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Deep oxidative desulfurization of fuels catalyzed by molybdovanadophosphoric acid on amino-functionalized SBA-15 using hydrogen peroxide as oxidant

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Abstract This study reports the usage of molybdovanadophosphoric acid catalyst on amino-functionalized SBA-15($PMoV_2$/SBA-15-NH_2) for the removal of sulfur from model oil (dibenzothiophene dissolved in *n*-hexane). To increase the tendency for adsorption of heteropoly acids, mesoporous SBA-15 silica was functionalized with amino groups by postsynthesis grafting, using 3-aminopropyltrimethoxy silane as the coupling agent. Immobilization of molybdovanadophosphoric acid on pure SBA-15 ($PMoV_2$/SBA-15) was also studied for comparison and the catalysts were characterized by physicochemical and spectroscopic methods. It was found that the catalysts exhibit high catalytic activities and $PMoV_2$/SBA-15-NH_2 is more durable than $PMoV_2$ impregnated on unmodified mesoporous SBA-15 silica. The results may bring about improvement for oxidative desulfurization of transportation fuels.

Introduction

Sulfur removal from fuels has become a very important and active research subject worldwide in the past decade since the production and use of environmentally friendly fuels have been attracting increasing attention in many countries. Furthermore, the regulations for sulfur contents in the liquid transportation fuels are becoming more and more stringent [1]. Therefore, deep desulfurization has become an urgent issue for the petroleum refining industry [2]. At present, hydrodesulfurization (HDS) is a very useful conventional method for the removal of aliphatic and alicyclic sulfur-containing compounds in the petroleum refining industry. However, it has its limit on the desulfurization of dibenzothiophene (DBT), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DBT) due to the steric hindrance effect of these compounds [3, 4]. To achieve ultra-low sulfur fuels, more severe conditions are required, such as higher temperature, higher hydrogen pressure and catalysts with higher activity, inevitably leading to higher operating cost. Therefore, it is desirable to develop some alternatives, such as oxidative desulfurization (ODS) [5, 6], adsorptive desulfurization [7], extractive desulfurization [8] and bio-desulfurization [9], to obtain ultra clean fuels. Because of moderate reaction conditions, high reactivity and no hydrogen requirement, oxidative desulfurization turned out to be one of the most promising desulfurization processes [10, 11]. In the ODS process, DBT and its derivatives can be selectively oxidized to their corresponding sulfoxides and sulfones, which can be then removed by extraction using water-soluble polar solvents as the extractants [12].

Various oxidants, including H_2O_2 [13], organic peroxide [14], potassium superoxide [15], molecular oxygen [10], ozone [16], and nitric acid/NO_2 [17], were investigated in ODS processes. Among them, H_2O_2 has been widely used due to its high reactivity and affordable cost. Moreover, the only product is water in the ODS process. Heteropoly acid (HPA) catalysts in H_2O_2 oxidation systems have also exhibited high catalytic activity for the oxidation of BTs and DBTs. HPA has been widely used as a catalyst in the oxidative desulfurization process due to its high catalytic activity for the oxidation of benzothiophene and its derivatives [18, 19]. However, the challenges for these catalysts are the difficulties in separation and recovery. Therefore,

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supported catalysts have been used in the ODS process to overcome these disadvantages. Yazu et al. [11] immobilized phosphotungstic acid on an anion-exchange resin to catalyze the oxidation of DBT with H_2O_2 as the oxidant. Results showed that the supported catalyst exhibited higher catalytic activities and could be easily recovered. Yan et al. [20] investigated the oxidation of DBT with H_2O_2 using phosphotungstic acid/TiO_2 as the catalyst. The selective desulfurization ratio reaches to 95.2 % under optimal conditions. Yang et al. [21] studied the supported phosphotungstic acid for the oxidative desulfurization and the catalyst turned out to be of high activity and easily recovered. Although immobilization of heteropolyacids on a suitable support can make them easily separated from the reaction mixture, weak bonding interaction of heteropolyanion with the silanol group of these silicate materials leads to partial leaching especially with polar solvent media [22, 23].

Herein, in the present work, we report on the molybdovanadophosphoric acid ($PMoV_2$) supported onto mesoporous silica both by adsorption to SBA-15 and by electrostatic binding to SBA-15 modified with amino groups (SBA-15-NH_2). Influences of reaction conditions, such as reaction time and temperature, catalyst amount, the molar ratio of H_2O_2 to DBT ($n(O)/n(S)$), were also investigated in detail. The results may bring some improvement in the application of oxidative desulfurization.

Experimental

Chemicals

The block copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) was purchased from Aldrich Corporation (USA). Tetraethoxysilane (TEOS), dibenzothiophene (DBT, 99 %) and 3-aminopropyltriethoxysilane were purchased from Acros Organics (USA). Disodium phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), hydrogen peroxide (H_2O_2), sodium metavanadate ($NaVO_3$), sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$), sulfuric acid, diethyl ether,toluene and acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used without any further purification.

Catalyst preparation

Synthesis of molybdovanadophosphoric acid and SBA-15

The pure siliceous SBA-15 and molybdovanadophosphoric acid were synthesized according to the procedures described previously, respectively [24, 25].

Synthesis of SBA-15-NH_2

Amine-functionalized SBA-15 was synthesized by the reaction of SBA-15 with 3-Aminopropyltriethoxysilane (APTES) using a grafting method [26]. In a typical preparation, freshly activated SBA-15 (1.0 g) was reacted with APTES in 50 mL toluene (distilled over sodium and dried) under reflux for 8 h. The resultant white solid was filtered off, washed with dried toluene and then dried under vacuum at room temperature for 12 h. The product was designated as SBA-15-NH_2.

Immobilization of $PMoV_2$ on mesoporous support

Molybdovanadophosphoric acid was impregnated on mesoporous SBA-15 support via incipient wetness technique. Mesoporous support (SBA-15, SBA-15-NH_2, 1.5 g) was added to an aqueous solution of $PMoV_2$ (1.0 g) with vigorously stirring for 24 h at room temperature. The mixtures were subjected to evaporation and dried to get the solid products. The solid was then dried at room temperature and designated as $PMoV_2$/SBA-15 and $PMoV_2$/SBA-15-NH_2.

Characterization of the samples

IR spectra of samples (KBr pellets) were recorded on a Perkin-Elmer infrared spectrometer in the range of 400–4,000 cm^{-1}. X-ray diffraction (XRD) measurements were performed on a D/MAX-RB X-ray diffractometer using a Cu Kα radiation (1.5406 Å) source at 40 kV and 30 mA, from 0.5 to 10° with a scan rate of 0.5°/min. Nitrogen adsorption–desorption data were measured with a BELSORP-Mini II analyzer at 77 K. Prior to the measurement, all samples were degassed under nitrogen atmosphere for 3 h at 200 °C. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method.

Catalytic experiments

Model oil was prepared by dissolving DBT in n-hexane containing 1,000 ppm corresponding to S-content. Catalytic oxidative desulfurization was performed in a round bottom flask in an oil bath under magnetic stirring at atmospheric pressure. The oxidative reaction was carried out with 20 mL of model oil, a certain amount of H_2O_2 as oxidant and 5 mL of acetonitrile as the extractant, using $PMoV_2$/SBA-15 and $PMoV_2$/SBA-15-NH_2 as catalysts, respectively. After the reaction, the mixture was cooled down to room temperature and then the catalyst was centrifuged. The upper reaction samples were withdrawn and subjected to GC-FID analysis. The catalyst was washed with acetonitrile three times, dried and used in the next run.

Results and discussion

Characterization

FTIR spectra are quite useful to identify structural and bonding changes in the Keggin unit present in the supported catalysts (The basic Keggin unit is composed of a central XO_4 tetrahedron ($X = $ P or Si) surrounded by 12 MO_6 octahedra ($M = $ Mo or W)) [27]. As can be seen from Fig. 1, the four IR bands characteristic of neat $PMoV_2$ appeared at 1,050–1,100 cm^{-1} (P–O stretching), 900–1,000 cm^{-1} (Mo–O stretching), 850–900 cm^{-1} (stretching of Mo–O–Mo inter bridges between corner-sharing MoO_6 octahedra) and 750–800 cm^{-1} (stretching of Mo–O–Mo intra bridges between edge-sharing MoO_6 octahedral) [28]. For pure SBA-15, a strong absorption band at 1,078 cm^{-1} assigned to Si–O–Si asymmetric vibrations was observed. Owing to the overlap of Mo–O–Mo and P–O bands with those of Si–O–Si stretching vibrations of mesoporous supports, only the bands corresponding to (Mo–O–Mo and Mo=O) were discernible after immobilization within the supports. As shown in Fig. 1, the reflections related to bulk $PMoV_2$ revealed that the Keggin structure was retained after immobilization. However, the bands at 958 and 859 cm^{-1} shifted to 938 and 796 cm^{-1}, respectively, after supporting HPA on amine-modified SBA-15. And a new band appeared at 938 cm^{-1} in $PMoV_2$/SBA-15-NH_2 compared with SBA-15-NH_2. All of these may be related to the interaction of HPA with the amine groups in the functionalized SBA-15.

Small-angle XRD patterns of catalyst samples are illustrated in Fig. 2. As can be seen from Fig. 2a, the three distinct Bragg diffractions, (100), (110) and (200), are characteristics of a highly ordered two-dimensional hexagonal mesoscopic structure of pure SBA-15 [24]. All three reflections are still detectable in Fig. 2b after immobilization of $PMoV_2$, suggesting that the hexagonal pore structure of the support is retained. However, intensities of these characteristic peaks are lower than those of pure SBA-15. This may be caused by the interaction between the mesoporous SBA-15 and $PMoV_2$ Keggin units. A similar pattern is observed for $PMoV_2$ interaction within SBA-15-NH_2 (Fig. 2d). This is in agreement with the results in the previous literature [29].

Evaluation of performance of various catalysts

The activities of various catalysts for oxidative desulfurization are compared in Table 1. All reactions were performed with hydrogen peroxide (H_2O_2) in Table 1. The difference between each entry was the catalyst. H_2O_2 is essentially used as the oxidant and $PMoV_2$ is the catalyst. In the first three entries (entry 1, 2 and 3), the conversions are similar to each other, and this could also illuminate that the supports actually made no more contributions for catalytic activity. Similar results were found in the previous literatures [31, 32]. The supported catalyst is made to increase the catalytic activity. After being supported on SBA-15, $PMoV_2$/SBA-15 showed lower catalytic activities than $PMoV_2$ which is due to the decrease in surface area. Compared with $PMoV_2$/SBA-15, $PMoV_2$/SBA-15-NH_2 exited a similar catalytic activity (98.1 % vs. 97.8 %). Considering the much lower surface area of $PMoV_2$/SBA-15-NH_2 than that of $PMoV_2$/SBA-15, it is certain that $PMoV_2$/SBA-15-NH_2 showed a higher activity per square meter of catalyst surface than $PMoV_2$/SBA-15.

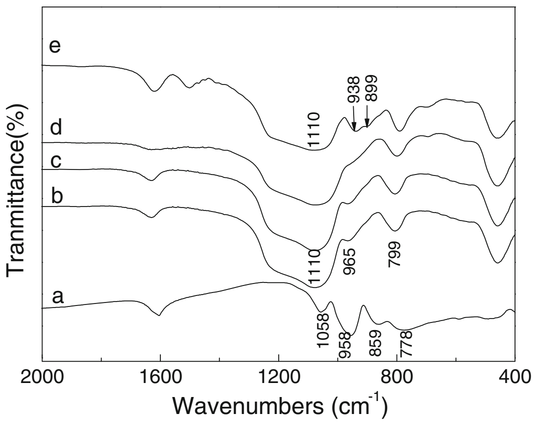


Fig. 1 IR spectra of various samples: *a* $PMoV_2$, *b* SBA-15, *c* $PMoV_2$/SBA-15, *d* SBA-15-NH_2, *e* $PMoV_2$/SBA-15-NH_2

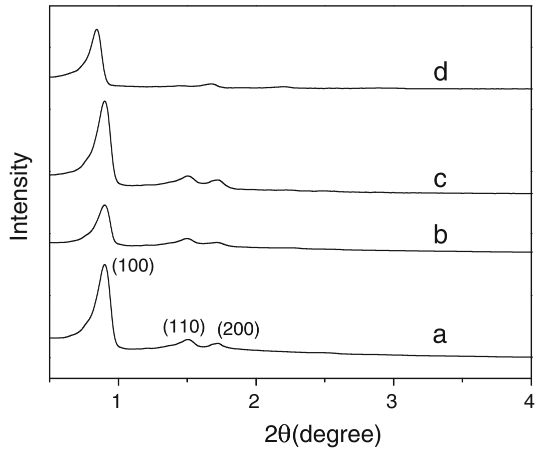


Fig. 2 Small-angle XRD patterns of *a* SBA-15, *b* $PMoV_2$/SBA-15, *c* SBA-15-NH_2, *d* $PMoV_2$/SBA-15-NH_2

Table 1 Oxidative desulfurization using H_2O_2 as the oxidant over different catalysts

Entry	Catalyst	S_{BET} (m^2/g)	DBT conversion
1	Blank	–	34.8 %
2	SBA-15	749	35.1 %
3	SBA-15-NH_2	404	34.6 %
4	$PMoV_2$	<10 [30]	98.7 %
5	$PMoV_2$/SBA-15	391	98.1 %
6	$PMoV_2$/SBA-15-NH_2	239	97.8 %

Reaction conditions: 20 mL model oil, 60 °C, 120 min, $n(O)/n(S) = 16$, 0.05 g $PMoV_2$, 0.108 g (37 %) $PMoV_2$/SBA-15, $PMoV_2$/SBA-15-NH_2

Catalytic stability and reusability

To assess the stability and reusability, the two different supported catalysts in the oxidative desulfurization were separated by centrifugation, washed off several times after completion of the reaction and dried before being applied to the subsequent run. It can be seen in Fig. 3, during the second run with $PMoV_2$/SBA-15, an 8.7 % reduction of DBT conversion was obtained comparing with the fresh $PMoV_2$/SBA-15. This may be attributed to the leaching of unstable immobilized $PMoV_2$, which caused the reduction in active sites. There is a further slight activity loss in the second recycle using $PMoV_2$/SBA-15-NH_2 as the catalyst. However, this significant activity loss is not evidenced with $PMoV_2$/SBA-15-NH_2 in the following recycles. It illustrated that $PMoV_2$/SBA-15-NH_2 is more durable than $PMoV_2$/SBA-15 in the oxidative desulfurization. The silanol groups, which are present at the surface and inside the channels of the mesoporous SBA-15, reacted with aminosilane molecules and $\equiv Si(CH_2)_3NH_3^+$ was formed [33, 34]. Then, after $PMoV_2$ was supported on the amino-functionalized SBA-15, the salt $\equiv Si(CH_2)_3NH_3 \cdot PMoV_2$ was formed. It was the chemical interaction between $\equiv Si(CH_2)_3NH_3^+$ and $PMoV_2$ that made $PMoV_2$/SBA-15-NH_2 more stable than $PMoV_2$/SBA-15. Therefore, $PMoV_2$/SBA-15-NH_2 was chosen as the catalyst in the following investigation into the oxidative desulfurization.

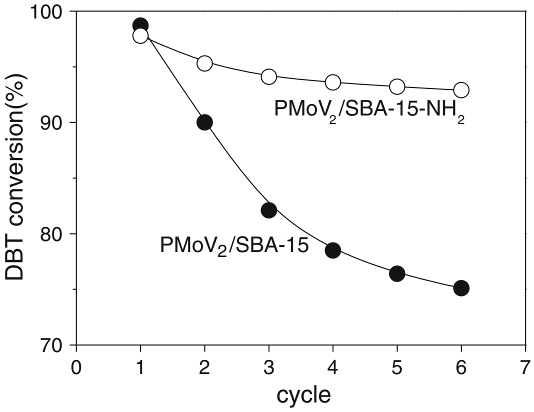


Fig. 3 Influence of recycle times on the DBT conversion. Reaction conditions: 20 mL model oil, 60 °C, 120 min, $n(O)/n(S) = 16$, 0.32 of molar ratio of [P]/DBT

Effect of reaction temperature

Reaction temperature is critical to the DBT conversion. Therefore, influence of the reaction temperature on the DBT conversion over the catalyst $PMoV_2$/SBA-15-NH_2 was investigated (Fig. 4). Increasing the reaction temperature could enhance the oxidation of DBT; however, this could also accelerate the decomposition of hydrogen peroxide. As can be seen in Fig. 4, the reaction rate increased with temperature. When the temperature was elevated from 30 to 60 °C, a drastic change in the rate of the reaction was found. Obviously, this may be ascribed to the rate of reaction governed by the temperature below 60 °C. However, if the temperature was higher than 60 °C, the DBT conversion rarely changed with further reaction time. This may be related to the decomposing of H_2O_2 paralleled with the increase in reaction temperature. Therefore, 60 °C was chosen as the reaction temperature.

Effect of reaction time

Figure 5 shows the influence of reaction time on the DBT conversion over $PMoV_2$/SBA-15-NH_2. It was obvious that the conversion increased greatly with the increase in reaction time up to 120 min, and after that, the DBT conversion increased comparatively slowly along with the increase in reaction time. This can be ascribed to the changes in reaction rate with the reaction time. The reaction rate increased quickly during the initial stage of reaction because of the higher concentration of DBT and H_2O_2.

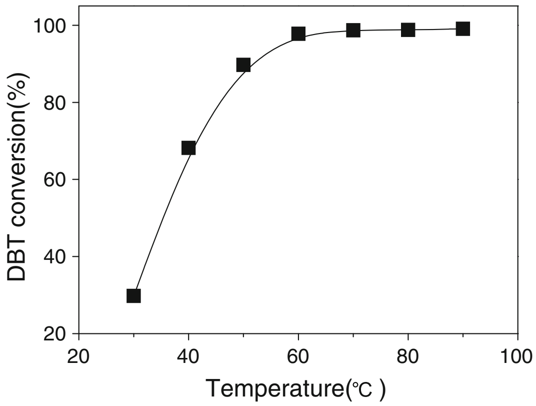


Fig. 4 Influence of reaction temperature on DBT conversion. Reaction conditions: 20 mL model oil, 120 min, $n(O)/n(S) = 16$, 0.32 of molar ratio of [P]/DBT

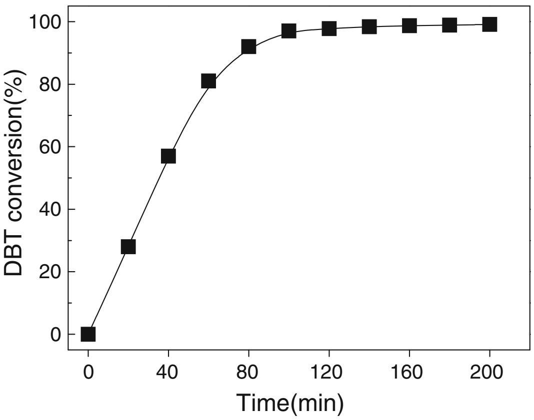


Fig. 5 Influence of reaction time on DBT conversion. Reaction conditions: 20 mL model oil, 60 °C, *n*(O)/*n*(S) = 16, 0.32 of molar ratio of [P]/DBT

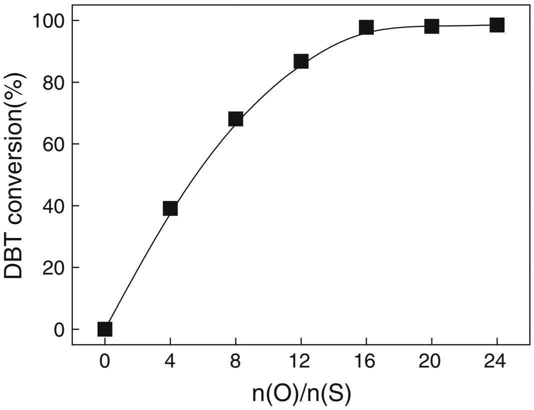


Fig. 6 Effect of the *n*(O)/*n*(S) on DBT conversion. Reaction conditions: 20 mL model oil, 60 °C, 120 min, 0.32 of molar ratio of [P]/DBT

Then with the reaction continued, the reaction rate decreased with the concentration. A slow change could be found between the reaction time of 80 and 120 min. And after the reaction continued for 120 min, the reaction rate was no longer changed, perhaps because hydrogen peroxide was used up. The DBT conversion reached the maximum and did not increase further. Therefore, 120 min was chosen as the optimal reaction time.

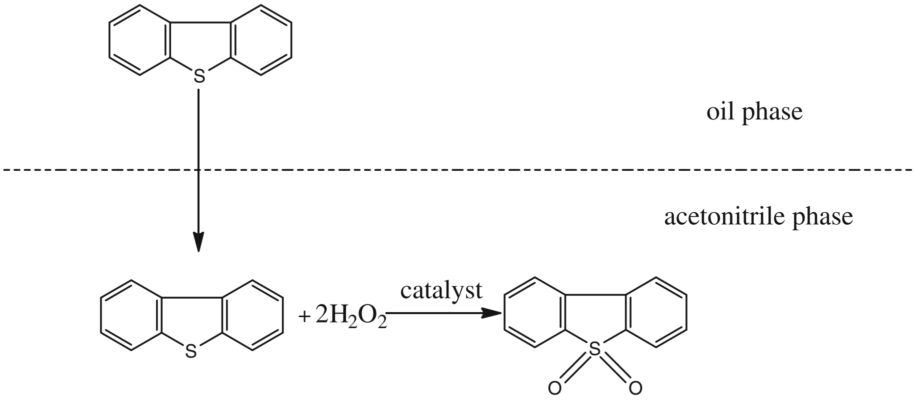
Effect of H_2O_2 amount

The amount of oxidant played an important role in the oxidative desulfurization of DBT. To investigate the influence of H_2O_2 amount on DBT conversion, oxidative desulfurization of DBT under various *n*(O)/*n*(S) was carried out. As can be seen from Fig. 6, the DBT conversion plot curve increased with *n*(O)/*n*(S) up to 16 and then the plot curve turned smoothly, which indicated that the DBT conversion slightly changed. However, as shown in scheme 1, in order to oxidize the sulfur-containing compounds to the corresponding sulfones using H_2O_2 as the oxidant, 2 mol of H_2O_2 is consumed for 1 mol of sulfur-containing compounds according to the stoichiometric reaction. The optimal *n*(O)/*n*(S) is much higher than stoichiometric *n*(O)/*n*(S) in DBT oxidation. The large excess of hydrogen peroxide, on the one hand, can be attributed to the thermal decomposition during the reaction. On the other hand, the excess of oxidant could increase the reaction rate [5, 18]. Therefore, with the economy and reaction rate taken into consideration, 16:1 molar ratio of O/S was chosen for further investigation.

Effect of catalyst dosage

To assess the influence of catalyst dosage on DBT conversion, different catalyst dosages were used and the results are shown in Fig. 7. It was found that the DBT conversion increased with the increasing of molar ratio of catalyst to DBT ([P]/DBT). This may be related to the increase in the total number of catalyst active sites. It was found that 97.8 % DBT conversion was obtained, when the molar ratio reached to 0.32. When [P]/DBT is lower than 0.32, it is unfavorable for the reaction rate. However, if [P]/DBT is further increased to higher than 0.32, the DBT conversion

Scheme 1 The process of oxidative reaction of DBT using H_2O_2 as the oxidant



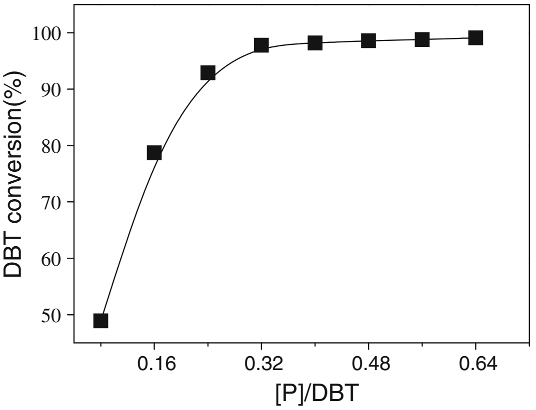


Fig. 7 Influence of catalyst amount on the DBT conversion. Reaction conditions: 20 mL model oil, 60 °C, 120 min, $n(O)/n(S) = 16$

increased comparatively slowly. From an economic point of view, this would be unconducive to the industrial application. Therefore, 0.32 of [P]/DBT was chosen in the investigation.

Conclusions

In this work, the catalyst $PMoV_2/SBA\text{-}15\text{-}NH_2$ was obtained by grafting the molybdovanadophosphoric acid onto the 3-aminopropyltrimethoxy silane-functionalized SBA-15. Such materials can be efficiently used for environmentally friendly heterogeneous catalysis. Compared with $PMoV_2/SBA\text{-}15$, $PMoV_2/SBA\text{-}15\text{-}NH_2$ shows good reusability during a six-cycle test due to the strong interaction of $PMoV_2$ and functionalized SBA-15. The results may bring improvements in the application of oxidative desulfurization.

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