Magnetically Recoverable Heterogeneous Catalyst: Tungstate Intercalated Mg–Al-Layered Double Hydroxides-Encapsulated Fe_3O_4 Nanoparticles for Highly Efficient Selective Oxidation of Sulfides with H_2O_2

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Abstract High catalytic activity of tungstate intercalated in hydrotalcite-encapsulated magnetic Fe_3O_4 nanoparticles have been prepared. High resolution transmission electron microscopy characterization demonstrated the formation of Fe_3O_4 nanoparticles within LDH matrix with a mean diameter of 1–3 nm. The catalyst of $WO_4^{2-}/LDH@Fe_3O_4$ exhibited excellent catalytic activity for the oxidation of various sulfides. The magnetic properties of the $WO_4^{2-}/$ LDH@Fe_3O_4 provided a convenient route for separation of the catalyst from the reaction mixture by application of an external permanent magnet. The spent catalyst could be recycled without appreciable loss of catalytic activity.

Keywords Hydrotalcite · Magnetic separation · Sulfides oxidation · Hydrogen peroxide

1 Introduction

Selective oxidation of sulfides to sulfoxides is an attractive and important reaction in organic chemistry, since sulfoxides are useful synthetic intermediates for the preparation of various chemically and biologically molecules, especially drugs and natural products [1–5]. Conventionally, this transformation is achieved using stoichiometric amounts of both organic and inorganic reagents, which inevitably lead to large volume of hazardous wastes [6–9]. Therefore, it is of great significance to develop new, efficient, highly selective, and widely applicable methods for this transformation under mild reaction conditions.

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The use of H_2O_2 as final oxidant has been very attractive. Aqueous H_2O_2 offers the advantages that it is a cheap, environmentally benign, and readily available reagent and produces waters as the only byproduct [10, 11]. These features have stimulated the development of useful procedures for H_2O_2 oxidation of sulfides, especially with various types of catalyst systems [12–15].

Recently, various types of tungsten-based heterogeneous catalysts such as silica-based tungstate interphase catalyst [16], tungstate nanoparticles on MCM-48 [17], silicatungstate core–shell nanoparticles [18] and Keggin heteropolycompounds [19] have been reported for the selective oxidation reaction with H_2O_2 as oxidant. Although these catalysts showed good activity, tedious procedures such as centrifugation and filtration were required for the recycle of catalysts, which inevitably lead to loss of solid catalyst in the separation process.

Magnetic separation provides a convenient method for removing and recycling magnetized species by applying an appropriate magnetic field. This technique may prevent the agglomeration of the catalyst particles during recovery and can increase the durability of the catalysts. In recent years, magnetic composites with core–shell structure have received growing attention owing to their unique properties and potential applications in various fields, such as catalysis, drug targeting and release and magnetic separation [20–28]. Various kinds of materials have been coated on the magnetic nanoparticles, such as hydroxyapatite [20– 22], mesoporous silica [23–27] and nonporous silica [28].

Mg–Al layered double hydroxides (Hydrotalcite, LDH) with ideal molecular formula $Mg_6Al_2(OH)_{16}CO_3$, possessing brucite-like octahedral layers with anions and water molecules occupying the interlayer space, are currently attracting intense research interest because of their novel properties such as good ion exchange ability and layered



Scheme 1 Preparation of WO₄²⁻/LDH@Fe₃O₄

structure [29–31].Recently, intense research interests have focused on accommodation of magnetic nanocrystallites into LDHs matrix. Presently, these novel magnetic LDH composites have been prepared and used in different areas such as catalysts [32, 33], luminescence [34] and drug delivery [35, 36].

In this work, LDH coated ultrafine and uniform Fe_3O_4 core–shell particles were synthesized and WO_4^{2-} was introduced into the layers of LDH by anion exchange. These magnetic composites were employed as highly active and reusable catalysts using magnetic separation for selective oxidation of sulfides to sulfoxides with 30 wt% hydrogen peroxide as oxidant.

2 Experimental

FeCl₂·4H₂O, FeCl₃·6H₂O, 25 wt% NH₄OH solution, $Mg(NO_3)_2$, $Al(NO_3)_3$, NaOH, Na₂CO₃, 30 wt% H₂O₂ and CH₃OH were of analytical grade and were used as received. Sulfides were purchased from Aldrich and Fluka without further purification.

2.1 Catalysts Preparation

The synthesis procedure is represented in Scheme 1. The detailed procedure was as follows. Firstly, FeCl₂·4H₂O and $FeCl_3 \cdot 6H_2O$ ($Fe^{3+}/Fe^{2+} = 2$) were dissolved in deionized water under N₂ atmosphere at room temperature. Then 25 wt% NH₄OH solution were added dropwise to the resulting solution under vigorous stirring to adjust the pH to 10, and a black Fe₃O₄ precipitate was produced instantly. In order to obtain small and uniform Fe₃O₄ particles, the drop rate was precisely controlled by constant dropper. After 15 min, 100 ml of Mg(NO₃)₂ and Al(NO₃)₃ solution (Mg/Al = 3) and 100 ml NaOH and Na₂CO₃ solution were added dropwise to the obtained Fe₃O₄ precipitate solution over 60 min under vigorous stirring, and the resulting solution was heated to 80 °C. After 8 h, the mixture was cooled to room temperature and aged overnight without stirring. The obtained precipitate was filtered, washed with deionized water till neutrality, and dried at 80 °C under vacuum for 12 h. The obtained sample was designated as LDH@Fe₃O₄.

The obtained LDH@Fe₃O₄ sample was calcined at 480 °C under N₂ protection for 4 h to remove CO_3^{2-} and water, and the LDH structure was destroyed simultaneity. Finally, the calcined sample was dispersed into a aqueous solution of Na₂WO₄ for 24 h to recover its LDH structure and in the same time absorb the WO₄²⁻ anions into the layers. Then, the product designated as WO₄^{2-/} LDH@Fe₃O₄ was collected by filtration and washed with deionized water, then dried under vacuum overnight.

2.2 Catalysts Characterization

The powder X-ray diffraction (XRD) was carried out on a PANalytical X'pert Pro Diffractometer. The BET surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. The Fourier transform infrared spectroscopy (FT-IR) measurements were carried out with a Bruker IFS 120HR FT-TR spectrometer, using KBr pellet technique. HRTEM micrographs were obtained with a JEM-2010 electron microscope. Magnetic properties were characterized by a VSM by Lakeshore 7304.

2.3 Catalytic Tests

To test the catalytic activity of $WO_4^{2-}/LDH@Fe_3O_4$, we selected the oxidation of thioanisole with 30 wt% H₂O₂ as model reaction. In a typical experiment, a mixture of substrate (2 mmol), 30 wt% H₂O₂ (6 mmol) and $WO_4^{2-}/LDH@Fe_3O_4$ (100 mg) in 10 ml methanol was stirred at room temperature for 6 h. After reaction, the catalyst was collected by an external magnet and washed repeatedly with methanol for next run. The resulting solution was treated with MnO₂ and anhydrous MgSO₄ for GC–MS and GC analyses. Qualitative analysis was conducted with a HP 6890/5973 GCMS with Chemstation and the NIST mass spectral database. Quantitative analysis was conducted with an Agilent 6820 GC equipped with an FID.

3 Results and Discussion

3.1 Catalysts Characterization

The N₂ adsorption–desorption isotherm of the $WO_4^{2-/}$ LDH@Fe₃O₄ is shown in Fig. 1. The isotherm exhibited a gradual increase in the amount of adsorbed N₂ with a hysteresis loop in rang of relative pressure from 0.6 to 1. According to the IUPAC, it can be classified as a type IV isotherm with a type III hysteresis hoop, indicating the existence of mesopores, which could be came from the



Fig. 1 N₂ adsorption-desorption isotherm for WO₄²⁻/LDH@Fe₃O₄

mesopores between the nanoparticles of the sample. The BET surface area of the obtained sample was found to be $91 \text{ m}^2/\text{g}$.

The XRD patterns of pure LDH, LDH@Fe₃O₄, sample after calcination and WO₄²⁻/LDH@Fe₃O₄ are shown in Fig. 2. As it shown in Fig. 2, compared with the pure LDH, the sample of LDH@Fe₃O₄ also exhibited characteristic diffraction peaks of hydrotalcite at around 11.4°, 22.9°, 34.7° , 38.8° , 45.9° , 60.6° and 61.9° , corresponding to the (003), (006), (012), (015), (018), (110) and (113) reflections, indicating the successful coating hydrotalcite on the Fe₃O₄ particles. The intensity of diffraction peaks for the LDH@Fe₃O₄ is lower than that of pure LDH, presumably due to the smaller size of the particles. The characteristic diffraction peaks of Fe₃O₄ were not found in the LDH@Fe₃O₄, which can be ascribed to the small size of the Fe₃O₄ particles in the sample. It can be clearly seen that the LDH structure was destroyed after calcination for the fact that the sample of after calcination did not show any diffraction peak of hydrotalcite other than that from the Fe₃O₄, suggesting the transformation of the Mg–Al LDH shell to amorphous mixed metal oxides. The LDH@Fe₃O₄ possessed versatile anion loading capability after calcination due to the unique property called "memory effect" of the hydrotalcite [37], which makes it ideal support for recoverable anionic functional material. Herein, we chose WO_4^{2-} as the structure recovery anion. After structure recovery by WO₄²⁻, the sample of WO₄²⁻/LDH@Fe₃O₄ became crystalline again, and four characteristic diffraction peaks (003, 006, 110 and 113) of hydrotalcite were appeared, implying the reconstruction of the LDH structure. Furthermore, compared to LDH@Fe₃O₄, the main (003) diffraction peak of WO₄²⁻/LDH@Fe₃O₄ shifted to lower angle, confirming the increasing of interlayer space, which was due to the larger ionic radius of WO_4^{2-}



Fig. 2 XRD patterns of *a* pure LDH, *b* LDH@Fe₃O₄, *c* after calcination, and $d \text{ WO}_4^{2-}/\text{LDH}@\text{Fe}_3\text{O}_4$ (*filled diamond* diffraction peaks of Fe₃O₄)



Fig. 3 FT-IR spectra of *a* LDH@Fe₃O₄, *b* after calcination, $c WO_4^{2-}/LDH@Fe_3O_4$

compared to CO_3^{2-} , indicating WO_4^{2-} was successfully inserted into the lays of the LDH in our process.

The FT-IR data shown in Fig. 3 are additional evidence for the chemical and structural modifications of the sample. There were two strong adsorption bands at 1,630 and at 3,400 cm⁻¹ for all the samples, which are attributable to the stretching and bending vibrations of water molecules in hydrotalcite structure. The band at 1,360 cm⁻¹ for the sample of LDH@Fe₃O₄ can be assigned as a vibration mode of carbonate ions in the layer. After calcination, this band disappeared, indicating the removal of interlayer ions of carbonate and the collapse of LDH layers during the calcination. Compared to LDH@Fe₃O₄ and the sample of after calcination, three additional peaks at 1,059, 801, and 760 cm⁻¹ for the sample of WO₄²⁻/LDH@Fe₃O₄ Fig. 4 HRTEM images of

WO₄²⁻/LDH@Fe₃O₄



Fig. 5 The magnetic hysteresis loops of LDH@Fe_3O_4 and WO_4^2-/ LDH@Fe_3O_4

appeared. All these bands can be ascribed to the vibration mode of WO_4^{2-} [38], indicating the inserting of WO_4^{2-} into the layers, which is consistent with the XRD results.

The morphological and structural features of $WO_4^{2-1}/LDH@Fe_3O_4$ were further examined by HRTEM. Fig. 4a gives clear image that Fe_3O_4 particles were coated with a layer LDH. The Fe_3O_4 nanopaticles (*black dot*) were found to be uniformly distributed within the host LDH matrix (*grey area*) and have a small particle size of around 1–3 nm. Moreover, Fig. 4b shows that $WO_4^{2-1}/LDH@Fe_3O_4$ has a typical layer structure of LDH with layer space of around 1 nm, again confirming the successful structure recovery by WO_4^{2-1} , which is in agreement with the XRD results.

The magnetic properties of LDH@Fe₃O₄ and WO₄^{2-/} LDH@Fe₃O₄ were investigated using a superconducting quantum interface device magnetometer. As shown in Fig. 5, the isothermal magnetization curve of LDH@Fe₃O₄



Table 1 The oxidation of thioanisole using various catalysts

Entry	Catalyst	Yield (%) ^a
1	Blank	No reaction
2	LDH@Fe ₃ O ₄	No reaction
3	WO ₄ ²⁻ /LDH@Fe ₃ O ₄	1st 89
		2nd 87
		3rd 88
		4th 86
		5th 85

Reaction conditions: 2 mmol substrate, 100 mg catalyst, 10 ml CH₃OH, 0.66 ml (6 mmol H_2O_2) of 30 wt% H_2O_2 , room temperature, 6 h

^a Determined by GC using an internal standard technique

increased rapidly with increasing applied magnetic field, with a saturation magnetization (M_s) value of 8 emu/g. The magnetic hysteresis was absent in low magnetic field region for the sample of LDH@Fe₃O₄, indicating the superparamagnetism of the sample. Compared to LDH@Fe₃O₄, there was no distinct difference in magnetic properties for the sample of WO₄²⁻/LDH@Fe₃O₄, suggesting there was no formation of ferromagnetic iron oxides such as α -Fe₂O₃ and γ -Fe₂O₃ during the process of calcination.

3.2 Catalytic Activity

The catalytic activities of various catalysts for the oxidation of thioanisole are shown in Table 1. In the absence of catalyst (entry 1), no reaction happed. Since the LDH@Fe₃O₄ gave the same result as that of no catalyst, LDH@Fe₃O₄ was not active for this reaction. However, when the reaction was conducted in the presence of the $WO_4^{2-}/LDH@Fe_3O_4$, the main product of methyl phenyl sulfoxide was efficiently formed in good yields, indicating WO_4^{2-} was the active component (entry 3). The catalyst of 6 h

LDH@Fe₃O₄ Entry Sulfide Yield/%^a 1 $\int S = 85$ 2 $\int S = 93$ 3 $\int S = 93$ 4 $\int S = 5$ 4 $\int S = 5$ 5 $\int S = 5$ 9 $\int S = 5$ 80 4 $\int S = 5$ 89

Table 2 The oxidation of different sulfides by the catalyst of WO_4^{2-1}

Reaction conditions: 2 mmol substrate, 100 mg catalyst, 10 ml CH_3OH , 0.66 ml (6 mmol H_2O_2) of 30 wt% H_2O_2 , room temperature,

^a Determined by GC using an internal standard technique

 $WO_4^{2-}/LDH@Fe_3O_4$ exhibited good performance in recycling, with no remarkable loss of activity after five times using (entry 3), indicating the slow deactivation of the catalyst. ICP analysis of the filtrate after reaction confirmed that tungstate contents were negligible. Also, it should be noted that our catalyst provided a simple way for the separation of the catalyst from the reaction mixture due to the heterogeneous nature and magnetic properties of the catalyst.

The WO₄²⁻/LDH@Fe₃O₄ catalyst can be applied for oxidation of a wide range of aryl and alkyl sulfides to corresponding sulfoxides with 30 wt% H₂O₂ as oxidant (Table 2). The catalyst seemed to be more active to the aryl alkyl sulfides with bigger alkyl (entries 1 and 2). The formation of sulfoxides from diaryl sulfide was relatively difficult to achieve (entry 3), probably due to the sterically hindrance. Compared to aryl alkyl sulfides, the catalyst was more effective to dialkyl sulfide (entry 5).

4 Conclusions

In this work, we have described a new magnetically recyclable and efficient nanocomposite catalyst for the oxidation of sulfides based on tungstate intercalated Mg–Al hydrotalcite-encapsulated Fe_3O_4 nanocrystallites. This catalyst exhibits several attractive features for practical applications. Firstly, Fe_3O_4 nanoparticles processed small particles size of 1–3 nm. Secondly, the magnetic core was isolated and protected by hydrotalcite, making its use under harsh reaction conditions possible. Thirdly, the magnetic

core could be readily utilized for the easy recovery and recycling of the catalyst with no significant loss of catalytic activity. Therefore, we expect this magnetic nanocomposite catalyst to find applications in many other industrially important catalytic processes such as catalytic oxidative desulfurization of gasoline.

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