Polymer Brushes Supported Polyoxometalate Catalyst for Ultra-Deep Desulfurization of Diesel

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In this paper, a novel catalyst ($PMo_{12}O_{40}$-PDMAEMA-SiO_2) with polymer brushes as support was synthesized in this paper. The catalysts were characterized by thermogravimetric analysis and fourier transform infrared spectroscopy and the results suggested that PDMAEMA was formed on the surface of SiO_2 and $[PMo_{12}O_{40}]^{3-}$ existed in the obtained catalyst. $PMo_{12}O_{40}$-PDMAEMA-SiO_2 was further used as oxidative catalyst in desulfurization process of dibenzothiophene dissolved in *n*-octane. $PMo_{12}O_{40}$-PDMAEMA-SiO_2 was found to be very effective for the oxidative removal of dibenzothiophene with desulfurization efficiency about 100 %. Experimental factors including type of different sulfur-containing compounds, O/S molar ratio, temperature, catalyst amount were evaluated and the optimal operating conditions were determined as O/S molar ratio, 24; reaction temperature, 60 ºC; the amount of catalyst, 0.008 g (5 mL model oil). Moreover, the new catalyst developed is reuseable. The recyclable $PMo_{12}O_{40}$-PDMAEMA-SiO_2 exhibited good catalytic performance and can be recycled for four times without significant decrease in catalytic activity. As a whole, $PMo_{12}O_{40}$-PDMAEMA-SiO_2 has high potential for using as an effective catalyst for deep desulfurization of diesel.

Key Words: Ultra-deep desulfurization, Diesel, Polyoxometalate, Polymer brushes, Recycleability.

INTRODUCTION

Sulfur compounds in diesel fuel burned at high temperature are changed into sulfur oxide (SO_x), which not only damage the engine, but also are easy to form acid rain in the atmosphere, causing serious damage to the environment[1]. In the past decade, many countries have set up environment legislations to limit sulfur content in transportation fuels[2]. According to the legislations in Japan and Europe, the sulfur content in diesel was limited to a maximum of 50 ppm by 2005 and further to 10 ppm by 2007. Emission and zero levels of sulfur content are being called for worldwide in the coming years[3]. Deep desulfurization of transportation fuels has become an important research subject due to the increasingly stringent regulations and fuel specifications in many countries for environmental protection purpose[4]. Hydrodesulfurization (HDS) is a traditional desulfurization technology, but reaction conditions of hydrodesulfurization are very harsh and refractory sulfur-containing compounds like dibenzothiophene (DBT) and its derivatives are difficult to remove from oils by hydrodesulfurization for steric hindrance of these compounds. Nevertheless, compared with hydrodesulfurization, oxidative desulfurization (ODS) can be carried out under very mild conditions. Especially, oxidative desulfurization is highly efficient

in oxidizing refractory organosulfur compounds to corresponding sulfones which are subsequently separated by extraction and adsorption. For this reason, oxidative desulfurization is considered as the most promising methods in deep desulfurization[6].

Many oxidants have been used in oxidative desulfurization, such as molecular oxygen, formic acid, hydrogen peroxide, NO_2, O_3, *tert*-butyl hydroperoxide. From an environmental and economic viewpoint, H_2O_2 is mostly chosen as an oxidant and water is the only by-product. H_2O_2 is effective in oxidative desulfurization with polyoxometalates as catalysts. In recent years, polyoxometalates with a Keggin structure such as $H_3PM_{12}O_{40}$ [M = Mo(VI), W(VI)] are of increasing interest in the oxidative desulfurization of dibenzothiophene[6] and good results were obtained. Li *et al.*[7] reported that a $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst, assembled in emulsion in diesel, could selectively oxidize dibenzothiophene and its derivatives into their corresponding sulfones using hydrogen peroxide as an oxidant under mild conditions. The sulfones can be easily separated from diesel by an extractant and the sulfur level of a prehydrotreated diesel can be lowered from 500 to 0.1 ppm after oxidation and then extraction. Wang *et al.*[8] reported that multi-walled carbon nanotube supported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was very effective for

the oxidative removal of dibenzothiophene, with a desulfurization efficiency of up to 100 %.

Separation and reuseability are important criteria of catalyst assessment. Although the homogeneous catalysts showed good activity in oxidative desulfurization process coupled with extraction, however, the used catalyst was very difficult to separate and recover. In view of these drawbacks, a superior and recoverable oxidative desulfurization catalyst, N,N-dimethylaminoethyl methacrylate (PDMAEMA) polymer brushes was used as support to prepare $PMo_{12}O_{40}$-PDMAEMA-SiO_2 catalyst. In the obtained novel catalyst, there are a mass of amino-groups in the PDMAEMA-SiO_2 polymer brushes, which can tightly immobilize $[PMo_{12}O_{40}]^{3-}$ on the chains of the polymer brushes in acid medium by electrostatic force between ammonium ion and $[PMo_{12}O_{40}]^{3-}$ anion, hence active components $[PMo_{12}O_{40}]^{3-}$ did not easily fell from the supports. Based on these viewpoint, a novel catalyst with high catalytic activity and reuseability can be synthesized with PDMAEMA-SiO_2 polymer brushes as the support of $[PMo_{12}O_{40}]^{3-}$.

EXPERIMENTAL

Silica nanoparticles 50 ± 5 nm in diameter was acquired from Aladdin and used after drying *in vacuo* at 110 ºC for 24 h to remove the physical adsorbed and chemical Materials. 3-Aminopropyltriethoxysilane (APTES, Aladdin, 99 %), 2-bromo-2-methylpropionyl bromide (Aladdin, 99 %) were used as received; N,N-dimethylaminoethyl methacrylate (DMAEMA, Aladdin, 99 %) were filtered through an basic aluminum oxide column before each polymerization for removal of inhibitor. Phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40} \cdot 24H_2O$), benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were analytical grade, commercially available and used without further purification.

Preparation of catalyst $PMo_{12}O_{40}$-PDMAEMA-SiO_2: In this paper we firstly report the polymer brushes supported polyoxometalate catalyst. In preparation of the catalyst, two steps are involved. At the first step, PDMAEM brushes on the surface of ATRP-initiator-anchored silica nanoparticles were prepared using atom transfer radical polymerization (ATRP) as previously reported[9]. In this step, silica nanoparticles were firstly modified with APTES to acquire NH_2-SiO_2 and then the ATRP-initiator-anchored silica nanoparticles (Br-SiO_2) were synthetized by reaction of amino groups in NH_2-SiO_2 with 2-bromo-2-methylpropionyl bromide. At last, the Br-SiO_2 was used to initiate DMAEMA polymerization. At the second step, for the preparation of $PMo_{12}O_{40}$-PDMAEMA-SiO_2, PDMAEMA-SiO_2 (1 g), double distilled water (100 mL), aceticacid (0.66 mL) were added into a 250 mL flask equipped with a mechanical stirring and then the $H_3PMo_{12}O_{40} \cdot 24H_2O$ (1 g, 0.44 mmol) dissolved in 10 mL of double distilled water was added dropwise into the flask. The resulting mixture was stirred for 24 h at room temperature. After reaction, the product were collected by filtration, washed thoroughly with methanol until the filtrate was colourless and dried in vacuum oven at 40 ºC. The synthesizing process of the catalyst was shown in Fig. 1.

Catalyst characterization: Fourier transform infrared spectra (FT-IR) were recorded on an Avatar 360 ESP FTIR
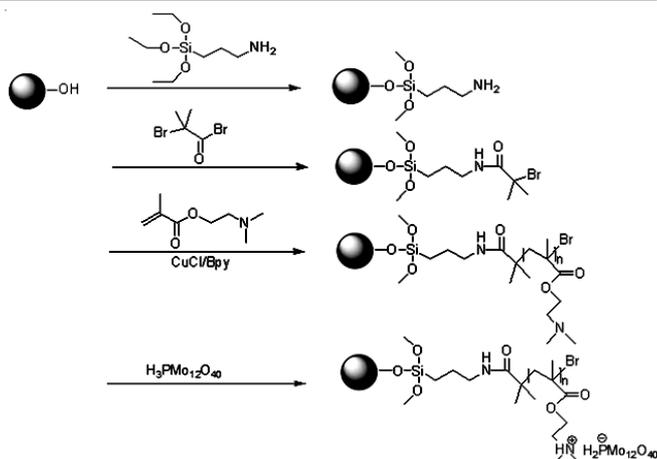
Fig. 1. Synthetic pathways for the synthesis of SiO_2-PDMAEMA-$PMo_{12}O_{40}$

spectrometer. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449 F3 with a heating rate of 20 ºC/min from 50 to 750 ºC under nitrogen atmosphere. The catalyst was analyzed on an inductively coupled plasma optical emission spectrometer (ICP-OES, GBC Integrn XL) to determine the $[PMo_{12}O_{40}]^{3-}$ content.

Evaluation of catalytic activity for desulfurization: The oxidative desulfurization of model fuels with H_2O_2 as oxidant was carried out in a mechanically stirred thermostated flask equipped with reflux condenser and a septum for withdrawing samples. The model oil with sulfur content of 34.7 ppm were obtained by dissolving sulfur-containing organic compounds (benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene) in *n*-octane. The oxidation of sulfur compounds were performed as follows: catalyst (0.01 mg), methanol (5 mL), model oil (5 mmol) and H_2O_2 (30 % aq., 0.66 μL) were added in the reaction flask. The reaction was carried out at a setting temperature. During the reaction, samples were withdrawn at regular time and the sulfone can be separated from the oil phase using acetonitrile as an extractant, then the oil phase was analyzed by a WK-2D microcoulometric detector. After reaction, the catalysts were separated from the reaction solvent by filtration, washed with acetonitrile until filtrate was colourless, dried under vacuum and used in the next run. With the same experimental method, the desulfurization experiments were carried out under other conditions.

RESULTS AND DISCUSSION

The successful preparation of the catalysts was verified by TGA and FT-IR analyses. All samples measured by TGA measurements were purified and dried before testing. TGA measurements were performed on SiO_2 nanoparticles, NH_2-SiO_2, Br-SiO_2 and PDMAEMA-SiO_2 to determine the amount of organics on the surface of SiO_2 nanoparticles (Fig. 2). As shown in Fig. 2a, a weight loss of 5.2 % for the unmodified SiO_2 nanoparticles may be attributed to the weight loss of hydroxyl groups or absorbed water on the SiO_2 nanoparticles surface. We can also discovered a weight loss of 9.07 % for the NH_2-SiO_2 (Fig. 2b) and 15.15% weight loss for Br-SiO_2 (Fig. 2c) when the samples are heated from about 50 to 750 ºC under nitrogen atmosphere. Therefore, the weight amount of ATRP initiator on the surface of SiO_2 was about 6 %. As

shown in Fig. 2d, the PDMAEMA-SiO₂ shows a main area of decreasing weight near 250 ºC due to the polymer content of PDMAEMA-SiO₂. According to the TGA analysis, the weight loss of the PDMAEMA-SiO₂ is about 35.59 %. In comparison with SiO₂-Br, the content of the grafted polymer was found to be about 20.44 %. From the synthetic schemes of PDMAEMA-SiO₂, the organic content on the surface of SiO₂ increases as the molecular weight of organics on the surface of SiO₂ increases. Meanwhile the results also indicate that the weight losses increase with increasing of the organic content on the surface of SiO₂. Hence the TGA results confirmed the synthesis of PDMAEMA-SiO₂ is successful.
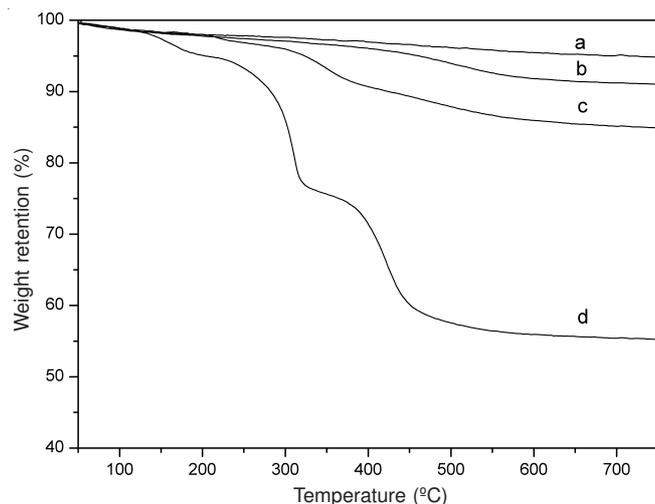
Fig. 2. TGA curves of silica nanoparticles (a), NH₂-SiO₂ (b), Br-SiO₂ (c), PDMAEMA-SiO₂ (d)

Additionally, Fig. 3 shows the FT-IR spectra of SiO₂, NH₂-SiO₂, Br-SiO₂, PDMAEMA-SiO₂ and PMo₁₂O₄₀-PDMAEMA-SiO₂, respectively. As seen in Fig. 3a, it exhibits a broad absorption peak around 3430 and 1060 cm⁻¹ assigned to the stretching vibration of -OH groups on the surface of silica nanoparticle and stretching of Si-O-Si, respectively. Comparing with the FT-IR spectra of silica nanoparticle, SiO₂-NH₂ shows new absorptions at 2920 and 1535 cm⁻¹ ascribed to -CH₂ and -NH₂ groups of NH₂-SiO₂[9] which indicated that the structure of sample NH₂-SiO₂ was formed as shown in Fig. 1. For the samples of Br-SiO₂, the peak at 1645 cm⁻¹ is attribute to the C=O stretching vibration covered up by the bending O-H bands of adsorbed water. After polymerization of DMAEMA on the surface of Br-SiO₂ a new strong absorption peak at 1730 cm⁻¹ ascribed to the stretching vibration of the ester carbonyl (C=O) associated with DMAEMA units[10]. The results of FT-IR qualitatively prove that the polymer brushes PDMAEMA-SiO₂ was synthesized successfully. It has been widely reported that phosphomolybdic acid with Keggin structures gives several strong, typical IR bands at 1065 cm⁻¹ (stretching frequency of P-O in the central P-O₄ tetrahedron), 962 cm⁻¹ (terminal bands for Mo=O in the exterior MoO₆ octahedron), 875 cm⁻¹ and 790 cm⁻¹ (bands for the Mo-Oᵦ-Mo and Mo-Oᵧ-Mo bridge, respectively)[11]. From Fig. 3, all of these absorption peaks were observed. The data indicated that the [PMo₁₂O₄₀]³⁻ anion with Keggin structures was successfully immobilized in the polymer brushes PDMAEMA-SiO₂ without structural changes.
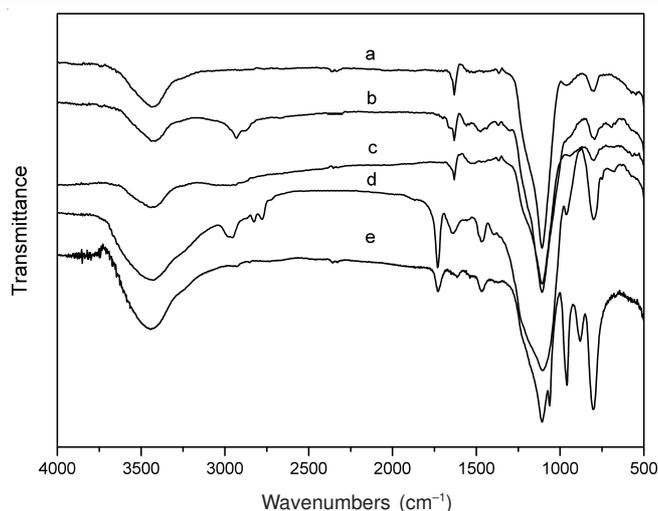
Fig. 3. FT-IR spectra of silica nanoparticle (a), NH₂-SiO₂ (b), Br-SiO₂ (c), PDMAEMA-SiO₂ (d), PMo₁₂O₄₀-PDMAEMA-SiO₂ (e)

To investigate the influence on the amount of oxidant on the desulfuration rate, various O/S molar ratios (equivalent to $2[H_2O_2]/[S]$) on the removal of dibenzothiophene are given in Fig. 4. In theory, the dibenzothiophene compounds were oxidized to their corresponding sulfones DBTO₂ using hydrogen peroxide as the oxidant and two molars of hydrogen peroxide are consumed for one molar of dibenzothiophene sulfur-containing compound, according to the stoichiometric reaction. The experimental results exhibited the O/S molar ratios had a strong effect on the reaction. As the O/S molar ratios increased from 10 to 24, the desulfurization efficiency of dibenzothiophene was increased quickly from about 87 to 100 % in 3 h. It is well-know that the increase in concentration of any reactant will result in the increase of the conversion of the rest reactants to a given chemical reaction. Moreover, hydrogen peroxide is known to be susceptible to disproportionation with oxygen evolution and some metal complexes are known to catalyze this process[12,13]. For this reason, the favourable O/S molar ratio is 24 from the results which are much more than the theoretical value.
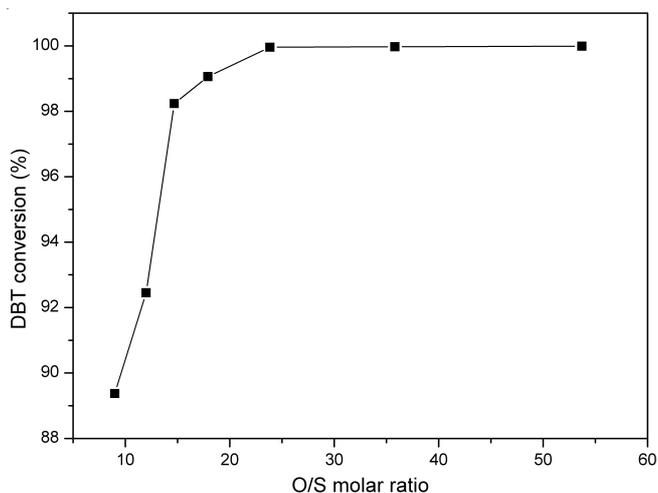
Fig. 4. Effect of O/S molar ratio on the desulfuration rate. Conditions: methanol = 5 mL, model oil = 5 mL, O/S = 24, PMo₁₂O₄₀-PDMAEMA-SiO₂ = 0.01 g, T = 60 ºC, t = 3 h

The amount of $PMo_{12}O_{40}$-PDMAEMA-SiO_2 catalyst plays an important role in the removal of dibenzothiophene. To investigate the effect of the amount of catalyst on the removal of dibenzothiophene, the amount of catalyst was changed under the same reaction condition. The desulfuration rate using different amount of catalyst are shown in Fig. 5. A rising trend is discovered from the Fig. 5. But the increased catalytic activity is not obvious when the amount of catalyst reaches 0.006 g and 100 % desulfurization rate of dibenzothiophene is obtained when the amount of catalyst gets up to 0.008 g. Since $[PMo_{12}O_{40}]^{3-}$ can react with H_2O_2, producing active intermediates known as peroxo-heteropoly compounds, including $[(PO_3(OH)\{MoO(O_2)_2\}_2)]^{2-}$, $[(PO_4)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]^{3-}$ and $[(PO_4)\{MoO(O_2)_2\}_4]^{3-}$ and so on and these peroxo-heteropoly compounds can react with dibenzothiophene more easily[14,15]. Hence, increasing the amount of catalyst, more peroxo-heteropoly compound species can be formed and deepens the reaction[8]. From Fig. 5, the optimal amount of catalyst can be recommended as 0.008 g under our study condition.
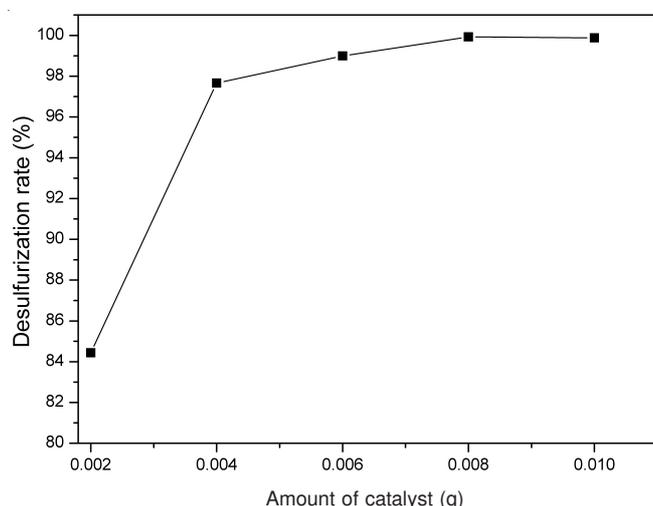
Fig. 5.   Effect of the amount of catalyst on desulfuration rate. Conditions: methanol = 5 mL, model oil = 5 mL, O/S molar ratio = 24, T = 60 °C, t = 3 h

The effect of reaction temperature on the desulfuration rate of dibenzothiophene was investigated from 30 to 70 °C. The desulfurization rate of dibenzothiophene in this catalytic system increased with increasing reaction temperature, as shown in Fig. 6, because the formation quantity of the peroxo-heteropoly compounds will increase with higher reaction temperature and its oxidative ability toward sulfide will be strengthened[16]. The desulfurization is only about 84 % at 30 °C, but the desulfurization rapidly go up to 97 % at 40 °C. When the temperature increases to 60 °C, the desulfurization rate reach up to 100 % and the desulfurization rate maintains at 100 % even the temperature increases to 70 °C continually. The results showed that the temperature of 60 °C is appropriate for this reaction system, so this temperature is used in the latter study.

The performance of catalyst $PMo_{12}O_{40}$-PDMAEMA-SiO_2 for benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), was investigated
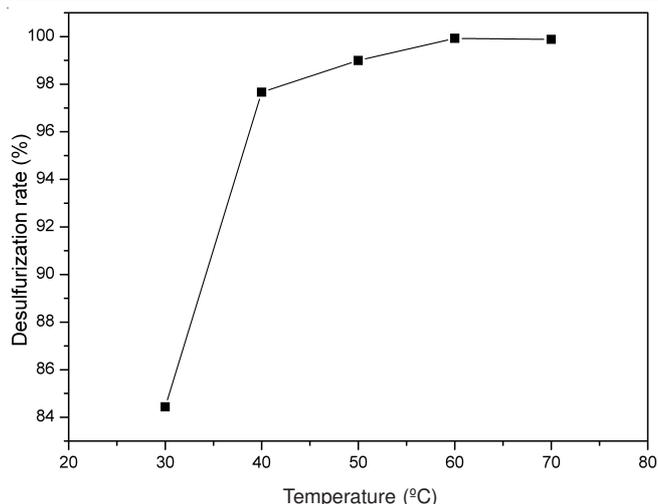
Fig. 6.   Effect of reaction temperature on desulfuration rate. Conditions: methanol = 5 mL, model oil = 5 mL, O/S molar ratio = 24, $PMo_{12}O_{40}$-PDMAEMA-SiO_2 = 0.008, t = 3 h

using hydrogen peroxide (H_2O_2) as the oxidant, as shown in Fig. 7. The relative desulfuration rates of these three model S-containing molecules allow not only to rank them in terms of reactivity but also to evaluate the potential of oxidative desulfurization process in fuel desulfurization[17]. Comparison of the catalytic oxidation reactivity of the three sulfur-containing compounds, the reactivity order was DBT > BT > 4,6-DMDBT. The results also indicated that the removal of three sulfur compounds increased with the increasing time, reaching 100, 99 and 94 %, respectively. The order can be explain as below. As calculated by Otstuki et al.[18], the electron densities on sulfur atoms are 5.758 for dibenzothiophene and 5.739 for BT. The electron density on sulfur atom of dibenzothiophene are higher than that of BT, which led to that dibenzothiophene has the higher oxidative reactivity than BT. The molecular diameter of 4,6-DMDBT is the biggest amongst these three sulfides. Because the distance between polymer chains of polymer brushes is very small, the sulfur atom of 4,6-DMDBT is difficult to approach the catalytic active species of $[PMo_{12}O_{40}]^{3-}$ between the chains of polymer brushes, due to the hindrance of big molecule of 4,6-DMDBT. Owing to this factor, the desulfurization efficiency of 4,6-DMDBT was lower than that of dibenzothiophene. The results indicated that the reactivity order was affected by both electron density and steric hindrance. Therefore, the obtained $PMo_{12}O_{40}$-PDMAEMA-SiO_2 is suitable for the desulfurization of dibenzothiophene, because dibenzothiophene has moderate sulfur atom electron density and molecule diameters.

Reusability and recycling of $PMo_{12}O_{40}$-PDMAEMA-SiO_2 catalyst was tested. After reaction was completed, the catalyst was recovered by simple filtration, washed with methanol, dried in vacuum oven at 40 °C and then reused in the next reaction. The results shown in Fig. 8 clearly display that there is nearly no decrease in catalyst activity after four recycled runs. These results show that $PMo_{12}O_{40}$-PDMAEMA-SiO_2 catalyst is highly efficient in sulfur removal and can be consider as effective and promising catalyst for oxidative desulfurization of refractory organosulfur compounds. The good reusability of catalyst could be due to the peculiar structure of polymer
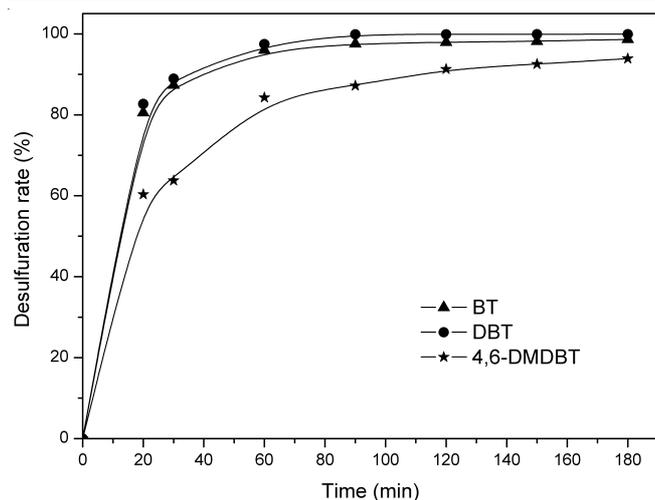
Fig. 7. Effect of different sulfur-containing compounds on the desulfuration rate. Conditions: methanol = 50 mL, model oil = 50 mL, $PMo_{12}O_{40}$-PDMAEMA-SiO_2 = 0.04 g, T = 60 °C, t = 3 h
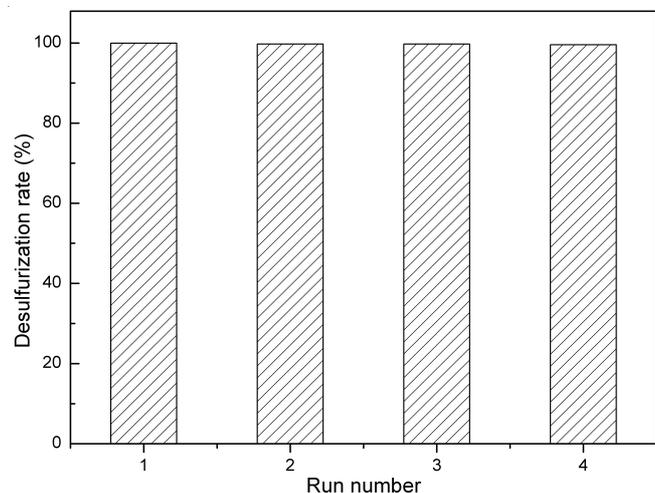
Fig. 8. Effect of the run number on the desulfuration rate. Conditions: methanol = 5 mL, model oil = 5 mL, $PMo_{12}O_{40}$-PDMAEMA-SiO_2 = 0.008 g, T = 60 °C, t = 3 h

brushes, densely grafted polymer chains and one amino-group in the every unit of polymer. That means that abundant amino-groups on the surface of SiO_2 nanoparticles which could hold tightly the polyoxometalate anion moiety, $[PMo_{12}O_{40}]^{3-}$, resulting in the catalytic active species did not drop easily from the supports. And this interpretation was further confirmed by ICP-OES results shown in Table-1. The $[PMo_{12}O_{40}]^{3-}$ contents of $PMo_{12}O_{40}$-PDMAEMA-SiO_2 were determined by using an inductively coupled plasma optical emission spectrometer. The $[PMo_{12}O_{40}]^{3-}$ content of fresh catalyst is about 52 % and the $[PMo_{12}O_{40}]^{3-}$ content of catalyst is about 47 % after four times recycling. Furthermore, a little amount of $[PMo_{12}O_{40}]^{3-}$ fell from the catalyst after the second recycle.

Conclusion

In conclusion, we have successfully prepared the polymer brushes supported catalyst, $PMo_{12}O_{40}$-PDMAEMA-SiO_2, by anchoring $[PMo_{12}O_{40}]^{3-}$ into polymer brushes PDMAEMA-SiO_2 successfully applied for the oxidative desulfurization of

TABLE-1
THE $[PMo_{12}O_{40}]^{3-}$ CONTENT OF CATALYSTS

Entry	Run	Mo content[a] (wt %)	$[PMo_{12}O_{40}]^{3-}$ content[b] (wt %)
1	Fresh catalyst	32.9	52.1
2	2	31.7	50.2
3	3	30.4	48.0
4	4	30.0	47.6
5	5	29.7	47.0

[a]Mo content was from ICP-OES experiment result.

[b]$W_{(H_3PMo_{12}O_{40})} = \dfrac{M_1}{M_2 \times 12} \times A$; M_1, M_2 and A represent molecular weight of $[PMo_{12}O_{40}]^{3-}$, atomic weight of Mo and Mo content from ICP OES results.

model oil. TGA and FT-IR of the $PMo_{12}O_{40}$-PDMAEMA-SiO_2 catalysts show the $[PMo_{12}O_{40}]^{3-}$ was immobilized into polymer brushes of PDMAEMA-SiO_2. Experimental factors affecting the oxidative desulfurization process, including O/S molar ratio, reaction temperature, the amount of catalyst and different sulfur-containing compounds were also evaluated.

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