

A novel [Bmim]PW/HMS catalyst with high catalytic performance for the oxidative desulfurization process

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Abstract—To effectively reduce the sulfur content in model fuel, [Bmim]PW/HMS catalyst was synthesized through impregnating the hexagonal mesoporous silica (HMS) support by phosphotungstic acid (HPW) and ionic liquid [Bmim]HSO₄. Physical structure characterizations of the catalysts showed that HMS retained mesoporous structure, and [Bmim]PW was well dispersed on the support of HMS. The catalytic activity of the [Bmim]PW/HMS was evaluated in the oxidative desulfurization process, and the optimal reaction conditions including loading of the catalysts, reaction temperature, catalyst amount, O/S (H₂O₂/sulfur) molar ratio and agitation speed were investigated. Under the optimal reaction conditions, the conversion of benzothiophene (BT), dibenzothiophene (DBT) and 4, 6-dimethyldibenzothiophene (4, 6-DMDBT) could reach 79%, 98%, 88%, respectively.

Key words: [Bmim]PW/HMS, Catalytic Oxidation Desulfurization, Dibenzothiophene

INTRODUCTION

In recent years, ultra-deep desulfurization from diesel fuel is attracting more and more attention due to the stringent regulations of sulfur level in many countries. At present, many desulfurization methods have been developed to reduce the sulfur compounds to an ultra-low level from diesel fuel. Oxidative desulfurization (ODS) is one of the alternative methods for ultra-deep desulfurization. In the ODS process, the sulfur compounds, such as benzothiophenes (BT), dibenzothiophene (DBT) and 4, 6-dimethyldibenzothiophene (4, 6-DMDBT), are oxidized to their corresponding sulfones, which can be easily separated from the diesel with extractant, and thus ultra-deep desulfurization of diesel fuel can be achieved.

Ionic liquid (IL) has been applied as phase transfer catalyst in ODS process. The sulfur compounds were extracted into IL phase, and then oxidized to their corresponding sulfones by oxidant [1,2]. IL-PA (HPA represents heteropolyacid) was also applied as ODS homogeneous catalyst in ODS process. Zhu et al. [3] reported four IL-PA catalysts including [MIMPS]₃PW₁₂O₄₀, [Bmim]₃PW₁₂O₄₀, [Bmim]₃PMo₁₂O₄₀ and [Bmim]₄SiW₁₂O₄₀ with high catalytic activity and selectivity to sulfur oxidation. With the presence of these homogeneous catalysts, the sulfur was first extracted into the IL phase and then catalyzed by the PW₁₂O₄₀ species in the presence of excess H₂O₂. However, although homogeneous IL-PA exhibited excellent catalytic effect for ODS process, it was difficult to be separated from the diesel fuel. The recovery rate of these catalysts was very low, which was the main obstacle for their industrial application.

To promote the recovery rate of the ODS catalyst, many researchers have developed heterogeneous catalysts by impregnating or incorporating the active HPA species into mesoporous materials. A series of heterogeneous catalysts including HPW/SBA-15 (HPW

represent phosphotungstic acid), HPMo/SBA-15 (HPMo represent phosphomolybdic acid) and HPW/SiO₂ etc., have been synthesized and applied in ODS process [4-6]. However, the molar ratio of H₂O₂/sulfur (O/S) in the ODS process of these catalysts is very high due to the slow kinetic process of sulfur oxidation. Li et al. [7] reported HPW/HMS (HMS represents hexagonal mesoporous silica) catalyst exhibited the optimal desulfurization effect with O/S=8. Yan et al. [8] found desulfurization rate of DBT on HPW/TiO₂ catalyst was close to 100% with O/S=12. These O/S values are much higher than the stoichiometric value of O/S=2.

In this study, we are synthesizing a heterogeneous catalyst with low O/S molar ratio in ODS process by introducing [Bmim] IL into HPW/HMS. It is supposed that [Bmim] IL can increase the sulfur concentration on surface of catalyst, and thus reducing the consumption of H₂O₂ in ODS process by a synthetic effect of PW and IL. The ODS optimal reaction conditions of the obtained [Bmim]PW/HMS catalyst, including temperature, O/S molar ratio, catalyst loading, amount of catalyst and agitation speed are investigated.

EXPERIMENTAL

1. Catalyst Preparation

The HMS support was synthesized by the process reported in the literature [9], which used a primary amine surfactant 1-dodecylamine (DDA, Tianjin GuangFu Fine Chemical Industry Research Institute, AR) as structure directing agent. In a typical synthesis procedure, under vigorous stirring, 1.25 g DDA was dissolved into the mixture solution of 14.3 g water and 7.6 g ethanol. Subsequently, 5.2 g tetraethyl orthosilicate (TEOS, Guangdong Shantou Xilong Chemical Product Company, AR) was added into the obtained mixture. The final mixture was aged for 18 h with continuous stirring at room temperature. The solid product was filtered, washed by ethanol, dried at 100 °C, and calcined at 600 °C for 4 h in air.

[Bmim]PW/HMS catalyst was prepared by the following pro-

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cess similar to the literature [10,11]. About 2 g HMS was added into 30 ml deionized water and spread out uniformly. A given amount of [Bmim]HSO₄ (Shanghai DiBo Chemicals Technologies Co. Ltd.) dissolved in 20 ml of water was dropped into HMS emulsion with stirring for 1 h. A certain amount of HPW (Tianjin GuangFu Fine Chemical Industry Research Institute, AR) was dissolved in 30 ml of deionized water, and then added to the above solution drop by drop with continuous stirring for 2 h. At last, the solid product was centrifuged, washed 2 or 3 times with deionized water and dried overnight at 100 °C. With the weight content of [Bmim]PW at 10 wt%, 20 wt%, 30 wt%, respectively, the samples were noted as 10 [Bmim]PW/HMS, 20[Bmim]PW/HMS, 30[Bmim]PW/HMS. HPW/HMS (the dosage of HPW was equal to 20[Bmim]PW/HMS) or [Bmim]PW was synthesized by similar procedure without the addition of [Bmim]HSO₄ or HMS.

2. Characterizations

The powder X-ray diffraction (XRD) was carried out on a Bruker advanced D8 X-ray diffractometer using Cu-K α irradiation ($\lambda=1.5406$ Å) as source at 40 kV and 40 mA. The samples were recorded from 1° to 10° (2θ) with a step scan of 0.01°/s for small-angle scan, and from 15° to 60° (2θ) with a step scan of 0.05°/s for wide-angle scan. The Fourier transform infrared spectra (FT-IR) were collected on the Nicolet AVATAR 360 FT-IR. Brunauer-Emmett-Teller (BET) surface area analysis was performed from the nitrogen adsorption isotherms at 77 K using a Micromeritics Model ASAP 2020 instrument. All samples were degassed at 100 °C under vacuum for 6 h. Thermogravimetric analysis (TGA) was performed on a Netzsch STA-449F3 (Jupiter OR, Germany) analyzer with heating rate of 10 °C/min under oxygen atmosphere. The gas flow through the system was 20 ml/min. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was obtained on the thermo scientific TCAP 6000 SERICS ICP spectrometer.

3. Catalytic Performance Testing

Model oils with content of 500 ppm sulfur compound (BT, DBT, 4, 6-DMDBT) were prepared by dissolving these compounds in n-octane. The catalytic performance testing was operated in a typical catalytic oxidation desulfurization method as follows: 10 ml model oil was added into a three-necked bottle, then a certain amount of H₂O₂ and [Bmim]PW/HMS catalyst was added. The reactor was fixed in an oil bath at different temperatures with stirring and reflux. Then the clarified oil was collected and sulfur content was analyzed by Microcoulometric Detector (WK-2D) after standing for a while. The solid catalyst was recovered by filtrated and washed with methanol for the next recycle.

RESULTS AND DISCUSSION

1. The Characterization of Samples

Fig. 1A compares the spectra of [Bmim]HSO₄, HPW and [Bmim]PW, respectively. The spectrum of HPW presents four main characteristic peaks at 1,080 cm⁻¹ (P-O), 980 cm⁻¹ (W=O), 890 cm⁻¹ (W-O₆-W) and 800 cm⁻¹ (W-O_c-W), respectively, representing the Keggin structure of HPW [7,8]. The peaks of [Bmim] IL at 2,960 cm⁻¹, 2,920 cm⁻¹ and 2,850 cm⁻¹ are attributed to the asymmetrical stretching vibration of H-C-H in -CH₂-CH₂-CH₂- and the symmetrical stretching vibration of terminal methyl in the structure of [Bmim] [12,13]. To prove that HPW is still present in [Bmim]PW/HMS samples

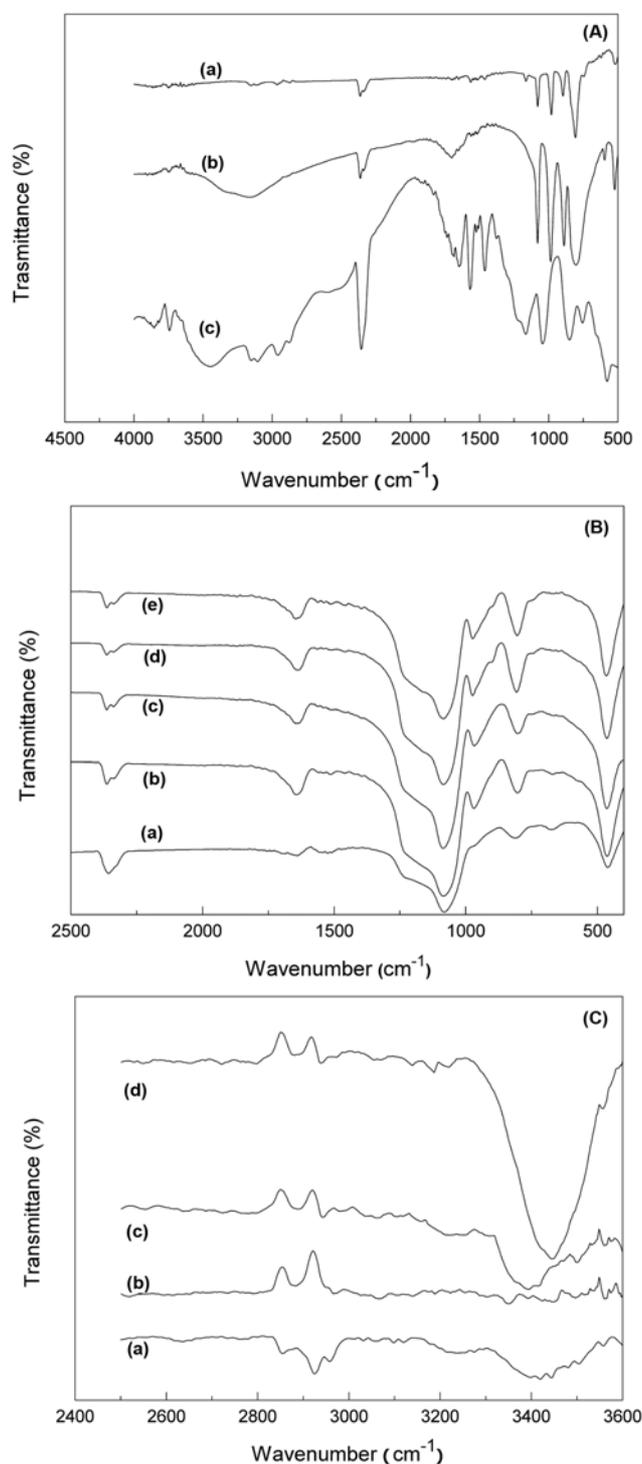


Fig. 1. (A) FT-IR spectra of (a) [Bmim]PW, (b) HPW, (c) [Bmim]HSO₄. (B) FT-IR spectra of (a) HMS, (b) HPW/HMS, (c) 10[Bmim]PW/HMS, (d) 20[Bmim]PW/HMS and (e) 30 [Bmim]PW/HMS in the range of 400 cm⁻¹ to 2,500 cm⁻¹. (C) FT-IR spectra of (a) 20[Bmim]PW/HMS, (b) HMS, (c) HPW, (d) HPW/HMS in the range of 2,500 cm⁻¹ to 3,600 cm⁻¹.

after [Bmim]PW loading on HMS support, Fig. 1B displays the FTIR results of HMS, HPW/HMS and [Bmim]PW/HMS with different [Bmim]PW loading in the range of 400 cm⁻¹ to 2,500 cm⁻¹.

The HMS sample presents three peaks at $1,080\text{ cm}^{-1}$, 970 cm^{-1} and 800 cm^{-1} , assigned with the asymmetric stretching vibrations of Si-O-Si bridges, vibrations of Si-OH and symmetric stretching vibrations of Si-O-Si bridges, respectively. Compared with HMS, HPW/HMS and [Bmim]PW/HMS catalysts, both display new absorption peaks at 890 cm^{-1} , and stronger peaks at $1,080\text{ cm}^{-1}$, 980 cm^{-1} and 800 cm^{-1} . These results prove that HPW with Keggin structure is presented in the [Bmim]PW/HMS samples. Fig. 1C compares the spectra of [Bmim]PW/HMS, HMS, HPW and HPW/HMS in the range of $2,500\text{ cm}^{-1}$ to $3,600\text{ cm}^{-1}$ to prove the presence of [Bmim] IL. The peaks of asymmetrical stretching vibration of H-C-H and the symmetrical stretching vibration of terminal methyl are only retained in the spectrum of the [Bmim]PW/HMS, which shows that [Bmim] can be effectively supported on the surface of HMS. The information obtained from Fig. 1 reveals that HPW and [Bmim] have been successfully supported on the surface of HMS.

Fig. 2 shows the N_2 adsorption-desorption curves of HMS and 20[Bmim]PW/HMS samples to identify the mesoporous structure of 20[Bmim]PW/HMS catalyst. Typical IV isotherms (according to IUPAC classification) and sharp increase at higher relative pressures ($P/P_0=0.8-1.0$) are observed in these two samples, indicating the mesoporous feature of them [14,15]. These results demonstrate that HMS support retains its mesoporous structure regardless of the loading of [Bmim]PW. The surface area is an important factor which will affect the catalytic performance. BET results of the structural properties of these samples used in the ODS reaction are listed in Table 1. The loading of [Bmim]PW on the surface of HMS reduces

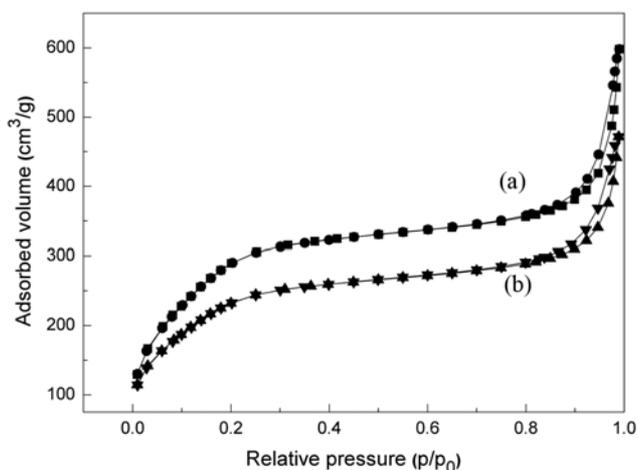


Fig. 2. Nitrogen physisorption results of representative samples: (a) HMS, (b) 20[Bmim]PW/HMS.

its surface area. The same decreased trend is also observed for the pore volume with the increment of [Bmim]PW content on HMS support. However, the content of [Bmim]PW hardly affects the pore size of these samples. To further understand the influence of [Bmim]PW species on the surface area and pore volume of HMS support, we tested the micropore surface area and micropore volume by the t-plot method, and calculated the external surface area and mesoporous surface area. The results are listed in Table 1. The micropore

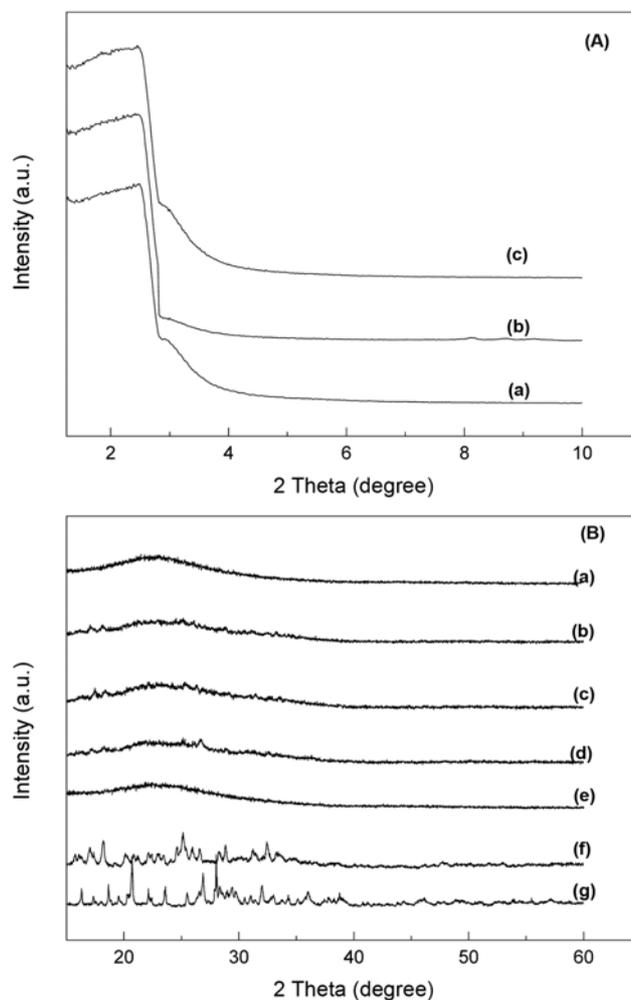


Fig. 3. (A) Small angle XRD patterns of (a) HMS, (b) 20[Bmim]PW/HMS, (c) HPW/HMS. (B) Wide angle XRD patterns of (a) HMS, (b) 10[Bmim]PW/HMS, (c) 20[Bmim]PW/HMS, (d) 30[Bmim]PW/HMS, (e) HPW/HMS, (f) [Bmim]PW and (g) HPW.

Table 1. Physical properties of various samples in DBT oxidation

Code	HMS	10[Bmim]PW/HMS	20[Bmim]PW/HMS	30[Bmim]PW/HMS	20[Bmim]PW/HMS _{spent}
S_{BET} (m^2/g)	1021	813	756	592	796
Pore volume ^a (cm^3/g)	0.56	0.47	0.42	0.35	0.45
Pore size ^b (nm)	2.2	2.3	2.2	2.3	2.2
$S_{External}^c$ (m^2/g)	917	718	684	520	722
S_{Micro}^c (m^2/g)	104	95	72	72	74
Pore volume _{Micro} ^c (cm^3/g)	0.047	0.041	0.033	0.033	0.034
Pore volume _{Meso} (cm^3/g)	0.513	0.426	0.387	0.317	0.416

surface area decreased from 104 m²/g to 72 m²/g, and external surface area decreased from 917 m²/g to 520 m²/g with [Bmim]PW content increasing to 30 wt%. These results indicate that both micropore space and mesopore space are occupied by loading of [Bmim]PW species. However, about 89% of the total BET surface area of HMS is contributed by the external surface area due to its mesoporous structure; therefore, the loading of [Bmim]PW mainly occupies the space of mesopore of HMS support. The same conclusion can also be obtained by analyzing the micropore volume and mesopore volume.

Fig. 3A shows the small angle XRD patterns of HMS, 20[Bmim]PW/HMS and PW/HMS, respectively. These three samples all display single low angle peaks at $2\theta=2.4^\circ$, assigned with the (1 0 0) diffraction of the HMS framework [16,17]. This result shows that the samples retain the uniform mesoporous structure of HMS after the loading of [Bmim]PW, being consistent with the N₂ adsorption-desorption analysis. Fig. 3B exhibits the wide angle XRD pattern of all samples. For all the supported [Bmim]PW/HMS catalysts, broad peaks centered at $2\theta=22.5^\circ$ are originated from the amorphous nature of HMS pore wall. The characteristic peaks of HPW are hardly observed in the samples of HPW/HMS and [Bmim]PW/HMS with [Bmim]PW content no more than 30 wt%, implying that high dispersion of HPW can be achieved in these catalysts [18].

2. The Catalytic Performance of Samples

The effect of catalyst loading on its catalytic performance is shown in Fig. 4. The ODS conversions of 10[Bmim]PW/HMS, 20[Bmim]PW/HMS and 30 [Bmim]PW/HMS catalyst are 95.9%, 98.3% and 94.4%, respectively. 20[Bmim]PW/HMS shows the highest catalytic activity for ODS process among the three samples, consistent with the literature [7]. These phenomena may be attributed to increment of the high dispersed active sites (PW) with HPW content increment. The decrease of catalytic activity with PW content from 20 wt% to 30 wt% may be assigned to the decrease of the surface area of the HMS support [19].

To investigate the effect of O/S molar ratio on the conversion of DBT, ODS process is carried out with different O/S molar ratio. As shown in Fig. 5(a), the removal rate of DBT increases with the

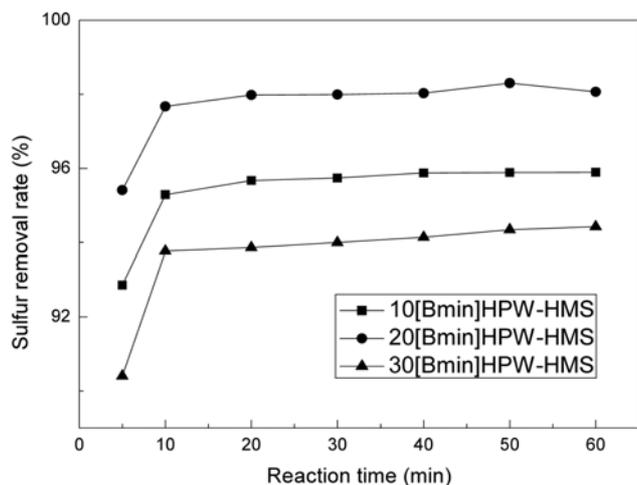


Fig. 4. ODS conversion of [Bmim]PW/HMS catalysts with different loadings; Temperature=60 °C, O/S=3, catalyst dosage=0.06 g/10 ml, rpm=600 r/min.

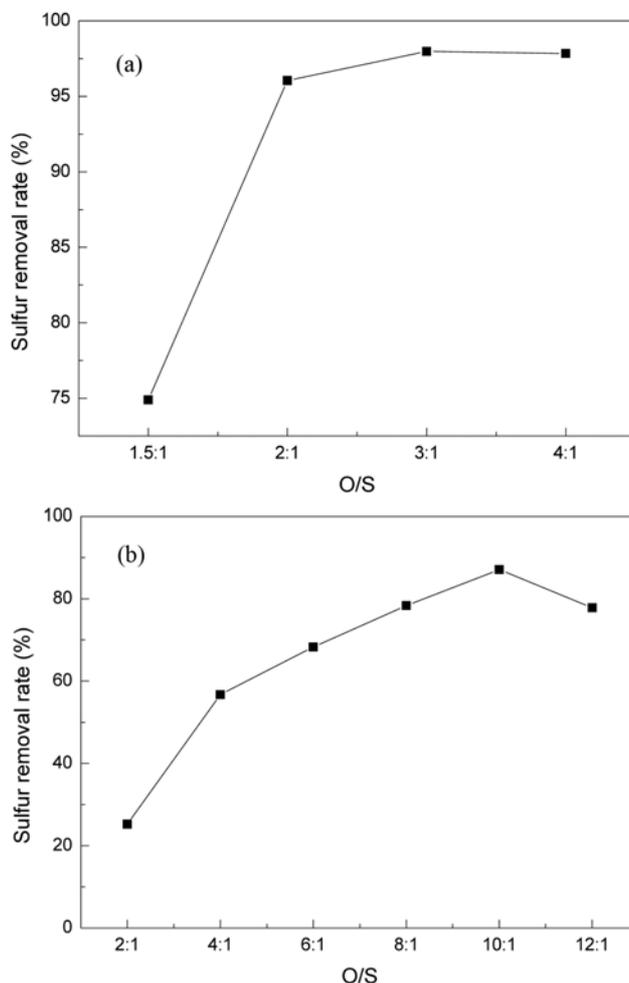


Fig. 5. The effect of O/S molar ratio in the oxidation of DBT of (a) 20[Bmim]PW/HMS and (b) HPW/HMS catalysts: Temperature=60 °C, reaction time=20 min, catalyst amount=0.06 g/10 ml, rpm=600 r/min.

increment of O/S. The sulfur removal tends to balance when the O/S molar ratio reaches 3. This O/S value is only 1.5 time of the stoichiometric value (O/S=2), close to the homogeneous catalyst reported in the literature [8,21]. For most heterogeneous catalysts, the O/S value is in the range of 8-12 to obtain the optimal desulfurization effect [7,8]. The lower O/S value of 20[Bmim]PW/HMS catalyst may be attributed to higher utilization of hydrogen peroxide with the presence of [Bmim] in the catalyst. In the ODS process, the reaction system consists of a three-phase system (liquid-solid-liquid, L-S-L), including a model diesel phase, a water phase (30% hydrogen peroxide) and a solid catalyst phase. When these three phases are mixed, DBT present in the diesel phase is easily extracted to the interface between diesel phase and solid catalyst phase due to the polarity of [Bmim] to diesel fuel. Therefore, on the interface of L-S-L system, the concentration of DBT is very high due to the presence of [Bmim], and thus the O/S value can be reduced in ODS process by promoting kinetic reaction rate of DBT oxidation. To demonstrate the effect of [Bmim] on the O/S value, we compared the O/S value of HPW/HMS catalyst with that of 20[Bmim]PW/HMS under the same reaction condition. As shown in Fig. 5(b), the ODS conversion of HPW/HMS exhibits the highest

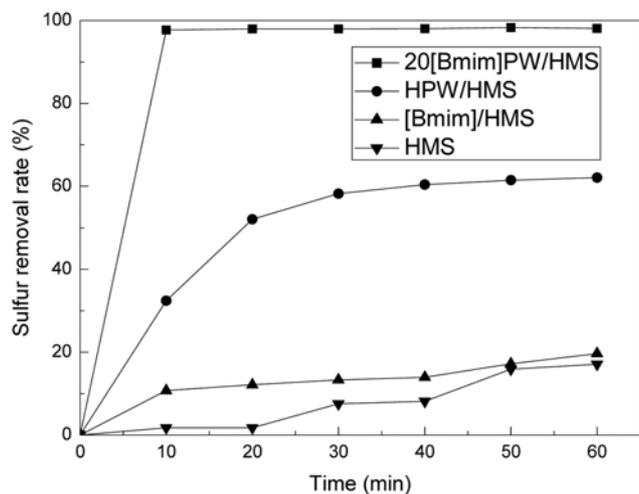


Fig. 6. ODS conversion of 20[Bmim]PW/HMS, HPW/HMS, [Bmim]/HMS and HMS, respectively: Temperature=60 °C, O/S=3, catalyst amount=0.06 g/10 ml, rpm=600 r/min.

ODS conversion when the O/S value is 10. The O/S value of HPW/HMS is much higher than that of 20[Bmim]PW/HMS catalyst, indicating that the introduction of [Bmim] into HPW/HMS can effectively reduce the O/S value used in ODS process.

To further demonstrate the effect of [Bmim] in ODS process, the DBT conversions of the HMS, [Bmim]/HMS, HPW/HMS and 20[Bmim]PW/HMS catalysts were investigated under the same reaction conditions. As shown in Fig. 6, the ODS conversions of DBT on these catalysts increase in the following order of HMS < [Bmim]/HMS < HPW/HMS < 20[Bmim]PW/HMS. This result shows that the individual extracting effect of [Bmim] in ODS process is very low, because the conversion of DBT on [Bmim]/HMS is only 20%. However, the ODS conversion of 20[Bmim]PW/HMS catalyst reaches up to 98.3%, much higher than the 56.7% of HPW/HMS catalyst, indicating that there may be a synergistic effect of [Bmim] and HPW active sites in the ODS process, as described above.

Fig. 7(a) illustrates the effect of catalyst amount in ODS process on the sulfur removal. As shown in Fig. 7(a), catalyst amount has a significant influence on sulfur removal. The ODS conversion increases from 80.5% to 97.98% with catalyst content increasing from 20 mg/10 ml to 60 mg/10 ml. However, the ODS conversion tends to a balance when catalyst amount is above 80 mg/10 ml. Therefore, the optimal amount of 20[Bmim]PW/HMS catalyst used in the ODS system is 60 mg/10 ml. Fig. 7(b) shows the effect of agitation speed (rpm) on sulfur removal. There is a steep increase of the sulfur removal with agitation speed increasing from 400 rpm to 600 rpm. When agitation speed is 600 rpm, the removal rate reaches up to 96% and then tends to a balance. When agitation speed is low, the solid catalyst and model oil might not form small and uniform emulsion droplets, thereby leading to mass transfer resistance [22]. In the catalytic oxidation reaction, temperature is the most important factor, because it can affect the kinetic constant of the ODS reaction. The effect of reaction temperature is investigated and the results are shown in Fig. 7(c). The information obtained from Fig. 7(c) shows that the ODS conversion increases with the temperature increasing from 40 °C to 70 °C.

Fig. 8 shows the ODS conversions of different sulfur substrates

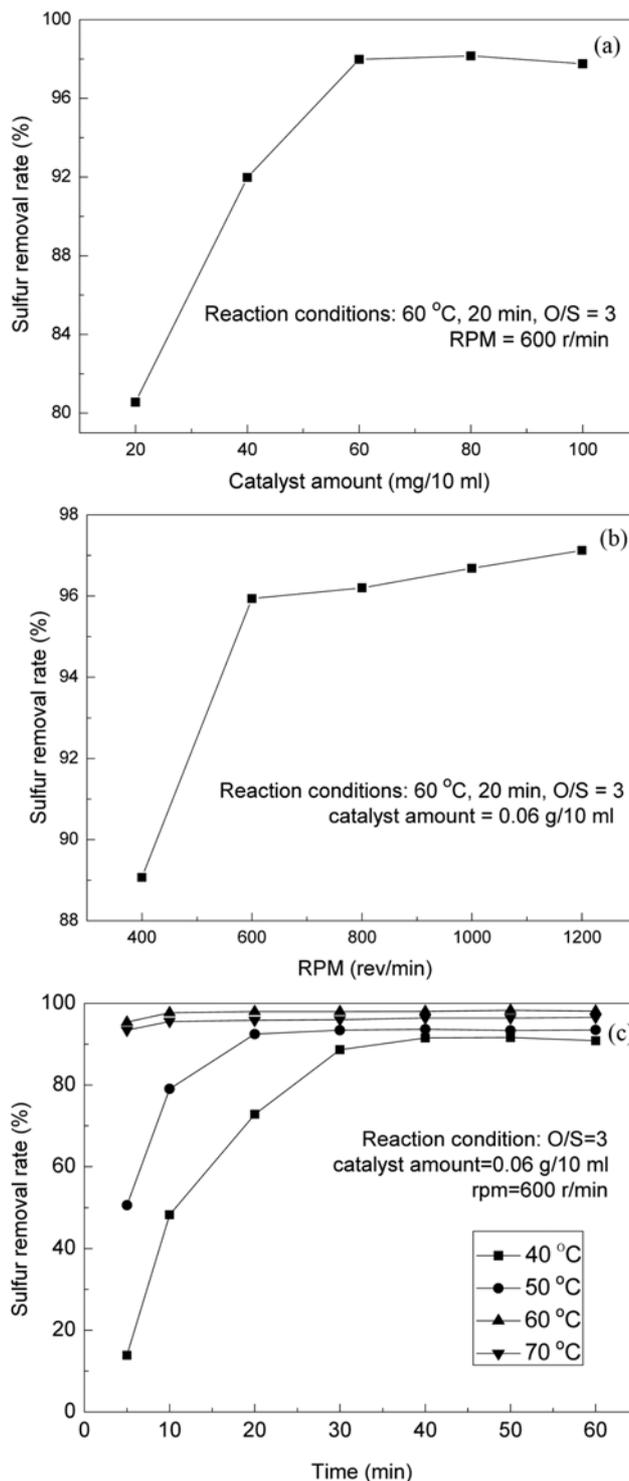


Fig. 7. The effect of agitation speed (a), catalyst amount (b) and reaction temperature (c) on the ODS conversion of 20[Bmim]PW/HMS.

in model oil. As shown, the removal rates of three representative thiophenes under the same reaction conditions decrease in the order of DBT > 4, 6-DMDBT > BT. Similar order was also observed in the ODS process based on liquids-H₂O₂ [3] and [Bmim]₃PMo₁₂O₄₀/SiO₂-H₂O₂ [11]. The electron densities of sulfur atoms on these sulfur substrates increase as the following order of BT (5.739) < DBT (5.758)

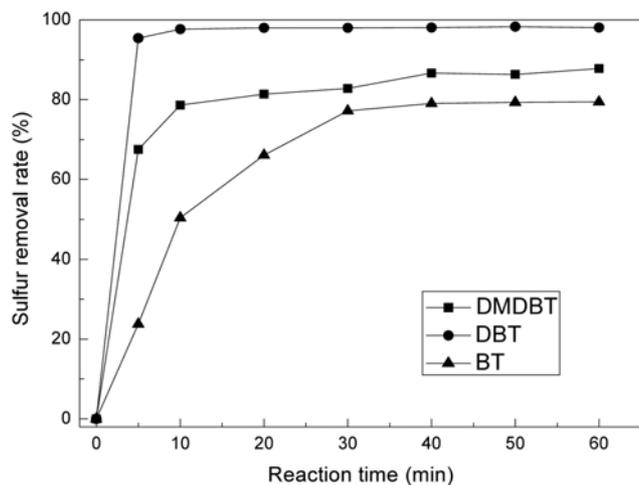


Fig. 8. The ODS conversion of different substrate with 20[Bmim]PW/HMS as catalyst: Temperature=60 °C, O/S=3, catalyst amount=0.06 g/10 ml, rpm=600 r/min.

<4, 6-DMDBT (5.760), and the steric hindrances increase in the order of BT<DBT<4, 6-DMDBT [3]. The low removal rate of BT may be related to its low electron density, and low removal of 4, 6-DMDBT may be assigned to its big steric hindrance as an obstacle for the approach of the sulfur atom to the catalytic active species.

It is necessary to investigate the recycle rate of the heterogeneous catalyst of 20[Bmim]PW/HMS. At the end of the reaction, the catalyst was recovered by simple filtration, washed with methanol for several times and dried at 100 °C to subject to next ODS process. The ODS conversions of the fresh and spent catalyst after 1-3 recycles are shown in Table 2. The conversions of BT, DBT and 4, 6-DMDBT all decrease after three recycles, and the decreasing speeds of three representative sulfur compounds are in the order of BT>4, 6-DMDBT>DBT. The conversion of BT, DBT and 4, 6-DMDBT decreases about 11.0%, 3.2% and 10.7% after three recycles, respectively. The spent catalyst of 20[Bmim]PW/HMS after recycles was characterized by FTIR spectra and XRD, and the results are shown in Fig. 9. The spent catalyst still exhibits the characteristic peaks of HPW at 1,080 cm⁻¹ and 800 cm⁻¹, and the characteristic peaks of [Bmim] at 2,960 cm⁻¹, 2,920 cm⁻¹ and 2,850 cm⁻¹ from FTIR. These results indicate that both HPW and ionic liquid species retain their physical structure after the ODS process. XRD patterns of the fresh and spent 20[Bmim]PW/HMS catalyst both display broad peaks centered at 2θ=22.5°, which originates from the amorphous nature

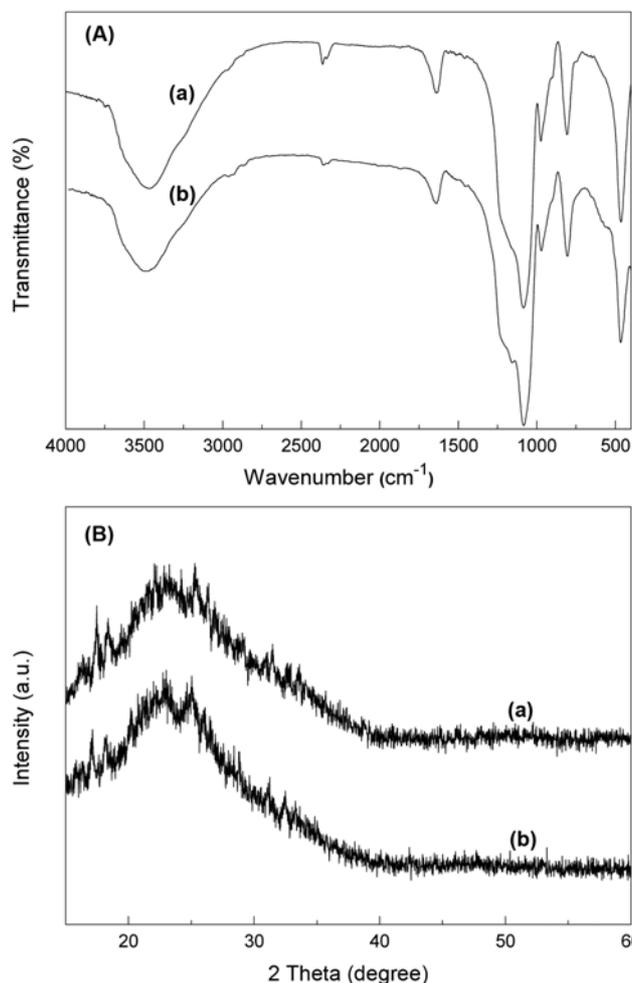


Fig. 9. (A) FTIR spectra and (B) Wide angle XRD patterns of (a) fresh 20[Bmim]PW/HMS and (b) spent 20[Bmim]PW/HMS.

of pore wall of HMS support. The BET results of the structural properties of spent catalyst are listed in Table 1. Surface area, pore volume and pore size of the spent 20[Bmim]PW/HMS catalyst are very close to those of the fresh catalyst. XRD and BET results both demonstrate that the ODS process has little influence on the HMS support. ICP-AES experiment was carried out to determine the W content in the 20[Bmim]PW/HMS catalyst after three cycles and calculate the corresponding content of [Bmim]PW. The results are shown in Table 2. The content of [Bmim]PW decreased from 17.1 wt% to

Table 2. DBT conversion in oxidation over fresh and repeated [Bmim]PW/HMS

Samples	Sulfur removal (%) ^a			W content (wt%) ^b	PW content (wt%) ^c	[Bmim]PW content (wt%) ^c
	BT	DBT	DMDBT			
Fresh catalyst	79.4	98.3	87.8	11.3	17.3	19.3
Recycle 1	75.3	97.9	84.1	10.0	15.3	17.1
Recycle 2	71.9	96.2	79.0	9.1	13.9	15.5
Recycle 3	68.4	95.1	77.1	8.5	13.0	14.5

^aReaction conditions: O/S molar ratio=3, catalytic amount=0.06 g/10 ml, temperature=60 °C, reaction time=60 min

^bDetermined by ICP-AES experiments

^cCalculated from the molecular weight of PW₁₂O₄₀ and [Bmim]

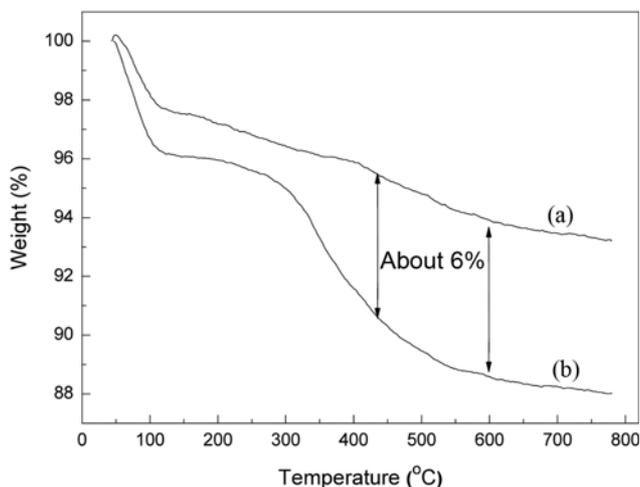


Fig. 10. TGA analysis of spent 20[Bmim]PW/HMS catalysts after ODS process: (a) with methanol washing, (b) without methanol washing.

14.5 wt% after three recycles, demonstrating about 14.7% [Bmim]PW active species are lost due to the leaching in ODS process or the dissolution in the methanol washing process. These results are assigned to the decrease of the ODS conversion of these three sulfur compounds in repetition test.

As the HMS support might suffer from the deposit of sulfones in ODS process, it is necessary to determine that whether the methanol washing process can remove the deposited sulfones from HMS support. The spent 20[Bmim]PW/HMS after ODS process was characterized by TGA. Fig. 10 compares the TGA results of two different spent catalysts with or without methanol washing. The spent catalyst without methanol treatment emerges with about 6% mass loss in the temperature range of 420–600 °C compared with methanol washing catalyst. That mass loss is attributed to the decomposition of sulfones [23,24], and value of 6% is very close to the theoretical sulfone content of 6.8%. This result shows that sulfones are deposited on the surface of HMS support in ODS process, and can be effectively removed by methanol washing before ODS repetition test.

CONCLUSIONS

[Bmim]PW/HMS catalyst was successfully synthesized by an impregnating method. The obtained catalyst displays typical mesoporous structure with the presence of [Bmim] and PW species. The introduction of [Bmim] into HPW/HMS reduced the O/S value in ODS process, due to the synthetic effect of [Bmim] and PW active sites. Under the optimal reaction conditions, the ODS conversion of 20[Bmim]PW/HMS catalyst reached up to 98%, and there was no significant catalytic performance decrease after the three recycles, indicating that an ultra-deep desulfurization of diesel fuel can be achieved.

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