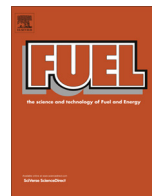




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Preparation of highly dispersed tungsten species within mesoporous silica by ionic liquid and their enhanced catalytic activity for oxidative desulfurization [☆]

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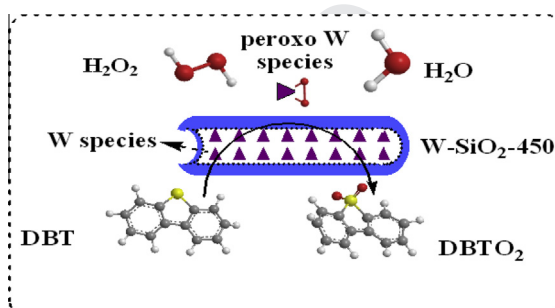
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HIGHLIGHTS

- W-mesoporous silicas were synthesized by functional IL [(n-C₈H₁₇)₃NCH₃]₂W₂O₁₁.
- The functional IL acted as template and W precursors during the synthesis process.
- W species were highly dispersed into the mesoporous silica.
- The catalysts showed good catalytic performance and reusability.

GRAPHICAL ABSTRACT

A series of W-containing mesoporous silicas were designed, prepared and evaluated as the catalysts of oxidative desulfurization.



interfacial reaction

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ABSTRACT

A series of W-containing mesoporous silicas with different calcination temperatures were *in situ* synthesized by using [(n-C₈H₁₇)₃NCH₃]₂W₂O₁₁ not merely as a novel template but also the W precursors. The catalysts were characterized by N₂ adsorption–desorption, XRD, XPS, HRTEM, EDS, ICP, FTIR, and UV–vis DRS analysis. The N₂ adsorption–desorption and HRTEM results indicated that these catalysts possessed mesoporous structure with relatively uniform pores and large internal surface areas. The XRD, ICP and HRTEM results indicated that the W species were highly dispersed on the surface and into the mesoporous silica matrix. The catalysts also showed excellent catalytic performance on the removal of refractory bulky molecule sulfur compounds from the model oil with H₂O₂. Based on the removal of DBT in the model oil, the optimal calcination temperature of the catalysts is 450 °C. The catalytic activity of different sulfur-containing substrates was also investigated. After 8-times recycling, the sulfur removal could still reach 99.2% without any significant decrease.

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1. Introduction

As the fact that the development of cost-effective and environmentally benign catalytic systems is becoming one of the main concerns of contemporary synthetic chemistry, ionic liquids (ILs) have attracted overwhelming attention due to their desirable

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properties such as negligible low vapor pressure, excellent thermal stability, low toxicity and good solubility characteristics [1]. Furthermore, sophisticated selections of cation and anion species allow the design of task-specific ionic liquids (TSILs) to deliver different chemical and physical function in the same compounds [2–5]. Polyoxometalates (POMs) are a large family of bulky clusters of transition metal oxide anions with structural diversity, which have been investigated carefully for their high activity in oxidative and catalytic reactions [6]. For the purpose of combining the excellent properties of ILs with functional POMs, enormous amount of POM-based ILs have been synthesized for a variety of catalytic processes [7–13]. Even though most POM-based ILs show efficient catalytic performance, widespread industrial applications of such homogeneous catalysts have been hampered by their intrinsic liquid nature, including difficulties in separation and recovery of the catalysts, the unsatisfactory recyclability, the large dosage of catalysts and high viscosities [14].

In order to overcome the problems mentioned above, a lot of efforts have been made to immobilize the ionic liquids to a solid support [15,16]. Mesoporous silicas are a class of inorganic materials, which possess interesting properties such as stable mesoporous structure, large surface areas, high pore volumes, well-ordered pore structures, and narrow pore-size distributions with relatively large-pore diameters (2–50 nm). Silicas have no inherent catalytic property but can be used as supports functionalized either by framework substitution or by post-synthesis surface modification. As a result, a series of novel mesoporous silica-supported functionalized ILs were designed and prepared. Compared with pure ILs, these silica-supported ILs exhibit additional advantages such as a remarkable decrease of the dosage, the facilitation of catalysts' separation from the reaction system, more rapid mass transfer, lower contamination of the product and excellent performance of recovery of the catalysts [17–21]. Meanwhile, a lot of efforts have also been made to synthesize the mesoporous silicas by using ILs as a template during the synthetic process. Hu et al. [22] synthesized micro/mesoporous silicate using dual templates consisting of an alkyl imidazole IL [C_n mim]Br and a surfactant cetyltriethylammonium bromide (CTAB). Wang and his groups [23] used the long-chain IL 1-hexadecyl-3-methylimidazolium chloride (C_{16} mimCl) as a template to prepare porous silica with a two-dimensional hexagonal p6 mm mesopore structure (MCM-41-type) as well as with a cubic Ia3d (gyroid, MCM-48-type structure) framework in basic synthesis medium via a hydrothermal synthesis procedure. Adams and coworkers [24] used a novel set of templates, 1-alkyl-3-methylimidazolium salts to prepare MCM-41. They studied systematically about subtle differences in the performance of novel templates and identified them as viable reagents in the synthesis of good quality MCM-41.

Oxidative desulfurization (ODS) has developed a simple, safe, reproducible and environmentally friendly post-treatment to the traditional hydrodesulfurization (HDS) in order to achieve ultra-deep desulfurization in recent years owing to its moderate operation conditions and easier removal of aromatic organosulfur compounds [25–37]. In the ODS process, organic sulfides are converted into their corresponding sulfoxides and sulfones, which are preferentially extracted due to their increased polarities [38]. Hydrogen peroxide has been widely used as the oxidant in oxidative desulfurization for the reason that it is cheap, commercially available, nontoxic, non-polluting and low corrosive. Various systems on the ODS process using different catalysts with H_2O_2 as oxidants have been reported, including liquid/liquid biphasic system (e.g., organic acid/ H_2O_2 and polyoxometalate/ H_2O_2) [39,40] and solid/liquid heterogeneous system (e.g., inorganic solid acids/ H_2O_2 and supported catalysts/ H_2O_2) [41,42]. In the liquid/liquid biphasic system, mass transfer limitations make it too slow for the ODS reaction to be applied to industrial use. Furthermore,

large amounts of catalysts and solvent, contamination of the oil and difficulties in separation of the catalysts may prevent industrial applications of the liquid/liquid biphasic system. In the field of solid/liquid heterogeneous system, a series of metal oxides (e.g., WO_3 , MoO_3 , V_2O_5) have been reported and they exhibited high performance in the ODS reaction. However, the metal oxide catalysts still suffer from some shortcomings, such as the low surface area, low adsorption rate and little number of accessible active catalytic sites. Therefore, the supported catalysts are attracting a great deal of attention in recent years.

Herein, we report a simple and reproducible synthesis of highly dispersed active sites and stable hybrid mesoporous silicas by an amphiphilic TSIL-templating approach. POM-based IL [$(n-C_8H_{17})_3NCH_3$] $_2$ [$W_2O_3(O_2)_4$] (abbreviated as $T_8W_2O_{11}$) was prepared and then used as a template to synthesize hybrid mesoporous silicas containing W which was incorporated into the silica. Mesoporous silicas were formed by first blending the silicate source tetraethyl orthosilicate (TEOS) with the amphiphilic $T_8W_2O_{11}$ under the synthetic conditions. Firstly, the liquid crystal phase was formed by the $T_8W_2O_{11}$ molecules and subsequently trapped by silicate condensation. After the structure had been formed, the organic cations of TSIL could be removed by calcination, leaving a mesoporous material. Through the very synthetic method, the active tungsten species were *in situ* introduced into the mesoporous silica framework. The sample showed highly catalytic activity in oxidative desulfurization process with low catalyst dosage and without organic solvents. The catalysts acted not only as absorbents to absorb sulfur-containing compounds but also as active species to activate H_2O_2 to oxidize sulfur compounds to corresponding sulfones.

2. Materials and methods

2.1. Preparation of the W-mesoporous silicas

A series of W-mesoporous silicas calcined from 350 to 850 °C were prepared through typical synthesis route via the following procedures. $T_8W_2O_{11}$ (1.1488 g) (synthesized based on our previously reported procedure [43]) was dissolved in ethanol (33.6 mL) under stirring at room temperature. Then deionized water (103 mL) was added into the above mixture. After that, TEOS (8 mL) was added dropwise into the solution. The PH of the solution was adjusted to 9–10 by adding $NH_3 \cdot H_2O$ (4 mL). After being stirred for 3 h at room temperature, the resultant precipitate was obtained by filtration, washed with deionized water and ethanol several times and dried in an oven at 120 °C for 3 h. The solid products were collected and calcined at 350, 450, 550, 650, 750, 850 °C at a heating rate of 10 °C/min for 0.5 h. The catalysts were denoted simply as “W-SiO₂-X”, where the X indicated the calcination temperature.

2.2. Characterization

The nitrogen adsorption-desorption isotherms at 77 K were investigated using a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corp.). Tungsten and silicon contents in W-SiO₂-450 were determined by inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima2000DV, USA). For ICP studies, 5 mg W-SiO₂-450 was digested with 2 mL HNO_3 and 0.5 mL HF and then diluted to 100 mL. The Fourier transform infrared spectroscopy (FT-IR) of all catalysts (KBr pellets) were recorded on Nicolet Model Nexus 470 FT-IR equipment. The diffuse reflectance spectra (DRS) were obtained by a ultraviolet-visible spectroscopy (UV-vis) (UV-2450, Shimadzu Corporation, Japan) in the range of 200 to 800 nm. BaSO₄ was used as the reflectance standard material. The crystalline phases of samples were analyzed by X-ray diffraction (XRD) by Bruker D8 diffractometer with Cu K α

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