



Research Paper

Superparamagnetic Mo-containing core-shell microspheres for catalytic oxidative desulfurization of fuel



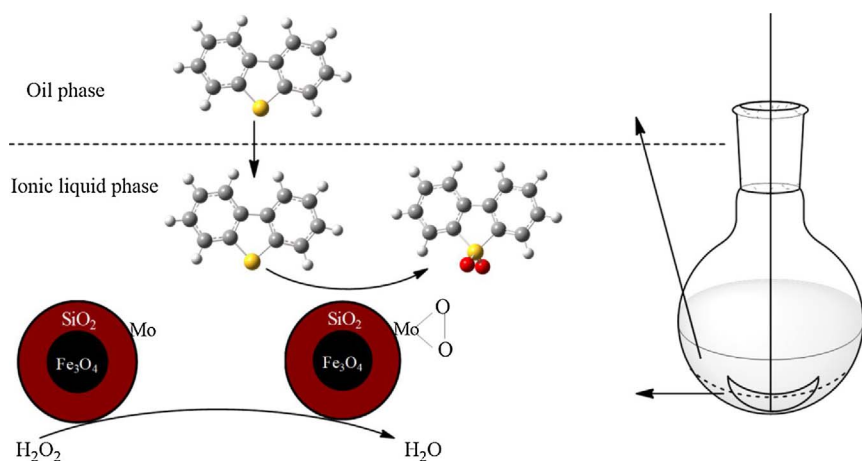
Tao Guo^a, Wei Jiang^b, Yijie Ruan^a, Lei Dong^a, Hui Liu^a, Hongping Li^b, Wenshuai Zhu^{a,*}, Huaming Li^{b,*}

^a School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China

^b Institute for Energy Research, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China

GRAPHICAL ABSTRACT

Dibenzothiophene (DBT) was extracted from the oil phase into the IL phase and then oxidized by the active peroxide species formed by magnetic catalysts and H₂O₂ to the corresponding sulfone.



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ABSTRACT

Magnetic core-shell structured materials as carriers have received extensive attention in heterogeneous catalysis due to their unique magnetic responsively properties. Herein, we report a synthetic route to obtain magnetic core-shell microspheres by a sol-gel approach. The Fe₃O₄ (ca. 8 nm) is completely coated with SiO₂ (ca. 15 nm) to prevent Fe₃O₄ from being oxidized in the reaction and the microspheres also show superparamagnetism, which allows the catalyst easy to separate. To explore their application, Mo-containing compound is loaded to their surface by impregnating and then calcined at different temperatures (100–800 °C). The obtained catalysts are used in oxidative desulfurization (ODS). The removal of DBT from model oil can reach 100% with calcination temperature at 400 °C and be recycled for at least five times without obvious decrease.

* Corresponding authors.

E-mail addresses: zhuws@ujs.edu.cn (W. Zhu), lihm@ujs.edu.cn (H. Li).

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1. Introduction

In recent years, an increasing number of attentions have been paid to the environmental pollution caused by the combustion of sulfur compounds in gasoline and diesel, which are the main source of SO_x in air [1,2]. Thus, lots of countries have released stricter regulations to limit the S-content in fuels [3]. Up to now, hydrodesulfurization (HDS) as a traditional desulfurization method has been generally used in industry because simple aliphatic sulfides can be efficiently removed in this process. However, it is less effective for aromatic sulfides such as dibenzothiophene (DBT) and its derivatives [4–6]. Compared with HDS, oxidative desulfurization (ODS) has gained more and more attention due to its simple, mild reaction conditions and most importantly its high performance on removal of aromatic organosulfur compounds [7–11]. In ODS process, aromatic organosulfur compounds can be easily removed by oxidation to the corresponding sulfones and extraction by polar solvent [12]. Multiple oxidants, including hydrogen peroxide [13–15], *tert*-butyl hydroperoxide [16,17] and molecular oxygen [18,19] are used in oxidative desulfurization process. Hydrogen peroxide as the oxidant is very common due to its cheap, nontoxic and non-polluting characteristic.

In the past, homogeneous catalysis was an important component of the desulfurization reaction [20,21]. However, catalysts suffered from deactivation during reaction and difficulty in recovering and recycling expensive reagents [22]. Despite heterogeneous catalysis is applied to desulfurization in recent years [23,24], researchers still want to find replaceable catalytic systems which offer nearly activity and selectivity but easier separation and reusability. Magnetic materials as catalyst carriers have received extensive attention in heterogeneous catalysis due to their unique magnetic responsively properties [25–27], low cytotoxicity [28,29] and chemically modifiable surface [30,31]. Meanwhile, they have large specific surface area which is conducive to the dispersion of matter [32,33].

Nowadays, magnetic materials have also a great attraction for desulfurization [34]. They make catalysts effectively separate from the oil under a magnetic field and recycle easily. However, the investigation of magnetic materials on desulfurization has few published literatures [35,36]. The early application of magnetic materials for oxidative desulfurization of diesel fuel was reported by Hasan Keypour et al. in 2012 [37]. In this paper, they synthesized a new heterogeneous magnetically separable oxidation catalyst by the covalent anchoring of $[\text{MoO}_2\text{Cl}_2(\text{DMSO})_2]$ complex on the amino propyl and Schiff base coated magnetic nanoparticles. Also, the obtained catalysts showed not only high chemical stability in a variety of organic solvents but also high catalytic activity in oxidation of sulfides. However, in catalytic oxidation of sulfides reaction, CH_2Cl_2 used as solvent may have bad effect to environment. Another article introduced a magnetic $\text{MoO}_3/\text{Fe}_3\text{O}_4$ catalyst synthesized by precipitation method [38]. The catalyst could be easily recovered from the reaction phase by adding a magnet and recycled, while Fe_3O_4 exposed to the outside could be easily oxidized in oxidation reaction.

In this work, we report a simple method to fabricate magnetically responsive core–shell catalysts $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ with MoO_3 on the surface, where MoO_3 are produced *in situ* by treating the precursor $\text{Fe}_3\text{O}_4@/\text{SiO}_2@[\text{C}_4\text{mim}]_3\text{PMo}_{12}\text{O}_{40}$ in different temperatures. All catalysts are characterized and tested for catalytic oxidation of aromatic sulfur compounds. The results show that the catalysts calcined in 400 °C can reach 100% desulfurization efficiency when using 30 wt.% H_2O_2 as oxidant and ionic liquid $[\text{C}_8\text{mim}]\text{PF}_6$ as extractant. The high desulfurization performance may be ascribed to the high dispersion of MoO_3 on the surface of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$, which may be resulted from the cation of organic polyoxometalates (POMs).

2. Experiment

2.1. Reagents

Ferric acetylacetonate ($\text{Fe}(\text{acac})_3$), benzyl alcohol, oleic acid,

oleylamine, cyclohexane, tetraethoxysilane (TEOS), dibenzothiophene (DBT), benzothiophene (BT), 3-methylbenzothiophene (3-MBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), 4-methyldibenzothiophene (4-MDBT) were purchased from Sigma-Aldrich. Acetonitrile, *n*-octane, 30 wt. % H_2O_2 , tetradecane and $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 26\text{H}_2\text{O}$ were bought from Sinopharm Chemical Reagent Co., Ltd. Polyethylene glycol hexadecyl ether (Brij 56) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. $[\text{C}_4\text{mim}]\text{Cl}$ and 1-octyl-3-methylimidazolium hexafluorophosphate ($[\text{O}mim]\text{PF}_6$) were gained from Shanghai Chenjie Chemical Co., Ltd. All chemicals were used without further purification.

2.2. Preparation of Fe_3O_4 nanoparticles

The Fe_3O_4 nanoparticles were synthesized through a solvothermal reaction according to the reported literature [35]. Typically, $\text{Fe}(\text{acac})_3$ (0.53 g) was added to benzyl alcohol (15 mL) and oleic acid (2.3 mL), oleylamine (2.3 mL) were subsequently joined, the mixture was magnetically stirred for 30 min. Brown solution was distributed to a 25 mL Teflon-sealed autoclave and heated at 180 °C for 10 h. The black magnetite product was washed three times with ethanol and dispersed in 13.5 mL of cyclohexane for the next step.

2.3. Preparation of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$

The above cyclohexane suspension of Fe_3O_4 nanoparticles was conducted under ultrasound for 1 h. Then, 1.2 mL of Fe_3O_4 nanoparticles cyclohexane suspension and 2 g of Brij56 were added to a round-bottom flask charged with 8.5 mL of cyclohexane, 0.12 mL of H_2O and 0.45 mL of concentrated ammonia. After stirring for 30 min, 0.4 mL of TEOS was added dropwise into the mixed solution under vigorous stirring at normal temperature. Then the reaction was performed for another 8 h at 50 °C in an oil bath. The product was collected with help of centrifuge and washed three times with ethanol and water, respectively.

2.4. Preparation of catalyst

$[\text{C}_4\text{mim}]_3\text{PMo}_{12}\text{O}_{40}$ was synthesized according to the reported literature [39]. Briefly, 0.3 g of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanoparticles and 0.09 g of $[\text{C}_4\text{mim}]_3\text{PMo}_{12}\text{O}_{40}$ were added in 10 mL of acetonitrile and the mixture was stirred at room temperature. The intermediate product was obtained after complete evaporation of the solvent. The percentage of Mo element on the resulted products was measured by ICP and the actual mass ratio of Mo is 10.1% lower than the theoretical value 11.9%. The solid products were calcined at 100, 200, 300, 400, 500, 600, 700, 800 °C respectively at a heating rate of 2 °C/min in air and held temperature for 4 h.

2.5. Characterization

Fourier transform-infrared (FT-IR) was recorded on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr disks at room temperature. Raman spectroscopy analysis was conducted by DXR Raman microscope using a 532 nm excitation laser power. Powder X-ray diffraction (XRD, Bruker D8) patterns of the crystal phase were measured on a diffractometer with high-intensity Cu-K α in the 2 θ range of 10–80° at normal temperature. Mo elemental content analysis was analyzed by inductively coupled plasma (ICP). The morphology features and sizes of the samples were characterized by a Tecnai 12 transmission electron microscope (TEM). Scanning electron microscopy (SEM, Leo Supra 35VP) was hired to study the surface morphologies of samples equipped with an energy dispersive spectrometer (EDS). X-ray photo-electron spectroscopy (XPS) was measured on a KRATOS (Shimadzu Corporation, Japan) with a monochromatic double anode Mg/Al K α source to explore the elements of the surface. Thermogravimetric and Differential Scanning Calorimetry (TG–DSC)

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