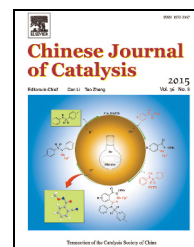


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Article

Selective oxidation of sulfurs and oxidation desulfurization of model oil by 12-tungstophosphoric acid on cobalt-ferrite nanoparticles as magnetically recoverable catalyst

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ABSTRACT

Silica-coated CoFe₂O₄ nanoparticles were prepared and used as a support for the immobilization of 12-tungstophosphoric acid, to produce a new magnetically separable catalyst. This catalyst was characterized using X-ray diffraction, wavelength-dispersive X-ray spectroscopy, Fourier-transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, laser particle size analysis, and vibrating sample magnetometry. The catalyst showed high activity in the selective oxidation of thioethers and thiophenes to the corresponding sulfones under mild conditions. The catalytic activity of the nanocatalyst in the oxidative desulfurization of model oil was investigated. The effect of nitrogen-containing compounds on sulfur removal from the model oil was also evaluated. The catalyst showed high activity in the oxidative desulfurization of diesel. The catalyst can be readily isolated from the oxidation system using an external magnet and no obvious loss of activity was observed when the catalyst was reused in four consecutive runs.

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1. Introduction

Among recent developments in catalysis, "clean oxidation catalysis", involving catalysis and H₂O₂, is receiving much attention because of the importance of oxidation reactions in the manufacture of fine chemicals. These catalytic systems promote the oxidation of organic substrates because of their oxygen content, and are low cost, safe to store and use, and, importantly, the use of H₂O₂ is environmentally friendly. These advantages have encouraged the development of practical procedures for the selective oxidation of organic sulfur compounds, not only because of the extensive use of sulfoxides and sulfones as synthetic intermediates in the pharmaceutical industry [1], but also because the oxidative desulfurization (ODS) process is an effective method for removing sulfur compounds

from fuels and industrial effluents, to satisfy new environmental legislation [2–5].

ODS is an alternative or complementary technology to hydrodesulfurization for deep desulfurization [6]. It has several advantages such as mild reaction conditions (ambient pressure and low temperature), high selectivity, and the potential for desulfurization of sterically hindered sulfur compounds such as dibenzothiophene (DBT) [7]. In the ODS process, aromatic sulfur compounds such as benzothiophene (BT), DBT, and their alkylated derivatives are oxidized to the corresponding sulfone or sulfoxide; these are highly polar and can be removed using organic extractants [8–14].

Various catalytic systems have been reported for ODS [15–22]. Among these, polyoxometalates (POMs) have higher sulfur removal efficiencies because of their unusual properties.

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The main obstacle to industrial applications of homogeneous POMs is that they are difficult to recover from the reaction medium. These materials are therefore usually impregnated on suitable materials [23–29].

Recently, progress has been achieved using amphiphilic POM catalysts, which are synthesized from a combination of quaternary ammonium cations and POM anions. These compounds can form emulsion droplets, which act as homogeneous catalysts at the interface of two immiscible liquids, giving high activities during oxidative processes [30–32].

We synthesized and characterized a novel, more effective, magnetically separable catalyst by the immobilization of 12-tungstophosphoric acid (PW) on the surfaces of silica-coated CoFe_2O_4 magnetic nanoparticles (CoFe@Si). This catalyst (denoted by CoFe@Si-PW) was characterized using various techniques. Selective oxidation of sulfur compounds and desulfurization of model oil were investigated using an $\text{H}_2\text{O}_2/\text{CoFe@Si-PW}$ catalytic system. The effects of reaction temperature, catalyst loading, and oxidant to sulfur (O/S) molar ratio were studied to optimize the reaction conditions. The ODS of model oil was investigated under the optimized reaction conditions. The effect of nitrogen-containing compounds on ODS were investigated by adding quinoline and indole to the oxidation system.

2. Experimental

2.1. Catalyst preparation

All materials were commercial reagent grade and obtained from Merck, Aldrich, and Fluka, and used without further purification.

The CoFe@Si-PW catalyst was synthesized according to the procedure shown in Scheme 1. The CoFe_2O_4 nanoparticles were prepared using a coprecipitation method. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (25 mL, 0.1 mol/L) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (25 mL, 0.2 mol/L) were dissolved in distilled water and kept at 70 °C. NaOH solution (24 mL, 3.0 mol/L) was added to the salt solution. The dark brown product was washed several times with distilled water and redispersed in distilled water to give a stable brown magnetic dispersion. CoFe_2O_4 nanoparticles (0.04 g) were dispersed in ethanol (160 mL). This dispersion was homogenized ultrasonically in a water bath for 10 min. Finally, water (40 mL), tetraethylorthosilicate (1 mL), and ammonia solution (5 mL) were slowly added to this dispersion. The obtained CoFe@Si nanoparticles were separated using a permanent magnet, washed with distilled water, and dried under vacuum. The synthesis of 40 wt% PW on CoFe@Si was performed by dissolving PW (0.5 g) in dry methanol (5 mL). This solution was added drop-wise to a suspension of CoFe@Si (1.0 g in 50 mL methanol) with dispersion

by sonication. The mixture was stirred to obtain CoFe@Si-PW magnetic nanoparticles. The catalyst was collected using a permanent magnet and dried under vacuum overnight.

2.2. Catalyst characterization

Fourier-transform infrared (FT-IR) spectroscopy was performed on KBr pellets using an FTIR-spectrometer (Alpha). X-ray diffraction (XRD) was performed using a D8 ADVANCE diffractometer (Bruker-AXS, Germany). The magnetic properties of $\text{CoFe@Si}_2\text{-PW}$ were determined using a BHV-55 (Riken, Japan) vibrating sample magnetometer (VSM). The morphology of the supported catalyst was examined using scanning electron microscopy (SEM; XL30, Philips). Transmission electron microscopy (TEM) was performed using a Zeiss EM900 transmission electron microscope with an accelerating voltage of 80 kV. The size distributions and zeta potentials of the samples were determined using a laser particle size analyzer (HPPS5001, Malvern, UK). The total S contents of the model oils were determined using an elemental analyzer (Analytik Jena AG-multi EA® 3100). The W content of the catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Spectro Ciros CCD spectrometer).

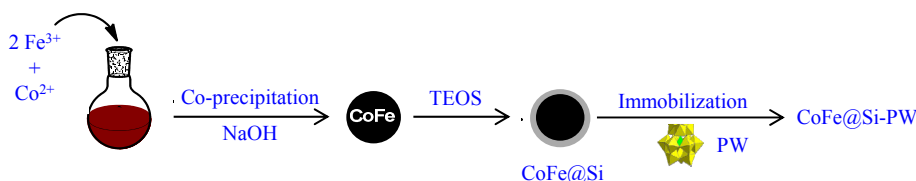
2.3. Catalytic tests

2.3.1. Oxidation of liquid sulfides

Liquid sulfides were oxidized to the corresponding sulfones by stirring a solution of the sulfide (1 mmol) and the catalyst (0.04 g) in *n*-heptane (4 mL). A certain amount of H_2O_2 (30% aq.) was added as the oxidant. The mixture was stirred for a specified time at room temperature. After completion of the reaction, the catalyst was separated from the reaction mixture using an external magnet. The corresponding sulfone products were extracted from the reaction mixture with Et_2O . The solvent was evaporated to generate the crude product. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent (method a).

2.3.2. Oxidation of solid sulfides

Solid sulfides were oxidized to the corresponding sulfones by stirring a solution of the sulfide (1 mmol) and the catalyst (0.15 g) in *n*-heptane-ethanol (*v/v*, 4:2). Then a certain amount of H_2O_2 (30% aq.) was added as the oxidant. The mixture was stirred for a specified time at 60 °C, and the reaction was monitored using thin-layer chromatography. After completion of the reaction, the catalyst was separated from the reaction solution using an external magnet. The corresponding sulfone products were separated from the reaction mixture. The solvent was evaporated to generate the crude product. The crude



Scheme 1. Schematic diagram of preparation of CoFe@Si-PW catalyst.

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