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Magnetic POM-based mesoporous silica for fast oxidation of aromatic sulfur compounds

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ABSTRACT

It is of great importance to develop efficient catalysts to achieve sulfur removal in fuel, protecting the world against the pollution caused by sulfur oxides. Aiming that, polyoxometalates supported materials have been employed as a vital class of heterogeneous catalysts for oxidative desulfurization. In this study, a serial of magnetic polyoxometalates-based mesoporous silica hybrid materials were successfully prepared over a facile hydrothermal and impregnation method, and evaluated in fast oxidation of aromatic sulfur. These hybrid materials exhibited interesting feature of rapid separation by external magnets, and excellent desulfurization performance to refractory sulfur compounds (benzothiophene, 3-methylbenzothiphene, dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiphene). Furthermore, the sulfur removal could still reach 94% after recycling for ten times, which could be potentially applied in industry production.

1. Introduction

Air pollution, as one of the by-product in human progress, has drawn wide attention for a long time, especially for the pollution of sulfur oxides from fuel combustion. Thus, it is essential to develop the desulfurization methods to make the fuel clean before combustion. In existing industry, hydrodesulfurization (HDS) plays an important role on desulfurization to effectively remove mercaptan, thioether, thiophene, benzothiophene and their derivatives from fuel. However, it could hardly remove aromatic sulfur compounds such as dibenzothiophene (DBT) under mild condition [1–3]. Owing to this restriction, it is vital to explore non-hydrodesulfurization technology to produce ultra-low sulfur containing fuel. Therein, oxidative desulfurization (ODS) method has been extensively studied since its mild operation, high sulfur removal and low-pollution property [4–9]. Therefore, ODS method could be employed to remove the residual aromatic sulfur compounds from the fuel after HDS operation.

For homogeneous catalysis, it is provided with numerous advantages such as high reactivity and selectivity [10–12]. However, there are also some problems for homogeneous catalysis in separation and regeneration of catalysts. Fortunately, heterogeneous catalysis has been developed to solve these problems. Ionic liquids (ILs), as an immense family of molten salts, have been employed as liquid catalysts in desulfurization to build liquid-liquid heterogeneous catalytic system [13–15]. Due to its non-volatile, good solvent ability, designable composition, chemical stability and easy separation, ILs have already been applied as extractant in extractive catalytic oxidative desulfurization (ECODS) and displayed good performance on sulfur removal of fuel [5,16–18]. However, the dosage of ILs in ECODS is relatively large, and there might be some residue of ILs in oil, reducing the quality of the fuel. Therefore, ILs supported materials have been developed as solid catalysts in desulfurization to reduce the dosage of ILs and promote sulfur removal of fuel [19–21].

Polyoxometalates (POMs), as a family of transition metal-oxide clusters, have been applied as active species in ODS method to the catalytic oxidation of sulfur-containing component in fuel. However, most POMs are difficult to disperse in the common organic solvents due to the crystalline feature and high lattice energy, resulting in obstacle for the pure POMs in desulfurization application. To solve this problem, emulsion system has been developed using a series of POMs modified ILs to improve the contact surface between catalysts and oil to achieve better desulfurization performance [22,23]. The organic cation from ILs could improve the lipophilic nature of POMs-anions and then shows better catalytic performance than that in organic reaction. However,

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limited by the property of emulsion droplets, another demulsification process is often required for the separation of POMs modified ILs from oil, which results in a challenge to the regeneration of catalysts. Thus, hybrid material is now becoming one of the hot spots to solve the problem above [19,21,24,25]. Mesoporous materials such as SBA-15 [26,27] and FDU-15 [28] have been widely used as supports to form multiphase and greatly accelerate reaction speed, which are the most important advantages of heterogeneous catalysis, due to its porous structure and large specific surface area in solid-liquid heterogeneous catalytic system. In this study, the mesoporous silica is employed to ODS process to improve the catalytic efficiency and recovery performance of the designed catalysts. Combining advantages of POMs modified ILs and mesoporous silica, this hybrid materials can be potentially used in industrial production.

Moreover, it is often difficult for catalysts to be separated and collected only by natural precipitation, while the centrifugation method costs much time and energy especially for the large scale in industry. Therefore, developing a kind of solid catalysts to be easily separated and collected turns into one of the task to industry. Hence, to further enhance the separability of material, we prepared a serial of magnetic POM-based mesoporous silica nanocomposites over a facile hydrothermal and impregnation method, which were evaluated in ODS system to remove aromatic sulfur compounds. The effects of γ-Fe_2O_3 in the hybrid materials were investigated on the magnetic properties and desulfurization performance. These hybrid materials were characterized in detail and tested on sulfur removal to investigate the catalytic performance. In recycling test, these materials showed good recyclability, and could be separated easily by external magnets, which could be potentially applied in industry. Furthermore, the oxidation products of aromatic sulfur compounds after catalytic oxidative desulfurization were also studied by gas chromatography-mass spectrometer (GC–MS) analysis.

2. Experimental section

2.1. Materials

Benzothiophene (BT, 97%), 3-methylbenzothiphene (3-MBT, 96%), dibenzothiophene (DBT, 98%), 4-methyldibenzothiophene (4-MDBT, 96%) and 4,6-dimethyldibenzothiphene (4,6-DMDBT, 97%) were purchased from Aladdin Chemical Co., Ltd. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_a = 5800$) was supplied by Sigma-Aldrich. 1-Hexadecyl-3-methylimidazolium chloride ($[C_{16}mim]Cl$) was obtained from Shanghai Chenjie Chemical Co., Ltd. Phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}\cdot 14H_2O$, AR grade), hydrogen peroxide (H_2O_2, 30 wt%, AR grade), citric acid (AR grade), sodium hydroxide (NaOH, AR grade), sodium nitrate ($NaNO_3$, AR grade), hydrochloric acid (HCl, AR grade), ethanol (EtOH, AR grade), acetonitrile (CH_3CN, AR grade), iron(II) sulfate heptahydrate ($FeSO_4\cdot 7H_2O$, AR grade), tetraethyl orthosilicate (TEOS) and n-octane (AR grade) were marketed from Sinopharm Chemical Reagents Co., Ltd.

2.2. Preparation of samples

POMs-based ionic liquid $[C_{16}mim]_3PMo_{12}O_{40}$ (IL) was obtained following previous research [20]. Magnetic iron oxide was obtained according to literature with modification [29]. In a typical procedure, 1 mmol citric acid and 7 mmol NaOH were dissolved in 19 mL aqueous solution containing 0.2 mol $NaNO_3$ at 100 °C, followed by facile addition of 1 mL aqueous solution containing 2 mmol $FeSO_4$ and then the mixture was stirred for 1 h. After cooling to room temperature, the magnetic iron oxide was separated and purified from solvent by a magnet for several times.

POM-based mesoporous silica nanocomposites were synthesized with a one-pot method. In a typical procedure, 2.668 g P123 was stirred and dissolved in 63 g of 1.9 mol/L HCl aqueous solution for 8 h, followed by addition of 4 mL acetonitrile containing 0.1 mmol $[C_{16}mim]_3PMo_{12}O_{40}$. Then, 4 mL of TEOS was added dropwise into above solution with continuous stirring for 24 h, followed by transferring all the solution to a Teflon-lined autoclave for 24 h at 100 °C. The resulting precipitate was separated, washed and dried at 80 °C overnight; Then, the solid was extracted by ethanol for 72 h using Soxhlet extractor to remove P123, and the remaining solid was collected and dried to obtain the POM-based mesoporous silica nanocomposites (PMS).

Magnetic POM-based mesoporous silica nanocomposites were synthesized with equivalent-volumetric ultrasonic impregnation method. In a typical procedure, 0 g/0.001 g/0.002 g/0.004 g/0.008 g magnetic iron oxide was dispersed into 4 g deionized water by ultrasonic, which was dropped in a small bottle containing 0.4 g POM-based mesoporous silica nanocomposites, named as 0-MPMS/0.25-MPMS/0.5-MPMS/1-MPMS/2-MPMS respectively, which was followed by impregnation with continuous ultrasonic for 1 h; it was then dried at 50 °C for 30 min and 200 °C for 8 h respectively to reinforce the connection between magnetic substance and silica nanocomposites.

2.3. Preparation of the model oil

All the sulfur-containing model oil was prepared as follows. To take DBT model oil as an example, the DBT model oil was obtained by dissolving desired amount of DBT in *n*-octane to get the S-content of 500 ppm. As internal standard, *n*-tetradecane was also dissolved into the solution above with the content of 4000 ppm.

2.4. Characterization

The as-prepared materials were characterized by multiple characterization techniques. The wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXD) were obtained using a Bruker D8 diffractometer with CuK_α radiation ($\lambda = 0.154$ nm) employing a scanning rate of $7^\circ\ min^{-1}$ in the 2θ range from 10° to 80° and $1^\circ\ min^{-1}$ in the 2θ range from 0.5° to 10°, respectively. X-ray photoelectron spectroscopy (XPS) on a ESCA-LAB250 (Thermo VG, UK), in which the standard monochromatic Al Ka excitation was at 1486.6 eV, was utilized to determine the element valence of materials. FT-IR and FT-Raman spectrums were obtained on Nexus 470 from Thermo Electron Corporation and DXR Raman microscope using 532 nm excitation laser power. Brunauer-Emmett-Teller method (BET) and density functional theory (DFT) on Quadrasorb *SI* (Quantachrome, USA) was employed to investigate the surface area and pore width distribution. Transmission electron microscopy (TEM) images were recorded with a JEM 2010 (JEOL, Japan) operated at 200 kV. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) was operated with a S-4800 (HITACHI, Japan) at an acceleration voltage of 15.0 kV and 20.0 kV respectively. Vibrating sample magnetometer (VSM) was employed to investigate the magnetization properties. The oxidized sulfur compound was characterized by GC–MS (Agilent 7890/5975 C-GC/MSD; HP-5 MS column, 30 m × 250 μm i.d. × 0.25 μm; temperature program: 100 °C-temperature increasing $15\ ^\circ C\ min^{-1}$ to 200 °C for 10 min).

2.5. Catalytic activity test

The catalytic activity test was carried out by mixing the catalyst and model oil in a two-necked kettle equipped with a magnetic stirrer and a condenser. After setting the reaction temperature, a desired amount of H_2O_2 was added into the mixture above under stirring at 800 rpm. The residual sulfur content was monitored via gas chromatography (GC, Agilent-7890 A) equipped with a capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm). The sulfur removal (%) was calculated by the formula as follows: