

Research Article

Preparation of FeO(OH) Modified with Polyethylene Glycol and Its Catalytic Activity on the Reduction of Nitrobenzene with Hydrazine Hydrate

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Abstract

Iron oxyhydroxide was prepared by dropping ammonia water to Fe(NO₃)₃·9H₂O dispersed in polyethylene glycol (PEG) 1000. The catalyst was characterized by X-ray powder diffraction, Fourier transform infrared spectroscopy and laser particle size analyzer. The results showed the catalyst modified with polyethylene glycol was amorphous. The addition of PEG during the preparation make the particle size of the catalyst was smaller and more uniform. The catalytic performance was tested in the reduction of nitroarenes to corresponding amines with hydrazine hydrate, and the catalyst showed excellent activity and stability. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: iron oxyhydroxide; hydrazine hydrate; nitroarenes; reduction; aniline

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1. Introduction

Aromatic amines are important intermediates in organic synthesis, which are widely used in production of agricultural chemicals, medicines, dyes, additive, surfactants and textile assistants. The major ways of reduction aromatic nitro compounds to aromatic amines include metal/acid reduction, sodium sulfide reduction, catalytic hydrogenation and catalytic transfer hydrogenation (CTH) [1,2]. Reduction with metal/acid is one of the most vigorous reduction methods, however, many byproducts are also produced. The sodium sulfide reduction is a selective and mild method, but it is ac-

companied by the production of a large amount of waste products that have to be disposed in an ecologically unfavorable way. The catalytic hydrogenation is suitable for most large-scale aromatic amines with high yields and without the production of waste products. Because of the exothermic nature of the reaction and the need for a closed high-pressure system, some safety precautions have to be taken [3]. Hydrogen donors such as hydrazine hydrate, alcohols, hydrides of boron, formic acid and formates were used in CTH which has real and potential advantages, including operational simplicity, high chemoselectivity and no special equipment required [4]. Among the hydrogen donors, hydrazine hydrate is a suitable alternative for CTH due to its high activity and low cost. The reduction of nitroarenes with hydrazine hydrate could be catalyzed by a variety of cata-

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lysts such as Pd [5], Rh [6], Raney Ni [7], activated carbon [8,9], Fe₃O₄ [10,11] and iron(III) compounds [12], etc. The iron-based compounds are generally cheaper, but their catalytic properties are not desirable. Thus, to develop the iron-based catalysts is necessary.

Different crystal forms of iron oxides have different catalytic activities in CTH using hydrazine hydrate as a hydrogen donor. Among the iron oxides, amorphous iron oxyhydroxide has highest activity [12]. However, amorphous FeO(OH) could convert into α -Fe₂O₃ easily in the reaction, which would decrease the catalytic activity [13]. To improve stability of FeCl₃ catalyst, FeCl₃/polyvinylpyrrolidone (PVP) was prepared using PVP as protective agent [14]. Polyethylene glycol (PEG) can also be used as a template [15] or a modifier [16] to improve catalytic performances of catalysts. Compared with PVP, PEG 1000 is very cheaper, so we prepared amorphous iron oxyhydroxide using PEG 1000 as a modifier to improve its catalytic performances in the reduction of nitrobenzene to aniline with hydrazine hydrate as a hydrogen donor (Scheme 1). The results indicate that the amorphous iron oxyhydroxide is a highly selective and efficient recyclable catalyst for the reduction.

2. Materials and Method

2.1. Materials

Fe(NO₃)₃·9H₂O was purchased from Xilong Chemical Company (China). Hydrazine hydrate (50 %) was purchased from China Medicine Group Shanghai Chemical Reagent Company (China). PEG 1000 was purchased from Shanghai Hengyuan Biological Company (China). Nitrobenzene was purchased from Tianjin Fucheng Chemical Company (China). Ethanol was purchased from Xilong Chemical Company (China). All reagents were of analytic grade and used without further purification.

2.2. Catalyst preparation

Fe(NO₃)₃·9H₂O (8.08 g) and PEG 1000 (5.0 g) were mixed in a mortar for 30 min and the mixture gradually became brownish. After the brown precursor was poured into a beaker, 2.0

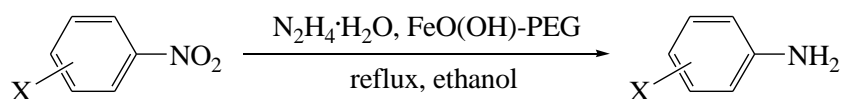
M ammonia water was dropped into the beaker with stirring, until its pH value became about 8. Subsequently, the slurry was washed with deionized water to be neutral. The product obtained was dried in an oven at 125 °C for 4 h, and then the catalyst was prepared and denoted as FeO(OH)-PEG. For comparison, the bare FeO(OH) was prepared following the same procedure in the absence of PEG 1000.

2.3. Catalyst characterization

XRD patterns were obtained on an X-ray diffraction (XRD) instrument (Ultima IV, Rigaku) equipped with a Cu K α radiation source. It was operated under the following conditions: tube voltage 40 kV, current 40 mA, and scanning range $2\theta = 10$ -80°. Fourier transform infrared spectra (FT-IR) were recorded between 400 and 4000 cm⁻¹ with a Bruker ALPHA spectrometer. The particle size distribution of the as-synthesized samples was measured by laser particle size analyzer (Winner 2008, Jinan Winner Particle Instrument Co.).

2.4. Catalytic reduction of nitroarenes over FeO(OH)-PEG

A mixture of nitroarene (10 mmol), FeO(OH)-PEG (0.1 g) and 10 mL ethanol was heated to reflux with stirring in a three-neck flask equipped with a condenser, followed by dropwise addition of hydrazine hydrate (20 mmol). The reaction mixture was stirred at refluxing temperature and the reaction progress was monitored by gas chromatography (GC-2014A, FID detector, Shimadzu). After completion of the reaction, the mixture was cooled to room temperature and the catalyst was filtered off for recycling tests. The filtrate was concentrated under a reduced pressure and dried over anhydrous magnesium sulfate. The relative contents of the aryl amines in the mixture were determined with normalization method by GC using *n*-decane as an internal standard. Product analyses were performed with GC-MS (HP6890/5973, Hewlett-Packard), and the products were identified by comparison with authentic.



Scheme 1. Reduction of nitroarenes with hydrazine hydrate

3. Results and Discussion

3.1. Characterization of FeO(OH)-PEG

Figure 1 shows the XRD patterns of as-synthesized FeO(H)-PEG and FeO(OH). The two patterns are very similar. The two broader peaks at $2\theta = 38^\circ$ and 65° indicate poorly ordered compounds, viz. amorphous materials. The patterns are similar to that of the so-called 2-line-ferrihydrite whose structure has not been fully established, but is assumed to resemble that of hematite [11,12]. However, no diffraction peak of PEG is observable for FeO(OH)-PEG, suggesting that the structure of PEG was destroyed.

FT-IR analysis can be used to determine the presence of surface functional groups on the samples. The FT-IR spectra of FeO(OH), FeO(OH)-PEG and PEG 1000 are shown in Figure 2. For the three samples the bands of stretching O-H vibrations are revealed in the range of $3150\text{--}3650\text{ cm}^{-1}$, which may be attributed to surface hydroxyl groups and chemisorbed water. The bands of the PEG 1000 sample at 2893 , 1639 , 1460 and 1109 cm^{-1} correspond to the C-H stretching vibration, O-H deformation vibration, $-\text{CH}_2$ deformation vibration and C-O-C stretching vibration, respectively [17]. Compared with that of PEG 1000, the bands in the spectrum of the FeO(OH)-PEG sample at 2893 , 1639 and 1109 cm^{-1} were observed, but not observed in the spectrum of the FeO(OH) sample. The results suggest that PEG linked with the FeO(OH)-PEG composite successfully. The bands at $400\text{--}600\text{ cm}^{-1}$ of FeO(OH)-PEG and FeO(OH) correspond to Fe-O stretching vibration. The peak of FeO(OH) at 846 cm^{-1} is ascribed to the absorption of NO_3^- , but the peak of FeO(OH)-PEG at 846 cm^{-1} is very weak. The results

indicate that NO_3^- can't be washed thoroughly in the FeO(OH) sample, whereas it can be washed thoroughly in the FeO(OH)-PEG sample. The PEG in FeO(OH)-PEG can coordinate with Fe^{3+} , which makes NO_3^- separate from Fe^{3+} easily [18].

The particle size distributions of FeO(OH)-PEG and FeO(OH) are showed in Figure 3. It can be seen from Figure 3 that most of the FeO(OH)-PEG particles are under $2.0\text{ }\mu\text{m}$ and the average dimension is around $0.95\text{ }\mu\text{m}$, and most of the FeO(OH) particles are under $25\text{ }\mu\text{m}$ and the average dimension is around $10.55\text{ }\mu\text{m}$. The results show that the particle size decreased significantly when PEG added during the preparation, for PEG on the particles hindering the aggregation [17].

3.2. Catalytic activity

The catalytic activities of FeO(OH)-PEG and FeO(OH) were investigated in the reduction of nitrobenzene with hydrazine hydrate as shown in Figure 4. It is clear from this figure that FeO(OH)-PEG shows higher activity than FeO(OH). It was taken about 1 h to complete the reduction catalyzed by FeO(OH)-PEG, however, it was taken about 2 h catalyzed by FeO(OH). Two reasons might contribute to the results. First, the particle size of FeO(OH)-PEG is smaller than that of FeO(OH). Second, a small amount of NO_3^- in FeO(OH) could decrease the activity [8,12].

The FeO(OH)-PEG catalyst also employed to catalyzed the reductions of several nitroarenes, which showed superior catalytic activity as well. As shown in Table 1, all the compounds were reduced with excellent yields. The reaction times needed to achieve the same results using FeO(OH)-PEG catalyst are less than the times in reference [12]. The method

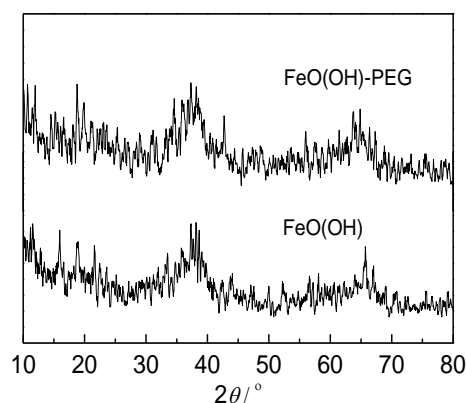


Figure 1. XRD patterns of FeO(OH)-PEG and FeO(OH)

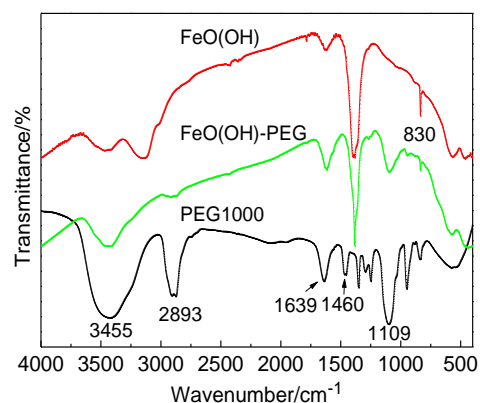


Figure 2. FT-IR spectra of PEG 1000, FeO(OH) and FeO(OH)-PEG

shows outstanding chemoselectivity for the reduction of nitroarenes with other hydrogenolysable or reducible groups in which amines were found to be the only product. Sensitive functional groups, such as: $-\text{Cl}$, $-\text{COOH}$, and $-\text{OCH}_3$, did not undergo any change under the reaction conditions. In most cases, the corresponding amines were obtained in good yields. According to Table 1, electron withdrawing/donating groups, such as: $-\text{CH}_3$, $-\text{Cl}$, $-\text{COOH}$ and $-\text{OCH}_3$, do not have a significant influence on the reaction. However, the activity is influenced by the position of the substituent on the aromatic ring. The presence of a groups, such as: $-\text{CH}_3$ or $-\text{Cl}$, ortho to the nitro group, decreased the yield to a larger extent than at the para or meta-position due to steric effects [19].

3.3. Reusability

The reusability of catalysts are very important issues for practical applications. To demonstrate the reusability of the catalyst, it was separated by filtration at the end of the reduction and washed with ethanol 3 times. The recovered catalyst was reused in the next run under the same conditions. The results in Figure

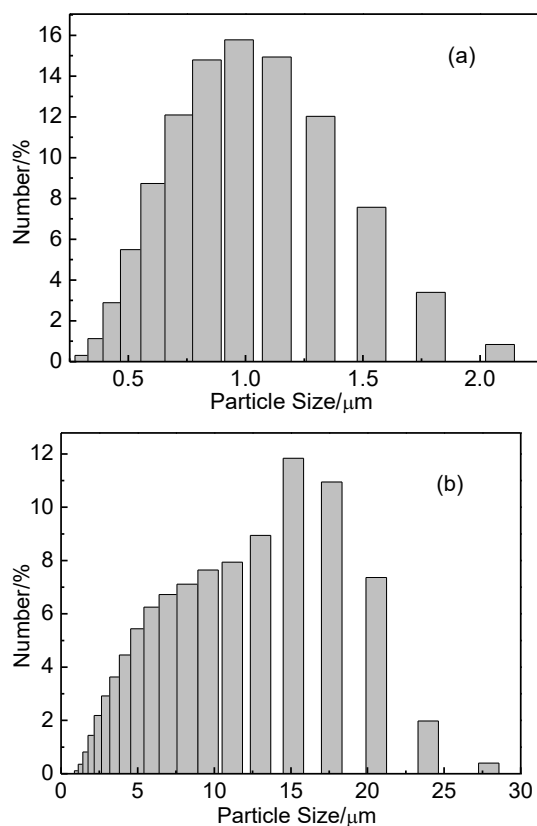


Figure 3. Particle size distribution of (a) FeO(OH)-PEG and (b) FeO(OH)

5 indicate that there is no appreciable difference in the yields after the FeO(OH)-PEG catalyst used six runs. In contrast, the FeO(OH) catalyst showed a loss in activity after four runs. To investigate the reasons for deactivation, the used catalysts after 4 runs were characterized by XRD and laser particle size analyzer. The XRD patterns of the two samples (Figure 6) showed notable difference from that of the fresh catalyst (Figure 1). The results showed that $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and $\alpha\text{-Fe}_2\text{O}_3$ (hematite) were produced from used FeO(OH), whereas only $\gamma\text{-Fe}_2\text{O}_3$ was produced from used FeO(OH)-PEG. The catalytic activity of $\gamma\text{-Fe}_2\text{O}_3$ is higher than $\alpha\text{-Fe}_2\text{O}_3$, hence the generated $\alpha\text{-Fe}_2\text{O}_3$ resulted in rapid activity decrease of FeO(OH) [13]. The particle sizes of the catalysts were tested after 4 runs, and the average sizes of FeO(OH)-PEG and FeO(OH) particles were about 2.76 μm and 14.04 μm respectively. This might be another reason for activity decreasing of FeO(OH) more quickly than that of FeO(OH)-PEG.

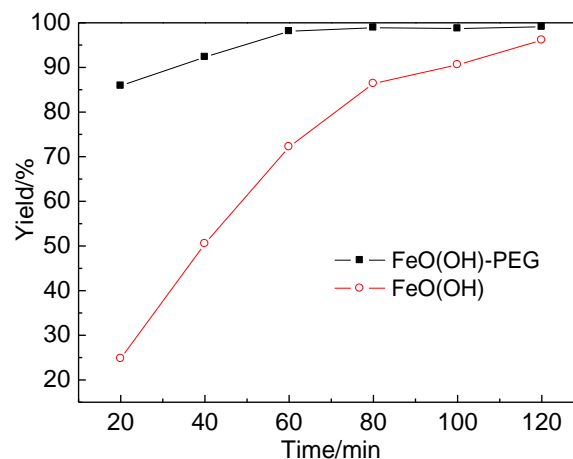


Figure 4. Activity of the catalysts

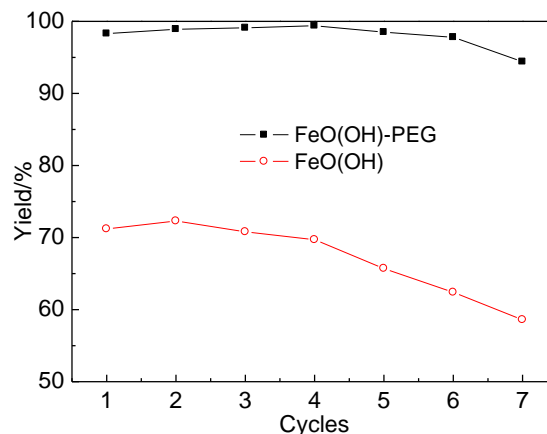


Figure 5. Reusability of the catalysts

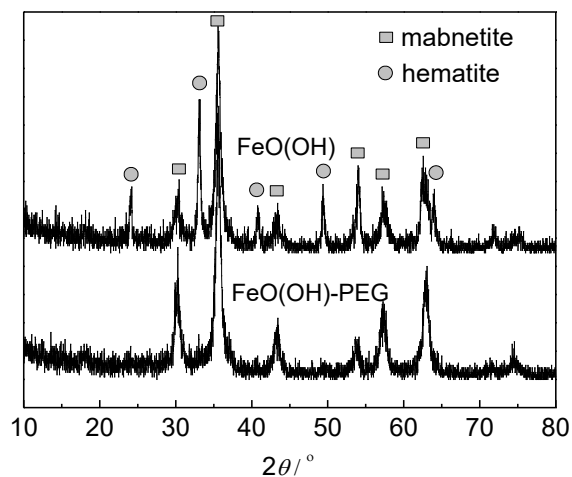


Figure 6. XRD patterns of FeO(OH)-PEG and FeO(OH) after used

4. Conclusions

In summary, a FeO(OH)-PEG composite was prepared by precipitation using PEEG 1000 as modifier conveniently. The presence of PEG prevented FeO(OH)-PEG particles from aggregating and enabled particle size to distribute well. Furthermore, the FeO(OH)-PEG composite showed efficient catalytic activity and excellent stability for the reduction of nitroarenes. The advantages of this reduction method are: high selectivity, ease of operation, high yields of the amines and no equipment of pressure apparatus. The present method offers an economical and efficient alternative to the currently available procedures.

Table 1. The reduction of nitroarenes with hydrazine hydrate over FeO(OH)-PEG (Reaction conditions: 10 mmol substrate, 20 mmol hydrazine hydrate, 0.1 g FeO(OH)-PEG, 15 mL ethanol, reaction time 1 h, refluxing)

Entry	Substrate	Product	Yield (%)
1			98.7
2			92.8
3			99.1
4			98.6
5			95.5
6			94.5
7			90.8
8			98.9
9			98.1

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