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One-pot synthesis, characterization and desulfurization of functional mesoporous W-MCM-41 from POM-based ionic liquids

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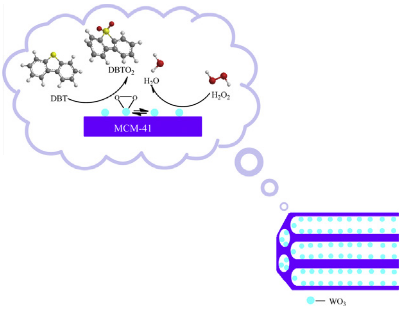
HIGHLIGHTS

- Functional W-MCM-41 have been successfully synthesized from POM-based ionic liquids.
- The materials characterized in detail demonstrated high performance in the deep desulfurization.
- The as-synthesized materials acted not only as absorbents but also catalysts in the reaction.
- The desulfurization process were conducted at mild reaction conditions without any organic solvents.

GRAPHICAL ABSTRACT

DBT was absorbed by the mesoporous material and then oxidized into $DBTO_2$ by the active peroxo species, which was formed by tungsten species in the presence of H_2O_2.



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ABSTRACT

Tungsten-containing functional meso-materials W-MCM-41 have been successfully synthesized and employed in the desulfurization of dibenzothiophene (DBT). The as-synthesized materials were characterized by XRD, XPS, TEM, Raman, FTIR, DRS, and BET analysis. The experimental results demonstrated that the mesoporous structure was well preserved after introduction of W species into the meso-materials. These materials presented a high dispersion of tungsten species and excellent catalytic activity on the removal of dibenzothiophene without any organic solvents as extractants, and the sulfur removal could reach 100.0% at 60 °C in 30 min. The catalytic performance on different sulfur compounds was also investigated in detail. After recycling for nine times, the removal of the oxidation desulfurization system could still reach 90.0%. According to the GC–MS analysis of the oxidation products, a mechanism was proposed for the absorptive oxidation process of DBT.

1. Introduction

Deep desulfurization of sulfur from gasoline and diesel has been an important and challenging issue for industrial and environmental reasons. Sulfur in transportation fuels is a major source of air pollution from automobiles, and the increasingly stringent fuel specifications worldwide also require reducing the sulfur content to a low level [1]. Nowadays, the conventional process for the removal of most sulfur compounds in industry is known as hydrodesulfurization (HDS), which is highly efficient in removing aliphatic and acyclic sulfur-containing compounds [2], but less effective for aromatic organosulfur compounds such as dibenzothiophene (DBT), benzothiophene (BT) [3]. Hence, it is necessary

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to develop new approaches for deep desulfurization, such as extraction [4,5], adsorption [6], oxidation [7,8], and biodesulfurization [9]. Oxidative desulfurization (ODS), especially employing green agent hydrogen peroxide as oxidant, is considered to be one of the most promising technologies, which has a significant advantage over HDS. It can be carried out under lower temperature and pressure, and the aromatic organosulfur compounds can be easily removed.

The design of effective, selective, and recyclable catalysts has become an important challenge for ODS process. Polyoxometalates (POMs) which have attracted wide attention for their unique properties exhibited high activity in oxidative and acid-catalyzed reactions [10]. Recently, various types of POM-based solid materials have been investigated in the desulfurization process [11–13]. However, the specific surface areas of these catalysts are not large and reaction times are long. To overcome the drawbacks above, mesoporous silicas (MCM-41 and SBA-15, etc.) which possess uniform pore size and large internal surface area are introduced to the solid materials for desulfurization [14,15]. Hence, a series of silica-based materials have been reported on ODS [16,17], but the desulfurization process often required high O/S molar ratio. Moreover, the wide usage of organic solvents as extractants in the desulfurization system may also obstruct them to the industrial application. After a careful survey of literatures, it was found that few detailed studies were about the application of POMs-based ionic liquids in the synthesis of meso-materials, which were used in the ODS process.

In the present work, in order to achieve the advantages of POMs and meso-materials, the active tungsten species were successfully introduced into the mesoporous MCM-41 by using $[C_{16}mim]Br$ as template and $[C_{16}mim]_3PW_{12}O_{40}$ as tungsten source. The absorptive process was combined with oxidative process in our desulfurization system where no organic solvents were added as extractants compare to our previous studies. The functional meso-materials were highly effective on the removal of DBT with a low O/S molar radio and easily separated for recycling, which could be potentially applied in future industry. The oxidation products in the reaction were studied with GC–MS analysis. Besides, the samples were also systematically characterized by XRD, XPS, TEM, FT-Raman, FTIR, DRS, and BET analysis.

2. Experimental section

2.1. Materials

Benzothiophene (BT, 99%), dibenzothiophene (DBT, 98%) and 4,6-dimethyldibenzothiophene (4,6-DMDBT, 99%) were purchased from Sigma–Aldrich. Commercially available H_2O_2 (aqueous solution, 30%), $H_3PW_{12}O_{40}\cdot 14H_2O$ (AR grade), WO_3 (AR grade), n-octane (AR grade), and tetradecane (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. $[C_{16}mim]Br$ was purchased from Shanghai Chengjie Chemical Co., Ltd.

2.2. Preparation of $[C_{16}mim]_3PW_{12}O_{40}$

$[C_{16}mim]_3PW_{12}O_{40}$ was prepared according to the reported literatures [18,19]. Stoichiometric amounts of $[C_{16}mim]Br$ and $H_3PW_{12}O_{40}\cdot 14H_2O$ were dissolved in deionized water under agitating for 30 min. The precipitate obtained was washed with distilled water until bromine-free ($AgNO_3$ aqueous test) and dried overnight at 80 °C.

2.3. Preparation of MCM-41

Mesoporous silica support MCM-41 was synthesized by nonhydrothermal method according to the previous studies with slight modification [20,21]: A 0.69 g portion of $[C_{16}mim]Br$ was dissolved in 25 mL of deionized water at room temperature. 2 mL of Tetraethyl orthosilicate (TEOS) was added into the solution above. And then, the mixture was adjusted to pH 10.0 by adding aqueous ammonia and stirred for 3 h. The resultant gel was filtered, washed with water, dried overnight at 120 °C and calcined for 6 h at 550 °C at a heating rate of 5 °C/min with an air flow rate of 400 mL/min.

2.4. Preparation of W-MCM-41

Hybrid functional material W-MCM-41 was prepared with an initial gel composition of $Si–0.2[C_{16}mim]^+–160H_2O–1.5NH_3\cdot H_2O–xW$ ($x = 0.025, 0.05, 0.1, 0.2$). In a typical synthesis, a 0.61 g portion of $[C_{16}mim]Br$ was dissolved in 25 mL of deionized water at room temperature. Then, 0.28 g of $[C_{16}mim]_3PW_{12}O_{40}$ was added into the mixture above. After that, 2 mL of Tetraethyl orthosilicate (TEOS) and 0.52 mL of $NH_3\cdot H_2O$ was added into the mixture and stirred for 3 h. The resultant gel was filtered, washed with water, dried overnight at 120 °C and calcined at 550 °C for 6 h at a heating rate of 5 °C/min with an air flow rate of 400 mL/min. The obtained sample was with a W/Si molar ratio of 0.1 in the gel and named as 0.1W-MCM-41. Besides, the samples with W/Si molar ratios of 0.025, 0.05, 0.2 in the gel were 0.025W-MCM-41, 0.05W-MCM-41, and 0.2W-MCM-41, respectively.

2.5. Characterization

The obtained functional materials W-MCM-41 and mesoporous MCM-41 were grounded into fine powder for characterization. The FTIR spectra of the catalysts (KBr pellets) were recorded with a Nicolet Nexus 470 FTIR instrument. Raman spectra were carried out at room temperature using a DXR Raman microscope with a 532 nm laser source. The diffuse reflectance spectra (DRS) were measured by a UV–vis spectrometer (UV-2450, Shimadzu) in the range of 200–800 nm. $BaSO_4$ was used as the reflectance standard material. Transmission electron microscopy (TEM) micrographs were taken with a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The samples used for TEM were prepared by dispersing some products in ethanol, then placing a drop of the solution onto a copper grid and letting the ethanol evaporate slowly in air. The crystalline phases of samples were analyzed by X-ray diffraction (XRD) by Bruker D8 diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å). X-ray photoelectron spectroscopy (XPS) was measured on a PHI5300 with a monochromatic Mg Kα source to explore the elements on the surface. The nitrogen adsorption–desorption isotherms at 77 K were investigated using a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corp.). ^{31}P MAS NMR spectra were recorded on Bruker AVANCE III 400WB with a MAS frequency of 8 kHz.

2.6. Oxidative desulfurization process

Model oil was prepared by dissolving DBT, BT, DT and 4,6-DMDBT in n-octane with a corresponding S-content of 500, 250, 250 and 250 ppm, respectively. The catalytic tests of oxidative desulfurization were performed in a 30 mL flask equipped with stirrer and condenser. In a typical run, the water bath was firstly heated and stabilized to 333 K. 10 mg of catalyst and 20 μL of H_2O_2 (O/S molar ratio = 2.5) were added to the reactor. Then, 5 mL of model oil was injected to start the reaction. The resulting mixture was stirred at 60 °C for 30 min in a water bath.

2.7. Analysis method of products

The remained sulfur-containing compounds in model oil after the reaction were analyzed by GC-FID with tetradecane as the