In situ synthesis, characterization, and catalytic performance of tungstophosphoric acid encapsulated into the framework of mesoporous silica pillared clay

Baoshan Lia, Zhenxing Liu, Chunying Han, Wei Ma, Songjie Zhao

Abstract

Mesoporous silica pillared clay (SPC) incorporated with tungstophosphoric acid (HPW) has been synthesized via in situ introducing P and W source in the acidic suspension of the clay interlayer template during the formation of the silica pillared clay. The samples were characterized by XRD, XRF, FT-IR, TG-DTA, N2 adsorption–desorption, and SEM techniques. The results showed that the HPW formed by in situ method has been effectively introduced into the framework of mesoporous silica pillared clay and its Keggin structure remained perfectly after formation of the materials. In addition, samples with similar HPW loadings were also prepared by impregnation method using SPC as the support. HPW in the incorporated samples was better dispersed into the silica pillared clay than in the impregnated samples. The results of catalytic tests indicated that the encapsulated materials demonstrated better catalytic performance than the impregnated samples in oxidative desulfurization (ODS) of dibenzothiophene (DBT).

1. Introduction

Heteropoly acids (HPAs) have attracted much interest owing to their very strong acidity and redox properties. HPAs, especially those having the Keggin structure, for example, H3PW12O40 (HPW), have shown excellent catalytic performance in both heterogeneous and homogeneous catalytic reactions [1–3]. However, the use of pure HPA is limited for their low surface area [4]. Plenty of works have been done to overcome these problems by loading HPA in porous materials, such as alumina, active carbon, titania, and ordered mesoporous silica [5–11]. But the HPA can be easily leached from the supporters in polar reaction media. Thus, many researchers have made efforts in encapsulating HPA into the frameworks and pores of some materials [12–14]. The diameter of Keggin heteropolyanion is about 1 nm. If HPA could be formed like a “ship in a bottle” in a “cage” whose size is slightly larger than the heteropolyanion, the formed HPA anions would not be able to diffuse out of the cages [14]. Recently, Chen et al. successfully in situ encapsulated H3PMo12O40 and Ni in the secondary pore of nanocrystalline HZSM-5 zeolites [15]. The material was prepared by adding molybdenum oxide, phosphoric acid, and nickel nitrate into a slurry mixture of nanocrystalline HZSM-5 zeolite crystals. Shi et al. reported that SiPMo-X and SiPW-X catalysts could be in situ synthesized with Keggin-type HPAs encapsulated into the framework of SBA-15 zeolite [16,17]. All these works had overcome the leaching problems of HPAs from the supporters.

Furthermore, a series of ordered mesoporous clay materials known as silica pillared clay (SPC) materials and metal ion doped SPC materials have been recently prepared [18–28]. These inorganic porous materials with a controlled pore structure have stimulated a great deal of interest for their potential application as selective catalysts, adsorbents, separating agents, and porous matrixes for encapsulation of specific functional molecules [29–31].

In the present work, an in situ synthetic method for incorporating HPW into the framework of mesoporous SPC materials without destruction of the clay gallery structure in order to combine the porous advantages of the SPC and the appropriate acidity of HPW was reported. The advantage of the result materials can overcome the unstable problem and leaching problem of HPW from supporters. The characterization results showed that HPW was in situ encapsulated in the framework of the samples and dispersed homogeneously. The catalytic performance of the result materials was studied by the oxidative desulfurization (ODS) of the model oil with 500 ppm dibenzothiophene (DBT), and the results are interesting.

2. Experimental

2.1. Materials

All solvents and reactants are commercially available and were used without further purification. The natural montmorillonite...
denoted as oven. The final HPW/SPC sample prepared by impregnation was SPC. After impregnation, the wet sample was dried at 110°C for 6 h in a furnace. The samples were desiccated at 115°C for 8 h before measurement, and the saturated vapor pressure (p0) was 0.11 MPa during measurement. The specific surface area (S_{BET}) was estimated by BET equation, and the pore size distribution and the mesopore analysis were obtained from the desorption branch of the isotherm using Barrett–Joyner–Halenda (BJH) method [2,18,32]. The scanning electron microscopy (SEM) micrographs were obtained on a Hitachi S-4700 microscope operated at 30 kV. The FT-IR spectra were obtained in KBr pellets using a Bruker VECTOR 22 spectrometer in the range of 400–4000 cm⁻¹, and all spectra were collected at room temperature with a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. The characterization of the samples

The X-ray fluorescence analysis for the HPW–SPC samples is shown in Table 1. It can be seen that the actual content of HPW were 5.9, 14.8, and 24.7 wt.% for the samples with nominal HPW content of 5, 15 and 25 wt.%, respectively. The molar ratio of P to W is estimated to be about 1:12 in all the samples, suggesting the formation of the Keggin structure of HPW in the mesoporous SPC.

2.2. Preparation

A given amount of MMT was suspended in 120 mL of deionized water in a round bottom flask, to which an ethanol solution of cetyltrimethylammonium bromide (CTAB) was added dropwise and stirred for 1 h, and a gel mixture was gained. Then, the pH of the gel was adjusted by HCl aqueous solution to 1.0. Subsequently, the requisite amount of Na₂WO₄ and Na₂HPO₄ was separately dissolved in water and added simultaneously dropwise into the above mixture to form a white precipitate [17]. After the mixture was stirred for 4 h, tetraethyl orthosilicate (TEOS) was added, followed by stirring for 12 h at room temperature. The molar ratio of clay, CTAB, TEOS, alcohol, and water was 1/0.4/1.6/6.3/258. Then, the mixture was put into an autoclave and heated in a furnace at 110°C for 24 h. Afterward, the autoclave was cooled, and the product was separated by filtration, thoroughly washed with deionized water, and dried in an oven at 110°C. Finally, the dried sample was calcined at 400°C for 6 h in a furnace. The samples were designated as x% HPW–SPC (where x% represents the weight percentage of HPW in the samples) and analyzed by X-ray fluorescence analysis (XRF). For comparison, the SPC sample was also prepared without addition of the P and W source following the same procedure as the HPW–SPC samples.

The impregnated samples with HPW content of 5–25 wt.% were prepared by an incipient wetness impregnation method using SPC as the support. Typically, a volume of 5 ml aqueous HPW solution with different concentration was mixed with 1 g of freshly calcined SPC. After impregnation, the wet sample was dried at 110°C in an oven. The final HPW/SPC sample prepared by impregnation was denoted as x% HPW–SPC–IM (where x% represents the weight percentage of HPW in the samples).

2.3. Catalytic performance in ODS

The model compound DBT was dissolved into n-octane to make a stock solution of model oil with sulfur content of 500 ppm. The reaction was performed in a three-neck flask with a water-bathed jacket. The mixture of 25 mL of the model oil and 0.15 g of catalyst was put into the reactor and heated to 60°C. Then, 0.12 mL of 30% H₂O₂ aqueous solution (molar ratio of H₂O₂/S = 3) was added into the mixture. After continuously stirring for 120 min, the oxidized model oil was extracted three times by acetonitrile using the volume ratio of total solvent to model oil 1:1. The desulfurization process was shown in Scheme 1. The amount of sulfur in the oil was determined by a Model WK-2D microcoulometric integrated analyzer (sulfur detection range from 0.2–5000 ppm, Jiangsu Jiang Fen Electroanalytical Instrument Co.).

2.4. Characterizations

The X-ray diffraction (XRD) was performed on a Rigaku D/Max 2500 VBZ+PC diffractometer using Cu Kα radiation at low-angle range (2θ value 0.5–10°) and at wide-angle range (2θ value 5–70°). The X-ray fluorescence analysis (XRF) was performed on a Philips Magix-601 X-ray fluorescence spectrometer. The samples were pressed into tablets before measurement, and the content of the element was analyzed. The thermogravimetric and differential thermal analysis (TG-DTA) was carried out in air on a HCT-1 thermal analyzer (Hengju Kexue Co.) using a heating rate of 10°C min⁻¹. The nitrogen adsorption isotherms were obtained using a Micromeritics ASAP2020M instrument. The samples were degassed at 115°C for 8 h before measurement, and the saturated vapor pressure (p0) was 0.11 MPa during measurement. The specific surface area (S_{BET}) was estimated by BET equation, and the pore size distribution and the mesopore analysis were obtained from the desorption branch of the isotherm using Barrett–Joyner–Halenda (BJH) method [2,18,32]. The scanning electron microscopy (SEM) micrographs were obtained on a Hitachi S-4700 microscope operated at 30 kV. The FT-IR spectra were obtained in KBr pellets using a Bruker VECTOR 22 spectrometer in the range of 400–4000 cm⁻¹, and all spectra were collected at room temperature with a resolution of 4 cm⁻¹.
The small angle X-ray diffraction patterns of the calcined MMT, SPC, and HPW–SPC samples are shown in Fig. 1. The calcined montmorillonite showed a diffraction peak (001) at 2Θ = 9.2. This corresponds to the montmorillonite layer spacing of 0.96 nm,1 which is consistent with the thickness of the montmorillonite clay sheet [33]. The phenomenon shows that the montmorillonite lamellar structure has collapsed during the calcination at 400 °C. The SPC sample showed a broad characteristic diffraction peak (001) at about 2Θ = 2.0, corresponding to the basal spacing of 4.24 nm. All the HPW–SPC samples also showed a broad characteristic diffraction peak (001) at about 2Θ = 2.0, which indicates that introducing P and W source during the intercalation of CTAB did not destroy the SPC mesoporous lamellar structure [34]. The basal spacing and gallery height of all the samples are summarized in Table 2. The HPW–SPC materials exhibited diffraction peak corresponding to the collapse of the mesoporous gallery structure [35].

The results of the XRF analysis of the HPW–SPC samples.  
Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>P2O5 (wt%)</th>
<th>W2O5 (wt%)</th>
<th>HPW (wt%)</th>
<th>P–W:Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% HPW–SPC</td>
<td>0.14</td>
<td>5.73</td>
<td>5.9</td>
<td>1:12.5:702:0:64.4</td>
</tr>
<tr>
<td>15% HPW–SPC</td>
<td>0.36</td>
<td>14.3</td>
<td>14.8</td>
<td>1:12.1:2004:10.9</td>
</tr>
<tr>
<td>25% HPW–SPC</td>
<td>0.58</td>
<td>23.9</td>
<td>24.7</td>
<td>1:12.6:122.2:12.6</td>
</tr>
</tbody>
</table>

The wide angle XRD patterns of samples: (a) calcined MMT, (b) SPC, (c) 5% HPW–SPC, (d) 15% HPW–SPC, and (e) 25% HPW–SPC.

The wide angle XRD patterns of samples: (a) MMT, (b) SPC, (c) 5% HPW–SPC, (d) 15% HPW–SPC–IM, and (e) pure HPW.

The results indicated that HPW was highly dispersed in the HPW–SPC samples [36,37]. But the characteristic peaks of HPW in the pattern of 15% HPW–SPC–IM sample can be evidently observed, indicating HPW has agglomerated in the HPW–SPC–IM sample. The results indicate that HPW formed by in situ method is much more highly dispersed in the HPW–SPC samples than that in the HPW–SPC–IM samples.

The TG–DTA curves of the SPC, HPW, and HPW–SPC samples before calcination in the region of 30–800 °C are shown in Fig. 3. For all the samples, the weight loss below 100 °C was due to the loss of the physisorbed H2O. There was a weight loss peak in the range of 210–400 °C for the SPC samples (Fig. 3a), which was due to the decomposition of CTAB in the sample. The corresponding DTA curves indicated that CTAB template elimination was associated with a sharp endothermic peak centered at 323 °C [38]. Another endothermic peak in the DTA diagram centered at 706 °C was corresponding to the collapse of the mesoporous gallery structure [39].

For the pure HPW (Fig. 3b), there was an endothermic peak in the temperature range of 100–215 °C (weight loss 2.94%) centered at 206 °C in the DTA diagram, accounting for the loss of H2O molecule of the Keggin unit of HPW. The broad endothermic peak between 215 and 538 °C centered at about 350 °C was corresponding to the loss of acidic protons and the decomposition of the Keggin structure. The peak centered at 572 °C in the DTA curve was assigned to the decomposition of heteropoly acid to form mixed oxides [40,41].

For all the HPW–SPC samples, the endothermic peak corresponding to the loss of the crystal water of HPW also appeared at about 200 °C (Fig. 3c–e). The endothermic peaks between 340 and 356 °C in the DTA diagrams can be attributed to the decomposition of surfactant. The decomposition temperature of surfactant...
shifted to higher temperatures was due to the interaction of the surfactant and HPW. The endothermic peak accounting for the loss of HPW acidic protons was also evidently observed at 478, 488, and 500 °C in the DTA diagrams of 5% HPW–SPC, 15% HPW–SPC, and 25% HPW–SPC samples, respectively (Fig. 3c–e). This phenomenon indicates that the HPW has been generated during the formation of the HPW–SPC samples. Comparing with the pure HPW, the thermal stability of the HPW in the HPW–SPC samples has been enhanced, which is due to the HPW formed by in situ method encaged in the framework of the SPC. Furthermore, the endothermic peak was gradually enhanced with the increase of the P and W content, which means the content of the formed HPW has increased in the HPW–SPC samples. Furthermore, compared with the DTA diagram of pure HPW (Fig. 3b), the complete decomposition of the heteropoly acid was observed at about 630 °C in the DTA diagram of the HPW–SPC samples (Fig. 3c–e), indicating that the HPW–SPC samples have evidently enhanced the thermal stability of the HPW heteropoly acid. The endothermic peak corresponding to the collapse of the mesoporous gallery structure also appeared in the DTA diagram of the HPW–SPC samples (Fig. 3c–e). This implies that the incorporation of the HPW did not destroy the interlayer gallery structures of the HPW–SPC samples. The TG–DTA curves also show that the HPW–SPC samples can be obtained after treating at 400 °C for 6 h.

The FT-IR spectra of the SPC, pure HPW, and HPW–SPC samples in the region of 700–1350 cm⁻¹ are shown in Fig. 4. The spectrum of HPW showed a broadened band at 802 cm⁻¹, which was assigned to $v_{\text{as}}$ (W=O=W) in edge shared octahedral [42]. In the spectrum of SPC sample, the band at 795 cm⁻¹ was attributed to the symmetric stretching frequency of Si–O–Si [43]. In the FT-IR spectra of the HPW–SPC samples, the band at 816 cm⁻¹ was attributed to the formation of Si–O–W bonds [44], which was due to the chemical interactions between the in situ formed HPW and SPC. With the increase of the P and W content, more HPW was in situ formed in the interlayer of the HPW–SPC samples, and the peak at 816 cm⁻¹ was evidently enhanced. Therefore, the phenomenon led to the conclusion that HPW has been in situ encaged in the mesoporous silica frameworks and formed new Si–O–W bonds within the silica wall of the SPC material. The characteristic bands of Keggin-type HPW were also observed at 1080, 980, and 890 cm⁻¹ (Fig. 4e), which were usually assigned to $v_{\text{as}}$(P=O), $v_{\text{as}}$(W=O), and $v_{\text{as}}$(W=O=W) in corner shared octahedral [42], respectively. However, in the FT-IR spectra of the HPW–SPC samples, the band at 1080 cm⁻¹ moved to a long wave scope. This may be due to the interactions of the Na₂HPO₄ and the silica wall of the SPC during the formation of HPW. Thus, the characteristic bands corresponding to the $v_{\text{as}}$(P=O) are ulteriorly effected by the frameworks of the SPC sample. In addition, the bands of the 25% HPW–SPC sample were evidently strengthened compared to that of SPC sample, which further indicates the formation of HPW and the incorporation of HPW into the SPC framework [45]. This is in accordance with the results of the XRD and TG–DTA.

Fig. 3. The TG–DTA curves of samples: (a) SPC, (b) pure HPW, (c) 5% HPW–SPC, (d) 15% HPW–SPC, and (e) 25% HPW–SPC.
The N₂ adsorption/desorption isotherms (A) and the pore size distribution curves (B) of the samples are shown in Fig. 5. All the HPW–SPC samples presented type IV isotherm patterns with H₄-type hysteresis loop starting at about 0.45 partial pressure (Fig. 5A), which is the characteristic of the mesoporous materials with the cylindrical pores formed in gallery region [46]. For the 25% HPW–SPC sample, the hysteresis loop of the isotherm was obviously smaller than these relatively low contents samples. Nevertheless, the main part of the hysteresis loop was still between 0.50 and 0.85. The MMT sample showed isotherm with adsorption at very low relative pressure \((P/P_0 < 0.3)\) and a small hysteresis loop at high relative pressures \((P/P_0 = 0.60–0.95)\), indicating that it possesses micropores (Type I) along with small amount of mesopores (Type IV). The results of the textural properties of the samples are summarized in Table 2. It is obvious that the \(S_{BET}\) and pore volume \((V_T)\) of the HPW–SPC samples are much larger than that of HPW–SPC–IM sample and MMT, but lower than that of the SPC sample. The significant loss of \(S_{BET}\) and \(V_T\) of the HPW–SPC–IM samples can be related to the agglomeration of HPW molecules on the external surface of the materials resulting in pore blockage [41,47]. \(S_{BET}\) and \(V_T\) also decreased with the increase of P and W content in the HPW–SPC samples, which is logical since the heteropoly acid formed in the framework of the HPW–SPC samples contributes to the sample weight.

The mesoporous pore size distribution is depicted in the Fig. 5B. The results indicate that the 5% HPW–SPC and the 15% HPW–SPC samples have the pore diameters around 4.2 nm, which are slightly smaller than that of the SPC sample (4.4 nm). However, the pore diameter of the 25% HPW–SPC sample is reduced to about 3.9 nm, which is about the same as that of the 15% HP–SPC–IM sample. This indicates that when excess HPW is formed in the HPW–SPC sample, it can clog in the mesopores and decrease the pore width as the impregnated sample [2]. This is in accordance with the results of the XRD.

The morphologies of the MMT, SPC, HPW–SPC, and 15% HPW–SPC–IM samples are shown in Fig. 6. The HPW–SPC sample exhibited slightly swelled natural mottorillite plate morphology [27], while all the HPW–SPC samples also exhibited plate structure, which was similar to the morphology of the SPC sample. This indicates that the interlayer gallery structure of the HPW–SPC samples is unaffected by the formation of HPW in the framework of the HPW–SPC samples. There were some fragmental particles in the images of the HPW–SPC samples, but the main laminated structure of the samples was retained. The small particles observed around the platelets are probably the broken platelets and the amorphous SiO₂ caused by the hydrolysis of TEOs in the extragallery region of the layered clay. As shown in Fig. 6, the 15% HP–SPC–IM sample also retained a mottorillite lamellar structure, but the surface of the sample was coarser than that of the HPW–SPC samples. This is because HPW has been incorporated into the framework of the HPW–SPC samples, while most of HPW in the 15% HPW–SPC–IM sample was impregnated on the surface of the sample.

### 3.2. The formation mechanism of the samples

Scheme 2 illustrates the proposed formation mechanism of the HPW–SPC materials. Firstly, MMT was suspended in aqueous solutions and had an ion-exchange with surfactant [48]. During this process, the surfactant formed micelle in the interlayer region. Then, the pH of the mixture gel was adjusted to 1.0 by using HCl aqueous solution, and an appropriate amount of Na₂WO₄ and Na₂HPO₄ was introduced. The WO₂⁴⁻/C₀⁴ and HPO₂⁻/C₀⁴ anions can be attracted into the interlayer by the electrostatic attraction and substitute Br⁻/C₀ and Cl⁻ in the shell surrounding the micelle, forming the complex of CTAB/polyheteroanions. Furthermore, the addition of HCl aqueous solution can keep the solution in a strong acidic environment to promote the formation of the PW₁₂O₃₄⁰ and retain the Keggin-type HPW heteropoly acid intact. When TEOS was finally added into the gel mixture, it would intercalate into the clay interlayer region by solvation and rapidly hydrolyze in acidic condition to form the protonated H₅SiO₄⁻ monomers. The silicate cations would interact with the anionic shell surrounding the
surfactant micelle to trap both X⁻ (Cl⁻, Br⁻) and heteropoly anions, leading to the formation of a silica layer around the surfactant template. Thus, the heteropoly anions would be present at the interface between the silica and the surfactant micelle. During the long time stirring and the hydrothermal treatment of the gel, the silica layer was polymerized and formed the Si—O—Si bonds between the interlayer regions. Washing and drying steps did not remove the heteropoly anions since they were trapped inside the clay interlayer. In the calcination step, the silica layer further condensed and yielded the completely cross-linked framework to strengthen the siloxane-pillars and the mesoporous structure, while the surfactant template decomposed and was eliminated from the pore system, but the HPW molecules remained fixed into the pore walls [2].

3.3. Catalytic performance of the samples

In order to examine the adsorption capacity for DBT of the catalysts, the tests without adding H₂O₂ and extraction were carried out and the results are shown in Table 3. It is evident that the adsorption capacity for DBT of the catalysts has no distinct difference as compared with the oxidation and extraction, which shows that the SPC and HPW–SPC samples cannot remove DBT effectively just by the adsorption and the best removal of DBT achieves merely 20.8% within 120 min on SPC sample. The best adsorption capacity of the SPC sample is due to the large pore size, S_{BET} and Vₜ of the SPC sample (Table 2), which conduce to the adsorption of DBT. Table 3 also shows the results of the sulfur removal over the different catalysts after oxidizing for 120 min at 60 °C. It is obviously that the HPW–SPC catalysts are highly efficient in catalytic ODS of DBT. The sulfur removal can reach up to 91.7% even over 5% HPW–SPC catalysts within 120 min. The results indicate that the sulfur removal enhanced with the increase of the HPW content in the HPW–SPC samples. But the 20% and 25% HPW–SPC samples exhibited comparatively lower activity than 15% HPW–SPC. This is because that the formation of high HPW contents in the HPW–SPC samples by introducing P and W leads to the decrease of the Vₜ and S_{BET} (Table 2), resulting from the agglomeration of HPW molecules on the surface and in the interlayer regions of the samples. For 15% HPW–SPC sample, the sulfur content can be reduced to 18.5 ppm from 500 ppm within 120 min. On the other hand, the catalytic performance of the HPW–SPC–IM samples was not so good. The sulfur removal was 70.7%, 73.7%, and 76.6% for the 5% HPW–SPC–IM, 15% HPW–SPC–IM, and 25% HPW–SPC–IM samples in

Fig. 6. The SEM images of samples: (a) MMT, (b) SPC, (c) 5% HPW–SPC, (d) 15% HPW–SPC, (e) 25% HPW–SPC, and (f) 15% HPW–SPC–IM.
120 min, respectively (Table 3). It is obviously that the catalytic performance of the HPW–SPC samples was more excellent than that of the HPW–SPC–IM sample. This is due to the $S_{BET}$ and $V_T$ of the HPW–SPC samples is much larger than that of the HPW–SPC–IM sample (Table 1), which induced by the most of HPW stacked on the surface and in the interlayer gallery for the HPW–SPC–IM sample.

The reusability of the 15% HPW–SPC catalyst was investigated in catalytic ODS. After each recycling, the catalyst was recovered by simple filtration, washing with methanol several times, and drying at 110 °C. The results (Table 4) show that the catalytic activity had no significant decrease after four runs. The excellent reusability of the HPW–SPC catalyst is due to that HPW has been in situ encaged in the silica pillared frameworks of SPC, leading to the better stability and negligible loss of the Keggin units of HPW.

4. Conclusions
The mesoporous HPW–SPC materials containing different contents of HPW were successfully synthesized via adding Na$_2$HPO$_4$ and Na$_2$WO$_4$ into the initial sol–gel system under strong acidic condition. The results show that HPW can be encapsulated into the gallery silica frameworks of the HPW–SPC samples and dispersed homogeneously in the samples. In addition, the HPW–SPC samples showed better catalytic performance than the HPW–SPC–IM samples in catalytic ODS of DBT-containing model oil. HPW in situ incorporated in the mesoporous silica pillared clay is insoluble during catalysis, and these materials can be easily separated and recycled. The prepared well-organized mesoporous HPW–SPC materials are promising and efficient catalysts for ODS of fuel oils.

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References