



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

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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).

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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.

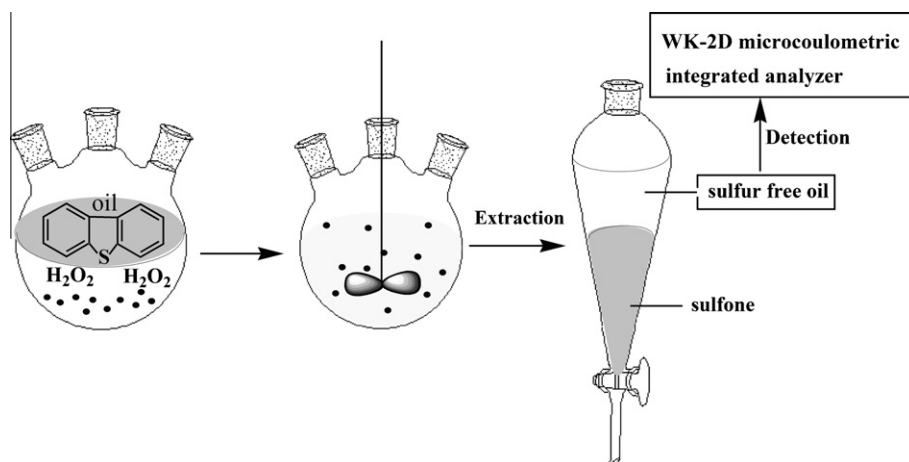
2. Experimental

2.1. Materials

All solvents and reactants are commercially available and were used without further purification. The natural montmorillonite

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Scheme 1. Catalytic oxidation desulfurization process of the model oil.

clay (MMT) was obtained from Inner Mongolia and used as the starting clay without any purification or ions exchanging. The raw clay had a basal (001) spacing of 15.4 Å and an anhydrous structural (layer) formula of $Ca_{0.48}Na_{0.03}K_{0.01}[Si_{7.86}Al_{0.14}][Al_{2.84}Fe_{0.30}Mg_{0.86}]O_{20}(OH)_4$, with a cation exchange capacity (CEC) of 91 meq/100 g [18].

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 Na_2WO_4 and Na_2HPO_4 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%

H_2O_2 aqueous solution (molar ratio of $H_2O_2/S = 3$) 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 $Cu K\alpha$ 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 (Hengjiu 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 (p_0) 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 results of the X-ray fluorescence analysis for the HPW–SPC samples are 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.

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