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**Deep oxidative desulfurization of model oil catalyzed by
magnetic MoO₃/Fe₃O₄**

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Abstract

The magnetic $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst was prepared and used in the oxidative desulfurization (ODS) of dibenzothiophene (DBT), benzothiophene, and thiophene. The morphology and components of the magnetic composite material were characterized by X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy techniques. Results indicated that MoO_3 as an active species was supported on Fe_3O_4 . High calcination temperature leads to the formation of $\text{Fe}_2(\text{MoO}_4)_3$ compounds which showed lower activity than MoO_3 . The highest conversion of 99.5 % for ODS of DBT can be achieved on $\text{MoO}_3/\text{Fe}_3\text{O}_4$ calcinated at 400°C . In addition, the amount of $\text{MoO}_3/\text{Fe}_3\text{O}_4$, TBHP/DBT molar ratio and reaction temperature played vital roles in desulfurization efficiency. This work showed the possibility for the utilization of low cost magnetic $\text{MoO}_3/\text{Fe}_3\text{O}_4$ composite in the oxidative desulfurization because it shows high activity and could be easily separated by applying an external magnetic field, achieving ten times recycling without significant decrease in activity.

Keywords: $\text{MoO}_3/\text{Fe}_3\text{O}_4$, magnetic composite particles, tert-butyl hydroperoxide, oxidative desulfurization

1. Introduction

The combustion of fuels results in sulfur oxide (SO_x) production, which leads to acid rain, haze, or many other environmental issues.¹ Thus, numerous countries have promulgated regulations to restrict the sulfur content in fuels.² Dibenzothiophene (DBT), benzothiophene (BT), and thiophene (Th), as well as their derivatives, are main sulfur-containing compounds.³ These substances are difficult to remove by traditional hydrodesulfurization technology. In recent years, oxidative desulfurization was developed to overcome this disadvantage and found to have the high removal efficiency with convenient and simple operating procedures.^{4,5}

In general, the catalysts for oxidative desulfurization can be divided into heteropolyacid^{6,7}, organic acids^{8,9}, ionic liquids,^{10,11} and nanometal oxides. The main focus in this field is deep oxidative desulfurization by nanometal oxides, such as V_2O_5 ¹², ZrO_2 ¹³, TiO_2 ¹⁴, MnO_2 ¹⁵, MoO_3 ¹⁶, and WO_3 ¹⁷. Compared with the traditional catalyst, nanocatalysts possess higher surface and more active sites. However, these nanocatalysts cannot be separated simply or rapidly in their applications. In recent years, magnetic materials have been widely used in various fields because of their high catalytic reaction activity and easy separation. The magnetic ionic liquids¹⁸⁻²⁰ and magnetizable complex^{21,22} have been used as catalysts in oxidative desulfurization to

enhance separation efficiency. As of this writing, no report has been published on the application of magnetic composite oxides in the oxidative desulfurization reaction.

In the current paper, the magnetic $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst was synthesized and used for the oxidative desulfurization of DBT model oil with tert-butyl hydroperoxide (TBHP) as oxidant. The catalyst exhibited high catalytic efficiency in oxidative desulfurization and could be quickly separated and recovered by an external magnetic field. The effects of reaction time, temperature, O/S molar ratio and catalyst amount were studied on the sulfur removal rate of model oil.

2. Experimental

2.1 Materials

FeCl_3 , $\text{C}_{19}\text{H}_{42}\text{BrN}$ (CTAB), anhydrous sodium acetate, ethylene glycol (EG), HNO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AMM), and N-octane were purchased from the Shanghai Chemical Factory. Tert-butyl hydroperoxide (TBHP), tetradecane, dibenzothiophene (DBT), benzothiophene (BT), and thiophene (Th) were purchased from the Aladdin Industrial Corporation. All reagents were commercially available and used as received without further purification. Deionized water was used throughout all experimental procedures.

2.2 Preparation

The Fe_3O_4 microspheres were prepared by hydrothermal treatment. Anhydrous FeCl_3 (2.43 g) was dissolved in $\text{C}_2\text{H}_6\text{O}_2$ (60 mL) to form a clear solution, in which anhydrous NaAc (4.92 g) and CTAB (0.72 g) were subsequently added under stirring. The obtained homogeneous mixed solution was transferred into Teflon-lined stainless

steel autoclave for hydrothermal treatment at 200 °C for 10 h. After the autoclave was cooled down to room temperature, the precipitate was collected by magnetic separation and washed several times with deionized water and anhydrous ethanol, then dried under vacuum at 50 °C before characterization and application.

The magnetic MoO₃/Fe₃O₄ particles were prepared by precipitation method. (NH₄)₆Mo₇O₂₄·4H₂O (0.3 g) was dispersed in deionized water (50 mL) to form a clear solution, followed by the addition of Fe₃O₄ (0.2 g). The obtained homogeneous solution by ultrasonication was transferred to a three-necked flask. Nitric acid was added into the solution to adjust pH value equal to 1.5, and then the mixture was heated in water bath at 70 °C for 10 h under mechanical stirring. After cooling down to room temperature, the precipitate was collected by magnetic separation and washed with deionized water for several times, then dried in vacuum oven at 60 °C for 8 h. Finally, the obtained sample was annealed in air at 400 °C for 4 h.

2.4 Oxidative desulfurization

Model oils were prepared by dissolving DBT, BT, or Th in n-octane separately, with the initial sulfur content of 500 ppm (µg/g). The catalyst, model oil (5 mL) and TBHP were added into a 50 mL two-necked flask in experimental proportion. Then the flask was heated in oil bath under stirring vigorously with a mechanical stirrer. After the reaction, the catalyst was separated from the reaction system under external magnetic field.

2.5 Characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained on a Philips X-ray diffractometer (PW 3040/60) using Cu K α target at 40 kV and 40 mA. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron microanalyzer with an accelerating voltage of 15 kV. The characterizations of surface information and valence state of the catalysts were carried out with X-ray photoelectron spectroscopy (XPS), using an ESCA System X-ray photoelectron spectrometer with Al K α X-ray as the excitation source. The FT-IR spectra of DBT oxidation products were recorded on a NEXUS 670 FT-IR spectrometer with KBr pellets prepared by manual grinding. The product was analyzed by gas chromatography-flame ionization detector (GC-FID) (Shanghai Tian Mei Scientific Instrument Co., Ltd., GC-7890) equipped with a TM-5 capillary column (30 m \times 0.32 mm i.d. \times 0.5 μ m) for the detection of DBT, BT and Th. The removal of the sulfides was calculated as follows: $X = \frac{C_0 - C_t}{C_0} \times 100\%$, where C_0 is the initial concentration of sulfur in the model fuel, and C_t is the concentration of sulfur in the oil phase after the reaction began for a period of time.

3 Results and discussion

3.1 Characterizations of catalysts

XRD patterns of the catalysts are shown in **Fig. 1**. For the Fe₃O₄ sample, the main peaks at 30.10°, 35.45°, 43.12°, 53.48°, 57.01°, and 62.58° corresponded to the (220), (311), (400), (422), (511) and (440) planes. For MoO₃/Fe₃O₄, the characteristic diffraction peaks of orthorhombic MoO₃ also appeared at $2\theta = 12.77^\circ, 23.31^\circ, 25.70^\circ, 27.33^\circ, \text{ and } 38.98^\circ$, aside from the characteristic diffraction peaks of Fe₃O₄.

The influence of the calcinations temperature on the catalyst was also analyzed by

XRD characterization. The characteristic diffraction peaks of MoO_3 weakened as the calcination temperature increased. Only the diffraction peaks of Fe_3O_4 and MoO_3 were detected for the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalysts calcined at 400 °C. When the calcination temperature was raised to 500 °C and 600 °C, new diffraction peaks appeared at 15.27°, 20.40°, 21.73°, 22.88°, 25.61°, 27.46°, 30.12°, 34.06°, 35.77°, and 40.89°, which were attributed to the characteristic diffraction peaks of $\text{Fe}_2(\text{MoO}_4)_3$ (JCPDS No. 00-035-0183). Moreover, the peak intensity increased when the calcination temperature was raised, and the Fe_3O_4 and MoO_3 diffraction peaks could not be detected. These results showed that the catalysts were converted to $\text{Fe}_2(\text{MoO}_4)_3$ compound with increasing calcination temperature. The optimal calcination temperature of catalyst was 400 °C because the performance of MoO_3 was much higher than that of $\text{Fe}_2(\text{MoO}_4)_3$ in the model oil desulfurization reaction.

Fig. 2 displays the scanning electron microscopy images of Fe_3O_4 and $\text{MoO}_3/\text{Fe}_3\text{O}_4$. The uniform Fe_3O_4 spherical structure was composed of small self-assembled Fe_3O_4 particles (**Fig. 2A** and **2B**). In comparison, the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst in **Fig. 2C** and **2D** presented a smoother surface, with a diameter of 600 and 700 nm. The result was due to the fact that the Fe_3O_4 particles were covered by small MoO_3 particles.

The surface chemical states of $\text{MoO}_3/\text{Fe}_3\text{O}_4$ calcined at 400 °C were studied by X-ray photoelectron spectroscopy (XPS). In **Fig. 3A**, a typical full XPS spectrum of $\text{MoO}_3/\text{Fe}_3\text{O}_4$ spheres showed photoelectron lines at binding energies of about 232, 711, 530 and 285 eV, corresponded to Mo3d, Fe2p, O1s, and C1s, respectively. In the Mo3d

spectrum (**Fig. 3B**), the binding energies of Mo3d_{3/2} and Mo3d_{5/2} were about 232.7 eV and 235.9 eV, respectively. The values were in accord with the MoO₃ binding energy. The result further proved the presence of MoO₃ in the MoO₃/Fe₃O₄ catalysts. The Fe2p_{3/2} and Fe2p_{1/2} peaks were located at 711.2 and 725.2 eV, respectively, consistent with the binding energy of Fe₃O₄. **Fig. 3C** shows the spectrum of O1s, and the peak at 530.4 eV may be attributed to anionic oxygen in Fe₃O₄ and MoO₃.

Table 1 shows XPS results of MoO₃/Fe₃O₄ calcined at different temperatures. The binding energy of Fe2p_{3/2} and O1s increased with increasing calcination temperature, implying that Fe element mainly existed in Fe₃O₄ form for MoO₃/Fe₃O₄ calcined at 400 °C. When the calcination temperature was raised to 500 °C, the formation of Fe₂(MoO₄)₃ resulted in the increase in the binding energy of Fe2p_{3/2}. In addition, the Mo/Fe ratio for MoO₃/Fe₃O₄ calcined at 400 °C was larger than that for MoO₃/Fe₃O₄ calcined at 500 °C. These results showed that higher calcination temperature led to Fe₂(MoO₄)₃ formation on the surface.

The magnetic properties of the Fe₃O₄ and MoO₃/Fe₃O₄ catalysts were studied using a magnetometer at room temperature. **Fig. 4** shows the magnetization of Fe₃O₄ and MoO₃/Fe₃O₄ at 300 K by cycling the field between -70 kOe and 70 kOe. The Fe₃O₄ and MoO₃/Fe₃O₄ catalysts presented a typical hysteresis loop phenomenon, and their coercivities were 12.41 and 10.05 Oe, respectively. This finding revealed the weak ferromagnetism behavior for Fe₃O₄ and MoO₃/Fe₃O₄. The saturation magnetizations were 76.40 and 27.91 emg/g, respectively. The decrease in saturation magnetization of MoO₃/Fe₃O₄ could be attributed to the addition of molybdenum oxide. The inset in **Fig.**

4 shows the magnetic separation renderings. The brown $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst was uniformly dispersed in an aqueous solution and the solution quickly changed to be clear by an external magnet. The $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst could be easily separated from the solution. Thus, this catalyst has great potential as a desulfurization catalyst carrier.

3.2 Catalytic Activity of $\text{MoO}_3/\text{Fe}_3\text{O}_4$

The sulfur-removal performance of catalysts is displayed in **Table 2**. Fe_3O_4 showed negligible performance, with sulfur removal rate of only 2%. By contrast, MoO_3 presented a high sulfur removal rate of 97.6%. $\text{MoO}_3/\text{Fe}_3\text{O}_4$ calcined at 400 °C exhibited the best sulfur removal of 99.5%. When the calcination temperature was raised to 500 °C and 600 °C, the sulfur removal rates of the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalysts were 40.9% and 37.9%, respectively. As shown in **Table 2**, $\text{Fe}_2(\text{MoO}_4)_3$ compounds were generated with the increase in calcination temperature, and the catalytic activity of this compounds was lower than MoO_3 . Therefore, the sulfur removal rate of the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalysts calcined under high temperature was reduced. The results suggested that MoO_3 was the active component for the catalytic oxidation of DBT in the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalysts system. Meanwhile, Fe_3O_4 mainly played the role of a magnetic mediator, which resulted in the separation of the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst from the reaction system under an extra magnetic field.

3.3 Influence of O/S Molar Ratios on Sulfur Removal

The amount of oxidant is one of the most important factors affecting DBT removal in the oxidative desulfurization system. According to the chemical reaction equation of DBT oxidation into dibenzothiophene sulfone, oxidation of 1 mol DBT requires 2 mol TBHP. In fact, however, more oxidants were required. **Fig. 5** shows that the effects of

oxidative desulfurization were dependent on the amount of oxidant for DBT desulfurization with different O/S molar ratios. The oxidative desulfurization rate of DBT maintained an upward trend with O/S molar ratios from 1:1 to 6:1, which may be attributed to increasing the concentration of the oxidizing agent TBHP greatly will promote the chances of sulfur compounds contact with the oxidant molecules and thus improve the desulfurization rate gradually. However, when the oxidizing agent TBHP was gradually depleted, the desulfurization rate remained almost unchanged 3 h later. Therefore, the most appropriate ratio of O/S was 4:1. Under this condition the desulfurization rate of 98.7% was achieved after reaction for 3 h.

3.4 Influence of the Amount of Catalyst on Sulfur Removal

Fig. 6 presents the sulfur-removal experimental results at varying usage amounts of the $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst under fixed conditions, as noted in the legend. The amount of catalyst significantly influenced the sulfur-removal performance. When the amount of catalyst increased from 3 mg to 8 mg, the desulfurization rate increased rapidly with the reaction time. The most suitable amount of catalyst for our experiment was 6 mg. The desulfurization rate of 97.6 % was obtained after reaction for 3 h.

3.5 Influence of Reaction Temperature on Sulfur Removal

The influence of temperature on the sulfur-removal kinetics was studied in the temperature range of 60°C to 110 °C, and the results are presented in **Fig. 7**. The reaction temperature greatly enhanced the sulfur removal rate. The sulfur removal of DBT was visibly advanced after reaction for 1 h. When the temperature was 90 °C, the sulfur removal of DBT reached 83.5% in 2 h and sulfur was nearly removed after 2.5 h, whereas the desulfurization efficiency appeared to be much lower at 60 °C. However, a

higher temperature at 110 °C resulted in the thermal decomposition of TBHP. Thus, for the present experiment and from a practical perspective, 90 °C and 3 h were selected as the appropriate temperature and reaction time, respectively.

3.6 Oxidation of Different Sulfur-Compounds

As mentioned above, the model oil of DBT could be effectively removed by MoO₃/Fe₃O₄. To examine the desulfurization efficiency of the MoO₃/Fe₃O₄ catalyst for other organic sulfides, the sulfur-removal performance of BT and Th was also studied and compared with the model oil of DBT under similar reaction conditions. The results are shown in **Fig. 8**. The reactivity of the three organic sulfides oxidized by TBHP followed the order of DBT > BT > Th, which was dependent on the electron density of the sulfur atom of different organic sulfides. In general, lower electron density on sulfur atom resulted in lower activity of the sulfur removal rate. For DBT, BT, and Th, the electron densities of the sulfur atom are 5.785, 5.739 and 5.696, respectively. Therefore, it is highly efficient for the removal of DBT which is a key organic sulfide of diesel oils. By contrast, the lower electron density of sulfur atom on BT and Th directly resulted in low catalytic activity over the MoO₃/Fe₃O₄ catalyst.

3.7 Influence of Recycle Times on Sulfur Removal

In the oxidative desulfurization system, the MoO₃/Fe₃O₄ catalyst with magnetic behavior was convenient and conducive to be separated under an external magnet. The magnetic catalysts were reused for oxidative desulfurization and the S-removal rates are presented in **Fig. 9**. After 10 cycles, no significant change in the desulfurization rate was observed, demonstrating the high stability of the magnetic MoO₃/Fe₃O₄ catalyst.

The structure of the obtained white precipitate was detected by IR and the result is presented in **Fig.10**. Compared with DBT, the product presented the absorption bands for sulfone at 1288 and 1166 cm^{-1} , and the absorption band for sulfoxide at 1047 cm^{-1} , suggesting that DBT was oxidized to DBTO and DBTO₂ by using the MoO₃/Fe₃O₄ catalysts.

4. Conclusions

In summary, the magnetic MoO₃/Fe₃O₄ catalyst was synthesized and applied in the oxidative sulfur removal of DBT. This study showed that the catalyst can be easily separated from the reaction system by adding a magnet and recycled. After 10 cycles, no obvious decrease was observed for oxidative sulfur removal using the MoO₃/Fe₃O₄ catalysts. In addition, the amount of catalyst used was relatively small, and the conversion of 99.5% was achieved under optimal conditions.

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Figure Captions

Fig. 1 XRD patterns of magnetic Fe_3O_4 and $\text{MoO}_3/\text{Fe}_3\text{O}_4$ with different calcination temperatures

Fig. 2 SEM images of magnetic Fe_3O_4 (A,B) and $\text{MoO}_3/\text{Fe}_3\text{O}_4$ (C,D)

Fig. 3 XPS spectra of magnetic $\text{MoO}_3/\text{Fe}_3\text{O}_4$ calcined at 400 °C: (A) full spectrum; (B) Mo3d spectrum; (C) Fe2p spectrum; (D) O1s spectrum.

Fig. 4 Magnetization curves of Fe_3O_4 (A) and $\text{MoO}_3/\text{Fe}_3\text{O}_4$ (B) and the photographs of $\text{MoO}_3/\text{Fe}_3\text{O}_4$ separated from the solution by applying an added magnet (inset)

Fig. 5 Influence of the mole ratio of O/S on sulfur removal

Fig. 6 Influence of the catalyst amount on sulfur removal

Fig. 7 Influence of reaction temperature on sulfur removal

Fig. 8 Sulfur removal of different sulfur compounds

Fig. 9 Influence of the recycle times on sulfur removal

Fig. 10 IR spectra of DBT (A) and its oxidation products (B)

Table 1 XPS results of the catalysts

Table 2 Oxidative desulfurization performance of the catalysts

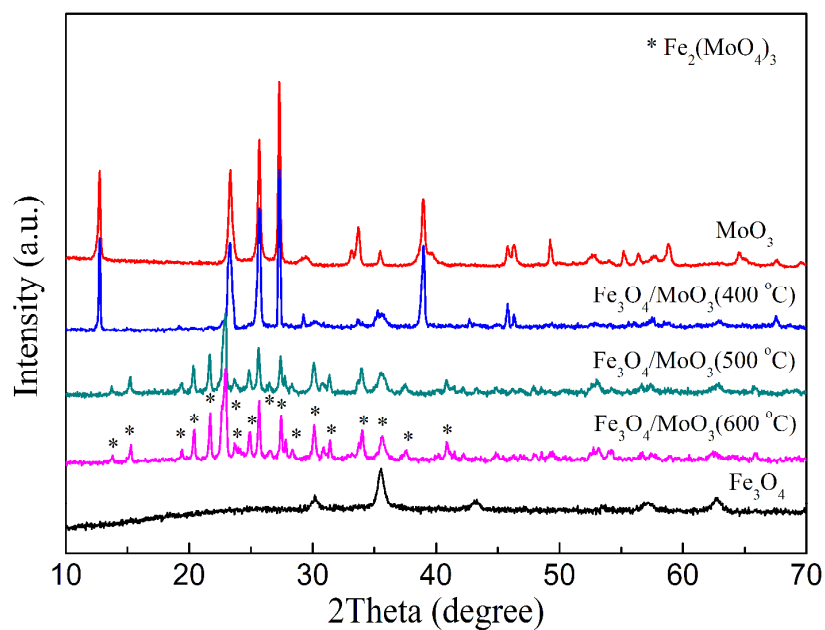


Fig. 1 XRD patterns of magnetic Fe₃O₄, MoO₃ and MoO₃/Fe₃O₄ with different calcination temperatures

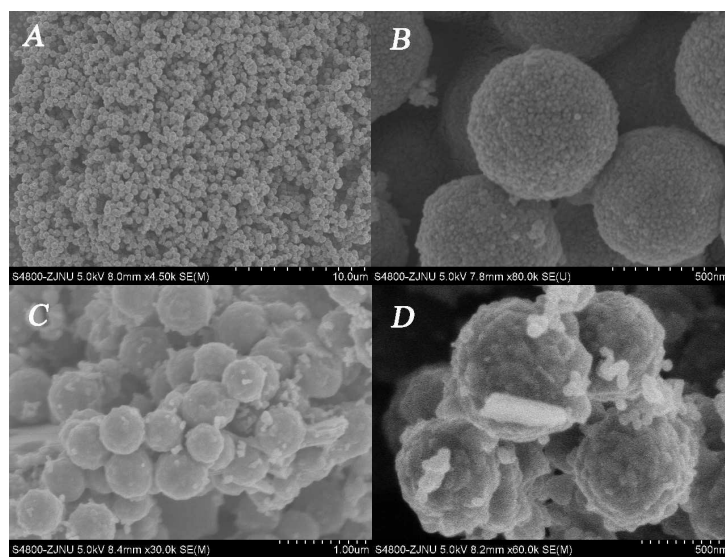


Fig. 2 SEM images of Fe_3O_4 (A,B) and $\text{MoO}_3/\text{Fe}_3\text{O}_4$ (C,D)

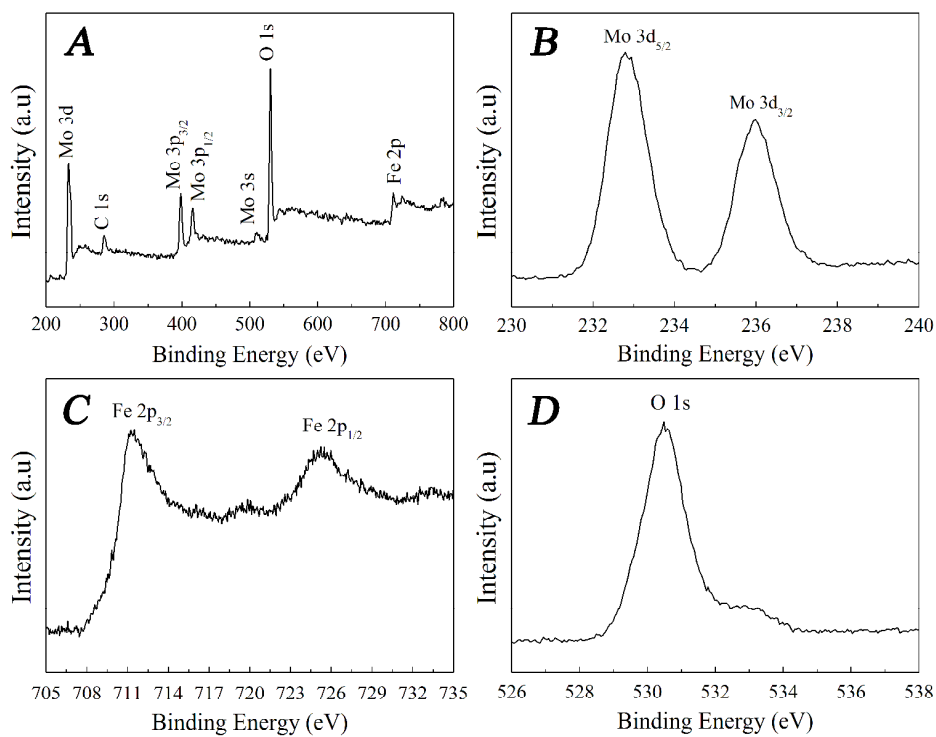


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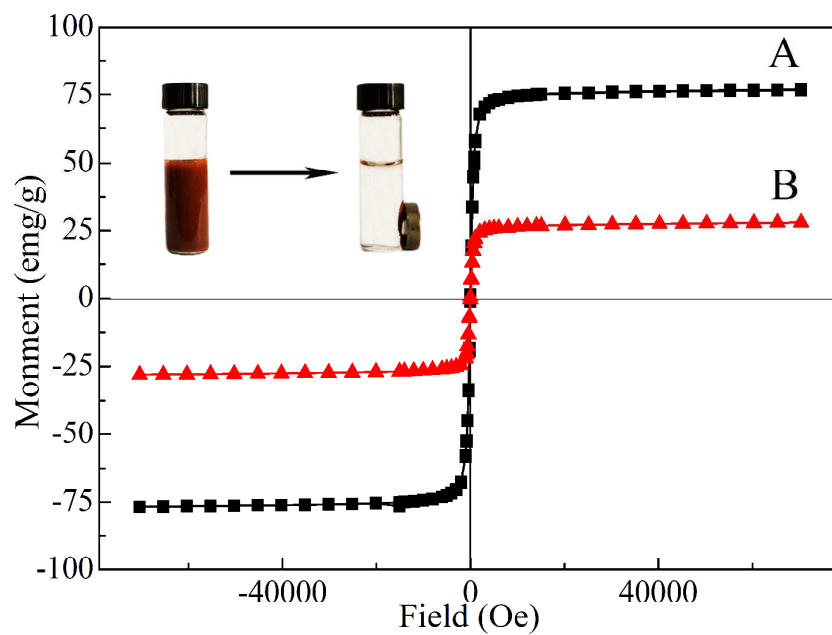


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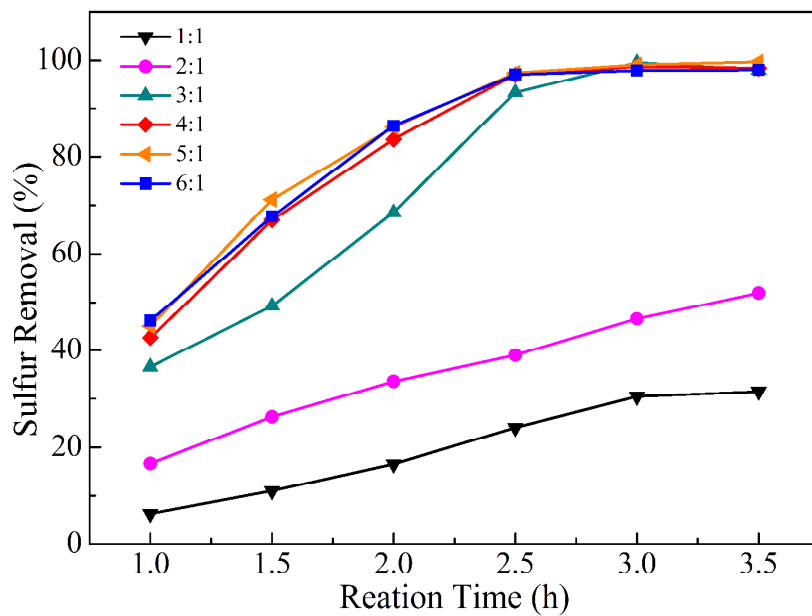


Fig. 5 Influence of the mole ratio of O/S on sulfur removal

Reaction Conditions: $T = 90\text{ }^{\circ}\text{C}$, $V(\text{DBT oil}) = 5\text{ mL}$, $m(\text{catalyst}) = 6\text{ mg}$.

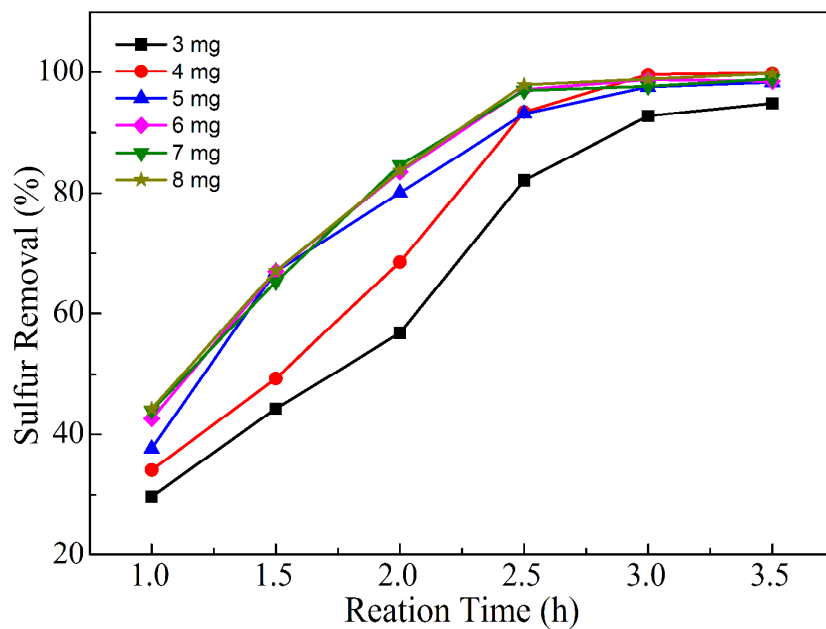


Fig. 6 Influence of the catalyst amount on sulfur removal

Reaction Conditions: $T = 90\text{ }^{\circ}\text{C}$, $V(\text{DBT oil}) = 5\text{ mL}$, $n(\text{O}):n(\text{S}) = 4:1$.)

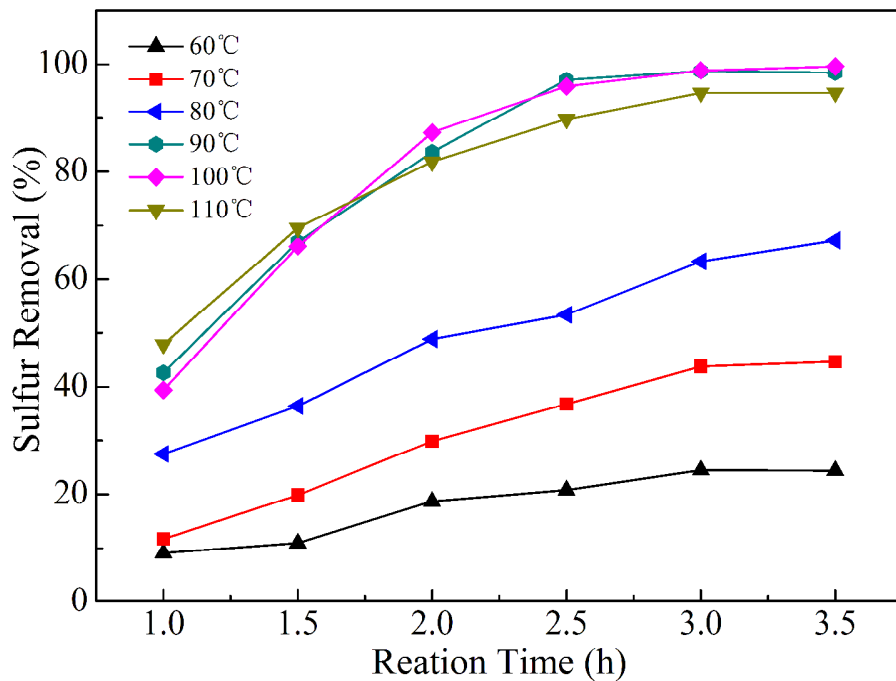


Fig. 7 Influence of reaction temperature on sulfur removal

Reaction Conditions: V(DBT oil) = 5 mL, m(catalyst) = 6 mg, n(O):n(S) =
4:1.

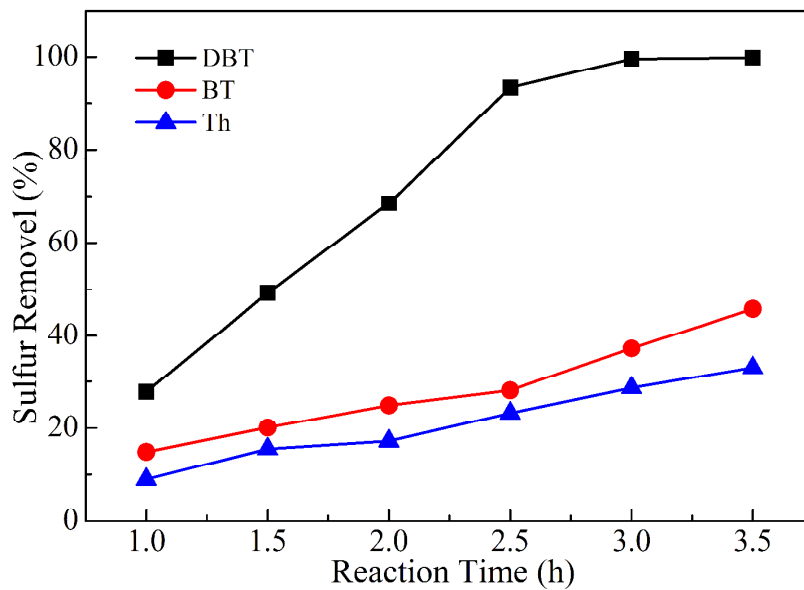


Fig. 8 Sulfur removal of different sulfur compounds

Reaction Conditions: $V(\text{DBT oil}) = 5 \text{ mL}$, $m(\text{catalyst}) = 6 \text{ mg}$, $n(\text{O}):n(\text{S}) = 4:1$.

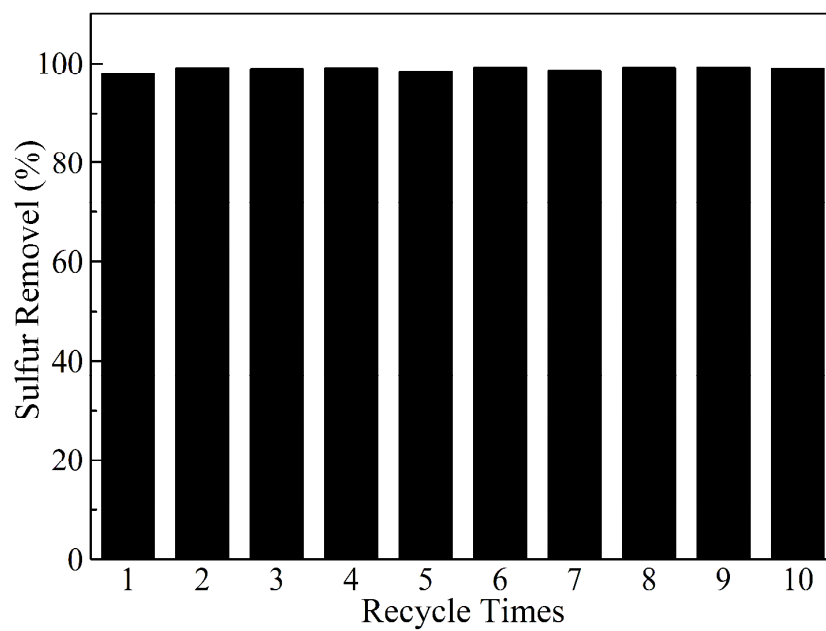


Fig. 9 Influence of the recycle times on sulfur removal

Reaction Conditions: $T = 90\text{ }^{\circ}\text{C}$, $m(\text{catalyst}) = 6\text{ mg}$, $n(\text{O}):n(\text{S}) = 4:1$.

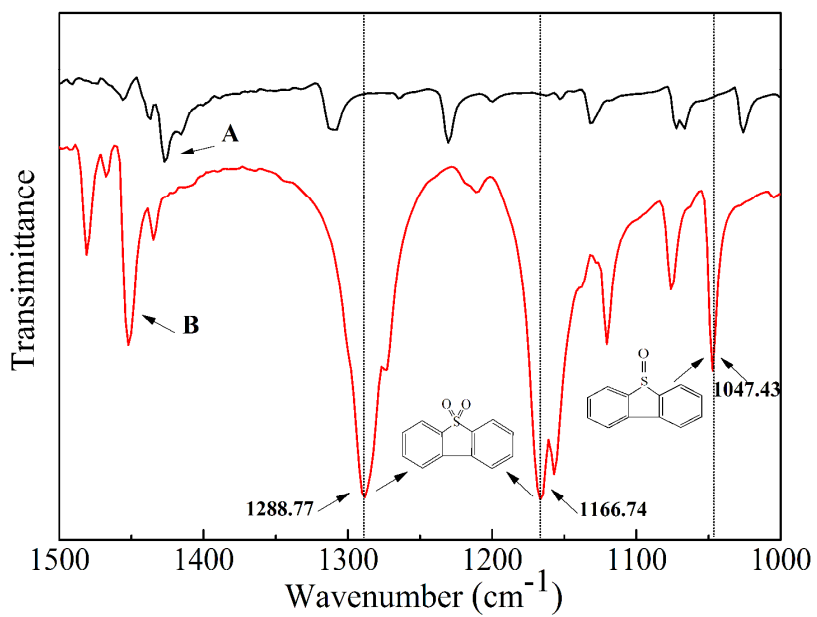


Fig. 10 IR spectra of DBT (A) and its oxidation products (B)

Table 1 XPS results of the MoO₃/Fe₃O₄ catalysts

Catalyst	Mo/Fe atomic ratio	Binding Energy (eV)		
		Fe 2p _{3/2}	Mo 3d _{5/2}	O 1s
MoO ₃ /Fe ₃ O ₄ (400 °C)	2.89	711.2	232.7	530.4
MoO ₃ /Fe ₃ O ₄ (500 °C)	1.25	711.4	232.8	530.6

Table 2 Oxidative desulfurization performance of the catalysts

Catalyst	S-removal Rate
Fe ₃ O ₄	2 %
MoO ₃	97.6 %
MoO ₃ /Fe ₃ O ₄ (400 °C)	99.5 %
MoO ₃ /Fe ₃ O ₄ (500 °C)	40.9 %
MoO ₃ /Fe ₃ O ₄ (600 °C)	37.9 %

(Reaction Conditions: V(DBT oil) = 5 mL, $m_{\text{catalyst}} = 6$ mg, n(O):n(S) = 4:1,
T = 90 °C.)

Graphical Abstract

The magnetic $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst showed good catalytic performance and stability for oxidation desulfurization of dibenzothiophene, and it could be easily separated by applying an external magnetic field.

