Chinese Journal of Catalysis 37 (2016) 2098–2105

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Article

Ultra-deep oxidative desulfurization of fuel with H_2O_2 catalyzed by phosphomolybdic acid supported on silica

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ARTICLE INFO

Article history:
Received 22 July 2016
Accepted 18 September 2016
Published 5 December 2016

Keywords:
Mesoporous silica
Phosphomolybdic acid
Oxidative desulfurization
Benzothiophene
Dibenzothiophene

ABSTRACT

A highly active catalyst of phosphomolybdic acid (HPMo) was prepared and applied in the catalytic oxidative desulfurization (CODS) system. The catalyst was characterized by FT-IR, XRD, XPS and superconducting NMR. The influences of *m*(catalyst)/*m*(oil), *V*(H_2O_2)/*V*(oil), reaction temperature and reaction time on the fractional conversion of benzothiophene (BT) and dibenzothiophene (DBT) were investigated. GC-MS and micro-coulometric methods were employed to investigate the reaction. The catalyst has high desulfurization activity in the removal of BT and DBT under mild conditions. The recycling experiments indicated that DBT and BT removal could still reach 95.2% and 95.7% after 10 cycles.

1. Introduction

With the rapid development of global industries, the consumption of fuel oil is increasing around the world, which has led to increasing toxic substance and carbon emissions. Crude oil-derived fuels contain a complex range of components including various sulfur compounds. Among these sulfur compounds, organosulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and their derivatives are the main source of SO_x which lead to air pollution and acid rain [1,2]. So, ultra-clean fuel production is needed. Many methods have been used to remove sulfur from fuels, such as biodesulfurization [3,4], selective adsorption [5,6], extraction by impregnant [7], extraction-oxidation [8], alkylationand [9], hydrodesulfurization (HDS) and oxidative desulfurization (ODS). HDS is highly efficient in removing thiols, sulfides and disulfides [10]. Nonetheless, there are two defects in HDS. The HDS process is operated at over 300 °C and hydrogen pressure of 2–10 MPa in the presence of a suitable catalyst (CoMo- or NiMo-based catalyst) [10–12], but it is considerably difficult to reach ultra-low sulfur levels, especially for DBT and its derivatives [13,14].Therefore, it is a challenge to develop facile approaches to effectively remove sulfur compounds under mild conditions.

As an ODS technique, a catalytic oxidative desulfurization (CODS) system does not need a hydrotreating process and an elevated temperature, and it has been extensively studied as a promising approach for ultra-deep desulfurization under mild reaction conditions [2,15]. In the CODS system, sulfur compounds in the oil phase are adsorbed by the catalyst first, and then oxidized to sulfones in the presence of an oxidant. The oxidation product is separated by extraction, distillation, or adsorption [9,16,17]. Zheng and coworkers [15] reported that a catalyst with titanium dioxide improved the desulfurization

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This work was supported by the National Natural Science Foundation of China (21473126).

DOI: 10.1016/S1872-2067(16)62558-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 12, December 2016

efficiency, and the desulfurization product was separated by extraction by an ionic liquid. To improve desulfurization efficiency, researchers need to develop suitable catalysts. Studies on the CODS process have employed different catalysts such as zeolites [18], formic acid [19,20], sodium bicarbonate [21], activated carbon [22], and peroxidase [23,24]. Among these, Mo-containing catalysts showed good performance in the CODS system because of the active radical species produced by the interaction between Mo(VI) sites and H_2O_2 and they have been widely investigated and employed [25–28]. For instance, García-Gutiérrez and coworkers [27] reported that a catalyst with Mo as the active phase and hydrogen peroxide (H_2O_2) as oxidant in the oxidation reaction improved the desulfurization efficiency. In the process of oxidative desulfurization, the catalyst support also plays an important role. Titanium dioxide (TiO_2) [15], zeolite [5], SBA-15 and MCM-4 [29] as the catalyst support have been extensively investigated, and many researchers have studied the effect of different morphologies. From the perspective of application, amorphous SiO_2 has found wide applications in the fields of selective separation and catalysis because of its high chemical and thermal stabilities, large surface area and good compatibility with other materials. Amorphous SiO_2 is also easy to synthesize and a cheap material compared to other supports [30]. In addition, the surface of amorphous mesoporous SiO_2 is rich in hydroxyl groups, which help the adsorption of the oxidation product [31]. Up to now, there are few reports on an amorphous SiO_2 loaded HPMo as the catalyst in an oxidative desulfurization system.

In this paper, catalysts of HPMo-SiO_2 was synthesized and applied in the CODS system. The reaction conditions, kinetic study of the catalytic oxidation and reuse of the catalyst were investigated in the desulfurization of a model oil. When HPMo-SiO_2 was employed as the catalyst, sulfur removal of DBT and BT approached 100.0% under mild reaction conditions. GC-MS and microcoulometric analysis were employed to investigate the reaction progress of the CODS system. DBT removal could still reach 95.2% (and 95.7% for BT) after 10 times recycling. This means that the HPMo-SiO_2 catalyst has high activity and stability in the CODS system. The catalyst prepared in this research can completely adsorb the oxidation products, and the further separation operation of oxidation products was not needed. The CODS system introduced in this paper effectively improved the economy of the desulfurization process and reduced the loss of fuels.

2. Experimental

2.1. Materials

All materials in this experiment were commercial reagent grade. Polyvinylpyrrolidone (PVP-k30), *n*-octane, concentrated sulfuric acid, phosphomolybdic acid (HPMo), tetraethylorthosilicate (TEOS), benzothiophene (BT), dibenzothiophene (DBT), and 30 wt% hydrogen peroxide (H_2O_2) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Catalyst preparation

For the preparation of the catalysts, 5.02 mL concentrated sulfuric acid and 0.8891 g PVP-k30 were dispersed in 57 mL of deionized water in a 200 mL conical flask under stirring at room temperature. TEOS (8.32 g) was added into the solution. Then HPMo was dropwise added into the mixture solution and pale yellow flocks were obtained. After that, the suspension was continuously stirred for 1 h before aging for 4 h at room temperature. Subsequently the powder obtained was dried at 105 °C in a vacuum oven. Finally, the resulting pale yellow powder was calcined at 420 °C for 12 h and labeled as HPMo-SiO_2 (the Mo/SiO_2 mass ratio was 15.9%).

2.3. Catalyst characterization

FT-IR spectra (4000–500 cm^{-1}) were recorded at room temperature on a Bruker VERTEX 70 FT-IR spectrometer using KBr in the ratio of 1:200. The X-ray diffraction (XRD) patterns were recorded on a Phillips Xpert Pro powder diffraction system using Cu K_α radiation with a Ni filter over the range $10° \le 2\theta \le 80°$. Solid-state ^{31}P NMR was recorded on an Agilent DD2 spectrometer (600 MHz). The X-ray photoelectron spectrum (XPS) measurements were performed with a Multilab 2000X-ray photoelectron spectrometer (VG, UK). The pore structure of the catalysts was obtained from nitrogen adsorption isotherms which were measured at −196 °C in the relative pressure range of 0.001–1 with a Quantachrome instrument (Autosorb-1-C-TCD-MS).

2.4. Catalytic evaluation

The oxidative desulfurization was studied by employing model oils containing refractory sulfur compounds which are commonly found in fuels, like DBT or BT. The model fuels were prepared by dissolving BT or DBT in *n*-octane to obtain the solution with a sulfur content of 400 mg/g. In these experiments, 10 mL of the model oil was introduced into a three-necked glass reactor equipped with a condenser, stirrer and thermometer. The reactor was placed in a water bath at a constant temperature and then HPMo-SiO_2 was added into the reactor. The reaction mixture was continuously stirred and heated to the set temperature. Subsequently, hydrogen peroxide was added to the reaction mixture, and this was recorded as the initial time of the reaction. After the reaction, the mixture was separated by centrifugation. The reaction products were then analyzed on an HP 6890 gas chromatograph equipped with an HP-5 capillary column and an FID detector.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows the FT-IR spectra of HPMo-SiO_2, SiO_2 and HPMo. The four FT-IR bands characteristic of HPMo with the Keggin structure appeared at 1065 cm^{-1} (stretching frequency of P–O in the center PO_4 tetrahedron of HPMo), 967 cm^{-1} (terminal Mo=O bands in the exterior MoO_6 octahedron), 871 and 788 cm^{-1} (Mo–O–Mo bands) [32]. Owing to the overlap of the

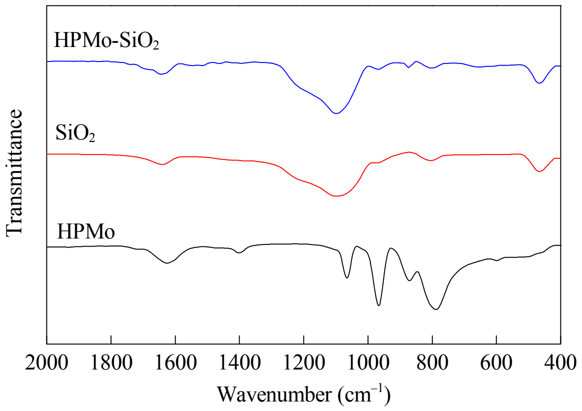

Fig. 1. FT-IR spectra of HPMo-SiO$_2$, SiO$_2$ and HPMo.

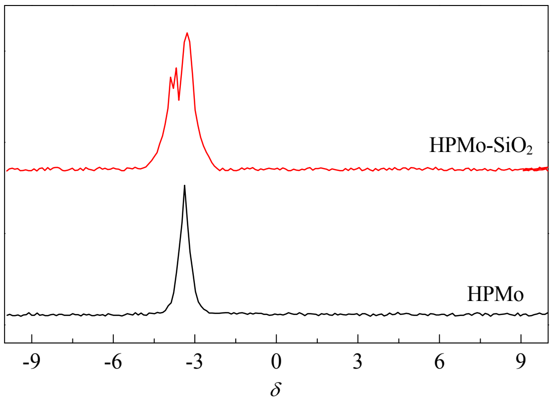

Fig. 3. ^{31}P NMR spectra of HPMo-SiO$_2$ and HPMo.

788 cm^{-1} Mo–O–Mo peak with that of the Si–O–Si stretching vibration of the mesoporous support, the bands corresponding to the Keggin structure of HPMo were weakened after the immobilization of HPMo on the support. As the detection of the peaks on bulk HPMo revealed, the Keggin structure was retained after immobilization. However, a slight shift occurred as a result of HPMo's interaction with the functional groups of the support.

Fig. 2 shows the powder XRD patterns of the catalysts. As shown in Fig. 2, the characteristic peaks of HPMo at 2θ = 12.7°, 23.3°, 25.7°, 29.7°, and 38.9° emerged, which belonged to the characteristic peaks of the MoO$_3$ unit [33]. The characteristic peaks of MoO$_3$ were almost not detected with HPMo-SiO$_2$, which indicated that the HPMo clusters were finely dispersed on the support of SiO$_2$.

The solid ^{31}P NMR spectra of the catalysts are shown in Fig. 3. The chemical shift of P is mainly determined by the chemical environment of P in the catalyst. For pure HPMo, a single absorption peak appeared at $\delta = -3.33$. The ^{31}P NMR spectrum of HPMo-SiO$_2$ presented a broad resonance centered at $\delta = -3.36$ [34] ($\delta = -3.33$ for HPMo, with a weak shoulder at $\delta = -4.09$). The shoulder peak can be attributed to the chemical interaction between HPMo and the SiO$_2$ skeleton. The compound of $[(\equiv SiOH_2)^+(H_2PMo_{12}O_{40})^-]$ was formed between HPMo and the hydroxyl groups on the surface of silica [35]. Therefore, it can be concluded that some HPMo was physical adsorbed by SiO$_2$, while another part of HPMo was immobilized on the mesoporous silica skeleton through chemical bonds. The chemical bond binds HPMo and SiO$_2$ with a stronger force, which significantly reduced the desorption of the catalysts in the process of desulfurization. In addition, ^{31}P NMR further confirmed that the integrity of the Keggin structure was maintained after immobilization on the SiO$_2$ supports.

In order to get further information on the chemical composition of the catalyst, XPS was performed to examine the surface chemical components. The results are exhibited in Fig. 4 and showed that the binding energy of the Mo 3*d* peak on the catalyst sample was 232.8 eV, indicating the presence of Mo in the catalyst. Fig. 4(b) presents the Mo 3*d* XPS spectrum of HPMo-SiO$_2$. Spectral deconvolution demonstrated the appearance of two signals at 232.8 and 235.8 eV for Mo 3$d_{5/2}$ and Mo

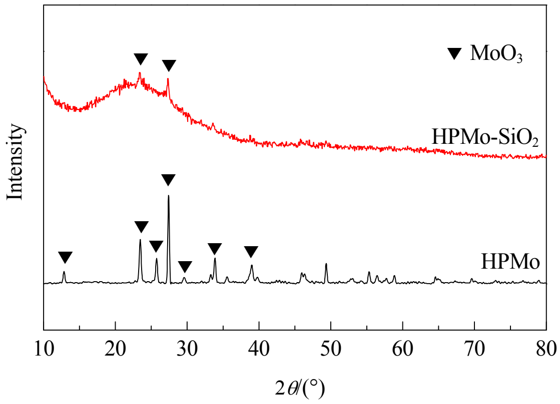

Fig. 2. X-ray diffractions of HPMo-SiO$_2$ and HPMo.

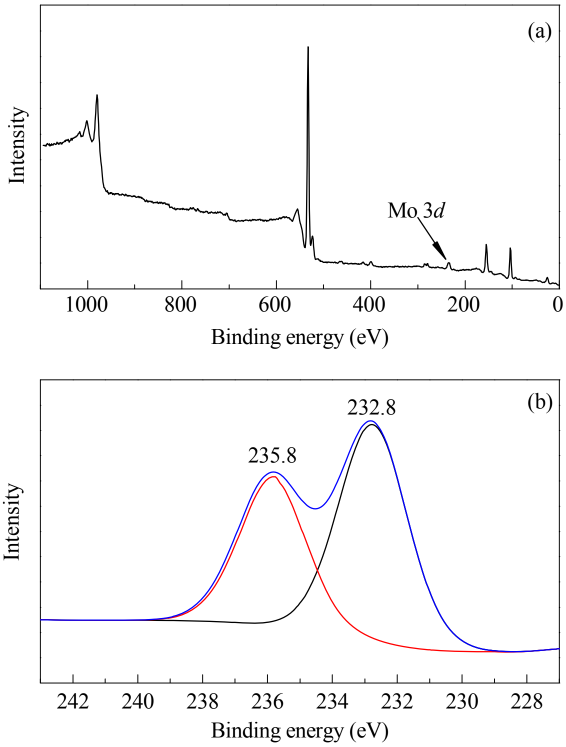

Fig. 4. XPS spectra of HPMo-SiO$_2$. (a) Survey; (b) Mo 3*d*.

3*d*3/2, respectively, and these binding energy values corresponded to Mo^{6+}. Some researchers have assigned the signal at 232.7 eV to the polymolybdate species in the highest oxidation state [36].

The adsorption isotherms of the catalysts are shown in Fig. 5. Using the IUPAC classification, the HPMo-SiO_2 adsorptionl isotherm with a H4 Type desorption hysteresis loop is a Type IV isotherm, which is characteristic of mesoporous materials [37]. The adsorption isotherm data were processed by the NLDFT equilibrium model. The pore size distribution of HPMo-SiO_2 was concentrated at the average pore diameter of 12.91 nm, the specific surface area was 365.0 m^2/g, and the total pore volume was 1.237 cm^3/g. The abundant pores of the structure and high pore content would assist the adsorption of BT and DBT on the catalyst surface and the oxidation reaction, which further improved sulfur removal from the fuel oil.

3.2. Oxidative desulfurization of the model fuel oil

3.2.1. Effect of mass ratio of catalyst/model oil

To verify the CODS activity, oxidative desulfurization experiments of DBT and BT were performed. The effect of *m*(catalyst)/*m*(model oil) on DBT or BT removal rate of the model oil was studied. As shown in Fig. 6, with the increase of HPMo-SiO_2, the desulfurization rate for both DBT and BT increased gradually, and the conversion of DBT was higher than that of BT with the same amount of catalyst. It was also observed that when the *m*(catalyst)/*m*(model oil) reached 0.7% for DBT (and 1.0% for BT), the removal rate of the sulfur compound in the model oil was 100.0%.

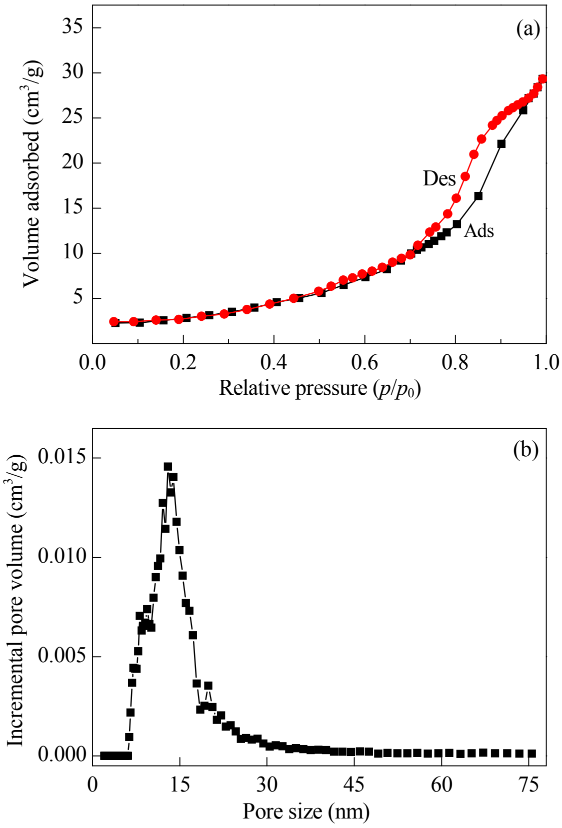

Fig. 5. Pore structure parameters of HPMo-SiO_2. (a) Adsorption isotherm; (b) Pore size distribution.

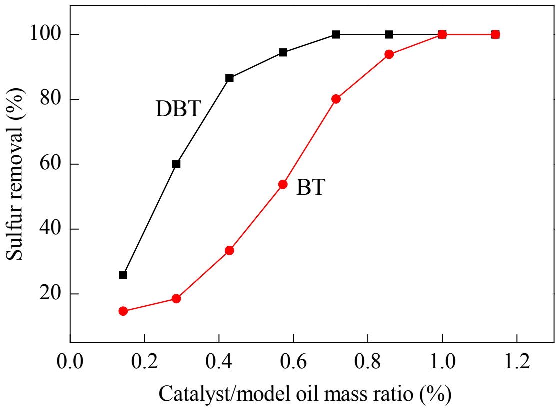

Fig. 6. Effect of catalyst/model oil on BT and DBT removal. Conditions for BT removal: *V*(H_2O_2)/*V*(model oil) = 0.3%, 60 °C, 30 min; Conditions for DBT removal: *V*(H_2O_2)/*V*(oil) = 0.3%, 55 °C, 15 min.

3.2.2. Effect of volume ratio of H_2O_2/model oil

The effect of *V*(H_2O_2)/*V*(model oil) on DBT and BT removal rate of model oil is shown in Fig. 7. With increasing H_2O_2, the removal rate of DBT and BT increased first and then decreased. When *V*(H_2O_2)/*V*(model oil) reached 0.3%, the removal rates of DBT and BT were 100.0%. With the further increase of hydrogen peroxide, the desulfurization efficiency decreased. The decline of sulfur removal rate was probably caused by that excess H_2O_2 caused a side reaction catalyzed by Mo that produced H_2O and O_2, and the side reaction occupied the active center and increased the consumption of H_2O_2 [33]. Furthermore, a part of the hydrophilic catalyst was transfered to the water phase which reduced the catalyst dispersed in the oil, which led to the reduction of the desulfurization rate.

3.2.3. Effect of temperature

Fig. 8 shows the conversion of BT and DBT catalyzed with HPMo-SiO_2 during the CODS process at different temperatures. The results indicated that the conversion of DBT catalyzed with

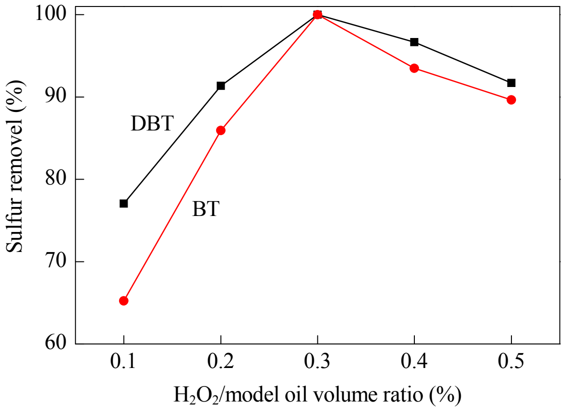

Fig. 7. Effect of hydrogen peroxide content on BT and DBT removal. Conditions for BT removal: *m*(catalyst)/*m*(oil) = 0.7%, 60 °C, 30 min; Conditions for DBT removal: *m*(catalyst)/*m*(oil) = 0.4%, 55 °C, 15 min.

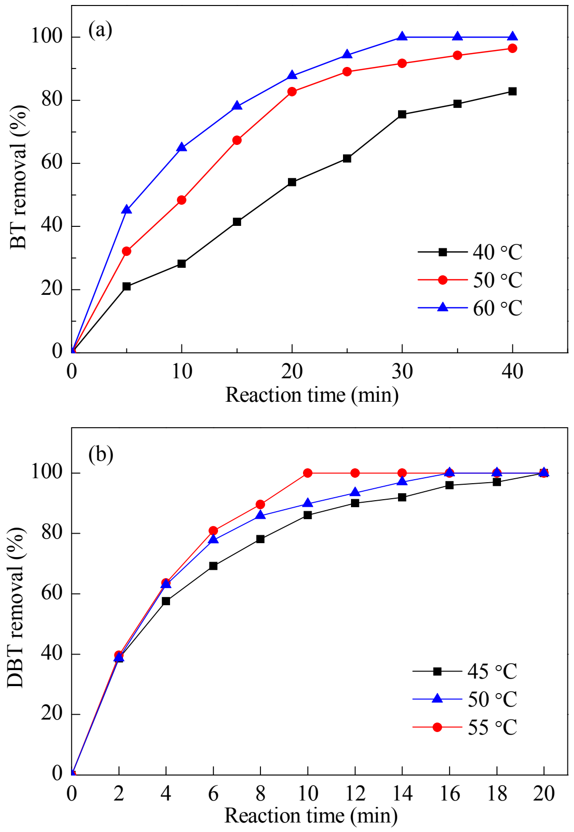

Fig. 8. Effect of reaction time on BT and DBT removal. (a) BT; (b) DBT. Conditions for BT removal: m(catalyst)/m(oil) = 1.0%, $V(H_2O_2)/V$(oil) = 0.3%; Conditions for DBT removal: m(catalyst)/m(oil) = 0.7%, $V(H_2O_2)/V$(model oil) = 0.3%.

HPMo-SiO_2 was higher than that of BT under the same conditions. This was because of the higher electron density on the sulfur atom in DBT. The electron density on the sulfur atoms is 5.758 for DBT and 5.739 for BT, which was calculated by Otsuki *et al.* [38]. The catalysts gave significantly higher CODS activity with the increase of reaction temperature because the formed quantity of metallic peroxide was increased by the higher reaction temperature [33].

3.2.4. *Apparent activation energy and reaction rate constant*

From the reaction rates determined at different temperatures (Table 1), the apparent activation energies for the CODS reactions (Fig. 9) were calculated by the Arrhenius equation. The CODS reactions fitted pseudo-first order reaction kinetics. The apparent activation energy of the DBT oxidation reaction (30.6 kJ/mol) was lower than that of the BT oxidation reaction (40.5 kJ/mol), which showed that DBT was easier to oxidize than BT. Qiu and coworkers [33] reported that the apparent activation energy of DBT in the HPMo/SiO_2-H_2O_2 catalytic system was 33.0 kJ/mol. The results indicated that the mesoporous HPMo-SiO_2-H_2O_2 catalytic system in the present work displayed a higher catalytic activity for DBT oxidation.

Table 1
Reaction rate constant (k) and correlation coefficient (R^2) for BT and DBT at different temperatures.

Sample	t (°C)	k (min^{-1})	R^2
BT	40	0.043	0.980
BT	50	0.083	0.993
BT	60	0.109	0.991
DBT	45	0.194	0.994
DBT	50	0.239	0.992
DBT	55	0.276	0.995

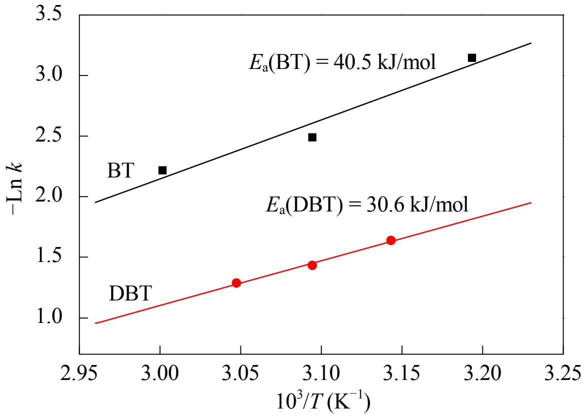

Fig. 9. Arrhenius activation energies for DBT and BT oxidation.

3.2.5. *Reuse cycles of the catalysts*

The relationship between DBT and BT removal rate in the CODS reactions and the utilization cycles is shown in Fig. 10. After the CODS reactions, the mixture of HPMo-SiO_2 and model fuel oil was separated by centrifugation. The filter was then dried at 105 °C in a vacuum oven for 12 h. After the regenera-

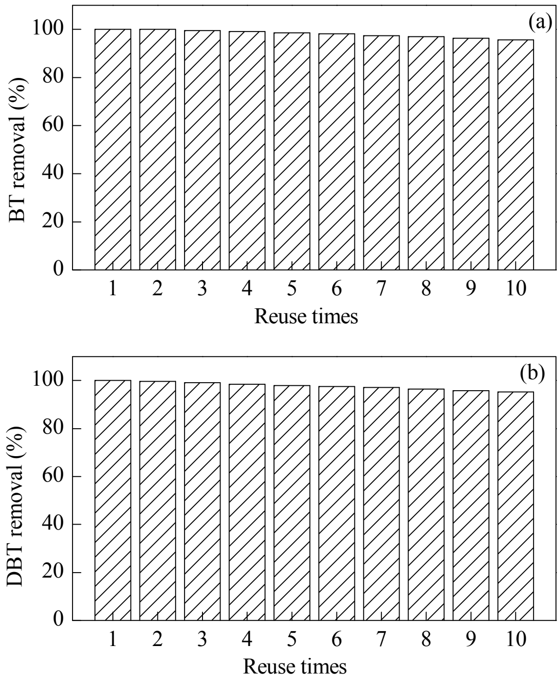

Fig. 10. Effect of reuse times on the oxidative desulfurization rate of BT and DBT. (a) BT; (b) DBT. Conditions for BT removal: m(catalyst)/m(oil) = 1.0%, $V(H_2O_2)/V$(oil) = 0.3%, 60 °C, 30 min; Conditions for DBT removal: m(catalyst)/m(oil) = 0.7%, $V(H_2O_2)/V$(oil) = 0.3%, 55 °C, 10 min.

tion was completed, the HPMo-SiO_2 was mixed with fresh model oil and used for a second CODS reaction cycle.

The Mo content in the catalyst before and after the oxidation reaction was detected by ICP-AES, and weak leaching of HPMo from the catalyst was seen in the desulfurization process (mass ratio of Mo/SiO_2 decreased from 15.9% to 14.8% after reuse 10 times). It is difficult to remove BTO_2 and $DBTO_2$ by direct drying at 105 °C because of their high melting points and boiling points, which led to a slight decrease in the desulfurization activity after repeated use of the catalyst.

3.2.6. *Analysis of oxidation products*

The S content of the model oil decreased from 400.0 mg/g to 0.0 mg/g with 100.0% sulfur removal rate and 99.2% model oil recovery in the reaction. In order to analyze the reaction process, GC-MS analysis was adopted to research the BT and DBT reaction process. After the reaction, the oil phase was separated by centrifugation and the solid catalyst was extracted by methanol. Subsequently, the oil phase and the methanol phase were analyzed by GC-MS. As shown in Fig. 11, only the peak of benzothiophene sulfone (BTO_2, Fig. 11(a)) (m/z = 166.1) or dibenzothiophene sulfone ($DBTO_2$, Fig. 11(b)) (m/z = 216.0) was found in the methanol phase. However, no peaks belonging to BT, DBT, BTO_2 or $DBTO_2$ were detected in the oil phase, which implied that there was enough oxidant to oxidize the DBT to $DBTO_2$ in 10 min (BT to BTO_2 in 30 min). Meanwhile, no sulfur compound was detected in the oil phase by the micro-coulometric method. Based on the results of GC-MS and micro-coulometric analysis, a reaction process can be proposed as the following. The catalyst, model oil and hydrogen peroxide formed a heterogeneous catalysis system. During the reaction process, BT or DBT was first adsorbed on the catalyst, and then oxidized by H_2O_2 [15]. The oxidation product of BT was BTO_2 ($DBTO_2$ for DBT), which remained on the solid catalyst because of its highly polar nature. As the BT or DBT was transferred from the oil phase to the catalyst and oxidized to BTO_2 or $DBTO_2$ continuously, a low sulfur model oil was achieved.

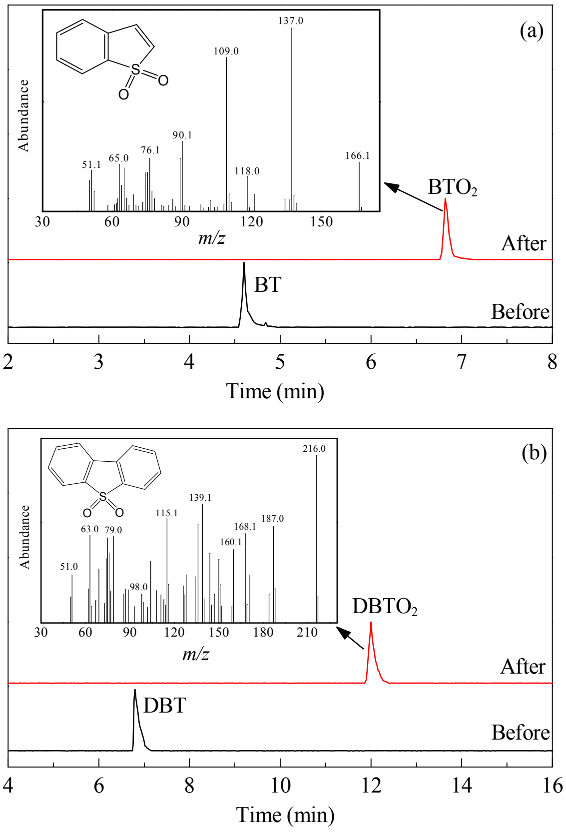

Fig. 11. GC-MS analysis of BTO_2 (a) and $DBTO_2$ (b) before and after reaction.

4. Conclusions

An amorphous HPMo-SiO_2 which kept the Keggin structure of HPMo was prepared and applied in the CODS system. The synthesis of the catalyst was simple and economical. The catalyst gave high desulfurization activity in the removal of BT and DBT under mild conditions. The catalytic oxidative activity for DBT was higher than that for BT under the same reaction conditions. The conversion of BT and DBT increased with the increase of reaction temperature. The apparent activation energy of the DBT oxidation reaction catalyzed by HPMo-SiO_2 was lower than that of BT. GC-MS and micro-coulometric analysis demonstrated that BTO_2 and $DBTO_2$ adsorbed by the catalyst were the only products of BT and DBT oxidation. The recycling experiments of HPMo-SiO_2 indicated that DBT and BT removal still reached 95.2% and 95.7% after 10 cycles.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 2098–2105 doi: 10.1016/S1872-2067(16)62558-5

Ultra-deep oxidative desulfurization of fuel with H_2O_2 catalyzed by phosphomolybdic acid supported on silica

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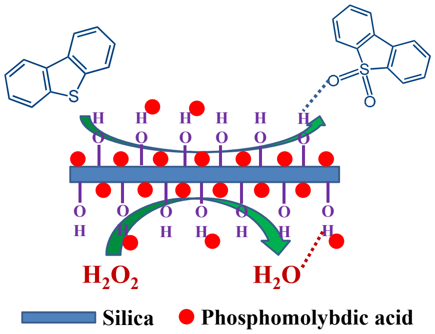

Benzothiophene or dibenzothiophene was adsorbed on the catalyst and oxidized by H_2O_2. The oxidation product remained on the solid catalyst because of its highly polar nature.

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