



Yao, Z., Miras, H. N., and Song, Y.-F. (2016) Efficient concurrent removal of sulfur and nitrogen contents from complex oil mixtures by using polyoxometalate-based composite materials. *Inorganic Chemistry Frontiers*.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/121455/>

Deposited on: 27 July 2016

Enlighten – Research publications by members of the University of Glasgow  
<http://eprints.gla.ac.uk>

## Efficient concurrent removal of sulfur and nitrogen content from complex oil mixtures by polyoxometalate-based composite materials

Zhixiao Yao,<sup>a</sup> Haralampos N. Miras<sup>b\*</sup> and Yu-Fei Song<sup>a\*</sup>

The increasingly stringent regulations in relation to the environmental impact of employed industrial processes makes compulsory the development of alternative routes towards the reduction of the sulfur and nitrogen content in large scale chemical mixtures. Herein, we demonstrate for the first time the highly efficient application of polyoxometalate (POMs)/layered double hydroxide (LDHs) composite in deep desulfurization (1000 ppm) and denitrogenation (100 ppm) of complex model oil system under mild conditions (65 °C), with a corresponding decrease of the content to less than 10 and 1 ppm, respectively. The high efficiency of the heterogeneous catalyst along with the high stability and easy recovery of the catalytic system renders them promising candidates for greener catalytic applications.

### Introduction

Deep desulfurization and denitrogenation of chemical mixtures becomes gradually a challenging issue for the chemical industry due to the increasingly stringent legislation around the world in relation to the sulfur and nitrogen content in chemical mixtures.<sup>1-3</sup> The sulfur and nitrogen compounds are common contaminants in gasoline, diesel and jet fuels, which can lead to the formation of SO<sub>x</sub> and NO<sub>x</sub> exhaust gases with known environmental consequences (e.g. acid rain *etc.*).<sup>4,5</sup> Thus, it is absolutely essential to develop economically viable solutions for the removal of sulfur and nitrogen content from chemical mixtures. Currently, the hydro-desulfurization (HDS) and hydro-denitrogenation (HDN) industrial solutions are mainly based on the utilization of Co–Mo or Ni–Mo catalysts operating at high temperature and pressure regimes in the presence of hydrogen atmosphere.<sup>6-9</sup> In addition to high operating costs, there are two main drawbacks associated with the hydro-treating process: 1) HDS and HDN are less effective for the removal of heterocyclic sulfur or nitrogen compounds such as thiophene (TPH), benzothiophene (BT), dibenzothiophene (DBT), pyridine, quinoline and indole, which are abundant in diesel fuels;<sup>10,11</sup> 2) most importantly, low content (~100 ppm) nitrogen-containing compounds present in fuels can compete with sulfur compounds for the catalytic active sites of Co–Mo or Ni–Mo catalysts, since HDN is a kinetically slower reaction, which finally suppresses significantly the deep desulfurization process.<sup>12-14</sup> Hence, it is crucial to develop environmentally greener and economically viable solutions for the removal of sulfur and nitrogen content from complex reaction mixtures *e.g.* during fuel production.

In the last decades, a number of alternative desulfurization or denitrogenation processes that operate under H<sub>2</sub>-free mild conditions have been extensively investigated. It has been demonstrated the use of adsorbents for the removal of either

sulfur or nitrogen compounds by adsorption of the relevant contaminant, such as Cu+Y zeolites,<sup>15,16</sup> activated carbon,<sup>17,18</sup> and metal–organic frameworks (MOF).<sup>19,20</sup> However, the limited maximum capacity at saturation of these adsorbents and the complicated desorption process for their restoration restricted their industrial application.

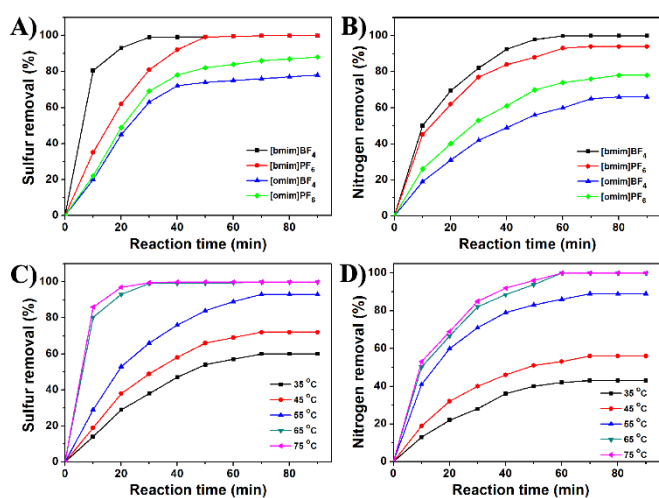
Ionic liquids (ILs) have attracted much interest as “green” solvents due to their non-volatile, non-explosive and recyclability properties. Recently, they have also been widely applied to remove sulfur compounds from fuels through an extraction process.<sup>21-23</sup> However, ILs exhibit a limited sulfur extraction ability which can reach a value of ~12–30%.<sup>24</sup> Interestingly, Zhang *et al.*<sup>25</sup> reported a promising simultaneous extraction and catalytic oxidative desulfurization and denitrogenation system using a functionalized ionic liquid component in a IL/M<sup>n</sup>X<sub>n</sub> (where M: Fe, Zn and n = 2 or 3) system in the presence of a rather simpler oil mixture of two sulfur (100 ppm) and nitrogen (500 ppm) containing substrates. Alternatively, many oxidative desulfurization systems, such as Ti-containing zeolites/O<sub>2</sub>,<sup>26</sup> polyoxometalates/H<sub>2</sub>O<sub>2</sub>,<sup>27</sup> heteropolyacid/SiO<sub>2</sub><sup>28</sup> and organic acid/H<sub>2</sub>O<sub>2</sub>,<sup>29</sup> have been widely investigated. For example, in 2003, one-pot desulfurization by chemical oxidation and solvent extraction using ILs has been demonstrated by Lo *et al.*<sup>30</sup> for the first time. More recently, Li *et al.*<sup>31,32</sup> investigated the efficiency of various extraction and catalytic oxidative desulfurization systems (ECODS), where they achieved efficient deep desulfurization utilizing Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, [PSPy]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·2H<sub>2</sub>O as catalysts in ILs medium in the presence of H<sub>2</sub>O<sub>2</sub>. Our previous studies<sup>33-35</sup> have demonstrated that deep desulfurization can be easily realized by using LaW<sub>10</sub>-based catalysts in ILs with H<sub>2</sub>O<sub>2</sub> as oxidant.

Interestingly, Hirai *et al.*<sup>29</sup> reported simultaneous extraction and catalytic oxidative desulfurization and denitrogenation system by using CH<sub>3</sub>COOH/H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>CN/H<sub>2</sub>O mixtures. However, the amounts of CH<sub>3</sub>COOH used in this catalytic system can eventually corrode the equipment whilst are highly

unlikely to be recovered during the recycling process, rendering it unsuitable for large scale application. Therefore, taking into consideration that sulfur and nitrogen-containing compounds are both common contaminants in fuels, it is of fundamental importance the development of efficient and recyclable heterogeneous catalysts which will allow the simultaneous desulfurization and denitrogenation process of complex chemical mixtures in an economic and greener fashion.

The ability of Polyoxometalates (POMs) species to act as oxidative catalysts<sup>36-39</sup> due to their redox stability and Lewis acidity renders them excellent active components on appropriate supporting platforms; the layered double hydroxides (LDHs),  $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are di- and tri-valent metal cations, and  $A^{n-}$  is a counter anion with modular interlayer galleries<sup>40</sup> and basicity are an exceptional support system for the immobilization of anionic POM catalysts.<sup>41-44</sup>

Herein, we report the efficient and greener simultaneous removal of sulfur and nitrogen content from complex chemical mixtures utilizing a POM/LDH composite as a robust heterogeneous catalyst. To the best of our knowledge, this is the first time that efficient and simultaneous deep desulfurization and denitrogenation using POM-based composite catalysts have been demonstrated under mild conditions.



**Figure 1.** (A) Sulfur and (B) nitrogen removal by Tris-LDH-LaW<sub>10</sub> in different ionic liquids at 65 °C. Effect of used temperature regimes on (C) sulfur and (D) nitrogen removal in 1 mL [bmim]BF<sub>4</sub>. Reaction condition: H<sub>2</sub>O<sub>2</sub> = 0.096 mL, mixed model oil = 5 mL (S = 1000 ppm, N = 100 ppm), H<sub>2</sub>O<sub>2</sub>/DBT/Tris-LDH-LaW<sub>10</sub> = 120:20:1.

## Results and Discussion

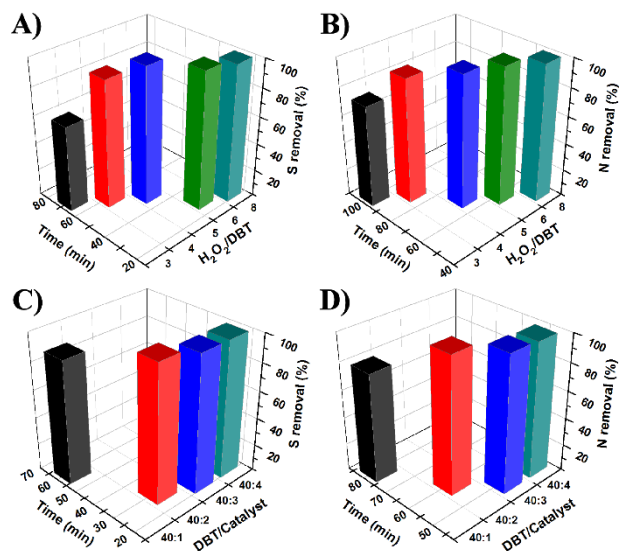
The composite of Tris-LDH-LaW<sub>10</sub> was synthesized according to our previous work<sup>44</sup> and fully characterized by XRD, FT-IR, <sup>13</sup>C NMR, XPS, TGA, BET, HRTEM and EDX (see supporting information).

## Optimization of parameters in simultaneous desulfurization and denitrogenation process

Initially, we would like to gauge the influence of different ionic liquids on the simultaneous desulfurization and denitrogenation of the mixed model oil containing both DBT and quinoline using Tris-LDH-LaW<sub>10</sub> as catalyst in the presence of H<sub>2</sub>O<sub>2</sub> at 65 °C. As shown in Figure 1A, catalytic oxidative desulfurization of DBT in the presence of [omim]BF<sub>4</sub> or [omim]PF<sub>6</sub> as extractants resulted in sulfur removal of 79% or 88% in 90 min. Alternatively, when [bmim]BF<sub>4</sub> or [bmim]PF<sub>6</sub> were used as extractants, 99% sulfur removal was observed for [bmim]PF<sub>6</sub> (50 min) and [bmim]BF<sub>4</sub> (30 min), respectively. Moreover, a 99% denitrogenation (removal of quinoline) was achieved only in the case of [bmim]BF<sub>4</sub> after 60 min (Figure 1B). In fact, [omim]BF<sub>4</sub>, [bmim]PF<sub>6</sub> and [omim]PF<sub>6</sub> all have good wettability for *n*-octane (model oil), but only [bmim]BF<sub>4</sub> shows good wettability for both H<sub>2</sub>O<sub>2</sub> and *n*-octane, which is highly beneficial for the oxidative desulfurization and denitrogenation process.<sup>45</sup> The initial studies showed that [bmim]BF<sub>4</sub> exhibited the optimal behavior for the simultaneous desulfurization and denitrogenation process and thus this was the IL of our choice for the following studies in this work.

Another known parameter that have a profound effect on the sulfur and nitrogen removal process, is the reaction temperature. Therefore, the following experiments were carried out in order to determine the optimum temperature regime on the simultaneous HDS and HDN of the mixed model oil containing DBT and quinoline (Figure 1C-D). The data revealed that 60%, 72% and 98% desulfurization can be achieved at 35, 45 and 55 °C in 70 mins, respectively. Further increase of the temperature to 65 or 75 °C resulted in 99% desulfurization of DBT in 30 min. Similarly, the nitrogen removal efficiency increases as a function of the temperature. As shown in Figure 1D, 99% denitrogenation can be achieved in 60 min at 65 °C. These data demonstrate that the desulfurization and denitrogenation efficiency is closely related to the reaction temperature, which reflects the thermodynamic nature of this process. Moreover, the optimum temperature that was used in the rest of our studies was 65 °C.

In an effort to study the influence of H<sub>2</sub>O<sub>2</sub> on sulfur and nitrogen removal of mixed model oil, we utilized different H<sub>2</sub>O<sub>2</sub>/DBT molar ratios under the identified optimum experimental conditions (Figure 2). Increase of the H<sub>2</sub>O<sub>2</sub>/DBT molar ratio from 3:1 to 4:1, increases the sulfur removal from 68% to 92% in 70 min (Figure 2A). When the molar ratio of H<sub>2</sub>O<sub>2</sub>/DBT increases to 5:1 and 6:1, 99% sulfur removal can be achieved in 30 min and 25 min, respectively. Meanwhile, the denitrogenation efficiency is also improved upon increase of the H<sub>2</sub>O<sub>2</sub>/DBT molar ratio (Figure 2B). When the H<sub>2</sub>O<sub>2</sub>/DBT molar ratio increased to 6:1 or 8:1, 99% denitrogenation is realized in 60 min and 50 min, respectively. Hence, the optimum H<sub>2</sub>O<sub>2</sub>/DBT molar ratio that was used in this work was 6:1.

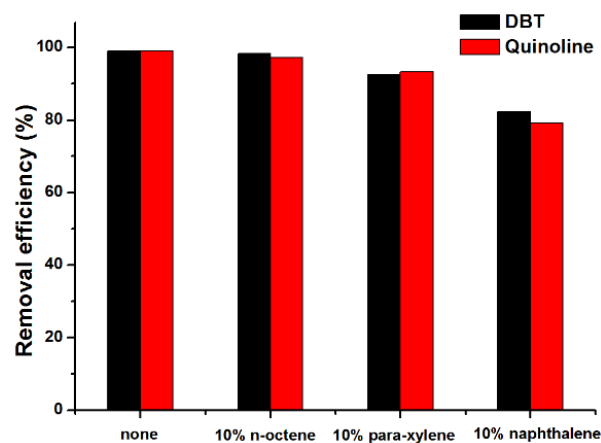


**Figure 2.** Effect of  $\text{H}_2\text{O}_2/\text{DBT}$  molar ratio on (A) sulfur and (B) nitrogen removal with  $\text{DBT}/\text{Tris-LDH-LaW}_{10} = 20:1$ . Effect of  $\text{DBT}/\text{Tris-LDH-LaW}_{10}$  molar ratio on (C) sulfur and nitrogen (D) removal with  $\text{H}_2\text{O}_2/\text{DBT} = 6:1$ . Reaction conditions:  $[\text{bmim}]\text{BF}_4 = 1$  mL, mixed model oil = 5 mL ( $\text{S} = 1000$  ppm,  $\text{N} = 100$  ppm),  $T = 65$  °C.

The amount of the catalyst present in the reaction mixture can affect as well the sulfur and nitrogen removal efficiency. As shown in Figure 2C, the required period of time to achieve 99% desulfurization can be shortened from 45 to 30 min when the  $\text{DBT}/\text{Tris-LDH-LaW}_{10}$  molar ratio decreases from 40:1 to 40:2. It can be found that when  $\text{DBT}/\text{Tris-LDH-LaW}_{10}$  molar ratio reaches up to 40:3, 99% sulfur removal can be achieved in 25 min. In a similar manner, upon increase of the  $\text{DBT}/\text{Tris-LDH-LaW}_{10}$  molar ratio from 40:1 to 40:2, the denitrogenation efficiency can be improved from 79% in 80 min to 99% in 60 min (Figure 2D). When the  $\text{DBT}/\text{Tris-LDH-LaW}_{10}$  molar ratio increases to 40:3 or higher, 99 % nitrogen removal of the mixed model oil can be obtained in 50 min. Thus, we used a  $\text{DBT}/\text{Tris-LDH-LaW}_{10}$  molar ratio of 40:2 for the subsequent study.

In general, the real oil contains a variety of both saturated and unsaturated hydrocarbons, such as aromatic compounds and alkenes. In order to evaluate the efficiency of the catalytic system in the presence of various oil compositions, three substrates including an alkene (*n*-octene), a mono-aromatic compound (*para*-xylene) and a polyaromatic compound (naphthalene) were chosen as model compounds (additives) for the mixed model oil under investigation. Simultaneous HDS and HDN of the mixed model oil was carried out under the optimized conditions as discussed above. As shown in Figure 3, in the presence of 10% *n*-octene in the mixed model oil the

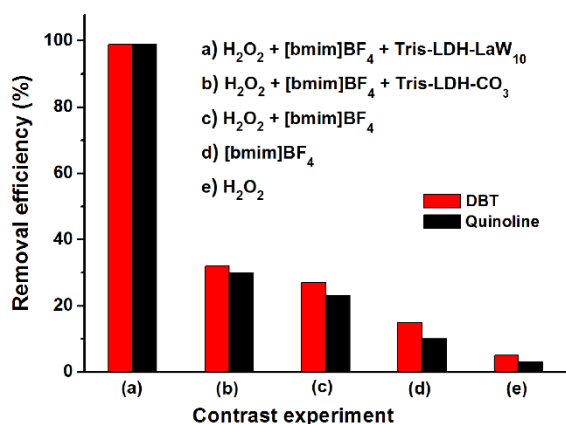
HDS and HDN efficiency remained nearly unchanged whilst, a slight decrease in sulfur and nitrogen removal efficiency to 92.6 and 93.3% was observed upon addition of 10% *para*-xylene. Moreover, the presence of naphthalene in the mixed model oil, seems to decrease slightly the HDS and HDN efficiency to a value of 82.3 and 79.2 %, respectively. As a result, the catalytic system of  $\text{Tris-LDH-LaW}_{10}/\text{H}_2\text{O}_2/[\text{bmim}]\text{BF}_4$  revealed great potential as a catalytic system for the removal of sulfur and nitrogen content from mixed model oil in the



presence of unsaturated compounds except for naphthalene due to the high solubility of the oxidized sulfur and nitrogen compounds in naphthalene.<sup>46</sup>

**Figure 3.** Effect of oil composition on sulfur and nitrogen removal; Compositions: pure *n*-octene, or  $x/\text{octane} = 1 : 9$  in mass,  $x = n$ -octene, *para*-xylene or naphthalene; Reaction condition:  $\text{H}_2\text{O}_2 = 0.096$  mL,  $[\text{bmim}]\text{BF}_4 = 1$  mL, mixed model oil = 5 mL ( $\text{S} = 1000$  ppm,  $\text{N} = 100$  ppm),  $\text{H}_2\text{O}_2/\text{DBT}/\text{Tris-LDH-LaW}_{10} = 120:20:1$ .

Finally, in order to verify the beneficial cooperative effect of the POM/LDH composite on the catalytic process, we carried out a set of comparative experiments using different catalytic systems for the simultaneous HDS and HDN of the model mixed oil system. As discussed above, in the presence of  $\text{H}_2\text{O}_2$  and  $[\text{bmim}]\text{BF}_4$ , simultaneous deep HDS and HDN of the mixed model oil can be realized using  $\text{Tris-LDH-LaW}_{10}$  as catalyst in 60 min. In contrast, the use of  $\text{Tris-LDH-CO}_3/\text{H}_2\text{O}_2/[\text{bmim}]\text{BF}_4$ ,  $\text{H}_2\text{O}_2/[\text{bmim}]\text{BF}_4$ ,  $[\text{bmim}]\text{BF}_4$  and  $\text{H}_2\text{O}_2$  for desulfurization resulted in markedly inferior performance where we only achieved 32, 27, 10 and 3 % sulfur removal in 60 min, respectively. A similar effect observed in the case of denitrogenation where we observed 30, 23, 15 and 5 % nitrogen removal during the same period of time. Noticeable, these results indicate that the  $\text{LaW}_{10}$  anion is the main active site for both processes.



**Figure 4.** Efficiency of different catalytic systems for sulfur and nitrogen removal.  $t = 60$  min,  $T = 65$  °C, mixed model oil = 5 mL ( $S = 1000$  ppm,  $N = 100$  ppm),  $H_2O_2 = 0.096$  mL,  $[bmim]BF_4 = 1$  mL,  $Tris-LDH-LaW_{10} = 54$  mg,  $Tris-LDH-CO_3 = 54$  mg.

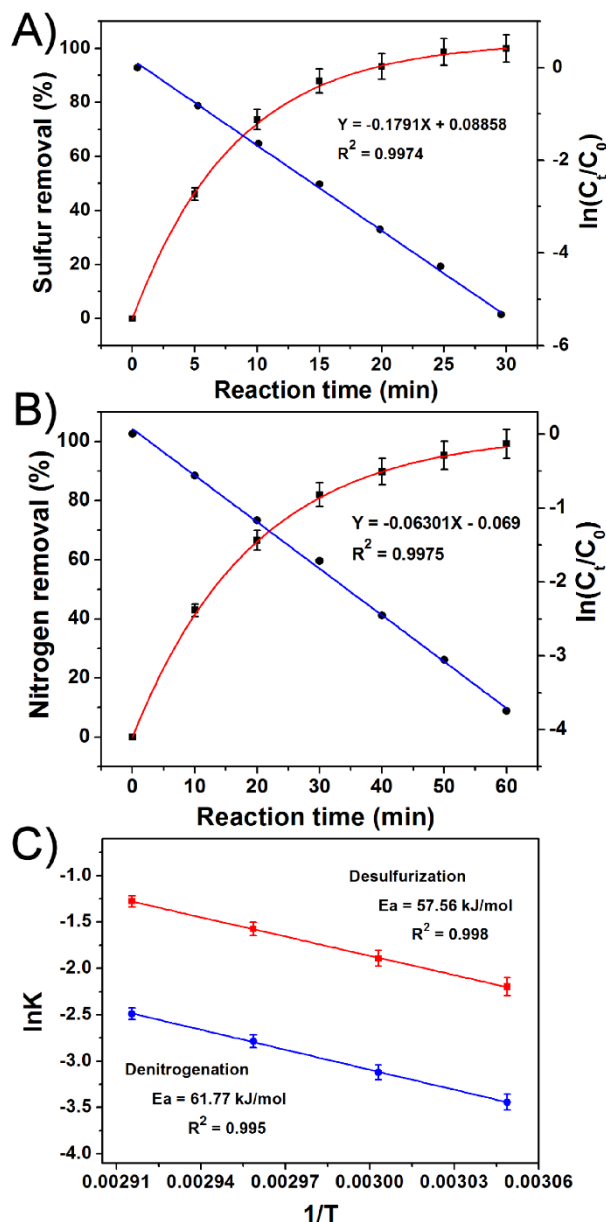
#### Kinetic study of the catalytic oxidation reactions

The kinetic parameters for the oxidation of DBT and quinoline, have been obtained from a series of experiments that have been performed using a ratio of  $H_2O_2/DBT/Tris-LDH-LaW_{10} = 120:20:1$  at  $65$  °C. The percentage of sulfur removal and the  $\ln(C_t/C_0)$  parameter were plotted against the reaction time, Figure 5A, where  $C_0$  and  $C_t$  are the DBT concentration at the beginning of the reaction and at time  $t$ , respectively. Similarly, the kinetic study of the denitrogenation process is also outlined in Figure 5B. The linear fit of the data indicate that the two catalytic reactions exhibit pseudo-first-order kinetics for the desulfurization of DBT ( $R^2 = 0.9954$ ) and denitrogenation of quinoline ( $R^2 = 0.9975$ ). Based on the Equations (1) and (2), the rate constant  $k$  of the oxidative desulfurization and denitrogenation is determined to be  $0.1791 \text{ min}^{-1}$  and  $0.0631 \text{ min}^{-1}$ , respectively, which demonstrates that the reaction rate of desulfurization is approximately 3 times faster than that of denitrogenation process. To calculate the activation energy, we carried out the simultaneous desulfurization and denitrogenation reaction at different temperature regimes. Figures S4-5, showed that the increase of the reaction temperature is associated with a sharp increase in the reaction rate of the two processes. This observation is consistent with the data shown in Figures 1C-D. According to the equation (3), the Arrhenius plots of the oxidative desulfurization and denitrogenation by  $Tris-LDH-LaW_{10}$  gave activation energies of  $57.56$  and  $61.77$  kJ/mol, respectively (Figure 5C).

$$\frac{-dC_t}{dt} = kC_t \quad (1)$$

$$\ln \frac{C_0}{C_t} = kt \quad (2)$$

$$\ln k = \frac{\ln A - E_a}{RT} \quad (3)$$



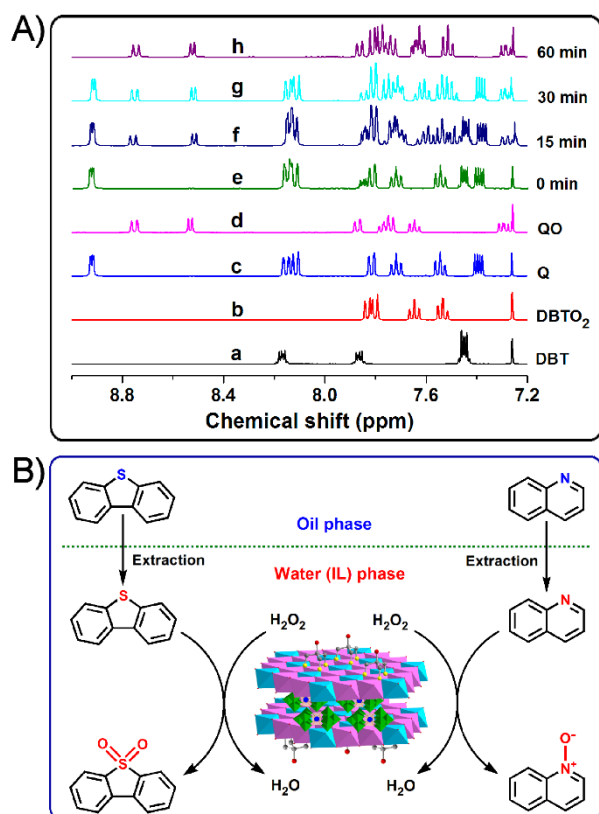
**Figure 5.** (A) Sulfur and (B) nitrogen removal and  $\ln(C_t/C_0)$  as a function of the reaction time at  $65$  °C; reaction conditions:  $H_2O_2 = 0.096$  mL,  $[bmim]BF_4 = 1$  mL, mixed model oil = 5 mL ( $S = 1000$  ppm,  $N = 100$  ppm),  $H_2O_2/DBT/Tris-LDH-LaW_{10} = 120:20:1$ . (C) Arrhenius plots of the desulfurization and denitrogenation.

#### Identification of the products and mechanistic analysis

The  $^1H$  NMR ( $CDCl_3$ ) spectra of standard DBT,  $DBTO_2$ , quinoline (Q), quinoline N-oxide (QO), and reaction products at different reaction time are presented in Figure 6A. The  $^1H$  NMR spectrum of the recovered products after 15 min is similar to a typical physical mixture of DBT,  $DBTO_2$ , quinoline and quinoline N-oxide. That means the mixed model oil contained



these four compounds at the particular reaction time. As the reaction progresses,  $t = 30$  min, all the peaks of DBT disappear in the  $^1\text{H}$  NMR spectrum of the recovered products.



**Figure 6.** (A)  $^1\text{H}$  NMR (CDCl<sub>3</sub>) spectra of (a) DBT, (b) DBTO<sub>2</sub>, (c) quinoline, (d) quinoline N-oxides, product at (e) 0 min, (f) 15 min, (g) 30 min, (h) 60 min. Reaction conditions: [bmim]BF<sub>4</sub> = 1 mL, mixed model oil = 5 mL (S content = 1000 ppm), DBT/Tris-LDH-LaW<sub>10</sub> = 20:1, T = 65 °C. (B) Proposed extraction and catalytic oxidative desulfurization and denitrogenation process by the catalytic system of H<sub>2</sub>O<sub>2</sub>/[bmim]BF<sub>4</sub>/Tris-LDH-LaW<sub>10</sub>.

This observation indicates that DBT has already been oxidized to DBTO<sub>2</sub> and removed completely from the mixed model oil. However, longer reaction time (60 min) is necessary for the removal of quinolone which is associated with the disappearance of the relevant signals from the  $^1\text{H}$  NMR spectrum of the recovered products. In the latter case, the quinoline has been converted to quinoline N-oxide and separated from the mixed model oil. Therefore, the desulfurization product and denitrogenation product is determined to be DBTO<sub>2</sub> and quinoline N-oxide, respectively. Moreover, the  $^1\text{H}$  NMR spectrum of the recovered products also demonstrate that DBT is removed much faster than quinoline from the mixed model oil. Based on the results discussed above, a proposed extraction and catalytic oxidative desulfurization and denitrogenation process is presented in Figure 6B. Initially, the immiscibility of [bmim]BF<sub>4</sub> with mixed model oil results in the formation of a biphasic catalytic system, where DBT and quinoline are in the oil phase, H<sub>2</sub>O<sub>2</sub> is

in the water (IL) phase, and the heterogeneous catalyst of Tris-LDH-LaW<sub>10</sub> is well dispersed in the hydrophilic (IL) phase. The catalytic active center of [LaW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> is immobilized tightly in the gallery of the Tris-modified LDHs, as a result of the strong electrostatic and hydrogen bonding interactions between POM anions and the LDHs layers. The [LaW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> anions located in the confined space of LDHs are oxidized to form the active peroxy species in the presence of H<sub>2</sub>O<sub>2</sub>. The extraction of DBT or quinoline by IL from oil phase to the aqueous (IL) phase is followed by their subsequent oxidation by the W-peroxy species to DBTO<sub>2</sub> or quinoline N-oxide, respectively. Additionally, the incorporation of metals (La<sup>3+</sup> in our case) to the POM's structure can modulate the acidic properties of the metal oxide framework which interacts with both substrates of DBT and quinolone promoting their catalytic conversion. Consequently, the accessibility of the substrates to the active W-peroxy species is largely improved by this coordination effect, which may contribute to the high efficiency of the catalyst of Tris-LDH-LaW<sub>10</sub>.

### Sulfur and nitrogen removal of complex model oil system

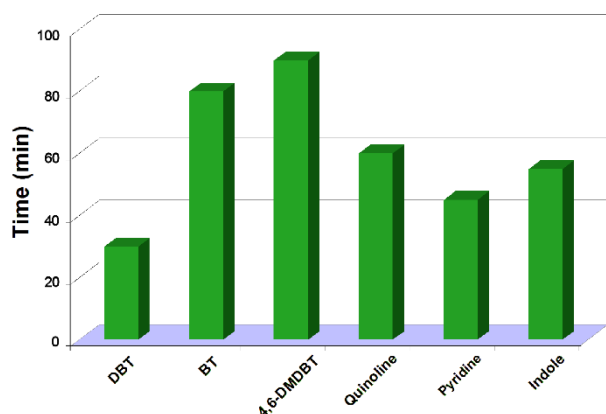
In an effort to test further the performance of the Tris-LDH-LaW<sub>10</sub> with H<sub>2</sub>O<sub>2</sub> system in more complex mixtures, we evaluated the efficiency of the catalyst in the presence of a mixed model oil containing BT, DBT, 4,6-DMDBT, pyridine, quinoline and indole, Figure 7. Interestingly, all the substrates can be completely removed from this highly complex mixed model oil at different but very reasonable time scales. More specifically, the sulfur removal of DBT can be achieved in 30 min whilst for substrates such as BT and 4,6-DMDBT, which are difficult to remove due to the relatively lower electron density of the sulfur atoms on both substrates,<sup>27</sup> the catalytic system exhibited a high desulfurization efficiency, with almost 99 % sulfur removal in 80 and 90 min, respectively. On the other hand, quinoline, pyridine and indole are relatively easier to remove than BT and 4,6-DMDBT. And the required time for 99% denitrogenation of these nitrogen compounds is 60, 45 and 55 min, respectively.

### Stability and recycling ability of the catalytic system

The Tris-LDH-LaW<sub>10</sub> composite exhibits a number of advantages as a catalyst such as easy separation and recyclability. In order to evaluate this possibility, we carried out the following recycling experiments: the upper layer of the model oil was separated using separatory funnel. Then, 50 mL of deionized water is added to the water phase to lower the viscosity of IL followed by separation of the catalyst by centrifugation. The diluted ionic liquid in deionized water was concentrated under vacuum to recycle the ionic liquid. As such, the IL and catalyst are both recyclable. The catalyst can be recycled at least ten times for simultaneous deep desulfurization and denitrogenation cycles without obvious decrease of its catalytic activity (Figure S6). ICP-AES measurement of the aqueous phase confirmed the absence of

La or W traces, which confirms further the stability of the catalyst and that there is no detectable leaching of the LaW<sub>10</sub> from the solid catalyst to the aqueous (IL) phase. Moreover, the structure of the recovered catalyst remained unchanged after comparison of the spectroscopic data (FT-IR, XRD and XPS) obtained for the fresh and the recycled catalyst (Figure S7).

**Figure 7.** Simultaneous 99% Sulfur and nitrogen removal of different substrates contained in a mixed model oil. Reaction conditions:  $t = 60$  min,  $T = 65$  °C, mixed model oil = 5 mL (Total S = 1000 ppm, Total N = 100 ppm, each sulfur compounds containing 333.3 ppm S, each nitrogen compounds containing 33.3 ppm),  $H_2O_2 = 0.096$  mL, [bmim]BF<sub>4</sub> = 1 mL, Tris-LDH-LaW<sub>10</sub> = 54 mg.



## Experimental Section

### Materials and reagents

Dibenzothiophene (DBT, 98%), benzothiophene (BT, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 95%), pyridine (99%), quinoline (98%), indole (99%), aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%), n-octane (99%) were obtained from Alfa Aesar and were used without further treatment. The ionic liquids [bmim]BF<sub>4</sub>, [bmim]PF<sub>6</sub> (bmim = 1-butyl-3-methylimidazolium) and [omim]BF<sub>4</sub>, [omim]PF<sub>6</sub> (omim = 1-octyl-3-methylimidazolium) were purchased from Sigma-Aldrich and used directly without further purification. The catalyst of Tris-LDH-LaW<sub>10</sub> was synthesized according to the literature methods.<sup>44</sup>

### Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). FT-IR spectra were recorded on a Bruker Vector 22 infrared spectrometer by using KBr pellets. The solid state NMR experiments were carried out at 75.6 MHz for <sup>13</sup>C on a Bruker

Avance 300M solid-state spectrometer equipped with a commercial 5 mm MAS NMR probe. <sup>1</sup>H NMR spectra were recorded on a Bruker AV400 NMR spectrometer at 400MHz, and the chemical shifts are given relative to TMS as internal reference. The N<sub>2</sub> adsorption-desorption isotherms were measured using Quantachrome Autosorb-1 system at liquid nitrogen temperature. HRTEM images were conducted on a JEOL JEM-2010 electron microscope operating at 200 kV. Thermogravimetric and differential thermal analyses (TG-DTA) were performed on a TGA/DSC 1/1100 SF from Mettler Toledo in flowing N<sub>2</sub> with a heating rate of 10 °C·min<sup>-1</sup> from 75 °C to 700 °C. X-ray photoelectron spectroscopy (XPS) measurements were performed with monochromatized Al K $\alpha$  exciting X-radiation (PHI Quantera SXM). Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500) was used to measure the concentration of W in the catalysts.

### Simultaneous desulfurization and denitrogenation procedure

In a typical experiment, a solution of DBT and quinoline in n-octane was used as mixed model oil with total S and N content of 1000 ppm and 100 ppm, respectively. The catalytic oxidative HDS and HDN experiments were performed in a 25 mL two-necked flask, to which 0.096 mL of 30 wt% H<sub>2</sub>O<sub>2</sub>, 5 mL of mixed model oil, 1 mL of IL, and 54 mg of freshly prepared Tris-LDH-LaW<sub>10</sub> were added. The resulting H<sub>2</sub>O<sub>2</sub>/DBT/Tris-LDH-LaW<sub>10</sub> molar ratio was 120:20:1. The reaction mixture was heated to a certain temperature (35, 45, 55, 65 or 75 °C). During the reaction, samples of the upper oil phase were periodically withdrawn and analysed by gas chromatography with a flame ionization detector (GC-FID). DBT and quinoline were identified using reference standards. The conditions were as follows: injection port temperature 340 °C; detector temperature 250 °C; oven temperature 70 °C; carrier gas: ultrapure nitrogen; sample injection volume 1  $\mu$ L.

## Conclusions

In this work, we demonstrated for the first time the applicability of the Tris-LDH-LaW<sub>10</sub> composite as a highly efficient and green catalyst for the simultaneous deep HDS and HDN of complex model oil mixtures under mild conditions. The catalytic system of H<sub>2</sub>O<sub>2</sub>/[bmim]BF<sub>4</sub>/Tris-LDH-LaW<sub>10</sub> can promote the concurrent deep desulfurization and denitrogenation at 65 °C in 60 min with S and N contents lower than 10 and 1 ppm, respectively. Leaching tests and recovery experiments demonstrated that the Tris-LDH-LaW<sub>10</sub> composite is a truly heterogeneous and highly stable catalyst which can be recycled at least 10 times without obvious decrease of its catalytic activity. The structural integrity of the recovered catalyst was confirmed by XRD, FT-IR and XPS analyses. Investigation of the scale-up effect of the heterogeneous catalyst and its applicability in large scale conditions are underway.

## Acknowledgements

This work was supported by National Basic Research Program (973 program, 2014CB932104), National Science Foundation of China (21222104, U1407127), the Fundamental Research Funds for the Central Universities (RC1302, YS1406) and Beijing Engineering Centre for Hierarchical Catalysts. H.N.M acknowledges the financial support from University of Glasgow.

## Notes and references

- P. Wiwel, K. Knudsen, P. Zeuthen and D. Whitehurst, *Ind. Eng. Chem. Res.* 2000, **39**, 533-540.
- X. Ma, S. Velu, J. H. Kim and C. Song, *Appl. Catal. B: Environ.* 2005, **56**, 137-147.
- K. A. Cychosz, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.* 2008, **130**, 6938-6939.
- X. Xu, J. A. Moulijn, E. Ito, R. Wagemans and M. Makkee, *ChemSusChem*. 2008, **1**, 817-819.
- M. S. Shannon, A. C. Irvin, H. Liu, J.D. Moon, M. S. Hindman, C. H. Turner and J. E. Bara, *Ind. Eng. Chem. Res.* 2015, **54**, 462-471.
- X. Liu, X. Li and Z. Yan, *Appl. Catal. B: Environ.* 2012, **121-122**, 50-56.
- R. T. Yang, A. J. Hernandez-Maldonado and F. H. Yang, *Science* 2003, **301**, 79-81.
- T. A. Zepeda, B. Pawelec, R. Obeso-Estrella, J. N. Díaz de León, S. Fuentes, G. Alonso-Núñez and J. L. G. Fierro, *Appl. Catal. B: Environ.* 2016, **180**, 569-579.
- N.-Q. Bui, C. Geantet and G. Berhault, *J. Catal.* 2015, **330**, 374-386.
- A. Rothlisberger and R. Prins, *J. Catal.* 2005, **235**, 229-240.
- D. Liu, J. Gui and Z. Sun, *J. Mol. Catal. A-Chem.* 2008, **291**, 17-21.
- R. G. Pearson, *J. Am. Chem. Soc.* 1963, **85**, 3533-3539.
- W. Kaernbach, W. Kisielow, L. Warzecha, K. Miga, R. Klecan, *Fuel* 1990, **69**, 221-224.
- M. Macaud, M. Sévignon, A. Favre-Réguillon, M. Lemaire, E. Schulz and M. Vrinat, *Ind. Eng. Chem. Res.* 2004, **43**, 7843-7849.
- A. J. Hernandez-Maldonado and R. T. Yang, *Angew. Chem. Int. Ed.* 2004, **43**, 1004-1006.
- A. J. Hernández-Maldonado and R. T. Yang, *Ind. Eng. Chem. Res.* 2003, **42**, 3103-3110.
- J. A. Arcibar-Orozco and J. R. Rangel-Mendez, *Chem. Eng. J.* 2013, **230**, 439-446.
- X. Han, H. Lin and Y. Zheng, *Chem. Eng. J.* 2014, **243**, 315-325.
- M. Maes, M. Trekels, M. Boulhout, S. Schouteden, F. Vermoortele, L. Alaerts, D. Heurtaux, Y. K. Seo, Y. K. Hwang, J. S. Chang, I. Beurroies, R. Denoyel, K. Temst, A. Vantomme, P. Horcajada, C. Serre and D. E. De Vos, *Angew. Chem. Int. Ed.* 2011, **50**, 4210-4214.
- M. Huang, G. Chang, Y. Su, H. Xing, Z. Zhang, Y. Yang, Q. Ren, Z. Bao and B. Chen, *Chem. Commun.* 2015, **51**, 12205-12207.
- L.-L. Xie, A. Favre-Réguillon, X.-X. Wang, X. Fu, S. Pellet-Rostaing, G. Toussaint, C. Geantet, M. Vrinat and M. Lemaire, *Green Chem.* 2008, **10**, 524-531.
- L.-L. Xie, A. Favre-Réguillon, S. Pellet-Rostaing, X.-X. Wang, X. Fu, J. Estager, M. Vrinat and M. Lemaire, *Ind. Eng. Chem. Res.* 2008, **47**, 8801-8807.
- H. Wang, C. Xie, S. Yu and F. Liu, *Chem. Eng. J.* 2014, **237**, 286-290.
- H. Gao, C. Guo, J. Xing, J. Zhao and H. Liu, *Green Chem.* 2010, **12**, 1220-1224.
- Y. Nie, X. Gong, H. S. Gao, X. P. Zhang and S. J. Zhang, *Sci. China. Chem.*, 2014, **57**, 1766-1773.
- L. Kong, G. Li and X. Wang, *Catal. Today* 2004, **93-95**, 341-345.
- C. Komintarachat and W. Trakarnpruk, *Ind. Eng. Chem. Res.* 2006, **45**, 1853-1856.
- A. M. Khenkin and R. Neumann, *ChemSusChem* 2011, **4**, 346-348.
- Y. Shiraishi, K. Tachibana, T. Hirai and I. Komasaawa, *Ind. Eng. Chem. Res.* 2002, **41**, 4362-4375.
- W.-H. Lo, H.-Y. Yang and G.-T. Wei, *Green Chem.* 2003, **5**, 639-642.
- W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He and J. Xia, *Green Chem.* 2008, **10**, 641-646.
- W. Huang, W. Zhu, H. Li, H. Shi, G. Zhu, H. Liu and G. Chen, *Ind. Eng. Chem. Res.* 2010, **49**, 8998-9003.
- J. Xu, S. Zhao, W. Chen, M. Wang and Y.-F. Song, *Chem. Eur. J.* 2012, **18**, 4775-4781.
- J. Xu, S. Zhao, Y. Ji and Y.-F. Song, *Chem. Eur. J.* 2013, **19**, 709-715.
- Y. Chen, S. Zhao and Y.-F. Song, *Appl. Catal. A-Gen.* 2013, **466**, 307-314.
- H. N. Miras, L. Vila-Nadal and L. Cronin, *Chem. Soc. Rev.* 2014, **43**, 5679-5699.
- S. S. Wang and G. Y. Yang, *Chem. Rev.* 2015, **115**, 4893-4962.
- S. Herrmann, M. Kostrzewa, A. Wierschem and C. Streb, *Angew. Chem. Int. Ed.* 2014, **53**, 13596-13599.
- H. N. Miras, J. Yan, D. L. Long and L. Cronin, *Chem. Soc. Rev.* 2012, **41**, 7403-7430.
- J. Han, Y. Dou, M. Wei, D. G. Evans and X. Duan, *Angew. Chem. Int. Ed.* 2010, **49**, 2171-2174.
- P. Liu, H. Wang, Z. Feng, P. Ying and C. Li, *J. Catal.* 2008, **256**, 345-348.
- P. Liu, C. Wang and C. Li, *J. Catal.* 2009, **262**, 159-168.
- S. Zhao, J. Xu, M. Wei and Y.-F. Song, *Green Chem.* 2011, **13**, 384-389.
- Y. Chen, Z. Yao, H. N. Miras and Y.-F. Song, *Chem. Eur. J.* 2015, **21**, 10812-10820.
- M. Li, M. Zhang, A. Wei, W. Zhu, S. Xun, Y. Li, H. Li and H. Li, 46 X. Zhang, Y. Shi and G. Liu, *Catal. Sci. Technol.* 2016, **6**, 1016-1024.



## ARTICLE

Efficient and simultaneous deep desulfurization and denitrogenation of complex oil systems under mild conditions is reported using a heterogeneous Tris-LDH-LaW<sub>10</sub> catalyst.

