel/[BMIM]PF$_6$ volume ratios and H_2O_2 (0.13 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The optimization of the ODS process using catalyst **2** was also performed and the parameters investigated were: type of extraction solvent, amount of catalyst and oxidant, volume of extraction solvent and temperature. Figure 4.8 displays the desulfurization profile obtained in the presence of different extraction solvents. $[BMIM]PF_6$ also presented the best desulfurization behaviour using catalyst **2**, achieving a complete desulfurization of the model diesel at 2 h of reaction.

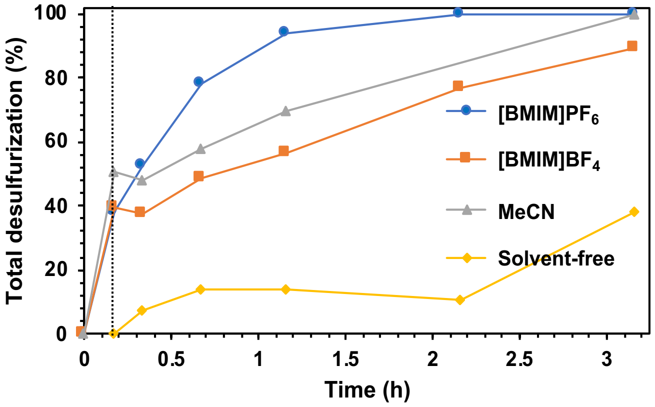


Figure 4.8. Desulfurization of a model diesel (3000 ppm S) using $[MoO_2Cl_2(DEO)]$ (**2**) (10 μmol) as catalyst, in the absence and presence of different extraction solvents and H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Regarding the oxidant amount, a different performance was observed in the presence of catalyst **2** (Figure 4.9). Using the catalyst **1**, the best desulfurization results were achieved using the lowest amount of oxidant, i.e. 0.13 mmol. However, using catalyst **2** higher desulfurization efficiency was obtained using 0.60 and 0.26 mmol of oxidant, achieving complete desulfurization after 2 h of reaction. Analysing the oxidant amount still present in the reaction medium after 2 h, it was verified that all the oxidant had been consumed. According to Kühn and Romão [17], the reaction rate for epoxidation catalysed by **2** decreased after a rapid increase in oxidation yield in the early stages. This is typical behaviour for $[MoO_2X_2L_n]$ catalysts in olefin epoxidation, which can occur due to several factors, such as the consumption of the oxidizing agent. In the present case, this reason was confirmed with sulfur-free model diesels obtained with the increase of the amount of oxidant. The amount of H_2O_2 chosen to continue the optimization studies with the catalyst **2**, was 0.26 mmol.

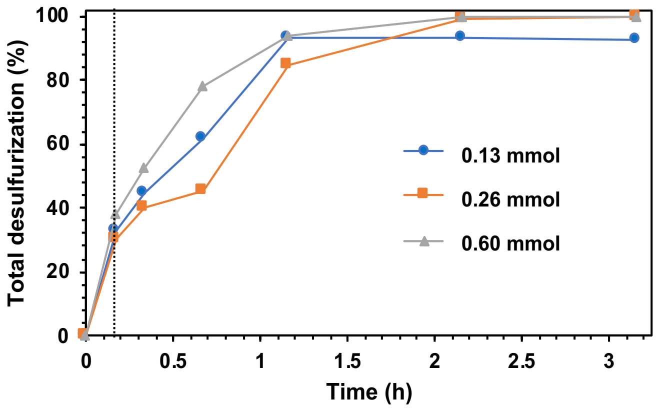


Figure 4.9. Desulfurization of a model diesel (3000 ppm S) using [MoO$_2$Cl$_2$(DEO)] (**2**) (10 *μ*mol) as catalyst, [BMIM]PF$_6$ (0.750 mL) as extraction solvent and different amounts of H_2O_2 as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The influence of the amount of catalyst **2** was also analysed for desulfurization of the model diesel, maintaining the remaining experimental conditions ([BMIM]PF$_6$ as extraction solvent, 0.26 mmol of H_2O_2 and 50 °C) (Figure 4.10). The best desulfurization result was obtained in the presence of the highest amount of catalyst **2** (20 *μ*mol). After 1 h, the treated model diesel only contained 3 ppm of sulfur compounds. However, the very interesting result obtained in the presence of 5 *μ*mol of catalyst, i.e. a completely desulfurized model diesel at 2 h of reaction, made it the chosen amount to continue the ODS studies.

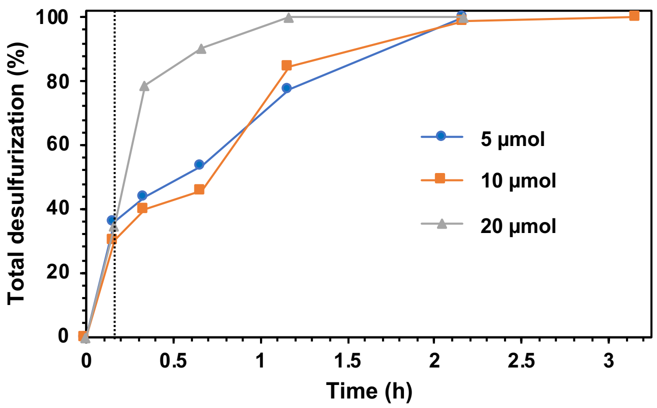


Figure 4.10. Desulfurization of a model diesel (3000 ppm S) using different amounts of [MoO$_2$Cl$_2$(DEO)] (**2**) as catalyst, [BMIM]PF$_6$ (0.750 mL) as extraction solvent and H_2O_2 (0.26 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Increasing the reaction temperature from 50 to 70 °C was very beneficial for the ODS process with **2** (allowing 99% sulfur removal after 40 min, and complete desulfurization after 1 h) (Figure 4.11). The higher temperature could not be used with **1** since it promoted a perceptible increase in miscibility between model diesel and IL phases. Nevertheless, it is remarkable that an ultra-low sulfur model diesel (< 10 ppm S) could be obtained using **1** as catalyst under the optimized conditions with a H_2O_2/sulfur molar ratio of 1.8, which is slightly lower than the molar ratio of **2** for the stoichiometric oxidation of the dibenzothiophene compounds to the corresponding sulfones. A higher H_2O_2/sulfur ratio of 3.7 was required for **2**, which may be indicative of an enhanced non-productive decomposition of the oxidant. Accordingly, titration analysis of the reaction mixture after 2 h showed that all the oxidant had been consumed.

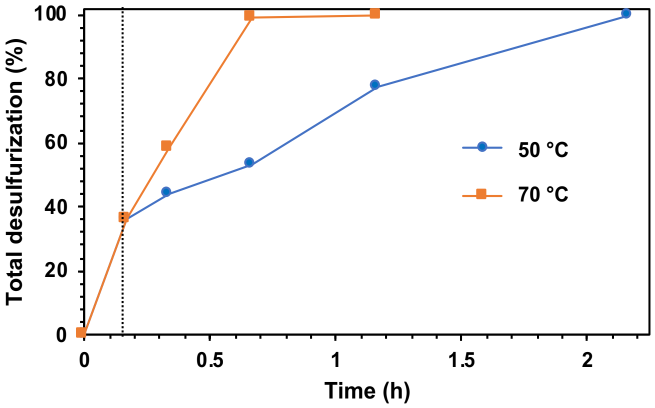


Figure 4.11. Desulfurization of a model diesel (3000 ppm S) using [MoO_2Cl_2(DEO)] (**2**) (5 μmol) as catalyst, [BMIM]PF_6 (0.750 mL) as extraction solvent and H_2O_2 (0.26 mmol) as oxidant, at different temperatures. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The effect of different model diesel/IL volume ratios in the ODS process was also analysed using catalyst **2**. Figure 4.12 displays the desulfurization profile of the model diesel using model diesel/[BMIM]PF_6 volume ratios of 1:1, 1:0.5 and 1:0.3. In the present case the highest amount of IL (1:1 of model diesel/[BMIM]PF_6 ratio) stands out, allowing a complete desulfurization after 1 h. Considering the optimized 1:0.5 ratio using catalyst **2**, complete desulfurization was only achieved after 4 h. In the presence of 1:0.3 ratio, after 4 h of reaction the model diesel still contained 41 ppm of sulfur content. It is interesting to note that during the initial extraction (before addition of H_2O_2) the amount of sulfur compounds transferred from the non-polar phase to the IL is proportional to the volume of [BMIM]PF_6, observing a decrease from 36.2% (1:1) to 23.2% (1:0.5) and 15.2% (1:0.3).

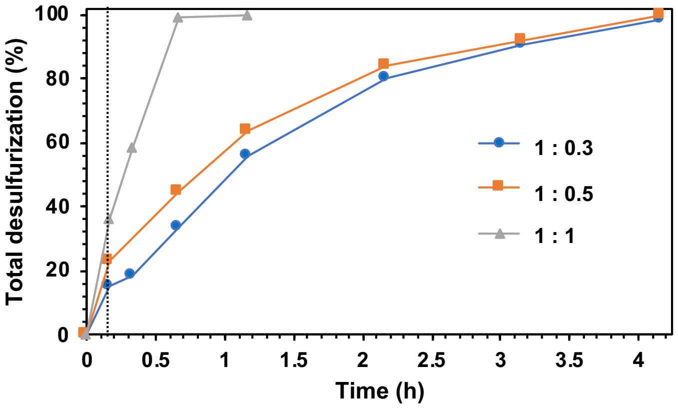


Figure 4.12. Desulfurization of a model diesel (3000 ppm S) using [MoO_2Cl_2(DEO)] (**2**) (5 μmol) as catalyst, in the presence of different model diesel/[BMIM]PF_6 volume ratios and using H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

4.2.2.2. Reutilization of catalysts 1 and 2

After ODS cycles performed under the optimized conditions with the model diesel (2 h reaction time), the IL ([BMIM]PF_6) liquid phases containing the dissolved catalysts were reused. The desulfurized model diesel phase was removed and then the next cycle was initiated simply by adding a fresh portion of model diesel, performing the extraction stage as usual during 10 min, and then adding a fresh portion of H_2O_2 to start the catalytic stage. The disadvantage of this procedure is that the concentration of oxidized sulfur compounds (sulfones) in the IL phase increases with the number of ODS cycles performed and may eventually reach the saturation point. Indeed, a white precipitate typically appeared after performing four cycles. Nevertheless, the desulfurization performances of the systems **1**/[BMIM]PF_6 and **2**/[BMIM]PF_6 were practically maintained across five ODS cycles (Figure 4.13). The similarity of the initial extraction results (22-29%) for the system **1**/[BMIM]PF_6, with no obvious decrease in sulfur removal capacity upon recycling, indicates that the accumulation of oxidized sulfur compounds in the IL phase over the various ODS cycles did not have a negative impact on the transfer of sulfur compounds from the model diesel to the IL medium, even though the volume of the latter was only half that of the model diesel.

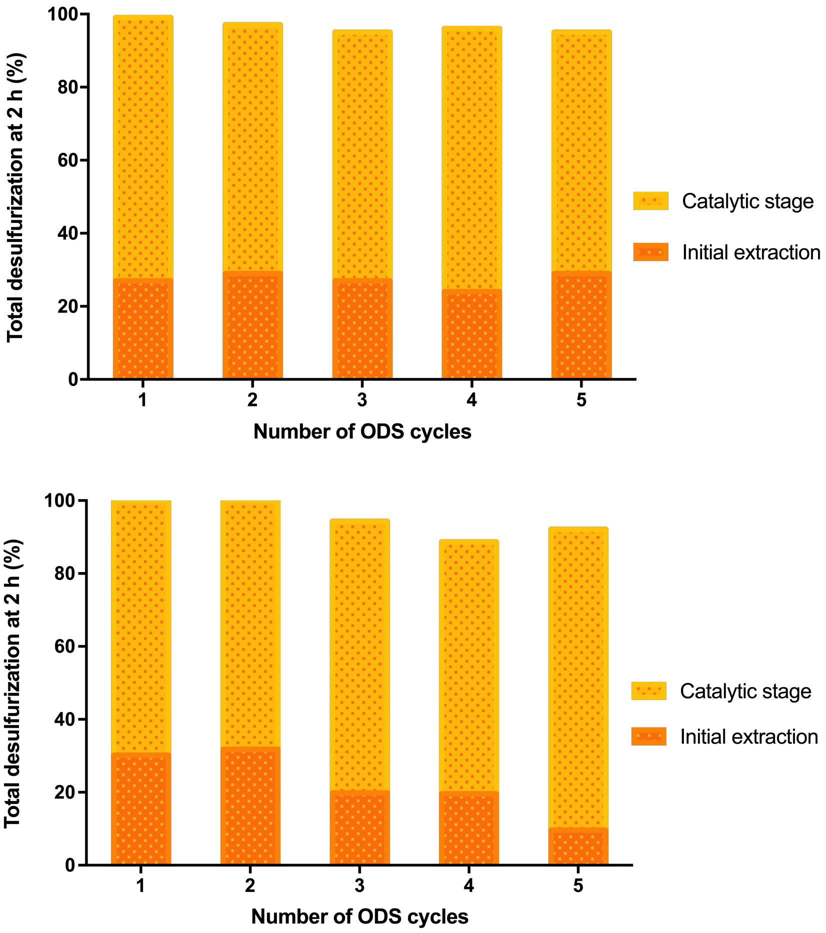


Figure 4.13. Desulfurization data for five consecutive reused ODS cycles, using $[MoO_2Cl_2(DMB)_2]$ (**1**) (10 μmol) (top) $[MoO_2Cl_2(DEO)]$ (5 μmol) (**2**) (bottom) as catalysts, a model diesel/$[BMIM]PF_6$ with a volume ratio of 1:0.5 (top) and 1:1 (bottom), with 0.13 mmol (top) and 0.26 mmol (bottom) of H_2O_2 as oxidant, and a reaction temperature of 50 °C (top) and 70 °C (bottom). Results obtained after 2 h of ODS reaction.

4.2.3. Desulfurization of untreated diesel

The ODS systems using catalysts **1** and **2** were investigated for the treatment of a high sulfur real diesel (2300 ppm S). In addition to the ODS step performed with the catalyst/$[BMIM]PF_6$ system under the optimized conditions determined previously, initial and/or final extractions with MeCN or DMF were performed. In agreement with the results obtained with the model diesel, the ODS system with **2** proved to be more efficient than that with **1** in the desulfurization of the untreated real diesel (Table 4.3). When the final extraction was performed with MeCN, the application of an initial extraction with the same solvent (before the oxidative catalytic stage) improved the overall desulfurization efficiency for both catalysts, albeit only slightly for **2**. On the other hand, for DMF, the application of an initial extraction was not beneficial, and actually led to a significantly lower desulfurization efficiency in the case of **2**. In fact, the exceptional results obtained for the ODS system using **2**, without an initial extraction, i.e. 93.1% and 89.7%, demonstrate that the initial extraction step can be omitted due to the high efficiency of **2** for the oxidative treatment of the real diesel.

In an effort to improve the performance of the ODS system **1**/[BMIM]PF_6 in the treatment of the real diesel, further experiments were performed (without any initial extraction treatment) in which the oxidant amount and/or diesel/IL volume ratio were varied (Table 4.4). With the lower amount of oxidant [$n(H_2O_2)/n(S) = 1.8$], similar desulfurization efficiencies were obtained for diesel/IL volume ratios of 1:1 and 1:0.5. We surmised that the failure to observe an increase in sulfur removal upon increasing the volume of IL might be due to sulfur oxidation being restricted by the low amount of oxidant, inhibiting a continuous transfer of sulfur compounds from the diesel to the IL. However, when the amount of oxidant was doubled [$n(H_2O_2)/n(S) = 3.7$], using equal volumes of IL and diesel, only a minor improvement in the desulfurization efficiency was obtained (from 49.8% to 53.4%). A remarkable increase in the sulfur removal from the real diesel, to 83.4%, was observed when the higher amount of oxidant was used but with the lower amount of IL, i.e. a diesel/IL volume ratio of 1:0.5. This behavior must be related with the two-fold increase in the concentration of the catalyst entrapped in the IL phase, which will result in a higher catalyst concentration at the interface of the immiscible aqueous and IL phases, thus promoting an increase in the reaction rate between the non-oxidized sulfur compounds (extracted from the diesel phase) and H_2O_2 over the catalyst.

Table 4.3. Experiments performed for ODS of an untreated real diesel, under the optimized model diesel ODS system conditions, using catalysts **1** and **2**

Catalyst	Extraction process[a]	ODS process[b,c]	S content (ppm)	Desulfurization efficiency (%)
1	---	MeCN[b]	1176	48.9
	---	DMF[b]	1000	56.5
	MeCN	MeCN[b]	657	71.4
	DMF	DMF[b]	1014	55.9
2	---	MeCN[c]	158	93.1
	---	DMF[c]	237	89.7
	MeCN	MeCN[c]	129	94.4
	DMF	DMF[c]	402	82.5

[a] Liquid-liquid diesel/organic solvent extraction of non-oxidized sulfur compounds during 10 min at 70 °C.

[b] Oxidative desulfurization in a biphasic diesel/[BMIM]PF_6 system during 2 h using the optimal experimental conditions (10 μmol of **1**, 0.13 mmol of H_2O_2, diesel/IL volume ratio = 1:0.5) obtained from model diesel desulfurization, with a final extraction with an organic solvent (MeCN or DMF) for 30 min at 50 °C.

[c] Oxidative desulfurization in a biphasic diesel/[BMIM]PF_6 system during 2 h using the optimal experimental conditions (5 μmol of **2**, 0.26 mmol of H_2O_2, diesel/IL volume ratio = 1:1) obtained from model diesel desulfurization, with a final extraction with an organic solvent (MeCN or DMF) for 30 min at 70 °C.

Table 4.4. Experiments performed for ODS of an untreated real diesel using catalyst **1** and different oxidant amounts and diesel/IL volume ratios.[a]

Catalyst	Amount of H_2O_2 (mmol)	Diesel/IL volume ratio	ODS process[a]	S content (ppm)	Desulfurization efficiency (%)
1	0.13	1:0.5	MeCN	1176	48.9
	0.13	1:1		1162	49.8
	0.26	1:0.5		381	83.4
	0.26	1:1		1071	53.4

[a] Oxidative desulfurization with a biphasic diesel/[BMIM]PF_6 system for 2 h at 50 °C, 10 μmol of **1**, with a final extraction with MeCN during 30 min at 50 °C.

4.3. Conclusions

In summary, two dioxomolybdenum(VI) complexes bearing *O*-donor monodentate and bidentate ligands were effectively used as catalysts for desulfurization of model and real diesels with high sulfur contents. The different ligands, *N,N*-dimethylbenzamide (DMB) and *N,N′*-diethyloxamide (DEO), coordinated to the molybdenyl derivative MoO_2Cl_2 resulted in distinct optimal operational conditions to achieve the highest catalytic performance for desulfurization of a multicomponent model diesel and an untreated diesel supplied by Galp Energia. Complete desulfurized model diesels were obtained in presence of catalyst **1** and **2** using very low oxidant/S ratios (H_2O_2/S = 1.8 for **1** and 3.7 for **2**) and model diesel/IL ratios of 1:0.5 and 1:1, at 50 and 70 °C, respectively. The catalyst **2** is one of the most effective ODS catalysts reported to date for removing sulfur from a real diesel, allowing under optimized conditions a reduction in the sulfur content from 2300 to 129 ppm, which corresponds to a desulfurization efficiency of over 94%.

4.4. Experimental Section

4.4.1. Materials and Methods

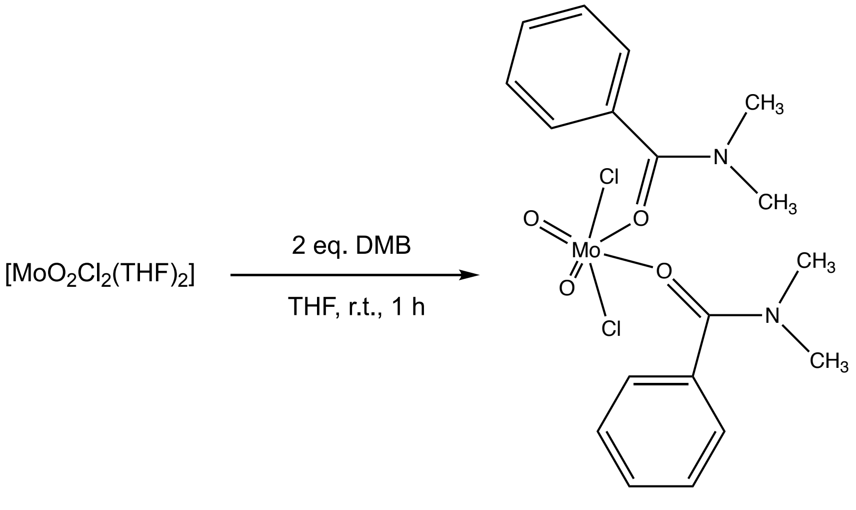
The following chemicals and reagents were purchased from commercial suppliers and used as received: MoO_2Cl_2 (Sigma-Aldrich), anhydrous tetrahydrofuran (Panreac), *N,N*-dimethylbenzamide (Alfa Aesar, ≥98%), *N,N'*-diethyl- oxamide (Alfa Aesar, 98%), dibenzothiophene (Sigma-Aldrich, 98%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), 1-butyl-3-methylimidazolium tetrafluoroborate (Sigma-Aldrich, ≥98%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical) and 30% w/v hydrogen peroxide (Sigma-Aldrich). The untreated diesel containing 2300 ppm of sulfur was supplied by Galp Energia.

The desulfurization of the model diesel was monitored using a Bruker 430-GC-FID gas chromatograph, equipped with a Supelco capillary column SPB-5 (30 m x 250 μm id.; 25 μm film thickness) and using hydrogen as the carrier gas (55 $cm^3 s^{-1}$). The analysis of the sulfur content in the treated diesel samples was performed at Galp

Energia by ultraviolet fluorescence using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

4.4.2. Catalyst synthesis

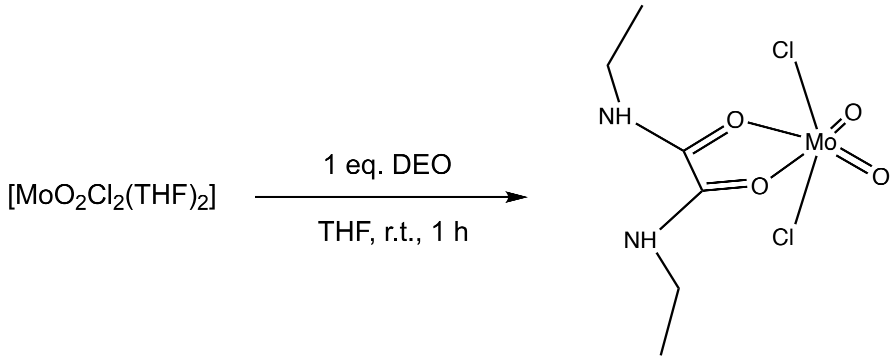
[$MoO_2Cl_2(DMB)_2$] (**1**) was prepared by dissolution of MoO_2Cl_2 (1.10 g, 5.53 mmol) in THF (15 mL) and posterior addition of *N,N*-dimethylbenzamide (1.65 g, 11.06 mmol), followed by stirring at room temperature for 1 h. The resultant pale-yellow precipitate was isolated by filtration, washed with diethyl ether (2 × 15 mL), and vacuum-dried. Yield: 2.51 g (91%). Anal. Calcd for $C_{18}H_{22}Cl_2MoN_2O_4$: C, 43.48; H, 4.46; N, 5.63. Found: C, 43.29; H, 4.54; N, 5.68%. FT-IR (KBr, cm^{-1}): ν = 3109 (w), 3057 (w), 3035 (w), 2966 (w), 2935 (w), 1587 (vs), 1566 (vs), 1510 (s), 1475 (s), 1444 (s), 1404 (s), 1286 (w), 1265 (s), 1217 (w), 1180 (w), 1161 (w), 1147 (w), 1097 (m), 1078 (m), 1057 (m), 1024 (m), 1003 (w), 991 (w), 947 (vs, ν_{sym}(Mo=O)), 910 (vs, ν_{asym}(Mo=O)), 852 (m), 783 (s), 741 (s), 719 (s), 700 (s), 652 (s), 559 (m), 447 (m), 395 (s), 332 (vs, ν(Mo–Cl)). FT-Raman (cm^{-1}): ν = 3067 (s), 2967 (w), 2939 (m), 2808 (w), 1601 (s), 1573 (w), 1514 (m), 1447 (m), 1414 (m), 1263 (w), 1217 (w), 1181 (w), 1162 (w), 1099 (w), 1025 (w), 1001 (s), 949 (vs), 910 (m), 782 (w), 741 (m), 725 (m), 651 (w), 615 (w), 561 (w), 447 (w), 397 (w), 347 (w), 322 (w), 302 (w), 259 (w), 207 (s), 144 (s), 107 (s). ^1H NMR (300 MHz, 298 K, CD_3CN): δ = 7.36 (overlapping signals, 10H), 3.01 (s, 6H), 2.88 (s, 6H).[8]



1

Figure 4.14. Preparation of complex [$MoO_2Cl_2(DMB)_2$] (**1**).

[MoO_2Cl_2(DEO)] (**2**) was prepared by dissolution of MoO_2Cl_2 (1.07 g, 5.38 mmol) in THF (15 mL) and posterior addition of *N,N′*-diethyloxamide (0.775 g, 5.38 mmol), followed by stirring at room temperature for 1 h. The resultant pale-yellow precipitate was isolated by filtration, washed with diethyl ether (2 × 15 mL), and vacuum-dried. Yield: 0.62 g (34%). Anal. Calcd for $C_6H_{12}Cl_2MoN_2O_4$: C, 21.01; H, 3.53; N, 8.17. Found: C, 20.81; H, 3.65; N, 8.24%. FT-IR (KBr, cm^{-1}): ν = 3330 (vs, ν(N–H)), 3178 (m), 3107 (w), 3057 (w), 2983 (m), 2939 (w), 2881 (w), 1643 (vs), 1523 (s), 1462 (s), 1446 (s), 1388 (m), 1379 (m), 1350 (m), 1288 (m), 1267 (m), 1232 (m), 1151 (s), 1097 (m), 1041 (m), 955 (vs, ν_{sym}(Mo=O)), 912 (vs, ν_{asym}(Mo=O)), 741 (m), 673 (m), 565 (s), 507 (s), 391 (s), 337 (vs, ν(Mo–Cl)). FT-Raman (cm^{-1}): ν = 3337 (w), 2981 (w), 2940 (s), 2878 (m), 1678 (w), 1636 (w), 1599 (m), 1554 (w), 1522 (w), 1447 (m), 1378 (s), 1332 (m), 1290 (w), 1267 (m), 1145 (w), 1058 (w), 1040 (w), 959 (vs), 913 (s), 803 (w), 505 (m), 390 (s), 316 (vs), 265 (s), 254 (s), 239 (vs), 192 (m), 140 (m). ^1H NMR (300 MHz, 298 K, CD_3CN): δ = 8.55 (br, 2H), 3.54 (br, 4H), 1.26 (br, 6H).[8]



2

Figure 4.15. Preparation of complex [MoO_2Cl_2(DEO)] (**2**).

4.4.3. Single-crystal X-ray diffraction

Single crystals of the compound [MoO_2Cl_2(DEO)]·THF were harvested from the crystallization vial, immersed in Fomblin® Y oil (Aldrich), and a suitable crystal for X-ray analysis was selected and mounted on the CryoLoops.[18] Full diffraction data were obtained at 150(2) K on a Bruker X8 APEX II CCD area-detector diffractometer (Mo K_α graphite-monochromated radiation, $\lambda = 0.71073$ Å; crystal positioned at 40 mm from the detector, 15 sec of exposure time per image), with the acquisition controlled by the APEX2 software.[19] Collected images were processed using SAINT+ program,[20] and the absorption effects were corrected by the multi-scan semi-empirical method implemented in SADABS.[21] The crystal structure was solved using the algorithms implemented in SHELXT-2014, [22, 23] and all non hydrogen atoms were located from difference Fourier maps calculated and refined by using anisotropic displacement from successive full-matrix least squares refinement cycles on F^2 using SHELXL-v.2014 [22, 24]

Hydrogen atoms connected to the distinct carbon atoms were positioned at geometrical positions using suitable *HFIX* instructions in SHELXL-v.2014 (*23* for the $–CH_2–$ and *137* for the terminal $–CH_3$ groups), while those bonded to nitrogen atoms of the DEO ligand were markedly visible in the difference Fourier maps, and included in subsequent refinement stages with the N–H distance restrained to 0.90(1) Å. All the hydrogen atoms were refined in riding-motion approximation with isotropic thermal displacement parameters (U_{iso}) fixed at 1.2 × or 1.5 × U_{eq} of the parent atom.

Table 4.5 shows selected information about the single-crystal X-ray data collection and the structure refinements. The CIF file was deposited with the Cambridge Crystallographic Data Centre as supplementary publication data No. CCDC--1895640. Copies of the data can be obtained online at https://www.ccdc.cam.ac.uk/structures/.

Table 4.5. Crystal and structure refinement data for the compound [MoO_2Cl_2(DEO)]·THF

Chemical formula	$C_{10}H_{20}Cl_2MoN_2O_5$
M_r	415.12
Crystal description	Yellow prism
Crystal size /mm	0.25 × 0.10 × 0.07
Crystal system, space group	Monoclinic, $P2_1/c$
a /Å	8.8771(7)
b /Å	9.5053(7)
c /Å	19.4997(16)
β /°	95.923(4)
Volume /Å^3	1636.6(2)
Z	4
$\rho_{calculated}$ /g cm^{-3}	1.685
F(000)	840
μ /mm^{-1}	1.145
θ range /°	3.651 to 28.281
Index ranges	$-11 \leq h \leq 11$ $-12 \leq k \leq 12$ $-25 \leq l \leq 25$
Reflections collected	31492
Independent reflections	4035 (R_{int} = 0.0753)
Final R indices [I>2σ(I)]	R_1 = 0.0305 wR_2 = 0.0753
Final R indices (all data)	R_1 = 0.0363 wR_2 = 0.0774
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ /e.Å^{-3}	0.724 and −0.649

4.4.4. ODS studies

4.4.4.1. Model diesel

The desulfurization studies were performed in 5 mL borosilicate flasks which were loaded with a magnetic stirring bar and a model diesel solution (0.750 mL) prepared by dissolving equal amounts (1000 ppm each) of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in *n*-octane. In a typical procedure, the catalyst **1** or **2** and an extraction solvent were added to the reaction vessel and the biphasic mixture was stirred vigorously for 10 min at 50 or 70 °C to perform an initial extraction. After this step, the oxidant was added to the system to initiate the catalytic oxidative stage. The reference (starting) conditions were 10 μmol of catalyst, 0.75 mL of extraction solvent, and 0.13 mmol of oxidant, which correspond to a *n*(cat):*n*(S):*n*(H_2O_2) molar ratio of 1:7:60. An optimization study was performed for each catalyst in which several reaction parameters were systematically varied, namely the effect of the absence or presence of different extraction solvents ([BMIM]PF_6, [BMIM]BF_4 and MeCN), the amount of 30% aq. H_2O_2 (0.13, 0.26 or 0.60 mmol) and catalyst (5, 10 or 20 μmol), the model diesel/extraction solvent volume ratio (1:1, 1:0.5 or 1:0.3), and the reaction temperature (50 or 70 °C).

The quantification of sulfur was performed by periodically taking aliquots from the model diesel phase, which were then diluted with tetradecane. For selected reactions the extent of non-productive oxidant decomposition was studied by titrating residual H_2O_2 with standardized ceric sulfate (full details are given in Section 4.4.5).

Catalyst reuse (for a total of five consecutive cycles) was performed by removal of the desulfurized model diesel from the ODS reactor, followed by addition of a fresh portion of model diesel and (after the 10 min initial extraction) a fresh portion of oxidant. The same reaction conditions were applied from one cycle to the next.

4.4.4.2. Untreated real diesel

The real diesel was treated by application of the optimized ODS conditions determined for the model diesel in the presence of catalysts **1** or **2**. To reach the best diesel desulfurization, some diesel samples were first desulfurized by liquid-liquid extractions with polar solvents, namely MeCN and DMF. After the oxidative catalytic process, all the diesel samples were washed with MeCN or DMF to remove the oxidized sulfur species still present.

4.4.5. Titration of H_2O_2

The hydrogen peroxide content was determined by titrating with standardized ceric sulfate, 0.093 M $Ce(SO_4)_2$, to a pale blue endpoint using ferroin indicator.

The standard solution of 0.093 M $Ce(SO_4)_2$ was prepared by dissolution of 16 g of $Ce(SO_4)_2$ in 28 mL of a mixture of H_2SO_4 and water (1:1, *v*/*v*). This solution was allowed to cool to room temperature and transferred to a 500 mL volumetric flask. The solution was standardized with 0.1 M $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$. In each titration procedure a solution prepared from 25 mL of 0.1 M $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 25 mL of 0.5 M H_2SO_4 was used.

The recovered reaction solution was weighed in an Eppendorf tube and added to a solution of 1 M H_2SO_4 (150 mL) along with 2-3 drops of ferroin indicator, and titrated with 0.093 M $Ce(SO_4)_2$ to a pale blue color. The reaction involved is defined as:

$$2Ce^{4+} + H_2O_2 \rightleftarrows 2Ce^{3+} + O_2 + 2H^+$$

The percentage of H_2O_2 was calculated through the following expression:

$$\%H_2O_2 = \frac{V \times [Ce^{4+}] \times 17.01}{10 \times m}$$

where V (mL) = volume of ceric sulfate solution (titrant); [Ce^{4+}] (mol.dm^{-3}) corresponds to the concentration of the titrant (0.093 M) and m (g) = weight of the reaction solution.

Using the same experimental procedure, the percentage of H_2O_2 present in the blank solution was also calculated, i.e. everything that would be present in an ODS reactor (except the solid catalyst) was transferred to an Eppendorf tube and weighed.

Knowing the percentage of H_2O_2 present in the sample and in the blank test, the amount of H_2O_2 consumed is calculated by the following expression:

$$100 - \%HP, where\ \%HP = \frac{\%H_2O_{2,\ sample}}{\%H_2O_{2,\ blank}}$$

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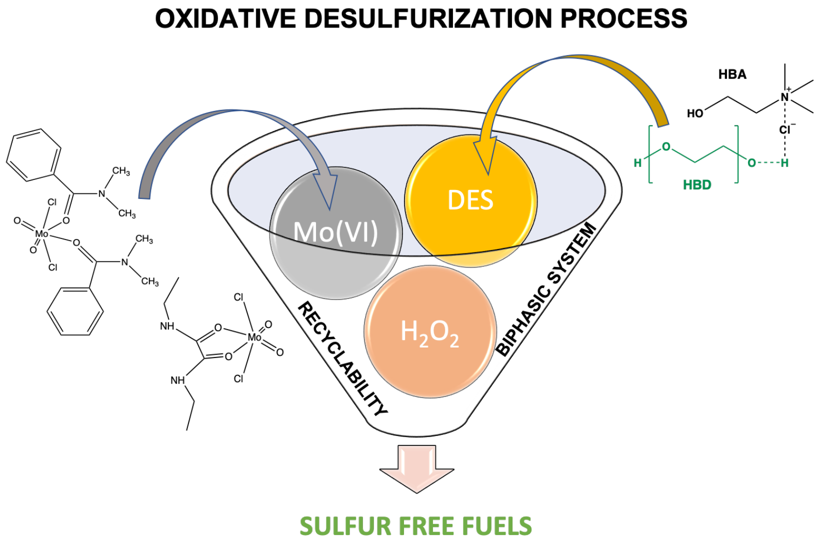
Chapter 5

NOVEL CATALYTIC SYSTEMS BASED ON $[MoO_2Cl_2L_n]$ COMPLEXES AND DEEP EUTECTIC SOLVENTS



5. Novel catalytic systems based on [$MoO_2Cl_2L_n$] complexes and deep eutectic solvents

5.1. Introduction

Green chemistry advocates a primary pollution prevention rather than waste remediation. A significant source of waste in industry and fine chemistry stems from the use of hazardous organic solvents.[1] It is therefore important to develop solvents that facilitate the reaction, the recovery and reuse to ensure an economic competitivity and minimize the impact on the environment and energy consumption.[2] An example are the so-called neoteric solvents, such as ionic liquids (ILs) [3], and supercritical fluids, in which are included water and carbon dioxide [4]. The ILs have been extensively studied due to their negligible vapor pressure, thermal stability and non-flammability. However, the possible choices of cation and anion results in a wide range of IL compositions and therefore different environmental impacts.[5, 6] Furthermore, their expensive preparation involves complex and time-consuming methods.[1, 7]

A new class of versatile, alternative green solvents, entitled deep eutectic solvents (DES), otherwise known as low-transition temperature mixtures (LTTMS) [1], have emerged with promising prospects in several areas, ranging from electrochemistry [8], catalysis [9-11], synthesis [12-14] to enzymatic reactions [15, 16]. DES present most of the advantageous inherent to ILs, but are obtained by simpler low cost synthetic routes composed of non-toxic and biodegradable components.[9] Their preparation involves gentle heating of a eutectic mixture of two or more components.[1] One of the components must possess relatively strong hydrogen bond donor ability (HBD), usually alcohols, polyols, carboxylic acids and amides, while the other components are for example ammonium or phosphonium salts used as hydrogen bond acceptors (HBA).[17] Most of them come from readily available, inexpensive, biocompatible and biodegradable renewable sources. Moreover, these solvents possess the highest possible atom economy.[1, 13] Many acids and bases are used to catalyse a wide range of organic reactions, thus by preparing DES with these components, it is possible to prepare DES that can act not only as a reaction medium but also as catalyst.[13] The extractive and catalytic behaviour of several types of DES have been investigated for the oxidative desulfurization of model diesel and real fuels.[10, 18-21]

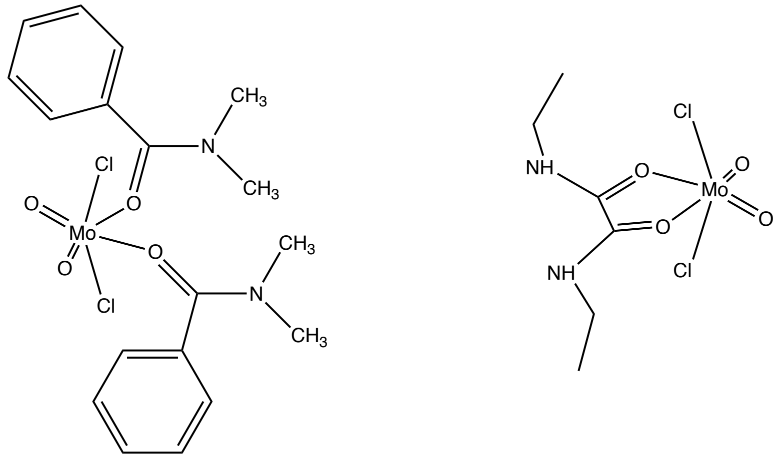
Oxidative desulfurization (ODS) technology is a low-cost process capable of an efficient removal of sulfur from liquid fuels under environmentally friendly conditions, such as low temperatures/pressures and without H_2 consumption.[22] This process is based on the oxidation of the sulfur compounds to the corresponding sulfoxides and/or sulfones, which are more easily removed by liquid-liquid extraction with appropriate polar solvents. The oxidative step is accomplished by the presence of an oxidant, usually the waste-avoiding H_2O_2. Its low intrinsic reactivity allows its selective activation by a suitable catalyst.[23] Molybdenum-based compounds are recognized as some of the most efficient catalysts for oxygen atom transfer reactions, such as olefin epoxidation and oxidation of sulfides.[24-27] A well-known example are the complexes based on dioxo dichloride, MoO_2Cl_2, bearing mono- and bidentate organic ligands with nitrogen or oxygen donor atoms.[28, 29] Only one report in the literature describes the use of a dioxomolybdenum(VI) complex, $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$, as an efficient homogeneous catalyst for the desulfurization of a model and real diesel using H_2O_2 as oxidant.[30] Despite the benefits of homogeneous catalysts, their recovery and recycling is challenging. This drawback can be overcome by the use of a solvent with recycling capacity, such as ILs and DES, permitting the reuse of the catalyst for several cycles. These solvents are also employed as sulfur extractants.

In the present chapter, two deep eutectic solvents were prepared and used as extraction solvents in desulfurization of a model diesel. The application of the dioxomolybdenum(VI) complexes, $[MoO_2Cl_2(DMB)_2]$ (**1**) and $[MoO_2Cl_2(DEO)]$ (**2**), using DES as extraction solvent and H_2O_2 as oxidizing agent, was studied for the first time for the desulfurization of model and real diesels. The systems containing the catalysts **1** or **2** were reused by distinct procedures for several ODS cycles. Moreover, real diesel samples were treated using the optimal model diesel conditions.

5.2. Results and Discussion

5.2.1. Dioxomolybdenum(VI) catalysts and DES

The dioxomolybdenum(VI) complexes applied as catalysts are the same as those described in Chapter 4, i.e. [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**) (Figure 5.1). DES were prepared and used as extraction solvents during the desulfurization studies. The DES were obtained by the dissolution in a proportion of 1:2 of different HBA (TBACl or ChCl) and polyethylene glycol (PEG) as HBD (Table 5.1). The DES were characterized by FT-IR and ^1H NMR. Some physical properties, such as viscosity and density, were also analysed. The detailed description of the syntheses can be found in the Section 5.4.2.



1 **2**

Figure 5.1. Dioxomolybdenum(VI) complexes: [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**).

Table 5.1. Schematic representation of components HBA and HBD and the corresponding proportions used in each DES

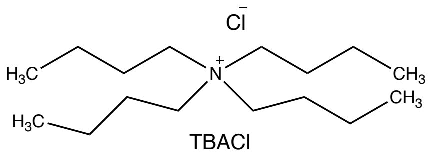
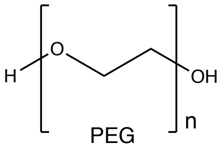
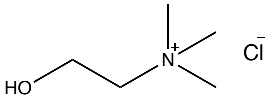
HBA	HBD	Molar ratio (HBA:HBD)
 TBACl	 PEG	1:2
 ChCl		

Figure 5.2 displays the FT-IR spectra of the DES and also the HBA and HBD components used in their preparation. The spectrum of PEG shows a strong band between 3400 and 3200 cm^{-1} attributed to the stretching vibration of hydroxyl groups (O-H). The formation of hydrogen bonding, characteristic of DES, was confirmed by the presence of the same band (albeit broader) in most of the spectra. The N-H stretching band, characteristic of ammonium-based HBA, was not observed in the DES spectra due to overlap with the broader O-H band.[31] The C-H stretching vibrations typical of saturated carbon chains were identified in the range of 2928-2873 cm^{-1}. The spectrum of TBACl presents two peaks at 2958 and 2874 cm^{-1} corresponding to CH_3 and CH_2 groups, respectively. The DES obtained from this HBA (TBA/PEG) presents a single peak, with a loss of definition, indicating the successful interaction between the TBA and PEG components.[20] In the fingerprint region of DES, namely from 1135 to 1037 cm^{-1}, bands characteristic of C-O stretching vibrations in PEG and ChCl were observed.[32] The purity of DES was confirmed using ^{1}H NMR.

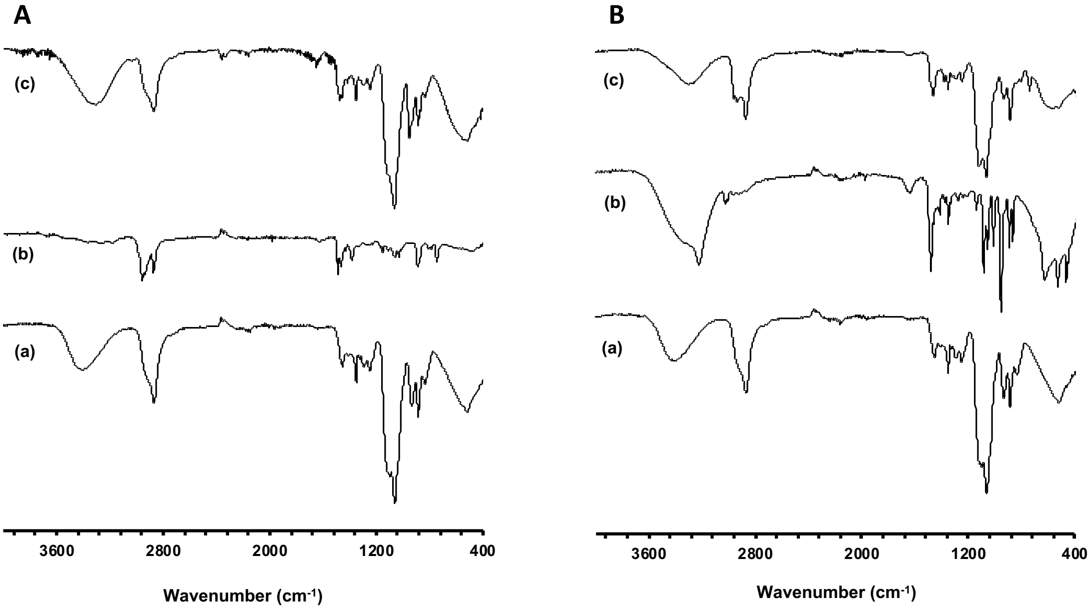


Figure 5.2. FT-IR spectra of **A** [(a) PEG, (b) TBACl and (c) TBA/PEG] and **B** [(a) PEG, (b) ChCl and (c) ChCl/PEG].

Viscosity is one of the most important physical properties of a fluid system. This parameter is usually affected by temperature, the types of HBD and HBA, and their molar ratio.[32, 33] The viscosity was measured at different temperatures in the range of 25-80 °C (Table 5.2). For both DES (TBA/PEG and ChCl/PEG) the reduction of viscosity was greater at the initial stage of temperature increment (from 25 to 50 °C). Increases in temperature above 50 °C had a diminished influence on the viscosity of the DES. As well described in the literature, high temperatures promote an increase in kinetic energy, which causes a decrease in contact between molecules and consequently a lowering of intermolecular forces, contributing to a decrease in the viscosity.[33] This dependence is described by the Arrhenius equation (1) where μ is the viscosity, μ^o is a preexponential constant, Ea is the activation energy of viscous flow, R is the gas constant and T is the temperature.

$$\mu = \mu^o + e^{Ea/RT} \qquad (1)$$

Table 5.3 shows the results when the equation 1 is applied. The values of activation energy show that both DES containing PEG as HBD are susceptible to the temperature variation. This can be related with the high carbon chain length of polyethylene glycol.[34]

Table 5.2. Viscosity (mPa.s) of the synthesized DESs at different temperatures and the corresponding HBD (PEG)

T (°C)	PEG	TBA/PEG	ChCl/PEG
25 °C	49.61	216.3	---
50 °C	17.49	60.99	66.55
70 °C	9.133	28.97	24.38
80 °C	6.863	21.08	18.68

Table 5.3. Viscosity-temperature model parameters

DESs	$\mu°$ / mPa.s	Ea* / $J.mol^{-1}$	R^2
TBA/PEG	6.035E-5	37148.2	0.9975
ChCl/PEG	1.565E-5	41008.4	0.9866
PEG	1.401E-4	31528.4	0.9989

* $Ea = m \times R$ ($R = 8.3144621\ J.K^{-1}.mol^{-1}$)

The density was also determined for the DES studied and found to decrease (linearly) with increasing temperature, although not as substantially as viscosity (Figure 5.3). The largest difference in density over the temperature range was 3.4% for TBA/PEG. In the presence of the same HBD (PEG), there is a considerable difference between the density of the TBA-based DES and that for ChCl/PEG, indicating a high influence of the HBA salt. The carbon chain of TBA has a considerably larger molar volume than those present in ChCl, exhibiting a lower density and a larger free volume, with this unique DES presenting a lower density when compared with its HBD component.[35]

The density follows a linear trend with temperature. The density values of the DESs were fitted as a function of temperature following equation 2, where ρ is the density, T is the temperature, and α and β are the fitted parameters. The values of α and β for the DES are presented in Table 5.4. The $R^2 > 0.9995$ indicate that the density-temperature relationship is linear for these DES.

$$\rho\left(\frac{g}{cm^3}\right) = \alpha + \beta(T/K) \qquad (2)$$

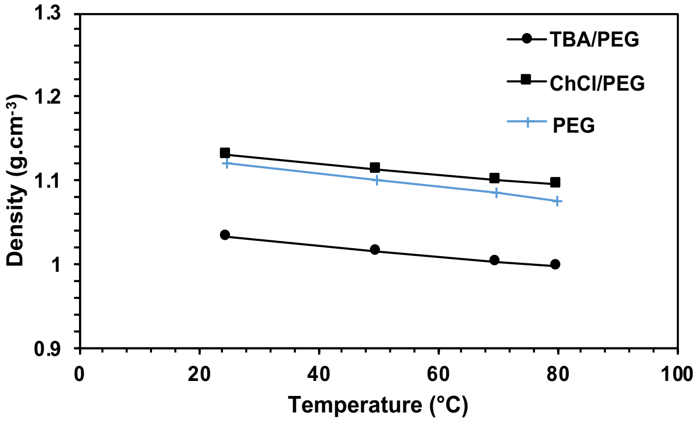


Figure 5.3. Density of DESs and corresponding PEG with respect to temperature.

Table 5.4. Density-temperature model parameters

DESs	α / g.cm^{-3}	β / g.cm^{-3}.K	R^2
TBA/PEG	1.2286	-0.0006	1.0000
ChCl/PEG	1.3407	-0.0007	1.0000
PEG	1.1409	-0.0008	0.9999

5.2.2. Desulfurization of a model diesel

A model diesel containing 3000 ppm of sulfur (DBT, 4-MDBT and 4,6-DMDBT) was desulfurized using the catalysts [$MoO_2Cl_2(DMB)_2$] (**1**) or [$MoO_2Cl_2(DEO)$] (**2**), the DES as extraction solvent and H_2O_2 as oxidant, at 50 or 70 °C. In a typical procedure the catalyst was dissolved in the extraction solvent, followed by addition of model diesel, resulting in a biphasic system. An initial extraction of sulfur compounds from the model diesel to the extraction solvent phase was achieved by stirring the mixture at 50 or 70 °C for 10 min. After this stage, H_2O_2 was added to the system to start the catalytic oxidative stage, in which occurs the oxidation of the sulfur compounds to the corresponding sulfones and/or sulfoxides. The similar polarities between the oxidized sulfur compounds and the extraction solvent allows an effective removal of these species.

5.2.2.1. Optimization of desulfurization process

The optimization of different experimental parameters is crucial to improve catalyst performance and desulfurization efficiency. In order to conciliate the highest desulfurization with the sustainability and economic viability of the process, numerous factors in the ODS system were investigated, such as the influence of different solvents, from volatile organic (MeCN) to ionic liquids ([BMIM]PF_6 and [BMIM]BF_4) and deep eutectic solvents (TBA/PEG and ChCl/PEG). Also, the amount of catalyst **1** (5, 10 and 20 μmol) and H_2O_2 oxidant (0.13, 0.26, 0.35 and 0.60 mmol), the model diesel/extraction solvent volume ratio (1:1, 1:0.5 and 1:0.3) and temperature (50 and 70 ºC) were investigated.

The first parameter analysed was the influence of different solvents (0.750 mL), with 0.750 mL of model diesel in the presence of 10 μmol of catalyst **1** and 0.60 mmol of H_2O_2, and a reaction temperature of 50 °C. A solvent-free system (without extraction solvent) was also tested. The results obtained are presented in Figure 5.4. The desulfurization efficiencies obtained after the initial extraction performed with the various solvents (i.e. before the oxidative catalytic stage) followed the order TBA/PEG (63.3%) > PEG (59.9%) > MeCN (52.8%) > [BMIM]PF_6 (41.2%) > [BMIM]BF_4 (28.3%) > ChCl/PEG (27.2%). The presence of TBA as hydrogen acceptor appears to be beneficial in comparison to ChCl, promoting an increase in the extraction capacity of this DES as solvent, being also superior to PEG. In fact, TBA/PEG possessed the lowest density (1.0167 $g.cm^{-3}$, Figure 5.3) and a low viscosity (60.99 mPa.s, Table 5.2) when compared to ChCl/PEG at 50 °C, which may explain its higher extraction capacity.

The catalytic stage of the ODS process is initiated by the addition of H_2O_2. Figure 5.4 shows that the most efficient solvents during the initial extractions are not the best reaction media for the catalytic oxidation. The highest desulfurization performances were achieved using the IL [BMIM]PF_6 and the DES ChCl/PEG as solvents. The main difference in their desulfurization profile occurs during the first hour of ODS process, which is related to the higher extraction capacity of the IL than the ChCl/PEG DES. The DES with the higher liquid-liquid extraction capacity did not promote a higher oxidative desulfurization using H_2O_2 as oxidant. Some authors have assumed that the presence of water dissolved in the DES can decrease its extraction capacity, promoting a return of sulfur compounds from the DES phase to the model diesel.[36] Considering the similarity between the desulfurization profiles found for [BMIM]PF_6 and ChCl/PEG and knowing the economic advantages of DES [1, 13], the solvent ChCl/PEG was chosen for the following optimization studies.

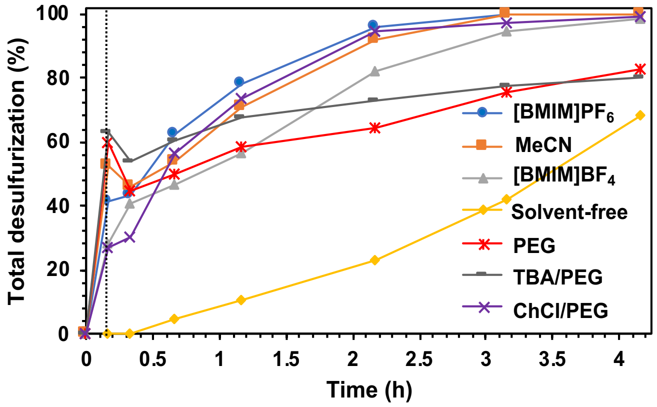


Figure 5.4. Desulfurization of a model diesel (3000 ppm S) using $[MoO_2Cl_2(DMB)_2]$ (**1**) (10 μmol) as catalyst, in the presence or absence of different extraction solvents and H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

From previous work it is clear that higher temperatures result in higher ODS efficiencies.[37] However, temperatures above 80 °C can promote side reactions, in which some compounds responsible for the quality of the fuel can suffer oxidation. Therefore, two temperatures were tested, namely 50 and 70 °C. The remaining experimental conditions were maintained (0.750 mL ChCl/PEG solvent, 0.750 mL of model diesel, 0.60 mmol of H_2O_2 and 10 μmol of catalyst **1**). The results are displayed in Figure 5.5. The fastest desulfurization performance was observed using a reaction medium with the highest temperature (70 °C), from which was obtained a sulfur-free model diesel after 2 h, instead of the 4 h needed using the lower temperature. The different desulfurization profiles observed at different temperatures may be partly related with a decrease in viscosity of DES (from 66.55 mPa.s at 50 °C to 24.38 mPa.s at 70 °C, Table 5.2).

Blank reactions were performed; an *oxidation* only with the solvent ChCl/PEG and H_2O_2 and an *extraction* without catalyst and oxidant. The reactions were performed for 2 h and the results are presented in Figure 5.6. During the oxidation, the desulfurization of the model diesel did not increase after the initial extraction stage, i.e. 30% (1655 ppm of S remained in the model diesel phase after 2 h). The same behaviour was observed for extraction (without catalyst and H_2O_2), from which resulted a desulfurization of 18% at 2 h. The difference between the 30% obtained during the oxidative reaction and the 18% achieved during the extraction is related to a lower oxidation that occurs in the presence of oxidant and absence of catalyst. However, the desulfurization profile obtained in the absence of catalyst is far from that obtained using catalyst **1** (100% desulfurization after 2 h).

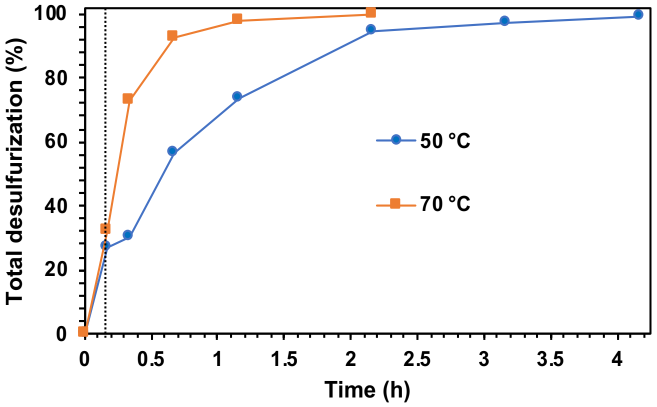


Figure 5.5. Desulfurization of a model diesel (3000 ppm S) using [$MoO_2Cl_2(DMB)_2$] (**1**) (10 μmol) as catalyst, ChCl/PEG (0.750 mL) as extraction solvent and H_2O_2 (0.60 mmol) at different temperatures. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

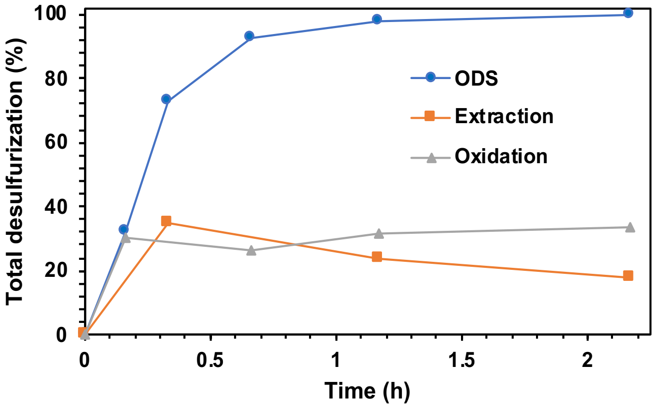


Figure 5.6. Desulfurization profiles for blank experiments (ODS process in absence of catalyst – Oxidation; and without catalyst and oxidant – Extraction), using a model diesel (3000 ppm S), in the presence of ChCl/PEG (0.750 mL) as extraction solvent, and H_2O_2 (0.60 mmol), at 70 °C.

Different amounts of oxidant, H_2O_2, ranging from 0.13 to 0.60 mmol, were tested using 0.750 mL of model diesel, 0.750 mL of ChCl/PEG, 10 μmol of catalyst **1** and a temperature of 70 °C. Similar results were achieved using the various H_2O_2 amounts (Figure 5.7); however, the worst behaviour was observed using 0.13 mmol, for which the ODS reaction did not reach a complete desulfurization (96.9% at 3 h). A sulfur-free model diesel was obtained in the presence of 0.35 and 0.60 mmol of H_2O_2 after 2 h of reaction. At the same reaction time, using 0.26 mmol of H_2O_2, almost 20 ppm of sulfur was still present in the model diesel phase. Therefore, the amount of oxidant chosen to continue the ODS studies was 0.35 mmol.

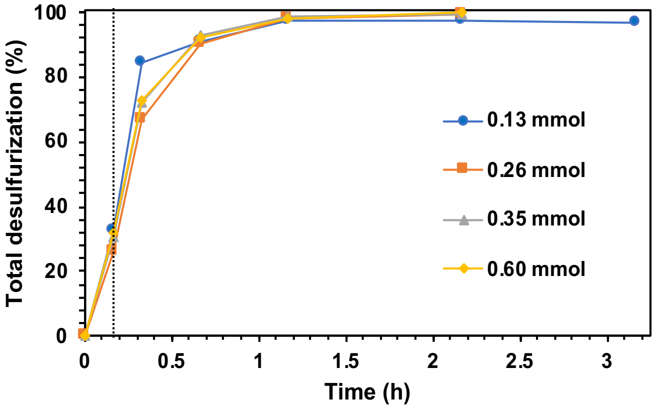


Figure 5.7. Desulfurization of a model diesel (3000 ppm S) using [$MoO_2Cl_2(DMB)_2$] (**1**) (10 μmol) as catalyst, ChCl/PEG (0.750 mL) as extraction solvent and different amounts of H_2O_2, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The influence of the amount of catalyst **1** was also analysed (5, 10 and 20 μmol), maintaining all the other experimental conditions (0.750 mL model diesel, 0.750 mL of ChCl/PEG, 0.35 mmol of H_2O_2 and a reaction temperature of 70 °C). Similar desulfurization profiles were found using the highest amounts of catalyst **1**, i.e. 100% and 98% of the sulfur present in model diesel phase was removed after 2 h, using 10 μmol and 20 μmol**,** respectively (Figure 5.8). Lower desulfurization efficiency was obtained using the lowest amount of catalyst (5 μmol) from which a complete desulfurization was achieved after 3 h. Therefore, 10 μmol of catalyst **1** was the amount chosen for the ongoing optimization studies.

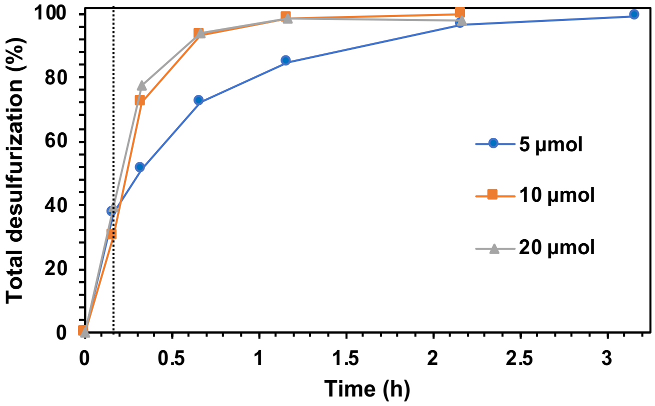


Figure 5.8. Desulfurization of a model diesel (3000 ppm S) using different amounts of catalyst [$MoO_2Cl_2(DMB)_2$] (**1**), ChCl/PEG (0.750 mL) as extraction solvent and H_2O_2 (0.35 mmol), at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The DES are generally made from non-toxic, biodegradable and inexpensive components. For example, choline chloride is a readily available and inexpensive feed additive produced in bulk quantities.[1] However, from an economic and environmental point of view, no solvent or the use of low amounts of solvents is preferable. Therefore, three model diesel/DES ratios were tested, namely 1:0.3, 1:0.5 and 1:1, using 10 *μ*mol of catalyst **1** in the presence of 0.35 mmol of H_2O_2 at 70 °C. A decrease in the volume of DES had a direct effect on the initial extraction and also on the oxidative catalytic stage, mainly during the first half hour (Figure 5.9). Using model diesel/DES volume ratios of 1:0.3 and 1:0.5 led to a sulfur removal of 83.9% and 97.9% after 3 h, respectively. Complete desulfurization was obtained at 2 h using 1:1 diesel/DES ratio. These results indicate that the efficiency of the ODS system using ChCl/PEG DES is dependent on the amount of solvent used.

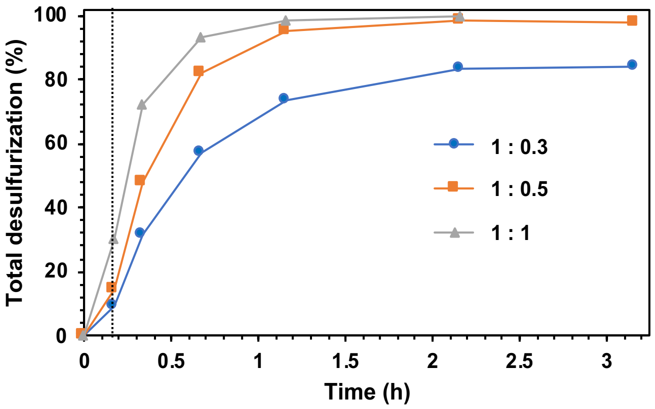


Figure 5.9. Desulfurization of a model diesel (3000 ppm S) using $[MoO_2Cl_2(DMB)_2]$ (**1**) (10 *μ*mol) as catalyst, in the presence of different volume ratios of model diesel/ChCl/PEG, using 0.35 mmol of H_2O_2 as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

5.2.2.2. Efficiency of catalysts 1 and 2

The desulfurization performance of complex $[MoO_2Cl_2(DEO)]$ (**2**) was studied under the optimal operational conditions found for complex $[MoO_2Cl_2(DMB)_2]$ (**1**), i.e. 10 *μ*mol of catalyst, 0.35 mmol of H_2O_2, 1:1 (*v*/*v*) model diesel/DES and a reaction temperature of 70 °C. Catalysts **1** and **2** present similar catalytic performance (Figure 5.10). The initial extraction in both systems was similar and the desulfurization efficiency for each sulfur compound followed the order DBT > 4-MDBT > 4,6-DMDBT (44.5%, 29% and 18%, respectively). These results are usually independent of the catalyst, depending only on the extraction solvent applied. The order obtained for each sulfur compound is related with their molecular diameter, geometry and solubility.[38]

The desulfurization increases greatly during the oxidative catalytic step. Catalysts **1** and **2** present similar desulfurization efficiencies; however, a sulfur-free model diesel was reached after 2 h using catalyst **1** and after 3 h using catalyst **2**. This difference in activity can be related with the higher facility that catalyst **1** has to interact with the oxidant to form active species. The presence of steric effects caused by the presence of mono- or bidentate organic ligands can have a strong influence on the catalyst interaction with the oxidant.[29] The presence of active species in the reaction medium is suggested by the modification of colour from colourless to yellow after oxidant addition.[30, 37]

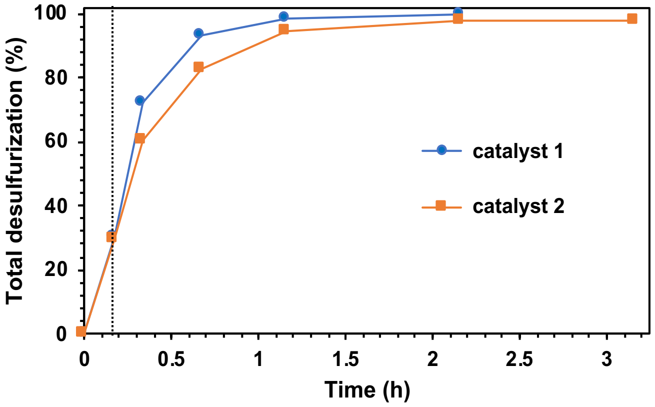


Figure 5.10. Desulfurization of a model diesel (3000 ppm S) using different catalysts (**1** and **2**, 10 μmol), ChCl/PEG as extraction solvent (0.750 mL) and H_2O_2 (0.35 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

5.2.2.3. Reusability of [$MoO_2Cl_2L_n$]@DES

Reusability tests were performed for five consecutive cycles using both complexes [$MoO_2Cl_2L_n$] **1** and **2** as homogeneous catalysts. The "reused" procedure was applied to the extraction solvent containing the dissolved catalyst. In this procedure the desulfurized model diesel phase is removed and a fresh portion of untreated model diesel and oxidant are added, maintaining the experimental conditions between cycles. Figure 5.11 shows that after the second cycle a decrease in desulfurization efficiency occurred for both systems. However, after 3 h of reaction, complete desulfurization was achieved for the third and fourth cycles using catalyst **1**. This loss of activity mainly after the second reused cycle using catalysts **1** and **2** can be related with a saturation of DES by the oxidized sulfur compounds.

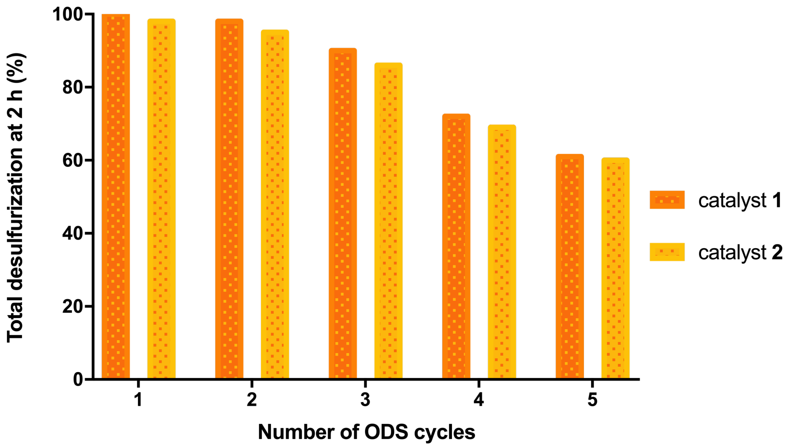


Figure 5.11. Desulfurization data for five consecutive “reused” ODS cycles, catalysed by [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**) (10 μmol), in the presence ChCl/PEG (0.750 mL) as extraction solvent and using 0.35 mmol of H_2O_2 as oxidant, at 70 °C. Results obtained after 2 h of ODS reaction.

5.2.3. Desulfurization of an untreated diesel

The high desulfurization performance demonstrated by both catalysts **1** and **2** led to their application in the treatment of a commercial untreated diesel supplied by Galp Energia. This diesel has a sulfur content of 2300 ppm, presented mostly by benzothiophenes and its derivatives.[39]

Some initial extraction tests were performed with solvents that had revealed higher extractive performance with model diesel, i.e. TBA/PEG, PEG and ChCl/PEG (Table 5.5). The results were similar to those obtained for the model diesel, where ChCl/PEG presented the lowest extractive capacity (4.1%). Higher extraction results were obtained using TBA/PEG (35.6%) and PEG (45.6%). These results were also higher than the previous ones obtained using organic solvents, e.g. DMF or MeCN.[37]

The ODS of the real diesel was performed using the same conditions applied for the desulfurization of model diesel. To a biphasic system composed of equal volumes of diesel and ChCl/PEG was added the catalyst **1** or **2** (10 μmol) and 0.35 mmol of H_2O_2 using a reaction temperature of 70 °C. In the previous work (Chapter 4) both catalysts showed high desulfurization performances in the IL [BMIM]PF_6 oxidative medium. Some of the best results from the oxidative desulfurization of the real diesel were obtained when the ODS treatments were applied to non-treated diesel samples (without an initial extraction treatment). Using this procedure replacing the IL by ChCl/PEG, desulfurization efficiencies of 79.9% and 81.3% were achieved in the presence of catalysts **1** and **2**, respectively. Comparing the present results with those presented in Chapter 4 using the IL oxidative reaction medium, it is possible to conclude that higher desulfurization efficiencies were achieved using catalyst **2** (94.4% in the presence of [BMIM]PF_6 and 81.3% in the presence of ChCl/PEG) than catalyst **1**, from which the best result was a diesel with 381 ppm (83.4%) obtained when [BMIM]PF_6 was used as reaction medium.

Table 5.5. Experiments performed for ODS of a commercial untreated real diesel[a]

Catalyst	Initial extraction	Extraction process after ODS[b]	S content (ppm)	Desulfurization efficiency (%)[c]
---	TBA/PEG	---	1480	35.6
	ChCl/PEG	---	2206	4.1
	PEG	---	1250	45.6
1	---	MeCN	1518	34.0
	---	DMF	462	79.9
	---	TBA/PEG	413	82.0
2	---	MeCN	1717	25.3
	---	DMF	430	81.3

[a] Reaction conditions: 70 °C, 2 h using the biphasic system diesel/(ChCl/PEG) 1:1 *v*/*v* and 0.35 mmol of H_2O_2.

[b] Liquid-liquid diesel/extraction solvent (30 min at 70 °C) of oxidized sulfur compounds after ODS.

[c] Calculated on the basis of a sulfur content of 2300 ppm in the commercial untreated diesel.

5.3. Conclusions

Deep eutectic solvents based on PEG-200 were prepared and applied as feasible substituents of conventional volatile solvents for desulfurization of model and real diesels. Their physical properties depend on the alkyl chain and the composition of the mixture. DES containing cations with long chain length, e.g. TBA/PEG, possessed higher sulfur extractive capacities but poor performance to promote a high oxidative catalytic desulfurization. The dioxomolybdenum(VI) catalysts **1** and **2** (10 μmol) showed high catalytic efficiency using as solvent ChCl/PEG and a H_2O_2/S molar ratio of 5, at 70 °C, from which resulted sulfur-free model diesels after 2 h and 3 h, respectively. Under the optimized model diesel conditions, the catalysts [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**) revealed similar desulfurization efficiencies, from which were achieved final treated diesels with 413 and 430 ppm of sulfur, respectively. These results open up the possibility of substitution of conventional volatile solvents used for real diesel extractions by more sustainable and cheap options, such as DESs.

5.4. Experimental Section

5.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: MoO_2Cl_2 (Sigma-Aldrich), anhydrous tetrahydrofuran (Panreac, 99.7%), *N,N*-dimethylbenzamide (Alfa Aesar, ≥98%), *N,N'*-diethyl- oxamide (Alfa Aesar, 98%), choline chloride (Sigma-Aldrich, ≥99%), polyethylene glycol (Sigma-Aldrich, BioUltra 200), tetrabutylammonium chloride (Sigma-Aldrich, 98%), dibenzothiophene (Sigma-Aldrich, 98%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), 1-butyl-3-methylimidazolium tetrafluoroborate (Sigma-Aldrich, ≥98%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical), and 30% w/v hydrogen peroxide (Sigma-Aldrich). The untreated diesel containing 2300 ppm of sulfur was supplied by Galp Energia.

Infrared absorption spectra were recorded in the 400–4000cm^{-1} region on a Perkin Elmer spectrum BX FTIR spectrometer with a resolution of 4 cm^{-1} and 64 scans. The viscosities were measured at 25 °C, 50 °C, 70 °C and 80 °C using Lovis 2000 ME and the obtained data were modulated and validated with a viscosity-temperature correlation. The densities were measured between 25 °C and 80 °C, using a DMA^{TM} 4500M, and the results were modulated as validated with a density-temperature correlation. The desulfurization of the model diesel was monitored by a Bruker 430-GC-FID gas chromatograph, using a Supelco capillary column SPB-5 (30 m x 250 μm id.; 25 μm film thickness) and hydrogen as carrier gas (55 cm^3 s^{-1}). The analysis of sulfur content of the treated diesel and jet fuel was performed by Galp Energia by ultraviolet fluorescence using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

5.4.2. Catalyst synthesis

The synthesis and characterization of complexes [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**) are described in Chapter 4, Section 4.4.2.

5.4.3. Synthesis of DES

Synthesis of 1:2 TBACl : polyethylene glycol (TBA/PEG): was prepared by an adaptation of the procedure described in reference [40]. TBACl (39.05 g, 0.140 mol) was used as the halide salt and polyethylene glycol (50 mL, 0.281 mol) as HBD. The mixture was heated at 100 °C with stirring, during 2 h. FT-IR (cm^{-1}): ν = 3310 (m), 2869 (m), 1474 (m), 1466 (m), 1458 (w), 1419 (w), 1350 (m), 1324 (w), 1297 (w), 1247 (w), 1116 (sh), 1063 (vs), 951 (vs), 886 (m), 833 (w), 548 (m). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.60 (t, 12H), 1.05 (m, 8H), 1.27 (m, 8H), 2.93 (m, 8H), 3.20 (br, 4H), 3.25 (br, 10H), 3.29 (br, 4H).

Synthesis of 1:2 ChCl : polyethylene glycol (ChCl/PEG): ChCl (19.61 g, 0.140 mol) was used as the halide salt and polyethylene glycol 200 (50 mL, 0.281 mol) as HBD. The mixture was left to stir for 8 h at 100 °C. FT-IR (cm^{-1}): ν = 3315 (w), 2934 (sh), 2906 (sh), 2873 (m), 1461 (m), 1382 (w), 1350 (w), 1322 (w), 1293 (w), 1246 (w), 1119 (s), 1064 (s), 1037 (w), 931 (w), 884 (m), 843 (w), 740 (w), 573 (w). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 3.06 (s, 9H), 3.32 (br, 4H), 3.38 (br, 12H), 3.43 (br, 6H).

In the end, all the DES samples were cooled to room temperature and kept in sealed flasks.

5.4.4. Oxidative desulfurization studies

5.4.4.1. Model diesel

The desulfurization studies were performed using a model diesel containing dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene dissolved in *n*-octane with 1000 ppm of each one. This solution was desulfurized in the presence of a DES as extraction solvent, dioxomolybdenum(VI) complexes [$MoO_2Cl_2(DMB)_2$] (**1**) and [$MoO_2Cl_2(DEO)$] (**2**) as catalysts and H_2O_2 as oxidant. All the experiments were performed under atmospheric pressure in a closed borosilicate reaction vessel (5 mL) equipped with a magnetic stirrer and immersed in a thermostated paraffin bath at 70 °C.

In order to achieve the best desulfurization results, some parameters were optimized, such as the influence of different extraction solvents ([BMIM]PF_6, [BMIM]BF_4, MeCN, PEG, TBA/PEG and ChCl/PEG), the amount of catalyst (5, 10 and 20 *µ*mol) and H_2O_2 (0.13, 0.26 and 0.60 mmol), the volume of the most efficient extraction solvent (0.250, 0.375 and 0.750 mL) and temperature (50 and 70 °C). The ODS reactions were performed under biphasic conditions in two main steps, an initial extraction and a catalytic oxidation. The initial extraction is performed before the addition of H_2O_2, and it is based on the transfer of sulfur compounds from the model diesel (non-polar phase) to the extraction solvent phase (polar phase) by vigorously stirring during 10 min, at 70 °C. After the addition of oxidant, the catalytic oxidative stage starts, in which occurs the oxidation of the sulfur compounds to the corresponding sulfoxides and/or sulfones.

The follow-up of the ODS reactions was performed by gas chromatography (GC). Aliquots removed from the reaction medium (model phase) were diluted in tetradecane (standard), allowing the quantification of the sulfur over time.

The systems containing the catalysts **1** and **2** were reused for several ODS cycles. In the reused cycles the same extraction solvent incorporating the catalyst was consecutively used without further cleaning process, occurring only the exchange of the desulfurized model diesel by fresh portions of non-treated model diesel and H_2O_2, maintaining the same initial experimental conditions.

5.4.4.2. Untreated diesel

A commercial untreated diesel containing 2300 ppm of sulfur content was treated by an extraction process with PEG and PEG-based DES (TBA/PEG and ChCl/PEG) alone. Also, some ODS studies were performed with the untreated samples using the best model diesel conditions (biphasic system based on equal amounts of diesel and ChCl/PEG, 10 *µ*mol of catalyst **1** or **2** and 0.35 mmol of H_2O_2 with a reaction temperature of 70 °C). At the end of each ODS treatment the resulting diesel samples were subjected to a final extraction with MeCN, DMF and TBA/PEG.

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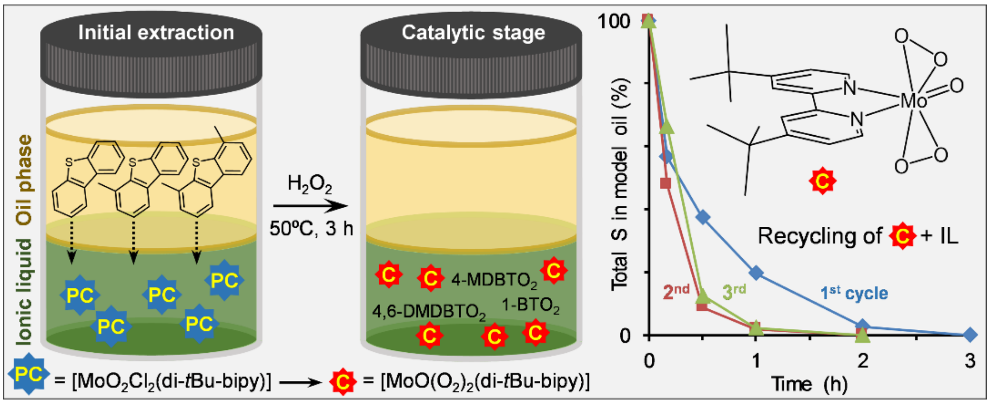
Chapter 6

EFFICIENT CATALYSTS BASED ON OXOMOLYBDENUM(VI) COMPLEXES CONTAINING A *N*-BIDENTATE LIGAND



6. Efficient catalysts based on oxomolybdenum(VI) complexes containing a *N*-bidentate ligand

6.1. Introduction

It is believed that the first metal-oxo molecular fragment, denominated as oxohalide complex, MoO_2Cl_2, was first described by J.J. Berzelius in 1826.[1] During the 19th and 20th centuries a continual interest in this type of molecular fragments MO_2X_2 (M = Mo, W) occurred, due to their application as catalysts for a wide variety of organic reactions.[2, 3] Donor solvent molecules or Lewis base ligands can fill the available positions around the metal center, giving rise to adducts of the composition $[MoO_2X_2L_2]$.[4]

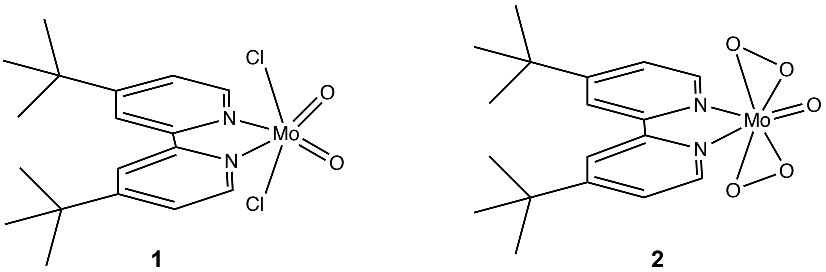
The catalytic efficiency of the oxo-molybdenum(VI) complexes is associated with the nature of the ligand L and X, which have a high influence on the solubility and stability of the complexes. Most of the catalytic applications of complexes of the type $[MoO_2X_2L_2]$ are in olefin epoxidation. From these studies some conclusions were made about ligand effects, such as the higher importance of the ligand L when compared with the ligand X, suggesting that the Lewis donor ligands stay bonded to the metal center, influencing the catalytic activity of the catalytic metal center. From among ligand L possibilities, the N-donors offer a great versatility in modifying the electron donor and acceptor properties of the ligand L.[5] Also, the presence of aromatic substituents at N is known to promote an increase in catalytic efficiency when compared to those bearing aliphatic substituents.[2, 6, 7] From this knowledge several active and selective catalysts based on bidentate N-donor ligands, such as 2,2'-bipyridine (bipy) and its derivatives, have been prepared, mainly for catalytic epoxidation.[2, 4, 8] A major drawback in using homogeneous catalysts like $[MoO_2X_2L_2]$ is related with their difficult recovery and reuse at the end of the catalytic reactions. This disadvantage can be contoured by the presence of ionic liquids (ILs) as a liquid phase, which due to their unique characteristics, allows the immobilization of the catalytic complex and the possibility of its reuse for several catalytic cycles.[9] Oxo-diperoxomolybdenum(VI) complexes of the type $Na_2[MoO(O_2)_2(OH)_2]$[10] and $[MoO(O_2)_2(L)_n]$ (L = H_2O [11], aminoacids [12] and 1,10-phenanthroline [13]) have yielded promising results for sulfide oxidation using H_2O_2 as oxidant and ILs as solvent. However, the use of $[MoO_2X_2L_2]$/ILs systems with the purpose of catalysing the oxidation of sulfides to the corresponding sulfoxides and sulfones has not yet been reported.

This chapter reports an oxidative catalytic system as strategic methodology to remove different refractory sulfur compounds from a model diesel, comprising a dioxomolybdenum(VI) complex based on a bidentate N-donor ligand ($[MoO_2Cl_2$(di-*t*Bu-bipy)] (**1**) (di-*t*Bu-bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine)) as catalyst, H_2O_2 as oxidant, and an IL as extraction solvent. The treatment of an authentic sample of untreated diesel is also reported.

6.2. Results and Discussion

6.2.1. Molybdenum(VI) catalysts

The reaction of $Na_2MoO_4 \cdot 2(H_2O)$ with the ligand 4,4'-di-*tert*-butyl-2,2'-bipyridine in the presence of dichloromethane and HCl, gave the dioxomolybdenum(VI) complex $[MoO_2Cl_2$(di-*t*Bu-bipy)] (**1**), which in contact with 30% aq. H_2O_2 supported the formation of the oxo-peroxomolybdenum(VI) complex $[MoO(O_2)_2$(di-*t*Bu-bipy)] (**2**). The several characterization data obtained for both complexes agreed with literature results and can be analysed in detail in Section 6.4.[14-16] In Figure 6.1 it is observable the structure corresponding to each molybdenum(VI) complex **1** and **2**.



1 **2**

Figure 6.1. Molybdenum(VI) complexes $[MoO_2Cl_2$(di-*t*Bu-bipy)] (**1**) and $[MoO(O_2)_2$(di-*t*Bu-bipy)] (**2**).

6.2.2. Desulfurization of a model diesel

A model diesel was prepared by dissolution of various sulfur compounds DBT, 4-MDBT and 4,6-DMDBT in *n*-octane, each with a sulfur concentration of 1000 ppm or 0.0312 mol dm^{-3}. These are the compounds more difficult to remove from real diesel samples by hydrodesulfurization technology used in refineries industry. In a typical oxidative desulfurization process (ODS), the catalyst $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$ (**1**) is added to the extraction solvent, followed by addition of the model diesel, forming a biphasic liquid-liquid system. This mixture is vigorously stirred for 10 min at 50 °C to promote an initial extraction of the refractory sulfur compounds from the model diesel to the extraction phase (IL). After this time, the oxidative catalytic stage is initiated by addition of the oxidant aq. 30% H_2O_2. During the ODS, the sulfur compounds present in the extraction solvent are oxidized to their corresponding sulfones and/or sulfoxides and consequently more of the non-oxidized sulfur compounds are transferred from the model diesel (Figure 6.2).

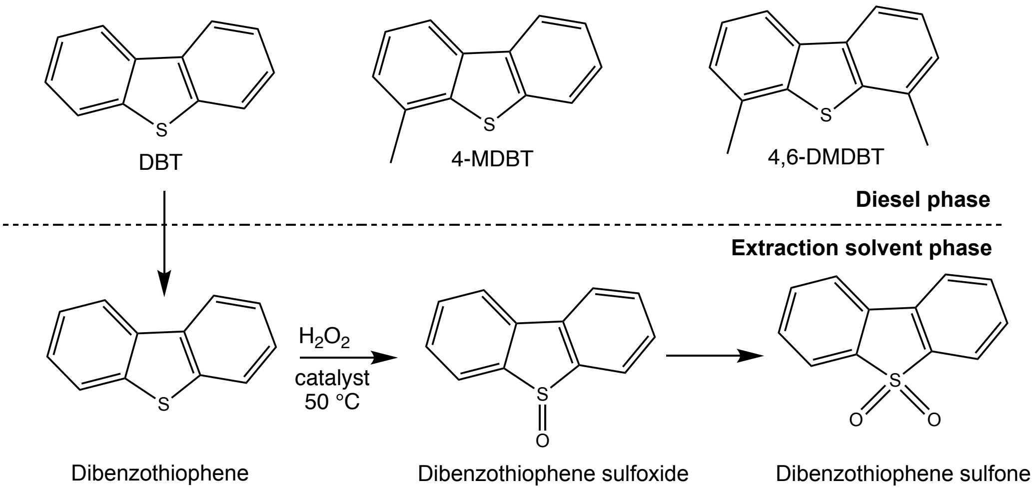


Figure 6.2. Schematic representation of the ODS system.

6.2.2.1. Optimization studies

Using a multicomponent model diesel containing DBT, 4-MDBT and 4,6-DMDBT, the influence of some experimental parameters was investigated. The evaluated parameters included the effect of different temperatures (60, 50 and 40 °C) and the influence of using different types of extraction solvents, such as MeCN and two different imidazolium salt type ILs ($[BMIM]PF_6$ and $[BMIM]BF_4$).

The effect of the temperature was the first parameter to be analysed. In this study was used equal amount of model diesel and the extraction solvent, that in this case was chosen the IL [BMIM]PF_6 due to its high extraction efficiency and stability as reaction medium demonstrated in some reported works of our research group.[17-19] The amount of catalyst [MoO_2Cl_2(di-*t*Bu-bipy)] (**1**) used corresponds to 10.7 μmol in the presence of H_2O_2 (0.60 mmol). The influence of each temperature (40, 50 and 60 °C) in desulfurization of the model diesel is illustrated in Figure 6.3. Analysing the desulfurization profiles, it is possible to conclude that the increase of the reaction temperature enhanced the desulfurization rate. After 2 h, complete desulfurization was only achieved for 60 °C. The influence of the temperature in the desulfurization performance after 2 h of reaction followed the order: 40 °C (77.4%) < 50 °C (97.3%) < 60 °C (100%). However, from the practical point of view, 50 °C was chosen as the preferred reaction temperature, since a higher temperature could result in a thermal decomposition of H_2O_2 and in potential loss of fuel quality, due to the possibility of oxidizing useful components, such as olefins and hydrocarbons.[20, 21] It is noteworthy refer that the ODS experiments performed in the absence of catalyst showed no oxidation of the sulfur compounds present in model diesel. Moreover, after a typical ODS cycle, FT-IR analysis to the model diesel was performed and revealed no bands in the region 800-1000 cm^{-1} that could be attributed to Mo=O stretching vibrations. Also, no bands were observed in the region 1350-1700 cm^{-1} corresponding to vibrational modes of the organic ligand di-*t*Bu-bipy, indicating that no leaching of the homogeneous catalyst from the IL phase to the model diesel phase occurred during the ODS cycles.

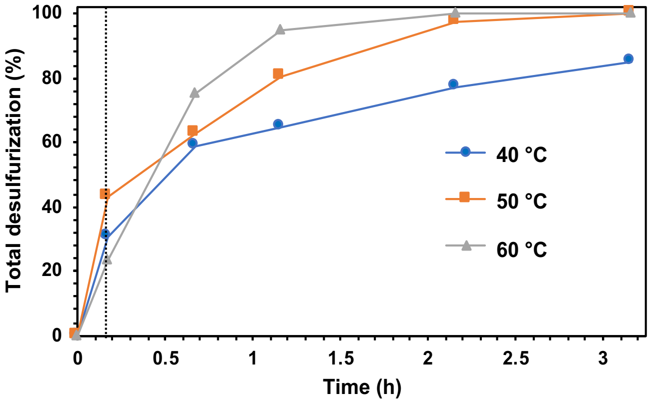


Figure 6.3. Desulfurization of a model diesel (3000 ppm S) using [MoO_2Cl_2(di-*t*Bu-bipy)] (**1**) (10.7 μmol) as catalyst, [BMIM]PF_6 (0.750 mL) as extraction solvent, at different temperatures and H_2O_2 (0.60 mmol) as oxidant. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The extraction capacity and the stability of the extraction solvent are important factors for the ODS efficiency. On the other hand, their flammable and volatile properties are important aspects to influence the sustainability of the ODS process. Therefore, three different extraction solvents, two IL and a polar volatile solvent were used as extraction solvents using equal volume (1:1) with model diesel: MeCN, [BMIM]PF_6 and [BMIM]BF_4, with a reaction temperature of 50 °C, in the presence of 10.7 μmol of catalyst **1** and 0.60 mmol of H_2O_2. Figure 6.4 displays the comparison of the desulfurization profile for different extraction solvents. Comparing the initial extraction step (before the addition of oxidant), it can be observed that the MeCN presents a higher extraction capacity (54.8%) than the ILs. Between these two ILs, the [BMIM]PF_6 presents a higher initial extraction (43.3%) than the [BMIM]BF_4 (16.6%). For all the studied extraction solvents, the initial extraction efficiency followed the order DBT > 4-MDBT > 4,6-DMDBT. As described in literature this order is related with the molecular diameter and geometry of each sulfur compound, as well with their different solubilities.[22] From the results obtained, it is possible to confirm that the proper combination of imidazolium cations and anions can result in ILs with higher extraction capacity. In general, the fluorinated anions promote an increase of the van der Waals interactions due to the volume of the anion, stimulating an intensification of the sulfur extraction. Furthermore, the extraction capacity of the ILs is also related with the C2-H imidazolium hydrogen bond with the anion and their availability to interact with the sulfur compounds via CH---π bonds. In other words, the decreasing of the strength of C2-H hydrogen bond with the anion increases the extraction capacity of the IL. This way, it is possible conclude that the [BMIM]PF_6 possesses a weak C2-H hydrogen bond to the anion, when compared to the homologues [BMIM]BF_4.[23]

The oxidative catalytic stage is initiated by addition of the oxidant H_2O_2, allowing the oxidation of the sulfur compounds to the corresponding sulfoxides and/or sulfones, which are more easily extracted due to their similar polarity with the extraction solvents. Analysing the Figure 6.4 it is possible to conclude that the best result was achieved in the presence of [BMIM]PF_6, reaching a complete desulfurization of the model diesel after 3 h of ODS reaction (at 2 h only 3% of sulfur remained in model diesel). For equal reaction time, the desulfurization efficiency of each extraction solvent followed the order, MeCN < [BMIM]BF_4 < [BMIM]PF_6. A total desulfurization in the presence of [BMIM]BF_4 was only achieved after 5 h of reaction and after 6 h there were still 2% of sulfur compounds in the model diesel phase when MeCN was used as extraction solvent. Curiously, the ILs that presented a lower extraction efficiency during the initial extraction stage (before the addition of H_2O_2) seems to allow a higher catalytic performance during oxidative stage than the MeCN. The high degree of oxidative desulfurization achieved with $[BMIM]PF_6$ has been already described in the literature for ODS systems and can be explained by the presence of a middle layer of H_2O_2 between diesel and the IL, resulted from the water-immiscibility property of $[BMIM]PF_6$, forming a pseudo-triphasic ODS system (diesel/ H_2O_2/$[BMIM]PF_6$).[17]

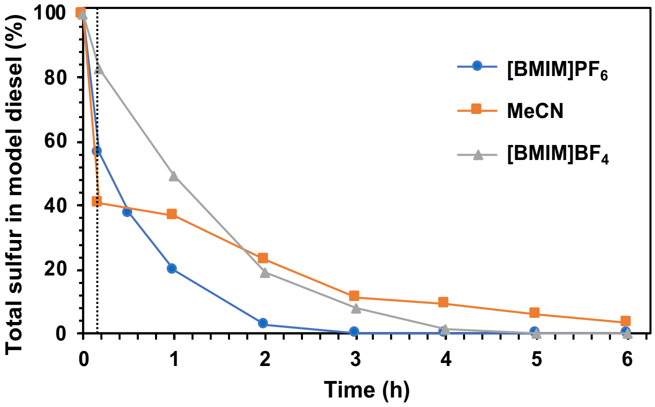


Figure 6.4. Desulfurization of a model diesel (3000 ppm S) using $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy}]$ (**1**) (10.7 μmol) as catalyst, in the presence of different extraction solvents and H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

In the ODS systems catalysed by complex **1** was observed that the initial colourless of the extraction phase turned to pale yellow after oxidant addition (Figure 6.5). Although the sulfoxidation mechanism is not well established for molybdenum catalysed reactions, it is assumed that the colour variation usually corresponds to the presence of active species (peroxo, oxo or hydroperoxo species), which are formed due to the interaction of the H_2O_2 oxidant with the dioxomolybdenum(VI) complex **1**.[24, 25] These species are the responsible for the oxidation of the sulfur compounds by oxygen transfer. In other words, an oxygen atom is transferred from the active species to the sulfur compound by a nucleophilic attack of the sulfur atom to the peroxo group.[26, 27]

To identify the possible active catalytic species resultant from the interaction of dioxomolybdenum(VI) complex **1** with H_2O_2 oxidant, a distinct experiment was performed in which an excess of H_2O_2 was added to a solution of complex $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$ (**1**) in MeCN. As result, was obtained a pale yellow precipitate, which was identified as the oxo-diperoxomolybdenum(VI) complex $[MoO(O_2)_2(\text{di-}t\text{Bu-bipy})]$ (complex **2** in Figure 6.9). To confirm the supposed complex structural transformation occurred during the ODS system, an oxidative desulfurization experiment with model diesel was performed using as catalyst the oxo-peroxo complex **2** (Figure 6.6). Comparing the desulfurization profiles present in Figure 6.6 it is possible to conclude that both complexes **1** and **2** presented a similar catalytic activity. During the first 2 h of ODS reaction the active species possesses a faster desulfurization performance comparing to the initial catalyst **1**. This behaviour can be related with the induction time that the catalyst [MoO_2Cl_2(di-*t*Bu-bipy)] (**1**) needs to form the active species [$MoO(O_2)_2$(di-*t*Bu-bipy)] (complex **2**) after the addition of the H_2O_2.

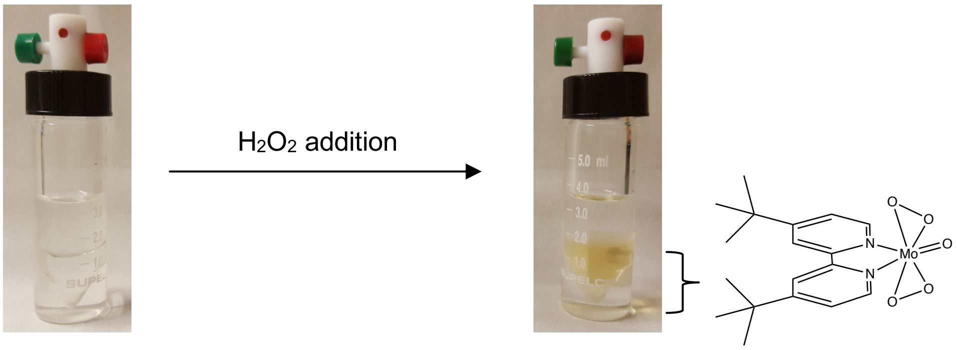


Figure 6.5. Schematic representation of the colour change after addition of H_2O_2.

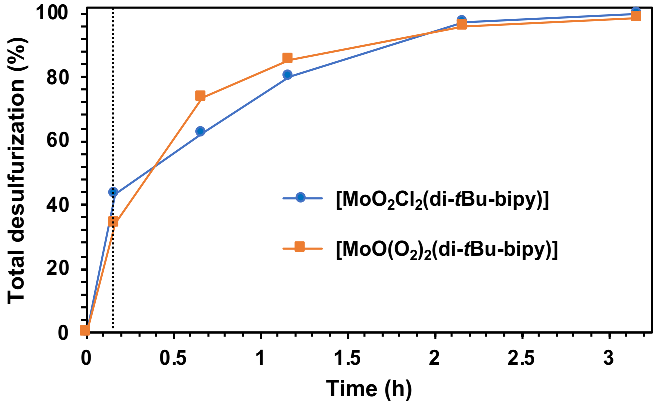


Figure 6.6. Desulfurization profiles using a model diesel (3000 ppm S), catalysed by complex MoO_2Cl_2(di-*t*Bu-bipy) (**1**) and $MoO(O_2)_2$(di-*t*Bu-bipy) (**2**) (10.7 *μ*mol), in the presence of [BMIM]PF_6 (0.750 mL) as extraction solvent and H_2O_2 (0.60 mmol) as oxidant, at 50 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

6.2.2.2. Catalyst recyclability

The recyclability of the two most efficient ODS systems, i.e. using [BMIM]PF_6 and [BMIM]BF_4 as extraction solvents, was investigated in consecutive ODS cycles. At the end of each ODS cycle the treated model diesel phase was removed and the IL phase containing the molybdenum species was washed with a mixture of ethyl acetate and diethyl ether (1:1 *v*/*v*) to remove the sulfur compounds resulting from the extraction/oxidation reactions and drying at 50 °C overnight. The reutilization in a new ODS cycle was performed adding a fresh sample of the model diesel and the oxidant H_2O_2. Figure 6.7 displays the recycling performance of the molybdenum(VI) catalyst **1** entrapped in different ILs phases ([BMIM]PF_6 and [BMIM]BF_4) for three consecutive desulfurization processes. Different recyclability efficiency was observed for each model diesel/IL system. While a notorious decrease in desulfurization efficiency was noticed using model diesel/[BMIM]BF_4 system over the cycles, for the model diesel/[BMIM]PF_6 system a slight increase in desulfurization was observed from the first to the consecutive cycles (97.3% for the 1st cycle and 100% for 2nd and 3rd cycles). The decrease of desulfurization efficiency observed for model diesel/[BMIM]BF_4 system can be related with the water excess from the addition of the oxidant H_2O_2 over the different cycles, that can promote a deactivation of the molybdenum(VI) catalyst **1**.[28] This behaviour was not observed to the model diesel/[BMIM]PF_6 system, since it is a pseudo-triphasic system, in which aq. H_2O_2 comprises the middle layer. On the other hand, the increase in desulfurization efficiency found for model diesel/[BMIM]PF_6 system can be related to the occurrence of active species preparation during the first cycle, i.e. the transformation of the complex [MoO_2Cl_2(di-*t*Bu-bipy)] (**1**) into more active catalytic species (complex **2**). After the first cycle, the active species are already in the reaction medium and no induction time is necessary after the addition of H_2O_2 oxidant, resulting in high degrees of desulfurization within short reaction times. In fact, after only 1 h of reaction only 2% of sulfur remained in model diesel phase. This corresponds to the 4,6-DMDBT compound, which is more difficult to extract from the model diesel phase to the IL phase, due to steric hindrance of the methyl groups, that prevent the access of the sulfur atom to the Mo active site. The catalytic stability of the catalyst was also confirmed by the persistent yellow colour for the IL phase during the different ODS cycles.

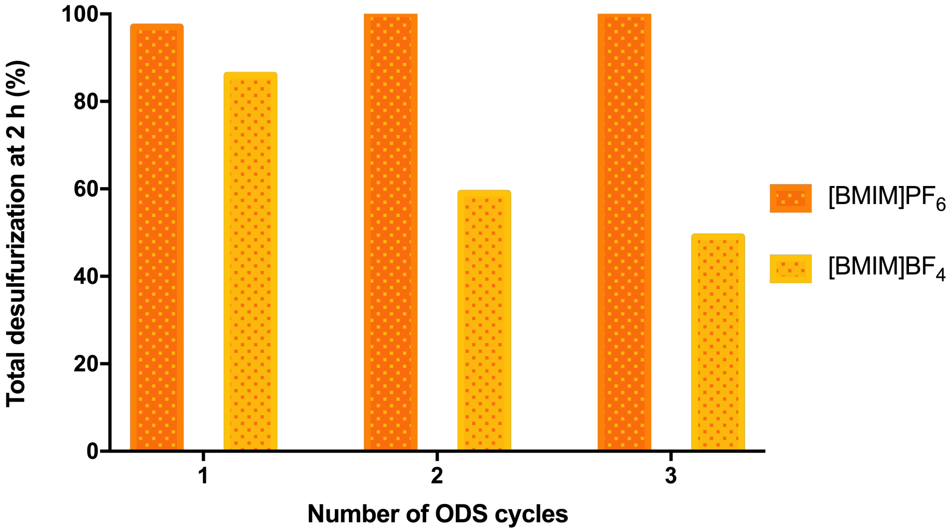


Figure 6.7. Results obtained for three consecutive cycles with a model diesel (3000 ppm S) and [MoO_2Cl_2(di-*t*Bu-bipy) (**1**) (10.7 *µ*mol) as catalyst, two different ILs as extraction solvents, with H_2O_2 (0.60 mmol) as oxidant, at 50 °C. Results obtained after 2 h of ODS reaction.

6.2.3. Oxidative desulfurization of a real diesel

The system containing the molybdenum(VI) complex **1** entrapped in [BMIM]PF_6 was the preferred choice to apply in desulfurization of an untreated diesel with a sulfur content of 2300 ppm, supplied by Galp Energia. The desulfurization process of the untreated diesel was initiated by performing six, nine and twelve consecutive extractions with MeCN, at 50 °C during 10 min (Table 6.1). The highest desulfurization was achieved with the maximum of extraction cycles; however, after the ninth cycle the extraction of sulfur compounds from the real diesel phase to the MeCN phase has increased less than the previous cycles and therefore, performing more than nine extraction cycles turn the desulfurization process less economical and environmental viable due to the high consumption of MeCN needed. Therefore, the oxidative desulfurization following step was performed using the diesel pre-treated with nine liquid-liquid extraction cycles (containing 771 ppm of sulfur) and the optimized experimental conditions found for the model diesel. The catalytic oxidative stage was performed for 3 h and 6 h. After 3 h, no substantial decrease of sulfur content present in the real diesel was observed (from 771 to 621 ppm), corresponding to a total sulfur removal of 73.0%. However, continuing the oxidative reaction for more 3 h, promoted a removal of additional 70 ppm S, increasing the total desulfurization efficiency to 76.0%.

The recycling capacity of the IL phase containing the molybdenum(VI) catalyst **1** was studied by using the pre-treated diesel (771 ppm of sulfur) and the [MoO_2Cl_2(di-*t*Bu-bipy)]/[BMIM]PF_6 phase for three consecutive ODS cycles without performing any cleaning treatment to the IL phase. After each desulfurization cycle, the treated diesel was removed from the system and a new portion of pre-treated diesel (771 ppm of sulfur content) and a fresh amount of H_2O_2 oxidant were added. Each cycle was performed for 6 h. The efficiency of desulfurization found for the first, second and third desulfurization cycles were 76.0%, 79.0% and 79.0%, respectively. The maintenance of these values is an indication of the high stability and recyclability of the Mo(VI) catalyst entrapped in IL.

Table 6.1. Experiments performed to test the influence of different number of initial extraction cycles

N° of liquid extraction cycles[a]	Diesel sulfur content (ppm)	Desulfurization efficiency (%)[b]
6	1057	54.0
9	771	66.5
12	613	73.3

[a] Liquid-liquid extraction of non-oxidized sulfur compounds in real diesel, stirring for 10 min at 50 °C the mixture 1:1 (v/v) of diesel/MeCN.

[b] Calculated based on the sulfur content of untreated real diesel (2300 ppm).

6.3. Conclusions

In summary, effective desulfurization processes conciliating extraction and oxidative stages were optimized for multicomponent model and real diesels, using the molybdenum(VI) complex $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$ (**1**) as catalyst in a sustainable system ($H_2O_2/S = 8.5$, 10.7 μmol of catalyst, at 50 °C). Ionic liquids were efficiently used as extraction solvents and an environmentally friendly oxidant (H_2O_2) under mild conditions allowed effective removal of sulfur compounds from model and untreated diesel samples after 3 h and 6 h, respectively. During the catalytic stages, a pale-yellow colour was observed, which was identified as an oxo-peroxomolybdenum(VI) complex $[MoO(O_2)_2(\text{di-}t\text{Bu-bipy})]$ (**2**), resulting from the interaction of the H_2O_2 oxidant with the complex $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$. This oxo-peroxomolybdenum(VI) complex proved to be the active catalytic species. The system formed by diesel/$[BMIM]PF_6$ (1:1) presented an excellent recycling capacity, suggesting high catalyst stability during consecutive cycles. This was the first recycling study performed with homogeneous oxo-metallic catalysts entrapped in ILs for the treatment of real fuel samples.

6.4. Experimental Section

6.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: Sodium molybdate dehydrate (Riedel-de-Haën, 99.5%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (Sigma-Aldrich), hydrochloric acid (Sigma-Aldrich, 37%), dibenzothiophene (Sigma-Aldrich, 98%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%) *n*-octane (Sigma-Aldrich, 98%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), 1-butyl-3-methylimidazolium tetrafluoroborate (Sigma-Aldrich ≥98%), ethyl acetate (Fisher Chemical, analytical grade), diethyl ether (Merck) and 30% w/v hydrogen peroxide (Sigma-Aldrich).

Infrared absorption spectra were recorded for 400–4000cm^{-1} region on a Perkin Elmer spectrum BX FTIR spectrometer, a resolution of 4 cm^{-1} and 64 scans. The desulfurization of the model diesel was monitored by a Bruker 430-GC-FID gas chromatograph, using a Supelco capillary column SPB-5 (30 m x 250 μm id.; 25 μm film thickness) and hydrogen as carried gas (55 cm^3 s^{-1}). The analysis of sulfur content in the real diesel was performed by Galp Energia through ultraviolet fluorescence test method (ISO 20846), using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry (ISO 8754), using an OXFORD LAB-X, LZ 3125.

6.4.2. Catalyst synthesis

[MoO$_2$Cl$_2$(di-*t*Bu-bipy)] (**1**) was synthesized by dissolution of $Na_2MoO_4 \cdot 2H_2O$ (0.59 g, 2.44 mmol) in 3.3 M HCl (30 mL) followed by the addition of a solution of di-*t*Bu-bipy (0.65 g, 2.44 mmol) in CH_2Cl_2 (60 mL). The solution was kept in stirring during 2 h at room temperature, resulting in a pale pink organic phase which was separated and dried over anhydrous $MgSO_4$ and evaporation, resulting in a pale pink solid (0.90 g, 80%) (Figure 6.8). The obtained complex was characterized by elemental analysis, infrared (FT-IR) and ^{1}H NMR spectroscopies, that confirmed the successful preparation. Anal. Calc. (%) for $C_{18}H_{24}N_2O_2Cl_2Mo$ (467.24): C, 46.27, H, 5.18; N, 5.99. Found: C, 46.24; H, 5.23; N, 5.94. FT-IR (KBr, cm^{-1}): 2966 (m), 2906 (w), 2870 (w), 1610 (s), 1545 (m), 1485 (m), 1465 (w), 1410 8s), 1365 (m), 1303 (w), 1250 (s), 1201 (w), 1122 (w), 1080 (w), 1028 (m), 939 (vs, v_{sym}(Mo=O)), 908 (vs, v_{asym}(Mo=O)), 850 (vs), 740 (w), 720 (w), 607 (m), 551 (m), 422 (m), 401 (m), 378 (m), 341 (vs, v(Mo-Cl)). ^{1}H NMR (400 MHz, $CDCl_3$, r.t., ppm): δ = 9.45 (d, H^6), 8.15 (d, H^3), 7.69 (dd, H^5), 1.47 (s, H_{tBu}).[15, 29]

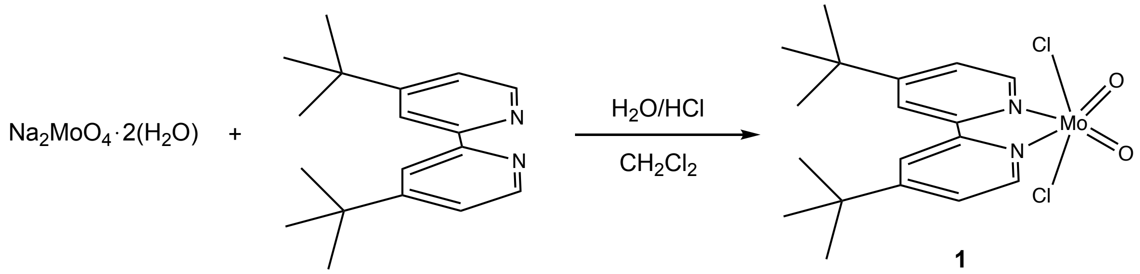


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Figure 6.8. Preparation of catalyst [MoO_2Cl_2(di-*t*Bu-bipy)] (**1**).

[$MoO(O_2)_2$(di-*t*Bu-bipy)] (**2**) was prepared by dropwise addition of 30% aq. H_2O_2 (0.032 mol) to a stirred solution of [MoO_2Cl_2(di-*t*Bu-bipy)] (0.10 g, 0.21 mmol) in MeCN (3 mL). The mixture was stirred at 50 °C for 2 h (Figure 6.9). A pale-yellow solid was precipitated and filtered. The obtained solid was washed twice with ethanol (5 mL) and diethyl ether (5 mL) and dried under vacuum (0.08 g, 86%). The obtained complex was characterized by elemental analysis, vibrational (FT-IR and FT-Raman) and ^{1}H and ^{13}C NMR spectroscopies, that confirmed the successful preparation. Anal. Calc. (%) for $C_{18}H_{24}N_2O_2Cl_2Mo$ (444.33): C, 48.66, H, 5.44; N, 6.30. Found: C, 48.76; H, 5.69; N, 5.93. FT-IR (KBr, cm^{-1}): 2968 (m), 2908 (w), 2871 (w), 1616 (s), 1550 (m), 1485 (m), 1460 (w), 1411 (s), 1371 (m), 1308 (w), 1253 (s), 1204 (w), 1123 (w), 1082 (w), 1025 (m), 941 (vs, v_{sym}(Mo=O)), 902 (m), 870 (vs, v(O-O)), 862 (vs, v(O-O)), 847 (sh), 744 (m), 719 (m), 657 (s), 604 (w), 588 (s), 553 (m), 530 (s), 428 (m), 401 (w), 358 (m), 349 (w), 328 (w). FT-Raman (cm^{-1}): 3086 (s), 2971 (vs), 2936 (w), 2909 (vs), 2876 (w), 1610 (s), 1543 (s), 1491 (m), 1418 (s), 1371 (m), 1321 (vs), 1254 (m), 1205 (m), 1128 (m), 1033 (vs), 939 (vs, v(Mo=O)), 918 (m), 902 (w), 874 (s, v(O-O)), 804 (m), 722 (s), 658 (w), 589 (m), 554 (w), 533 (s), 405 (w), 297 (m), 248 (m), 172 (m), 126 (s). ^{1}H NMR (400 MHz, $CDCl_3$, r.t., ppm): δ = 9.33 (d, H^6), 8.19 (d, H^3), 8.17 (d, $H^{6'}$) 7.88 (s, $H^{3'}$), 7.33 (dd, H^5), 7.31 (dd, $H^{5'}$), 1.46 (s, H_{tBu}), 1.29 (s, H_{tBu}). ^{13}C{^{1}H} NMR (100.51 MHz, $CDCl_3$, r.t., ppm): δ = 168.80 ($C^{2,2'}$), 164.46 ($C^{2,2'}$), 155.29 (C^6), 154.34 ($C^{4,4'}$), 147.46 ($C^{6'}$), 124.24 ($C^{5,5'}$), 124.08 ($C^{5,5'}$), 119.53 (C^3), 117.60 ($C^{3'}$), 35.51 (C_{tBu}), 30.32 (C_{tBu}).[16]

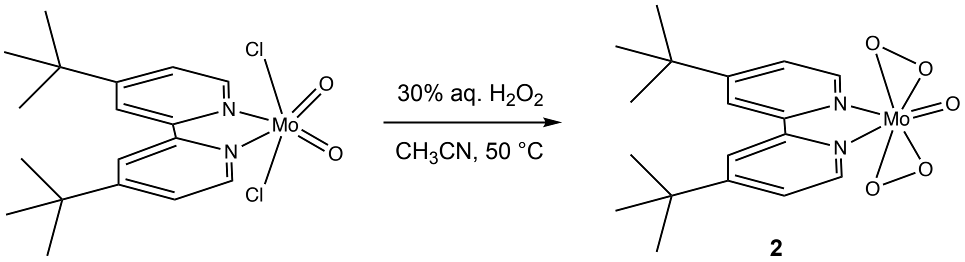

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Figure 6.9. Preparation of catalyst $[MoO(O_2)_2(\text{di-}t\text{Bu-bipy})]$ (**2**).

6.4.3. ODS studies

6.4.3.1. Model diesel

The ODS studies were performed using a multicomponent model diesel containing 1000 ppm of each sulfur compound: dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene dissolved in *n*-octane. The ODS system was performed in a biphasic liquid-liquid system (1:1 (v/v) model diesel/ extraction solvent proportion) in the presence of the oxidizing agent aq. 30% H_2O_2 (0.60 mmol) and using the $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$ (**1**) (10.7 μmol) as catalyst. The catalyst was added to the extraction solvent, followed by the addition of the model diesel. In general, the ODS process combines oxidation and extraction. Firstly, occurs an initial extraction, where some of the sulfur compounds present in model diesel are transferred to the extraction solvent. This stage has a duration of 10 min and is performed at 50 °C under vigorous stirring. After the addition of the oxidant, H_2O_2, starts the oxidative stage, from which the sulfur compounds are oxidized to the corresponding sulfones and/or sulfoxides, facilitating their extraction to the extraction solvent due to the similar polarities, allowing thus a decrease of non-oxidized sulfur compounds present in extraction phase to continue the transfer of these compounds from the model diesel to the extraction phase. The sulfur content in the model diesel was quantified periodically by GC analysis. Tetradecane was used as standard. In a typical procedure, an aliquot (10 μL) of standard solution was added to the aliquot removed from the model diesel phase (10 μL). When $[BMIM]PF_6$ or $[BMIM]BF_4$ were used, the extraction phase containing the homogeneous catalyst could be recycled. The sulfur compounds from these extracting solvents were removed by stirring this phase for 10 min with a mixture composed by an equal volume of ethyl acetate and diethyl ether.

6.4.3.2. Untreated real diesel

An untreated real diesel sample (containing 2300 ppm of sulfur) supplied by Galp Energia was used. By application of a simple liquid-liquid extraction process with equal volumes of diesel and MeCN, six, nine and twelve consecutive extractions cycles were performed. After each extraction cycle, the MeCN phase was removed and replaced by a fresh portion of clean solvent. In the next step, the oxidative catalytic process was carried out using a biphasic diesel/[BMIM]PF_6 system containing dissolved the [MoO_2Cl_2(di-*t*Bu-bipy)] (**1**) catalyst and using H_2O_2 as oxidant at 50 °C. The catalytic reactions were performed during 3 and 6 h. After each catalytic cycle the diesel sample was removed and washed with an equal volume of MeCN for 10 min at 50 °C.

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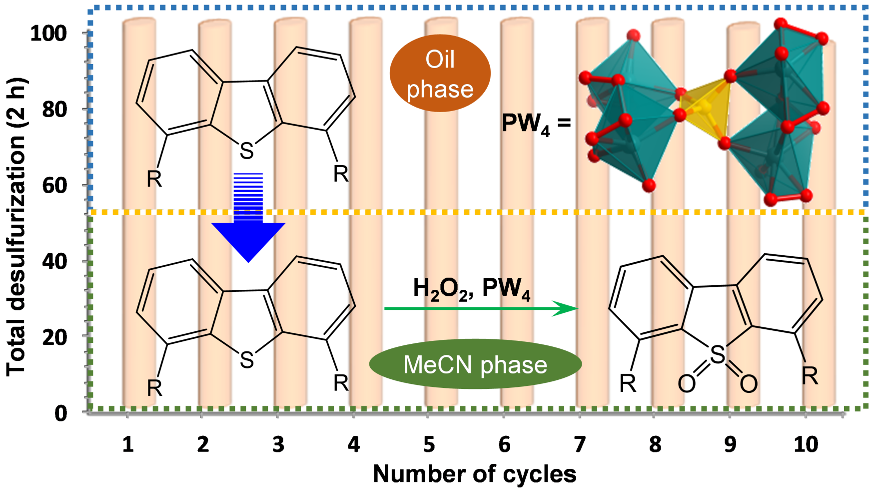
Chapter 7

PEROXOTUNGSTATE CATALYSTS: HOMOGENEOUS AND HETEROGENEOUS BY IMMOBILIZATION ON FUNCTIONALIZED SBA-15



7. Peroxotungstate catalysts: homogeneous and heterogeneous by immobilization on functionalized SBA-15

7.1. Introduction

The oxygen transfer chemistry of tungsten has not benefited of an adequate investment from a mechanistic point of view in comparison to other transition metals.[1] Environmental concerns have been playing a fundamental role in the development of catalytic systems based on hydrogen peroxide, which is known to be efficiently activated by high valent d^0 tungsten, making these catalysts interesting for the development of greener catalytic systems.[2, 3]

Tungsten catalysts such as H_2WO_4, $W(CO)_6$, polyoxotungstates, peroxotungstates, Na_2WO_4, among others, have attracted considerable interest in the oxidation of sulfides.[4-12] Among these, the phosphorous-containing tetranuclear peroxotungstate $\{PO_4[WO(O_2)_2]_4\}^{3-}$, also known as the Venturello ion and denoted as PW_4, has been considered one of the best catalysts, in part as a result of its synthetic versatility.[2] Despite the favourable catalytic abilities of peroxotungstates, their good solubility in polar media is a disadvantage since at the industrial level the recovery and reuse of the catalyst is very important.[13] Thus, the development of heterogeneous systems is of significant industrial interest. The heterogenization of a homogeneous catalyst should ideally combine the selectivity and efficiency of the catalytically active center with the robustness of the support. Examples of success are frequently associated with the use of ordered mesoporous silicas (e.g. MCM-48, MCM-41, SBA-15) that have the advantage of easy surface modification by reaction with organosilanes presenting the appropriate functional groups.[13, 14] SBA-15 possesses walls with thickness between about 3.1 and 6.4 nm, which gives the material a higher hydrothermal and mechanical stability, when compared for instance to MCM-41.[15] Its high internal surface area (400-900 m^2 g^{-1}), the hexagonal pores with a narrow pore distribution and tuneable pore diameter between 5 and 15 nm make SBA-15 a favourable catalyst support.[16, 17]

In the present chapter, the synthesis of a quaternary ammonium salt of the peroxophosphotungstate anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and a composite based on its immobilization in a trimethylammonium-functionalized SBA-15 (PW_4@TM-SBA-15) were prepared and investigated as homogeneous and heterogeneous catalysts for the oxidative desulfurization of a model diesel and real liquid fuels (diesel and jet fuel) supplied by Galp Energia. An ionic liquid and acetonitrile were used as extraction solvents, and H_2O_2 as oxidant. The reusability of these systems was tested for several ODS cycles.

7.2. Results and Discussion

7.2.1. Catalyst characterization

The peroxophosphotungstate anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (Figure 7.1) was isolated as a tetrabutylammonium salt by addition of an aqueous solution of tetrabutylammonium chloride to an aqueous solution formed by the addition of 30% aq. H_2O_2 to phosphotungstic acid.[18]

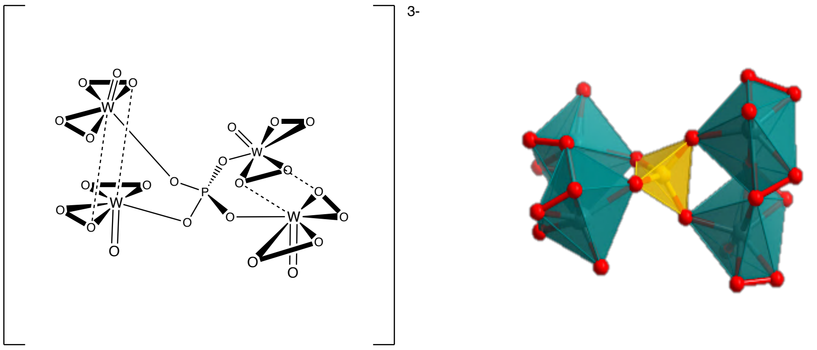


Figure 7.1. Different representations of the molecular structure of the anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$.

The supported catalyst PW_4@TM-SBA-15 was prepared by functionalizing SBA-15 with a spacer ligand containing terminal trimethylammonium groups and then treating this material with a solution of the peroxophosphotungstate $(nBu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ (PW_4) (Figure 7.2).

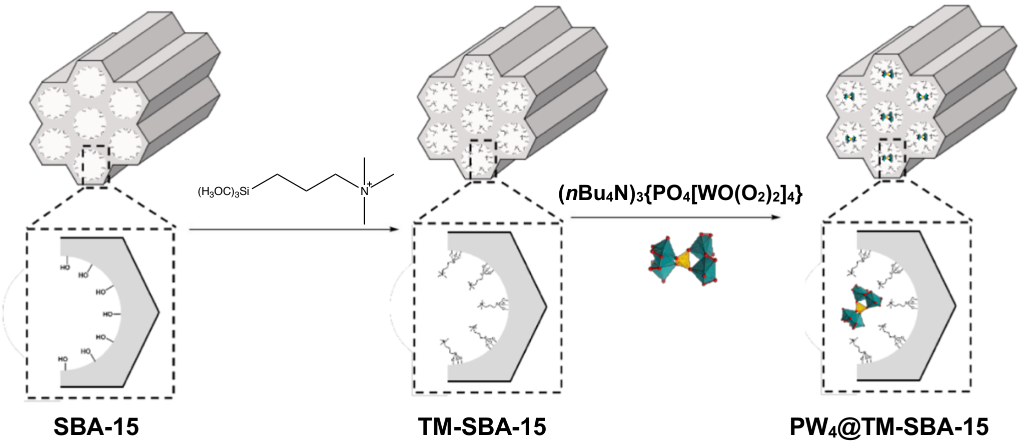


Figure 7.2. Representative pathway for the preparation of TM-SBA-15 support and the corresponding PW_4@TM-SBA-15 composite. Adapted from reference

The resultant material, denoted as PW_4@TM-SBA-15, had a tungsten content of 3.3 mmol.g^{-1} (determined by ICP-MS). The composite material was further characterized by several techniques including vibrational spectroscopies (FT-IR and FT-Raman), PXRD, ^{31}P and ^{13}C MAS NMR spectroscopy, SEM and EDS. The FT-IR spectrum of PW_4@TM-SBA-15 was practically unchanged from that for TM-SBA-15 and, due to the intense broad band centered at 1088 cm^{-1} (asymmetric Si—O—Si stretch), no bands due to immobilized peroxophosphotungstate species could be discerned (Figure 7.3). Other bands due to the SBA-15 support include those at 951 cm^{-1} (symmetric Si—O—Si stretch) and 804 cm^{-1} (Si—O—Si bending mode). Some O—H stretching and bending vibrations were observed around 3000-3800 cm^{-1} and at 1637 cm^{-1}, respectively, which may be related with the surface silanol groups and adsorbed water molecules.[19, 20]

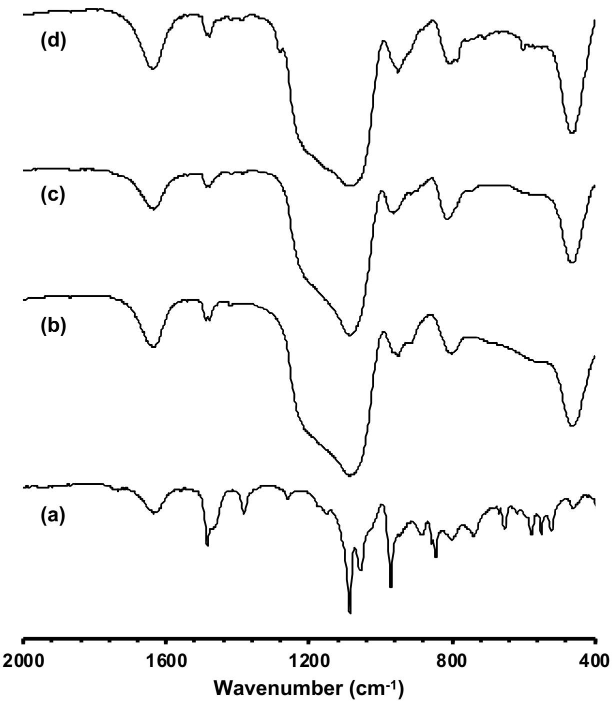


Figure 7.3. Infrared spectra of PW_4 (a), the support TM-SBA-15 (b), and the composite material before [(c) PW_4@TM-SBA-15] and after [(d) PW_4@TM-SBA-15_ac] use in the ODS process.

The FT-Raman spectrum of PW_4@TM-SBA-15 was more informative regarding the nature of immobilized tungsten-containing species since several new bands appeared that are not displayed by the starting material TM-SBA-15 (Figure 7.4). Some key bands displayed by PW_4 [ν(O-O) at 859 cm^{-1}, $\nu(W(O_2))$ at 531 and 591 cm^{-1}] [21] are not evident in the spectrum of PW_4@TM-SBA-15. A strong band centered at 987 cm^{-1} (or a shoulder on this band at ca. 975 cm^{-1}) may be due to ν(W=O) of supported PW_4 species since the latter typically display a band for this mode at 980 ± 3 cm^{-1}.[21, 22] However, considering the failure to observe bands related with W-coordinated peroxo groups, alternative assignments must be considered. The supported material PW_4@TM-SBA-15 exhibits an additional sharp and intense band at 1004 cm^{-1}. By reference to published data, the main bands at 987 and 1004 cm^{-1} can be confidently attributed to the α-Keggin heteropolyanion, $[PW_{12}O_{40}]^{3-}$ (PW_{12}).[23-26] The transformation of PW_4 to PW_{12} during the immobilization process is not altogether surprising since previous reports have shown the two species to be in equilibrium during oxidative processes, and the formation of PW_{12} from PW_4 is likely to be favored in the absence of excess H_2O_2.[27]

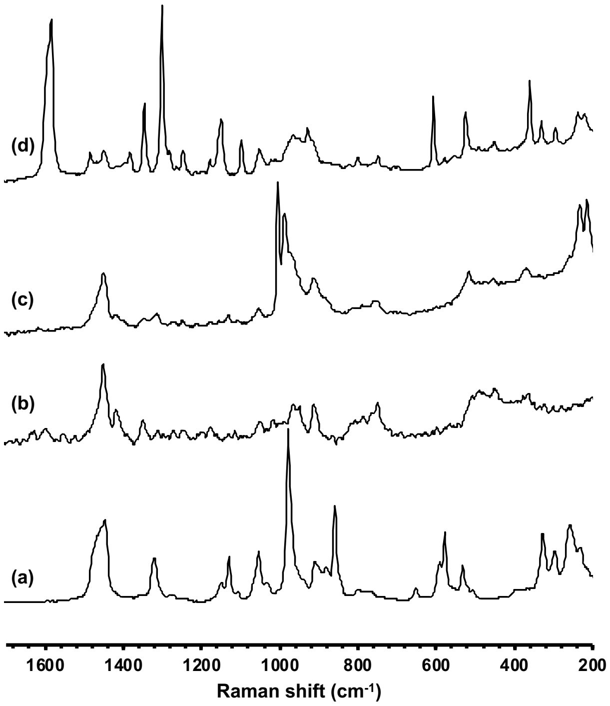


Figure 7.4. Raman spectra of PW_4 (a), the support TM-SBA-15 (b), and the composite material before [(c) PW_4@TM-SBA-15] and after [(d) PW_4@TM-SBA-15_ac] use in the ODS process.

The ^{31}P HPDEC MAS NMR spectrum of PW_4@TM-SBA-15 provided further confirmation for the presence of the α-Keggin anion (Figure 7.5). Thus, the sharp line at -15 ppm is attributed to PW_{12} species in accordance with literature data.[22, 26] A strong and broad peak centered at 0 ppm may be due to free phosphate ions formed in the conversion of PW_4 species to PW_{12} species. However, it is likely that this peak and the shoulder at 5.4 ppm have contributions from peroxo species with low W/P ratios, e.g. tetranuclear PW_4 and dinuclear $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ (PW_2). The ^{31}P chemical shift for PW_4 species (dissolved in nonaqueous media or recorded in the solid-state) is typically reported to be in the range of 0.5-4.5 ppm, being sensitive to the solvent and type of counter-cation.[21, 22, 28, 29] Accordingly, in this work the solution ^{31}P spectrum of PW_4 in CD_3CN displayed a single sharp line at 4.5 ppm, while the ^{31}P HPDEC MAS NMR spectrum displayed a single sharp line at 2.7 ppm (Figure 7.5). The ^{31}P chemical shift for PW_4 species can fall out of this range depending on the surrounding medium. For example, chemical shifts between 1.0 and -3.5 ppm have been reported for PW_4 in aqueous phase.[28, 29] Brégeault et *al.* [30] reported a chemical shift of 0 ppm for the PW_2 complex supported on silica. The presence of both PW_2 and PW_4 in PW_4@TM-SBA-15 is probable since chemical exchange between these two species is known to occur.[31] Several overlapping peaks between -5 and -14.5 ppm in the spectrum of

PW_4@TM-SBA-15 may be assigned to lacunary phosphotungstate species of the type $[PW_xO_y]^{z-}$ (e.g., $x = 9$ or 11) and/or derivatives of these such as the well-known Wells-Dawson anion $[P_2W_{18}O_{62}]^{6-}$ and the sandwich-like cluster $[P_2W_{21}O_{71}]^{6-}$. Typical chemical shifts for these anions are -10.5 ± 0.5 for $[PW_{11}O_{39}]^{7-}$,[32, 33] and -12.4 ppm for the Wells-Dawson anion.[34] Zhao *et al.* [35] reported a similar ^{31}P MAS NMR spectrum (and reached similar conclusions to ours) for a supported catalyst prepared by immobilization of PW_4 on the mesoporous silica KIT-1 grafted with quaternary ammonium groups.

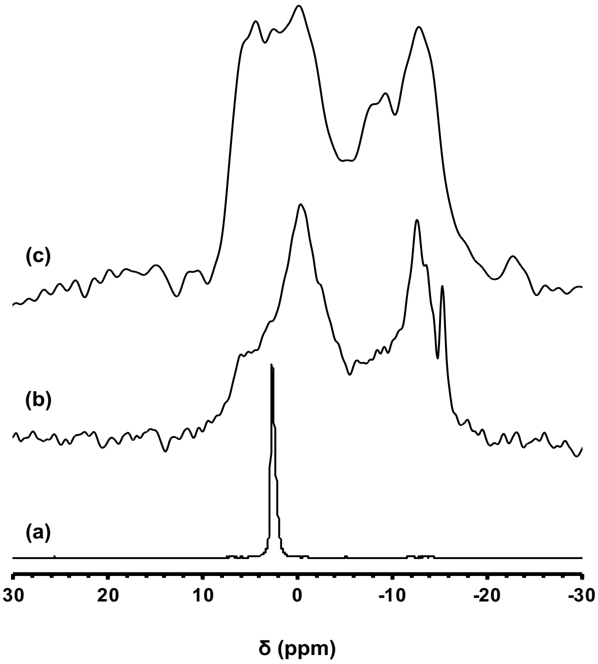


Figure 7.5. ^{31}P HPDEC MAS NMR spectra of PW_4 (a), and the composite material before [(b) PW_4@TM-SBA-15] and after [(c) PW_4@TM-SBA-15_ac] use in the ODS process.

The $^{13}C\{^1H\}$ CP MAS NMR spectrum of the functionalized support TM-SBA-15 displays four main peaks at 68.5 (NCH_2), 53.4 ($(CH_3)_3N$), 16.7 ($CH_2\mathit{C}H_2CH_2$) and 8.9 ppm (CH_2Si) that correspond to the tethered propyltrimethylammonium group (Figure 7.6). These four peaks are present in the spectrum of PW_4@TM-SBA-15 and are unshifted relative to those of TM-SBA-15. The spectrum contains additional weaker peaks (marked with an asterisk in Figure 7.6) that can be assigned to tetrabutylammonium groups. Hence, treatment of TM-SBA-15 with a dichloromethane solution of the salt PW_4 resulted in the co-immobilization of some $(nBu_4N)^+$ cations in addition to peroxophosphotungstate species.

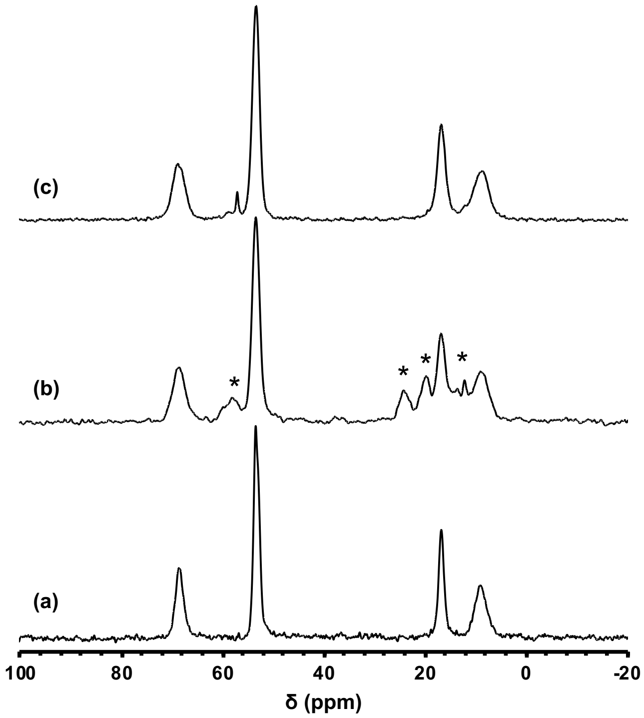


Figure 7.6. $^{13}C\{^{1}H\}$ CP MAS NMR spectra of the support TM-SBA-15 (a), and the composite material before [(b) PW_4@TM-SBA-15] and after [(c) PW_4@TM-SBA-15_ac] use in the ODS process. Peaks due to co-encapsulated tetrabutylammonium ions are indicated with an asterisk.

Figure 7.7 compares the PXRD patterns of the derivatized support TM-SBA-15 and the composite material PW_4@TM-SBA-15. Both materials exhibit a single very strong peak at a 2θ value of 0.81-0.84° and weaker higher-order peaks at 1.44-1.51° and 1.68-1.75°, which are typical of SBA-15 materials and are indexed as the (100), (110) and (200) reflections of the *p*6*mm* hexagonal structure. The similarity of the two patterns indicates that the highly-ordered SBA-15 mesostructure was preserved upon immobilization of peroxophosphotungstate anions. The reflections for PW_4@TM-SBA-15 are shifted slightly to higher angles compared with those for TM-SBA-15, revealing a slight contraction of the unit cell (unit cell parameter $a_0 = 2d_{100}/\sqrt{3}$ = 12.58 nm for TM-SBA-15 and 12.19 nm for PW_4@TM-SBA-15). Similar results were found previously after immobilization of the titanium-polyoxometalate $[(PW_{11}O_{39}Ti)_2OH]^{7-}$ in TM-SBA-15.[36]

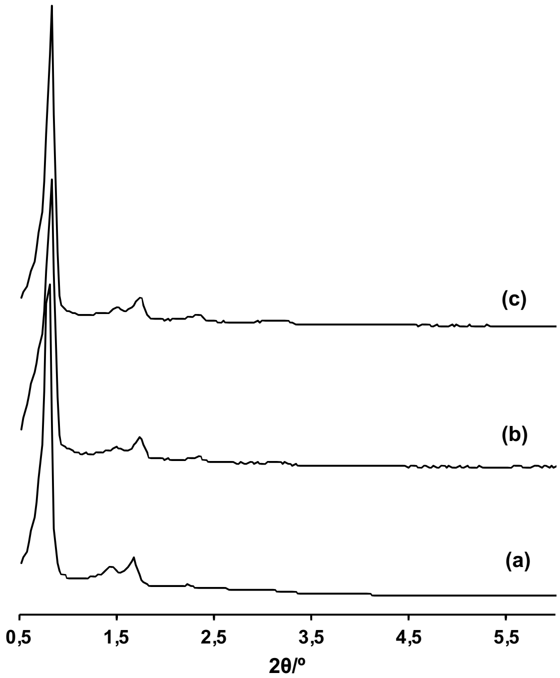


Figure 7.7. PXRD patterns of the support TM-SBA-15 (a) and the composite material before [(b) PW_4@TM-SBA-15] and after [(c) PW_4@TM-SBA-15_ac] use in the ODS process.

SEM micrographs of TM-SBA-15 and PW_4@TM-SBA-15 indicated that the typical SBA-15 morphology consisting of bean-shaped particles with lengths in the range of 700-1100 nm was not affected by the immobilization of peroxophosphotungstate anions in TM-SBA-15 (Figure 7.8).[37] EDS analyses confirmed the presence of W and P in the composite material PW_4@TM-SBA-15 (Figure 7.9).

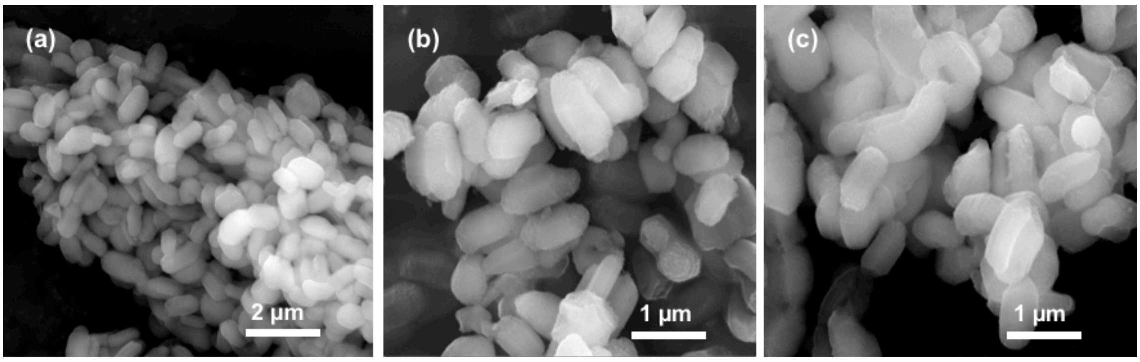


Figure 7.8. SEM images of the solid support TM-SBA-15 (a), and the composite material before [(b) PW_4@TM-SBA-15] and after [(c) PW_4@TM-SBA-15_ac] use in ODS process.

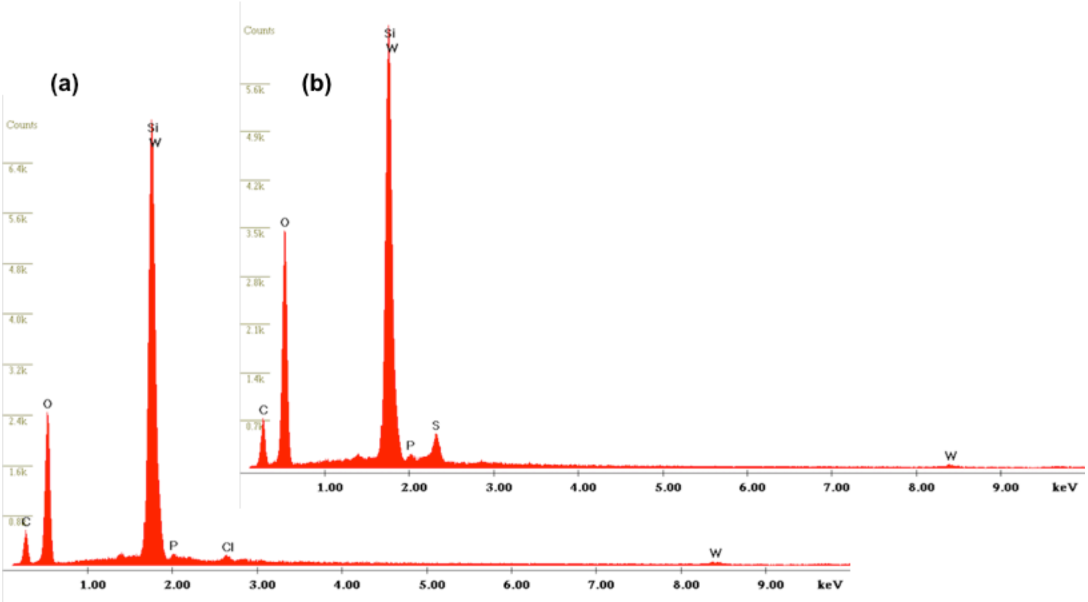


Figure 7.9. EDX spectrum of composite material before [(a) PW_4@TM-SBA-15)] and after [(b) (PW_4@TM-SBA-15_ac)] use in ODS process.

7.2.2. Desulfurization of a model diesel

The model diesel containing the three refractory sulfur compounds most commonly found in liquid fuels, namely DBT, BT and 4,6-DMDBT, was desulfurized through the application of a biphasic system composed by equal volumes of model diesel and extraction solvent using 30% aq. H_2O_2 as oxidant and either the composite PW_4@TM-SBA-15 or homogeneous PW_4 as catalysts. The desulfurization occurred in two fundamental steps. Firstly, the biphasic diesel/solvent system was vigorously stirred for 10 min at 70 °C to promote the initial extraction of the sulfur compounds from the model diesel to the extraction solvent. After this period a transfer equilibrium between the two phases is reached and the desulfurization continues with an oxidative catalytic step to achieve sulfur-free diesel. Thus, after the initial extraction step the oxidant is added (0.26 mmol; H_2O_2/S molar ratio = 7) to the biphasic system and the sulfur compounds present in the extraction solvent phase are oxidized to the corresponding sulfones and/or sulfoxides, which due to their high polarity remain in the extraction solvent phase. The oxidation of the sulfur compounds in the extraction solvent phase promotes a continual transfer of more non-oxidized sulfur compounds from the model diesel to the solvent phase. No oxidative products were detected in the model diesel or extractant phases in the absence of the catalyst.

7.2.2.1. Optimization studies

An optimization study was performed using the homogeneous catalyst PW_4. Two different parameters were investigated: the effect of the extraction solvent and the amount of oxidant. The initial conditions adopted were 5 μmol of catalyst, 0.26 mmol of H_2O_2, 0.750 mL of model diesel and 0.750 mL of extraction solvent, using a thermostatic bath at 70 °C.

The desulfurization efficiency using different extraction solvents (MeCN and $[BMIM]PF_6$) or in absence of extraction solvent was analysed in the treatment of a model diesel containing 1500 ppm of sulfur. Using the biphasic system, the initial extraction of sulfur compounds from the model diesel to the polar solvent was significantly more pronounced for the system containing the MeCN (68.1%) than $[BMIM]PF_6$ (43.4%) (Figure 7.10). This result is in agreement with those presented in the literature by Balula's research group.[37, 38] Figure 7.10 displays the kinetic profile obtained for the oxidative catalytic stage using different extraction solvents. In the presence of MeCN the model diesel was completely desulfurized after 2 h, while during the same reactional time, no complete desulfurization was obtained in the presence of $[BMIM]PF_6$ (73.5%) and in the absence of extraction solvent (62.8%). The higher catalytic capacity of PW_4 in the presence of MeCN can be attributed to the affinity of the PW_4 complex to this solvent. It is well-known that the peroxophosphostungstate complex is an intermediate active species in a variety of oxidative reactions, being formed from the reaction of Keggin-type polyoxometalates with H_2O_2.[39] As an intermediate active oxygen species, this complex interacts with the sulfur compounds present in the MeCN phase, forming the corresponding sulfoxides and sulfones. Posteriorly, the peroxo-compound is regenerated by the reaction with H_2O_2 oxidant that is present in the same phase of the catalyst due to its miscibility in MeCN.

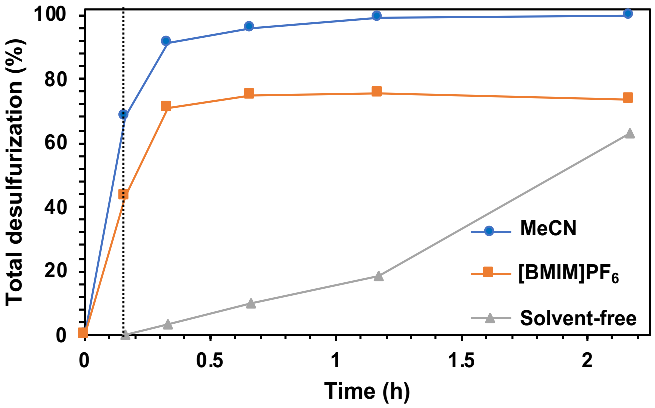


Figure 7.10. Oxidative desulfurization of a model diesel (1500 ppm S) using PW_4 (5 µmol) as catalyst, in the presence or absence of different extraction solvents and H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The influence of oxidant amount (0.26 or 0.39 mmol) was analysed for the desulfurization of the model diesel. A similar desulfurization profile was obtained for both amounts of H_2O_2 used, obtaining in both cases a complete desulfurization after 2 h of ODS reaction (Figure 7.11). Therefore, the amount of oxidant used in the subsequent experiments was 0.26 mmol. The efficiency of H_2O_2 usage was found to be 98% under the optimized conditions. This result indicates that an excess of $H_2O_2/S = 7$ is needed to achieve complete desulfurization after 2 h of ODS reaction.

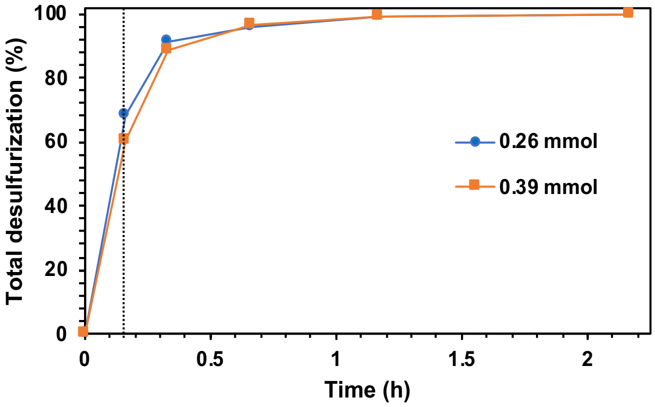


Figure 7.11. Oxidative desulfurization of a model diesel (1500 ppm S) using PW_4 (5 µmol) as catalyst, MeCN (0.750 mL) as extraction solvent and different amounts of H_2O_2 (0.26 and 0.39 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

From an industrial point of view, the ODS process requires some improvements to become a commercially competitive process. Some of these requirements are high efficiency at moderate temperature, and low consumption of oxidant to avoid parallel oxidation reactions (i.e. oxidation of alkenes and aromatics present in fuels). Most of the published studies in this area do not fulfil these requirements, using H_2O_2/S ratios higher than 8 and applying the catalysts in the desulfurization of poor model diesel solutions which only contain a single sulfur compound (generally the most easily oxidized, DBT).[37, 40-42] The present work demonstrates that PW_4 is an efficient catalyst for deep desulfurization of a multicomponent model diesel in short reaction times (2 h) under mild conditions (H_2O_2/S = 7, 70 °C).

7.2.2.2. PW_4 stability and reusability

The peroxophosphotungstate PW_4 complex has revealed a high catalytic efficiency under the optimized conditions, i.e. model diesel/MeCN system and 0.26 mmol of H_2O_2 with a reaction medium temperature of 70 ºC. In order to test its stability, reusability tests were performed for several consecutive ODS cycles. The PW_4/MeCN phase was reused after each cycle by removing the desulfurized model diesel phase and initiating a new cycle by the addition of fresh portions (0.750 mL) of sulfurized model diesel and H_2O_2. Figure 7.12 presents the desulfurization results obtained for ten consecutives cycles after 2 h of reaction. The results show that the desulfurization catalytic activity of the PW_4/MeCN system remained stable for the eight consecutive cycles, with only a slight decrease in the ninth and tenth cycle, in which 17 ppm of sulfur remaining after 3 h. This loss of desulfurization capacity may be related with the saturation of the PW_4/MeCN phase with the oxidized sulfur compounds which curtail the extraction of more sulfur compounds from the model diesel and therefore decrease the desulfurization efficiency of the system.

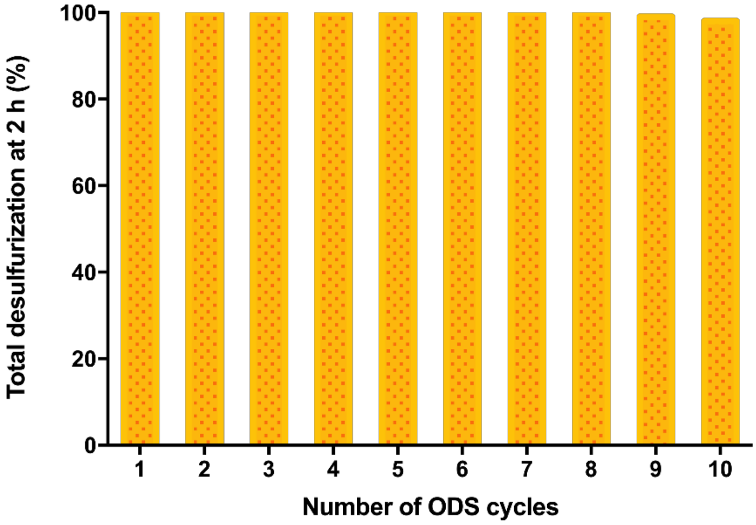


Figure 7.12. Reusability of the homogeneous PW_4 (5 μmol) catalyst dissolved in the extraction solvent MeCN for the desulfurization of a model diesel (1500 ppm S) at 70 °C for ten consecutive ODS cycles, using H_2O_2 (0.26 mmol) as oxidant. Results obtained after 2 h of ODS reaction.

The stability of the catalyst PW_4 after the second cycle was investigated by ^{31}P NMR (Figure 7.13). As discussed in Section 7.2.1, the ^{31}P NMR spectrum of as-synthesized PW_4 catalyst exhibits a single peak at 4.5 ppm (in CD_3CN solution), which is in agreement with the chemical shift of 4.2 ppm reported previously by Aubry *et al.* [22] ($CH_3CN/CDCl_3$). However, after the second ODS cycle three resonance lines were observed at 4.5, 3.7 and 0.24 ppm. The line at 4.5 ppm can be assigned to PW_4, while the other two lines may be due to other PW_n peroxophosphotungstate species (e.g., PW_2, for which a chemical shift of 3.0±0.1 ppm has been previously reported in $CD_3CN/CDCl_3$ [28]), or free phosphate ions. These new species formed during the catalytic process proved to be stable during the consecutive ODS cycles.

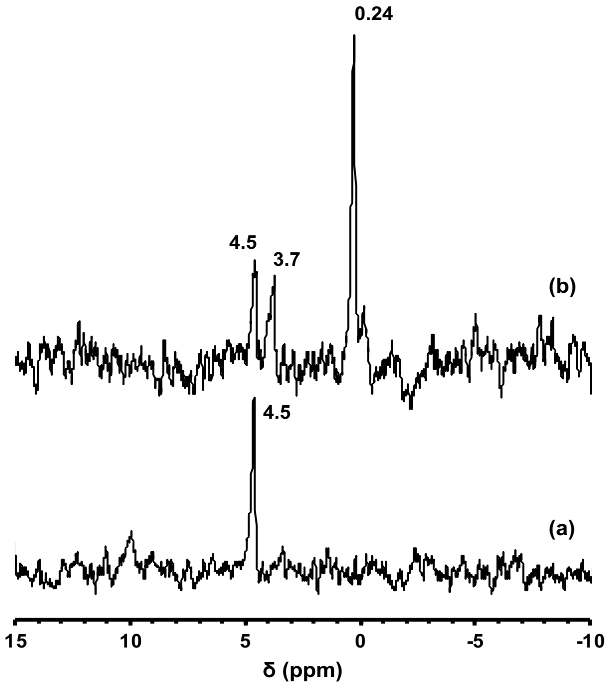


Figure 7.13. ^{31}P NMR spectra of the PW_4 in CD_3CN, before (a) and after (b) the 2nd ODS cycle.

7.2.2.3. Desulfurization efficiency using PW_4@TM-SBA-15

The peroxophosphotungstate PW_4 catalyst reveals high desulfurization performance. However, as a homogeneous catalyst, its recovery from the reaction medium is not straightforward. For this reason, the homogeneous catalyst was immobilized in the derivatized SBA-15 support (through electrostatic interactions) to obtain a supported catalyst that could be more easily recovered and reused. The ODS reactions with the supported catalyst PW_4@TM-SBA-15 were performed using the same optimized conditions obtained with the homogeneous PW_4. Comparing both homogeneous and supported catalysts, the initial extraction stage of each sulfur compound followed the same order BT > DBT > 4,6-DMDBT, since this extraction order only depends on the molecular diameter and geometry of each sulfur compound, and their solubility.[43] Figure 7.14 shows the desulfurization profiles of the model diesel using PW_4 and PW_4@TM-SBA-15 catalysts. A similar kinetic profile was observed for the homogeneous and supported catalyst, and a complete desulfurization was reached at 2 h and 3 h, respectively. Regardless of catalyst applied, during the catalytic stage, the BT showed to be the most refractory sulfur compound, due to its significantly lower electron density when compared to the remaining benzothiophene derivatives.

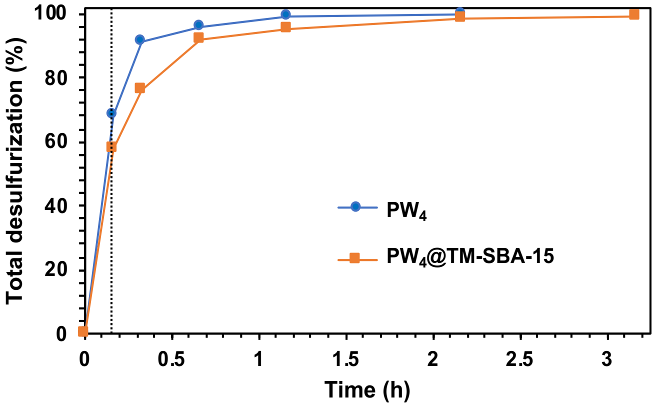


Figure 7.14. Desulfurization of a model diesel using the homogeneous PW_4 and supported PW_4@TM-SBA-15 catalyst in the presence of MeCN (0.750 mL) as extraction solvent and H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The reusability of the composite material PW_4@TM-SBA-15 was investigated for ten consecutive ODS cycles. As performed for the homogeneous catalyst, the solid catalyst was maintained in the MeCN extraction phase and a new ODS cycle was performed by removal of the desulfurized diesel and adding a new portion (0.750 mL) of model diesel and oxidant (0.26 mmol). The results obtained are displayed in Figure 7.15 and demonstrate that the PW_4@TM-SBA-15 catalyst maintains its activity from the first to eighth desulfurization cycle. After the eighth cycle a slight decrease in the desulfurization efficiency was observed (98.6% for the 8th cycle, 97.9% for the 9th cycle and 96% for the 10th cycle), obtaining a complete desulfurization of the model diesel after 4 h. This behaviour is similar to the obtained for the reusability of the homogeneous ODS process, and the loss of efficiency after the eighth cycle can be also attributed to the saturation of the MeCN phase with oxidized sulfur compounds, which causes a decrease in the transfer of sulfur compounds from the model diesel phase to the extraction solvent and consequently limits the efficiency of the catalytic system.

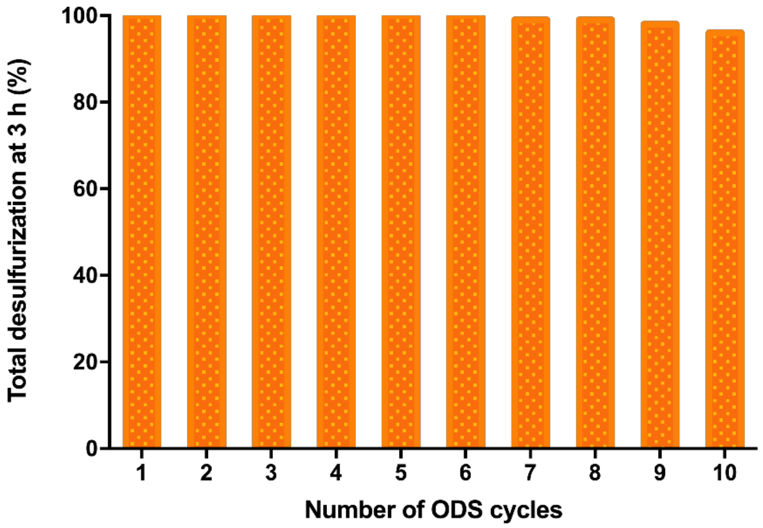


Figure 7.15. Reusability of the supported catalyst PW_4@TM-SBA-15 and the extraction solvent MeCN for the desulfurization of a model diesel (1500 ppm S) for ten consecutive cycles, using H_2O_2 (0.26 mmol) as oxidant, at 70 °C. Results obtained after 3 h of ODS reaction.

7.2.2.4. Stability of the supported catalyst

To evaluate the catalyst stability after catalytic use, the composite (PW_4@TM-SBA-15_ac, where ac stands for after catalysis) was recovered in the end of the tenth ODS cycle and posteriorly characterized. The FT-IR spectra of PW_4@TM-SBA-15 and PW_4@TM-SBA-15_ac match very closely, suggesting that no significant chemical or structural alteration occurred with the SBA-15 support framework during the various ODS cycles (Figure 7.3). In stark contrast, the FT-Raman spectra of the as-synthesized composite and PW_4@TM-SBA-15_ac are very different (Figure 7.4). Bands for PW_4@TM-SBA-15 at 987 and 1004 cm^{-1} that were attributed to the α-Keggin heteropolyanion, PW_{12}, are not present in the spectrum of the recovered solid, indicating that this species had either undergone chemical transformation to a different (supported) species or had been leached into solution. The ^{31}P HPDEC MAS NMR spectrum of PW_4@TM-SBA-15_ac is consistent with these results since it does not contain the sharp line at ca. -15 ppm characteristic of PW_{12}. On the other hand, a clear increase in the relative intensity of the peak at 5.4 ppm (assigned above as supported PW_4) is observed, which can be explained by a progressive reaction of supported PW_{12} and/or supported lacunary phosphotungstate species with H_2O_2 to give supported PW_4 species. The FT-Raman spectrum of PW_4@TM-SBA-15_ac presents several new bands that are not observed for PW_4@TM-SBA-15. These are attributed to sulfones adsorbed in the composite after catalytic use (Figure 7.4). Thus, the bands at 1150 and 1301 cm^{-1} are compatible with vibrations of the SO_2 moiety in thiophene 1,1-dioxides.[44] The intense band at 1584 cm^{-1} and a shoulder at 1592 cm^{-1} are attributed to C-C stretching modes of the C=C double bond in BTO_2 and/or the benzene rings in BTO_2, $DBTO_2$ and 4,6-$DMDBTO_2$.[45, 46] EDS analysis confirmed the presence of sulfur-containing compounds in the recovered catalyst (Figure 7.9). While the $^{13}C\{^1H\}$ CP MAS NMR spectrum of PW_4@TM-SBA-15_ac display the four peaks expected for the tethered propyltrimethylammonium group, peaks due to $(n\text{Bu}_4\text{N})^+$ cations were not observed, indicating that these species were extracted into solution during the ODS cycles (Figure 7.6). The spectrum showed weak signals in the aromatic region around 130-135 ppm (not shown) that probably arose from the adsorbed sulfones.

The Si/W ratio before and after catalytic use of the composite was quantified by elemental analysis. The results indicated that some leaching had occurred since the Si/W ratio increased from 0.13 (before catalysis) to 0.23 (after catalysis). The PXRD pattern of the composite after catalysis exhibited the same profile as that found for the as-prepared material (Figure 7.7), indicating that the ordered mesostructure of the SBA-15 support was preserved during the ODS process. Accordingly, SEM analysis showed that the morphology of the recovered catalyst was unchanged from that for PW_4@TM-SBA-15 (Figure 7.8).

7.2.3. Desulfurization of untreated real diesel

PW_4 and PW_4@TM-SBA-15 were used as catalysts for the oxidative desulfurization of a diesel and jet fuel with a sulfur content of 2300 ppm and 1100 ppm, respectively. From previous work it is known that the main sulfur constituents of untreated fuels supplied by Galp Energia are benzothiophene and dibenzothiophene derivatives.[11] An extractive pre-treatment was performed for the diesel sample using liquid-liquid extraction with the immiscible polar solvents DMF or MeCN. After one liquid-liquid extraction during 5 min at 70 °C, the sulfur content in diesel decreased from 2300 to 1920 ppm for MeCN and 1438 ppm for DMF (experiments A and B in Table 7.1). Therefore, DMF showed a higher extraction capacity for non-oxidized sulfur compounds than MeCN. In the next step, the catalytic oxidative desulfurization of this pre-treated diesel was performed using the model diesel conditions with PW_4 as catalyst. To test the efficiency of each polar solvent to the oxidized sulfur compounds, in the end of experiment C and D, was performed a final extraction to remove the sulfoxides and sulfones from the diesel. By the results obtained, namely 349 and 377 for MeCN and

DMF, respectively, it is possible to conclude that despite the DMF had promoted a far better initial extraction capacity, this had no effect on the overall efficiency of the desulfurization process. These results were corroborated by the experiments E and F, in which were achieved the best desulfurization efficiencies without an initial extraction step. It is important to point out that the results obtained in these experiments (E and F), namely 86.7% and 88.7% are among the best results ever achieved from a diesel with such a high sulfur content (2300 ppm S), using MeCN as extraction solvent and a tungsten-based catalyst.[10, 11, 38, 47, 48] The similar results obtained in presence of both solvents indicate similar extraction capacity behaviour.

Regarding to the PW_4@TM-SBA-15 two desulfurization tests were performed (experiments G and H in Table 7.1) using also an untreated diesel (2300 ppm S) and a pre-treated diesel (obtained in experiment A). To remove the oxidized sulfur compounds from the diesel samples, all the experiments suffered an extraction step after the catalytic oxidative stage. The desulfurization efficiencies obtained in both cases are in accord with the results obtained in the presence of the homogeneous catalyst. The small differences are coherent with the results posteriorly obtained during the model diesel tests, in which the best results were obtained when the initial extraction step was not applied.

An untreated jet fuel (1100 ppm S) was also desulfurized by PW_4 under the optimized conditions obtained with the homogeneous catalyst. Through previous work with this liquid fuel and by the results obtained with the diesel, was concluded that the initial extraction is not so an important parameter for a successful desulfurization.[49] Therefore, was performed two treatments, in which was performed the oxidative step and final extractions with MeCN and DMF. As can be observed in Table 7.2, the highest desulfurization was obtained when the MeCN was employed as final extraction solvent. The obtained results contrast with that obtained for diesel, where the most efficient desulfurization results were very similar using DMF and MeCN as final extraction solvents (experiments E and F). This difference can be related with a different constitution of jet fuel when compared to diesel.

Therefore, the desulfurization process employed in this work using the homogeneous peroxophosphotungstate catalyst PW_4 or the corresponding heterogeneous catalyst, MeCN as extraction solvent, with a H_2O_2/S ratio of 7, and a reaction time of only 2 h, constitutes a competitive and cost-effective process that may have potential to replace the actual industrial HDS process.

Table 7.1. Experiments performed for desulfurization of an untreated diesel (2300 ppm S) using the model diesel conditions

Experiment	Initial extraction[a]	Catalyst	ODS time	Final extraction[b]	S content (ppm)	Desulfurization efficiency (%)
A	MeCN	---	---	---	1920	16.5
B	DMF	---	---	---	1438	37.5
C	MeCN	PW_4	2 h	MeCN	349	84.8
D	DMF	PW_4	2 h	DMF	377	83.6
E	---	PW_4	2 h	MeCN	306	86.7
F	---	PW_4	2 h	DMF	259	88.7
G	MeCN	PW_4@TM-SBA-15	2 h	MeCN	524	77.2
H	---	PW_4@TM-SBA-15	2 h	MeCN	405	82.4

[a] Liquid-liquid diesel/organic solvent extraction of non-oxidized sulfur compounds during 5 min at 70 °C.

[b] Liquid-liquid diesel/organic solvent extraction of oxidized sulfur compounds during 30 min at 70 °C.

Table 7.2. Experiments performed for desulfurization of an untreated jet fuel (1100 ppm S) using the model diesel conditions

Experiment	Initial extraction	Catalyst	ODS time	Final extraction[a]	S content (ppm)	Desulfurization efficiency (%)
I	---	PW_4	2 h	MeCN	230	79.1
J	---	PW_4	2 h	DMF	596	45.8

[a] Liquid-liquid fuel/organic solvent extraction of oxidized sulfur compounds during 30 min at 70 °C.

7.3. Conclusions

This chapter reports a highly efficient process for the oxidative desulfurization of model and real liquid fuels through the application of a peroxophosphotungstate complex PW_4 as homogeneous catalyst and the corresponding composite material PW_4@TM-

SBA-15 as supported catalyst. For both materials, the desulfurization efficiency was maintained for ten consecutive cycles under environmentally friendly conditions (H_2O_2/S = 7 at 70 °C and using 5 μmol of catalyst). In treating the diesel samples (2300 ppm S) supplied by Galp Energia, the PW_4/MeCN/H_2O_2 combination promoted a desulfurization efficiency of 88.7%, achieving a final diesel with a sulfur content of only 259 ppm.

7.4. Experimental Section

7.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: phosphotungstic acid hydrate (Sigma-Aldrich), tetra-*n*-butylammonium chloride (Sigma-Aldrich, 98%), pluronic P123 (Aldrich), hydrochloric acid (Fluka), tetraethyl orthosilicate (Aldrich, 98%), *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (ABCR, 50% in methanol), anhydrous toluene (Aldrich, 99.8%), dibenzothiophene (Aldrich, 98%), 1-benzothiophene (Fluka, 95%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical), dimethylformamide (Fischer) and 30% w/v hydrogen peroxide (H_2O_2, Sigma-Aldrich).

Elemental analysis for C, H, and N was performed at the University of Aveiro with a Leco TruSpec 630-200-200 analyzer and at the University of Santiago de Compostela on a Leco CHNS-932. Powder X-ray diffraction (PXRD) analyses were performed at ambient temperature on a PANalytical Philips X'Pert MPD diffractometer (Cu-Kα X-radiation, λ = 1.54060 Å) fitted with a curved graphite monochromator and a flat plate sample holder, in a Bragg–Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.02°), in continuous mode, in the range of ca. $1 \leq 2\theta \leq 50°$. Infrared absorption spectra were collected using KBr (Sigma-Aldrich, 99%, FT-IR grade) pellets and a Mattson-7000 infrared spectrophotometer. FT-Raman spectra were recorded on a RFS-100 Bruker FT-Spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm (resolution 4 cm^{-1}, 1000 scans). ^{31}P NMR spectra were recorded at ambient temperature for liquid solutions using a Bruker Avance III 400 spectrometer at 161.9 MHz. Solid-state NMR spectra were recorded at 79.49 MHz for ^{29}Si and 125.76 MHz for ^{13}C on Bruker

Avance 400/500 spectrometers. ^{29}Si magic-angle-spinning (MAS) NMR spectra were recorded with 40° pulses, spinning rates of 5.0–5.5 kHz and 60 s recycle delays. ^{13}C CP MAS NMR spectra were recorded with 3.5 μs ^{1}H 90° pulses and 2 ms contact time with a spinning rate of 7 kHz and 4 s recycle delays. Solid-state ^{31}P high power decoupled (HPDEC) NMR spectra were recorded on a 9.4 T Bruker Avance spectrometer at 161.9 MHz, using a 5.5 µs ^{1}H 90° pulse, a spinning rate of 12 kHz, and a recycle delay of 60 s. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at the "Centro de Materiais da Universidade do Porto" (CEMUP, Porto, Portugal) using a JEOL JSM 6301F scanning electron microscope operating at 15 kV equipped with an Oxford INCA Energy 350 energy-dispersive X-ray spectrometer. GC-FID analysis was carried out with a Bruker 430-GC-FID gas chromatograph using hydrogen as the carrier gas (55 cm^{3} s^{-1}) and fused silica SPB-5 Supelco capillary columns (30 m × 0.25 mm i.d.; 25 μm film thickness). The analysis of sulfur content in real diesel and jet fuel was performed at Galp Energia by ultraviolet fluorescence, using a Thermo Scientific instrument with a TS-UV module, and by Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

7.4.2. Catalyst synthesis

(nBu$_4$N)$_3${PO$_4$[WO(O$_2$)$_2$]$_4$} (PW$_4$) was prepared by following a published procedure.[18] An aqueous solution of $H_3PW_{12}O_{40}\cdot nH_2O$ (1.65 g, 0.58 mmol) was added to 30% H_2O_2 (10 mL, 100 mmol) and the solution was stirred for 30 min. The mixture was then added to an aqueous solution of tetrabutylammonium chloride (0.445 g, 1.6 mmol), forming a white precipitate. The solid was filtered and washed several times with water, dried and stored in a vacuum desiccator. Yield: 1.34 g (41%). Anal. Calcd. (%) for $(C_{16}H_{36}N)_3[PO_4(WO(O_2)_2)_4]\cdot 3H_2O$ (1931.76): C, 29.84; H, 5.95; N, 2.17. Found: C, 30.26; H, 5.86; N, 2.17. ^{31}P NMR (161.9 MHz, CD$_3$CN, 25 °C): δ = 4.5 ppm. Selected FT-IR (cm^{-1}): ν = 1087 (vs, ν(PO$_4$)), 1055 (m, ν(PO$_4$)), 971 (s, ν(W=O)), 845 (m, ν(O-O)), 577 (w, ν_{asym}[W(O$_2$)]), 522 (w, ν_{sym}[W(O$_2$)]). FT-Raman (cm^{-1}): ν = 1447 (m), 1320 (m), 1129 (m), 1054 (m), 1031 (w), 978 (vs), 909 (m), 881 (m), 859 (s), 651 (w), 591 (sh), 577 (s), 531 (m), 327 (s).

$$H_3[PW_{12}O_{40}]/H_2O \xrightarrow[\text{ii) }(n\text{Bu}_4\text{N})\text{Cl}]{\text{i) excess aq. 30\% }H_2O_2} (n\text{Bu}_4\text{N})_3\{PO_4[WO(O_2)_2]_4\}\ (PW_4)$$

Figure 7.16. Preparation of peroxotungstate **($(n\text{Bu}_4\text{N})_3\{PO_4[WO(O_2)_2]_4\}$) ($PW_4$)**.

PW_4@TM-SBA-15: The parent material SBA-15 was synthesized according to a previously reported procedure [50], using triblock copolymer surfactant P123 dissolved in aqueous HCl and at room temperature was added dropwise TEOS; the mixture was stirred, put in an oven at 35 °C for 24 h and more 24 h at 100 °C. The solid was filtered and calcined at 550 °C for 5 h. Mesoporous SBA-15 functionalized with *N,N,N*-trimethylammonium groups at a loading of 0.1 mmol g^{-1} (**TM-SBA-15**) was performed following a procedure adapted from literature.[40, 41] Initially, the SBA-15 was dried at 120 °C under vacuum in order to remove physisorbed water. Afterwards, activated SBA-15 (2 g) was refluxed with TM (5 mmol) in anhydrous toluene (25 mL) for 24 h under argon. The functionalized support (TM-SBA-15) was filtered, washed with toluene and dried. The immobilization of PW_4 in TM-SBA-15 was performed by an impregnation procedure similar to those described previously for the immobilization of other POMs in SBA-15 materials.[32] A solution of PW_4 (0.313 g, 0.16 mmol) in dichloromethane (10 mL) was added to TM-SBA-15 (0.5 g) and the mixture stirred vigorously for 72 h at room temperature and then filtered under vacuum and washed with dichloromethane. ICP-MS analysis gave a W content of 61% (3.3 mmol g^{-1}). FT-IR (cm^{-1}): ν = 3450 (vs, bd), 1637 (m), 1490 (w), 1479 (w), 1419 (vw), 1388 (w), 1280 (w), 1088 (vs), 951 (m), 914 (sh), 804 (m), 460 (s). FT-Raman (cm^{-1}): ν = 1450 (s), 1131 (vw), 1055 (w), 1004 (vs), 987 (s), 912 (m), 755 (w), 516 (w), 370 (w), 232 (s), 214 (s).

7.4.3. ODS studies

7.4.3.1. Model diesel

The initial ODS studies were performed using a model diesel containing a total sulfur concentration of 1500 ppm composed of equal amounts of refractory sulfur compounds: DBT, BT and 4,6-DMDBT, dissolved in *n*-octane. These experiments were performed at atmospheric pressure in a closed borosilicate reaction vessel (5 mL) loaded with a magnetic stirring bar and immersed in a paraffin bath heated to 70 °C. The processes were carried out using a biphasic (1:1 *v*/*v*) system composed of a polar extraction solvent and the model diesel, in the presence of homogeneous (PW_4) or heterogeneous (PW_4@TM-SBA-15) catalysts, using aq. 30% H_2O_2 as oxidizing agent.

Process optimization was executed in the presence and absence of the extraction solvent. Two different solvents were tested, an ionic liquid ([BMIM]PF_6) and MeCN. Using these extractants, an initial extraction between the immiscible phases (model diesel/extraction solvent) was performed by vigorously stirring the mixtures for 10 min at 70 °C. To quantify the initial amount of sulfur transferred from the model diesel to the extraction solvent, an aliquot from the upper model diesel phase was taken and analysed by GC. After this stage, the oxidation step begins by addition of the oxidant H_2O_2 (0.26 mmol). To follow the catalytic reaction, aliquots were periodically taken from the model diesel phase, and analysed by GC. Tetradecane was used as standard.

7.4.3.2. Untreated real diesel

Untreated liquid fuels containing a total sulfur content of 2300 ppm (diesel) and 1100 ppm (jet fuel) were provided by Galp Energia to treat by oxidative desulfurization studies. A prior initial extraction was performed with the untreated diesel using MeCN or DMF as solvents with a 1:1 diesel/solvent ratio, for 5 min at 70 °C. ODS was performed using the experimental conditions applied for the model diesel. Both homogeneous and heterogeneous catalysts were used for the ODS of the fuel samples.

7.4.4. Titration of H_2O_2

The hydrogen peroxide content was determined by titrating with standardized ceric sulfate, 0.093 M $Ce(SO_4)_2$, to a pale blue endpoint using ferroin indicator.

The standard solution of 0.093 M $Ce(SO_4)_2$ was prepared by dissolution of 16 g of $Ce(SO_4)_2$ in 28 mL of a mixture of H_2SO_4 and water (1:1, *v*/*v*). This solution was allowed to cool to room temperature and transferred to a 500 mL volumetric flask. This solution was standardized with 0.1 M $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$. In each titration procedure a solution prepared from 25 mL of 0.1 M $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ and 25 mL of 0.5 M H_2SO_4 was used.

The recovered reaction solution was weighed in an Eppendorf tube and added to a solution of 1 M H_2SO_4 (150 mL) along with 2-3 drops of ferroin indicator, and titrated with 0.093 M $Ce(SO_4)_2$ to a pale blue color. The reaction involved is defined as:

$$2Ce^{4+} + H_2O_2 \rightleftarrows 2Ce^{3+} + O_2 + 2H^+$$

The percentage of H_2O_2 was calculated through the following expression:

$$\%H_2O_2 = \frac{V \times [Ce^{4+}] \times 17.01}{10 \times m}$$

where V (mL) = volume of ceric sulfate solution (titrant); $[Ce^{4+}]$ ($mol.dm^{-3}$) corresponds to the concentration of the titrant (0.093 M) and m (g) = weight of the reaction solution.

Using the same experimental procedure, the percentage of H_2O_2 present in the blank solution was also calculated, i.e. everything that would be present in an ODS reactor (except the solid catalyst) was transferred to an Eppendorf tube and weighed.

Knowing the percentage of H_2O_2 present in the sample and in the blank test, the amount of H_2O_2 consumed is calculated by the following expression:

$$100 - \%HP, where\ \%HP = \frac{\%H_2O_{2,\ sample}}{\%H_2O_{2,\ blank}}$$

7.5. References

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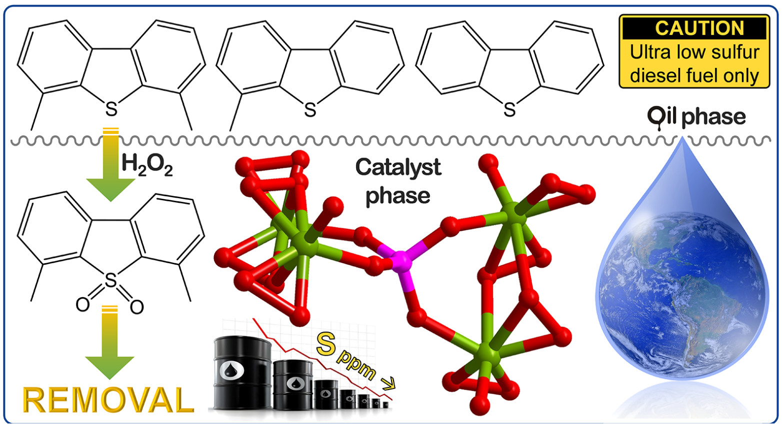
Chapter 8

A PEROXOMOLYBDATE CATALYST



8. A peroxomolybdate catalyst

8.1. Introduction

Oxidative desulfurization (ODS) is one of the most promising processes because it uses mild conditions that are more energy efficient, does not use expensive hydrogen, and has the potential to remove sterically hindered thiophenes such as 4,6-DMDBT.[1-5] ODS generally consists of oxidation of organosulfur compounds in fuel using appropriate oxidants in the presence of a catalyst. The resultant sulfoxides and/or sulfones are then amenable to removal by solvent extraction or adsorption. Hydrogen peroxide is one of the more favoured oxidants due to its low cost, high reactivity and lack of toxic by-products. Among the many different types of catalysts used, molecular catalysts based on molybdenum have consistently yielded promising results. The Mo-based catalysts include discrete mononuclear complexes such as $[CpMo(CO)_3Me]$ (Cp = η^5-cyclopentadienyl)) [6], $[MoO_2Cl_2$(4,4′-di-*tert*-butyl-2,2′-bipyridine] [7] and oxoperoxo complexes of the type $[MoO(O_2)_2(L)]$ (L = 1,10-phenanthroline, amino acid) [8,9], organic salts of polyperoxomolybdates such as $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (hereafter abbreviated as PMo_4)[10-12] and $[Mo_2O_3(O_2)_4]^{2-}$ [13], and salts of polyoxomolybdates such as $[MMo_6O_{24}H_6]^{n-}$ (M = Ni, Co) [14,15], $[Mo_7O_{24}]^{7-}$ [16], $[Mo_8O_{26}]^{4-}$ [17,18], and $[PMo_{12}O_{40}]^{3-}$ (hereafter abbreviated as PMo_{12}) [19-22]. With H_2O_2 as oxidant, polyoxomolybdate anions act as precursors and the actual active species are polyperoxomolybdates. The most well characterized example of this is the conversion of the Keggin anion, PMo_{12}, to the peroxophosphomolybdate PMo_4.[23,24]

In the present work, the tetrabutylammonium salt $(n\mathrm{Bu4N})_3\{PO_4[MoO(O_2)_2]_4\}$ has been applied in processes for the ODS of a model diesel and untreated real fuels (diesel, gasoline and jet fuel). The optimization of the catalytic performance was investigated, including reaction temperature, H_2O_2/S molar ratio, dosage of catalyst and the use of an extraction solvent. The peroxophosphomolybdate displayed no loss of catalytic activity during ten consecutive ODS cycles. An exhaustive study was performed with the real diesel to achieve high desulfurization levels.

8.2. Results and Discussion

8.2.1. Peroxomolybdenum catalyst

The peroxophosphomolybdate salt PMo_4 was prepared by the reaction of phosphomolybdic acid hydrate with excess H_2O_2 followed by the addition of tetrabutylammonium chloride.[10,23] FT-IR, FT-Raman and ^{31}P NMR data for PMo_4 were in agreement with those reported previously for the same salt [10,23,25] or for other organic salts of the PMo_4 anion [24,26,27].

Crystal structures of compounds containing the tetrakis(oxodiperoxomolybdo)-phosphate anion PMo_4 are extremely rare. A search in the literature and in the Cambridge Structural Database (CSD, Version 5.38 - with several updates [28-30]) revealed only two examples involving the PMo_4 cluster ion with organic molecules: Tris(tetra-*n*-hexyammonium)·$\{PO_4[MoO(O_2)_2]_4\}$ [31] and (4-methoxyquinoline-N-oxide)·$\{H_3P[OMo(O_2)_2O]_4\}$ [32]. We therefore set out to determine the structure of PMo_4 and found that single-crystals suitable for X-ray diffraction analysis could be obtained by recrystallization of the compound from MeCN. The crystal structure was determined in the orthorhombic space group *P*bca, with the asymmetric unit comprising only one peroxophosphomolybdate anion $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ and three charge-balancing tetrabutylammonium cations. The tetranuclear anion contains four crystallographically independent molybdenum centers with similar coordination environments (Figure 8.1, a): each metal center is seven-coordinated by two peroxo groups and three other oxygen atoms, which culminates in a coordination geometry that resembles a distorted pentagonal-bipyramid. The main structural features, particularly the Mo–O bond lengths and O–Mo–O angles, are comparable to those reported previously for the two related compounds mentioned above.[31,32] An inspection of the crystal packing arrangement reveals that the charge-balancing and space-filling tetrabutylammonium cations surround each individual anion, and interact by an extensive network of cooperative C–H···O hydrogen bonds (Figure 8.1, b and Table 8.1 for geometric details concerning the potential weak hydrogen bonds). Besides this hydrogen bonding network, the typical electrostatic and van der Waals interactions further reinforce the ordered packing of the inorganic anions and organic cations, ultimately leading to a three-dimensional supramolecular framework (Figure 8.1, c).

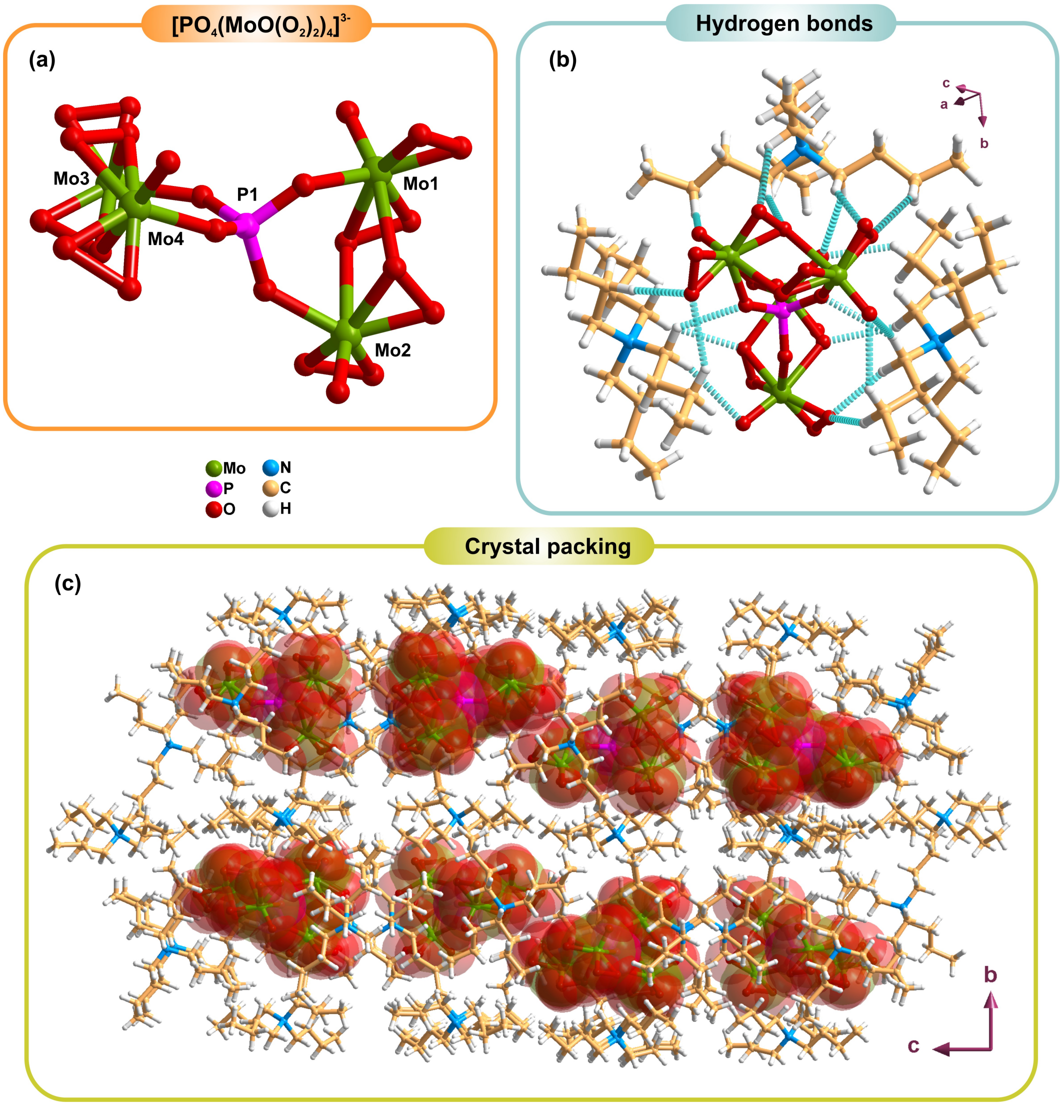


Figure 8.1. Selected features of the crystal structure of the compound $(n\mathrm{Bu_4N})_3\{PO_4[MoO(O_2)_2]_4\}$: (a) Ball-and-stick representation of the structure of $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, with labelling of the Mo and P centres; (b) C–H···O hydrogen bond interactions (drawn as dashed blue lines) between adjacent inorganic anions and organic cations; (c) crystal packing viewed along the [1 0 0] direction of the unit cell, with the $n\mathrm{Bu_4N}$ cations represented in ball-and-stick and the $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ anions shown in semi-transparent space-filling model.

Table 8.1. Hydrogen bonding geometry (distances in Å and angles in degrees) for peroxophosphomolybdate (nBu$_4$N)$_3${PO$_4$[MoO(O$_2$)$_2$]$_4$} [a]

C−H···O	*d*(H···O)/Å	*d*(C···O)/Å	∠(CHO)/°
C37–H37A···O19$^{\text{i}}$	2.62	3.57(2)	159.5
C37–H37B···O13$^{\text{i}}$	2.58	3.43(2)	144.5
C42–H42A···O8$^{\text{i}}$	2.63	3.34(4)	128.8
C45–H45A···O9$^{\text{i}}$	2.52	3.49(3)	166.4
C5–H5B···O17$^{\text{ii}}$	2.64	3.520(19)	148.1
C6–H6B···O12	2.52	3.45(2)	155.3
C9–H9B···O6$^{\text{iii}}$	2.53	3.33(2)	137.9
C9–H9B···O7$^{\text{iiii}}$	2.23	3.21(3)	171.9
C13–H13B···O1$^{\text{ii}}$	2.44	3.218(19)	134.9
C14–H14A···O7$^{\text{iii}}$	2.64	3.42(2)	135.2
C14–H14B···O11$^{\text{iii}}$	2.40	3.31(2)	151.6
C17–H17B···O20$^{\text{i}}$	2.47	3.46(2)	172.6
C21–H21B···O22	2.44	3.39(2)	160.4
C25–H25A···O21	2.47	3.288(19)	139.5
C29–H29A···O23$^{\text{i}}$	2.62	3.22(2)	118.6
C29–H29B···O18$^{\text{i}}$	2.60	3.51(2)	153.2

[a] Symmetry transformation used to generate equivalent atoms:
(i) *x–1/2, y, –z+1/2;* (ii) *x–1, y, z;* (iii) *x–1/2, –y+3/2, –z+1.*

8.2.2. Desulfurization of a model diesel

A model diesel containing 500 ppm of each sulfur compound (DBT, BT and 4,6-DMDBT) was desulfurized using a peroxophosphomolybdate as catalyst and H_2O_2 as oxidant at 70 °C. The ODS studies were performed under a solvent-free system. It is important to refer that under the mentioned conditions and in absence of catalyst was not obtained a desulfurized model diesel.

8.2.2.1. Optimization studies

Using a model diesel containing DBT, BT and 4,6-DMDBT, an optimization of the experimental parameters was performed. The evaluated parameters included the catalyst (1, 2, 5 and 8 μmol) and oxidant (0.13, 0.26 and 0.39 mmol) amounts, reaction temperature (25, 50 and 70 °C), stirring speed rate and the use of a solvent-free system (catalytic oxidation occurs in the absence of an extraction solvent and without initial sulfur extraction) or biphasic systems (1:1 *v*/*v* model diesel/extraction solvent) in which MeCN (miscible with aq. H_2O_2) or the IL [BMIM]PF_6 (immiscible with aq. H_2O_2) were employed as extraction solvents.

We first analysed the influence of an extraction solvent. For this purpose, ODS experiments were performed using the same amount of catalyst (5 μmol) and oxidant (0.13 mmol H_2O_2), and a reaction temperature of 70 °C. Under these conditions, when no extraction solvent was present the PMo_4 catalyst was not dissolved in the model diesel operating as a heterogeneous catalyst. Instead of it, in the presence of MeCN or [BMIM]PF_6, the catalyst was completely dissolved acting as a homogeneous catalyst.

When the model diesel/extraction solvent system was applied (using equal amounts (0.750 mL) of model diesel and extraction solvent), an initial extraction was performed prior to addition of the oxidant. During this extractive desulfurization step the removal of sulfur compounds followed the order BT > DBT > 4,6-DMDBT (Table 8.2). This order is related to the molecular size, geometry and polarity of the sulfur compounds. As BT possesses the smallest molecular size, its transfer from the model diesel to the extraction phase is easier, while the presence of methyl substitutes at the sterically hindered positions in 4,6-DMDBT makes the extraction of this compound more difficult. Regarding the extractive capacity of each solvent tested, MeCN was more effective than the IL. Regardless of the initial extractions obtained for each solvent, the solvent-free system showed the highest ODS performance (i.e. after addition of the oxidant), promoting complete desulfurization after 4 h of reaction (Figure 8.2). Therefore, the solvent-free system was elected as the preferred ODS system to continue the desulfurization studies, avoiding the negative impact on the environment from the use of the organic (MeCN) or IL extraction solvents.

Table 8.2. Values (%) corresponding to the initial extraction of each sulfur compound in the presence of different extraction solvents

Sulfur compounds	**[BMIM]PF_6**	**MeCN**
DBT	29.3	58.4
BT	37.8	60.2
4,6-DMDBT	7.5	47.6

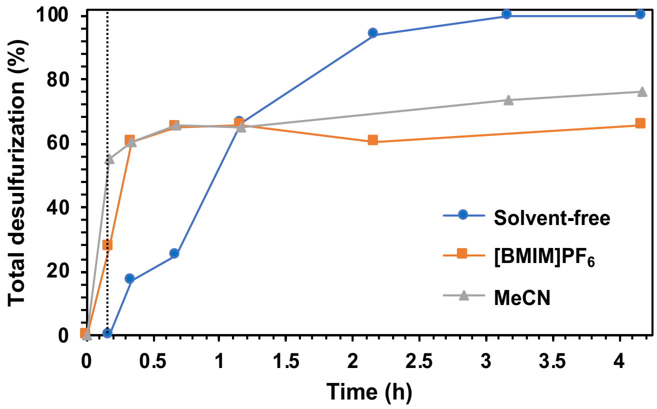


Figure 8.2. Oxidative desulfurization of a model diesel (1500 ppm S) using PMo_4 (5 µmol) as catalyst, in the presence or absence of different extraction solvents and H_2O_2 (0.13 mmol) as oxidant with a reaction temperature of 70 °C. The vertical dashed line indicates the instant the ODS stage started by addition of oxidant.

Figure 8.3 shows the influence of the amount of PMo_4 (1, 2, 5 and 8 μmol) on catalytic ODS using the solvent-free system (0.13 mmol of H_2O_2, 0.750 mL of model diesel, and a reaction temperature of 70 °C). The desulfurization performance improved immensely on increasing the catalyst amount from 1 μmol (n(S)/n(catalyst)/n(H_2O_2) = 35:1:130) to 5 μmol (n(S)/n(catalyst)/n(H_2O_2) = 7:1:26), followed by only a modest improvement on increasing the amount to 8 μmol. Sulfur-free model diesel was obtained after 3 h of ODS in the case of 5 μmol, and after 5 h of ODS in the case of 2 μmol. Based on these results, the optimal amount of catalyst was chosen as 5 μmol. Results reported by He *et al.* [10] for the same catalyst PMo_4 are consistent with these findings. In particular, for n(S)/n(catalyst)/n(H_2O_2) = 100:1:200, He *et al.* obtained 16.8% desulfurization for a model diesel containing only DBT (1000 ppm), in an ODS reaction performed at 70 °C for 3 h. However, these authors did not study the effect of increasing the catalyst amount.

Having determined that the diesel/catalyst/H_2O_2 ODS system with 5 μmol of catalyst was optimal, the influence of three other factors was studied, namely the amount of oxidant, the reaction temperature, and the stirring speed. Figure 8.4 displays the desulfurization profile of the model diesel using the solvent-free system, in the presence of different amounts of H_2O_2 (0.13, 0.26 and 0.39 mmol), with a reaction temperature of 70 °C. Surprisingly, the best performance was achieved using the lower amount of oxidant (0.13 mmol; oxidant/S molar ratio = 3.7). Generally, nucleophilic attack of H_2O_2 on the Mo(VI) centers of polyoxometalates (POMs) leads to the formation of hydroperoxo or peroxo active species which can oxidize the sulfur compounds of interest to the corresponding sulfoxides and/or sulfones, with concomitant regeneration of the starting Mo(VI) POM species.[33,34] However, in the present case, the chosen catalyst (PMo_4) is already in the peroxo form, which may account for why a lower amount of H_2O_2 is sufficient to guarantee good ODS performance. Using a larger excess of H_2O_2 may lead to an increased production of water, which may decrease the performance of the catalyst for oxidation of the sulfur compounds present in the model diesel.

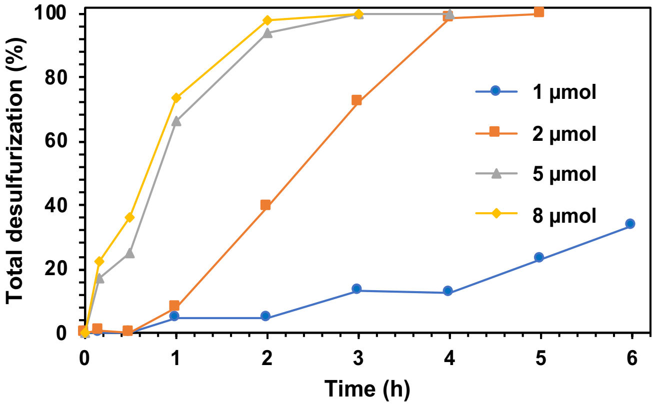


Figure 8.3. Oxidative desulfurization of a model diesel (1500 ppm S) using different amounts of PMo_4 as catalyst and H_2O_2 (0.13 mmol) as oxidant, at 70 °C.

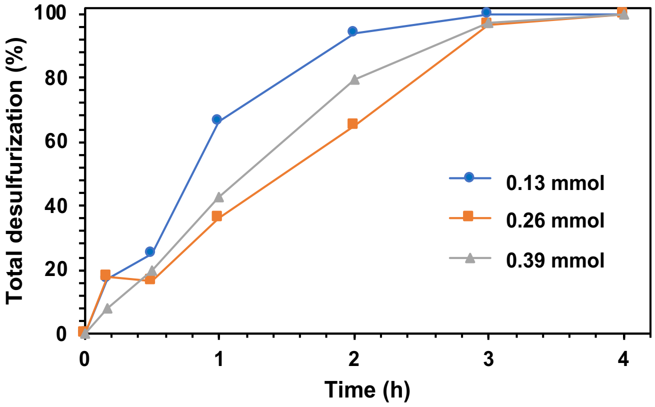


Figure 8.4. Oxidative desulfurization of a model diesel (1500 ppm S) using PMo_4 (5 µmol) as catalyst and different amounts of H_2O_2 as oxidant, at 70 °C.

The influence of the reaction temperature was studied for the oxidative desulfurization process carried out using the optimal amounts of catalyst (5.0 *µ*mol) and oxidant (0.13 mmol) using the solvent-free system. As shown in Figure 8.5, an increase in the reaction temperature from 25 to 70 °C led to an increase in sulfur oxidation, with complete desulfurization only being reached at 70 °C. This behaviour is related with the strong dependence of the oxidation reaction rate of the sulfur compounds present in the model diesel on the reaction temperature.[35,36] Oxidation above 80 °C can decrease the quality of diesel fuel due to the possibility of oxidizing useful components, such as olefins and hydrocarbons typically present in fuels.[37] For this reason, 70 °C is considered the maximum temperature at which the reactions can be conducted.

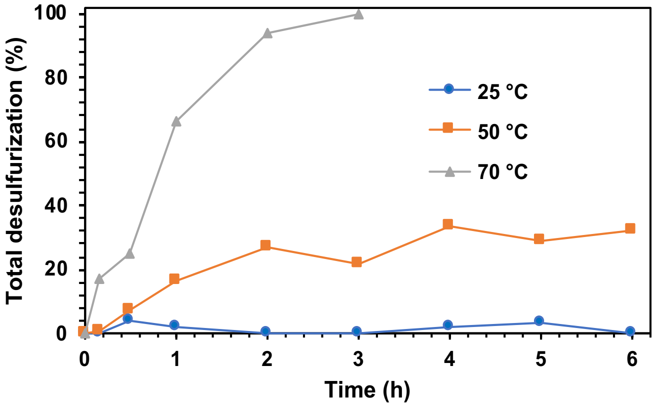


Figure 8.5. Oxidative desulfurization of a model diesel (1500 ppm S) using PMo_4 (5 μmol) as catalyst and H_2O_2 (0.13 mmol) as oxidant, at different reaction temperatures.

To assess the importance of the stirring rate applied during the ODS reactions, two rotation speeds (2000 and 3000 rpm) were tested for reactions performed under the optimized experimental conditions (5 μmol of catalyst, 0.13 mmol of H_2O_2, absence of an extraction solvent and a thermostated oil bath set at 70 °C). The increase in the stirring rate resulted in a measurable increase in the desulfurization rate (Figure 8.6). These results are likely to be related with a higher dispersion of the catalyst in the model diesel for the higher stirring rate, which probably facilitates contact between the catalyst, oxidant and substrate, thus promoting the efficient oxidation of the sulfur compounds.

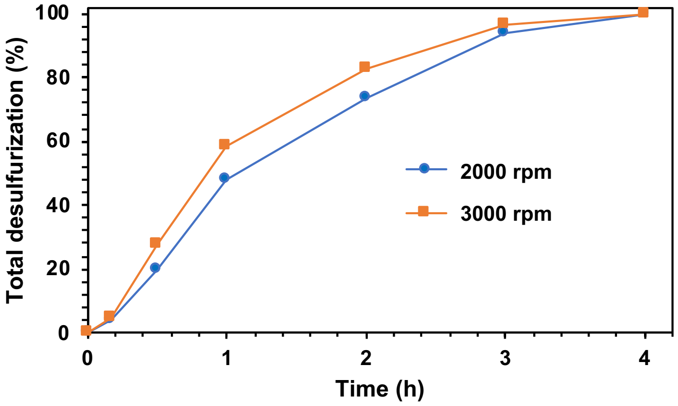


Figure 8.6. Oxidative desulfurization of a model diesel (1500 ppm S), catalysed by PMo_4 (5 µmol), using H_2O_2 (0.13 mmol) as oxidizing agent, a reaction temperature of 70 °C, and different rotation speeds.

8.2.2.2. Catalyst stability and reusability

The promising performance of PMo_4 in the absence of an extraction solvent (solvent-free ODS system) using mild conditions, that include a H_2O_2/S molar ratio of 3.7, motivated the investigation of its reusability in consecutive ODS cycles of a model diesel. The reusability of the catalyst after each cycle was evaluated by simple removal of the treated model diesel, followed by addition of fresh portions of model diesel and H_2O_2, with consecutive ODS cycles being performed under the same experimental conditions. No significant decrease in desulfurization efficiency at 3 h of reaction was observed during ten consecutive cycles (Figure 8.7). Only a slight decrease was observed between the sixth and seventh cycles, after which the sulfur removal at 3 h remained between 96% and 97%. Complete sulfur removal was achieved after 4 h for the last four cycles. During all cycles, the sulfur oxidation followed the order DBT > 4,6-DMDBT > BT. This order is attributed to the significantly lower electron density of BT compared with the other two sulfur compounds. The electron density on the sulfur atom is similar in DBT (5.758) and 4,6-DMDBT (5.760), and consequently the reactivity difference is essentially due to steric hindrance associated with the methyl groups.[38]

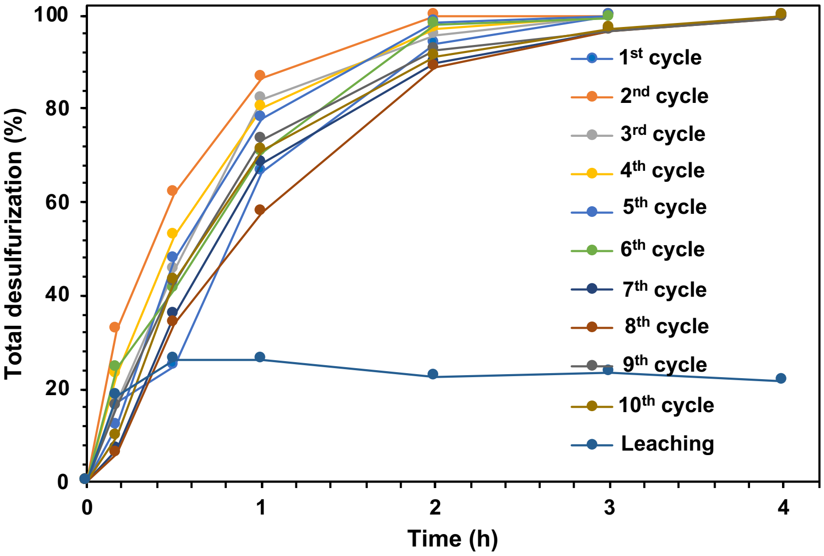


Figure 8.7. Oxidative desulfurization for ten consecutive cycles of ODS of a multicomponent model diesel (1500 ppm S) using PMo_4 (5 μmol) as catalyst and H_2O_2 (0.13 mmol) as oxidant, at 70 °C.

To investigate the stability of PMo_4 during the ODS cycles, a leaching test was performed (Figure 8.7). No further reaction took place after removal of the catalyst at 30 min of reaction, suggesting that no significant dissolution of the catalyst had occurred to the reaction medium. The structure of the recovered catalyst was analysed by FT-IR, FT-Raman and ^{31}P NMR spectroscopies. No significant alterations were detected in the vibrational spectra, suggesting that the structure of the PMo_4 anion was retained during the ODS cycle (Figure 8.8). Accordingly, the ^{31}P NMR spectrum of the recovered catalyst (in CD_3CN solution) presented a single line at 8.25 ppm, in agreement with that displayed by the as-synthesized compound (Figure 8.9).

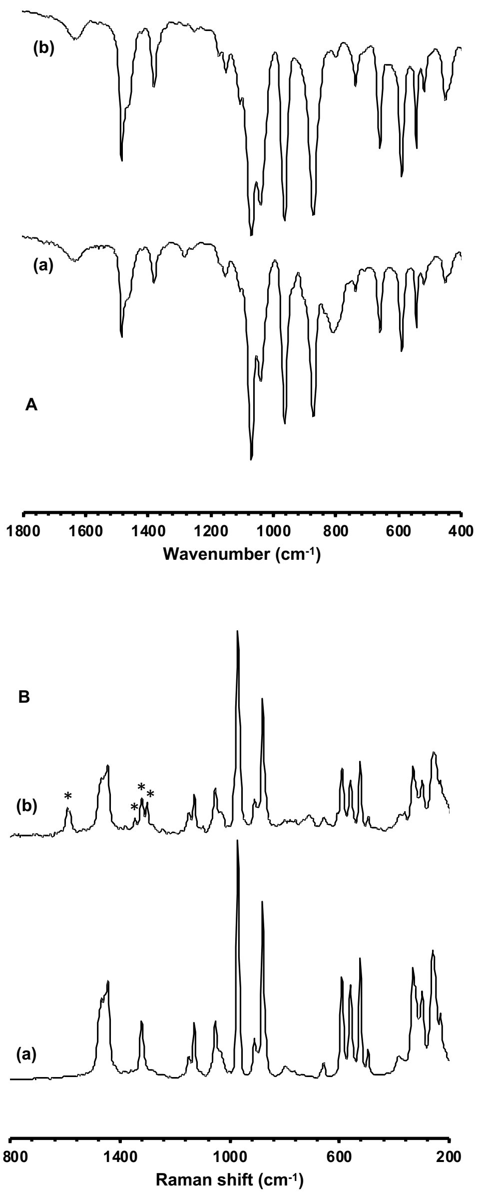


Figure 8.8. FT-IR (A) and FT-Raman spectra (B) of PMo_4 catalyst before (a) and after (b) an ODS cycle under the optimized conditions (solvent-free system, 5 μmol catalyst, 0.13 mmol 30% aq. H_2O_2, 70 °C). The bands marked with asterisks in the Raman spectrum of the recovered catalyst are attributed to residual amounts of oxidized sulfur compounds ($DBTO_2$, BTO_2, 4,6-$DMDBTO_2$; the band at 1593 cm^{-1} is assigned as a benzene ring C=C stretch [39]).

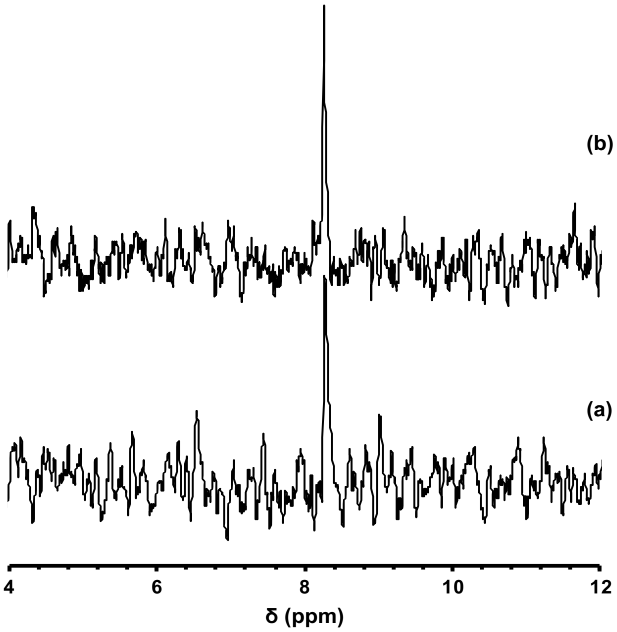


Figure 8.9. ^{31}P NMR spectra (in CD_3CN) of PMo_4 catalyst before (a) and after [(b) PMo_4_ac] oxidative catalytic use for desulfurization of a model diesel using a solvent-free system.

8.2.3. Desulfurization of untreated liquid fuels

The good results obtained with PMo_4 as a catalyst in the ODS of the multi-component simulated diesel prompted its evaluation for the much more demanding task of removing sulfur from a real commercial diesel. For this purpose, an untreated diesel sample with a sulfur content of 2300 ppm supplied by Galp Energia was used. In general, the desulfurization of the untreated real diesel was investigated in two fundamental steps: (i) extraction before and/or after the ODS process with an appropriate extraction solvent (MeCN or DMF); (ii) catalytic oxidation, using PMo_4 catalyst and H_2O_2 as oxidizing agent, at 70 °C. The desulfurization efficiency during catalytic oxidation stage was studied in the presence ([BMIM]PF_6 or MeCN) and absence of an immiscible polar solvent (solvent-free system).

Liquid fuels are known to be composed of a complex mixture of compounds besides the innumerable sulfur-containing derivatives, which makes the desulfurization process more difficult. Some optimization experiments were therefore performed with the real diesel. The amounts of catalyst and oxidizing agent, and the use of different solvents for the extraction of the oxidized and non-oxidized sulfur compounds before and after oxidative catalytic stage, were studied using the solvent-free system, i.e. without the presence of a polar solvent (MeCN or [BMIM]PF_6) during the ODS step.

Catalyst amounts of 5 and 8 μmol were tested, using 0.13 mmol of H_2O_2. Following previous work [7,33], MeCN was used as an extraction solvent to remove the oxidized sulfur compounds obtained after 3 h of oxidation. The results show that a higher amount of catalyst did not promote a higher desulfurization efficiency (Table 8.3, experiments A and B), which parallels the results obtained with the multicomponent model diesel (Figure 8.3).

When considering the ODS of real diesels using H_2O_2 as oxidant, one of the most important experimental parameters is the amount of oxidant since, given the complexity of the diesel matrix, the oxidation of other compounds can compete with that of the sulfur-containing ones, degrading fuel quality and decreasing desulfurization efficiency. Therefore, to minimize these possible drawbacks, it is important to optimize H_2O_2/S ratios. Different amounts (from 0.13 to 0.39 mmol) of oxidant were used in the desulfurization of the untreated real diesel, maintaining the amount of catalyst (5 μmol), reaction time (3 h) and temperature (70 °C) constant, and using MeCN as final extraction solvent. The desulfurization efficiency followed the order 0.39 mmol (51.3%) > 0.13 mmol (48.2%) > 0.26 mmol (38.0%) (experiments A, C and D in Table 8.3). When these results are compared with those presented in Figure 8.4 for the ODS of the multicomponent model diesel, it is noteworthy that both systems indicate that there is no major gain to be had with a 3-fold increase in the amount of oxidant. Hence, the desulfurization studies were continued using the lower amount of oxidant (0.13 mmol, $H_2O_2/S = 3.7$).

The next parameter to be analysed was the nature of the extraction solvent (MeCN or DMF) used after the ODS reactions ($H_2O_2/S = 3.7$, 5 μmol PMo_4) to extract oxidized sulfur compounds. In Chapter 2 we ascertained that the highest extraction efficiencies were achieved by performing the extraction at 70 °C for 30 min [6], so these were the conditions used in the present work. When no extraction was performed (experiment F in Table 8.3), the remaining S content was 2100 ppm, which indicates that most of the oxidized sulfur compounds remained in the diesel phase (the quantification technique used does not distinguish between the oxidized and non-oxidized sulfur species), since in this case a solvent-free ODS system was used. When an extraction was performed after catalytic oxidative step (experiments A and E), the performance with MeCN (48.2%) was significantly better than that with DMF (41.1%). These results confirm that the union of oxidation and final extraction steps is fundamental to obtain an effective desulfurization performance, since the oxidized sulfur compounds resulting from the oxidation process are retained in the treated diesel using a solvent-free ODS system.

An initial extraction (i.e., before the ODS process) can contribute for the improvement of total desulfurization efficiency by using a suitable polar solvent. For extraction studies using MeCN or DMF (Table 8.3, experiments G-J), a temperature of 70 °C was used and the initial extraction was only performed for 5 min, since this type of extraction is not time dependent (see Chapter 2, Table 2.1).[6] The highest desulfurization efficiencies were achieved when using MeCN as the solvent for initial extraction (experiments H and J), indicating that this solvent probably possesses a high affinity towards the non-oxidized sulfur compounds. Notably, the best result for the desulfurization of the real diesel was obtained when the initial and final extractions (after ODS processes) were performed with different solvents, i.e. MeCN and DMF, respectively (experiment J). The results suggest that these solvents, in addition to having an affinity for non-oxidized (in the case of MeCN) and oxidized (DMF) sulfur compounds, may promote the extraction of different families of sulfur compounds.

The optimization studies with the model diesel revealed that the highest level of desulfurization occurred when no extraction solvent was used during the ODS reaction. However, since the model and real diesel media have completely different compositions, with the latter being much more complex, the effect of dissolving the catalyst PMo_4 in an extraction solvent (MeCN or $[BMIM]PF_6$) was tested again in the process for the desulfurization of the real diesel. The results (experiments K-N in Table 8.3) show that the use of an extraction solvent to dissolve the catalyst was indeed beneficial, with the highest desulfurization efficiency being 78.3% for the system using $[BMIM]PF_6$ as the extraction solvent during the ODS step and DMF as the solvent used after ODS to further extract oxidized sulfur compounds (experiment L). Considering that no pre-treated diesel was used in these experiments, the results are striking and demonstrate the high catalytic efficiency of the anion PMo_4 for the oxidation of sulfur compounds.

Table 8.3. Experiments performed for ODS of a commercial untreated real diesel[a]

Experiment	Amount of PMo_4 (µmol)	Amount of H_2O_2 (mmol)	ODS reaction	Extractive process before ODS[b]	Extractive process after ODS[c]	Diesel sulfur content (ppm)	Desulfurization efficiency (%)[d]
A	5	0.13	---	---	MeCN	1192	48.2
B	8	0.13	---	---	MeCN	1234	46.3
C	5	0.26	---	---	MeCN	1425	38.0
D	5	0.39	---	---	MeCN	1120	51.3
E	5	0.13	---	---	DMF	1354	41.1
F	5	0.13	---	---	---	2100	8.7
G	5	0.13	---	DMF	MeCN	1345	41.5
H	5	0.13	---	MeCN	MeCN	1206	47.6
I	5	0.13	---	DMF	DMF	1275	44.6
J	5	0.13	---	MeCN	DMF	881	61.7
K	5	0.13	$[BMIM]PF_6$	---	MeCN	710	69.1
L	5	0.13	$[BMIM]PF_6$	---	DMF	500	78.3
M	5	0.13	MeCN	---	MeCN	791	65.6
N	5	0.13	MeCN	---	DMF	620	73.0

[a] Reaction conditions: 70 °C, 3 h.

[b] Liquid-liquid diesel/extraction solvent (5 min at 70 °C) of non-oxidized sulfur compounds before ODS.

[c] Liquid-liquid diesel/extraction solvent (30 min at 70 °C) of oxidized sulfur compounds after ODS.

[d] Calculated on the basis of a sulfur content of 2300 ppm in the commercial untreated diesel.

After a desulfurization process using the real diesel (experiment J), the solution ^{31}P NMR spectrum of the catalyst was acquired and found to display a single resonance at 8.25 ppm (similar to the ^{31}P NMR spectrum for PMo_4_ac displayed in Figure 8.9), thereby confirming that the structural integrity of the peroxophosphomolybdate PMo_4 was retained during the whole process.

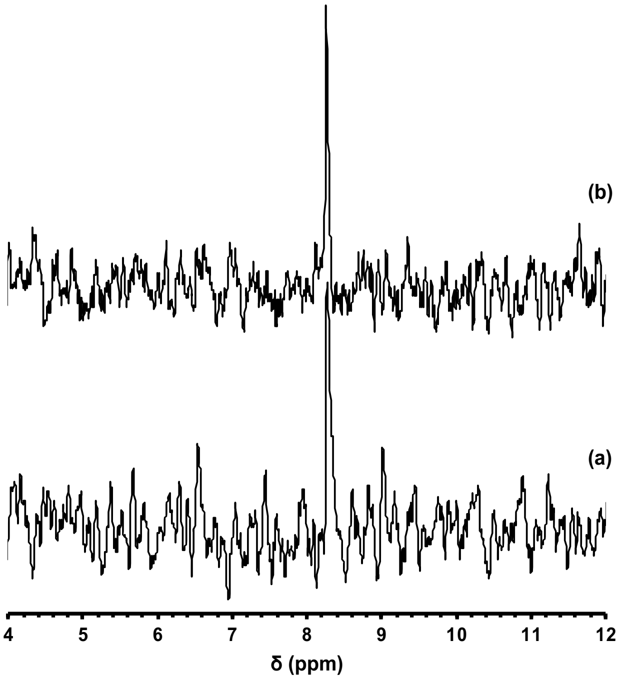


Figure 8.10. ^{31}P NMR spectra of PMo_4 before (a) and after [(b) PMo_4_ac] use in the ODS process of an untreated real diesel (2300 ppm S).

For last, few desulfurization tests were performed in gasoline (151 ppm S) and jet fuel (1100 ppm S). In this study were applied the optimal conditions obtained from model diesel studies. From the previous work described in Chapter 2 was verified that the initial extraction is not a fundamental parameter to get a jet fuel successfully desulfurized.[6] Therefore, the same decision of non-initial extraction was applied to gasoline due to its low content in sulfur. Although has been used a solvent-free system and a low H_2O_2/S ratio, the result obtained for jet fuel (experiment P, Table 8.4) is similar to those obtained using biphasic systems (Chapter 2 and 6), highlighting the catalytic power of the peroxophosphomolybdate when compared to other molybdenum and tungsten catalysts. The desulfurization treatment of a gasoline revealed to be more “difficult” due to its high volatility and to some observable miscibility with the extraction solvent. However, a good result was obtained, in which an almost complete desulfurized gasoline was obtained (experiment O).

Table 8.4. Experiments performed for oxidative desulfurization of a gasoline and jet fuel after 3 h of reaction at 70 °C, using 5 μmol of PMo_4 and 0.13 mmol of H_2O_2

Experiment	Fuel	Extractive process after ODS[a]	Diesel sulfur content (ppm)	Desulfurization efficiency (%)
O	gasoline	MeCN	33	78.1[b]
P	jet fuel	MeCN	307	72.1[c]

[a] Liquid-liquid diesel/extraction solvent (30 min at 70 °C) of oxidized sulfur compounds after ODS.

[b] Calculated based on untreated gasoline containing 151 ppm of sulfur supplied by Galp Energia.

[c] Calculated based on untreated jet fuel containing 1100 ppm of sulfur supplied by Galp Energia.

8.3. Conclusions

In this work, we performed a complete optimization study for oxidative desulfurization of model and real diesels using a peroxophosphomolybdate as a highly efficient catalyst under eco-sustainable conditions. The benzothiophenes BT, DBT and 4,6-DMDBT could be completely removed from the model diesel under the optimal condition of $H_2O_2/S = 3.7$, 5 μmol of catalyst, at 70 °C for 3 h, and in the absence of any additional solvent. The catalyst could be directly reused without any treatment and showed excellent stability and reusability through ten consecutive cycles. Leaching of active Mo species into the model diesel phase was negligible. The catalyst was further applied for the desulfurization of a real untreated diesel with a sulfur content of 2300 ppm. A desulfurization efficiency of 78.3% was reached by using an extractive and catalytic ODS system in which the catalyst was dissolved in the ionic liquid $[BMIM]PF_6$, H_2O_2 was used as oxidant with a low H_2O_2/S molar ratio of 3.7, and DMF was used in a final extraction step to remove oxidized sulfur compounds. Conciliating the catalytic activity, stability and reusability of the salt PMo_4 under ODS conditions suggest that it could be a viable catalyst in an industrial setting for the production of low sulfur fuels.

8.4. Experimental Section

8.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used as received: phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}\cdot nH_2O$, Fluka, ≥99.99%), tetrabutylammonium chloride (Sigma-Adrich, 98%), dibenzothiophene (Aldrich, 98%), benzothiophene (Fluka, 95%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical, 99.99%), dimethylformamide (Fischer, 99.99%) and 30% w/v hydrogen peroxide (H_2O_2, Sigma-Aldrich).

Elemental analysis for C, H, and N was performed at the University of Aveiro with a Leco TruSpec 630-200-200 analyser. Infrared absorption spectra were recorded on a Mattson-7000 infrared spectrophotometer using KBr (Sigma-Aldrich, 99%, FT-IR grade) pellets. FT-Raman spectra were recorded on a RFS-100 Bruker FT-Spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm. Liquid ^{31}P NMR spectra were recorded in 5 mm tubes at ambient temperature on a Bruker Avance III 400 spectrometer operating at 161.9 MHz. Chemical shifts (δ ppm) are referenced with respect to external 85% H_3PO_4. GC-FID was carried out on a Varian V3800 chromatograph to monitor catalytic reactions and a Bruker 430-GC to follow the reactions. In both experiments, hydrogen was the carrier gas (55 $cm^3\ s^{-1}$) and fused silica SPB-5 Supelco capillary columns (30 m × 0.25 mm i.d.; 25 μm film thickness) were used. The analysis of sulfur content of the treated diesel was performed in Galp Energia by ultraviolet fluorescence using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

8.4.2. Synthesis of $(nBu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$

The peroxophosphomolybdate salt PMo_4 was prepared by following published procedures with slight modifications [10,23]. A solution of tetrabutylammonium chloride (0.861 g, 3.1 mmol) in 30% aq. H_2O_2 (40 mL) was added to phosphomolybdic acid hydrate (1.82 g, 1.0 mmol) in 30% aq. H_2O_2 (10 mL). The mixture was stirred vigorously at 40 °C for 5 h. After cooling to ambient temperature, the mixture was vigorously stirred for a further 48 h. The resultant yellow precipitate was filtered off, washed with water, air-dried and stored in a vacuum desiccator. Yield: 1.30 g (85% based on phosphorus). Anal. Calcd for $C_{48}H_{108}Mo_4N_3O_{24}P$ (1526.11): C, 37.78; H, 7.13; N, 2.75. Found: C, 36.87; H, 6.75; N, 2.58. ^{31}P NMR (CD_3CN): $\delta = 8.25$ ppm. FT-IR (cm^{-1}): 3442 (m), 2962 (vs), 2935 (sh), 2875 (s), 1628 (m), 1485 (vs), 1381 (m), 1284 (w), 1253 (w), 1174 (w), 1151 (w), 1070 (vs, $\nu(PO_4)$), 1041 (s, $\nu(PO_4)$), 964 (vs, $\nu(Mo{=}O)$), 872 (vs, $\nu(O\text{-}O)$), 800 (w), 734 (m), 659 (s), 590 (s, $\nu_{asym}[Mo(O_2)]$), 544 (s, $\nu_{sym}[Mo(O_2)]$), 519 (w), 451 (m). FT-Raman (cm^{-1}): 2963 (sh), 2932 (vs), 2872 (vs), 2737 (w), 1468 (sh), 1447 (m), 1321 (m), 1150 (w), 1129 (m), 1054 (m), 970 (vs), 911 (w), 880 (s), 799 (w), 658 (w), 590 (m), 560 (m), 523 (m), 494 (w), 384 (w), 332 (m), 299 (m), 259 (m), 176 (m), 139 (m).

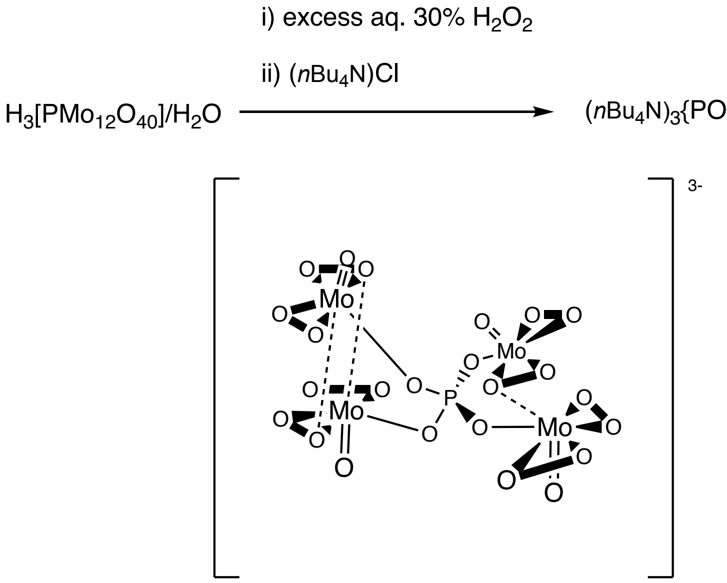


Figure 8.11. Preparation of peroxophosphomolybdate **PMo4.**

8.4.3. Single-crystal X-ray diffraction

Single-crystals of PMo4 suitable for X-ray diffraction analysis were obtained by recrystallization of the tetrabutylammonium salt from MeCN. A selected crystal was manually harvested and mounted on a cryoloop using viscous Fomblin Y perfluoropolyether vacuum oil (LVAC 140/13, Sigma-Aldrich) [41]. Diffraction data were collected on a Bruker X8 Kappa APEX II CCD area-detector diffractometer controlled by the APEX2 software package [42]: Mo-K$_\alpha$ graphite-monochromated radiation, $\lambda = 0.71073$ Å; crystal was positioned at 50 mm from the detector; 75 s of exposure time per frame; temperature of acquisition (150 K) was set up with a liquid nitrogen stream from an Oxford Cryosystems Series 700 monitored by the interface Cryopad [43]. Images were processed using SAINT+ [44], and absorption correction was carried out using the multi-scan semi-empirical method implemented in SADABS [45]. The structure was solved using the algorithm implemented in SHELXT-2014 which allowed the immediate location and identification of a considerable number of the heaviest atoms composing the asymmetric unit. [46,47] The remaining absent and misplaced non-hydrogen atoms were located from difference Fourier maps from successive full-matrix least-squares refinement cycles on F^2 using SHELXL-v.2014. [46,48] All the non-hydrogen atoms were successfully refined using anisotropic displacement parameters.

H-atoms of the organic cations were placed at their geometrical positions using the appropriate HFIX instructions (*137* for the terminal $-CH_3$ and *23* for the $-CH_2-$ groups) and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacement parameters (U_{iso}) fixed at 1.2 or 1.5 × U_{eq} of the adjacent atom.

Crystal data for PMo_4: $C_{48}H_{108}Mo_4N_3O_{24}P$, $M = 1526.11$, Orthorhombic, *P*bca, $a = 13.5996(7)$ Å, $b = 24.6708(14)$ Å, $c = 13593.3(12)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 13593.3(12)$ Å^3, $T = 150.0(2)$ K, $Z = 8$, $\mu = 0.816$ mm^{-1}, $\rho_c = 1.491$ g cm^{-3}, yellow prism crystal with 0.17 × 0.09 × 0.05 mm^3; 78543 reflections measured with 11971 being independent ($R_{int} = 0.0621$); the final R_1 and $wR(F^2)$ values were 0.1422 [$I > 2\sigma(I)$] and 0.3084 (all data), respectively; data completeness to $\theta = 25.03°$, 99.7%. Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-1879540. Copies of the data can be obtained online at: https://www.ccdc.cam.ac.uk/structures/.

8.4.4. ODS studies

8.4.4.1. Model diesel

The oxidative desulfurization procedures were performed using a model diesel containing dibenzothiophene, benzothiophene and 4,6-dimethyldibenzothiophene dissolved in *n*-octane with approximately 500 ppm of each one. The ODS studies were performed using either an extraction solvent-free system and a biphasic system formed by equal volumes of model diesel and an extraction solvent. In the solvent-free system only a catalytic stage was performed in which the salt PMo_4 (5 μmol) was dispersed in the model diesel phase (0.750 mL) in the presence of an appropriate amount of oxidant (30% aq. H_2O_2). All these reactions were carried out using a borosilicate reaction vessel loaded with a magnetic stirring bar and immersed in a thermostated oil bath at 70 °C under air (atmospheric pressure).

The optimum ODS reaction conditions were investigated through the evaluation of several parameters, such as the presence (biphasic system) or absence (solvent-free system) of an extraction solvent during the oxidative catalytic stage. In the case of biphasic system different extraction solvents were employed, namely acetonitrile or 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6). In the model diesel/[BMIM]PF_6 system, the aqueous H_2O_2 oxidant is immiscible in the extraction solvent phase and also in the model diesel phase. The amount of H_2O_2 (0.13, 0.26 or 0.39 mmol), dosage of PMo_4 (1, 2, 5 or 8 μmol), and reaction temperature (25, 50 or 70 °C) were also optimized.

The ODS reactions performed with MeCN or [BMIM]PF_6 combine extraction and catalytic oxidation. The PMo_4 catalyst is dissolved in these extraction solvents. Before addition of H_2O_2, an initial extraction of sulfur compounds present in the model diesel to the extraction solvent phase was performed by vigorously stirring the model diesel/extraction solvent mixture for 10 min at 70 °C. After this stage, H_2O_2 (0.13 mmol; H_2O_2/S molar ratio = 3.7) was added to the biphasic liquid-liquid system, initiating the catalytic stage.

Aliquots were taken with a microsyringe directly from the model diesel phase during the ODS reaction, allowing the periodic quantification of sulfur content by GC analysis. In a typical procedure, an external standard (tetradecane) was used to dilute the aliquot removed from the model diesel of the ODS system. The same quantification procedure was performed for all systems. Since the oxidized products (sulfones) are nearly insoluble in *n*-octane, they precipitated when no extraction solvent was used. For the reusability tests (performed for the system without extraction solvent), the model diesel phase was removed at the end of each cycle and the catalyst solid residue was not washed since it remained stuck to the walls of the reaction vessel. Each cycle was performed under the same experimental conditions through the addition of fresh samples of model diesel and oxidant.

8.4.4.2. Untreated diesel

The ODS system for the untreated real diesel with a sulfur content of approximately 2300 ppm (supplied by Galp Energia) was optimized by starting from the model diesel conditions (H_2O_2/S/catalyst at 70 °C for 3 h). The elements tested were the amount of 30% aq. H_2O_2 (0.13, 0.26 or 0.39 mmol), the dosage of catalyst (5 or 8 μmol), and the effect of introducing an extraction solvent (MeCN or [BMIM]PF_6) during the oxidative process. The extraction capacity of the oxidized and non-oxidized sulfur compounds was also evaluated by application of two different solvents, namely MeCN and dimethylformamide (DMF). Some experimental tests were also performed in a jet fuel and gasoline containing 1100 and 151 ppm of sulfur, respectively. In these fuels was performed ODS reactions using the optimal conditions achieved during the model diesel studies. In the end, the jet and gasoline samples suffered final extractions with MeCN to remove the oxidized sulfur compounds.

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Chapter 9

HYBRID ORGANIC-INORGANIC MATERIALS: $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ AND $[Mo_8O_{22}(OH)_4(di\text{-}t\text{Bu-bipy})_4]$

9. Hybrid organic-inorganic materials: $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ and $[Mo_8O_{22}(OH)_4(di\text{-}t\text{Bu-bipy})_4]$

9.1. Introduction

Half of the World's total supply of energy is produced from crude oil, which is composed by a complex mixture of different compounds, including hydrocarbons, aromatics and molecules containing sulfur, nitrogen, among others.[1] The decrease in resources of light crude oils has increased the use of heavy oils, which are more viscous mainly formed by heavy molecules, some of these containing sulfur. These heavy oils are more difficult to desulfurize, needing to be treated under high severe conditions to follow the stricter environmental protection regulations. The hydrodesulfurization can be strongly inhibited by the presence of nitrogen compounds, through the deactivation of the acidic sites on hydrotreating catalysts as a result of a competition with sulfur compound on the catalyst surface. Some nitrogen compounds are also corrosive and when combusted, have carcinogenic and mutagenic properties.[2-4] In addition, they are also responsible for the colour and gum as well as for the formation of deposits.[2] The nitrogen compounds combustion are also responsible for drastic effects on environment, such as the increase concentration of the greenhouse gas nitrous oxide and as contributor to acid rain and to the photochemical smog that afflicts rural and urban areas around the world.[5] Thus, the denitrogenation of feeds would enhance the depth of desulfurization and consequently would reduce the impact of fuels on the environment by decreasing the NO_x and SO_x emissions. The oxidative desulfurization (ODS) process can promote an effectively removal of both fuel components. Several reported works have demonstrated the high ability of ILs to remove simultaneously sulfur and nitrogen compounds from model diesel and real liquid fuels, being an asset as extraction solvents to the simultaneous ODS/ODN process.[2, 4, 6]

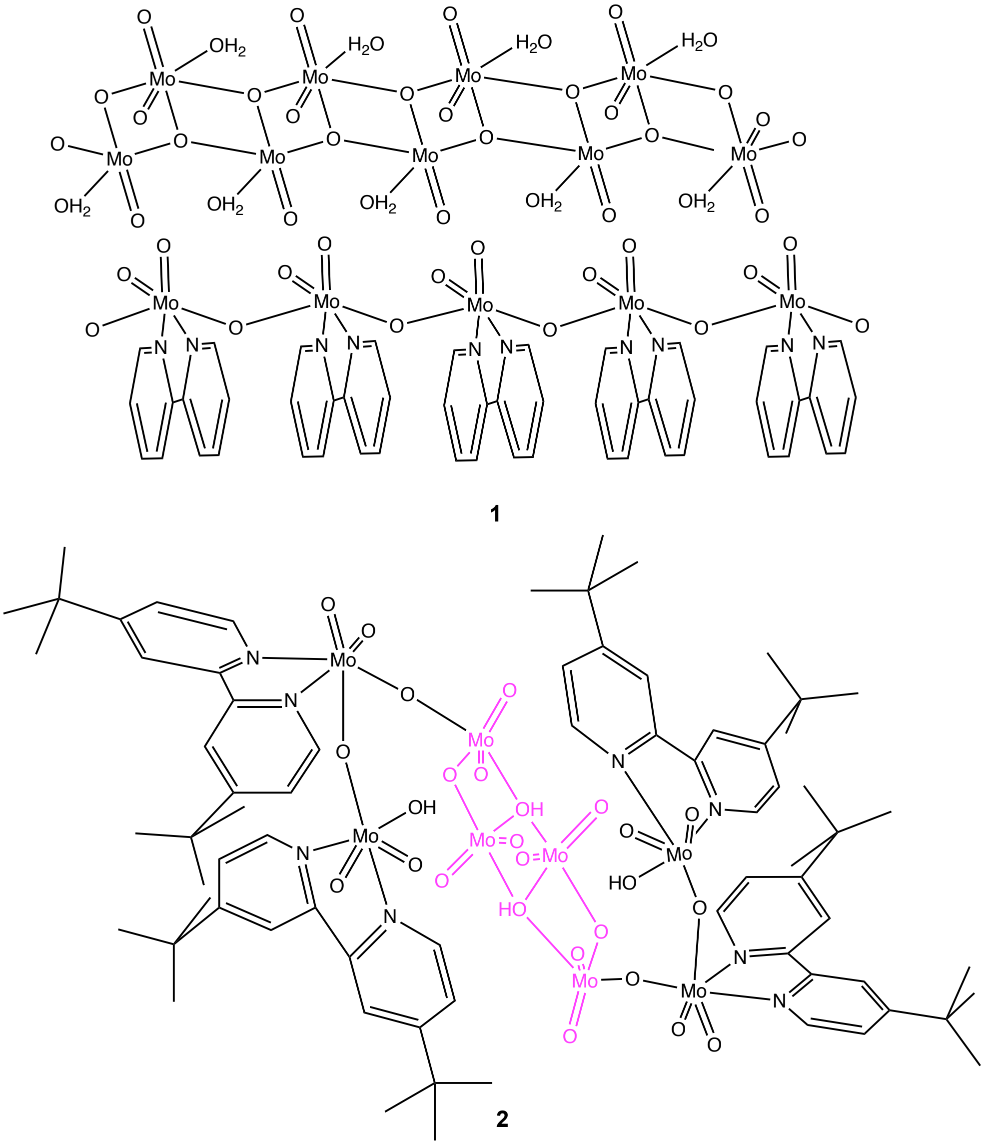
A variety of compounds bearing different metal centers, such as Mo(VI), W(VI), V(V) and Re(VII) has been reported as successful catalysts for oxidation of sulfur and nitrogen-containing compounds in the presence of H_2O_2 or less sustainable oxidants.[7-9] An example of success are the Mo(VI) complexes containing the *cis*-dioxomolybdenum(VI) structural unit.[10-14] From this class of Mo(VI) complexes, the [MoO_2Cl_2] bearing organonitrogen ligands has been used as a precursor of interesting molybdenum(VI) oxide based hybrid materials with one-dimensional (1D) chains, two-dimensional (2D) sheets, and three-dimensional (3D) networks structures, in which the ligand are bonded directly to a molybdenum oxide of the oxide structure.[15-17] The nature of the ligand chosen is an important parameter for the formed specie and corresponding catalytic performance.[15, 18] For example, when the monomer [[MoO_2Cl_2(L)] with L = 2,2'-bipyridine was used as precursor, the polymer {[MoO_3(bipy)][$MoO_3(H_2O)$]}$_n$ was obtained; however, only by substituting the L to 4,4'-di-*tert*-butyl-2,2'-bipyridine, the octameric complex [$Mo_8O_{24}(OH)_4$(di-*t*Bu-bipy)$_4$] was isolated instead.[16] Hybrid molybdenum compounds have revealed to be stable, selective and active for catalytic epoxidation with *t*BHP (in decane).[16, 18] Their application as active catalysts for oxidation of sulfides is still unknown.

In the present chapter, the {[MoO_3(bipy)][$MoO_3(H_2O)$]}$_n$ and [$Mo_8O_{24}(OH)_4$(di-*t*Bu-bipy)$_4$] hybrid materials were efficiently applied for the first time as homogeneous catalysts in oxidative desulfurization/denitrogenation process (ODS/ODN) of a model diesel containing 3000 and 400 ppm of sulfur and nitrogen compounds, respectively. Eco-sustainable conditions (low temperature, low H_2O_2/S molar ratio and an environmentally friendly solvent, [BMIM]PF_6) are used. Both systems containing the materials were reused and recycled for several ODS and ODN cycles. Using the best model diesel conditions, an untreated real diesel was desulfurized through the reutilization of the systems containing the catalyst **1** or **2** for three consecutive cycles.

9.2. Results and Discussion

9.2.1. Molybdenum hybrid materials

The monomer $[[MoO_2Cl_2(L)]$ with L = 2,2'-bipyridine or L = 4,4'-di-*tert*-butyl-2,2'-bipyridine, gives the polymer $[MoO_3(bipy)][MoO_3(H_2O)]_n$ (**1**) and the octameric complex $[Mo_8O_{24}(OH)_4$(di-*t*Bu-bipy)$_4]$ (**2**), respectively (Figure 9.1). The synthesis and detailed characterization can be conferred in Section 9.4.2.



1

2

Figure 9.1. Schematic representation of each molybdenum hybrid material **1** and **2**.

9.2.2. Desulfurization of a model diesel

The desulfurization performance of each molybdenum hybrid catalyst **1** and **2** was performed in the treatment of a model diesel containing 3000 ppm of some of sulfur compounds more difficult to remove under the currently processes applied in petroleum refining industry, namely DBT, 4-MDBT and 4,6-DMDBT. The catalyst **1** or **2** was applied together with H_2O_2, which is the oxidizing agent and an IL as extraction solvent with a reaction medium temperature of 70 °C. The combination of all reaction elements results in a biphasic system, in which occurs an initial extraction of some of sulfur compounds present in model diesel phase to the IL phase. This stage is performed under constant stirring with a duration of 10 min, at 70 °C. After this time, is added the oxidant, starting the catalytic oxidative stage, where the sulfur compounds are oxidized to the corresponding sulfones and/or sulfoxides. These oxidized species possess a similar polarity to the extraction solvent phase, allowing its removal during the ODS reaction.

9.2.2.1. Optimization studies

To study the influence of some parameters and subsequently achieve exceptional desulfurization results, an optimization study was performed, using a multicomponent model diesel containing the sulfur compounds commonly found in fuels: DBT, 4-MDBT and 4,6-DMDBT. The parameters analysed were the influence of different extraction solvents, such as MeCN and two room temperature ionic liquids (ILs) with imidazolium cations ($[BMIM]PF_6$ and $[BMIM]BF_4$), the effect of omitting the extraction solvent (solvent-free system), the amount of catalyst **1** (5, 10 and 15 μmol) and H_2O_2 oxidant (0.13, 0.26 and 0.60 mmol), the influence of different temperatures (50 °C and 70 °C) and the volume of extraction solvent (0.750, 0.375 and 0.250 mL).

The efficiency of the extraction stage of desulfurization process depends on a number of factors, among which are the polarity and selectivity of the solvents chosen, which must be geared towards having a solvent with high affinity for the products resulting from oxidation (sulfones and sulfoxides). Another important factor is the density of the solvent, which is responsible for a suitable separation from the fuel. Considering these factors, three different polar solvents were elected, which were tested using equal amounts of model diesel (0.750 mL), 10 μmol of catalyst **1** and 0.60 mmol of H_2O_2 at 70 °C. Under the same reaction conditions, the influence of omitting the extraction solvent (solvent-free system) was also tested. The ODS performance of catalyst **1** using solvent-free system and biphasic system using various solvents is presented in Figure 9.2. During the initial extraction step (before the addition of oxidant) it was possible to analyse the influence of the extractive capacity of each solvent for the removal of the sulfur compounds. MeCN (45.4%) showed the highest extraction performance, followed by [BMIM]PF$_6$ (37%) and [BMIM]BF$_4$ (30.5%). The highest extraction capacity demonstrated by MeCN can be related with its low viscosity when compared to the ILs, which allows a superior mass transfer.[19] On the other hand, the differences observed between [BMIM]PF$_6$ and [BMIM]BF$_4$ extraction capacities are strongly influenced by the chemical nature of the anion. Large anions, such as the fluorinated ones, are usually responsible for the weakening of Coulombic forces between the ions, enabling the selective and extractive removal of sulfur compounds, which are accommodated into the ionic pair structure of the IL.[20-22] After the addition of oxidant, the oxidative catalytic stage starts, during which a change in behaviour was observed for each extraction solvent. The catalytic performance of catalyst **1** was higher when in the presence of [BMIM]PF$_6$, achieving complete desulfurization of the model diesel after 1 h. For the same reaction time, the catalyst **1** led to conversions of 94.8% for [BMIM]BF$_4$, 94.1% for MeCN, and only 11.7% for solvent-free system. The better results obtained in the presence of ILs can be related with the polarity, which is similar to that for the oxidized sulfur compounds, improving the sulfur removal during the oxidative catalytic stage.[23] The outstanding result observed in the presence of [BMIM]PF$_6$ has already been noted in literature reports and can be explained by the water-immiscibility of this IL, which leads to the formation of a middle layer upon addition of aqueous H$_2$O$_2$, giving a triphasic ODS system (diesel/H$_2$O$_2$/[BMIM]PF$_6$).[24]

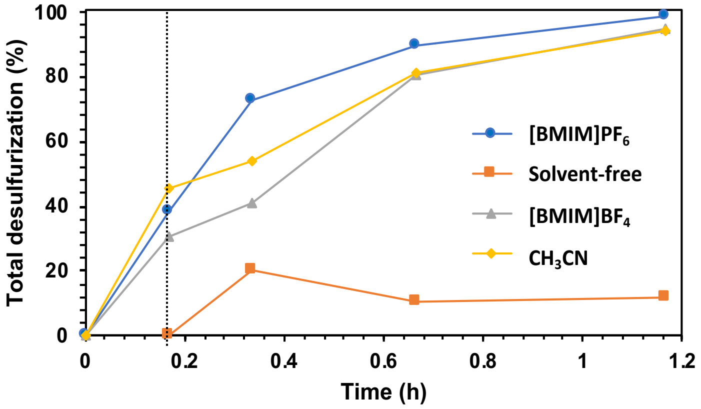


Figure 9.2. Desulfurization of a model diesel (3000 ppm S) using {[MoO$_3$(bipy)][MoO$_3$(H$_2$O)]}$_n$ (**1**) (10 μmol) as catalyst, in the presence or absence of different extraction solvents, and H$_2$O$_2$ (0.60 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

As referred to above, the ODS technology is composed of two important steps, oxidation and extraction, so the nature and quantity of the oxidant are important factors since they control, together with catalyst, the oxidative step through oxygen donation. The oxidant chosen was H_2O_2 due to its environmental friendliness and availability. Three different amounts of this oxidant were tested, i.e. 0.13, 0.26 and 0.60 mmol, maintaining the remaining conditions: 0.750 mL of model diesel and $[BMIM]PF_6$, 10 μmol of catalyst **1** and a reaction temperature of 70 °C. Similar kinetic profiles were obtained for all the amounts of oxidant (Figure 9.3); however, in the presence of 0.26 mmol the desulfurization of the model diesel was faster. For an equal reaction time (1 h, after oxidant addition), the final sulfur contents in the model diesel were 30 ppm for the higher amount of oxidant, and 230 ppm for the lower amount. The sulfur removal differences observed between the 0.26 and 0.60 mmol amounts may be related with the water formed from the degradation of the oxidant, which can decelerate the oxidative desulfurization performance.[25]

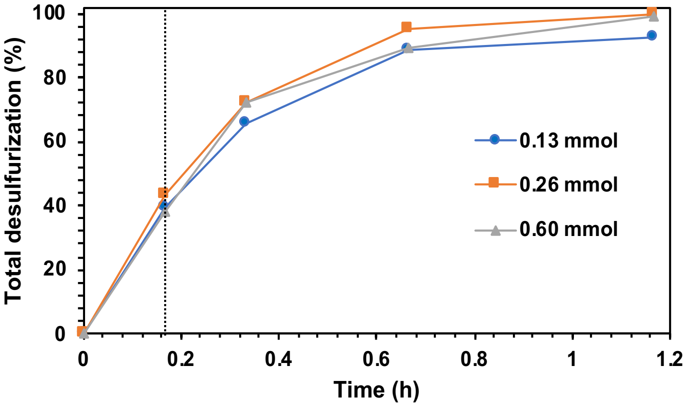


Figure 9.3. Desulfurization of a model diesel (3000 ppm S) using $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**1**) (10 μmol) as catalyst, $[BMIM]PF_6$ (0.750 mL) as extraction solvent and different amounts of H_2O_2 as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The influence of different amounts of catalyst **1** (5, 10 and 15 μmol) was also studied, maintaining the best experimental conditions obtained so far (model diesel (0.750 mL), $[BMIM]PF_6$ as extraction solvent (0.750 mL), H_2O_2 (0.26 mmol) at 70 °C). The efficiency of the ODS system increased with the amount of catalyst, reaching a completely desulfurized model diesel after 1 h using the higher amount of catalyst **1** (Figure 9.4). Considering that the best results were achieved with the highest amounts (15 and 10 μmol) of catalyst **1** and knowing that from an industrial point of view the investment costs are of huge importance, the amount chosen to continue the optimization studies was 10 μmol.

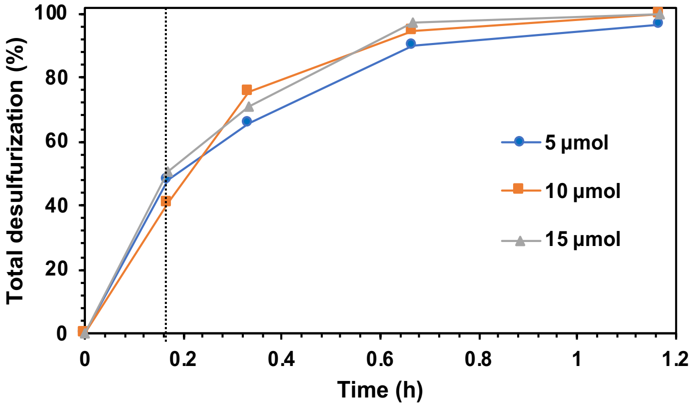


Figure 9.4. Desulfurization of a model diesel (3000 ppm S) catalysed by different amounts of {[MoO_3(bipy)][$MoO_3(H_2O)$]}$_n$ (**1**) in the presence of [BMIM]PF_6 (0.750 mL) as extraction solvent, using H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The effect of temperature (50 °C and 70 °C) on the oxidative desulfurization process was also analysed. Temperatures higher than 70 °C were not studied since oxidation at temperatures between 80 and 90 °C can promote the decomposition of the oxidant, as well as parallel undesirable oxidation reactions that can degrade the quality of liquid fuels.[26] An increase in the reaction temperature led to an improvement in the desulfurization rate, obtaining a sulfur-free model diesel after 1 h (after oxidant addition) when a higher temperature (70 °C) is used (Figure 9.5).

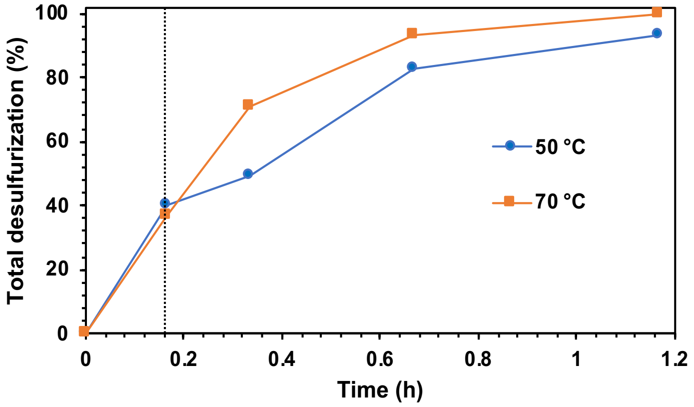


Figure 9.5. Desulfurization of a model diesel (3000 ppm S) using {[MoO_3(bipy)][$MoO_3(H_2O)$]}$_n$ (**1**) (10 μmol) as catalyst, [BMIM]PF_6 (0.750 mL) as extraction solvent and H_2O_2 (0.26 mmol) as oxidant, at different

temperatures. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

To make ODS a competitive choice when compared to the actual desulfurization process used in the refining industry (hydrodesulfurization, HDS), it is important to have an effective mass transfer from the fuel phase to the polar phase (extraction solvent). Accordingly, the next parameter to be analysed was the influence of the model diesel/[BMIM]PF_6 volume ratio in desulfurization (Figure 9.6). All the other experimental conditions were maintained. During the initial extraction step, the amount of sulfur compounds transferred from the model diesel phase to the extraction phase was similar using 1:1 and 1:0.5 of model diesel/[BMIM]PF_6. After the addition of oxidant to the system (oxidative catalytic stage), a noticeable difference in ODS efficiency was observed, where the system containing equal volumes of model diesel and IL revealed a faster desulfurization performance, obtaining a sulfur-free model diesel after 1 h of ODS reaction. For the same reaction time, the model diesels desulfurized in the presence of lower volumes of [BMIM]PF_6 still contained 142 ppm (1:0.3 diesel/IL) and 44 ppm (1:0.5 diesel/IL) of sulfur compounds.

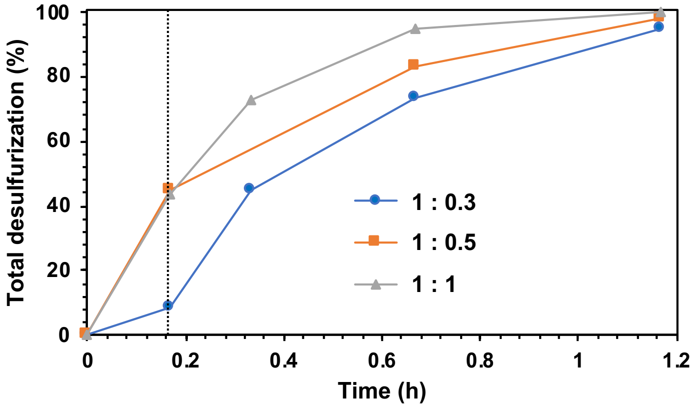


Figure 9.6. Desulfurization of a model diesel (3000 ppm S) using $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**1**) (10 μmol) as catalyst, in the presence of different volumes of [BMIM]PF_6 and H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

The optimization studies were also performed using the catalyst **2** and varying the same parameters (type of solvent, amount of catalyst and oxidant, temperature and volume of extraction solvent). Most of the results obtained for each parameter evaluated were similar to those achieved for the catalyst **1**, namely the amounts of catalyst (10 μmol) and oxidant (0.26 mmol) and temperature of the reaction medium (70 °C) as can be observed in Figures 9.7, 9.8 and 9.9. However, when different solvents were tested, a completely desulfurized model diesel was obtained using both MeCN and [BMIM]PF$_6$ after 2 h of ODS reaction (Figure 9.10). Therefore, the catalyst **2** possesses high catalytic efficiency in a water-immiscible system ([BMIM]PF$_6$) and also a water-miscible (MeCN) one, indicating that the catalyst **2** is not sensitive to aqueous environments, as seems to happen with the catalyst **1**. The bulky ligand presents in catalyst **2** may be responsible for protecting the Mo center from the water (by-product from the H_2O_2), avoiding a possible catalyst deactivation. Despite the similar results obtained for MeCN and [BMIM]PF$_6$, the IL was the solvent chosen to continue the ODS studies, due to its unique properties, such as thermal stability, negligible volatility and the capacity to be recycled.[27, 28]

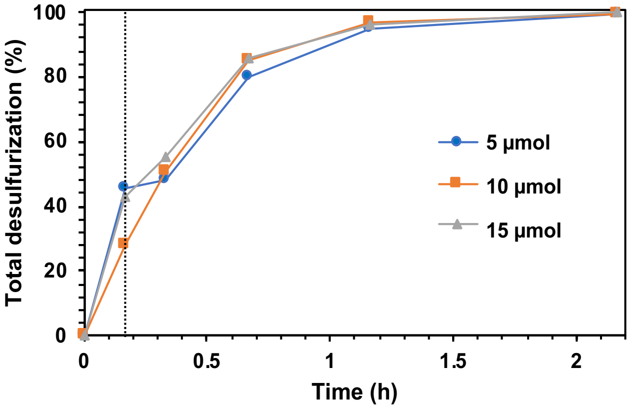


Figure 9.7. Desulfurization of a model diesel (3000 ppm S) catalysed by different amounts of [Mo$_8$O$_{22}$(OH)$_4$(di-tBu-bipy)$_4$] (**2**) in the presence of [BMIM]PF$_6$ (0.750 mL) as extraction solvent with H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

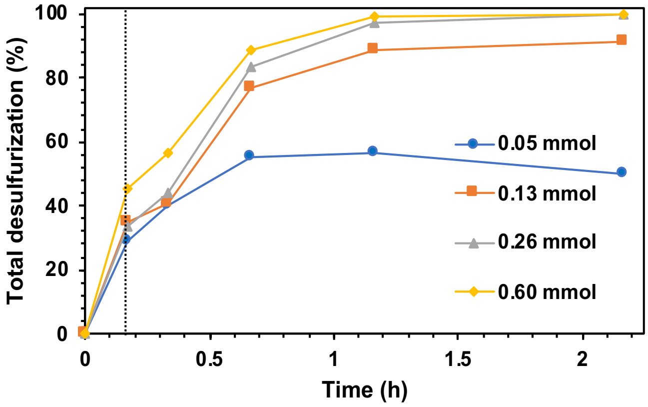


Figure 9.8. Desulfurization of a model diesel (3000 ppm S) using [$Mo_8O_{22}(OH)_4$(di-*t*Bu-bipy)$_4$] (**2**) (10 μmol) as catalyst, [BMIM]PF_6 (0.750 mL) as extraction solvent and different amounts of H_2O_2 as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

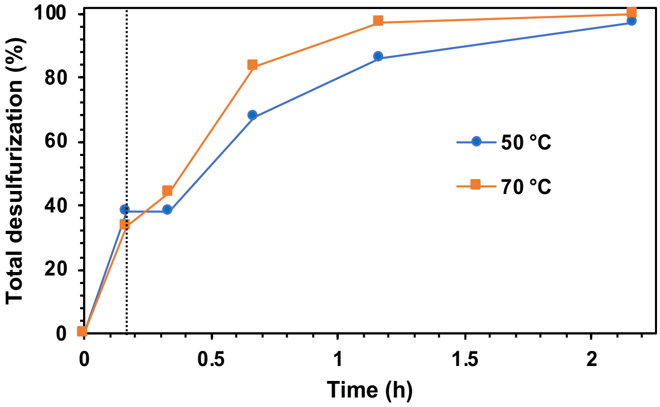


Figure 9.9. Desulfurization of a model diesel (3000 ppm S) using [$Mo_8O_{22}(OH)_4$(di-*t*Bu-bipy)$_4$] (**2**) (10 μmol) as catalyst, [BMIM]PF_6 (0.750 mL) as extraction solvent, H_2O_2 (0.26 mmol) as oxidant, at different temperatures. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

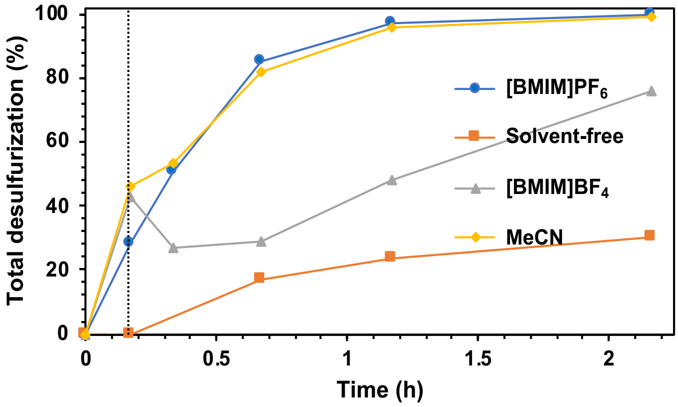


Figure 9.10. Desulfurization of a model diesel (3000 ppm S) using [Mo$_8$O$_{22}$(OH)$_4$(di-tBu-bipy)$_4$] (**2**) (10 μmol) as catalyst, in the presence or absence of different extraction solvents, H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Interestingly, the other parameter which gave results that were slightly different from those obtained with catalyst **1** is also related to the solvent, namely the model diesel/IL volume ratio (Figure 9.11). Considering the results obtained with the catalyst **1**, we only analysed the IL volumes that provided the best desulfurization rates (0.375 mL for 1:0.5 ratio and 0.750 mL for 1:1 ratio). In the presence of catalyst **2** the kinetic profiles obtained for each model diesel/IL volume ratio were very similar, obtaining in both ratios sulfur-free model diesels after 2 h of ODS reaction. Although the results obtained for the catalysts **1** and **2** seem to be different, the reaction time must be taken into account. For the same reaction time (1 h), desulfurization efficiencies were 98.9% (1:0.5) and 98.2% (1:1) for catalyst **1**, and 98.3% (1:0.5) and 100% (1:1) for catalyst **2**. Hence the behaviour of each catalyst is practically the same in the presence of the different amounts of [BMIM]PF$_6$.

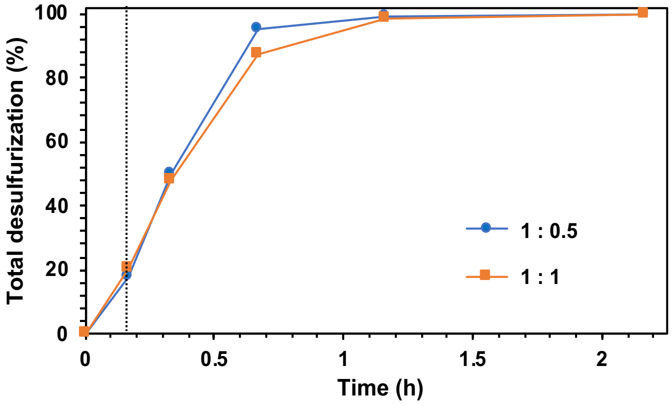


Figure 9.11. Desulfurization of a model diesel (3000 ppm S) using $[Mo_8O_{22}(OH)_4(di\text{-}tBu\text{-}bipy)_4]$ (**2**) (10 μmol) as catalyst, in the presence of different volumes of $[BMIM]PF_6$, H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

9.2.2.2. Relative efficiency of catalysts 1 and 2

After the optimization tests were completed, the desulfurization performance of each catalyst $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**1**) and $[Mo_8O_{22}(OH)_4(di\text{-}tBu\text{-}bipy)_4]$ (**2**) was compared using the best conditions achieved (10 μmol of each catalyst **1** and **2**, 0.26 mmol of H_2O_2 and equal amounts of model diesel/$[BMIM]PF_6$, at 70 °C). The desulfurization profiles obtained are presented in Figure 9.12. Generally, the initial extraction step is only affected by the extraction capacity of the solvent. However, Figure 9.12 shows some significant differences between the initial extraction occurring in the presence of each catalyst. The presence of catalyst **2** in the IL phase appears to induce some restraining effects on the extraction of sulfur compounds. After the addition of oxidant, a sulfur-free model diesel was obtained in the presence of catalyst **1** at 1 h of ODS reaction, while at the same reaction time, the reaction containing the catalyst **2** still comprised 66 ppm of sulfur compounds in the model diesel phase, which corresponds to a percentage of sulfur removal of 97.8%. Therefore, under the same reaction conditions, the catalyst **1** is the most efficient. This difference may be related to the different *N*-donor ligands present in each compound, i.e. the catalyst **2** possesses a derivative of the ligand 2,2'-bipyridine present in catalyst **1**, but in the case of **2** the *tert*-butyl substituent groups may be responsible for greater steric repulsions, inhibiting the connection between the catalyst and the oxidant, promoting a slower formation of the active species (the catalyst/$[BMIM]PF_6$ system changed colour to bright yellow during the ODS reaction).[29] In the actual system, H_2O_2 is present in a middle phase between the model diesel and IL phases, creating a triphasic system.

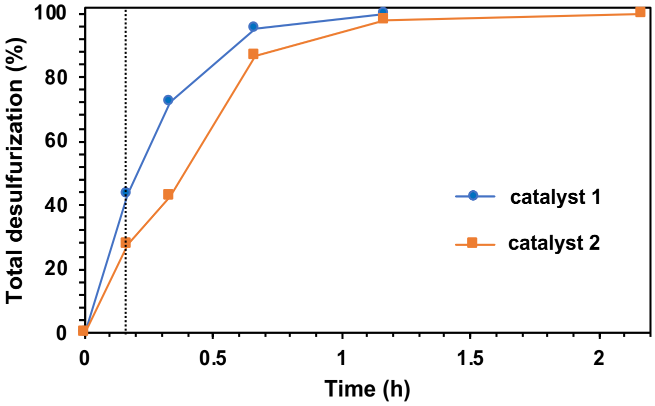


Figure 9.12. Desulfurization of a model diesel (3000 ppm S) using different catalysts (**1** and **2**, 10 *μ*mol) in the presence of [BMIM]PF_6 (0.750 mL) as extraction solvent, and H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

9.2.2.3. Hybrid catalysts recyclability and reusability

The stabilities of the catalysts **1** and **2** were tested for several cycles through the recycling and reutilization of the catalysts/[BMIM]PF_6 systems. Two different methods were applied to perform consecutive ODS catalytic cycles. In both methods "reused" and "recycled", the model diesel phase is removed, but while the reused process is based only on the addition of fresh portions of model diesel and H_2O_2, the recycled method involves a washing step, where the catalyst/[BMIM]PF_6 systems are cleaned with a mixture of ethyl acetate/diethyl ether (1:1 *v*/*v*) to remove the sulfur compounds resulting from extraction/oxidation reactions. Each cycle is performed under the same experimental conditions applied during the first cycle.

Recyclability and reutilization tests of the catalysts **1** and **2** were executed for five consecutive ODS cycles (Figure 9.13). Until the third cycle, both systems presented the same behaviour, maintaining the desulfurization efficiency. However, the system containing the catalyst **1** suffered a notable decrease after the third cycle, in which the reused cycle showed an efficiency loss from 97% (3rd cycle) to 49.3% and 38.9% in the fourth and fifth cycle. This type of occurrence has been attributed to the saturation of the extraction phase by the oxidized sulfur species (Figure 9.14), which prevents the further transfer of sulfur compounds from the nonpolar phase to the IL phase, decreasing the system efficiency.[30] The recycled **1**/[BMIM]PF_6 system also lost catalytic activity after the third ODS cycle, but in a more gradual way, possibly due to the reason described above, that in this case is delayed by the cleaning process applied between each cycle.

Besides the saturation of the systems, another reason for the decrease in catalytic activity may be the deactivation of catalyst **1**, which could occur by contact with water resulting from the use of H_2O_2 as oxidizing agent. A possible change in the catalyst structure was indicated by the observation of a change in the system colour from yellow (supposedly derived from the active species) to colourless in the last cycles. This loss of efficiency presented during the "reused" and "recycled" systems was not so noticeable for the system containing the catalyst **2**, possibly due to its higher resistance to water, as was observed during the optimization of the solvents ([BMIM]PF_6 and MeCN) presented in Figure 9.10.

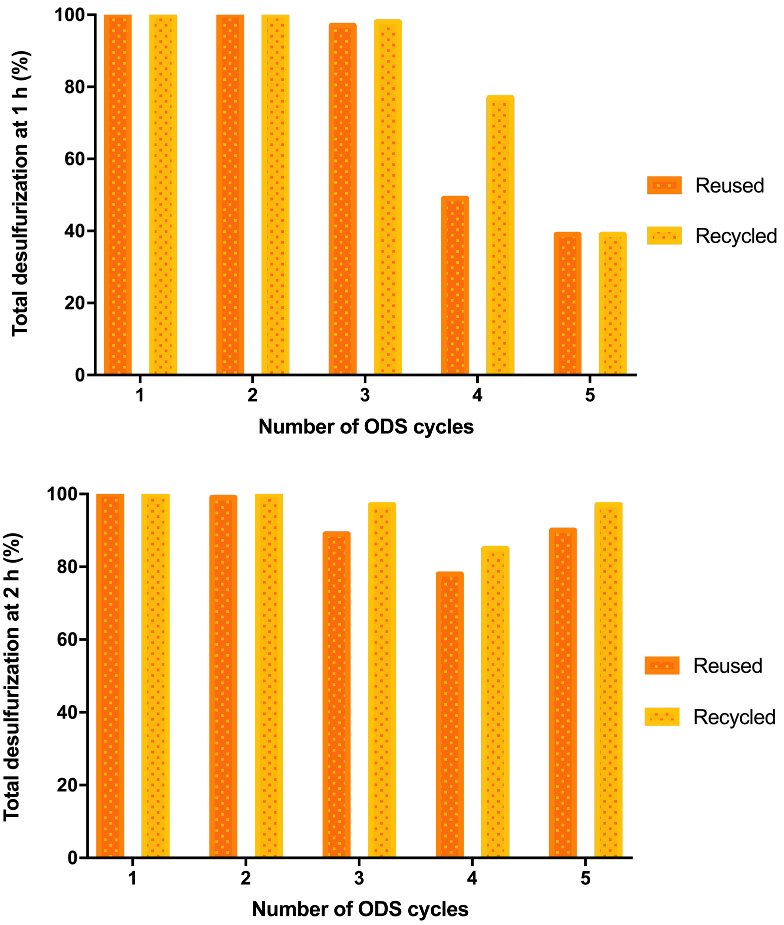


Figure 9.13. Desulfurization results for five consecutive reused and recycled ODS cycles, using catalyst **1** (top) and catalyst **2** (bottom), a model diesel (3000 ppm S) and [BMIM]PF_6 with a volume ratio of 1:1, at 70 °C with H_2O_2 (0.26 mmol) as oxidant. Results obtained after 1 h and 2 h of ODS reaction, respectively.

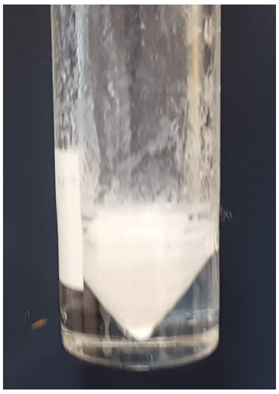


Figure 9.14. Photograph of the resulting ODS mixture after five consecutive cycles.

9.2.2.3.1. Simultaneous ODS and ODN of a model diesel

A model diesel containing 400 ppm of two different nitrogen compounds (indole and quinoline) was prepared. The nitrogen compounds in crude oils are predominantly present as heterocyclic aromatic compounds and in smaller amounts as non-heterocyclic nitrogen compounds such aliphatic amines and nitriles. The latter ones are not worrisome due to their easy treatment. The heterocyclic nitrogen compounds are classified as basic (six-membered pyridines) and neutral (five-membered pyrroles). Thus, the choice of indole and quinoline is related to their different molecular properties; one of which is a neutral nitrogen compound and the other is a basic nitrogen compound, respectively (Figure 9.15).[31]

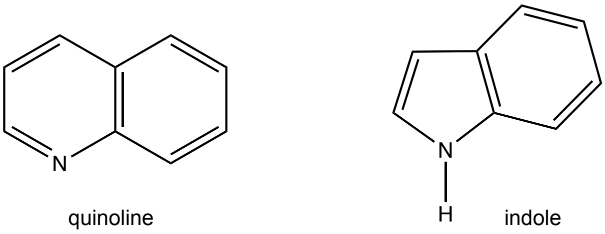


Figure 9.15. The structure of the heterocyclic nitrogen compounds used for the denitrogenation tests.

First, we tested the catalytic efficiency of our ODS system in the ODN process maintaining the same optimized conditions (model diesel (400 ppm N)/[BMIM]PF_6 volume ratio = 1:1, 10 μmol of catalyst **1** and **2**, and 0.26 mmol of H_2O_2). The kinetic profiles obtained for each nitrogen compound (quinoline and indole) were very similar for both catalysts, so herein only the results obtained using the system **1**/[BMIM]PF_6 are presented. Figure 9.16 displays the total denitrogenation of the model diesel *versus* time. The largest amount of indole (97.3%) is extracted during the initial extraction (before addition of H_2O_2), while the removal/oxidation of quinoline is performed over time, obtaining a model diesel with only 5 ppm of quinoline after 2 h of ODN reaction. This different denitrogenation behaviour may be related to a possible interaction between the proton donor molecule indole and the PF_6^- anion which promotes a selective extraction from the model diesel. In the basic nitrogen compounds containing a six-membered pyridine ring, this behaviour is not so evident, since a lone pair electron on the nitrogen atom is not part of the aromatic system and it is extended in the plane of the ring, being responsible for the negative charge that is higher than in neutral nitrogen compounds.[32-34] Due to this, the basic nitrogen compounds are better extracted by Lewis acid ionic liquids.[31]

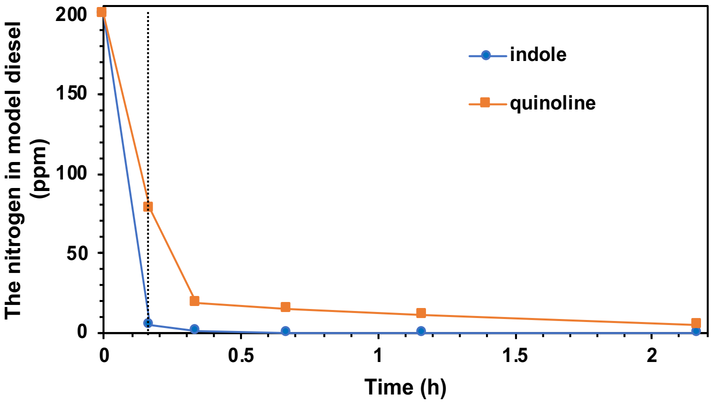


Figure 9.16. Denitrogenation of a model diesel containing different nitrogen compounds (400 ppm) using $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**1**) (10 μmol) as catalyst, $[BMIM]PF_6$ (0.750 mL) as extraction solvent, H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

With the knowledge that the nitrogen compounds can be effectively extracted/oxidised under the same conditions used during the desulfurization tests, a model diesel containing sulfur (3000 ppm) and nitrogen (400 ppm) compounds was prepared and treated. Figure 9.17 displays the desulfurization and denitrogenation results obtained simultaneously using catalyst **1** and **2** (10 μmol)**,** 0.26 mmol of H_2O_2 and $[BMIM]PF_6$ as extraction solvent at 70 °C. Table 9.1 presents the initial extraction results for sulfur and nitrogen compounds. When the desulfurization and denitrogenation occur separately, the nitrogen and sulfur compounds presented certain initial extraction values (Table 9.1). However, when the denitrogenation and desulfurization occur simultaneously, almost only nitrogen compounds were initially extracted, in the order indole > quinoline > DBT (Table 9.1). The sulfur compounds with alkyl-substituents on the aromatic rings were not extracted during this stage, probably due to steric hindrance when compared to the other sulfur and nitrogen compounds. These results show that during the initial extraction stage a competition between the compounds with different heteroatoms seems to occur, which only appears to affect the sulfur extraction, since the extraction obtained with the nitrogen compounds was practically the same as that obtained for denitrogenation as a single process (Figure 9.16). Hansmeier *et al.* [35] reported that nitrogen compounds are significantly better extracted than sulfur-containing compounds when ILs are used as extraction solvents. Interestingly, despite the results obtained for desulfurization process during the initial extraction, the ODS process did not suffer from serious consequences resulting from the poor initial extraction obtained in the presence of the nitrogen compounds, since a completely desulfurized model diesel was obtained after 2 h (at 1 h of ODS reaction only 34 and 36 ppm of 4,6-DMDBT remained in the systems containing the catalysts **1** and **2**, respectively). Concerning the removal of nitrogen compounds from the model diesel, indole was completely removed/oxidized within 30 min of reaction, while the N content relating to the basic nitrogen compound quinoline suffer only a small decrease from 10 min to 3 h, remaining 13 ppm and 6 ppm in model diesel phase for the systems based in catalyst **1** and **2**, respectively. These results may be related with the use of an insufficient amount of H_2O_2, which because of competitive oxidation could halt the continuous oxidation of the quinoline compound to the corresponding quinoline *N*-oxide.[36]

Table 9.1. Values (%) obtained for each extractable compound after the initial extraction using the separated or simultaneous processes in the presence of the different catalysts **1** and **2**

Compounds	**Simultaneous ODS/ODN (%)**		**ODS (%)**		**ODN (%)**	
	Catalyst 1	**Catalyst 2**	**Catalyst 1**	**Catalyst 2**	**Catalyst 1**	**Catalyst 2**
DBT	11.4	11.7	56.4	40.2		
4-MDBT	0	0	41.8	25.7		
4,6-DMDBT	0	0	29.9	13.5		
Indole	96.8	97.4			97.5	97.2
Quinoline	58.0	61.6			61.0	64.1

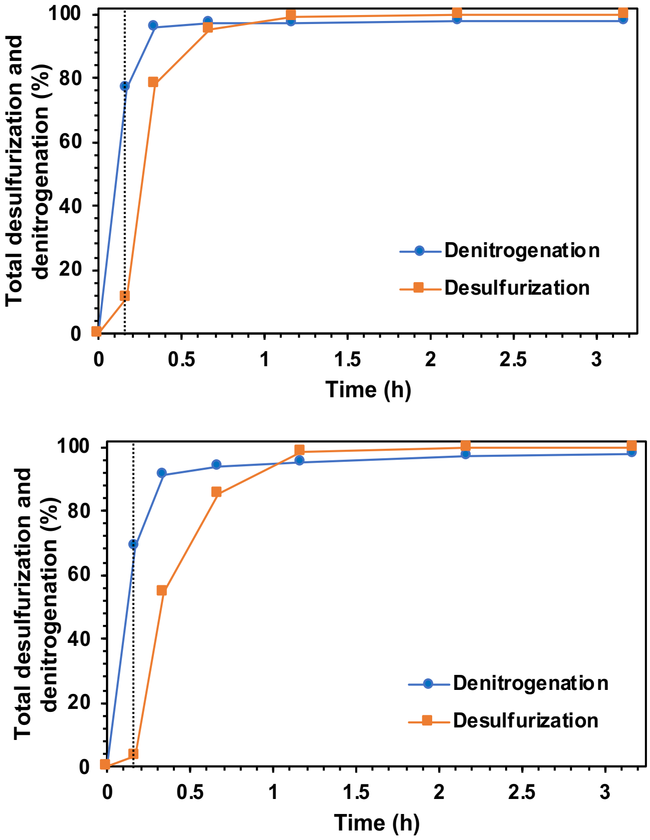


Figure 9.17. Simultaneous desulfurization and denitrogenation of a model diesel (3000 ppm of S and 400 ppm of N) catalysed by complex **1** (top) and **2** (bottom) (10 µmol) in the presence of [BMIM]PF_6 as extraction solvent and H_2O_2 (0.26 mmol) as oxidant, at 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

To understand if the oxidant H_2O_2 possesses an active role during the simultaneous desulfurization and denitrogenation process, a blank reaction was performed where no oxidant and catalyst were applied. The remaining conditions were maintained ([BMIM]PF_6 as extraction solvent, model diesel containing 3000 ppm of S and 400 ppm of N and a reaction medium of 70 °C) being the results presented in Figure 9.18. Clearly, is observable that without the oxidative step, no complete desulfurization or denitrogenation was achieved, i.e., both nitrogen and sulfur compounds only can be efficiently removed from the model diesel phase when the oxidation and extraction process are conciliated.

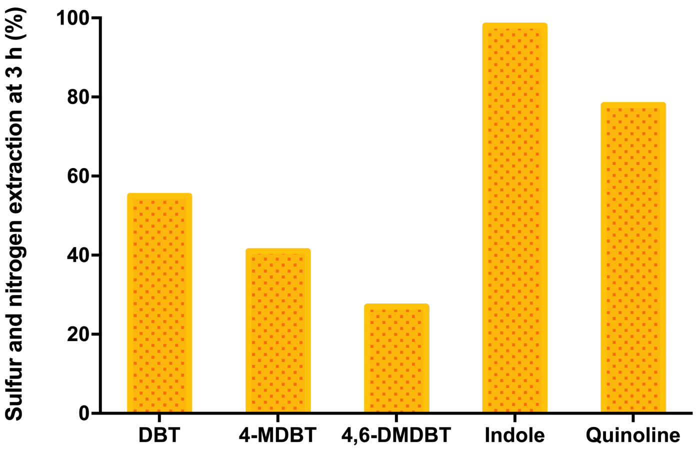


Figure 9.18. Extractive desulfurization and denitrogenation results (3 h) obtained by using an equal amount of [BMIM]PF_6 and model diesel (3000 ppm of S and 400 ppm of N) at 70 °C.

In order to evaluate the catalytic efficiency of the **1**/[BMIM]PF_6 and **2**/[BMIM]PF_6 systems for several cycles of simultaneous ODS and ODN processes, some reusability and recyclability tests were performed (Figure 9.19 and 9.20). The tests were executed under the optimized conditions. The systems containing both catalysts maintained the catalytic efficiency for five consecutive cycles, and no substantial differences were observed between the “reused” and the “recycled” systems, showing that despite the high content of sulfur and nitrogen compounds in the model diesel, the number of oxidized compounds is not sufficient to provoke a saturation of the **1**/[BMIM]PF_6 and **2**/[BMIM]PF_6 systems during the 2 h of reaction. Also, the complete removal of sulfur compounds, shows that the presence of nitrogen compounds has practically no influence on the ODS reaction mechanism. However, an excess of the oxidant appeared to be required to promote the complete removal of quinoline from the model diesel.

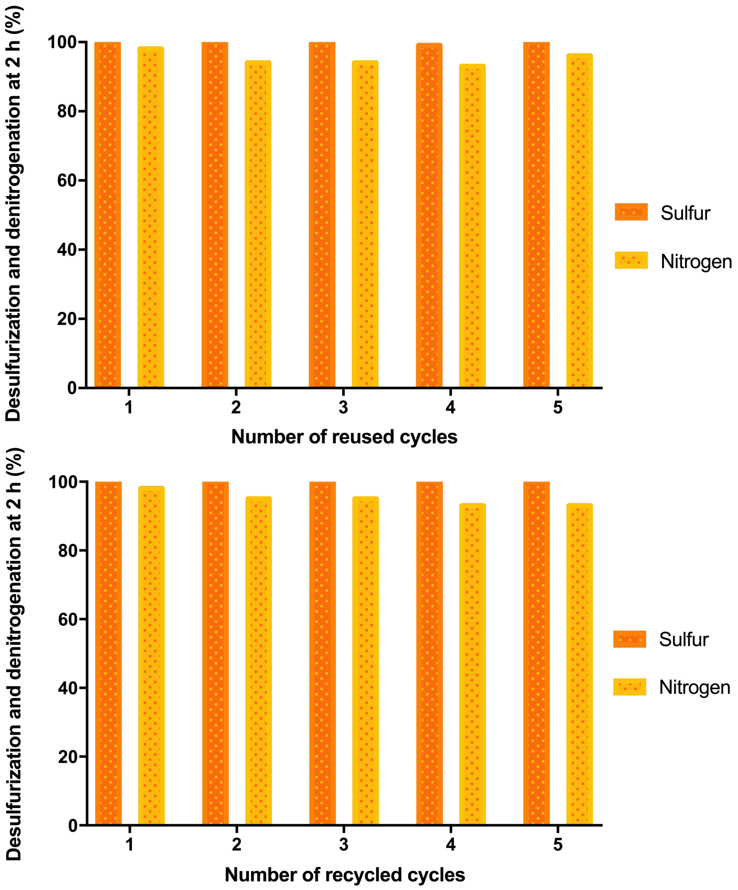


Figure 9.19. Desulfurization and denitrogenation data for five consecutive reused (top) and recycled (bottom) cycles using a model diesel containing 3000 ppm of S and 400 ppm of N, catalysed by $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ (**1**) (10 μmol) in the presence of $[BMIM]PF_6$ as extraction solvent, using 0.26 mmol of H_2O_2 at 70 °C. Results obtained after 2 h of ODS/ODN reaction.

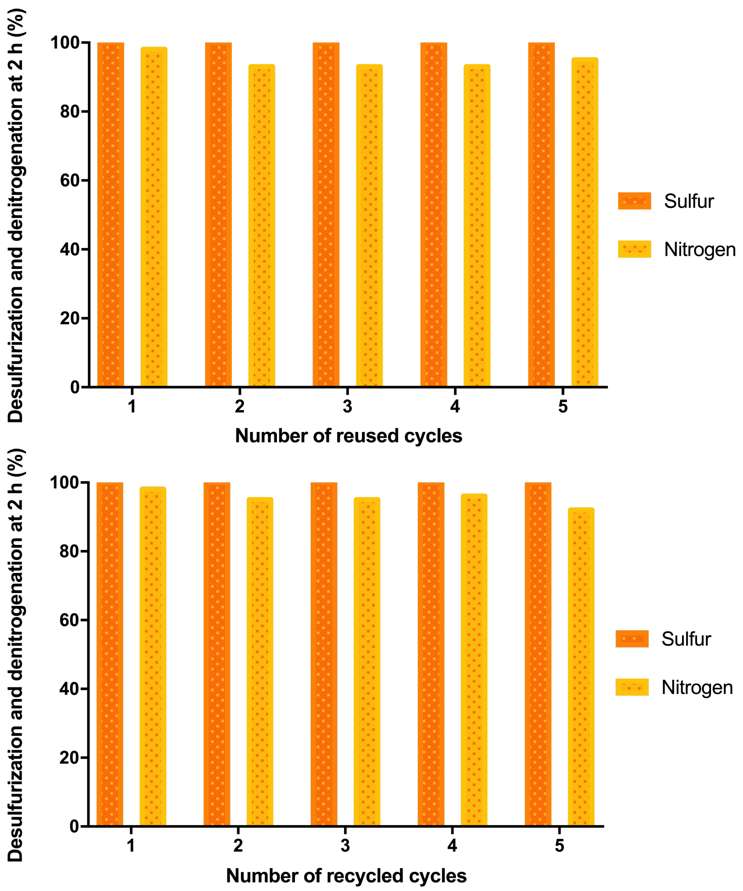


Figure 9.20. Desulfurization and denitrogenation data for five consecutive reuse (top) and recycle (bottom) cycles using a model diesel containing 3000 ppm of S and 400 ppm of N, catalysed by [$Mo_8O_{22}(OH)_4$(di-tBu-bipy)$_4$] (**2**) (10 μmol) in the presence of [BMIM]PF_6 as extraction solvent, using 0.26 mmol of H_2O_2 at 70 °C. Results obtained after 2 h of ODS/ODN reaction.

The good results obtained for the "reused" cycles show that the washing step is not an important parameter in these systems using catalysts **1** and **2**. The same type of reutilization process was therefore used to study the influence of the volume of the extraction solvent ([BMIM]PF_6) (0.750 or 0.375 mL) on the efficiency of the desulfurization and denitrogenation for the consecutive and simultaneous ODN and ODS cycles for each catalyst/[BMIM]PF_6 system. While the use of different amounts of [BMIM]PF_6 did not influence the desulfurization process, the removal/oxidation of quinoline (but not indole) was affected, such that the denitrogenation efficiency was lower when a lower amount of IL was used (Figures 9.21 and 9.22). This may be related with a saturation of the system arising from the high amount of different species in the model diesel and the lower quantity of IL used. The application of a washing step between cycles avoided this loss of denitrogenation efficiency (Figure 9.23).

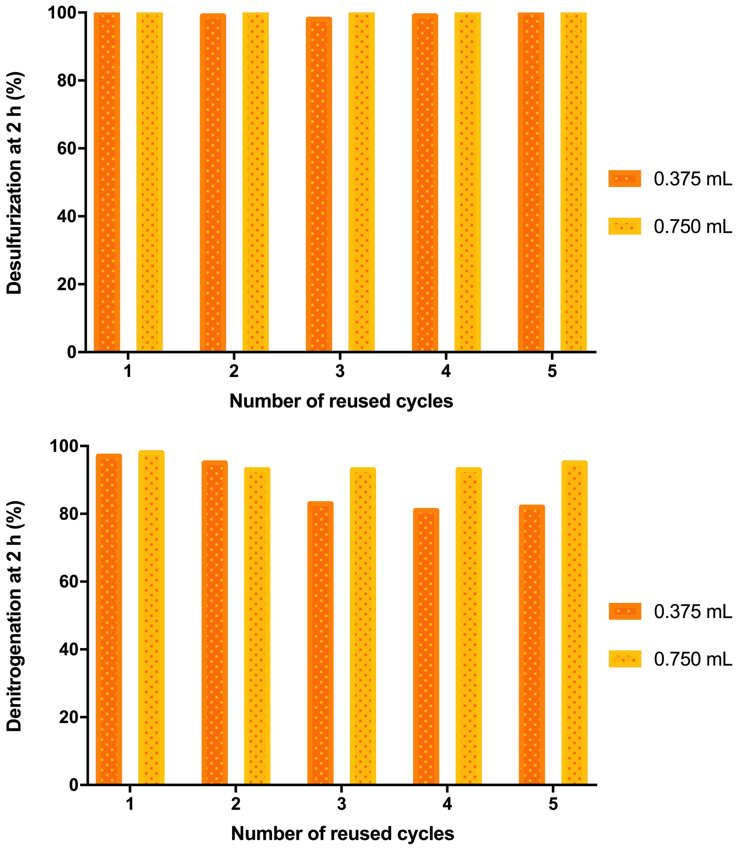


Figure 9.21. Comparative studies of desulfurization (top) and denitrogenation (bottom) reutilizations for five consecutive cycles using a model diesel containing 3000 ppm of S and 400 ppm of N and {[MoO_3(bipy)][MoO_3(H_2O)]}n (**1**) (10 μmol) as catalyst in the presence of 0.750 and 0.375 mL of [BMIM]PF_6 as extraction solvent, using 0.26 mmol of H_2O_2 at 70 °C. Results obtained after 2 h of ODS/ODN reaction.

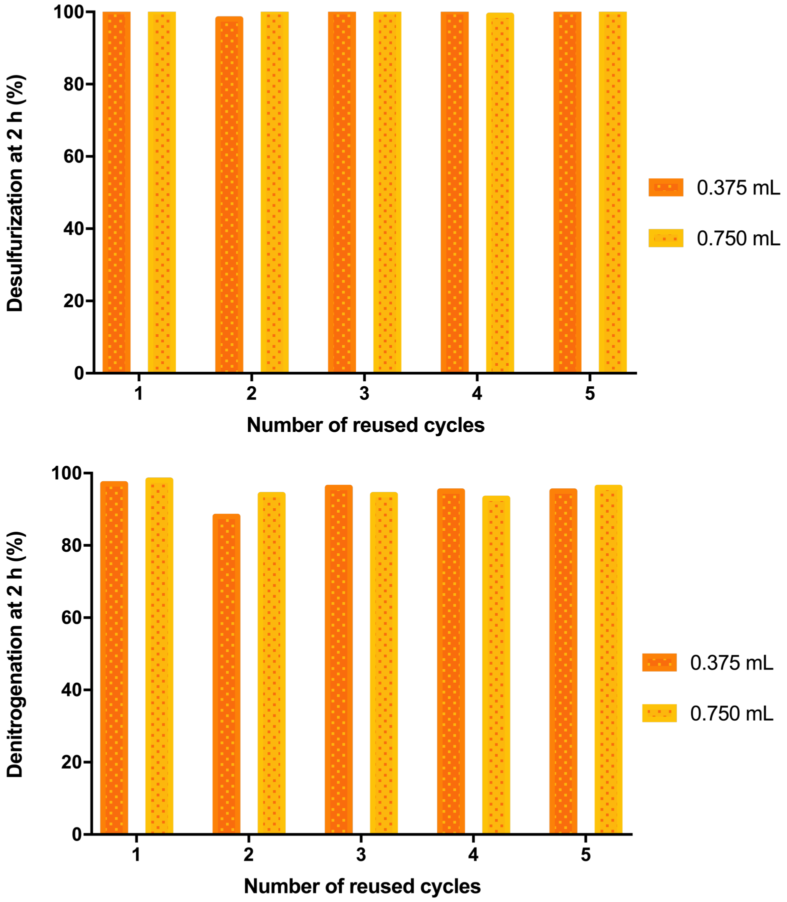


Figure 9.22. Comparative studies of desulfurization (top) and denitrogenation (bottom) reutilizations for five consecutive cycles using a model diesel containing 3000 ppm of S and 400 ppm of N and $[Mo_8O_{22}(OH)_4(di\text{-}t\text{Bu-bipy})_4]$ (**2**) (10 μmol) as catalyst in the presence of 0.750 and 0.375 mL of $[BMIM]PF_6$ as extraction solvent, using 0.26 mmol of H_2O_2 at 70 °C. Results obtained after 2 h of ODS/ODN reaction.

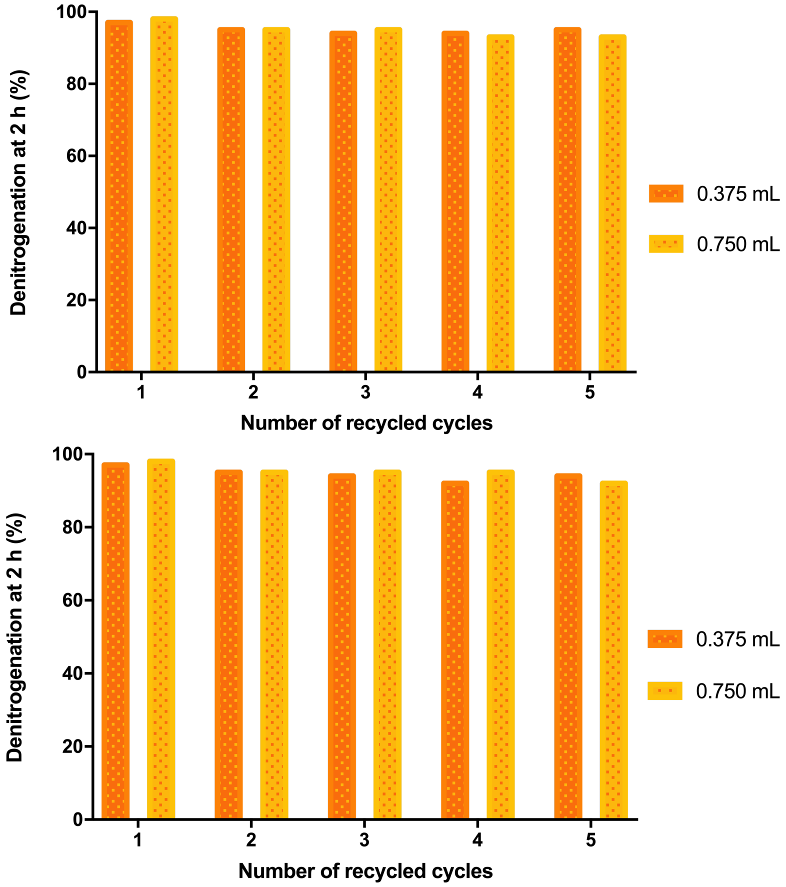


Figure 9.23. Comparation of denitrogenation results obtained from a simultaneous desulfurization and denitrogenation processes recycled for five consecutive cycles using different amounts of [BMIM]PF_6 (0.750 and 0.375 mL), with a model diesel containing 3000 ppm of S and 400 ppm of N, catalysts **1** (top) and **2** (bottom) (10 μmol) and 0.26 mmol of H_2O_2 at 70 °C. Results obtained after 2 h of ODS/ODN reaction.

9.2.3. Desulfurization of a real diesel

The ODS of an untreated real diesel containing 2300 ppm of sulfur was performed under the conditions resulted from model diesel optimization studies, i.e. an equal amount of [BMIM]PF_6 and diesel, 0.26 mmol of H_2O_2 and 10 μmol of catalyst **1** or **2**, with a reaction temperature of 70 °C. The systems containing the catalysts **1** and **2** were reused for three consecutive cycles. No cleaning process was applied to the catalyst/[BMIM]PF_6 system between ODS cycles. Considering that no pre-treatment was applied to the diesel, the results obtained demonstrated high catalytic efficiencies for both catalysts, from which resulted sulfur removals of 1560 ppm corresponding to a catalytic efficiency of 67.8% observed for the first cycle (Table 9.2). From the first to the second cycle was observable a loss of efficiency of 15.1% and 5.8% for catalyst **1** and

2, respectively. Similar desulfurization efficiency was found for the second and third cycles. The results are in accordance with those obtained during the reutilization of model diesel (Section 9.2.2.3), where the system containing the catalyst **1** suffered a considerable efficiency decrease when compared to that containing the catalyst **2**.

Table 9.2. Experiments performed for desulfurization of untreated diesel using 1:1 diesel/[BMIM]PF_6 system catalysed by **1** or **2** for several consecutive cycles under model diesel conditions

Catalyst	**1st ODS cycle**[a]		**2nd ODS cycle**[a]		**3rd ODS cycle**[a]	
	S content (ppm)	Desulfurization efficiency (%)[b]	S content (ppm)	Desulfurization efficiency (%)[b]	S content (ppm)	Desulfurization efficiency (%)[b]
1	741	67.8	1087	52.7	1024	55.5
2	740	67.8	874	62.0	871	62.1

[a] Oxidative desulfurization in a biphasic/diesel system during 2 h under the optimal model diesel conditions with a final extraction with MeCN during 30 min at 70 °C.

[b] Calculated based on the sulfur content of untreated real diesel (2300 ppm).

9.3. Conclusions

Using {[MoO_3(bipy)][$MoO_3(H_2O)$]}$_n$ (**1**) and [$Mo_8O_{22}(OH)_4$(di-*t*Bu-bipy)$_4$] (**2**) as catalysts for desulfurization studies, a model diesel containing 3000 ppm of S and 400 ppm of N was successfully desulfurized and denitrogenized using a low oxidant/sulfur ratio (H_2O_2/model diesel = 3.7), 10 μmol of each catalyst, an ionic liquid as extraction solvent and a reaction temperature of 70 °C. Performing simultaneously the ODS and the ODN processes, both catalysts **1** and **2** seemed to possess similar activities for both processes. Their oxidative desulfurization capacity was also confirmed for reused and recycled cycles, showing that in the presence of catalysts **1** and **2** the washing step is not vital.

The desulfurization efficiency of catalysts **1** and **2** was also verified using an untreated high sulfur diesel and similar performance was obtained for both catalysts achieving an efficiency of 67.8% after 2 h. As the first application of these catalysts in the treatment of fuel samples, these results open up a large number of possible applications for these or related hybrid molybdenum oxide compounds as efficient catalysts for desulfurization and denitrogenation of liquid fuels.

9.4. Experimental Section

9.4.1. Materials and Methods

The following chemicals and reagents were purchased from Sigma-Aldrich unless otherwise indicated, and used as received: MoO_2Cl_2 (Sigma-Aldrich), bipyridine (Sigma-Aldrich, 99%), 4,4′-di-tert-butyl-2,2′-bipyridine (Sigma-Aldrich), tetrahydrofuran anhydrous (Sigma-Aldrich, 99%), acetone (Fluka, puriss, p.a.), diethyl ether (Sigma-Aldrich, puriss, p.a.), dibenzothiophene (Sigma-Aldrich, 98%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), 4-methyldibenzothiophene (Sigma-Aldrich, 96%), quinoline (Sigma-Aldrich, 98%), indole (Sigma-Aldrich, ≥99%), *n*-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Aldrich, 97%), tetradecane (Aldrich, 99%), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium tetrafluoroborate (Sigma-Aldrich, ≥98%), ethyl acetate (Fischer Chemical, analytical grade), diethyl ether (Merck), and 30% w/v hydrogen peroxide (Sigma-Aldrich).

Microanalyses (CHN) were acquired at the University of Aveiro with a Truspec Micro CHNS 630-200-200 elemental analyser. Powder X-ray diffraction (PXRD) data were collected at ambient temperature using a PANalytical Empyrean instrument equipped with a PIXcel 1D detector set at 240 mm from the sample. Cu-K$\alpha_{1,2}$ X-radiation (λ_1 = 1.540598 Å; λ_2 = 1.544426 Å) filtered with a nickel foil was used along with a standard transmission sample holder. Working operating conditions for the X-ray tube: 45 kV and 40 mA. Intensity data were collected in continuous mode in the ca. $3.0 \leq 2\theta \leq 70.0°$ range. FT-IR spectra were recorded as KBr pellets using a Unicam-Mattson 7000 spectrophotometer equipped with a DTGS CsI detector (128 scans and resolution of 4 cm^{-1}). FT-Raman spectra were recorded on a RFS-100 Bruker FT-Spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm. ^{13}C cross-polarization (CP) magic-angle-spinning (MAS) NMR spectra were obtained using a Bruker Avance 400 spectrometer (9.4 T) at 100.62 MHz, with 3.6 μs ^1H 90° pulses, 2 ms contact time, spinning rates of 7 and 11 kHz, and 5 s recycle delays. Chemical shifts are quoted in parts per million (ppm) with respect to TMS. The desulfurization of the model diesel was monitored using a Bruker 430-GC-FID gas chromatograph, equipped with a Supelco capillary column SPB-5 (30 m x 250 *μ*m id.; 25 *μ*m film thickness) and using hydrogen as carrier gas (55 cm^3 s^{-1}). The analysis of sulfur content of the treated diesel was performed in Galp Energia by ultraviolet fluorescence using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

9.4.2. Catalysts synthesis

The monomers **[MoO_2Cl_2(bipy)]**[29] and **[MoO_2Cl_2(di-*t*Bu-bipy)]**[37] were synthesized according to the published procedures.

{[MoO_3(bipy)][MoO_3(H_2O)]}$_n$ (**1**) was prepared by addition of [MoO_2Cl_2(bipy)] (0.85 g, 2.39 mmol) and water (25 mL) to a Schlenk tube. The mixture was left under reflux during 12 h under air using an external oil bath as a heating source. The resultant white solid was separated from the pink aqueous mother liquor (pH ≅ 2) by filtration and washed with water (2 x 10 mL), acetone (2 x 10 mL) and diethyl ether (2 x 10 mL) and dried under vacuum. The characterization performed to the compound **1** is in excellent agreement with previous literature data.[15] Yield: 0.50 g, 90%. Anal. Calcd for $C_{10}H_{10}Mo_2N_2O_7$ (462.08): C, 25.99; H, 2.18; N, 6.06. Found: C, 25.85; H, 2.32; N, 6.04. Selected FT-IR (KBr, cm^{-1}): 3224 (m, (ν(OH)), 3121 (w), 3086 (w), 1679 (m, (*δ*(OH_2)), 1608 (m), 1600 (m), 1575 (w), 1565 (w), 1496 (m), 1475 (m), 1444 (m), 1315 (m), 1248 (w), 1179 (w), 1159 (w), 1028 (m), 1017 (m), 955 (s, ν(Mo=O)), 930 (s, ν(Mo=O)), 916 (s, ν(Mo=O)), 868 (s, ν(Mo=O)), 757s, 682 (s, br, (ν(Mo-O-Mo)), 654 (m), 636 (sh), 514 (s,br, (ν(OMo_3)), 439 (w), 415 (w), 400 (m), 368 (w), 317 (w). Selected FT-Raman (cm^{-1}): 3079 (w), 1597 (m), 1565 (w), 1494 (w), 1431 (w), 1319 (m), 1268 (w), 1160 (w), 1060 (w), 1023 (m), 961 (m), 911 (vs), 870 (m), 768 (w), 735 (w), 674 (vs), 653 (m), 437 (w), 396 (w), 362 (w), 315 (m), 255 (m), 236 (w), 183 (vs), 131 (w).

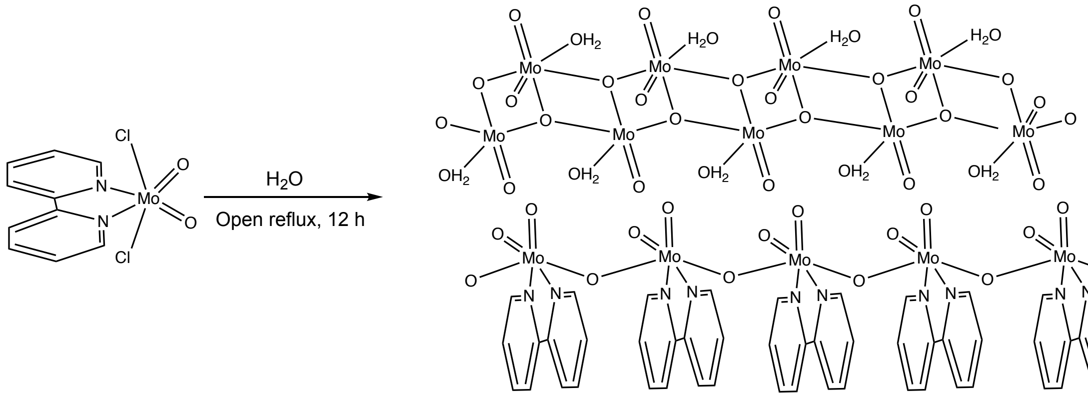


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Figure 9.24. Illustration of the synthesis route to {[MoO_3(bipy)][MoO_3(H_2O)]}$_n$ (**1**).

$[Mo_8O_{22}(OH)_4$(di-*t*Bu-bipy)$_4]$ (**2**) was prepared by addition of $[MoO_2Cl_2$(di-*t*Bu-bipy)] (0.75 g, 1.61 mmol) and water (25 mL) to Schlenk tube, which were refluxed for 12 h under air using an external oil bath as a heating source. The resultant white solid was separated from the pink aqueous mother liquor (pH ≅ 2) by filtration and washed with water (2 x 10 mL), acetone (2 x 10 mL) and diethyl ether (2 x 10 mL) and dried under vacuum. The characterization performed to the compound 2 is in excellent agreement with previous literature data.[16] Yield (0.36 g, 79 %). Anal. Calcd for $C_{72}H_{100}Mo_8N_8O_{26}$ (2261.12): C, 38.24; H, 4.45; N, 4.95. Found: C, 37.80; H, 4.31; N, 4.94. Selected FT-IR (cm^{-1}): v = 3262 (m), 2967 (s), 2936 (sh), 2906 (m), 2870 (m), [1615 (vs), 1548 (m), 1410 (vs) (bipy C=C and C=N str)], [935 (vs), 923 (s), 914 (vs), 899 (vs), 882 (vs), 865 (vs) v(Mo=O)], 850 (vs) (ligand mode), [829 (vs), 777 (vs), 751 (s), 719 (s), 640 (vs,br) v(Mo–O–Mo) and v(OMo_3)]. Selected FT-Raman (cm^{-1}): v = 3072 (m), 2972 (s), 2929 (m), 2905 (m), 1608 (s), 1541 (vs), 1415 (s), 1318 (vs), 957 (s), 934 (vs), 922 (vs), 900 (s), 863 (s), 827 (m), 802 (m), 781 (m), 718 (s). ^1H NMR (400 MHz, CD_3CN, 25 °C, ppm): δ = 8.56 (d, bipy), 8.44 (s, bipy), 7.43 (d, bipy), 1.37 (s, $C(CH_3)_3$). ^{13}C CP MAS NMR: δ = 31.0, 31.6 ((CH$_3)_3$C, (CH$_3)_3$C′), 34.9, 36.0 (($CH_3)_3$*C*, ($CH_3)_3$*C′*), 117.3–120.0, 126.3, 150.1, 151.1, 151.9, 153.4, 162.7, 163.9, 167.3 (C(2,2′)-C(6,6′)).

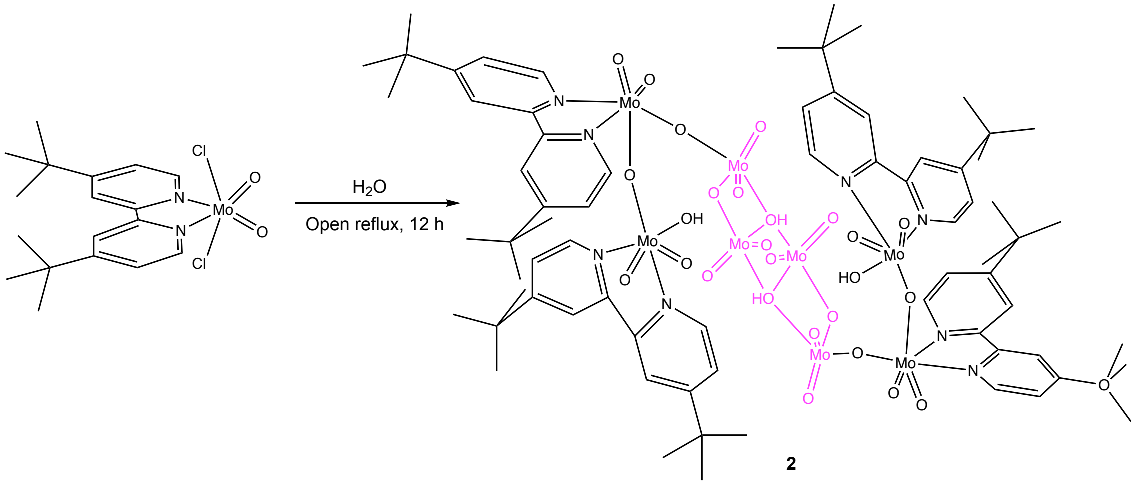

Figure 9.25. Illustration of the synthesis route to the octanuclear complex $[Mo_8O_{22}(OH)_4$(di-*t*Bu-bipy)$_4]$ (**2**). The purely inorganic core $Mo_4O_8(\mu_3\text{-}OH)_2(\mu_2\text{-}O)_2$ is highlighted in pink.

9.4.3. ODS of a model diesel

The desulfurization experiments were carried out using a multicomponent model diesel containing 3000 ppm of sulfur. The sulfur compounds present in the model diesel were dibenzothiophene (1000 ppm), 4-methyldibenzothiophene (1000 ppm) and 4,6-dimethyldibenzothiophene (1000 ppm), which were dissolved in *n*-octane. Model diesel and extraction solvent ([BMIM]PF_6) were added to a 5-mL borosilicate vessel under atmospheric pressure, followed by 0.26 mmol of H_2O_2 and 10 μmol of catalyst **1** or **2**, at 70 °C.

The final conditions applied resulted from the optimization of different parameters: amount of catalyst (5, 10 and 15 μmol), extraction solvent (MeCN, [BMIM]PF_6 and [BMIM]BF_4) and absence of solvent, temperature (50 and 70 °C), amount of H_2O_2 (0.13, 0.26 and 0.60 mmol) and volume of the chosen extraction solvent (0.250, 0.375 and 0.750 mL). The ODS reactions are generally composed by a biphasic liquid-liquid system combining two different processes, extraction and catalytic oxidation. The extraction step, which occurs before the addition of oxidant, results from the transfer of sulfur compounds from the non-polar phase (model diesel) to the polar solvent phase by vigorously stirring for 10 min at 70 °C. After this time, the desired amount of 30% aq. H_2O_2 is added and the catalytic oxidative stage starts, where the transferred compounds are oxidized to the corresponding sulfones and/or sulfoxides.

The periodic quantification of sulfur content was performed by GC analysis through the injection of aliquots withdrawn from the model diesel phase during the ODS reactions. Tetradecane was used as standard to dilute the aliquot removed. The recyclability tests were performed by the removal of the model diesel phase at the end of each catalytic cycle. Depending on the recycling process applied, the extraction phase containing the catalyst was washed with a mixture of ethyl acetate and diethyl ether (1:1 v/v) to remove the oxidized species (cycles denoted “recycled”) or used without any cleaning treatment (cycles denoted “reused”). All reused and recycled cycles were performed under the same initial experimental conditions by the addition of fresh portions of model diesel and H_2O_2.

9.4.4. ODN of a model diesel

The denitrogenation studies were performed using a model diesel containing 400 ppm of nitrogen compounds known to be present in fuel compositions: quinoline (200 ppm) and indole (200 ppm) dissolved in *n*-octane. All the applied conditions (extraction solvent, amount of catalyst and H_2O_2) as well the reaction steps performed were provided by the optimized desulfurization studies (Section 9.2.2.1).

9.4.5. Simultaneous ODS and ODN of a model diesel

The removal/oxidation of nitrogen and sulfur compounds from the model diesel was performed using a *n*-octane solution with a sulfur and nitrogen content corresponding to 3000 and 400 ppm, respectively. The conditions applied during these studies came from the optimized desulfurization studies. The catalytic stabilities of catalysts **1** and **2** were tested for several recycling and reutilization cycles, using the methods described in Section 9.2.2.3.

9.4.6. ODS of an untreated diesel

An unrefined diesel sample containing 2300 ppm of sulfur supplied by Galp Energia was treated applying the best model diesel conditions (H_2O_2/S/catalyst/[BMIM]PF_6 (catalyst = **1** and **2**) at 70 °C) for 2 h. The systems containing each catalyst were reused for three consecutive cycles, through the removal of diesel phase (to be analysed) and addition of new fresh portions of untreated diesel and oxidant.

9.5. References

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Chapter 10

CONCLUSIONS AND FINAL CONSIDERATIONS

10. Conclusions and final considerations

10.1. Conclusions

The global impact, over the last 200 years, of SO_x emissions resulting from the burning of fossil fuels has led to the imposition of environmental restrictions regarding the sulfur level in transportation fuels. The production of ultra-low sulfur fuels is very costly for refineries, due to the harsh conditions (high temperatures and high H_2 pressures) needed that are incompatible with other fuel requirements, some of them responsible for the quality of fuel.

Oxidative desulfurization (ODS) is a promising technology for the removal of sulfur at low temperatures and under atmospheric pressure. This process is based on the oxidation of sulfur compounds to the corresponding sulfoxides and/or sulfones and subsequent removal by extraction or adsorption. The key to improving the selectivity of the oxidant towards sulfoxidation while minimizing waste and preventing the oxidation of olefins or aromatic compounds present in fuels consists of the application of suitable catalysts with atom economical oxidants, such as H_2O_2.

Oxometal complexes, especially those containing molybdenum as the metal center, have been extensively studied as catalysts for several oxygen atom transfer reactions involving a variety of substrates, from alkenes, olefins, amines and alcohols, to sulfides. Their importance is easily recognized by the number of catalytic systems described based on these reactions, which have, however, usually employed less sustainable oxidants such as *t*BHP.

In the light of current environmental concerns, this PhD project had as its main target the development of efficient and sustainable catalytic ODS systems based on the unexplored Mo(VI)/H_2O_2 combination. Therefore a wide-range of different Mo(VI) complexes, from organometallic tricarbonyl molybdenum complexes to dioxomolybdenum complexes bearing mono- and bidentate organic ligands with nitrogen or oxygen donor atoms, and peroxomolybdates (and peroxotungstates), were applied for the first time in the oxidation of refractory sulfur compounds in the presence of H_2O_2 as oxidant. Although the general idea had been to achieve complete desulfurization of model and real diesels, it was also important to make the ODS process competitive and sustainable. Therefore, attention was given to several parameters by constantly performing optimization studies. An important example is the H_2O_2/S ratio. Most of the catalytic systems present in the literature are active for the oxidation of sulfur compounds, but using high H_2O_2/S ratios. Besides the cost associated with the use of “industrial” amounts of oxidant it is important to understand that liquid fuels are complex mixtures of hydrocarbons, aromatics and molecules containing a heteroatom, such as sulfur, nitrogen and oxygen, which can also be oxidized, consuming part of the oxidant and impairing the quality of the fuel. These side reactions may accelerate at temperatures above 80 °C, so the use of low amounts of H_2O_2 and mild temperatures is important. The conventional ODS systems are generally composed of a biphasic liquid-liquid system formed by the diesel and an immiscible extraction solvent phase, in which are usually used flammable and volatile organic polar solvents. The solvent chosen is a crucial parameter, since it allows the extraction of the refractory sulfur compounds, usually following the order BT > DBT > 4-MDBT > 4,6-DMDBT, which is related with their molecular diameters and geometry, as well as with their solubility in different polar solvents. Most of these harmful solvents have been substituted by ionic liquids (ILs) due to their unique physical and “greener” properties (nonvolatility, ability to dissolve organic and inorganic compounds, good thermal and chemical stability, non-flammability and recycling capacity). Also, the many possible combinations of cation and anion allows the extraction capacity of ILs to be improved. Despite all the advantages inherent to the use of ILs, their production cost and the energy necessary to promote their regeneration are important concerns. These potential drawbacks can be minimized by decreasing the dosage of IL during the ODS process, using biphasic systems with a higher amount of diesel than the extraction solvent. More recently, a new class of versatile solvents prepared by the combination of non-toxic and biodegradable substrates has emerged as an alternative environmentally friendly reaction medium. These solvents, known as deep eutectic solvents (DES), are in a growth stage, with their potential as extraction solvents for the removal of sulfur compounds from model diesel and real liquid fuels still being largely unknown. Despite all the advantages that come from the application of biphasic systems composed of ILs or DES, the best solvent for oxidative desulfurization should be “no solvent”, which besides the low associated costs and the use of mild conditions, would promote an improvement of fuel specifications, such as octane/cetane number or aromatics content, which are essential for high fuel quality.

Molybdenum complexes, such as IndMo(CO)$_3$Me (Chapter 3) and the peroxomolybdate $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (Chapter 8), showed high performances in solvent-free systems with low H_2O_2/S ratios, i.e. 6.5 and 3.7, respectively, giving sulfur-free model diesels after 2 h and 3 h of ODS reaction. In model and real diesel media these catalysts behave as heterogeneous catalysts since they can be recovered at the end of each cycle. Their desulfurization efficiencies were maintained for several continuous cycles, without the application of any “cleaning” process. Despite the outstanding results obtained for the model diesel treatment, the same effective behaviour was not observed for the treatment of real diesel samples (2300 ppm S) supplied by Galp Energia. This drawback was overcome by the use of a biphasic medium based on MeCN or [BMIM]PF$_6$. In fact, in a biphasic liquid-liquid system, the carbonyl complex IndMo(CO)$_3$Me revealed the highest desulfurization performance ever obtained for the treatment of a real diesel, i.e. maintaining all the model diesel conditions and using an IL as extraction solvent, 95.9% of sulfur compounds were removed from an untreated diesel containing an initial amount of sulfur corresponding to 2300 ppm (Figure 10.1), leading to a final sulfur content of 95 ppm. Following the same pattern, real diesels containing 129, 381, 372 and 259 ppm of sulfur were obtained in the presence of [MoO$_2$Cl$_2$(DEO)] and [MoO$_2$Cl$_2$(DMB)$_2$] (Chapter 4), CpMo(CO)$_3$Me (Chapter 2) and $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (Chapter 7), respectively (Figure 10.2). Albeit less prominently, initial extraction treatments with MeCN or DMF also had some influence on the final sulfur values. These results are an indication of the remarkable influence of the diesel’s composition for the success of the ODS process. The presence of an extraction solvent during the catalytic stage appears to work as a barrier, avoiding the interaction of other potentially oxidizable species. The complexes [MoO$_2$Cl$_2$(DEO)] and [MoO$_2$Cl$_2$(DMB)$_2$] (Chapter 5) were also applied in ODS of a real diesel, using a DES (ChCl/PEG) as extraction solvent. From this combination, diesels containing 462 and 430 ppm of sulfur were obtained, respectively. These results reveal the possibility of substitution of ILs, maintaining the recycling possibilities and also high extraction efficiencies.

The identification of active species and the related mechanism responsible for their formation was not a priority of the present thesis, in which the main concern was to develop novel catalytic systems that allowed sulfur-free model and real liquid fuels to be achieved. Also, reaction media based on ILs, such as [BMIM]PF$_6$ and [BMIM]BF$_4$, are known to complicate the isolation and possible characterization of the active species. However, the appearance of a pale-yellow colour during most of the ODS reactions, namely in those employing molybdenum complexes, with the exception of the peroxomolybdate present in Chapter 8, was a validation of the presence of active species. The use of molybdenum complexes as efficient catalysts for sulfoxidation reactions is still an unexplored area, with most of the experimental and theoretical research having been performed for epoxidation reactions. By using data obtained from these epoxidation studies and, whenever the reaction conditions allowed, performing experimental tests between the catalyst and H_2O_2, some of the active species could be identified. The carbonyl complexes bearing a cyclopentadienyl ligand (Chapter 2) act as precursors of the oxo-peroxo species $[CpMoO(O_2)R]$, in which the metal coordinated CO ligands disappear and the Mo-bonded R group remains coordinated to the metal center, thereby influencing the catalytic performance obtained for each $[CpMo(CO)_3Me]$, $[CpMo(CO)_3PhCO_2Me]$ and $[CpMo(CO)_3CH_2COOH]$ precatalyst. Nitrogen donor ligands containing aromatic substituents are known to improve the catalytic efficiency, resulting in the preparation of several active and selective catalysts based on these ligands. An example is the dioxomolybdenum(VI) catalyst $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$ (Chapter 6) which showed to efficiently oxidize/remove refractory sulfur compounds from model and real diesels (Figure 10.2). The pale-yellow colour observed during the catalytic stage was identified as the oxo-peroxomolybdenum(VI) complex $[MoO(O_2)_2(\text{di-}t\text{Bu-bipy})]$. This was the first work presenting the recyclability of oxo-metal complexes entrapped in ILs with the aim of treating real diesel samples. The same process was later applied for two hybrid molybdenum compounds (Chapter 9), which also maintained their catalytic efficiencies for diesel treatment for three consecutive ODS cycles. In the case of the complex $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, a solvent-free system was employed for desulfurization of a model diesel and real diesel, enabling the recovery of the catalyst and its characterization by several techniques. In this type of medium the complex behaves like a heterogeneous catalyst. The characterization revealed a high structural stability during the ODS reactions, i.e. the peroxomolybdate catalyst maintained its structure over ten consecutive cycles and when applied in different diesel solutions. Interestingly, an analogous catalyst containing a different transition metal as metal center (tungsten instead of molybdenum) (Chapter 7) was not structurally stable during the ODS reactions, with new peroxophosphotungstate species being formed. It should be noted, however, that despite the low structural stability, its activity remained constant for nine consecutive cycles. Its immobilization in a derivatized SBA-15 support resulted in a composite material with similar activity and structural fragility after ODS application. Although the incorporation did not bring improvements in terms of desulfurization efficiency and stability, the development of heterogeneous systems based on the immobilization of homogeneous catalysts in solid supports is an important strategy at the industrial level in order to overcome separation and recycling problems.

The environmental pollution caused by sulfur emissions, such as SO_2 and SO_3 resulting from the combustion of liquid fuels, has gained worldwide attention and for that reason many industrialized countries have modified their legislations to limit the sulfur content in diesel and gasoline to less than 10 ppm. Interestingly, nitrogen that is also a harmful element present in liquid fuels has been ignored, continuing to contribute indiscriminately to the increased concentration of greenhouse gases. Also, the presence of nitrogen compounds during the hydrodesulfurization treatments decreases the effectiveness of the process, limiting the number of sulfur compounds removed from the liquid fuels. Therefore, under the same desulfurization conditions obtained from the optimization studies in the presence of the hybrid molybdenum complexes $[MoO_3(bipy)][MoO_3(H_2O)]_n$ and $[Mo_8O_{24}(OH)_4(di\text{-}t\text{Bu-bipy})_4]$, some denitrogenation studies were performed. When both treatments were performed together, i.e. with a model diesel containing all the sulfur and nitrogen compounds, the initial extraction occurred in the order indole > quinoline > DBT. The sulfur compounds with alkyl-substituents were not extracted during this stage, showing the possible occurrence of a competition between the compounds with the different heteroatoms. During the catalytic stage, substantial differences were not observed. The systems containing each of the hybrid complexes were reutilized and recycled for five consecutive cycles, from which resulted a continuously efficient desulfurization and denitrogenation.

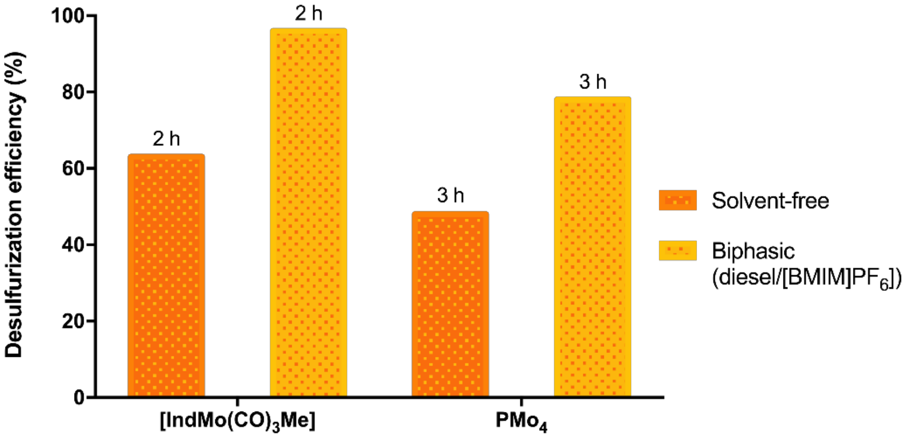

Figure 10.1. Desulfurization data for ODS of a real diesel (2300 ppm), using $[IndMo(CO)_3Me]$ (Chapter 3) and PMo_4 (Chapter 8) as catalysts, under solvent-free and biphasic (diesel/IL) systems with H_2O_2 as oxidant, at 70 °C. Results obtained for 2 h and 3 h of ODS reaction.

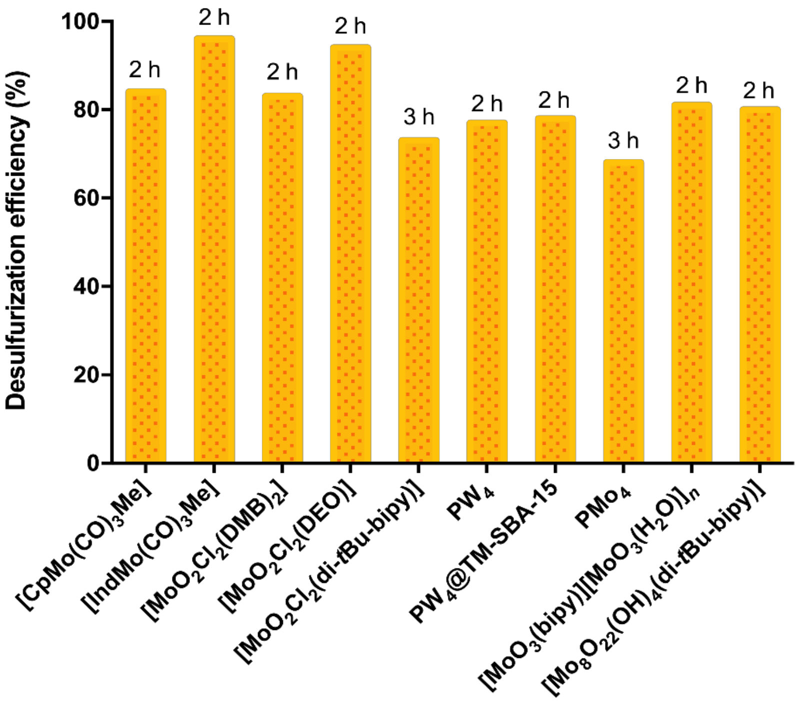

Figure 10.2. Desulfurization data for ODS of a real diesel (2300 ppm), using different catalysts (Chapter 2-9), $[BMIM]PF_6$ or MeCN as extraction solvent and H_2O_2 as oxidant, at 50 °C or 70 °C. Results obtained for 2 h or 3 h of ODS reaction.

10.2. Final Considerations

The results presented in this thesis opened a new route to design efficient ODS and ODN processes to treat efficiently real fuels, using molybdenum complexes as catalysts in the presence of H_2O_2 as environmentally friendly oxidant. ODS and ODN optimization was performed through ligand design, application of other types of Mo(VI) families or as mentioned above by the heterogenization of these complexes on suitable solid supports. The final heterogeneous materials should combine the best features of homogeneous catalysts, such as selectivity and catalytic activity, with the advantages of support solids. Also, a continuous application in different DES must be investigated as biodegradable and cheap reaction media, being a sustainable solution for substituting ILs while maintaining similar recyclability capacities. However, from a sustainability point of view, in order to reduce possible waste, the best option is the use of solvent-free systems, in which these molybdenum complexes present non-miscibility, allowing their removal and later characterization, and favouring the possible identification of active species. Regarding ODS, it is well known that the desulfurization of real fuels is much more difficult than model diesels. Besides sulfur compounds which are present in several forms (mercaptans, sulfides, disulfides, thiophenes and their derivatives), the fuels also possess a complex mixture of hydrocarbons, which has a strong impact on the ODS process, promoting a competitive oxidation, decreasing the effectiveness of the catalyst/oxidant. The remarkable diversity of fuels results in a variety of physical properties, which have numerous important roles in fuel technology and utilization, e.g. boiling point, viscosity and density. Thus, it is important to understand all the fundamental links between composition, structure and properties to estimate expected properties and clean efficiently the fuels without modifying important properties. This can be achieved by the development of more complex model diesels more similar to real fuels or, if possible, performing all the studies, from optimization of the reaction parameters to the final application, with the real liquid fuels. Also, the identification of the sulfur families that remain in desulfurized diesel, e.g. benzothiophenes, aliphatics or others, would be an important achievement that would bring new developments in this area.