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An Efficient Heterogeneous Catalyst Based on Highly Dispersed Na₇H₂LaW₁₀O₃₆·32H₂O Nanoparticles on Mesoporous Silica for Deep Desulfurization

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Highlights

The LaW₁₀ is highly-dispersed on modified mesoporous silica. Deep desulfurization of DBT, BT, and 4,6-DMDBTcan be achieved by $SiO_2/NH_3^+/LaW_{10}$. The desulfurization catalyst is highly efficient with the model oil of 1000 mL. The $SiO_2/NH_3^+/LaW_{10}$ can be easily recovered and reused at least ten times.

Abstract

A lanthanide-containing polyoxometalate of Na₇H₂LaW₁₀O₃₆·32H₂O (LaW₁₀) have been chemically anchored to the amino-modified mesoporous silica through an organic linker. The catalysts have been characterized by ICP-ES, FT-IR, N₂ sorption measurements, UV-vis, MAS-NMR, and HR-TEM. It is found that the LaW₁₀ nanoparticles are highly dispersed on mesoporous silica, and the resulting catalysts show highly efficient deep desulfurization in only 35 min with almost 100% conversion of dibenzothiophene by using $(SiO_2/NH_3^+/LaW_{10})/[bmim]BF_4$ (bmim=1-butyl-3-methylimidazolium) in the presence of H_2O_2 as oxidant. Furthermore, deep desulfurization proceeds smoothly in model oil with S content as low as 100 ppm. A scaled-up experiment, in which the volume of model oil increases from 5 to 1000 mL with S content of 1000 ppm, indicates that almost 100% sulfur removal can be achieved in 45 mins. Additionally, the catalyst could be recycled and reused at least ten times without any decrease of the catalytic efficiency. To the best of our knowledge, the (SiO₂/NH₃⁺/LaW₁₀)/[bmim]BF₄ catalyst system with H₂O₂ as oxidant exhibits great potential for practical application as desulfurization systems reported so far.

Keywords: Polyoxometalates, Desulfurization, Lanthanides, Mesoporous silica

1. Introduction

Sulfur-containing compounds in transportation fuels such as gasoline and diesel oil can be converted to SO_x and NO_x during combustion, which not only are responsible for the formation of smog, sour gases, acid rain and haze, but also poison noble metal catalysts for reducing SO_x and NO_x emissions. The recent presence of haze continuously in China has drawn attention to the quality of fuels. It is known that thiophene sulfides account for more than 80% of the total sulfur content in diesel fuel, and benzothiophene (BT) and dibenzothiophene (DBT) account for 70% of thiophene sulfides. As a result, the removal of thiophene sulfides is a top priority in industry.[1, To date, hydrodesulfurization (HDS) has been applied in industry, and this 2] method is efficient in removing thiols, sulfides, and disulfides from fuels.[3] However, conventional HDS is less effective for removing the refractory sulfur-containing compounds such as DBT and its derivatives.[4] In addition, HDS requires harsh conditions such as high temperature, high pressure, the catalysts with high activity, and high operating cost. Under such circumstances, oxidative desulfurization (ODS) has been explored intensively as a promising alternative to HDS in recent years since the operating conditions are mild and no hydrogen is necessary.[5-7] To the best of our knowledge, the development of non-HDS technologies for the production of clean diesel fuel with little-to-no sulfur content under mild conditions remains to be highly demanding and challenging.

Ionic liquids (ILs) exhibit many desirable properties such as nonvolatility, sparing solubility in nonpolar organic solvents, good solvent power, and high thermal stability, and thus show great potential in various research areas. Recently, the use of extractive catalytic oxidative desulfurization (ECODS) in the presence of polyoxometalates (POMs) as catalysts has attracted wide interest and attention.[8-12] Our previous studies have demonstrated that highly efficient deep desulfurization can be realized by using lanthanide-containing POMs of $Na_7H_2LaW_{10}O_{36}\cdot 32H_2O$ as catalysts under mild conditions.[6, 7]

Polyoxometalates (POMs) constitute a group of discrete anionic metal-oxides of V,

Mo, W and Nb *etc.* and they are thermally and oxidatively stable compared with commonly used organic ligands. The chemical properties of POMs such as redox potential, electron-transfer properties, acidities, and solubility *etc.* can be finely tuned by adjusting the metal ions, the heteroatoms and the counter ions. These properties endow POMs to be superior catalytic materials for oxidative catalysis.[13-20] It is known that most oxidative desulfurization (ODS) processes reported so far are homogeneous catalysis, which causes the catalyst separation an added step. As a result, many catalysts are not applicable in the practical industrial application. To overcome the above-mentioned limitation, LaW_{10} has been immobilized onto mesoporous silica to prepare a heterogeneous catalyst that incorporates the properties of both the active LaW_{10} and a high surface area of silica support. The desulfurization experiments have indicated that an efficient and recyclable heterogeneous catalyst of $SiO_2/NH_3^+/LaW_{10}$ presents great potential for industrial application.

2. Experimental Section

2.1. Chemical materials

Na₂WO₄·2H₂O (99%), acetic acid (99%), LaCl₃·7H₂O (99%), dibenzothiophene (DBT, 98%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, 95%), benzothiophene (BT, 98+%), hydrogen peroxide (30 wt% $H_2O_2),$ *n*-octane (99%) (3-aminopropyl)triethoxysilane (APTES) and trifluoromethanesulfonic acid were obtained from Alfa and were used without further treatment. Mesoporous silica (Silica gel, 227196 SIGMA-ALDRICH, particle size: 40-63µm, pore size: 60 Å, amorphous state) and the ionic liquids [bmim]BF₄, [bmim]PF₆, (bmim=1-butyl-3-methylimidazolium) [omim]BF4, and [omim]PF6 (omim=1-octyl-3methyl-imidazolium) were purchased from Sigma-Aldrich and used directly without further purification. All solvents were of analytical grade, purchased from Alfa Aesar, and used without further purification.

2.2. Measurements

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 59.6 MHz for ²⁹Si on a Bruker Avance 300M solid-state spectrometer equipped with a commercial 5 mm MAS NMR probe. The N₂ 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. The specimen was dispersed in ethanol using an ultrasonic washer, and dropped on a holey ultrathin carbon film. Diffuse reflectance UV–vis (DRUV–vis) spectra of catalyst samples were obtained using a Shimadzu UV-2101 PC spectrometer equipped with a diffuse–reflectance attachment, with BaSO₄ as the reference. Inductively coupled plasma emission spectroscopy (ICP-ES, Shimadzu ICPS-7500) was used to measure the concentration of La or Eu in the catalysts. The content of DBT, BT, and 4,6-DMDBT was analyzed on an Agilent 7820A GC system by using a 30 m 5% phenymethyl silicone capillary column with an ID of 0.32 mm and 0.25 mm coating (HP-5).

2.3. Preparation of lanthanide-containing POMs

 $Na_7H_2LaW_{10}O_{36}$ ·32H₂O was synthesized and characterized according to the literature method. The ICP and FT-IR data were summarized in Table S1.[21]

2.4. Catalyst preparation

The surface modification of mesoporous silica by (3-aminopropyl) triethoxysilane (APTES) was carried out as follows: In a typical preparation, 0.5 g of mesoporous silica (particle size: 40-63 μ m, pore size: 60 Å) was pretreated at 393 K for 3 h under reduced pressure (<10⁻² torr). The activated mesoporous silica was refluxed in 50 cm³ of freshly-distilled toluene for 4 h. Then, 0.25 g of APTES was added and the reaction mixture was stirred under reflux conditions for 24 h. After the solvent was evaporated under vacuum, the solid was filtered and washed with distilled toluene, and then dried for 8 h at 80 °C under vacuum.

The amine-functionalized mesoporous silica was treated with trifluoromethanesulfonic acid to enhance POMs' loading. Protonation was carried out by adding 6 mole equivalent of trifluoromethanesulfonic acid per mole of LaW_{10} to amine-functionalized mesoporous silica. The more positively charged NH_3^+ group on the support, the stronger the electrostatic binding of LaW_{10} to the support. Freshly protonated amine-functionalized mesoporous silica (0.5g) was added to 50 mL of methanol solution containing 0.3 g of LaW_{10} and refluxed for 24 h. The sample was then filtered, washed with deionized water and dried at 100 °C under vacuum. The final materials are designated as $SiO_2/NH_3^+/LaW_{10}$.

2.5. Desulfurization procedure and analysis of S content

In a typical experiment, a solution of DBT, BT, and 4,6-DMDBT in *n*-octane was used as model oil with an S content of 1000 ppm. The catalytic oxidative desulfurization experiments were performed in a 50 mL two-necked flask, to which 0.08 mL of 30 wt% H₂O₂, 5 mL of model oil, 1 mL of [bmim]BF₄, and 60 mg of freshly prepared SiO₂/NH₃⁺/LaW₁₀ were added. The resulting H₂O₂/DBT/LaW₁₀ molar ratio was 150:30:1. The reaction mixture was stirred at 70 °C. During the reaction, the upper layer of the model-oil phase was periodically withdrawn and analyzed by gas chromatography with a flame ionization detector (GC-FID). DBT, BT, and 4,6-DMDBT were identified by 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 mL.

3. Results and discussion

3.1. Synthetic approach and characterization of the highly dispersed LaW_{10} nanoparticles on modified mesoporous silica

Scheme 1 shows the synthetic approach for preparation of supporting LaW_{10} on silica supports. Firstly, 3-aminopropyl groups (APTES groups) were grafted on mesoporous silica to obtain amine-functionalized material. Secondly, after the

protonation of the amine-functionalized mesoporous silica, the freshly activated material was added into the methanol solution of LaW_{10} and refluxed in order to load LaW_{10} onto the mesoporous silica.[22] The electrostatic interactions allow LaW_{10} to be chemically anchored strongly to the surfaces of the functionalized supports, resulting in the formation of POM-immobilized mesoporous silica $SiO_2/NH_3^+/LaW_{10}$. It should be noted that the lanthanum content in $SiO_2/NH_3^+/LaW_{10}$ is 87 µmol/g analyzed by inductively coupled plasma emission spectroscopy (ICP-ES).



Scheme 1. Schematic representation of the LaW₁₀ immobilization and dispersion result on mesoporous silica.



Figure 1. The ²⁹Si CP/MAS NMR profile of (a) SiO₂ and (b) SiO₂/NH₂.

As shown in Figure 1, the ²⁹Si CP/MAS NMR spectrum of SiO₂/NH₂ exhibit two visible resonances at -59 and -67 ppm, which correspond to RSi(OH)(OSi)₂ (T²) and RSi(OSi)₃ (T³), respectively (R = CH₂CH₂CH₂NH₂).[23] Additionally, the resonances at -101 and -110 ppm that are associated with (SiO)₃SiOH (Q³) and Si(OSi)₄ (Q⁴) can be observed, indicating that (3-aminopropyl) triethoxysilane (APTES) groups have been bound to the surface with two or three Si-O-Si linkages. Since no peak appears at -45 ppm, which is normally the chemical shift of silicon in liquid (3-aminopropyl) trialkoxysilane, this result indicates that no free silane molecules have been physically adsorbed on the amine-functionalized mesoporous silica surface.[24] Contrast experiment shows that no T² and T³ resonance can be observed in the ²⁹Si CP/MAS NMR spectrum of SiO₂.



Figure 2. FT-IR spectra of (a) SiO_2 , (b) SiO_2/NH_2 , (c) SiO_2/NH_3^+ (d) $SiO_2/NH_3^+/LaW_{10}$ and (e) LaW_{10} .

FT-IR spectra of $SiO_2/NH_3^+/LaW_{10}$, SiO_2/NH_3^+ , SiO_2/NH_2 , SiO_2 and LaW_{10} have been shown in Figure 2. The insertion of amino propyl groups on the mesoporous silica is confirmed by the presence of N–H bending mode vibrations at 1552 cm⁻¹ in the FT-IR spectrum of SiO₂/NH₂.[25] In the FT-IR spectrum of SiO₂/NH₃⁺/LaW₁₀, the original N-H bending at 1552 cm⁻¹ is shifted to 1519 cm⁻¹ (Figure 2d), indicating

the transformation of NH₂ to NH₃⁺. FT-IR spectrum of LaW₁₀ shows four characteristic peaks of W-O stretching bands at 944, 844, 785, and 710 cm⁻¹, which have shifted to 946, 883, 792, and 716 cm⁻¹, respectively, in the corresponding FT-IR spectrum of SiO₂/NH₃⁺/LaW₁₀.

Table 1. Physico-chemical properties of the materials.				
Materials	Surface area	Pore volume	Average pore	
	(m ² /g)	(cm ³ /g)	diameter (nm)	
SiO ₂	490	0.82	6.6	
SiO ₂ /NH ₂	322	0.73	5.6	
SiO ₂ /NH ₃ ⁺ /LaW ₁₀	135	0.34	4.9	



Figure 3. Adsorption-desorption isotherms of (a) SiO₂, (b) SiO₂/NH₂ and (c) SiO₂/NH₃⁺/LaW₁₀.



Figure 4. Pore size distribution of (a) SiO₂, (b) SiO₂/NH₂ and (c) SiO₂/NH₃⁺/LaW₁₀.

The BET measurements were carried out on the organo-functionalized mesoporous silica with and without LaW₁₀. The specific surface area, pore volume, and pore diameters (estimated from N₂ adsorption–desorption isotherms) are presented in Table 1. BET surface areas and BJH pore distributions were calculated using N₂ adsorption at 77 K. It can be seen clearly that the aminosilylation and introduction of LaW₁₀ significantly affected the surface area and pore distribution of the modified samples. The samples display a type IV isotherm with H₁ hysteresis (Figure 3). The textural properties of mesoporous silica are substantially maintained over amine functionalization and on subsequent anchoring of LaW₁₀.[26] The parent mesoporous silica sample exhibits a maximum pore diameter (6.6 nm) and surface area (490 m²/g) (Table 1). The aminosilylation of the mesoporous silica results in a shift of the pore maximum to smaller diameters (Figure 4) and a decrease in surface area (322 m²/g). Moreover, the introduction of LaW₁₀ leads to a further decrease in surface area and pore volume.



Figure 5. HRTEM images of (a) SiO_2 , (b) SiO_2/NH_2 , (c) $SiO_2/NH_3^+/LaW_{10}$, (d) (e) LaW_{10} highly dispersed on mesoporous silica and (f) magnification of selected region in (e) of mesoporous silica.

The HRTEM images of the parent mesoporous silica (Fig. 5a) and grafted samples (Fig. 5b and 5c) provide strong evidence that the mesoporous structure of supports has been retained. As shown in Figure 5d and 5e, LaW_{10} nanoparticles are highly dispersed on mesoporous silica and these nanoparticles are isolated and almost evenly distributed throughout the entire mesoporous silica without severe agglomeration. In addition, according to the HRTEM image, the LaW_{10} particle size is in the range of 1–2 nm and the lattice fringe of LaW_{10} nanoparticles can also be clearly observed, which indicates the LaW_{10} molecules are mono-dispersed on the mesoporous silica.



Figure 6. The UV/Vis spectra of (a) LaW_{10} and (b) $SiO_2/NH_3^+/LaW_{10}$.

As shown in Fig 6, the diffuse-reflectance UV/Vis spectroscopy of LaW_{10} exhibits characteristic absorption bands centered at 265 nm, whereas that of SiO₂/NH₃⁺/LaW₁₀ exhibits O→W ligand-metal charge-transfer (LMCT) transition at around 262 nm, which is very close to that of neat LaW₁₀. The result indicates the presence of LaW₁₀ in the corresponding mesoporous silica. The band shift suggests the interactions exist between LaW₁₀ and mesoporous silica. It should be noted that LaW₁₀ is under the constraint environment of mesoporous silica after immobilization.

3.2. Influence of different extractants on sulfur removal

Previous studies have shown that the selection of ionic liquids could have a significant influence on the catalytic desulfurization.[6,7] In this study, different ionic liquids have been added to the catalytic system, respectively, to investigate the effect

on the catalytic desulfurization of DBT by $SiO_2/NH_3^+/LaW_{10}$ (Table 2). In a typical catalytic oxidation reaction, DBT and freshly prepared $SiO_2/NH_3^+/LaW_{10}$ have been added to the model oil in the presence of H_2O_2 and different ionic liquids. Catalytic oxidative desulfurization of DBT with [omim]BF₄ or [omim]PF₆ as extractant shows sulfur removal of 51% or 95% in 80 min (Table 2). In contrast, when [bmim]BF₄ or [bmim]PF₆ is applied as extractant, >99% sulfur removal could be reached for [bmim]PF₆ in 40 min and [bmim]BF₄ in 35 min. As such, [bmim]BF₄ is used for the following studies.

		1			
Entry	Catalyst	IL	<i>t</i> [min]	S removal [%]	
1	SiO ₂ /NH ₃ ⁺ /LaW ₁₀	[omim]BF ₄	80	51	
2	SiO ₂ /NH ₃ ⁺ /LaW ₁₀	[omim]PF ₆	80	95	
3	SiO ₂ /NH ₃ ⁺ /LaW ₁₀	[bmim]BF ₄	35	99	
4	SiO ₂ /NH ₃ ⁺ /LaW ₁₀	[bmim]PF ₆	40	99	

Table 2. Effect of different ionic liquids on sulfur removal of DBT.

Reaction conditions: T=70°C H₂O₂ 0.080 mL, model oil 5 mL (S content 1000 ppm), [omim]BF₄ or [omim]PF₆ or [bmim]BF₄ or [bmim]PF₆ 1 mL, H₂O₂/DBT/LaW₁₀ 150:30:1.

3.3. Effect of temperature on sulfur removal of DBT

To investigate the effect of temperature on sulfur removal, oxidation of DBT has been performed at different temperatures (Table 3). The $SiO_2/NH_3^+/LaW_{10}$ shows desulfurization of DBT for 36%, 69% and 92%, 99%, at 30, 40, 50 and 60°C in 80 min, respectively. In contrast, this system reaches more than 99% sulfur removal in 35 min at 70 °C. Therefore, DBT can be completely removed in a relatively short reaction time at 70 °C.

Entry	temperature	<i>t</i> [min]	S removal [%]
1	30°C	80	36
2	$40^{\circ}C$	80	69
3	50°C	80	92
4	60°C	80	99
5	70°C	35	99

Table 3. Effect of different temperatures on sulfur removal of DBT

Reaction conditions: H₂O₂ 0.080 mL, model oil 5 mL (S content 1000 ppm), [bmim]BF₄, 1 mL H₂O₂/DBT/LaW₁₀ 150:30:1.

3.4. Effect of H_2O_2/DBT molar ratio on the desulfurization of model oil

To elucidate the influence of H_2O_2 on the desulfurization, different H_2O_2/DBT molar ratios have been applied under the optimized experimental conditions of T = 70 °C, 5 mL of model oil (S content 1000 ppm), 1 mL of [bmim]BF₄, DBT:LaW₁₀ = 30:1. With the increase of the H_2O_2/DBT molar ratio from 1:1 to 8:1 (Table 4, entries 1–5), the catalytic desulfurization of DBT increases gradually. When excess amount of H_2O_2 is applied, DBT is completely oxidized to DBTO₂, whereas only part of DBT transforms into DBTO₂ when one eqiv of H_2O_2 is applied. (Figure S1). The observed competition between H_2O_2 decomposition and DBT oxidation is in line with the results of Li and co-workers.[27]

Entry	H ₂ O ₂ /DBT	H ₂ O ₂ [µL]	<i>t</i> [min]	S removal [%]	
1	1	16	80	44	
2	2	32	80	74	
3	3	48	80	97	
4	5	80	35	99	
5	8	128	30	99	

Table 4. Effect of H₂O₂/DBT molar ratio on sulfur removal of DBT

Reaction conditions: $T = 70^{\circ}C$, model oil = 5 mL (S content 1000 ppm), [bmim]BF₄ = 1 mL, DBT/LaW₁₀ = 30:1.

3.5. Effect of DBT/LaW₁₀ molar ratio on the desulfurization of model oil

As shown in Table 5, the time for deep desulfurization could be shortened from 45 to 35 min when the DBT/LaW₁₀ molar ratio increases from 60:1 to 60:4 in the presence of 0.080 mL of H_2O_2 (Entries 1–3). It can be found that when DBT/LaW₁₀ molar ratio reaches to 60:8, sulfur removal reaches 86% in 35 min and 91% in 80 min, which might be caused by the catalyst poison. Furthermore, slight increase of the amount of H_2O_2 to 0.128 mL leads to almost 100% sulfur removal in only 20 min at T = 70 °C with the $H_2O_2/DBT/LaW_{10}$ molar ratio of 480:60:8 (Entry 9).

Entry	$H_2O_2/DBT/LaW_{10}$	H_2O_2 [µL]	<i>t</i> [min]	S removal [%]
1	300:60:1	80	45	99
2	300:60:2 = 150:30:1	80	35	99
3	300:60:4 = 75:15:1	80	35	99
4	300:60:8 = 75:15:2	80	35	86
5	300:60:8 = 75:15:2	80	80	91
6	480:60:1	128	35	99
7	480:60:2 = 240:30:1	128	30	99

Table 5. Effect of DBT/LaW₁₀ molar ratio on sulfur removal of DBT

8	480:60:4 = 120:15:1	128	30	99
9	480:60:8 = 240:15:2	128	20	99

Reaction conditions: $T = 70^{\circ}C$, model oil = 5 mL (S content 1000 ppm), [bmim]BF₄ = 1 mL.

3.6. Kinetic study on catalytic oxidation of sulfur compounds

To obtain the kinetic parameters for oxidation of DBT, experiments have been performed with the H₂O₂/DBT/LaW₁₀ = 150:30:1 at 70 °C. Percentage sulfur removal and ln(C_t/C₀) are plotted against reaction time in Figure 9, in which C₀ and C_t are initial DBT concentration and DBT concentration at time t, respectively. The linear fit of the data reveals that the catalytic reaction exhibits pseudo-first-order kinetics for the desulfurization of sulfides (R²=0.9946). The rate constant *k* of the oxidation reaction can be determined to be 0.10 min⁻¹. From the data of *k*(70°C), *k*(60°C), *k*(50°C) and *k*(40°C) (Figure 7, Figure S2), the calculated activation energy (*E*_a) for DBT oxidation is 58 kJ/mol. The oxidation of DBT to DBTO₂ could be complete in about 35 min. Thus, the catalystic reaction strictly obeys pseudo-first-order kinetics with 100% selectivity for DBTO₂.



Figure 7. Sulfur removal of DBT and $\ln(C_t/C_0)$ as functions of reaction time at 70°C. $H_2O_2 = 0.080$ mL, model oil = 5 mL (S content 1000 ppm), [bmim]BF₄ = 1 mL, $H_2O_2/DBT/LaW_{10} = 150:30:1$.

Further investigation of the activity and potential application of $SiO_2/NH_3^+/LaW_{10}$ has been carried out. First of all, it has been demonstrated that 100% desulfurization could be achieved in 5 min in model oil with S content as low as 100 ppm, indicating that deep desulfurization can be realized in oil with low S contents. Secondly, scaled-up experiment by increasing the model oil from 5 mL to 1000 mL shows that deep desulfurization can be reached in 45 mins, which suggest the $SiO_2/NH_3^+/LaW_{10}$ has a great potential for practical application.

Entry	volume of model oil	S content	<i>t</i> [min]	S removal [%]	
1	1000 mL	1000 ppm	45	99	
4	5 mL	100 ppm	5	99	

 Table 6. Effect of S content decrease and scaled-up experiments

Reaction conditions: T=70°C, H_2O_2 0.080 mL, model oil 5 mL (S content 1000 ppm), [bmim]BF₄ 1 mL, H_2O_2/LaW_{10} 150:1.

3.7. Sulfur removal of BT and 4,6-DMDBT

The performance of $SiO_2/NH_3^+/LaW_{10}$ with H_2O_2 as oxidant for different substrates including BT, DBT, and 4,6-DMDBT was evaluated (Table 7). It is known that, due to steric hindrance, it is very difficult to remove 4,6-DMDBT in the HDS process. Under our experimental conditions, the catalyst $SiO_2/NH_3^+/LaW_{10}$ proves to be highly efficient for removing sulfur of different substrates with 99% conversion of DBT in only 35 min, 92% conversion of BT and 86% conversion of 4,6-DMDBT in 80 min, respectively.

Table 7. Sulfur removal of DBT, BT, and 4,6-DMDBT.				
Entry	Substrates	<i>t</i> [min]	S removal [%]	
1	DBT	35	99	
3	BT	80	92	
4	4,6-DMDBT	80	86	

Reaction conditions: T = 70°C, $H_2O_2 = 0.080$ mL, model oil = 5 mL (S content 1000 ppm), [bmim]BF₄ = 1 mL, H_2O_2 /substrate/LaW₁₀ = 150:30:1.

3.8. recycling catalyst

The main advantage of using solid catalysts in a liquid-phase reaction is the ease of separation and reuse of the catalyst in catalytic cycles. The recycled $SiO_2/NH_3^+/LaW_{10}$ catalytic system has been applied for further oxidation of DBT.

After the desulfurization procedure, the upper layer was separated by decantation or using separatory funnel. Then, 50 mL of deionized water was added to the water phase to decrease the viscosity of IL. After that, the catalyst was separated by centrifugation and filtration. The diluted ionic liquid in deionized water was concentrated under vacuum to recycle the ionic liquid. As such, the IL and catalyst are both reusable. The catalyst could be recycled and reused at least ten times without any decrease of the catalytic efficiency (Figure S3).

3.9. Proposed desulfurization process



Figure 8. The proposed catalytic oxidative desulfurization process using the $(SiO_2/NH_3^+/LaW_{10})$ catalyst system.

As shown in Figure 8, the immiscibility of [bmim]BF₄ with model oil and catalyst results in the formation of triphasic catalyst system, in which DBT is in the oil phase, H_2O_2 is in the IL phase, and LaW_{10} immobilized onto the amine-modified mesoporous silica is in the solid phase. It should be mentioned that the presence of strong electronic interactions between LaW_{10} and the protonated $-NH_3^+$ group makes LaW_{10} anchored tightly onto SiO₂. At the interface of water phase/solid phase, LaW_{10} is continuously oxidized to active peroxo species in the presence of H_2O_2 . With the extraction of DBT from oil phase to IL phase, it can be oxidized by the

W-peroxo species to DBTO₂. ICP-ES measurement of the water phase shows no presence of La and W, indicating no bleach of LaW_{10} from solid catalyst to IL phase. The La (LaW₁₀) content is 86.6 µmol/g in the recycled catalyst, which is almost the same as new prepared catalyst. Additionally, the catalyst can be recycled and reused at least ten times without any decrease of the catalytic efficiency.

Conclusions

Immobilization of Na₇H₂LaW₁₀O₃₆·32H₂O onto amine-functionalized mesoporous silica leads to the formation of new heterogeneous catalyst of SiO₂/NH₃⁺/LaW₁₀. Deep oxidative desulfurization of DBT, BT, and 4,6-DMDBT has been achieved by applying the catalytic system of $(SiO_2/NH_3^+/LaW_{10})/[bmim]BF_4$ in the presence of H₂O₂ as oxidant. Furthermore, such desulfurization proceeds smoothly and efficiently in model oil with an S content as low as 100 ppm. The scaled-up experiment, in which the volume of model oil increases from 5mL to 1000 mL, shows that deep desulfurization can be realized in only 45 min. It has been demonstrated that 99% desulfurization of DBT in only 35 min, 92% conversion of BT and 86% conversion of 4,6-DMDBT can be achieved at 70 °C in 80 min, respectively. In addition, the heterogeneous catalyst can be recycled at least ten times without any decrease of the catalytic efficiency. Therefore, the SiO₂/NH₃⁺/LaW₁₀ is one of the most efficient heterogeneous desulfurization catalysts reported so far with great potential for further application.

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Graphic Abstract:

