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Three-dimensionally Ordered Macroporous Phosphotungstic Acid/SiO_2 for Efficient Catalytic Oxidative Desulfurization

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Abstract: Three-dimensionally ordered (3DOM) macroporous phosphotungstic acid/SiO_2 (HPW/SiO_2) materials were prepared by using colloidal crystal as templates and applied for oxidative desulfurization (ODS) of the model fuel oil. The obtained HPW/SiO_2 materials were characterized through scanning electron microscopy, powder X-ray diffraction, N_2 sorption, and Fourier transform infrared spectroscopy. The results indicated that 3DOM HPW/SiO_2 possessed hierarchical pore architectures which contained ordered macropores and disordered mesopores, with the Keggin type HPW embedded in the framework of pore structure. The removal rate of dibenzothiophene (DBT) could reach 100% under the optimum conditions, moreover. The performance was only slightly decreased for the regenerated catalyst after 7 cycles.

Key words: three-dimensionally ordered macroporous SiO_2; phosphotungstic acid; oxidative desulfurization

1 Introduction

With increasing environmental pollution, the deep desulfurization of fuel oil has attracted more and more attention[1]. To solve the problem, catalytic oxidation of thiophene and its derivatives in fuel oil has been researched as a promising technology. Over the past years, many researchers have made ongoing effort to develop efficient and reusable supported heteropoly acid catalysts, such as mesoporous $H_3PW_{12}O_{40}/TiO_2$[2], mesoporous $H_3PMo_{12}O_{40}/SiO_2$[3], mesoporous silica pillared clay supported HPW[4, 5], well-ordered hexagonal mesoporous HPW/SiO_2[6], MCM-41 supported $(C_{19}H_{42}N)_4H_3(PW_{11}O_{39})$[7] and ionic liquid-modified SBA-15 supported HPW[8]. Since Velev *et al* reported to synthesize porous silica via colloidal crystallization[9], owing to the well-arranged and stable 3DOM structures of the composite, it was widely studied in the field of catalysis[10]. Han DZ *et al* prepared highly ordered 3DOM γ-Al_2O_3 as hydrodesulfurization (HDS) catalyst, and the activity increased from 70% to 98% compared with mesoporous γ-Al_2O_3[11]. Dou J *et al* also found that 3D silica nanowires supported MoO_3 catalyst showed better oxidation desulfurization activity than MoO_3/SBA-15[12]. What we know so far, 3DOM SiO_2 supported HPW used as catalyst for ODS has little been heard yet. Choosing 3DOM SiO_2 as support, there may be possible advantage as follows: as is well known, the high surface area can be good for catalyst to obtain more exposed active sites and enhance the catalytic activity for ODS process[13]. However, pore structure of catalyst, as one of the most influential factors, not merely influenced the surface area of SiO_2 supported HPW catalyst, but also affected the diffusion of the reactant and reaction product molecules (namely thiophenic compounds and sulfones), especially for the liquid-solid reaction. Hence, to explore the influence of porestructure and surface area of supported POM catalysts on ODS process can be a valuable work.

In the present work, we specially designed a series of 3DOM SiO_2 supported HPW catalysts and investigated the feasibility of applying the as prepared catalysts for oxidative desulfurization. Their catalytic performance was explored through the ODS of the model oil. And effects of loading amount of HPW, catalyst dosage, oxidant consumption, and temperature were also studied systematically, which was in relation to the change of the sulfur removal rates. Besides, regeneration performance of the catalysts was tested.

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2 Experimental

2.1 Preparation

Monodispersed polystyrene spheres (PS) were adopted as a macroporous template, synthesized by emulsion polymerization technique[14]. The catalyst 3DOM macroporous phosphotungstic acid SiO_2 was prepared as follows: 2.833 g of tetraethyl silicate (Aladdin), 0.1495 g of hydrochloric acid (HCl, 36wt%, Aladdin) and 0.44 g of distilled water were dissolved in 2.439 g of ethanol with strong stirring, and then an amount of HPW (Aladdin) was added slowly and magnetically stirred for another 0.5 h to form transparent sol. Dried PS latex spheres were added to a Buchner funnel with back pressure, obtained sol was carefully added by pipetting till the spheres were completely wetted. The infiltration process was repeated 3 times. The inorganic/organic composites were dried for 24 h at 60 ℃ and calcined at 400 ℃ in air for 10 h (at a ramp rate of 1 ℃/min). The catalyst was denoted as 3DOM HPW/SiO_2-x (where x represented the weight percentage of HPW in the catalyst).

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffractometer with Cu source (λ=1.5406 Å) operating at 40 kV, and 50 mA. Scanning electron microscopic (SEM) images were obtained on a Hitachi S-4800 field emission scanning electron microscope. N_2 sorption isotherms was measured with a Micromeritics Tristar II 3020 analyzer at 77 K. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, the pore size distributions were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared spectra (FT-IR) were recorded on a Digilab-FTS60 spectrometer, and the samples were pressed with KBr. The HPW content in solid samples was determined by the results of inductively coupled plasma analysis (ICP, Perkin-Elmer 3300DV).

2.3 Desulfurization of model fuel

All model fuels with sulfur content of 500 mg/L (S) were prepared by dissolving DBT, BT or 4, 6-DMDBT in petroleum ether, respectively. In the typical run, the water bath was heated to the given temperature under stirring at 600 rpm and a certain amount of catalyst was added to a mixture of 10 mL model fuel oil and 10 mL acetonitrile. And then, a specific amount of 30% aqueous H_2O_2 was added into the mixture to start the reaction. The amount of oxidant was expressed as *O/S* mole ratio. The resulting mixture was stirred for 2 h at the reaction temperature and analyzed periodically. After reaction, the catalyst was separated by centrifugation, washed with methanol, dried at 100 ℃, and subjected to the next ODS process. The upper oil was collected and the sulfur content was analyzed by high performance liquid chromatography (HPLC). The HPLC system was LC-20A (Shimadzu, Japan), which consisted of LC-20AT pumps, a SPD 20A ultraviolet detector and a SinoChrom ODS-BP column (4.6 mm×200 mm, 5 μm).

3 Results and discussion

The wide-angle powder XRD patterns of 3DOM HPW/SiO_2 samples with different HPW loadings are presented in Fig.1. The characteristic peaks of amorphous silica were found on wide-angle XRD patterns of all these samples. There were no indication of PWA crystalline phases present on the patterns, which meant that HPW has successfully introduced into SiO_2 framework rather than existing in free solid acid[15]. Calculated with the Scherrer equation, nanocrystalline size of SiO_2 decreased significantly with increasing content of HPW (Table 1), which can be attributed to the import of HPW hindered crystal growth of SiO_2[16]. Fig.2 shows the SEM images of 3DOM HPW/SiO_2-20. The macropores were approximately 340 nm and interconnected by windows pores (Fig.2(a)), the mean diameter were 50 nm and the pore size was much smaller than that of the PS template (480 nm), which is because of the shrinkage of the HPW/SiO_2 composite during calcination. Moreover, Fig.2(b) demonstrates the well-ordered macroporous structure of 3DOM HPW/SiO_2-20 material and the presence of periodicity of orderly structures preserved throughout the sample. In order to further illustrate the inner architectures of the 3DOM HPW/SiO_2, Fig.3(a) exhibits the N_2 adsorption isotherms of 3DOM HPW/SiO_2-20, which displayed

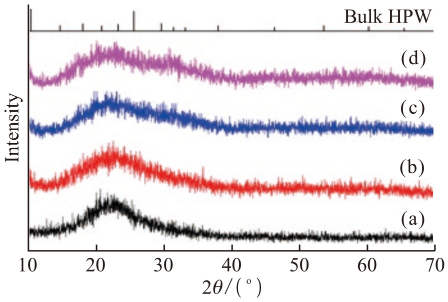

Fig.1 Powder XRD patterns of 3DOM HPW/SiO_2: (a) SiO_2, (b) HPW/SiO_2-10, (c) HPW/SiO_2-20, (d) HPW/SiO_2-30

Table 1 Physico-chemical parameters and total desulfurization efficiency of various samples

Sample	HPW content /wt%	S_{BET} /(m^2/g)	Sulfur removal^b /%
SiO_2	-	230.5	81.6
HPW/SiO_2-10	9.4	256.4	98.2
HPW/SiO_2-20	19.2	288.1	100
HPW/SiO_2-30	29.1	301.5	100
Mesporous HPW/SiO_2^{a}	19.3	398.2	95.6

^{a} Meso-HPW/SiO_2: mesoporous HPW/SiO_2 with 20wt% HPW prepared by the literature method[18]

^{b} The reaction conditions are as follows: T=60℃, O/S=12, catalyst dosage=0.1 g, t=2 h

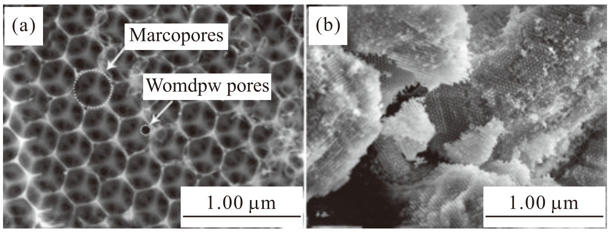

Fig.2 SEM images of macroporous HPW/SiO_2 sample with 20wt% HPW content

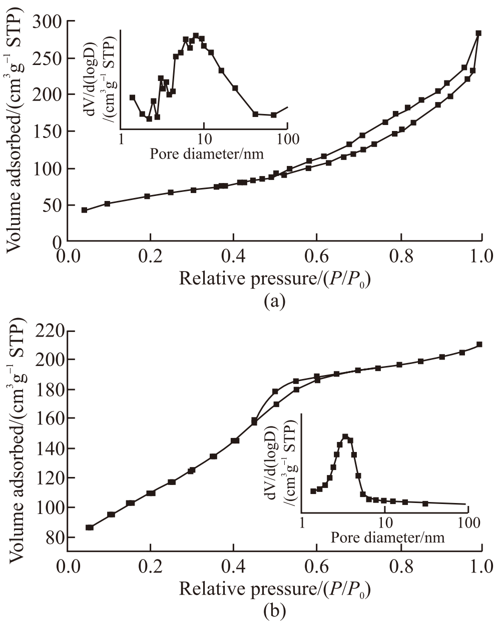

Fig.3 The nitrogen adsorption isotherms and the pore distributions of order 3DOM HPW/SiO_2-20(a) and mesoporous HPW/SiO_2-20(b)

a type of H3 hysteresis loops, meaning that the close-packed agglomeration of these nanoparticles formed the mesoporous structure[14, 17], the sample showed a broad distribution of pore size and the average mesopore size was 8 nm. Table 1 summarizes the specific surface area of 3DOM SiO_2 and 3DOM HPW/SiO_2 samples, which clearly showed that S_{BET} of the composite was increased with HPW dosage firstly, and decreased then, a proper dosage of phosphomolybdic acid could improve the pore structure and increase the specific surface area. However, excess HPW will damage the pore structure of the catalyst and reduce the specific surface area[2, 3]. At the same time, mesoporous HPW/SiO_2 with 20wt% HPW was prepared by the literature method (Fig.3(b))[18].

Fig.4 displays the FT-IR spectra of HPW, 3DOM SiO_2 and 3DOM HPW/SiO_2 samples. Bulk HPW showed several absorption bands as follows: 1 079 cm^{-1} ν_{as}(P-O), 983 cm^{-1} ν_{as}(W=O), 889 cm^{-1} ν_{as}(W-O_b-W), and 805 cm^{-1} ν_{as}(W-O_c-W)[19]. However, silica showed typical framework bands at 805 cm^{-1}, 960 cm^{-1}, and 1 060-1 250 cm^{-1} (Fig.4(a)), which overlapped with the typical absorption bands of Keggin-type HPW, while there was still weak characteristic band of HPW between 983 cm^{-1} and 889 cm^{-1} with the increase of HPW loading, mode shifts at 889 cm^{-1}（W-O_b-W）and 960 cm^{-1}（W=O） were observed compared with HPW and SiO_2, which can be attributed to the effect of chemical interactions between HPW and SiO_2 framework[19].

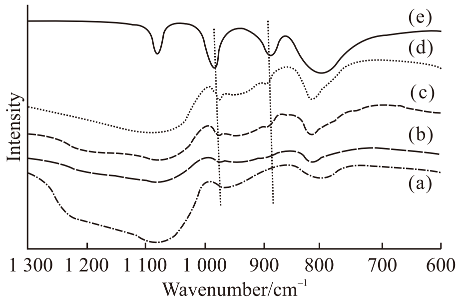

Fig.4 FT-IR spectra of 3DOM HPW/SiO_2: (a) SiO_2, (b) HPW/SiO_2-10, (c) HPW/SiO_2-20, (d) HPW/SiO_2-30, (e) HPW

Initially, the catalytic performance of 3DOM HPW/SiO_2 of different loadings was investigated (Fig.5). The removal rate of DBT was increased with the HPW content. When the HPW loading of 3DOM SiO_2 was 10%, 20%, and 30%, the sulphur removal of DBT was 83.6%, 97.39%, and 100% within 2 h, respectively. This can be attributed to the increase of the active tungsten species in unit volume and specific surface area[3]. However, 20% HPW/SiO_2 and 30% HPW/SiO_2 catalysts demonstrated similar desulfurization ability. This could be ascribed to the diffusion process of DBT, dominating the catalytic reaction[20]. Therefore, 3DOM HPW/SiO_2-20 was chosen in the following investigation.

In the oxidation reaction of DBT process, molar ratio of O/S plays a critical role. It affects not only the efficiency but also the economy of the reaction system. In order to investigate the effect of the consumption of hydrogen peroxide on the oxidation process, Fig.6 shows the catalytic activity of 3DOM HPW/SiO_2-20 under various *O/S* molar ratios at 60 ℃. A pretty clear trend can be drawn out that the removal rates of DBT increased along with the amount of hydrogen peroxide. At the value of stoichiometric molar ratio of *O/S*, the desulfurization rate reached 70.6% after 2 h, which means that there are 29.4% of hydrogen peroxide unreacted because of thermal decomposition[2]. However, with the *O/S* molar ratio up to 20, a significant downswing appeared unexpectedly, which is possibly attributed to the concentration increase of H^+ in the catalytic process, which facilitates the attack of the H^+ on the P=O species and hinders the procedure of P=O species reacting with hydrogen peroxide to form catalytic active intermediate species, such as $\{PO_4[WO(O_2)_2]_4\}$ [21]. Taking the desulfurization efficiency into account, *O/S* molar ratio of 12 was the optimal condition.

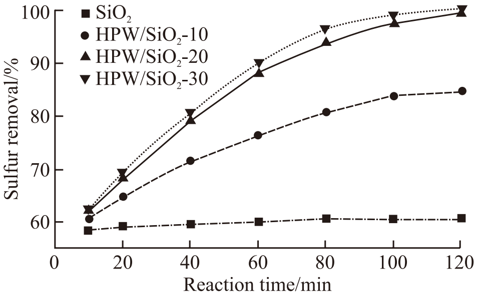

Fig.5 Variation of DBT removal rate with time in oxidation over 3DOM HPW/SiO_2 under different loadings. The reaction conditions are as follows: *T* = 60 ℃, *O/S* = 12, and *m* (dosage) = 0.1 g

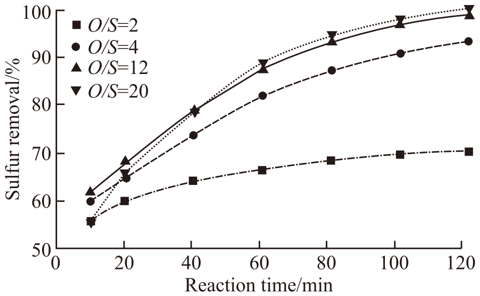

Fig.6 Variation of the DBT removal rate with reaction time in oxidation over HPW/SiO_2-20 at different O/S molar ratio. The reaction conditions are as follows: *T* = 60 ℃, and *m* (dosage) = 0.1 g

The effect of reaction temperature on desulfurization process was investigated and the results are presented in Fig.7. At lower temperature (40, 50, 60, and 70 ℃), desulfurization reaction might be in the kinetic control[22], the reaction rate was promoted and the desulfurization rate of DBT increased significantly with time. At higher temperatures, diffusion was the speed control procedure[23]. Desulfurization rate curves were alike. So, it is favorable for us to conduct the oxidation of DBT over 3DOM HPW/SiO_2-20 at lower and more appropriate temperatures, such as 60 ℃.

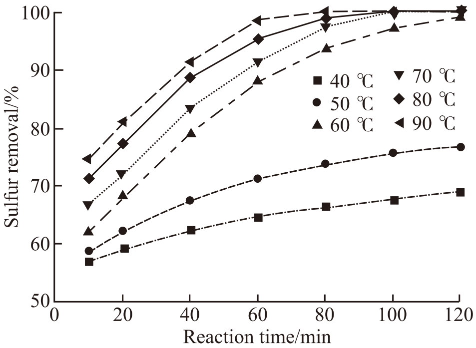

Fig.7 Variation of the DBT removal rate with reaction time in oxidation over 3DOM HPW/SiO_2-20 at different temperatures. The reaction conditions are as follows: *O/S*=12, and *m* (dosage) = 0.1 g

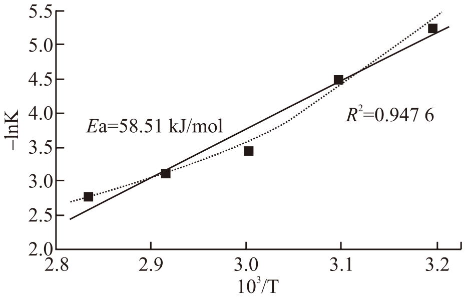

Fig.8 The apparent activation energy for DBT oxidation

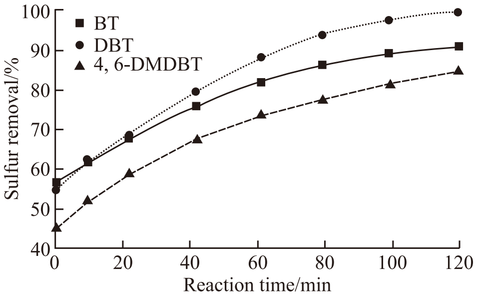

Fig.9 The sulfur removal of different substrates with 3DOM HPW/SiO_2-20. The reaction conditions are as follows: *T* = 60 ℃, *O/S* = 12, and *m* (dosage) = 0.1 g

The reaction kinetics of removal of DBT was further examined. The oxidative reaction of sulfur-containing compound was a pseudo first-order reaction, where the rate is apparently dependent on the concentration of the limiting reactant[24]. The value of ln $[1/1-X_T]$ versus reaction time was obtained at 40, 50, 60, 70, 80, and 90 ℃ (Fig.8), where X_T means the desulfurization rate, and the apparent rate constants are 0.0052, 0.0113, 0.0319, 0.0440, and 0.0628 min^{-1} for reaction, corresponding R^2 values are 0.9948, 0.9976, 0.9819, 0.9916, and 0.9901, respectively. Via apparent rate constants, the apparent activation energy can be calculated from the Arrhenius equation at different temperatures. The Arrhenius plot is shown in Fig.8 giving a linear plot with the R^2 of 0.9476 and the apparent activation energy was calculated to be 58.51 kJ/mol, Fig.9 compares the reactivity of BT, DBT, and 4, 6-DMDBT in the oxidation reaction. After a reaction time of 2 h, the desulfurization efficiencies of DBT, 4, 6-DMDBT and BT were 100%, 84.4%, and 90.6%, respectively. The removal rates decreased in order: DBT > 4, 6-DMDBT > BT, in accordance with the result of polyoxometalate/H_2O_2 system[5]. Electron density and steric hindrance of sulfur compounds are major impacts of the desulfurization reaction. The electron densities of sulfur atoms in BT, DBT, and 4, 6-DMDBT are 5.739, 5.758, and 5.760, respectively[25]. The lowest sulfur removal rate of BT was related to its lowest electron density, the reactivity of 4, 6-DMDBT, however, was lower than that of DBT, which can be attributed to the steric hindrance of two methyl groups in 4, 6-DMDBT molecule.

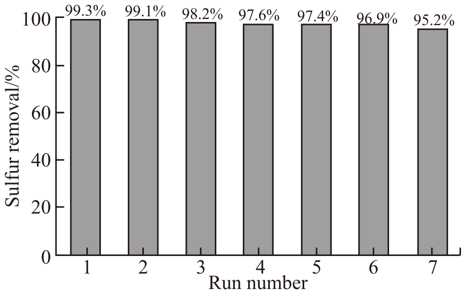

Fig.10 Effect of the recycles on the conversion of DBT with 3DOM HPW/SiO_2-20 as catalyst. The reaction conditions are as follows: T=60 ℃, O/S=12, m (dosage) = 0.1 g, and t = 2 h

According to the previous work of our project group, mesoprous HPW/SiO_2-20 (398.2 m^2/g) has been prepared and investigated by the N_2 adsorption isotherms (Fig.3(b)), and the result was in good agreement with the Ref.[18]. With the similar surface areas, 3DOM HPW/SiO_2-20 catalyst (288.1 m^2/g) exhibited much higher removal rates of DBT (Table 1). Since it was a liquid-phase reaction for ODS, only when the reactants and the products moving into or out of the nanostructured material are included as an integral part of the nanostructure, will the catalytic process be more effective[26]. Moreover, the hierarchical pore structure of catalyst makes the reactant molecules easier to enter the inner pores, and thus more flexible to approach the active sites[27]. This result suggested that rather than the surface area but the pore structure played the crucial role in our catalyst systems. The intrinsic interconnected 3DOM structure may render quicker transport of guest species to catalytic active site[11, 28].

Fig.10 shows the reusing potential of heterogeneous catalyst in desulfurization of DBT. At the end of reaction, 3DOM HPW/SiO_2-20 was recovered by filtration and washed with methanol 3 times, then dried at 100 ℃ overnight. After 7 times of regeneration, the desulfurization rate of 3DOM HPW/SiO_2-20 was slightly lower than that of the fresh catalyst. The catalyst has excellent reusing capability, which can be attributed to the strong chemical interactions between the HPW and SiO_2 framework, preventing HPW from leaching in polar solution. Hence, the 3DOM HPW/SiO_2-20 was easy to restore the catalytic activity.

4 Conclusions

The 3DOM HPW/SiO_2 catalyst has been successfully prepared at room temperature via Polystyrene colloidal crystals method and used as catalyst for ODS process. 3DOM HPW/SiO_2 catalysts possessed a hierarchical porous structure, with Keggin type HPW fixed in the wall of the pore structure. Besides, the 3DOM HPW/SiO_2 catalysts showed excellent desulfurization performance under the optimum conditions, and 100% conversion of the sulfur removal of DBT could be achieved within 2 h .The 3DOM pore structure of catalyst played an important role in the ODS, which has been confirmed by experimental results, and the kinetic studies indicated that the DBT removal presented a pseudo first-order kinetic process, and the apparent activation energy was 58.51 kJ/mol. The order of desulphurization efficiency decreased in line: DBT > 4, 6-DMDBT > BT. Furthermore, the 3DOM HPW/SiO_2 was very active catalyst for refractory sulfides such as DBT. After 7 times of regeneration, the activity loss of desulfurization was negligible.

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