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Article

Synthesis and characterization of $PMoV/Fe_3O_4/g\text{-}C_3N_4$ from melamine: An industrial green nanocatalyst for deep oxidative desulfurization

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ABSTRACT

A facile approach to the preparation of a novel magnetically separable $H_5PMo_{10}V_2O_{40}/Fe_3O_4/g\text{-}C_3N_4$ ($PMoV/Fe_3O_4/g\text{-}C_3N_4$) nanocomposite by chemical impregnation is demonstrated. The prepared nanocomposite was characterized and its acidity was measured by potentiometric titration. $PMoV/Fe_3O_4/g\text{-}C_3N_4$ showed high catalytic activity in the selective oxidative desulfurization of sulfides to their corresponding sulfoxides or sulfones. The catalytic oxidation of a dibenzothiophene (DBT)-containing model oil and that of real oil were also studied under optimized conditions. In addition, the effects of various nitrogen compounds, as well as the use of one- and two-ring aromatic hydrocarbons as co-solvents, on the catalytic removal of sulfur from DBT were investigated. The catalyst was easily separated and could be recovered from the reaction mixture by using an external magnetic field. Additionally, the remaining reactants could be separated from the products by simple decantation if an appropriate solvent was chosen for the extraction. The advantages of this nanocatalyst are its high catalytic activity and reusability; it can be used at least four times without considerable loss of activity.

1. Introduction

Research on the desulfurization of fuels and the technical importance of this process for clean energy production and removal of environmental pollutants has been increasing in recent years. Deep desulfurization of diesel fuels has attracted a lot of attention owing to the increasingly stringent regulations and fuel specifications for the purposes of environmental safekeeping in various countries [1]. Oxidative desulfurization (ODS) is considered to be one of the most promising approaches for ultra-deep desulfurization of diesel fuel. In the ODS process, organosulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are oxidized to their corresponding sulfones in the presence of an oxidizing agent, and removal of these oxidized products is carried out by extraction or adsorption processes [2,3]. Reported oxidative desulfurization catalysts have included ionic liquids (ILs) [4–9], composites [10,11], polyoxometalates (POMs) [12,13], organic acids [14], Fenton's reagent [15], and molecular sieves [16,17]. Catalytic processes based on these systems have many advantages and have attracted global attention. ILs can be used as novel solvents for extraction, POM-based homogeneous catalysts show high performances under mild reaction conditions, composites are easily separated from the reaction mixture and show high reuse capabilities, and organic acids and Fenton's reagent demonstrate high reac-

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tion rates for the removal of sulfur containing-compounds from fuel oils.

The design of an efficient catalyst for this oxidation process is challenging. Nanosized metal–oxygen cluster anions, or heteropoly acids (HPAs), form a class of compounds that is unique in its structural variety and functional versatility [18]. These compounds, which consist of O-sharing MO_x polyhedra (most often M = Mo^{VI}, W^{VI} or V^{V}), have found applications in various fields. Of these, their catalytic applications are the most important [19–22]. Owing to their unique metal–oxygen framework and reversible electron transfer abilities [23,24], HPAs have been investigated extensively as catalysts for a variety of oxidation reactions, including epoxidation and desulfurization [25–27]. $H_5PMo_{10}V_2O_{40}$ (PMoV) is a vanadium-containing HPA, which is recognized as an efficient homogeneous catalyst because of its bifunctional nature (Brönsted acidity and electron transfer properties) and ease of modification for acidic and oxidative reactions [28]. Immobilizing HPAs onto the surface of a solid support is necessary to obtain a heterogeneous catalyst. This enhances their low surface area and reduces their high solubility in polar media, thus overcoming some of the difficulties in catalyst recovery. Recently, graphitic carbon nitride (g-C_3N_4), the most stable allotrope of carbon nitride [29], has attracted increasing attention as a convenient support for the immobilization of HPAs owing to its environmentally friendly properties, high chemical stability, reasonable thermal stability, low-cost, 2D layered structure, and the abundant availability of its precursors [30–32]. An important hindrance in the large-scale application of nanosized catalysts is the difficulty of their separation from the reaction mixtures. This is due to prolonged equipment operation, complicated technical requirements, and the high operational costs of classical separation methods. However, using magnetic nanoparticles as special immobilizing carriers for the catalysts would provide a way to separate the nanocatalysts from the reaction mixtures by simply using an external magnetic field [33,34]. Therefore, preparation of magnetically separable nanocomposites based on g-C_3N_4 would enable their easy separation from the solution with an external magnet. Hence, we have developed a facile and large-scale method for the preparation of a novel magnetically separable PMoV/Fe_3O_4/g-C_3N_4 nanocomposite for the first time. For this purpose, we first prepared the Fe_3O_4/g-C_3N_4 nanocomposite as a magnetically separable support. Then, PMoV was immobilized on this magnetic support to give the PMoV/Fe_3O_4/g-C_3N_4 nanocomposite. These two synthetic processes were achieved using a chemical co-precipitation method, and the resulting PMoV/Fe_3O_4/g-C_3N_4 composite showed considerable catalytic activity in the selective oxidation of organic sulfur compounds. In addition, the desulfurization of model and real oil was investigated in the presence of the newly synthesized catalyst under optimized reaction conditions. The problem of separating the catalyst from the reaction mixture was resolved by using this novel magnetic nanocatalyst, and excellent reusability with almost no change in yield after four runs was observed.

2. Experimental

2.1. Materials and methods

$FeCl_3·6H_2O$ (99%), $FeSO_4·7H_2O$ (99%), NaOH (98%), HCl (37%), melamine, PMoV (> 99%), and all other reagents and solvents were obtained from Merck, Aldrich or Fluka and were used without further purification. Transmission electron microscopy (TEM) images were obtained with a transmission electron microscope (Jeol JEM-2100 with an accelerating voltage of 200 kV). Scanning electron microscopy (SEM) was performed using an AIS2300C microscope with scanning range from 0 to 20 keV. Energy-dispersive X-ray (EDX) spectroscopy measurements were recorded with an IXRF model 550i attached to the scanning electron microscope. SEM/EDX samples were prepared by coating the solid particles with a conductive layer. X-ray diffraction (XRD) patterns were obtained using a STOE powder diffraction system, 2θ diffraction, and a scintillation counter detector. Electrochemical experiments were performed with a computer-controlled Autolab modular electrochemical system (Eco Chemie, Utrecht, the Netherlands) equipped with GPES software (Eco Chemie). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro Ciros CCD spectrometer was used to investigate the leaching of the active sites. Fourier transform infrared (FT-IR) spectra were acquired on an ALPHA FT-IR spectrometer with samples as KBr pellets. Magnetic properties were determined using a vibrating sample magnetometer (BHV-55, Riken, Japan). Ultraviolet-visible (UV-vis) spectra were measured using an Agilent (8453) UV-vis diode-array spectrometer in quartz cells with 1 cm optical path. The potential variation was recorded using a Hanna 302 pH meter and a double junction electrode. NMR spectra were carried out on a Bruker Avance 200 MHz NMR spectrometer with TMS as the internal standard and $CDCl_3$ as solvent. Thin layer chromatography on precoated silica gel (fluorescent at 254 nm, 0.2 mm) on aluminum plates was used to monitor the reactions. The total sulfur content was analyzed using a multi EA 3100 Element Analyzer (Analytik Jena AG).

2.2. Preparation of the catalysts

2.2.1. Preparation of g-C_3N_4

Pure g-C_3N_4 was fabricated by directly calcining melamine in air. Briefly, 2.0 g melamine was put into an alumina crucible with a loose cover and heated to 250 °C from room temperature in a muffle furnace at a heating rate of 5 °C/min. The temperature was then raised to 550 °C with a heating rate of 10 °C/min and the sample was maintained at this temperature for another 2 h. Finally, the resulting yellow g-C_3N_4 sample was cooled to room temperature.

2.2.2. Preparation of the Fe_3O_4/g-C_3N_4 nanocomposite

The Fe_3O_4/g-C_3N_4 nanocomposite was prepared by chemical co-precipitation. In a typical synthesis, 0.5 g g-C_3N_4 was ultrasonically dispersed into 150 mL distilled water for 20 min at room temperature. Then 0.58 g $FeCl_3·6H_2O$ was dissolved in 25 mL degassed distilled water (solution A), and 0.2 g $FeSO_4·7H_2O$ was dissolved in a solution containing 10 mL distilled water