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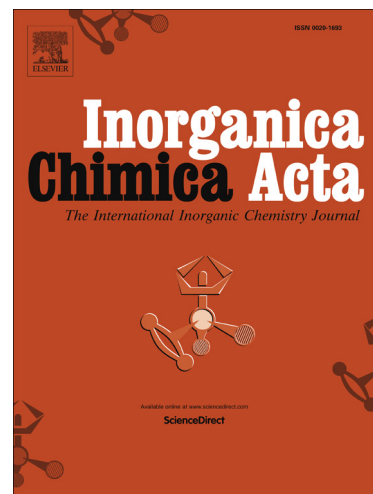Tingting Wang, Ying Lu, Hongli Wu, Enbo Wang

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# Surfactant-Encapsulated High-nuclear Polyoxometalate Complexes for Catalytic Oxidative Desulfurization of Model Oil

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**Abstract**

Two novel surfactant-encapsulated high-nuclear polyoxometalates catalysts $(DODA)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6] \cdot 27H_2O$ and $(DODA)_{10}[(HPMo_6O_{21})_2(C_2O_4)_3] \cdot 11H_2O$ have been prepared and characterized by TG, FT-IR, ^{1}H NMR and UV-vis. They were used for the oxidative desulfurization of model oil containing sulfur compounds such as dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), benzothiophene (BT) with $H_2O_2$ as an oxidant under mild conditions. The removal of DBT, 4,6-DMDBT and BT could reach above 98% under the optimal conditions of $n(S)/n(catalyst)/n(H_2O_2) = 220 : 1 : 880$ at 60 ℃ for 2.5 h, 4.5 h and 5 h respectively, which improved to be a promising catalyst in the ODS process. The oxidative reactivity of the sulfur-containing compounds decreased according to DBT > 4,6-DMDBT > BT. We investigated the main factors affecting the process including temperature, the polymeric structures of catalysts, and O/S ($H_2O_2$/DBT) molar ratio in detail. Moreover, the catalyst can be reused 5 times with high recycling efficiency.

*Key words:* surfactant-encapsulated; high-nuclear polyoxometalates; oxidative desulfurization; model oil.

## 1. Introduction

Polyoxometalates (POMs), as one kind of important molecule-based nanomaterials of the early transition metal oxides, have been applied in almost all fields, such as catalysis, photoelectric functional materials, and medicinal chemistry [1-8]. The studies of POMs as catalysts have attracted the most attention of POMs chemists, and design and syntheses of high activity, high stability and recycled POMs catalysts are the goals that researchers committed to achieve. We all know that most homogeneous catalysts are usually efficient, but they are difficult to separate and reuse from the solution. Nevertheless, heterogeneous catalysts can be recovered easily except they show relative long reaction time. Therefore, people committed to make catalysts both have good efficiency and easy recycling such as temperature-responsive catalyst, self-separation catalyst and phase-transfer catalyst [9-12]. Normally, POMs exist in solid and crystalline states, which limit their activity due to their poor solubility in organic solvents. In this context, a lot of new organic-inorganic salts were synthesized such as the surfactant-encapsulated POMs which usually consists of various quaternary ammonium cations and POMs anions [13-14]. Various POMs have been encapsulated by surfactants, for example, Keggin-, Dawson-, Anderson- and Preyssler-type POMs, etc [15]. The surfactant cations and POMs anions connected via electrostatic interaction [16-17]. Due to the encapsulation of surfactant, the resulting hybrids no longer dissolve in water but can be soluble in chloroform, benzene and other organic solvents increasing their processability and miscibility with organic matrices. For this reason, the sufactant-encapsulated POMs catalysts usually exhibit

high activity because they were soluble in the organic solvents. Apart from this, the sufactant-encapsulated POMs catalysts can be easily recovered by many methods, for example, some of which were temperature-controlled, which can precipitate from the reaction solution when the temperature decreased and be recovered by centrifugation [18]; and extraction with a polar extractant is also a common approach to separating and recovering these catalysts [19-20].

Conventional hydrodesulfurization (HDS) is the currently adopted method in industry to remove the sulfur compounds in fuel [21], but it will cost much to remove the refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives to become the ultra low sulfur diesel (ULSD) [22]. Oxidative desulfurization (ODS) is regarded as a promising strategy to remove the refractory aromatic thiophenes [23-24]. In recently years, POMs as catalysts for ODS processes have been widely researched [25-28], especially the surfactant-encapsulated POMs (SEPs) which not only exhibit high activity and selectivity but also can be easily recovered. In recent years, many SEPs as catalysts were applied in ODS process. Li and co-workers [29] have reported that SEP catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ can selectively oxidize the sulfur-containing molecules present in diesel using $H_2O_2$ as an oxidant under mild conditions, which exhibits high performance (96% efficiency of $H_2O_2$, is easily recycled, and ~100% selectivity to sulfones). Wu [30-31] *et al* have empolyed $(DODA)_3PW_{12}$ (DODA = dimethyldioctadecylammonium) as catalyst for catalytic sulfoxidation reactions, and demonstrated that supramolecular interactions plays a crucial role in promoting the activity of the catalyst. Beyond that,

the reported SEPs applied in the ODS process were formed by various POMs including Keggin-type $[PW_{12}O_{40}]^{3-}$, $[PMo_{10}V_2O_{40}]^{3-}$ [31-32], Dawson-type $[P_2W_{18}O_{62}]^{6-}$ [33], Anderson-type $[IMo_6O_{24}]^{5-}$ [34], Weakly-type $[EuW_{10}O_{36}]^{9-}$ [29a] and isopolyoxovanadate $[V_{10}O_{28}]^{6-}$ [35], *et al.* However, the studies on the SEPs formed by highnuclear POMs and their application in the ODS process are rare.

Recently, Niu and his co-workers [36] have synthesized a series of highnuclear complexes formed up by the polymerization of $[HPMo_6O_{21}]^{2-}$ units. Considering that the polymeric structure of the highnuclear complexes may increase active sites and catalytic efficiency, we synthesized SEP catalyst combing the highnuclear POMs anions built by $[HPMo_6O_{21}]^{2-}$ units with surfactant cations (**Fig. 1** and **Fig. 2**), $(DODA)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]•27H_2O$(**SEP-1**) and $(DODA)_{10}[(HPMo_6O_{21})_2(C_2O_4)_3]•13H_2O$ (**SEP-2**). We investigated the oxidation desulfurization of **SEP-1** and **SEP-2** in the model oil with the hydrogen peroxide as oxidant under optimized reaction conditions and studies the influence of the different polymeric structure on catalytic performance.

## 2. Experience

### 2.1. Materials and Methods

Commercially available 30 wt% $H_2O_2$, n-hexane, were purchased from Sinopharm Chemical Reagent Co. Ltd. Dimethyl distearylammonium chloride (DODACl) was commerical products from Aladdin Reagent Co. Ltd. (Shanghai, China) and used without further purification. DBT, BT and 4,6-DMDBT were obtained by Sigma-Aldrich. $(NH_4)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]•27H_2O$ **(POM-1)** and

$(NH_4)_8H_2[(HPMo_6O_{21})_2(C_2O_4)_3] \cdot 13H_2O$ (**POM-2)** was prepared according to literature procedure [36]. FT-IR spectra were recorded in the range of 400-4000 cm$^{-1}$ on an Alpha Centaurt FT-IR Spectrophotometer with pressed KBr pellets. $^1$H NMR spectrum (CDCl$_3$) was recorded on an AV-400 spectrometer (Bruker Corporation, Germany). UV-vis spectra were performed on an Agilent (8453) UV-vis diode-array spectrometerusing quartz cells of 1 cm optical path. TGA ware recorded with the powder sample on a Perkin-Elmer TGA instrument flowing N$_2$ with a heating rate of 10 °C min$^{-1}$. Elemental analyses (H, C, and N) were obtained with performed on a Perkin-Elmer 2400 C, H, N elemental analyzer. Mo and P were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The products were analyzed by GC-MS on a agilent 5975-6890N. The HPLC analysis were carried out using a Shimadzu LC-15C instrument on a C18 column and detected by UV detector (254 nm) at 30 °C through eluting with CH$_3$CN/H$_2$O (90 : 10) at a flow rate of 1 mL min$^{-1}$.

*2.2. Syntheses*

*2.2.1. Synthesis of SEP-1*.

**POM-1** (238 mg, 0.05 mmol) was dissolved in water (20 mL), and then DODACl (587 mg, 1 mmol) in chloroform (30 mL) was slowly added dropwise to the resultant solution with stirring. The initial molar ratio of **POM-1** to DODACl was controlled at 1 : 20. After the solution was stirring for about 6 h at room temperature, the organic phase was separated and evaporated the chloroform to dryness then the solid **SEP-1** was obtained. The product was stored in a vacuum desiccator for the measurements. The complex was characterized by FT-IR, TG, elemental analysis, $^1$H NMR

spectroscopy and UV-vis. IR (KBr, cm$^{-1}$): $v$ = 3424 (w), 2930 (s), 2851 (s), 1585 (w), 1469 (m), 1347 (w), 1102 (w), 894 (s), 800 (w), 692 (s), 570 (w), 527 (w).

*2.2.2. Synthesis of **SEP-2**.*

The synthesis of **SEP-2** followed the same procedure as for **SEP-1**, using the **POM-2** instead of the **POM-1**. The initial molar ratio of DODA·Cl to **POM-2** was kept at 10 : 1. IR (KBr, cm$^{-1}$) for **SEP-2**: $v$ = 3463 (s), 2932 (s), 2847 (s) 1640 (s), 1462 (m), 1336 (m), 1069 (s), 1001(w), 886 (s), 780 (w), 675 (s), 568 (w), 532 (w).

*2.3. Preparation of Model Oils.*

Different model oils were prepared in the following processes. 1.466 g DBT was dissolved in 500 mL n-hexane to obtain the model oil, the sulfur content of which was 500 μg mL$^{-1}$. Other kinds of model oil were prepared by dissolving the corresponding moles of 4,6-DMDBT and BT in n-hexane which the sulfur contents were both 500 μg mL$^{-1}$.

*2.4. Catalytic Oxidation of Dsulfurization in Model Oil*

For a typical catalytic oxidation reaction, freshly prepared **SEP-1** catalyst (6.0 mg, 0.365 μmol) was added to the model oil (5 mL) in the 10 mL round-bottom flask. The reaction system was allowed to stabilize at 60 ℃ under continuous stirring, meanwhile the catalyst was dissolved in the model oil. Then H$_2$O$_2$ (4 eq, 30 wt%) was added dropwise when temperature stabilized. During the reaction, these oxygenated DBTs were highly polarized and decreased the solubility in the model oil [37]. The reaction progress was determined by TLC (n-hexane/ethyl acetate 2:1) at different time intervals. When the reaction finished, the round-bottom flask was immersed in

an ice-water bath. Both DBT-sulfone and catalyst were precipitated as white solids [38]. The upper clear solution was removed after separation by means of centrifugation and analyzed by HPLC. The catalytic oxidation reactions of 4,6-DMDBT and BT were also performed using similar procedure. The catalytic oxidation reaction of **SEP-2** followed the same procedure as for **SEP-1**, using the **SEP-2** (5.6 mg, 0.730 μmol) instead of **SEP-1** as the catalyst, the initial molar ratio of **SEP-1** to **SEP-2** was kept at 1 : 2.

## 3. Result and discussion

### 3.1. Characterization of the Catalyst and Product

In the IR spectra of the solid-state **SEP-1**, **SEP-2** (**Fig. S1**), bands at 2923 (vas $CH_2$), 2844 (vs $CH_2$), and 1469 $cm^{-1}$ (d $CH_2$) (2932, 2847, 1462 $cm^{-1}$ for **SEP-2**) are assigned to $CH_2$ antisymmetric and symmetric stretching modes of DODA alkyl chains, and strong bands are observed at 1589, 1347, 894, 800, 699 $cm^{-1}$ (1640, 1336, 886, 780, 675 $cm^{-1}$ for **SEP-2**) for vibrations of **POM-1**. Some characteristic peaks at such as 1589, and 1347 $cm^{-1}$ (1640, 1336 $cm^{-1}$ for **SEP-2**) become weaker and also the position of these peaks moved a little, which confirms the success of the encapsulation step. Comparing the $^1H$ NMR spectra of DODACl and **SEP-1**, **SEP-2** (**Fig. S2**), we find that the $^1H$ signal of the -$CH_2$- group shifts from 1.25 ppm to 1.35 ppm (1.25 ppm to 1.27 ppm for **SEP-2**) and the $^1H$ signal of the -$CH_3$ group shifts from 0.89 to 0.98 ppm (0.89 ppm to 0.90 ppm for **SEP-2**). All these signals of the complexes have moved to the higher field, which confirms the existence of electrostatic interactions between the organic cations and **POM-1**. Similar absorption

bands are observed in the UV-vis spectra of **POM-1** at 221 nm (209 nm for **POM-2**) and **SEP-1** at 251 nm (245 nm for **SEP-2**) (**Fig. S3**). The band at 221 nm of **POM-1** (209 nm for **POM-2**) removes to 251 nm (245 nm for **SEP-2**), which demonstrates that the interaction between $DODA^+$ and polyoxometalate anions. All the test above proved that the surfactant has replaced the counter cation of **POM-1** and **POM-2**. The TGA analysis suggests a mass loss of 3.1 % (2.6 % for **SEP-2**) in the range of 20-100 °C (**Fig. S4**) resulting from the loss of water molecules in **SEP-1** and **SEP-2**. The number of crystallized water molecules established by elemental analysis and TG analysis is 27 for **SEP-1** (11 for **SEP-2**). Anal. Calc. For **SEP-1** ($C_{778}H_{1650}O_{125}N_{20}P_4Mo_{24}$): C, 58.7; H, 10.4; N, 1.76; P, 7.8; Mo, 14.5. Found: C, 57.7; H, 11.0; N, 1.36; P, 7.0; Mo, 14.1. According to the elemental analysis, ICP, TG analysis, the chemical formula of **SEP-1** was determined as $(DODA)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6] \cdot 27H_2O$. The chemical formula of **SEP-2** was determined as $(DODA)_{10}[(HPMo_6O_{21})_2(C_2O_4)_3] \cdot 11H_2O$. Anal. Calc. For **SEP-2** ($C_{386}H_{824}O_{65}N_{10}P_2Mo_{12}$): C, 58.9; H, 10.5; N, 1.8; P, 0.8; Mo, 14.6. Found: C, 57.7; H, 11.0; N, 1.56; P, 0.4; Mo, 13.9.

When the reaction finished, the round-bottom flask was immersed in an ice-water bath. Both product and catalyst were precipitated as white solids and were separated from the solution by centrifugation. The product was extracted by $CH_3CN$ at room temperature. Then the $CH_3CN$ solution was distilled at room temperature until a white crystal solid was produced and characterized by GC-MS (shown in **Fig. S5**) and IR (shown in **Fig. S6**). The appearance of characteristic frequencies at 1288 cm$^{-1}$ (vas,

$SO_2$) and 1161 cm$^{-1}$ (vs, $SO_2$) confirmed that sulfone was the only product, which was in accordance with the results of the GC-MS, the GC-MS analysis of model oil in the reaction process indicated that the DBT, 4,6-DMDBT and BT were oxidized to $DBTO_2$, 4,6-DMDBTO$_2$ and $BTO_2$.

*3.2. Effect of H$_2$O$_2$/DBT on the Desulfurization of Model Oil*

The effect of the amount of $H_2O_2$ on the oxidation desulfurization of model oil system under various $H_2O_2$/sulfur (O/S) molar ratios at 60 °C catalyzed by **SEP-1** was shown in **Table 1.** 1 mol sulfide usually need 2 mol hydrogen peroxide when the substrate all convert to sulfone in theory, but the actual experiment data show that the removal of sulfide can only reach 86.2 %, because the oxidant decomposed in the actual reaction inevitably. The removal of sulfide could reach 99.4% when the equivalent of hydrogen peroxide is 4. We can see from the results of the experiments that when the $H_2O_2$/DBT molar ratio was increased from 2 : 1 to 8 : 1, the removal of DBT increased from 86.2% at O/S = 2 to 99.4% at O/S = 4 in 2.5 h, when increasing the amount of oxidant slightly. Further increasing the O/S ratio to 6 and 8, the removal of DBT didn't change too much. So in view of the cost of the oxidant and the productivity, O/S molar ratio at 4 was the appropriate condition. (**Entry 3**).

*3.3. Effect of Temperature on the Desulfurization of Model Oil.*

The effect of temperature on the desulfurization of DBT in the model oil catalyzed by **SEP-1** was investigated in **Table 2** The removal of substrate increased significantly with the reaction temperature changed from 45 °C to 60 °C. It can be found that DBT was almost eliminated completely at 60 °C after 150 min. Moreover,

when the temperature dropped to 55, 50, or 45°C, the removal of DBT was not so perfect as the 60 °C, which can only reach 92.2%, 82.3%, and 72.5% respectively. In view of the desulfurization effect, 60 °C was better than the others and too high temperature will contribute to the decomposition of $H_2O_2$, so the reaction temperature of 60 °C was recommended.

*3.4. Effect of Different Desulfurization System*

DBT, 4,6-DMDBT, and BT were selected as sulfur compound representatives of those refractory sulfur compounds in fuels. Removals of sulfide in different desulfurization systems are shown in **Table 3**. 4,6-DMDBT and BT exhibited a much lower reactivity than that of DBT. Remove all the DBT needs about 2.5 h, however the other two sulfides 4,6-DMDBT and BT need 4.5 h, 5 h respectively. Without the catalyst **SEP-1**, the removals of DBT, 4,6-DMDBT and BT were merely 5.1 %, 2.1 %, and 1.4 % respectively. When **SEP-1** was used as a catalyst, the removal of DBT, 4,6-DMDBT and BT increased remarkable, reaching 99.4 %, 98.8 %, 98.6 % respectively indicating that the catalyst **SEP-1** played a important role in catalytic oxidation desulfurization.

Compared with DBT and 4,6-DMDBT, the electron density of BT (5.696) in the sulfur atom is lowest, resulting to its lowest reactivity. The electron density differences of DBT and 4,6-DMDBT (5.758, and 5.760 for DBT and 4,6-DMDBT respectively) [39, 40] is so small that they can be ignored, the activity of 4,6-DMDBT is lower than DBT because of its steric hindrance. From the experiment result we can know that the oxidant reactivity of the sulfide occurs in the following order: BT <

4,6-DMDBT < DBT and the reaction rates of these sulfur-containing compounds are sensitive to the electron density on sulfur atoms and the steric hindrance of the substituted groups of sulfur-containing compounds [34b].

*3.5. The Effect of the Polymeric Structure on the Desulfurization of Model Oil*

In 2013, Niu [36] group reported two highnuclear POMs formed by the polymerization of $[HPMo_6O_{21}]^{2-}$ units, $(NH_4)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]\cdot 27H_2O$ (**POM-1**) and $(NH_4)_8H_2[(HPMo_6O_{21})_2(C_2O_4)_3]\cdot 11H_2O$ (**POM-2**). **POM-1** possesses a cage-type structure built by four $[HPMo_6O_{21}]^{2-}$ units joined together by six V-type dicarboxylate ligands. While **POM-2** exhibits a pillar-type structure constructed by two $[HPMo_6O_{21}]^{2-}$ units connected through three oxalate linkers. In order to investigate the influence of the different polymeric structure on catalytic performance, we synthesized SEP catalysts **SEP-1** and **SEP-2** combing the **POM-1** and **POM-2** with surfactant cations respectively and compared their catalytic performance on the oxidative desulfurization of DBT. As shown in **Table 3** (**Entry 5, 6**), the catalyst **SEP-1** exhibited higher catalytic activity than the catalyst **SEP-2**. It can be ascribed to the effect of the different polymeric structure, as we control the two catalysts with the same amount $\{HPMo_6\}$ catalytic active units during the catalytic process.

*3.6. The Recycle of the Catalyst*

The recycling of the **SEP-1** catalyst was investigated by choosing DBT as a substrate in the ODS system. When the first run was over, the round-bottom flask was immersed in an ice-water bath. Both DBT-sulfone and catalyst were precipitated as white solids, then were separated from the solution by centrifugation. Sulfone was

extracted by $CH_3CN$ at room temperature leaving the catalyst for the next experiment. The catalyst could be recycled 5 times without significant decrease in activity (**Fig. 3**), with the data 99.4%, 98.6%, 97.9%, 96.0%, 95.1% respectively. The desulfurization rate of the catalyst decreased from 99.4% to 95.1% after five recycles may be caused by the slight loss of catalyst during the catalyst seperation process. The catalyst was characterized by IR (**Fig. S7**) and $^1$H NMR (**Fig. S8**) after being recycled 5 times, from the IR spectra and the $^1$H NMR we find that the catalyst didn't change after the oxidative desulfurization of the model oil.

*3.7. Supposed mechanism of desulfurization system*

Based on the experiments and literatures [41-42], the overall mechanism of catalytic desulfurization can be supposed as follows. **Scheme 1** presents a schematic illustration of the oxidation of DBT to sulfone over the active species from the **SEP-1**. When **SEP-1** (abbreviated as **Mo**) reacting with excess $H_2O_2$, the catalyst with active oxygen (abbreviated as **Mo(O)**) was generated. Then an oxygen transmitted from the **Mo(O)** to the substrate, the transition state (DBTO) that a sulfide with an active oxygen formed, at the same time the initial **Mo** regenerated for the next cycle. The active peroxo species **Mo(O)** transmitted an oxygen atom to the transition state which lead to the formation of corresponding sulfone (DBTO$_2$) and the regeneration of the **Mo**, **Mo** is available to restart the catalytic cycle.

**4. Conclusion**

In this study, two novel surfactant-encapsulated high-nuclear polyoxometalate catalysts composed of the high-nuclear poly-{HPMo$_6$} POMs have been synthesized

and characterized by TGA, FT-IR, ^{1}H NMR and UV-vis. They were used as catalysts for the oxidation of model oil with $H_2O_2$ as an oxidant under mild conditions. We investigated the main factors affecting the process including the experiment temperature, the polymeric structure of catalyst, and O/S ($H_2O_2$/DBT) molar ratio in detail. The reaction activity decreased according to the following order: DBT > 4,6-DMDBT > BT. The catalytic activity has a relationship with the polymeric structures, as the two catalysts exhibited different catalytic activities when controling the two catalysts with the same amount {HPMo$_6$} catalytic active units during the process. Moreover, the oxidation system can recycle 5 times with high recycling efficiency. Therefore, this process provides a green, low-cost, and effective strategy to remove sulfur from diesel.

**Supplementary materials**

IR spectra, TG, ^{1}H NMR, UV-vis, GC-MS, and additional figures are available.

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**References**

[1] J. T. Rhule, C. L. Hill, D. A. Judd, R. F. Schinazi, Chem. Rev. 98 (1998) 327.

[2] R. Neumann, M. Gara, J. Am. Chem. Soc. 116 (1994) 5509.

[3] D. Mansuy, J. F. Bartoli, P. Battioni, D. K. Lyon, R. C. Finke, J. Am. Chem. Soc. 113 (1991) 7222.

[4] J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle, C. L. Hill, J. Am. Chem. Soc. 133 (2011) 16839.

[5] R. Xing, A. P. Zheng, F.Wang, L.Wang, Y. P. Yu, A. H. Jiang, Food. Chem. 175 (2015) 292.

[6] E. Rafiee, S. Eavani, Journal of Molecular Catalysis A: Chemical 380 (2013) 18.

[7] C. Ritchie, A. Ferguson, H. Nojiri, H. N. Mirs, Y. F. Song, D. L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin, L. Cronin, Angew. Chem. Int. Ed. 47 (2008) 5609.

[8] (a) X. X. Xu, X. Gao., T. T. Lu, X. X. Liu, X. L. Wang, J. Mater. Chem. A 3 (2015) 198; (b) X. L. Wang, J. Luan, H. Y. Lin, C. Xu, G. C. Liu, J. W. Zhang, A. X. Tian, CrystEngComm 15 (2013) 9995; (c) Y. Y. Zhou, S. Yao, J. H. Yan, L. Chen, T. T. Wang, C. J. Wang, Z. M. Zhang, Dalton Trans. 44 (2015) 20435.

[9] M. Wende, J. A. Gladysz, J. Am. Chem. Soc. 125 (2003) 5861.

[10] L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, Angew. Chem. Int. Ed. 43 (2004) 2924.

[11] Y. Leng, J. Wang, D. Zhu, X. Q. Ren, H. Q. Ge, L. Shen, Angew. Chem. Int. Ed. 48 (2009) 168.

[12] H. Hamamoto, Y. Suzuki, Y. M. A. Yamada, H. Tabata, H. Takahashi, S. Ikegami, Angew. Chem. Int. Ed. 44 (2005) 4536.

[13] Y. Z. Wang, H. L. Li, W. Qi, Y. Yang, Y. Yan, B. Li, L. X. Wu, J. Mater. Chem. 22 (2012) 9181.

[14] B. F. Zhang, P. C. Yin, F. D. Haso, L. Hu, T. B Liu, J. Cluster Sci. 25 (2014) 695.

[15] (a) H. L. Li, H. Sun, W. Qi, M. Xu, L. X. Wu, Angew. Chem. Int. Ed. 46 (2007) 1300; (b) W. Li, W. F. Bu, H. L. Li, L. X. Wu, M. Li, Chem. Commun. 30 (2005) 3785; (c) Y. Yang, L. Yue, H. L. Li, E. Maher, Y. G. Li, Y. Z. Wang, L. X. Wu, V. W. W. Yam, Small 8 (2012) 3105; (d) W. F. Bu, H. L. Li, H. Sun, S. Y. Yin, L. X. Wu, J. Am. Chem. Soc. 127 (2005) 8016; (e) A. Nisar, Y. Lu, J. Zhuang, X. Wang, Angew. Chem. Int. Ed. 50 (2011) 3187.

[16] P. C. Yin, J. Wang, Z. C. Xiao, P. F Wu, Y. G. Wei, T. B. Liu, Chem. Eur. J. 18 (2012) 9174.

[17] D. G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M. J. Koop, A. Müller, A. D. Chesne, Chem. Eur. J. 6 (2000) 385.

[18] H. Y. Lü, J. B. Gao, Z. X. Jiang, Y. X. Yang, B. Song, C. Li, Chem. Commun. 2 (2007) 150.

[19] C. Li, Z. X. Jiang, J. B. Gao, Y. X. Yang, S. J. Wang, F. P. Tian, F. X. Sun, X. P. Sun, P. L. Ying, C. R. Han, Chem. Eur. J. 10 (2004) 2277.

[20] P. P. Zhao, M. J. Zhang, Y. J. Wu, J. Wang, Ind. Eng. Chem. Res. 51 (2012) 6641.

[21] R. Prins, Angew. Chem. Int. Ed. 40 (2001) 1551.

[22] Y. Shiraishi, K. Tachibana, T. Hirai, I. Komasawa, Ind. Eng. Chem. Res. 41 (2002) 4362.

[23] H. X. Zhang, J. J. Gao, H. Meng, Y. Z. Lu, C. X. Li, Ind. Eng. Chem. Res. 51 (2012) 4868.

[24] P. D. Filippis, M. Scarsell, Ind. Eng. Chem. Res. 47 (2008) 973.

[25] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199.

[26] C. L. Hill, C. M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.

[27] N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944.

[28] K. Sato, M. Hyodo, M. Aoki, X. Q. Zheng, R. Noyori, Tetrahedron 57 (2001) 2469.

[29] (a) J. Gao, Y. Zhang, G. Jia, Z. Jiang, S. Wang, H. Lu, B. Song, C. Li, Chem. Commun. 3 (2008) 332; (b) H. Lü, J. Gao, Z. Jiang, F. Jing, Y. Yang, G. Wang, C.

Li, J. Cat. 239 (2006) 369; (c) C. Li, Z. Jiang, J. Gao, Y. Yang, S. Wang, F. Tian, F. A. Sun, X. Sun, P. Ying, C. Han, Chem. Eur. J. 10 (2004) 2277.

[30] M. Xu, H. L. Li, L. Y. Zhang, Y. Z. Wang, Y. Yuan, J. M. Zhang, L. X. Wu, Langmuir 28 (2012) 14624.

[31] W. Qi, Y. Z. Wang, W. Li, L. X. Wu, Chem. Eur. J. 16 (2010) 1068.

[32] C. Komintarachat, W. Trakarnpruk, Ind. Eng. Chem. Res. 45 (2006) 1853.

[33] Y. N. Zhang, L. Wang, Y. L. Zhang, Z. X. Jiang, C. Li, Chin. J. Catal. 32 (2011) 235.

[34] (a) H. Y. Lü, Y. Zhang, Z. X. Jiang, C. Li, Green Chem. 12 (2010) 1954; (b) H. Lü, W. Z. Ren, H. Y. Wang, Y. Wang, W. Chen, Z. H. Suo, Applied Catalysis A: General 453 (2013) 376.

[35] N. F. Tang, Y. N Zhang, F. Lin, H. Y. Lü, Z. X. Jiang, C. Li, Chem. Commun. 48 (2012) 11647.

[36] D. H. Yang, S. Z. Li, P. T. Ma, J. P. Wang, J. Y. Niu, Inorg. Chem. 52 (2013) 8987.

[37] W. S. Zhu, P. W. Wu, Y. H. Chao, H. M. Li, F. Zou, S. H Xun, F. X. Zhu, Z. Zhao, Ind. Eng. Chem. Res. 52 (2013) 17399.

[38] C. Li, Z. X. Jiang, J. B. Gao, Y. X. Yang, S. J. Wang, F. P. Tian, F. X. Sun, X. P. Sun, P. L. Ying, C. R. Han, Chem. Eur. J. 10 (2004) 2277.

[39] S. Otsuki, T. Nonaka, N. Takashima, W.H. Qian, A. Ishihara, T. Imai, T. Kabe, Energy Fuels 14 (2000) 1232-1239.

[40] Y. Shiraishi, K. Tachibana, T. Hirai, I. Komasawa, Ind. Eng. Chem. Res. 41 (2002) 4362-4375.

[41] A. M. Al-Ajloun, T. M. Daiafla, M. El-Khateeb, Journal of Molecular Catalysis A: Chemical 275 (2007) 139.

[42] Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, J. Org. Chem. 52 (1987) 1868.

**Figure and Table Caption**

**Scheme 1** The mechanism of desulfurization process.

**Table 1** Effect of $H_2O_2$/DBT on the desulfurization of model oil.

**Table 2** Effect of temperature on the desulfurization of model oil.

**Table 3** Effect of Different Desulfurization System.

**Figure 1** Schematic view of the synthesis of **SEP-1, (a) POM-1, (b)** surfactant

DODA⁺, **(c) SEP-1**.

**Figure 2** Schematic view of the synthesis of **SEP-2**, **(a) POM-2**, **(b)** surfactant

DODA⁺, **(c) SEP-2.**.

**Figure 3** The recycle times on the DBT removal with **SEP-1** as catalyst.

Scheme 1

Figure 1

(a)　(b)　(c)
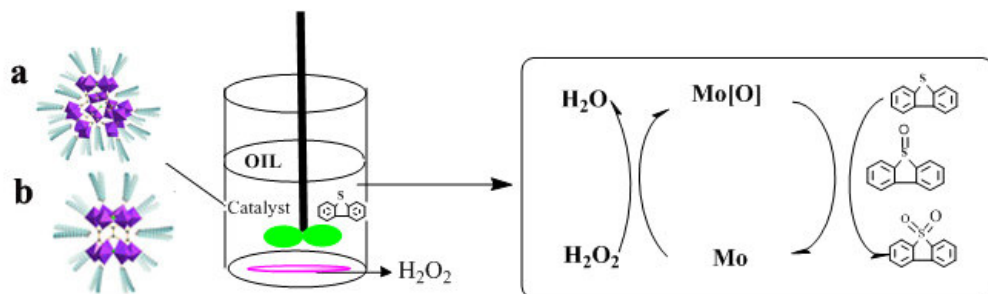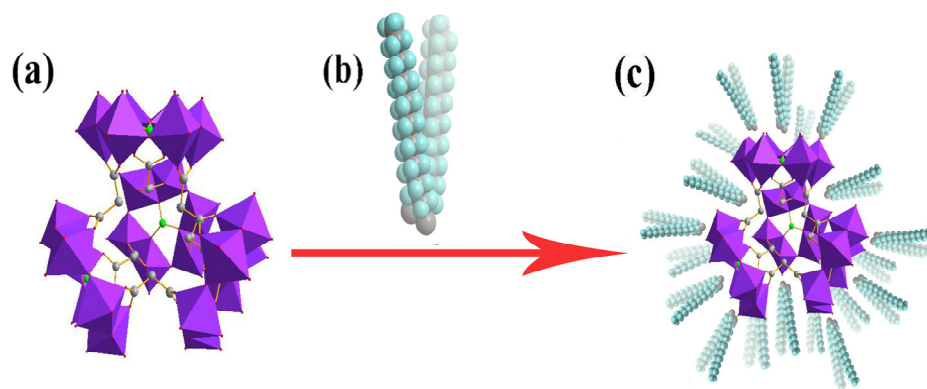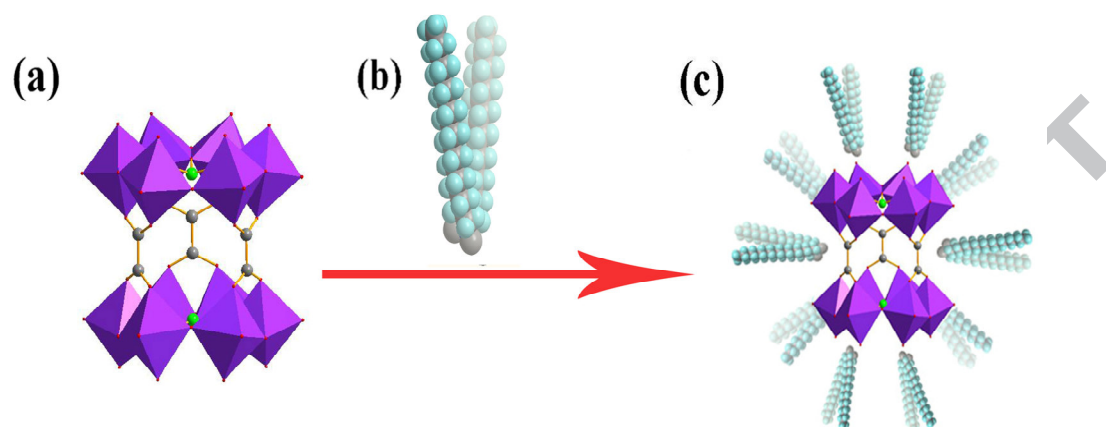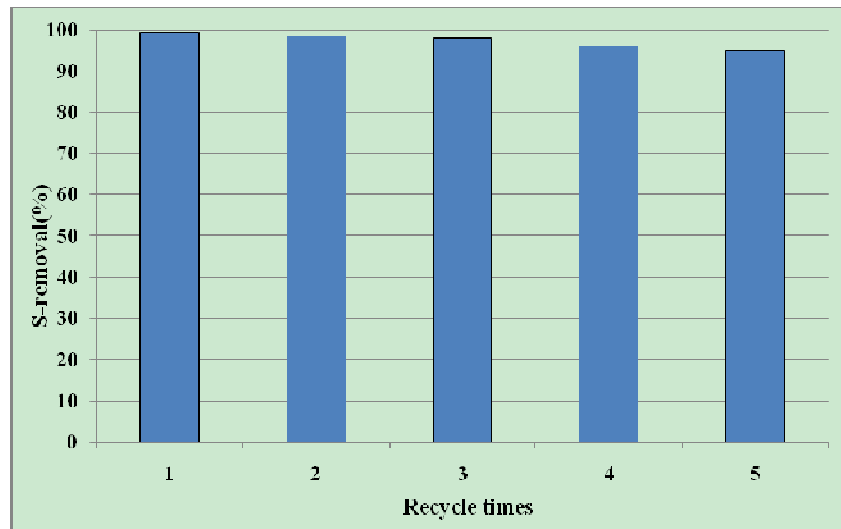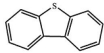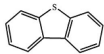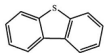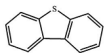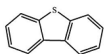
Figure 2

Figure 3

Table 1

| Entry | $H_2O_2$[eq] | Substrate | Product | $t$ [min] | Removal [%] |
|-------|--------------|-----------|---------|-----------|-------------|
| 1 | 2 | | | 150 | 86.2 |
| 2 | 3 | | | 150 | 92.3 |
| 3 | 4 | | | 150 | 99.4 |
| 4 | 6 | | | 150 | 99.6 |
| 5 | 8 | | | 150 | 99.6 |

Reaction conditions: $V$ (model oil) = 5 mL, $T$ = 60 °C, $n$(catalyst **1**) / $n$(DBT) = 1 : 220.

Table 2

| Entry | 温度[℃] | Substrate | Product | $t$ [min] | Removal, [%] |
|-------|---------|-----------|---------|-----------|--------------|
| 1 | 45 | | | 150 | 72.5 |
| 2 | 50 | | | 150 | 82.3 |
| 3 | 55 | | | 150 | 92.2 |
| 4 | 60 | | | 150 | 99.4 |

Reaction conditions: *V* (model oil) = 5 mL, *T* = 60 °C, *n*(catalyst **1**) / *n*(DBT) = 1 : 220.

Table 3

| Entry | Substrate | Product | Catalyst | $t$ [h] | Removal, [%] |
|-------|-----------|---------|----------|---------|--------------|
| 1 | | | **SEP-1** | 5 | 98.6 |
| 2 | | | none | 5 | 1.4 |
| 3 | | | **SEP-1** | 4.5 | 98.8 |
| 4 | | | none | 4.5 | 2.1 |
| 5 | | | **SEP-1** | 2.5 | 99.6 |
| 6 | | | **SEP-2** | 2.5 | 92.1 |
| 7 | | | none | 2.5 | 5.1 |

Reaction conditions: n(H$_2$O$_2$)/n(DBT) = 4, $V$ (model oil) = 5 mL, $n$(catalyst)/$n$(DBT) = 1 : 220, $T$ = 60 ℃

Two new surfactant-encapsulated high-nuclear polyoxometalate catalysts composed of the poly-$\{PMo_6\}$ POMs, $(DODA)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]\cdot 27H_2O$ (**SEP-1**) and $(DODA)_{10}[(HPMo_6O_{21})_2(C_2O_4)_3]\cdot 13H_2O$ (**SEP-2**), have been synthesized, and used as catalysts for the oxidative desulfurization of model oil with $H_2O_2$ as an oxidant. The removal of sulfide could reach above 98% under the optimal conditions.

## Surfactant-Encapsulated High-nuclear Polyoxometalate Complexes for Catalytic Oxidative Desulfurization of Model Oil

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*Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Renmin Street No. 5268, Changchun, Jilin 130024, PR China*
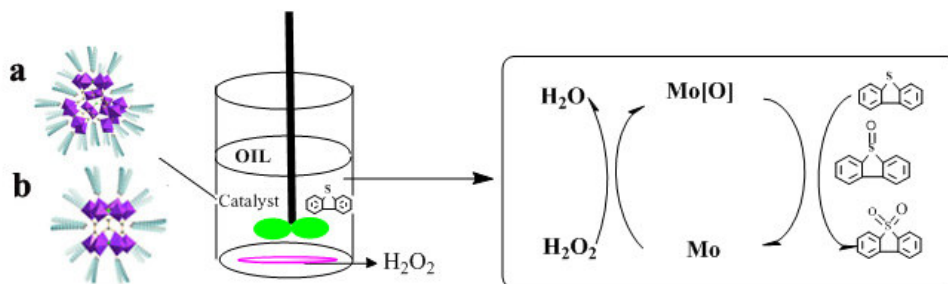
## Highlight

(1) The catalyst is a rare example of surfactant-encapsulated POMs formed by high-nuclear poly-{HPMo$_6$} POMs.

(2) The removal of sulfide could reach above 98% under the optimal conditions.

(3) The catalyst can be reused 5 times with high recycling efficiency.