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Article (Special Issue on Environmental Catalysis and Materials)

Fabrication and characterization of tungsten-containing mesoporous silica for heterogeneous oxidative desulfurization



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ARTICLE INFO

Article history:

Received 29 January 2016

Accepted 7 April 2016

Published 5 June 2016

Keywords:

Heterogeneous oxidative desulfurization
Tungsten species
Mesoporous silica
One-pot synthesis
Organosulfur

ABSTRACT

A series of functional, tungsten-containing mesoporous silica materials (W-SiO₂) have been fabricated directly from an ionic liquid that contained imidazole and polyoxometalate, which acted as mesoporous template and metal source respectively. These materials were then characterized through X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectra (FTIR), diffuse reflectance spectra (DRS), and N₂ adsorption-desorption, which were found to contain tungsten species that were effectively dispersed throughout the structure. The as-prepared materials W-SiO₂ were also found to possess a mesoporous structure. The pore diameters of the respective sample W-SiO₂-20 determined from the TEM images ranged from 2 to 4 nm, which was close to the average pore size determined from the nitrogen desorption isotherm (2.9 nm). The materials were evaluated as catalysts for the heterogeneous oxidative desulfurization of dibenzothiophene (DBT), which is able to achieve deep desulfurization within 40 min under the optimal conditions (Catalyst (W-SiO₂-20) = 0.01 g, temperature = 60 °C, oxidant (H₂O₂) = 20 μL). For the removal of different organic sulfur compounds within oil, the ability of the catalyst (W-SiO₂-20) under the same conditions to remove sulfur compounds decreased in the order: 4,6-dimethyldibenzothiophene > Dibenzothiophene > Benzothiophene > 1-dodecanethiol. Additionally, they did not require organic solvents as an extractant in the heterogeneous oxidative desulfurization process. After seven separate catalytic cycles, the desulfurization efficiency was still as high as 90.3%. From the gas chromatography-mass spectrometer analysis, DBT was entirely oxidized to its corresponding sulfone DBT₂O₂ after reaction. A mechanism for the heterogeneous desulfurization reaction was proposed.

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1. Introduction

As the worldwide demand for fuel continues to increase rapidly, the industrial desulfurization of diesel fuel faces increasing technological challenges to comply with environmental concerns and legal requirements [1,2].

Hydrodesulfurization (HDS) is a mature technology and efficiently removes aliphatic and acyclic sulfur compounds (e.g. thiols, sulfides, and disulfides) [3–5] but not thiophene sulfides, such as dibenzothiophene and its derivatives [6–8]. Additionally, further improvements to the HDS process for deep desulfurization are limited to increasingly harsh operating condi-

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This work was supported by the National Nature Science Foundation of China (21276117, 21376111, 21406092).

DOI: 10.1016/S1872-2067(15)61103-2 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 37, No. 6, June 2016

tions with high associated costs [9,10]. Hence, it is critical to develop supplementary strategies for deep desulfurization, including extraction [11–14], adsorption [15,16], oxidation [17–22], and biodesulfurization [23]. Oxidative desulfurization (ODS) can remove aromatic organosulfur compounds under mild conditions. As such, it is considered as a promising technique for deep desulfurization.

Ionic liquids (ILs) are organic salts with low melting points and vapor pressures, and have attracted wide attention owing to their unique physicochemical properties, including negligible volatility, low toxicity, excellent thermal stability, good solubility characteristics, and the variety of available structures [24]. Task-specific IL anions that are tethered to functional groups (e.g. polyoxometalates) show great potential for the modification and control of different chemical and physical functions in a material [25–27]. Polyoxometalates (POMs) are a vast class of well-defined, early transition metal oxoanion clusters that exhibit distinctive physicochemical properties, including adjustability of composition, size, shape, acid-base properties, and redox potential [28–32]. As such, POMs are extensively used as green catalysts, particularly in oxidation reactions [33,34]. A number of studies have demonstrated that POM-based ILs exhibited efficient catalytic ODS [35–37]. However, the widespread use of these materials for homogeneous desulfurization in an industrial setting has been hindered because of their intrinsic liquid nature and high viscosity, which leads to difficulties in separation and recovery, recyclability, cost, and the large amounts of ILs that are required [38].

To overcome some of these problems, considerable efforts have been made to introduce active POM-based species into heterogeneous desulfurization systems, where materials such as zeolites, porous carbon, clays, siliceous materials, and metal-organic frameworks were employed as a support [39–44]. Among these supports, mesoporous silica possesses a number of desirable properties, including a stable mesoporous structure, a large surface area and pore volume, well-ordered pore structure, and narrow pore-size distributions. Moreover, silica has no inherent catalytic property and can be used as a support that can be functionalized by framework substitution or post-synthesis surface modification. As such, POM-based IL-supported mesoporous silica has been fabricated for ODS, but required relatively excessive oxidants. Additionally, the requirement for organic solvents (e.g. acetonitrile and dimethylformamide) may limit future applications of these materials [45,46].

In this work, active tungsten species were introduced directly into mesoporous silica from a POM-based IL ($[\text{C}_{16}\text{mim}]_3\text{PW}_{12}\text{O}_{40}$), where the imidazole cation and polyoxometalate anion acted as template and metal source, respectively. The hybrid materials (W-SiO_2) were highly effective on removing organosulfur compounds under mild conditions and were separated easily for recycling. Additionally, organic solvents were not required for the heterogeneous desulfurization. All samples were characterized using X-ray diffraction, Transmission electron microscopy, Raman spectroscopy, Fourier transform infrared spectra, Diffuse reflectance spectra, and Brunauer-Emmett-Teller analysis.

2. Experimental

2.1. Materials

H_2O_2 (aqueous solution, 30 wt%), $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 14\text{H}_2\text{O}$ (AR grade), WO_3 (AR grade), *n*-octane (AR grade), $\text{NH}_3\cdot\text{H}_2\text{O}$ (aqueous solution, 25 wt%), acetonitrile (AR grade), tetraethyl orthosilicate (TEOS, AR grade) and tetradecane (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. Benzothiofene (BT, 99%), dibenzothiofene (DBT, 98%) 1-dodecanethiol (DT, 99%), and 4,6-dimethyldibenzothiofene (4,6-DMDBT, 99%) were purchased from Sigma-Aldrich. $[\text{C}_{16}\text{mim}]\text{Br}$ was purchased from Shanghai Chengjie Chemical Co., Ltd. All the materials are used without further purification.

2.2. Sample preparation

The POM-based IL $[\text{C}_{16}\text{mim}]_3\text{PW}_{12}\text{O}_{40}$ was prepared according to a literature procedure [47]. The mesoporous hybrid material (W-SiO_2) was prepared using a one-pot method from an initial gel that consisted of $\text{TEOS}:[\text{C}_{16}\text{mim}]_3\text{PW}_{12}\text{O}_{40}:\text{H}_2\text{O}:\text{NH}_3\cdot\text{H}_2\text{O} = 1:x:160:1.5$ ($x = 0.002, 0.004, 0.008$). In a typical synthesis, $[\text{C}_{16}\text{mim}]_3\text{PW}_{12}\text{O}_{40}$ (0.14 g) was added into acetonitrile (4 mL) with constant stirring. Subsequently, TEOS (2 mL) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (0.52 mL) were added into the mixture and stirred for 3 h. The resulting gel was filtered, washed with water (200 mL), dried overnight at 120 °C, and then calcined at 550 °C with a heating rate of 5 °C/min for 6 h. The samples were named based on the Si/W molar ratio used in the gel ($\text{W-SiO}_2\text{-}y$, where $y = \text{Si}/\text{W} = 10, 20$ and 40).

2.3. Characterization and methods

The samples were ground into a fine powder for characterization. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet Nexus 470 FT-IR instrument using KBr pellets. Raman spectroscopy was recorded at ambient temperature using a DXR Raman microscope with an excitation wavelength of 532 nm from a laser source. Diffuse reflectance spectra (DRS) were measured between 200 and 800 nm with BaSO_4 used as the reflectance standard using a UV-visible spectrometer (UV-2450, Shimadzu). The surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method, while the pore-size distribution was obtained from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. Transmission electron microscopy (TEM) was recorded using a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The crystalline phases within the samples were analyzed using X-ray diffraction (XRD) spectroscopy with a Bruker D8 diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.154$ nm).

2.4. Catalytic activity test

A model oil sample was prepared by dissolving DBT, BT, DT and 4,6-DMDBT in *n*-octane with a corresponding sulfur content of 500, 250, 250 and 250 ppm, respectively. Desulfurization was performed in a flask equipped with a magnetic stirrer

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