

One step non-hydrodesulfurization of fuel oil: Catalyzed oxidation adsorption desulfurization over HPWA-SBA-15

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Abstract

HPWA-SBA-15 has the typical structure of mesoporous molecular sieve SBA-15 and Keggin structure of $H_3PW_{12}O_{40}$ (HPWA). It was initially used in the catalyzed oxidation adsorption desulfurization of model fuel composed of dibenzothiophene (DBT) and isooctane, using *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant. A series of catalysts including SBA-15 modified with different kinds of acid and several microporous materials containing HPWA were tested in the desulfurization of model fuel, it is shown that HPWA-SBA-15 has the best desulfurization capacity as catalyst and sorbent, it can remove DBT in nine tenths in one-step. Several comparison experiments were designed for the exploration of the function of HPWA-SBA-15 in the desulfurization. It is concluded that HPWA-SBA-15 has both catalytic oxidation ability and adsorption ability. The non-polar DBT can be converted into polar DBT sulfone that is easily absorbed on HPWA-SBA-15. FTIR characterization indicates the existence of intermediate of [O–O] structure in the desulfurization. Both the ^{31}P NMR spectra of HPWA-SBA-15 before and after regeneration and the desulfurization results of these two samples indicate that HPWA-SBA-15 has good regenerating ability. © 2006 Elsevier B.V. All rights reserved.

Keywords: Desulfurization; Oxidation; Adsorption; DBT; HPWA-SBA-15

1. Introduction

Deep desulfurization of transportation fuels is receiving increasing attention in the research community worldwide due to increasingly stringent regulations and fuel specifications in many countries for environmental protection purpose [1]. The oxidative desulfurization (ODS) is considered to be one of the promising new methods for super deep desulfurization of fuel oil [2]. Compared with conventional catalytic hydrodesulfurization (HDS), ODS can be carried out under very mild conditions (room temperature and atmospheric pressure), especially, such process is much more efficient for the removal of dibenzothiophene (DBT) which is difficult to be removed in the HDS of the fuel [3]. In oxidation, dibenzothiophene (DBT) can be oxidized into sulfone that can be subsequently removed by conventional separation operations (e.g. solvent extraction, adsorption, etc.) because their properties are signif-

icantly different from those of the hydrocarbons in the fuel oils [4].

Some authors have reported two-step process for desulfurization of fuel, for example, oxidation–extraction or oxidation–adsorption using liquid catalysts [5,6]. Such catalysts are not so easily separated as solid catalysts and this process is not as profitable as one-step process.

Recently, polyoxometalates with a Keggin structure such as $H_3PM_{12}O_{40}$ [M, Mo(VI), W(VI)] is of increasing interest in the oxidation of DBT [7,8]. In this paper, an effective oxidative catalyst HPWA-SBA-15 is obtained by supporting $H_3PW_{12}O_{40}$ (HPWA) on the mesoporous molecular sieves SBA-15, and it exhibits excellent performance in the desulfurization of model fuel. Its function in the desulfurization and its regenerating ability are systematically studied.

2. Experimental

2.1. Synthesis of HPWA-SBA-15

Tetraethoxy silane (TEOS, 8.48 g) was dissolved in a mixture of 4.0 g P123 and 25.1 g HCl (36 wt%) while stirring at 313 K in

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a water bath. To this solution HPWA was added in a calculated amount to reach 30 wt% heteropoly acid loading in the final (calcined) sample.

The gel composition was $\text{SiO}_2\text{:HPWA:P123:HCl:H}_2\text{O} = 4.07\text{:}x\text{:}0.7\text{:}2.4\text{:}544$ (x is mol (HPWA)/mol (HPWA + SiO_2)). This gel was stirred for 24 h at 313 K, and then crystallized in a propylene vessel at 373 K for 24 h. After crystallization, the white precipitate solid was dried in vacuum oven at 383 K overnight. The dried precipitate was calcined in air for 5 h at 723 K to decompose the template and obtain a white powder. The final sample is HPWA-SBA-15.

2.2. Characterization of the catalysts

XRD patterns were recorded at $2\theta = 0.7\text{--}40.0^\circ$ on a Rigaku D/max-RB diffractometer instrument operating at 40 kV and 100 mA with Cu target $K\alpha$ -ray irradiation.

FTIR spectra ($1200\text{--}600\text{ cm}^{-1}$) were recorded on a Nicolet 5Dx-FTIR spectrometer. The samples were pressed with KBr in the ratio 1:150.

TEM results were obtained on Hitachi H-600 transmission electron microscope.

^{31}P NMR spectra were obtained at 202.45 MHz on an Infinity Plus 300WB NMR spectrometer with a 5 mm solid MAS probe by using 85% H_3PO_4 as the internal standard.

2.3. Desulfurization of model fuel

A model fuel with given concentration was prepared by dissolving calculated amount of dibenzothiophene (DBT) in fixed amount of isoctane, which was inert in the oxidation of DBT at 343 K. The desulfurization experiments were carried out in a 250 ml flask equipped with magnetic stirrer and condenser. The reaction was carried out with *t*-BuOOH as oxidant and HPWA-SBA-15 as catalyst and absorbent. The amount of oxidant was expressed as O/S, i.e. the mole ratio of *t*-BuOOH to DBT. The total sulfur content and sulfur compounds types, including DBT, DBOT (dibenzothiophene sulfoxide) and DBOOT (dibenzothiophene sulfone) were measured on WK-2 total sul-

fur analyzer and a gas chromatograph (PFPD: agilent-6890), respectively.

2.4. Regeneration of HPWA-SBA-15

When HPWA-SBA-15 is saturated with sulfur compounds, it needs regeneration. The saturated HPWA-SBA-15 was washed with toluene for several times to remove the physisorption sulfide according to “like dissolves like” principle. Then HPWA-SBA-15 is heated at 513 K for 4 h to break down the chemical action between sulfur compounds and HPWA-SBA-15. HPWA-SBA-15 can be reused after being washed with toluene again and drying for 12 h.

3. Results and discussion

3.1. XRD patterns

XRD patterns of SBA-15 and HPWA-SBA-15 were shown in Fig. 1. Fig. 1A is the small angle XRD patterns, the typical XRD patterns consisting of a strong peak (at 2θ around 0.8°) along with two weak peaks (at 2θ around 1.6° and 1.8°) are corresponding to the (1 0 0), (1 1 0) and (2 0 0) planes of SBA-15 [9]. Intensities of these characteristic peaks are lower than those of pure SBA-15, whereas no remarkable peaks at high angle (Fig. 1B) indicate that HPWA is probably finely dispersed in the samples.

3.2. FTIR Spectra

FTIR spectra ($1200\text{--}600\text{ cm}^{-1}$) of SBA-15, HPWA-SBA-15 and HPWA are shown in Fig. 2. Bands observed at 1083, 982, 890 and 808 cm^{-1} , which are the fingerprint of Keggin structure of HPWA, are usually assigned to $\nu_{\text{as}}(\text{P-O})$, $\nu_{\text{as}}(\text{W=O})$, $\nu_{\text{as}}(\text{W-O}_b\text{-W})$ in corner shared octahedral and $\nu_{\text{as}}(\text{W-O}_c\text{-W})$ in edge shared octahedral, respectively [10]. These characteristic bands are regarded as experimental evidences to the existence of HPWA molecules or molecular fractions such as phosphorous oxides and/or tungstate ions, and the red shift of

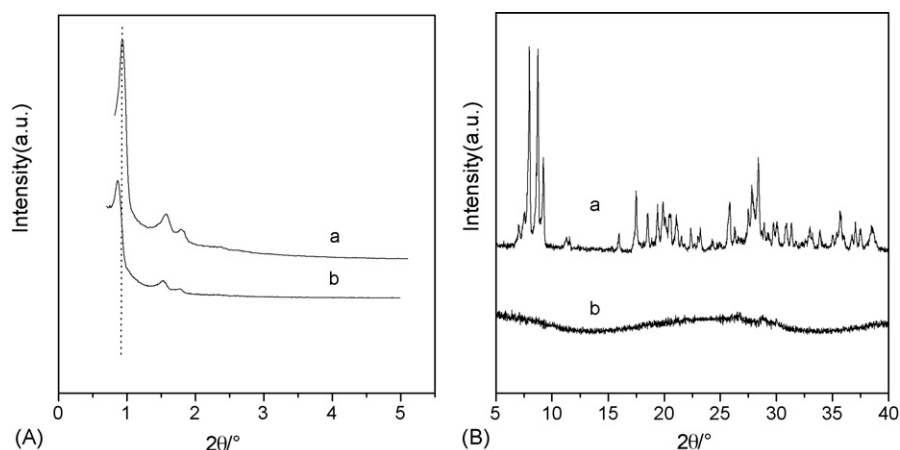


Fig. 1. XRD patterns of (A) SBA-15 (a), HPWA-SBA-15 (b) and (B) SBA-15 (a), HPWA (b).

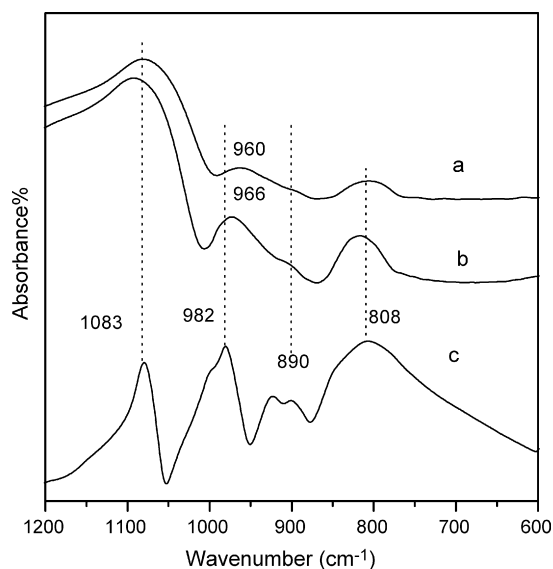


Fig. 2. FTIR spectra of SBA-15 (a), HPWA-SBA-15 (b), and HPWA (c).

$\nu_{\text{as}}(\text{W}=\text{O})$ indicate the chemical interaction between HPWA and SBA-15.

3.3. TEM

The pore size, pore shape, pore distribution and active constituent's dispersion of HPWA-SBA-15 can be obviously observed in TEM spectra (Fig. 3). Fig. 3A indicates the reg-

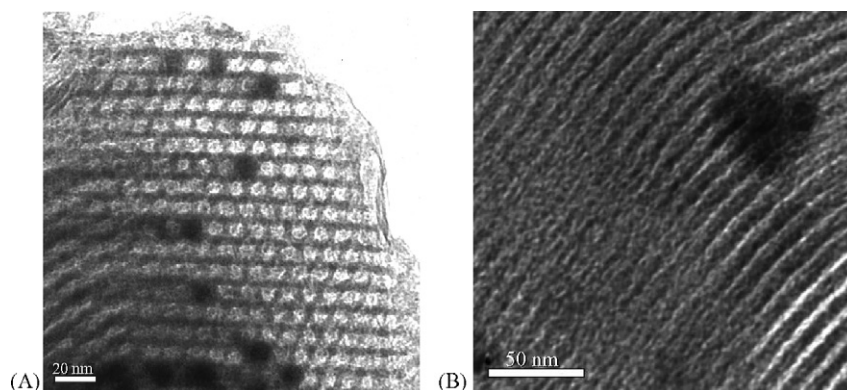


Fig. 3. TEM of HPWA-SBA-15: (A) electron beam parallel to the channel and (B) electron beam vertical to the channel.

Table 1
Comparison experiments

Serial number	Catalysts and oxidants	Feed composition ($\mu\text{g g}^{-1}$)		Products composition ($\mu\text{g g}^{-1}$)		Total desulfurization (%)
		DBT	DBOOT	DBT	DBOOT	
1	<i>t</i> -BuOOH and HPWA-SBA-15	174.00	0.00	2.33	2.15	97.43
2	<i>t</i> -BuOOH and HPWA	174.00	0.00	69.76	104.24	0.00
3	<i>t</i> -BuOOH	174.00	0.00	113.99	60.01	0.00
4	<i>t</i> -BuOOH and SBA-15	174.00	0.00	–	–	7.28
5	HPWA-SBA-15	174.00	0.00	–	–	12.87
6	SBA-15	174.00	0.00	–	–	1.63

–: the parameters need not to be decided; DBT: dibenzothiophene; DBOT: dibenzothiophene sulfoxide; DBOOT: dibenzothiophene sulfone. Operating parameters—feedstock: $174 \mu\text{g g}^{-1}$ model fuel; reaction time: 2 h; reaction temperature: 343 K; O/S:25; catalysts amount: 1.07 wt%.

ular two-dimensional hexagonal structure of the pores and the uniform pore size about 5–6 nm. In Fig. 3B, small quantities of HPWA, i.e. the black parts disperse well in the channels of HPWA-SBA-15.

3.4. Desulfurization over HPWA-SBA-15

Desulfurization capacity of HPWA-SBA-15 was compared with that of other catalysts including SBA-15 modified with phosphorous acid or boric acid and microporous materials involving USY, H β and ZSM-5 molecule sieves modified with HPWA. The experiment results (Figs. 3 and 4) indicate that HPWA-SBA-15 has the highest desulfurization rate among so many catalysts involved in this paper at low temperature and atmospheric pressure.

The model fuel with sulfur concentration of $174 \mu\text{g g}^{-1}$ was made to study the function of HPWA-SBA-15 in the desulfurization. Several comparison experiments were carried out according to Table 1, the catalysts and oxidants in the experiments were different from each other. The sulfur content and sulfur types of the experiments were also shown in this table. It is evident that neither pure adsorption with SBA-15 or HPWA-SBA-15 nor the pure oxidation can remove DBT effectively. However, 97.43% of sulfur was removed in the single experiment 1 mainly due to the catalytic function of HPWA-SBA-15. The conversion of DBT in experiment 2 is much higher than experiment 3, which shows that the catalytic active constituent is HPWA. And such conclusion is also validated by the experiment 4, in which only 7.28% of DBT was removed (Fig. 5).

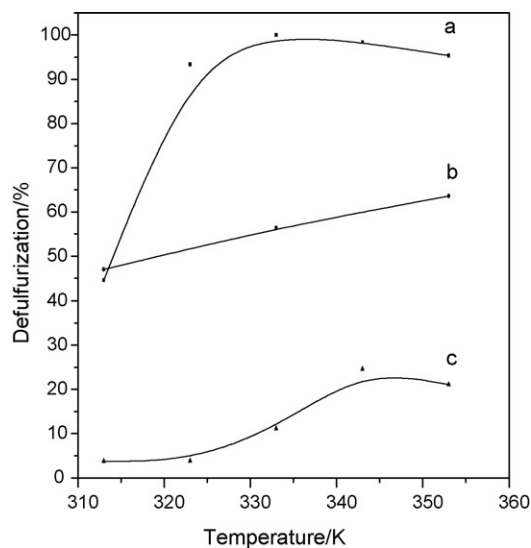


Fig. 4. Desulfurization abilities of HPWA-SBA-15 (a), H₃BO₄-SBA-15 (b), and H₃PO₄-SBA-15 (c) (feedstock: 174 $\mu\text{g g}^{-1}$ model fuel; reaction time: 2 h; reaction temperature: 343 K; O/S: 25; catalysts amount: 1.07 wt%).

DBT is a relatively large molecule with molecular dynamics diameter of 1.7 nm. The pore of HPWA-SBA-15 is much larger than it, thus diffusion resistance of the catalyzed oxidation is reduced, and as a result DBT was almost fully converted into polar DBOOT in experiment 1.

Attushi and Hai Mei think that peroxide of HPWA formed in situ when it is used as a catalyst in the oxidation reac-

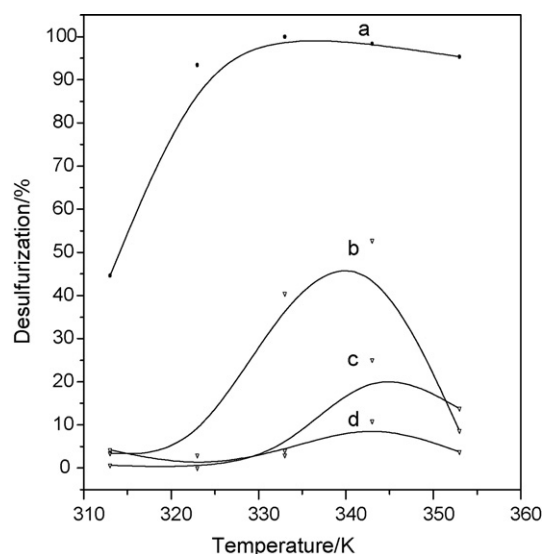


Fig. 5. Desulfurization abilities of HPWA-SBA-15 (a), HPWA-USY (b), HPWA-H β (c) and HPWA-ZSM-5 (d) (feedstock: 174 $\mu\text{g g}^{-1}$ model fuel; reaction time: 2 h; reaction temperature: 343 K; O/S: 25; catalysts amount: 1.07 wt%).

tion involving hydroperoxide [4,11]. Original HPWA-SBA-15, HPWA-SBA-15 after adding the oxidant and HPWA-SBA-15 after desulfurization were studied with FTIR (Fig. 6) in this paper, and an apparent conclusion was obtained in this study. It can be concluded that HPWA-SBA-15, after treatment with *t*-BuOOH, has the peroxide structure [O–O], from which the

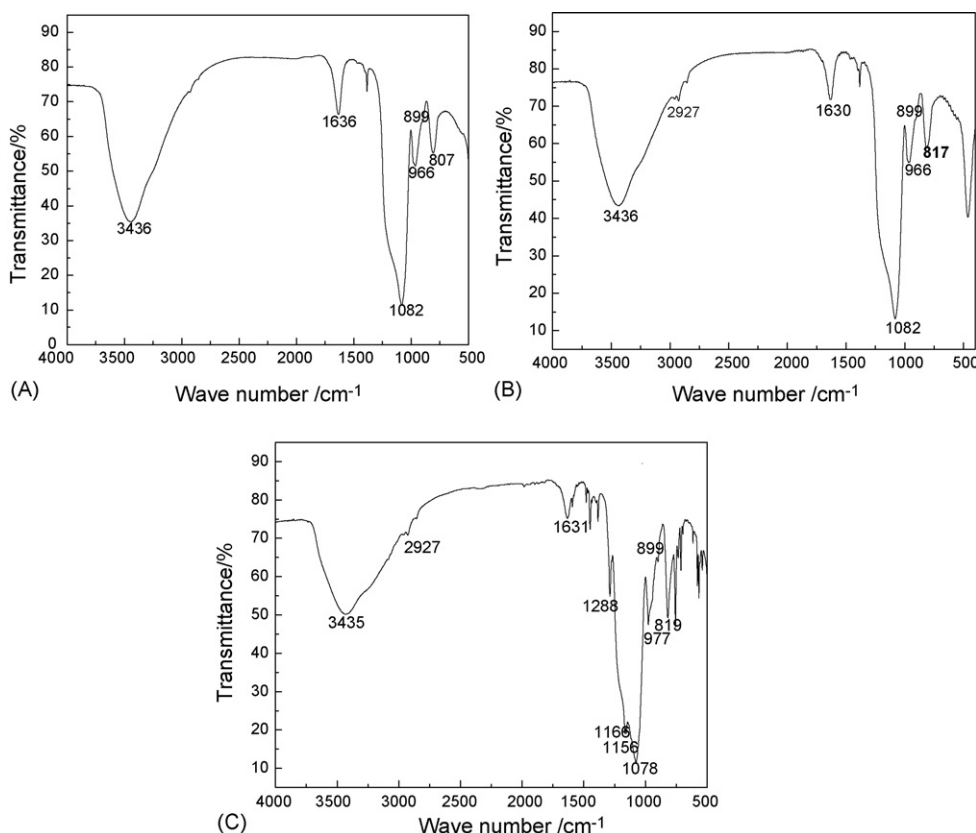


Fig. 6. FTIR of (A) HPWA-SBA-15, (B) HPWA-SBA-15 after adding oxidants, and (C) HPWA-SBA-15 after desulfurization.

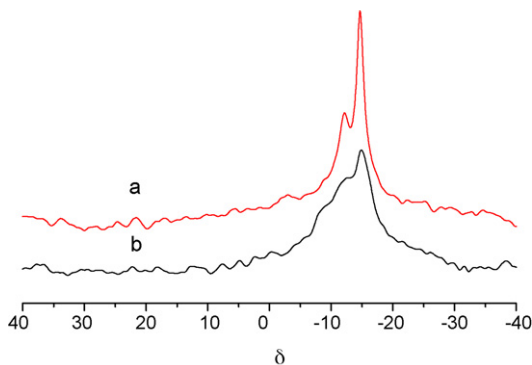


Fig. 7. ^{31}P NMR spectra of HPWA-SBA-15 (a), and HPWA-SBA-15 after regeneration (b).

817 cm^{-1} peak originates [12]. The peaks of 1156 cm^{-1} and 1166 cm^{-1} both originate from the $-\text{SO}_2-$ functional group, i.e. the DBT oxidation product sulfone [13]. The Keggin structure characteristic peaks including $\nu_{\text{as}}(\text{W}=\text{O})$ and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ originally observed at $966, 807\text{ cm}^{-1}$ in HPWA-SBA-15 have changed to 977 and 819 cm^{-1} , respectively, this result indicates that the sulfone not only has the chemical action with the end oxygen of HPWA, but also the chemical action with the bridge oxygen of it, this result indicates the sulfone's chemical adsorption on HPWA-SBA-15. After oxidation, the conjugate system of DBT is broken, the dipole moment of the sulfur compound increases greatly, hereby the adsorption of sulfur compound is strengthened (Fig. 7).

In order to investigate the regenerating ability of HPWA-SBA-15 in the desulfurization, ^{31}P NMR spectra of HPWA-SBA-15 and HPWA-SBA-15 after regeneration are obtained (Fig. 8). HPWA-SBA-15 sample shows two typical resonances at $\delta_{\text{p}} - 14.68$ and $\delta_{\text{p}} - 12.19$, but HPWA shows a single resonance at $\delta_{\text{p}} - 14.98$ [14]. The similar result has been observed for polyoxometalates supported on silica and mobilized $\text{PW}_{12}\text{O}_{40}^{3-}$ on FSM-16 [15]. The two different circumstances for the $\text{PW}_{12}\text{O}_{40}^{3-}$ anions result from the internal and external surfaces of SBA-15 [16].

After regeneration, the sulfur compounds and solvent on HPWA-SBA-15 were removed. Compared with the ^{31}P NMR spectra of HPWA-SBA-15, few changes can be seen in the ^{31}P NMR spectra of the regenerated HPWA-SBA-15, except for the unobvious broadness of the peaks. Therefore the obvious decomposition of HPWA-SBA-15 can be ruled out.

The reusing ability of HPWA-SBA-15 in the desulfurization was also studied (Fig. 8), it can be seen that HPWA-SBA-15 has good reusing ability, and the desulfurization of HPWA-SBA-15 after regeneration is a little lower than fresh HPWA-SBA-15. On one side, direct synthesis method may effectively reduce the loss of HPWA [17]. On the other side, not strong chemical action exists between sulfone and HPWA through hydrogen bond, and this chemical action is broken at 513 K , at this temperature HPWA and the molecular sieve are both stable, therefore the HPWA-SBA-15 may easily restore the catalytic activity.

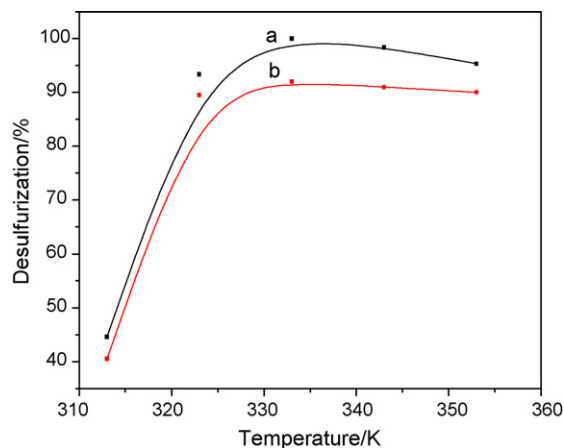


Fig. 8. Desulfurization over HPWA-SBA-15 (a), and HPWA-SBA-15 after regeneration (b).

4. Conclusions

- (1) HPWA-SBA-15 has the typical Keggin structure of HPWA, uniform mesopores and crystal structure of SBA-15.
- (2) HPWA-SBA-15 realizes the catalyzed oxidation–adsorption desulfurization of DBT with high desulfurization rate under the mild operating conditions, beneficial to the energy saving and environmental protection.
- (3) As catalyst and sorbent, HPWA-SBA-15 plays an important role in the desulfurization, the intermediate of $[\text{O}-\text{O}]$ structure is found in the desulfurization.
- (4) HPWA-SBA-15 has good stability and regenerability in the desulfurization of DBT.

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