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A sustainable peroxophosphomolybdate/H$_2$O$_2$ system for the oxidative removal of organosulfur compounds from simulated and real high-sulfur diesels

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GRAPHICAL ABSTRACT
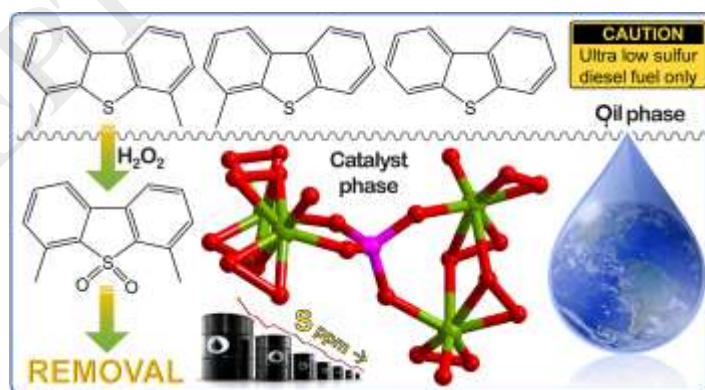
HIGHLIGHTS

- **Crystal structure of the peroxophosphomolybdate [(*n*-C$_4$H$_9$)$_4$N]$_3$\{PO$_4$[MoO(O$_2$)$_2$]$_4$\}.**

- Complete desulfurization of a multicomponent model diesel (3 h, 70 °C).

- Catalyst pluses include high stability, low H_2O_2/S ratios, and no leaching effects.

- Easy catalyst separation promotes its efficient reuse in many desulfurization cycles.

- Desulfurization efficiency of 78% achieved with a high-sulfur untreated real diesel.

ABSTRACT

Highly efficient, deep desulfurization of a multi-component model diesel containing benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) has been achieved by using the peroxophosphomolybdate [(n-C_4H_9)$_4$N]$_3${PO$_4$[MoO(O$_2$)$_2$]$_4$} (Q$_3$PMo$_4$) directly as catalyst, and aqueous H_2O_2 as oxidant. Q$_3$PMo$_4$ behaves as a heterogeneous catalyst in the complete oxidation of the various sulfur compounds to the corresponding sulfones within 3 h at 70 °C, using a relatively low H_2O_2/S molar ratio of 3.7, and could be recycled for ten times with only a minimal decrease in activity. A study was performed to adapt the catalyst Q$_3$PMo$_4$ for the removal of sulfur from a real untreated diesel while maintaining a low, economically desirable, H_2O_2/S molar ratio of 2.4. The highest desulfurization performance was achieved in the presence of an extraction solvent during the catalytic oxidative stage, reinforced by two extraction steps before and after sulfur oxidation. Under these conditions, the sulfur content of the real diesel was reduced from 2300 to 500 ppm (78% desulfurization efficiency) after 3 h.

1. Introduction

Of all the refined products obtained from crude oil, transportation fuels (e.g. gasoline, diesel and jet fuel) have the highest value. One of the central conversion requirements in refineries is the removal of sulfur compounds that are carried over from crude oil during the distillation process [1]. In middle-distillate-range fractions, such as diesel, sulfur is present in the form of condensed heterocyclic compounds like benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives [2,3]. These compounds are detrimental to the oil-refining process since they may

cause catalyst deactivation and equipment corrosion. Upon combustion, the sulfur in fuels is emitted in the form of sulfur oxide (SO_x) gases and sulfate particulate matter, which can poison emission control catalysts, reduce engine performance, and lead to undesirable effects on human health (e.g. respiratory disorders) and the environment (e.g. acid rain) [3,4]. Current regulations require the removal of sulfur in transportation fuels to very low levels (10 ppm or less), forcing existing technologies to be pushed into inefficient operating regimes.

Hydrodesulfurization is the most commonly used method in the petroleum-refining industry to reduce the sulfur content of fuels [1-4]. However, benzothiophenes and dibenzothiophenes, and especially their sterically-hindered derivatives such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), are much more difficult to remove by HDS, requiring larger reactor volumes, longer processing time, high temperatures from 300 °C to 450 °C, and high hydrogen pressures from 3.0 to 5.0 MPa, which affect the economic viability of the process and fuel specifications [3]. Therefore, the development of alternative and/or complementary desulfurization methods to produce sulfur-free fuels is necessary, but still a challenge for both academia and industry. A few novel desulfurization processes have proved to be capable of achieving the ultra-low sulfur levels. 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 [1-7]. 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 favored 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)$_3$Me] (Cp = η^5-cyclopentadienyl)) [8], [MoO$_2$Cl$_2$(4,4′-di-*tert*-butyl-2,2′-bipyridine] [9] and oxoperoxo complexes of the type [MoO(O$_2$)$_2$(L)] (L = 1,10-phenanthroline, amino acid) [10,11], organic salts of polyperoxomolybdates such as $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (hereafter abbreviated as PMo$_4$) [12-14] and $[Mo_2O_3(O_2)_4]^{2-}$ [15], and salts of polyoxomolybdates such as $[MMo_6O_{24}H_6]^{n-}$ (M = Ni, Co) [16,17], $[Mo_7O_{24}]^{7-}$ [18], $[Mo_8O_{26}]^{4-}$ [19,20], and $[PMo_{12}O_{40}]^{3-}$ (hereafter abbreviated as PMo$_{12}$) [21-24]. With H$_2$O$_2$ 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 heteropolyperoxomolybdate PMo_4 [25,26].

In the present work, the tetrabutylammonium salt $[(n\text{-}C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$ has been applied in processes for the ODS of a model diesel and an untreated real diesel. 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.

2. Experimental Section

2.1. 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-Aldrich, 98%), dibenzothiophene (Sigma-Aldrich, 98%), 1-benzothiophene (Fluka, 95%), 4,6-dimethyldibenzothiophene (Alfa Aesar, 97%), n-octane (Sigma-Aldrich, 98%), 1-butyl-3-methylimidazolium hexafluorophosphate (Sigma-Aldrich, 97%), tetradecane (Sigma-Aldrich, 99%), acetonitrile (Fisher Chemical, 99.99%), dimethylformamide (Fischer, 99.99%) and 30% aqueous hydrogen peroxide (Sigma-Aldrich).

Elemental analysis for C, H, and N was performed at the University of Aveiro with a Leco TruSpec 630-200-200 analyzer. 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 ($55 \text{ cm}^3 \text{ s}^{-1}$) and fused silica SPB-5 Supelco capillary columns (30 m × 0.25 mm i.d.; 25 μm film thickness) were used.

4

The analysis of the sulfur content of the real diesel sample received from Galp Energia was carried out by ultraviolet fluorescence, using a Thermo Scientific equipment with TS-UV module for total sulfur detection, and by Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

2.2. Synthesis of $[(n-C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$ (Q_3PMo_4)

The peroxophosphomolybdate salt Q_3PMo_4 was prepared by following published procedures with slight modifications [12,25]. A solution of tetrabutylammonium chloride (0.861 g, 3.1 mmol) in 30% H_2O_2 (40 mL) was added to phosphomolybdic acid hydrate (1.82 g, 1.0 mmol) in 30% H_2O_2 (10 mL). The mixture was stirred vigorously at 40 °C for 5 hours. After cooling to ambient temperature, the mixture was vigorously stirred for a further 48 hours. 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, $\nu(O-O)$), 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).

2.3. Single-crystal X-ray diffraction

Single-crystals of Q_3PMo_4 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) [27]. Diffraction data were collected on a Bruker X8 Kappa APEX II CCD area-detector diffractometer controlled by the APEX2 software package [28]: 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 [29]. Images were processed using SAINT+ [30], and absorption correction was carried out using the multi-scan semi-empirical method implemented in SADABS [31]. 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 [32,33]. 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 [32,34]. 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 Q_3PMo_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 $0.17 \times 0.09 \times 0.05$ 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/.

2.4. ODS of a model diesel

The oxidative desulfurization procedures were performed using a model diesel containing dibenzothiophene (DBT), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) dissolved in *n*-octane with approximately 500 ppm of S or 0.0156 mol dm^{-3} of each one. The ODS studies were performed using either an extraction solvent-free system or 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 Q_3PMo_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 the 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 30% aq. H_2O_2 (0.13, 0.26 or 0.39 mmol), dosage of Q_3PMo_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 Q_4PMo_4 catalyst is dissolved in these extraction solvents. Before addition of 30% aq. 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, 30% aq. 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 recyclability tests (performed for the system without extraction solvent), the model diesel phase was removed at the end of each cycle and the solid catalyst 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.

The miscibility between model diesel/acetonitrile phases was analyzed during the ODS process. A loss of model diesel volume after desulfurization treatment was observed. This was of 4% after initial extraction and 9% after the oxidative catalytic step.

2.5. ODS of an untreated real 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 hours). 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).

The miscibility between real diesel/acetonitrile phases was also analyzed. Similar to the model diesel, a loss of real diesel volume occurred, which amounted to 7% after the oxidative catalytic step and 16% after the final extraction with acetonitrile.

3. Results and Discussion

3.1. Catalyst preparation and crystal structure

The peroxophosphomolybdate salt Q_3PMo_4 was prepared by the reaction of phosphomolybdic acid hydrate with excess H_2O_2 followed by the addition of tetrabutylammonium chloride [12,25]. FT-IR, FT-Raman and ^{31}P NMR data for Q_3PMo_4 were in agreement with those reported previously for the same salt [12,25,35] or for other organic salts of the PMo_4 anion [26,36,37].

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 [38-40]) revealed only two examples involving the PMo_4 cluster ion with organic molecules: Tris(tetra-*n*-hexyammonium)·{$PO_4[MoO(O_2)_2]_4$} [41] and (4-methoxyquinoline-N-oxide)·{$H_3P[OMo(O_2)_2O]_4$} [42]. We therefore set out to determine the structure of Q_3PMo_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

8

tetrabutylammonium cations. The tetranuclear anion contains four crystallographically independent molybdenum centers with similar coordination environments (Fig. 1a): 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 [39,40]. 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 (Fig. 1b; see Table S1 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 (Fig. 1c).

3.2. Optimization of the ODS system

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 model diesel/extraction solvent) in which MeCN (miscible with aq. H_2O_2) or the ionic liquid (IL) [BMIM]PF_6 (immiscible with aq. H_2O_2) were employed as extraction solvents.
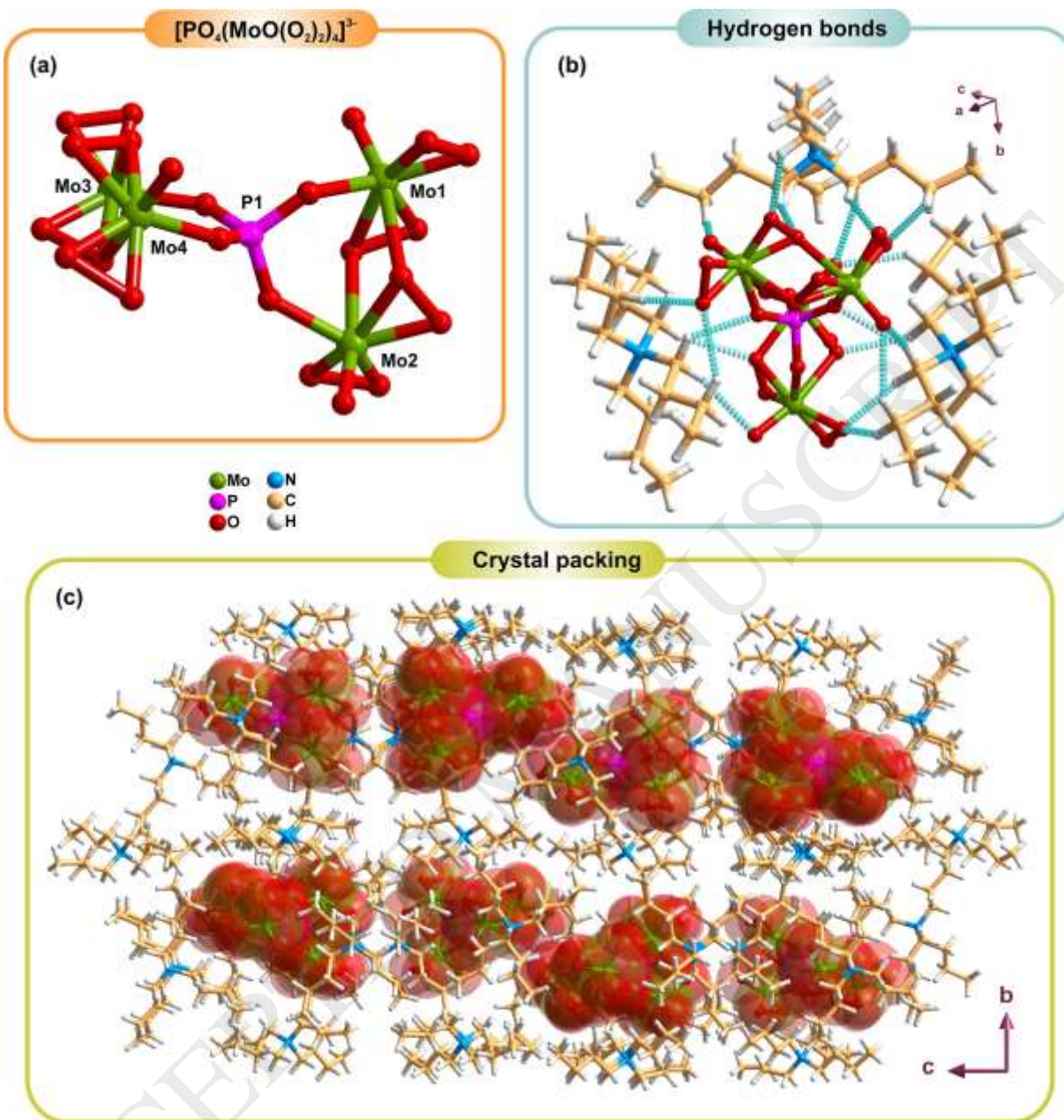
Fig. 1 Selected features of the crystal structure of the compound $[(n\text{-}C_4H_9)_4N]_3\{PO_4[MoO(O_2)_2]_4\}$: (a) Ball-and-stick representation of the structure of $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, with labelling of the Mo and P centers; (b) C–H···O hydrogen bonding interactions (drawn as dashed blue lines) between adjacent inorganic anions and organic cations; (c) crystal packing viewed along the [1 0 0] direction of the unit cell, with the tetrabutylammonuim cations represented in ball-and-stick mode and the $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ anions shown in semi-transparent space-filling mode.

We first analyzed 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 catalyst Q_3PMo_4 was not dissolved in the model diesel, operating as a heterogeneous catalyst. Conversely, 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 (0.75 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 1). 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 model diesel/water system showed the highest ODS performance (i.e. after addition of the oxidant), promoting complete desulfurization after 4 hours of reaction (Fig. 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 prevenient from the use of the organic (MeCN) or IL extraction solvents.

Table 1 Values (%) corresponding to the initial extraction of each sulfur compound in the presence of different extraction solvents.

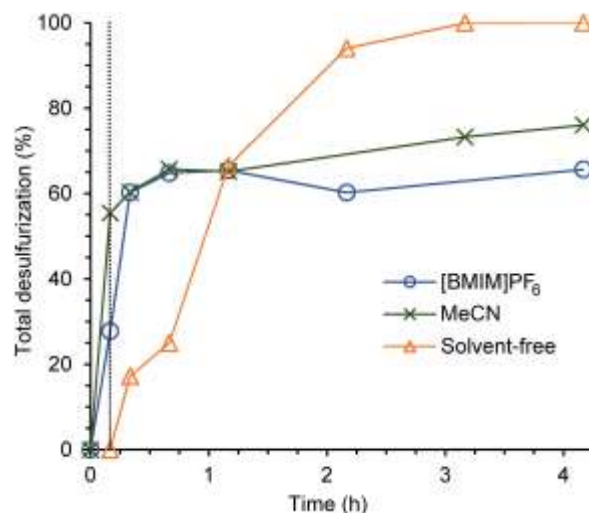| Sulfur compounds	[BMIM]PF_6	MeCN
DBT	29.3	58.4
BT	37.8	60.2
4,6-DMDBT	7.5	47.6

Fig. 2 Desulfurization profile for the ODS system using a multicomponent model diesel (1500 ppm S), catalyst Q_3PMo_4 (5 µmol), 30% aq. H_2O_2 (0.13 mmol), in the absence or presence of an extraction solvent ([BMIM]PF$_6$ or MeCN), and with a reaction temperature of 70 °C. The vertical dashed line indicates the instant the ODS reaction was started by addition of oxidant.

Fig. 3 shows the influence of the amount of Q_3PMo_4 (1, 2, 5 and 8 µmol) on catalytic ODS using the solvent-free system (0.13 mmol of 30% aq. H_2O_2, 0.75 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. for the same catalyst Q_3PMo_4 are consistent with these findings [12]. 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.
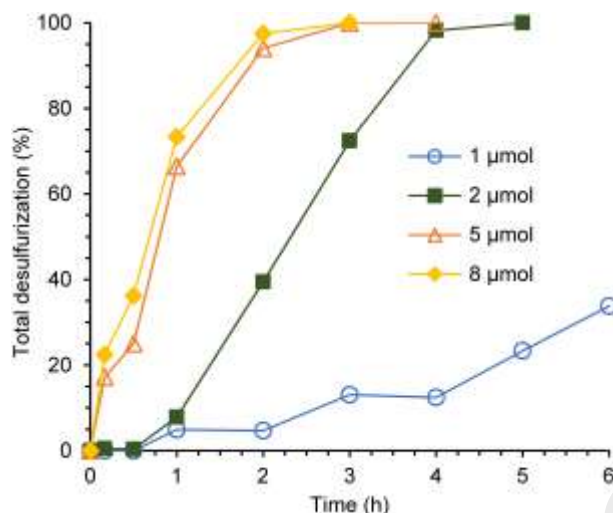
12

Fig. 3 Kinetic profiles for the ODS of a multicomponent model diesel (1500 ppm S), catalyzed by different amounts of Q_3PMo_4, in the presence of H_2O_2 (0.13 mmol) as oxidizing agent, at 70 °C.

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. Fig. 4 displays the desulfurization profile of the model diesel using the solvent-free system, in the presence of different amounts of 30% aq. 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 [43,44]. However, in the present case, the chosen POM (Q_3PMo_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. Zhu et al. proposed a detailed mechanism involving the same peroxophosphomolybdate catalyst for sulfur oxidation [13]. The sulfur compounds are oxidized to sulfoxides and consecutively to sulfones by interaction with the peroxo groups ($Mo(O_2)$) of the catalyst. The oxygen from the peroxo $Mo(O_2)$ group is transferred to the sulfur compound, forming an $Mo(O)$ group. This latter group interacts with the H_2O_2 oxidant to regenerate the $Mo(O_2)$ group [13].

13

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.
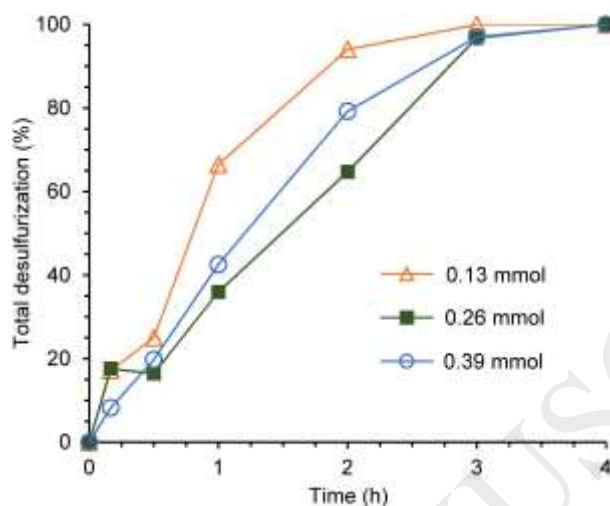

Fig. 4 Kinetic profiles for the ODS of a multicomponent model diesel (1500 ppm S), catalyzed by Q_3PMo_4 (5 µmol), using different amounts of 30% aq. H_2O_2, and a reaction temperature of 70 °C.

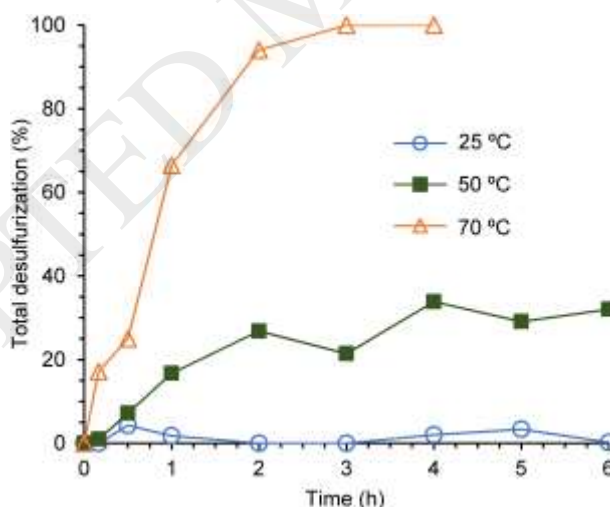**Fig. 5** Kinetic profiles for the ODS of a multicomponent model diesel (1500 ppm S), catalyzed by Q_3PMo_4 (5.0 µmol), using 30% aq. H_2O_2 as oxidizing agent (0.13 mmol), at different reaction temperatures.

The influence of the reaction temperature was studied for the oxidative desulfurization process carried out using the optimal amounts of catalyst (5.0 µmol) and oxidant (0.13 mmol)

using the solvent-free system. As shown in Fig. 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 behavior is related with the strong dependence of the oxidation reaction rate of the sulfur compounds present in the model diesel on the reaction temperature. Reaction temperatures higher than 70 ℃ were not studied since under these conditions there exists the possibility of oxidizing useful components, such as olefins and hydrocarbons typically present in fuels [45].

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 30% aq. 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 small but measurable increase in the desulfurization rate (Fig. 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.
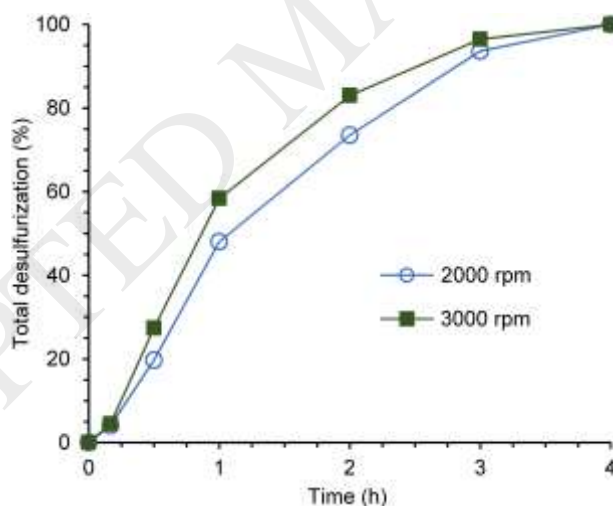

Fig. 6 Kinetic profiles for the ODS of a multicomponent model diesel (1500 ppm S), catalyzed by Q_3PMo_4 (5.0 µmol), using 30% aq. H_2O_2 as oxidizing agent (0.13 mmol), a reaction temperature of 70 °C, and different rotation speeds.

3.3. Catalyst stability and recyclability

15

The promising performance of Q_3PMo_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 recyclability 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 30% aq. H_2O_2, with consecutive ODS cycles being performed under the same experimental conditions. No significant decrease in desulfurization efficiency at 3 hours of reaction was observed during ten consecutive cycles (Fig. 7). Only a slight decrease was observed between the 6th and 7th cycles, after which the sulfur removal at 3 hours 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 [46].
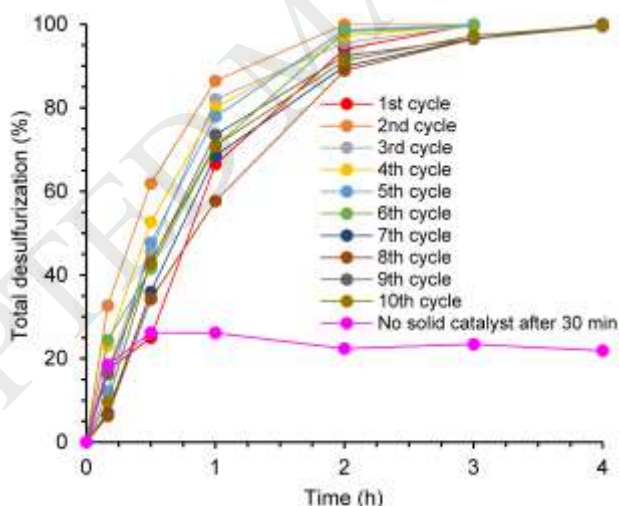

Fig. 7 Kinetic profiles for ten consecutive cycles of ODS of a multicomponent model diesel (1500 ppm S) using Q_3PMo_4 (5 µmol) as catalyst and 30% aq. H_2O_2 (0.13 mmol) as oxidant, at 70 °C.

To investigate the stability of Q_3PMo_4 during the ODS cycles, a leaching test was performed (Fig. 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 analyzed by FT-IR, FT-Raman and ^{31}P NMR

16

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 (Fig. 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 (Fig. 9).
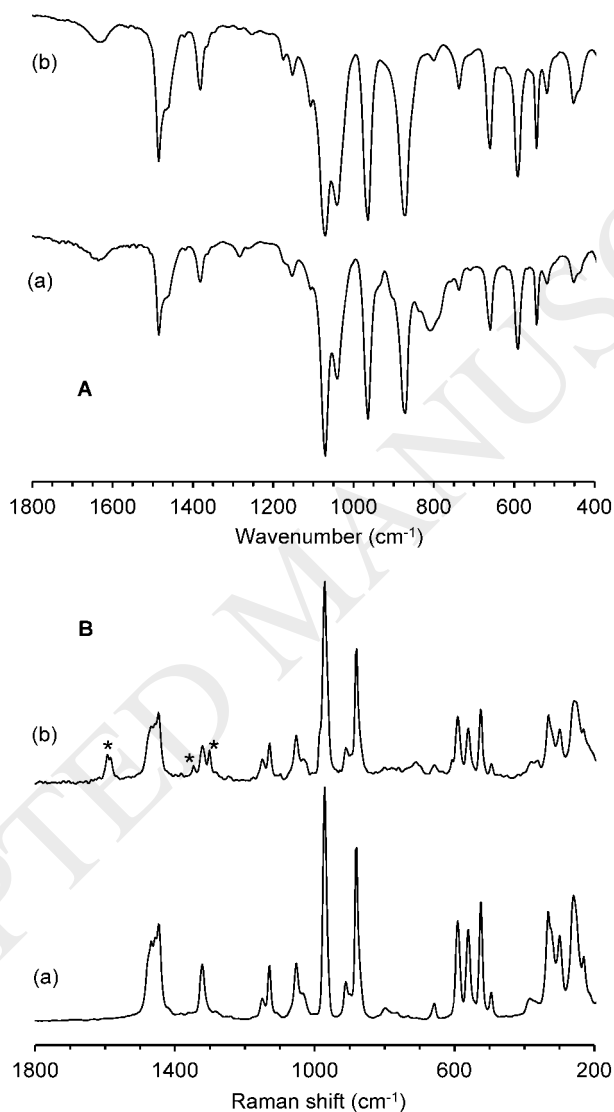

Fig. 8 FT-IR (A) and FT-Raman spectra (B) of Q_3PMo_4 catalyst before (a) and after (b) an ODS cycle under the optimized conditions (solvent-free system, 5 μmol catalyst, 0.13 mmol 30% aq. H_2O_2, 70 °C). The bands marked with asterisks in the Raman spectrum of the recovered catalyst are attributed to 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 [47]).
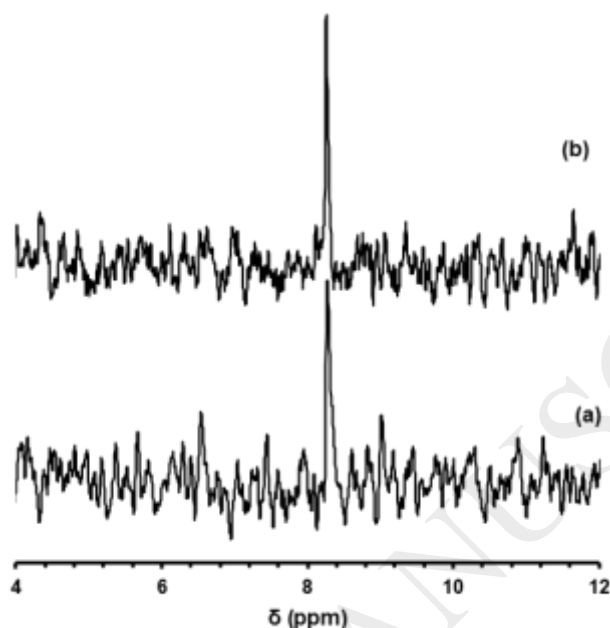
17

Fig. 9 ^{31}P NMR spectra (in CD$_3$CN) of Q$_3$PMo$_4$ catalyst before (a) and after (PMo4_ac) oxidative catalytic use (b) for desulfurization of a model diesel using a solvent-free system.

3.4. Oxidative desulfurization of a commercial untreated diesel

The good results obtained with Q$_3$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 with two fundamental steps: (i) extraction before and/or after the ODS process with an appropriate extraction solvent (MeCN or DMF); (ii) catalytic oxidation, using Q$_3$PMo$_4$ as catalyst and H$_2$O$_2$ as oxidizing agent, at 70 °C. The desulfurization efficiency during the 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.

18

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 30% aq. H$_2$O$_2$. Following previous work [9,48], MeCN was used as an extraction solvent to remove the oxidized sulfur compounds obtained after 3 hours of oxidation. The results show that a higher amount of catalyst did not promote a higher desulfurization efficiency (Table 3, experiments A and B), which parallels the results obtained with the multicomponent model diesel (Fig. 3).

When considering the ODS of real diesels using H$_2$O$_2$ 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$_2$O$_2$/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%) > 0.13 mmol (48%) > 0.26 mmol (38%) (experiments A, C and D in Table 3). When these results are compared with those presented in Fig. 4 for the ODS of the multi-component 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$_2$O$_2$/S = 2.4).

The next parameter to be analyzed was the nature of the extraction solvent (MeCN or DMF) used after the ODS reactions (H$_2$O$_2$/S = 2.4, 5 μmol PMo$_4$) to extract oxidized sulfur compounds. In previous work we ascertained that the highest extraction efficiencies were achieved by performing the extraction at 70 °C for 30 min [8], so these were the conditions used in the present work. When no extraction was performed (experiment F in Table 2), 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%) was significantly better that that with DMF (41%). 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) using a suitable polar solvent can contribute to the improvement of total desulfurization efficiency. For extraction studies using MeCN or DMF (Table 2, 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 [8]. 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, i.e. a biphasic diesel/H_2O system. 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 Q_3PMo_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 3) show that the use of an extraction solvent to dissolve the catalyst was indeed beneficial, with the highest desulfurization efficiency being 78% for the system using [BMIM]PF_6 as the cosolvent 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 2 Experiments performed for ODS of a commercial untreated real diesel.[a]

Experiment	Amount of PMo$_4$ (μmol)	Amount of H$_2$O$_2$ (mmol)	ODS cosolvent	Extractive process before ODS[b]	Extractive process after ODS[c]	Diesel sulfur content (ppm)	Desulfurization efficiency (%)[d]
A	5	0.13	---	---	MeCN	1192	48
B	8	0.13	---	---	MeCN	1234	46
C	5	0.26	---	---	MeCN	1425	38
D	5	0.39	---	---	MeCN	1120	51
E	5	0.13	---	---	DMF	1354	41
F	5	0.13	---	---	---	2100	9
G	5	0.13	---	DMF	MeCN	1345	41
H	5	0.13	---	MeCN	MeCN	1206	48
I	5	0.13	---	DMF	DMF	1275	45
J	5	0.13	---	MeCN	DMF	881	62
K	5	0.13	[BMIM]PF$_6$	---	MeCN	710	69
L	5	0.13	[BMIM]PF$_6$	---	DMF	500	78
M	5	0.13	MeCN	---	MeCN	791	66
N	5	0.13	MeCN	---	DMF	620	73

[a] Reaction conditions: 70 °C, 3 h.

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

[c] Liquid-liquid diesel/solvent extraction (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.

21

Comparing the desulfurization performance reported in this work with literature data for the ODS of real diesels, it is evident that the present system leads to a superior performance in terms of desulfurization efficiency under eco-sustainable operation conditions (low H_2O_2/S ratio using an untreated diesel, i.e. 0.13 mmol of H_2O_2 was used in this work ($H_2O_2/S = 2.4$), while relatively higher amounts of oxidant (H_2O_2/S between 5 and 13) were required in previous studies with different Mo or W-based catalysts to achieve desulfurization efficiencies of 72-80% for the same real diesel. For example, an ODS system comprising the complex $[MoO_2Cl_2(4,4'$-di-*tert*-butyl-2,2'-bipyridine]$ in $[BMIM]PF_6$ required a H_2O_2/S molar ratio of 11.3 to achieve a final sulfur removal of 76% (ODS step performed at 50 ºC for 6 h) [9]. 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 PMo4_ac displayed in Fig. 9), thereby confirming that the structural integrity of the peroxophosphomolybdate Q_3PMo_4 was retained during the whole process.

4. 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 $n(S)/n(catalyst)/n(H_2O_2) = 7:1:26$, 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 recyclability 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 very good desulfurization efficiency of 78% 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 2.4, and DMF was used in a final extraction step to remove oxidized sulfur compounds. The high catalytic activity, stability and recyclability of the salt Q_3PMo_4 under ODS conditions suggest that it could be a viable catalyst in an industrial setting for the production of low sulfur fuels.

Acknowledgements

References

[1] Y. S. Al-Degs, A. H. El-Sheikh, R. Z. Al Bakain, A. P. Newman, M. A. Al-Ghouti, Conventional and Upcoming Sulfur-Cleaning Technologies for Petroleum Fuel: A Review, Energy Technol. 4 (2016) 679-699.

[2] R. Javadli, A. de Klerk, Desulfurization of heavy oil, Appl. Petrochem. Res. 1 (2012) 3-19.

[3] A. Stanislaus, A. Marafi, M. S. Rana, Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production, Catal. Today 153 (2010) 1-68.

[4] V. C. Srivastava, An evaluation of desulfurization technologies for sulfur removal from liquid fuels, RSC Adv. 2 (2012) 759-783.

[5] J. M. Campos-Martin, M. C. Capel-Sanchez, P. Perez-Presas, J. L. G. Fierro, Oxidative processes of desulfurization of liquid fuels, J. Chem. Technol. Biotechnol. 85 (2010) 879-890.

[6] S. Houda, C. Lancelot, P. Blanchard, L. Poinel, C. Lamonier, Oxidative desulfurization of heavy oils with high sulfur content: a review, Catalysts 8 (2018) 344-370.

[7] M.N. Hossain, H.C. Park, H.S. Choi, A comprehensive review on catalytic oxidative desulfurization of liquid fuel oil, Catalysts 9 (2019) 229-241.

[8] 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)$_3$R] as catalysts, Appl. Catal. B: Environ. 230 (2018) 177-183.

[9] 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 Trans. 45 (2016) 15242-15248.

[10] W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, J. Xia, Oxidative Desulfurization of Fuels Catalyzed by Peroxotungsten and Peroxomolybdenum Complexes in Ionic Liquids, Energy Fuels 21 (2007) 2514-2516.

[11] W. Zhu, H. Li, Q. Gu, P. Wu, G. Zhu, Y. Yan, G. Chen, Kinetics and mechanism for oxidative desulfurization of fuels catalyzed by peroxo-molybdenum amino acid complexes in water-immiscible ionic liquids, J. Mol. Catal. A: Chem. 336 (2011) 16-22.

24

[12] L. He, H. Li, W. Zhu, J. Guo, X. Jiang, J. Lu, Y. Yan, Deep Oxidative Desulfurization of Fuels Using Peroxophosphomolybdate Catalysts in Ionic Liquids, Ind. Eng. Chem. Res. 47 (2008) 6890-6895.

[13] W. Zhu, G. Zhu, H. Li, Y. Chao, M. Zhang, D. Du, Q. Wang, Z. Zhao, Catalytic kinetics of oxidative desulfurization with surfactant-type polyoxometalate-based ionic liquids, Fuel Process. Technol. 106 (2013) 70-76.

[14] J. Xu, H. Li, S. Wang, F. Luo, Y. Liu, X. Wang, Z. Jiang, Ultra-deep desulfurization via reactive adsorption on peroxophosphomolybdate/agarose hybrids, Chemosphere 111 (2014) 631-637.

[15] W. Zhu, P. Wu, Y. Chao, H. Li, F. Zou, S. Xun, F. Zhu, Z. Zhao, A Novel Reaction-Controlled Foam-Type Polyoxometalate Catalyst for Deep Oxidative Desulfurization of Fuels, Ind. Eng. Chem. Res. 52 (2013) 17399-17406.

[16] H. Lü, W. Ren, W. Liao, W. Chen, Y. Li, Z. Suo, Aerobic oxidative desulfurization of model diesel using a B-type Anderson catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18} \cdot 3H_2O$, Appl. Catal. B: Environ. 138-139 (2013) 79-83.

[17] H. Lü, W. Ren, H. Wang, Y. Wang, W. Chen, Z. Suo, Deep desulfurization of diesel by ionic liquid extraction coupled with catalytic oxidation using an Anderson-type catalyst $[(C_4H_9)_4N]_4NiMo_6O_{24}H_6$, Appl. Catal. A: Gen. 453 (2013) 376-382.

[18] H. Lü, C. Deng, W. Ren, X. Yang, Oxidative desulfurization of model diesel using $[(C_4H_9)_4N]_6Mo_7O_{24}$ as a catalyst in ionic liquids, Fuel Process. Technol. 119 (2014) 87-91.

[19] X. Zhang, Y. Shi, G. Liu, Direct preparation of $[(CH_3)_3NC_{16}H_{33}]_4Mo_8O_{26}$ and its catalytic performance in oxidative desulfurization, Catal. Sci. Technol. 6 (2016) 1016-1024.

[20] S. Yue, Q. Song, S. Zang, G. Deng, J. Li, Synthesis of polyoxomolybdate-quinoline compounds beads for catalytic oxidative desulfurization, Mol. Catal. 455 (2018) 88-94.

[21] M. Te, C. Fairbridge, Z. Ring, Oxidation reactivities of dibenzothiophenes in polyoxometalate/H_2O_2 and formic acid/H_2O_2 systems, Appl. Catal. A: Gen. 219 (2001) 267-280.

[22] W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He, J. Xia, Commercially available molybdic compound-catalyzed ultra-deep desulfurization of fuels in ionic liquids, Green Chem. 10 (2008) 641-646.

[23] W. Trakarnpruk, K. Rujiraworawut, Oxidative desulfurization of gas oil by polyoxometalate catalysts, Fuel Process. Technol. 90 (2009) 411-414.

[24] J. Zhang, A. Wang, X. Li, X. Ma, Oxidative desulfurization of dibenzothiophene and diesel over [Bmim]$_3$PMo$_{12}$O$_{40}$, J. Catal. 279 (2011) 269-275.

[25] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, G. Huet, H. Ledon, Reinvestigation of Epoxidation Using Tungsten-Based Precursors and Hydrogen Peroxide in a Biphase Medium, Inorg. Chem. 30 (1991) 4409-4415.

[26] F. P. Ballistreri, G. A. Tomaselli, R. M. Toscano, V. Conte, F. Di Furia, Spectroscopic and structural properties of some molybdenum and tungsten polyoxoperoxo complexes. A comparison with mononuclear complexes, J. Mol. Catal. 89 (1994) 295-301.

[27] T. Kottke, D. Stalke, Crystal Handling at Low-Temperatures, J. Appl. Crystallogr. 26 (1993) 615-619.

[28] APEX2, Data Collection Software Version 2012.4, Bruker AXS, Delft, The Netherlands, 2012.

[29] Cryopad, Remote monitoring and control, Version 1.451, Oxford Cryosystems, Oxford, United Kingdom, 2006.

[30] SAINT+, Data Integration Engine v. 8.27b©, Bruker AXS, Madison, Wisconsin, USA, 1997-2012.

[31] G.M. Sheldrick, SADABS 2012/1, Bruker AXS Area Detector Scaling and Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 2012.

[32] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. Sect. A: Found. Adv. 64 (2008) 112-122.

[33] G.M. Sheldrick, SHELXT v. 2014/3, Program for Crystal Structure Solution, University of Göttingen, 2014.

[34] G.M. Sheldrick, SHELXL v. 2014/3, Program for Crystal Structure Refinement, University of Göttingen, 2014.

[35] L. Salles, R. Thouvenot, J.-M. Brégeault, Redistribution and fluxionality in heteropolyoxoperoxo complexes: [PO$_4${M$_2$O$_2$(μ-O$_2$)$_2$(O$_2$)$_2$}$_2$]$^{3-}$ with M = Mo and/or W, Dalton Trans. (2004) 904-907.

[36] F.P. Ballistreri, A. Bazzo, G.A. Tomaselli, R.M. Toscano, Reactivity of Peroxopolyoxo Complexes. Oxidation of Thioethers, Alkenes, and Sulfoxides by Tetrahexylammonium Tetrakis(diperoxomolybdo)phosphate, J. Org. Chem. 57 (1992) 7074-7077.

[37] A.C. Dengel, W.P. Griffith, B.C. Parkin, Studies on polyoxo- and polyperoxo-metalates. Part 1. Tetrameric heteropolyperoxotungstates and heteropolyperoxomolybdates, J. Chem. Soc., Dalton Trans. (1993) 2683-2688.

[38] F.H. Allen, The Cambridge Structural Database: a quarter of a million crystal structures and rising, Acta Crystallogr. Sect. B: Struct. Sci. Cryst. Eng. Mater. 58 (2002) 380-388.

[39] F.H. Allen, W.D.S. Motherwell, Applications of the Cambridge Structural Database in organic chemistry and crystal chemistry, Acta Crystallogr. Sect. B: Struct. Sci. Cryst. Eng. Mater. 58 (2002) 407-422.

[40] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, The Cambridge Structural Database, Acta Crystallogr. Sect. B: Struct. Sci. Cryst. Eng. Mater. 72 (2016) 171-179.

[41] L. Salles, C. Aubry, F. Robert, G. Chottard, R. Thouvenot, H. Ledon, J.M. Brégeault, Preparation of various onium tetrakis(oxodiperoxomolybdo)phosphates. 3. Structure and reactivity towards olefins under biphasic conditions, New J. Chem. 17 (1993) 367-375.

[42] O.V. Larionov, D. Stephens, A.M. Mfuh, H.D. Arman, A.S. Naumova, G. Chavez, B. Skenderi, Insights into the mechanistic and synthetic aspects of the Mo/P-catalyzed oxidation of N-heterocycles, Org. Biomol. Chem. 12 (2014) 3026-3036.

[43] D. Julião, R. Valença, J. C. Ribeiro, B. Castro, S. S. Balula, Efficient eco-sustainable ionic liquid-polyoxometalate desulfurization processes for model and real diesel, Appl. Catal. A: Gen. 537 (2017) 93-99.

[44] C. M. Granadeiro, P. M. C. Ferreira, D. Julião, L. A. Ribeiro, R. Valença, J. C. Ribeiro, I. S. Gonçalves, B. Castro, M. Pillinger, L. Cunha-Silva, S. S. Balula, Efficient Oxidative Desulfurization Processes Using Polyoxomolybdate Based Catalysts, Energies 11 (2017) 1696-1707.

[45] M.F. Ali, A. Al-Malki, B. El-Ali, G. Martinie, M.N. Siddiqui, Deep desulphurization of gasoline and diesel fuels using non-hydrogen consuming techniques, Fuel 85 (2006) 1354-1363.

[46] S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai, T. Kabe, Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction, Energy Fuels 14 (2000) 1232-1239.

[47] Z. Huo, F. Jin, G. Yao, H. Enomoto, A. Kishita, An in situ Raman Spectroscopic Study of Benzothiophene and Its Desulfurization under Alkaline Hydrothermal Conditions, Ind. Eng. Chem. Res. 54 (2015) 1397-1406.

[48] D. Julião, R. Valença, J.C. Ribeiro, B. de Castro, S.S. Balula, Efficient eco-sustainable ionic liquid-polyoxometalate desulfurization processes for model and real diesel, Appl. Catal. A: Gen. 537 (2017) 93-99.

[49] S.O. Ribeiro, D. Julião, L. Cunha-Silva, V.F. Domingues, R. Valença, J.C. Ribeiro, B. de Castro, S.S. Balula, Catalytic oxidative/extractive desulfurization of model and untreated diesel using hybrid based zinc-substituted polyoxometalates, Fuel 166 (2016) 268-275.