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Article

Synthesis and characterization of PMoV/Fe₃O₄/g-C₃N₄ 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 H₅PMo₁₀V₂O₄₀/Fe₃O₄/g-C₃N₄ (PMoV/Fe₃O₄/g-C₃N₄) nanocomposite by chemical impregnation is demonstrated. The prepared nanocomposite was characterized and its acidity was measured by potentiometric titration. PMoV/Fe₃O₄/g-C₃N₄ 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.

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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 $\text{M} = \text{Mo}^{\text{VI}}$, 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]. $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (PMoV) is a vanadium-containing HPA, which is recognized as an efficient homogeneous catalyst because of its bifunctional nature (Brønsted 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 ($\text{g-C}_3\text{N}_4$), 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 $\text{g-C}_3\text{N}_4$ 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 $\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite for the first time. For this purpose, we first prepared the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite as a magnetically separable support. Then, PMoV was immobilized on this magnetic support to give the $\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite. These two synthetic processes were achieved using a chemical co-precipitation method, and the resulting $\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ 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

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (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 $\text{g-C}_3\text{N}_4$

Pure $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ sample was cooled to room temperature.

2.2.2. Preparation of the $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite

The $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite was prepared by chemical co-precipitation. In a typical synthesis, 0.5 g $\text{g-C}_3\text{N}_4$ was ultrasonically dispersed into 150 mL distilled water for 20 min at room temperature. Then 0.58 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 25 mL degassed distilled water (solution A), and 0.2 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in a solution containing 10 mL distilled water

and 2 mL HCl (2 mol/L, solution B). Afterwards, solutions A and B were mixed under mechanical stirring and nitrogen degassing at 60 °C to form a yellow suspension of g-C₃N₄. After stirring for 30 min, an aqueous solution of ammonia was added until the pH reached 10.0. The resulting dark brown suspension was then stirred at 80 °C for another 30 min. After cooling to room temperature, the precipitate was washed twice with ethanol and double-distilled, magnetically separated water. The obtained dark brown precipitate was then dried in an oven at 60 °C for 24 h.

2.2.3. Preparation of the PMoV/Fe₃O₄/g-C₃N₄ nanocomposite

To immobilize the PMoV on the as-prepared Fe₃O₄/g-C₃N₄ supports, 0.7 g PMoV was dissolved in 5 mL dry methanol. This solution was added dropwise to a suspension of 1.0 g Fe₃O₄/g-C₃N₄ in 50 mL methanol while being dispersed by sonication. The mixture was stirred for 24 h at room temperature to give the PMoV/Fe₃O₄/g-C₃N₄ nanocomposite. Finally, the obtained catalyst was collected using a permanent magnet and dried in a vacuum oven overnight.

2.3. Voltammetry experiments

Electrochemical reduction of the samples was performed in phosphate buffer (0.1 mol/L, pH = 5) with Ag/AgCl as the reference electrode and glassy carbon as the working electrode. Cyclic voltammograms of the samples (v, 0.1 V/s) were prepared at room temperature (20 ± 5 °C).

2.4. Acidity measurement

For the potentiometric titration, 0.05 g solid catalyst was added to 90 mL acetonitrile and magnetically stirred for 3 h. The suspension was then titrated with a solution of *n*-butylamine (0.05 N) in acetonitrile.

2.5. Catalytic reactions

2.5.1. Oxidation of liquid sulfides to sulfoxides

A mixture of 0.01 g of the catalyst and 30% H₂O₂ (4 mmol) aq. was added to a solution of the sulfide (1 mmol) in a mixed solvent of EtOH and hexane (1:1; 2 mL), and the resulting mixture was stirred at room temperature. At the end of the reaction, the catalyst was separated using an external magnetic field. The corresponding sulfoxide was then extracted with EtOH from the reaction mixture (Method a, Table 1).

2.5.2. Oxidation of liquid sulfides to sulfones

A similar method to that described above was utilized for sulfone synthesis, but the reactions were performed in the presence of 0.02 g of the catalyst and put a blank 30% H₂O₂ (8 mmol) aq., and at 60 °C (Method b, Table 2, entries 1–7).

2.5.3. Oxidation of solid sulfur compounds to sulfones

A mixture of 0.03 g of the catalyst and 30% H₂O₂ (10 mmol) aq. was added to a solution of the sulfide (1 mmol) in a mixed solvent of EtOH and hexane (1:1; 2 mL), and the resulting mixture

was stirred at 80 °C. The reaction mixture was cooled to room temperature and the catalyst was separated using an external magnetic field. The corresponding sulfones were extracted with EtOH from the reaction mixture (Method c, Table 2, entries 8–11).

2.5.4. Oxidative desulfurization of a model oil containing DBT

The ODS catalytic tests were performed by dissolving 5 mL of a model oil containing DBT (500, 800, 1000, 1200 ppm) in a mixed solvent of EtOH and hexane (1:1; v/v ratio). Then, 0.03 g of the catalyst and 30% H₂O₂ (10 mmol) aq. was added to the mixture. The mixture was stirred under air (atmospheric pressure) in a flask equipped with a condenser at 80 °C. At the end of the reaction, the catalyst was separated from the reaction mixture using an external magnet, and the corresponding sulfone was extracted with EtOH.

2.5.5. Effect of nitrogen-containing compounds on ODS

The oxidation reaction was carried out by first stirring 5 mL of the model oil containing 1000 ppm of DBT in a mixed solvent of EtOH and hexane (1:1; v/v ratio) at 80 °C. Then, 0.03 g of the catalyst and 30% H₂O₂ (10 mmol) aq. were added to the mixture. To investigate the effect of nitrogen-containing compounds on the oxidation of DBT, indole, quinolone, pyridine or pyrrol (60 ppm) were added to the model oil. After completion of the reaction, the catalyst was separated from the reaction mixture using an external magnet. When EtOH was used as the solvent for extraction, the products could be separated from the polar phase by simple decantation, which provided a simple way to separate the products from the reaction mixture.

2.5.6. Effect of aromatic hydrocarbons on ODS

The oxidation reaction was carried out by first stirring 5 mL of the model oil containing 1000 ppm of DBT in a mixed solvent of EtOH and hexane (1:1; v/v ratio) at 80 °C. Then, 0.03 g of the catalyst and 30% H₂O₂ (10 mmol) aq. was added to the mixture. The influence of one-ring aromatic hydrocarbons (toluene, xylene, mesitylene or benzene) and a two-ring aromatic hydrocarbon (naphthalene) on the conversion of the model oil was investigated by addition of 40% ratio (v/v) of these aromatic compounds to the mixture. The catalyst and products were separated as described above.

2.5.7. Oxidative desulfurization of real oil

For the ODS of real oil, 5 mL of oil (sulfur content: 500, 1900 ppm, API 41.67) was used. First, 5 mL of the oil was stirred in a mixed solvent of EtOH and hexane (1:1; v/v ratio) at 80 °C. Then, 0.03 g of the catalyst and 30% H₂O₂ (10 mmol) aq. were added to the mixture and it was heated at 80 °C with vigorous stirring for 200 min. After completion of the reaction, the solid catalyst was separated from the reaction mixture using an external magnet. When EtOH was used as the solvent for extraction, the products could be separated from the polar phase by simple decantation. The sulfur content of the real oil was measured using a total sulfur analyzer.

2.5.8. Leaching test

To investigate the leaching stability of the PMoV/Fe₃O₄/g-C₃N₄ nanocomposite, the contents of the PMoV filtrates were quantitatively evaluated by ICP-AES after completion of the oxidation reaction of methyl phenyl sulfide (MPS, 10 mmol) in a mixed solvent of EtOH and hexane (1:1; 20 mL) in the presence of 0.3 g of the catalyst and 30% H₂O₂ (100 mmol) aq.

3. Results and discussion

3.1. Catalyst preparation and characterization

The PMoV/Fe₃O₄/g-C₃N₄ nanocomposite was fabricated by the following procedure. First, the g-C₃N₄ sheets were ultrasonically dispersed in water and then Fe salts were added. The Fe ions were converted into Fe₃O₄ nanoparticles with controlled growth in the presence of ammonia as a precipitating agent. As a result, finely distributed and uniform Fe₃O₄ nanoparticles were effectively deposited on the surface of the g-C₃N₄ sheets to give the Fe₃O₄/g-C₃N₄ nanocomposite, which was then used as a support for the immobilization of PMoV. The in situ growth mechanism also prevented the aggregation of the Fe₃O₄ nanoparticles. The Keggin units of PMoV connect to the g-C₃N₄ sheets by forming covalent Mo–O–C bonds as a result of the interactions between either terminal Mo=O bonds or bridge Mo–O–Mo bonds within the Keggin units and the NH₂ groups on the edge of C₃N₄ sheets. Hydrogen bonding or acid–base interactions may also play a role.

Fig. 1 illustrates the FT-IR spectra of Fe₃O₄/g-C₃N₄, PMoV/Fe₃O₄/g-C₃N₄ and the recovered PMoV/Fe₃O₄/g-C₃N₄ nanocomposites. In the spectrum of Fe₃O₄/g-C₃N₄, the bands in the range of 1200–1700 cm^{−1} correspond to the stretching vibrations of the C–N and C=N bonds in the g-C₃N₄ heterocycles [35]. The broad absorption band at 3000–3500 cm^{−1} is at-

Fig. 1. FT-IR spectra of Fe₃O₄/g-C₃N₄ (1), PMoV/Fe₃O₄/g-C₃N₄ (2) and recovered PMoV/Fe₃O₄/g-C₃N₄ (3).

Fig. 2. Magnetization curves for Fe₃O₄/g-C₃N₄ (1) and PMoV/Fe₃O₄/g-C₃N₄ (2).

tributed to the stretching vibrational modes of the primary (=NH) and secondary (–NH) amines on the g-C₃N₄ aromatic rings [36]. Furthermore, the two characteristic peaks at around 650 and 485 cm^{−1} are assigned to the stretching vibrations of the Fe–O bond [37]. In the spectrum of PMoV/Fe₃O₄/g-C₃N₄, the vibrational modes of PMoV at 1163, 1038, 944 and 854 cm^{−1} are attributed to P–O, Mo=O_a, Mo–O_b and Mo–O_c, respectively. The characteristic bands for Fe₃O₄/g-C₃N₄ are found at the same wavenumbers in the spectrum of PMoV/Fe₃O₄/g-C₃N₄, with a small shift corresponding to the interaction between the support and the PMoV. The characteristic FT-IR bands of the recovered PMoV/Fe₃O₄/g-C₃N₄ nanocomposite are similar to those of the fresh nanocomposite, which means that the principal structure of the catalyst is retained after use.

Plots of the magnetization versus the applied external magnetic field for the as-prepared Fe₃O₄/g-C₃N₄ and PMoV/Fe₃O₄/g-C₃N₄ magnetic nanocomposites at room temperature are shown in Fig. 2. The saturated magnetization values for the Fe₃O₄/g-C₃N₄ and PMoV/Fe₃O₄/g-C₃N₄ nanocomposites are about 65 and 35 emu/g, respectively. There is no hysteresis, which suggests that this magnetic nanocatalyst has a superparamagnetic character. It is clear that the saturated magnetization value of Fe₃O₄/g-C₃N₄ was reduced in the presence of PMoV, thus confirming the presence of nonmagnetic materials on the surface of the g-C₃N₄.

Fig. 3 illustrates the excellent and easy separation of the

Fig. 3. Separation of the PMoV/Fe₃O₄/g-C₃N₄ nanocatalyst from the reaction mixture using an external magnet. (a) at the start of the reaction; (b) after completion of the reaction.

Fig. 4. Potentiometric titration curves (a) and cyclic voltammograms (b) of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ and $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$.

magnetic nanocatalyst from the solution using an external magnet. It can thus be concluded that magnetization of the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite is sufficient to magnetically separate the nanocatalyst from the reaction solution.

Investigation of the acidity of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ was performed by potentiometric titration with *n*-butylamine (Fig. 4(a)). The nature of the support and the type of HPA are believed to affect the acidity of the supported HPA. The initial electrode potential (E_i) demonstrates the maximum strength of the acid sites. In addition, the value at which the plateau is reached (mmol amine/g solid, n) indicates the total number of acid sites that are present in the titrated solids [38]. The acidic strength of the acid sites is classified according to the following scale: $E_i > 100$ mV (very strong acid sites), $0 < E_i < 100$ mV (strong acid sites), $-100 < E_i < 0$ mV (weak acid sites) and $E_i < -100$ mV (very weak acid sites) [39]. According to this scale, the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ magnetic catalyst presents very strong acid sites ($E_i = 204$ mV), whereas $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ presents weaker acid sites ($E_i = 63$ mV). Immobilization of PMoV on the support led to an increase in both the acid strength (E_i) and the total number of acid sites (n) due to the dispersion of the PMoV anions on the support. As a bifunctional catalyst, $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ provides two different properties, namely Brönsted acidity and electron transfer properties. To investigate the electron transfer behavior of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, we studied the electrochemical behavior of the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ and $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites. Fig.

4(b) illustrates the cyclic voltammetry (CV) responses of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ and $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ -modified glassy carbon electrodes in a phosphate buffer solution at pH = 5. In the voltammogram of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, Fe_3O_4 shows two sharp and well-defined redox waves that correspond to the reversible reduction/oxidation processes [40]. A sharp cathodic peak at around -0.28 V, which clearly corresponds to the reduction of Fe^{3+} to Fe^{2+} (Eq. (1)), and an anodic peak at approximately 0.15 V, which corresponds to the oxidation of Fe^{2+} by HPO_4^{2-} (Eq. (2)), could be detected.

Two pairs of reversible redox peaks were observed in the potential range between $E = -0.9$ V and $E = 0.2$ V for the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ -modified electrode [41]. These can be attributed to the electron-transfer reactions of the $\text{Mo}^{5+}/\text{Mo}^{4+}$, $\text{Mo}^{4+}/\text{Mo}^{3+}$ couples, and further confirm that the two-electron exchange is accompanied by two protonation reactions in the $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ heteropolyanion reduction process. The electron exchange process can therefore be assigned as follows (Eq. (3)):

Comparing the CV of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ with that of $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, we can deduce that the presence of the PMoV species facilitates the oxidation and reduction of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ in catalytic cycles of the desulfurization reaction.

The morphological evolution of the as-prepared $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite can be confirmed by SEM and TEM observation, as presented in Fig. 5. Fig. 5(a) shows the TEM image of the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite. It is clear that spherical particles of Fe_3O_4 and PMoV with average diameters of about 23 nm are deposited on the $\text{g-C}_3\text{N}_4$ sheets. Microstructure measurement was performed by measuring particle sizes at several spots in the TEM image to obtain a histogram of the size distribution of the nanocomposite particles. Deposition of the Fe_3O_4 and PMoV nanoparticles on the $\text{g-C}_3\text{N}_4$ sheets was also confirmed by the SEM image of the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite (Fig. 5(b)).

The crystal structures of the samples were investigated using powder XRD diffraction patterns. Fig. 6(a) shows the typical XRD patterns of the as-prepared $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$, $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ and recovered $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposites. The strong peak at 27.41° corresponds to the characteristic inter-planar stacking of the conjugated aromatic systems and the inter-layer structural packing of $\text{g-C}_3\text{N}_4$ [42]. Peaks are observed at $2\theta = 30.2^\circ, 35.5^\circ, 43.2^\circ, 53.4^\circ, 57.3^\circ$ and 62.6° for the Fe_3O_4 crystal phase [43]. The $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ contains the important characteristic peaks of pure PMoV (at $2\theta = 12.5^\circ$ and 25.5°). The presence of these peaks confirms our FT-IR spectroscopic results, which suggested that there was no significant variation in the structure of PMoV during the preparation of the nanocatalyst. When the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite was recovered, the diffraction pattern was similar to that of fresh $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$. This lack of change in the diffraction pattern confirms that the structure is retained even after recovery and reuse.

Fig. 5. TEM image with particle size distribution histogram (a) and SEM images of the PMoV/Fe₃O₄/g-C₃N₄ nanocatalyst (b).

The compositions of the PMoV/Fe₃O₄/g-C₃N₄ and recovered PMoV/Fe₃O₄/g-C₃N₄ nanocomposites were determined by EDX

Fig. 6. (a) XRD patterns of Fe₃O₄/g-C₃N₄, PMoV/Fe₃O₄/g-C₃N₄, and recovered PMoV/Fe₃O₄/g-C₃N₄ nanocatalysts. EDX spectra of PMoV/Fe₃O₄/g-C₃N₄ (b) and recovered PMoV/Fe₃O₄/g-C₃N₄ nanocatalysts (c).

analysis (Fig. 6 (b), and (c)). The peaks of the as-prepared nanocomposite clearly correspond to C, Fe and Mo with molar ratios of 9.13%, 21.01% and 47.12% respectively. Therefore, similarly to the results obtained from the XRD patterns, EDX also confirms that particles of Fe₃O₄ and PMoV were anchored on the g-C₃N₄ sheets. The EDX analysis of the recovered PMoV/Fe₃O₄/g-C₃N₄ nanocomposite is presented in Fig. 6(c). The presence of Fe₃O₄, PMoV and the g-C₃N₄ sheets as constituents of the PMoV/Fe₃O₄/g-C₃N₄ nanocomposite after reuse was confirmed with EDX analysis. Moreover, the molar ratios of C, Fe and Mo were 10.3%, 23.2% and 40.1%, respectively. The decrease in the percentage of Mo could be due to leaching of the initial PMoV content into the reaction mixture.

3.2. Catalytic reactions

The activity of the magnetic nanocatalyst was demonstrated by oxidation of various sulfides to the corresponding sulfoxides and sulfones in the presence of hydrogen peroxide as an oxidant. The influence of different reaction parameters, including the solvent system, amount of catalyst and H₂O₂/MPS (O/S) molar ratio was evaluated for a model system, the selective oxidation of MPS to methyl phenyl sulfoxide (MPSO) in the presence of PMoV/Fe₃O₄/g-C₃N₄ (Scheme 1, Fig. 7), to study the various factors affecting the selectivity and efficiency of the catalyst. First, the effect of the solvent system on the product conversion was investigated (Fig. 7(a)). The results indicated that the use of a non-polar solvent, such as hexane, was unfavorable for this conversion. The best conversion data were found in the presence of MeCN and EtOH: hexane. The biphasic solvent system EtOH/hexane was selected as the best solvent system for two reasons. First, ethanol is the most suitable solvent for extraction because it is derived from agricultural

Scheme 1. Model reaction.

Fig. 7. Effect of (a) solvent (1 mmol MPS, O/S ratio = 4:1, catalyst amount = 0.01 g, room temperature), (b) catalyst amount (O/S ratio = 4:1, reaction time = 10 min, room temperature), and (c) molar ratio of $\text{H}_2\text{O}_2/\text{MPs}$ (catalyst amount = 0.01 g, reaction time = 10 min, room temperature) on the selective oxidation of MPS to MPSO in the presence of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$.

products and is renewable, biologically less objectionable in the environment and less toxic than acetonitrile. Second, as a non-polar solvent with a texture similar to that of the model oil, hexane holds promise for application in the ODS process. As shown in Fig. 7(b), the quantity of the catalyst used for the oxidation of MPS to MPSO was optimized. When 0.01 g of the nanocatalyst was used, MPSO was obtained in high yields. Decreasing the amount of catalyst to 0.005 g resulted in a lower conversion. Catalyst quantities above 0.01 g led to lower selectivity for MPSO. The effect of the O/S ratio was also investigated (Fig. 7(c)). At an O/S ratio of 3:1, the yield of MPSO was low, but when the ratio was increased to 4:1 the yield increased to 95% with 96.9% selectivity. Further increases in the O/S ratio (to 6:1 and 8:1) resulted in a lower selectivity for MPSO. Thus, O/S = 4:1 was chosen as the optimized ratio for MPSO production. Finally, the reusability of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ was investigated using the conditions for method a (see the Experimental section) (Fig. 8), and excellent yields were still obtained after the

Fig. 8. Reusability of $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ in the model reaction (under the conditions for method a).

fourth run (90% yield of MPSO after 20 min).

To understand the reason for the lower rate of sulfur removal when using the recycled catalyst, leaching of the active site in the model reaction was studied by ICP-AES. The results show that 12% of the initial PMoV content leached into the reaction mixture over four successive runs, and this was confirmed by EDX analysis.

The results from the acidity and CV measurements shown in Fig. 4(b) suggest that the catalyst can catalyze the reaction via two different pathways, through its Brønsted acid and electron transfer abilities.

We attempted to selectively produce sulfone MPSO_2 as the main product by increasing the temperature to 60 °C (Fig. 9(a)); however, selectivity was not achieved without increasing the O/S ratio. When the O/S ratio was increased to 8:1, the yield of MPSO_2 was also increased (Fig. 9(b)). In addition, increasing the catalyst quantity from 0.01 to 0.02 g also led to an increase in the selectivity of the reaction (95% selectivity for MPSO_2) (Fig. 9(c)).

Encouraged by these results; we subjected a series of sulfides to oxidation under the optimized conditions for sulfoxide or sulfone formation (Tables 1 and 2). The experimental results show that various types of liquid sulfides could be oxidized to the corresponding sulfoxides with excellent selectivities (Table 1).

We also tested the reactions of various liquid and solid sulfides at 60 and 80 °C and with O/S ratio = 8:1 and 10:1, respectively. The obtained results show that various types of sulfides could be oxidized into their corresponding sulfones with excellent selectivities (Table 2).

Based on the above results, the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite was used in the ODS reaction for a model oil containing DBT, one of the major sulfur-containing compounds present in fuels. Model oils with various sulfur concentrations were used, and the reaction was carried out in 5 mL of a mixed solvent of EtOH and hexane (Fig. 10). The $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite catalyst efficiently oxidized the model DBT-containing oils with sulfur concentrations of up to 1000 ppm. A concentration of 1000 ppm DBT was selected for further experiments.

It is accepted that nitrogen-containing compounds have a negative effect on the ODS process. To clarify the effects of nitrogen-containing compounds, we investigated the behavior of

Fig. 9. Effect of (a) temperature (catalyst amount = 0.01 g, O/S ratio = 4:1, reaction time = 10 min), (b) molar ratio of H₂O₂ (catalyst amount = 0.01 g, reaction time = 10 min, 60 °C) and (c) catalyst amount (O/S ratio = 4:1, reaction time = 10 min, 60 °C) in the selective oxidation of MPS to MPSO₂.

quinoline, indole, pyridine and pyrrole in the oxidation system (Fig. 11(a)). The nitrogen-containing compounds were oxidized to the corresponding products in short reaction times (about 20 min). The reaction rate for the oxidation of DBT in the presence of these nitrogen-containing compounds decreased in the order: indole > quinoline > pyrrole > pyridine. These results thus suggest that nitrogen-containing compounds have a negative effect on the ODS process owing to competition with the sulfides for adsorption on the catalytic sites, as well as their basic character. However, this negative effect is minimal. To verify the effect of co-solvents on the reaction, ODS of the model oil was carried out using various one-ring aromatic compounds (toluene, xylene, mesitylene and benzene) and the two-ring aromatic hydrocarbon naphthalene as co-solvents under optimized reaction conditions (40% v/v ratio of co-solvent to mixture) (Fig. 11(b)). The one-ring aromatic compounds had a positive effect on ODS conversion.

Table 1

Selective oxidation of liquid sulfides to sulfoxides with 30% H₂O₂ aq. using Fe₃O₄/g-C₃N₄/PMoV as a catalyst *.

		$\text{R}-\text{S}-\text{R}' \xrightarrow[\text{H}_2\text{O}_2]{\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4/\text{PMoV}} \text{R}-\text{S}(=\text{O})-\text{R}' + \text{R}-\text{S}(=\text{O})_2-\text{R}'$		
Entry	Sulfide	Time (min)	Isolated yield (%)	
			Sulfoxide	Sulfone
1		10	95	3
2		5	96	2
3		10	90	5
4		10	94	2
5		25	90	7
6		35	90	5

* Method a.

Table 2

Selective oxidation of sulfides to sulfones with 30% H₂O₂ aq. using PMoV/Fe₃O₄/g-C₃N₄ as a catalyst.

		$\text{R}-\text{S}-\text{R}' \xrightarrow[\text{H}_2\text{O}_2]{\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4/\text{PMoV}} \text{R}-\text{S}(=\text{O})-\text{R}' + \text{R}-\text{S}(=\text{O})_2-\text{R}'$		
Entry	Method	Sulfide	Time (min)	Isolated yield (%)
				Sulfoxide Sulfone
1	b		10	3 95
2	b		5	6 92
3	b		10	4 94
4	b		5	3 95
5	b		30	7 91
6	b		45	8 90
7	b		50	7 90
8	c		60	5 90
9	c		65	6 92
10	c		70	2 93
11	c		65	4 90
12	—		120	5 50
13	—		120	5 45

The reaction rate for the oxidation of DBT decreased in the order toluene > xylene > benzene > mesitylene, in agreement with the increasing steric hindrance in these compounds. It should be noted that the two-ring aromatic compound naphthalene had a negative effect on the ODS reaction and reduced the reaction rate. This negative effect is attributed to the greater steric hindrance from the two aromatic rings.

The activity of the PMoV/Fe₃O₄/g-C₃N₄ nanocomposite in the presence of H₂O₂ was evaluated in the ODS of real oil. Under optimum conditions, 24.3% and 29.8% of the sulfur was re-

Fig. 10. Effect of dibenzothiophene concentration on the ODS reaction of dibenzothiophene (under the conditions of method c).

Fig. 11. (a) Comparison of the ODS reaction of DBT in the presence of different nitrogen-containing compounds (DBT concentration = 1000 ppm, nitrogen-containing compound concentration = 60 ppm, method c); (b) ODS reaction of DBT in the presence of various aromatic compounds (40% v/v) as co-solvent (DBT concentration = 1000 ppm, method c).

moved from real oil with sulfur contents of 500 and 1900 ppm, respectively.

The proposed mechanism for the ODS reaction is shown in Scheme 2. The catalytic behavior of polyoxometallic anions has previously been demonstrated [44–47]. In the first step, $\text{PMo}_{10}\text{V}_2\text{O}_{40}^{5-}$ in the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ catalyst is oxidized by H_2O_2 (step 1). After removal of one water molecule, the heteropolyanion peroxide is produced in the next step (step 2). Subsequently, the heteropolyanion peroxide reacts with DBT in step 3. During this step the corresponding sulfone of DBT is generated and the original state of the catalyst is restored in final step (step 4).

4. Conclusions

In summary, a $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite has been successfully prepared by a simple, effective and reproducible method. The structure, morphology, electrochemical

Scheme 2. Proposed mechanism for the ODS reaction with a $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ catalyst in the presence of H_2O_2 .

behavior and magnetic properties of the nanocomposite were investigated using XRD, FT-IR spectroscopy, EDX spectroscopy, SEM, TEM, CV, ICP-AES and vibrating sample magnetometry techniques. The nanocomposite catalyst showed high catalytic activity and good selectivity for the oxidation of sulfides to the corresponding sulfoxides or sulfones under mild reaction conditions. This catalyst also showed excellent activity in the removal of sulfur from DBT-containing model oil and from real oil containing 500 and 1900 ppm of sulfur compounds. The effect of quinoline, indole, pyridine and pyrrole as nitrogen-containing compounds on ODS activity was also investigated. In the presence of these compounds, the overall ODS activity was slightly reduced owing to competitive oxidation between the sulfur- and nitrogen-containing compounds. Nevertheless, this negative effect was low. The addition of aromatic co-solvents such as toluene, xylene, benzene, mesitylene or naphthalene on the ODS reaction was also investigated. Most importantly, the $\text{PMoV}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ nanocomposite could be recovered using an applied magnetic field and reused without significant loss of catalytic activity even after four successive cycles. Therefore, this nanocomposite can be considered a promising catalytic material for environmental applications.

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Graphical Abstract

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Synthesis and characterization of PMoV/Fe₃O₄/g-C₃N₄ from melamine: An industrial green nanocatalyst for deep oxidative desulfurization

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H₅PMo₁₀V₂O₄₀ was supported on a Fe₃O₄/g-C₃N₄ magnetic support to produce a PMoV/Fe₃O₄/g-C₃N₄ nanocomposite. This catalyst was characterized and used for selective oxidative desulfurization of sulfides. Oxidation of dibenzothiophene-containing model oils and real oil was also studied under optimized reaction conditions. Moreover, the effects of various nitrogen-containing compounds and aromatic hydrocarbons on dibenzothiophene removal were investigated.

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从三聚氰胺制得工业用深度脱硫的绿色纳米催化剂 $\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$: 合成与表征

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摘要: 采用简便的化学浸渍法制备了新型磁性可分离的纳米复合物 $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ ($\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$), 并进行了详细的表征, 采用电位滴定法测定了催化剂酸性. 该 $\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ 纳米复合物在硫化物选择氧化为砷或亚砷的反应中表现出较高的催化活性; 考察了在优化反应条件下, 它在含硫(包括二苯并噻吩DBT)模拟油或真实石油的催化氧化反应中的催化性能; 特别考察了各种含氮化合物, 以及1-环和2-环芳香烃作为共溶剂对DBT脱硫效果的影响. 采用外加磁场即可方便地将该催化剂从反应混合物中分离和回收. 选取最好的萃取剂, 通过简单的倾滤就可很容易地将剩余反应物从产物中分离出来. 该纳米催化剂具有高催化活性, 且容易重复使用, 至少可以重复使用4次而未见催化活性明显下降.

关键词: 石墨化氮化碳; 纳米复合物; 三聚氰胺; 杂多酸; 氧化脱硫; 石油

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