



Short communication

Ultrathin γ -Fe₂O₃ nanosheets as a highly efficient catalyst for the chemoselective hydrogenation of nitroaromatic compounds

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ARTICLE INFO

Keywords:

Ultrathin γ -Fe₂O₃ nanosheets
Catalytic hydrogenation
Nitroaromatic compounds
N₂H₄H₂O

ABSTRACT

Ultrathin γ -Fe₂O₃ nanosheets (γ -Fe₂O₃-UNSSs) were successfully prepared through a simple strategy. The as-prepared γ -Fe₂O₃-UNSSs were used for the chemoselective hydrogenation of nitroaromatic compounds to corresponding aniline compounds using N₂H₄H₂O as a hydrogen donor. An excellent catalytic activity and 100% selectivity for the aniline products were obtained. Moreover, γ -Fe₂O₃-UNSSs can be easily separated from the reaction solution by an external magnet due to its superparamagnetic property, and recycled at least six cycles without any obvious decrease in its catalytic activity.

1. Introduction

Aniline compounds are very important chemical intermediates that are frequently used in the synthesis of dyes, agrochemicals, pharmaceuticals and polymers [1–3]. Many useful strategies have been reported for the synthesis of aniline and its derivatives, such as hydrogenation of nitroarenes [4] and nitriles [5], reduction of nitroarenes and azides [6], amination of alcohols [7] and alkyl halides [8]. Among these strategies, the catalytic hydrogenation or reduction of nitroarenes is regarded as the most efficient strategy for the production of aromatic anilines, given the fact that nitroarenes are easily available chemical feedstocks. However, the reduction strategy traditionally used needs a stoichiometric amount of metal/acid or hydride [9] reagents as reductants, and a lot of undesirable waste is produced during the reaction, which is not environment-friendly. Besides these reduction methods, the catalytic hydrogenation of nitroarenes is classified as an environmentally benign process, and is compatible with industrial processes since H₂O is always the only byproduct during the reaction process [10]. But still limiting factors exist in the catalytic hydrogenation strategy, such as the use of noble metal catalysts that can increase the production cost [11]. Moreover, when noble metal catalysts and H₂ (as hydrogen donor) are used for the catalytic hydrogenation of nitroarenes with reducible groups, such as halogen-, aldehyde and C=C groups, the chemoselectivity is always not ideal [12,13]. A feasible way to resolve the above limitations is to replace the noble metal catalysts with earth-abundant transition metal based catalysts and avoid using H₂ for the catalytic hydrogenation of various nitro compounds [14].

Up to now, significant efforts have been made to design efficient catalytic systems for the hydrogenation of nitroarenes using hydrogen donors, namely: formic acid [15], formate salts [16], alcohols and N₂H₄H₂O [17]. Recently, Beller's group has reported iron oxide-based catalysts for the chemoselective catalytic hydrogenation of nitroarenes using N₂H₄H₂O as hydrogen donor [18–20]. Since then, other iron oxide nanoparticles (NPs)-based catalysts have also been reported [21–23]. A Co₃O₄ NPs immobilized on an Al/Si-mixed metal oxide support has recently been reported for chemoselective hydrazine-mediated transfer hydrogenation of nitroarenes [24]. All the above efforts have demonstrated that the use of earth-abundant transition metal-based catalysts for catalytic hydrogenation is entirely feasible in order to replace noble metal-based catalytic hydrogenation in the sustainable chemistry point of view. Thus, it is strongly desirable to design new and easily prepared transition metal-based catalysts for the catalytic hydrogenation of nitroarenes.

In this effort, via a facile method, we successfully prepared ultrathin γ -Fe₂O₃ nanosheets (γ -Fe₂O₃-UNSSs). γ -Fe₂O₃-UNSSs proved to be a highly efficient catalyst for the chemoselective hydrogenation of nitroarenes to corresponding aniline compounds, using N₂H₄H₂O as hydrogen donor. It is worth mentioning that, in the catalytic hydrogenation of halogenated nitro-compounds and other nitrobenzenes with reducible groups to the corresponding amines, 100% selectivity can be achieved. On the other hand, the catalyst can be easily recycled and the catalytic activity without an obvious decrease undergoes six consecutive reaction cycles. Hence, the γ -Fe₂O₃-UNSSs catalyst not only exhibits excellent catalytic activity and selectivity but also has excellent recyclability and reusability. Thus, it should be a potential candidate for

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the catalytic hydrogenation of nitroarenes in a large scale.

2. Experimental

2.1. Synthesis of γ -Fe₂O₃-UNSSs

Firstly, 190 mL ice-cooled aqueous solution containing 4 mmol of FeCl₃·6H₂O and 500 mg of 2-(2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy)ethanol was stirred for 10 min in an ice-bath. Next, 8.8 mmol of KBH₄ was dissolved into 8 mL ice-cooled water and quickly injected into the above solution. At the moment, the yellow Fe³⁺ solution quickly became colorless. After stirring for a few minutes at 0 °C, the solution gradually changed into gray black. Then, the above solution was aged at 4 °C for another 2 h, where a black precipitate appeared. This black precipitate was separated by a magnet and washed twice with ethanol and dried overnight at 25 °C.

2.2. Catalytic hydrogenation of nitroarenes

Typically, 1 mmol of nitrobenzene (123 mg), 10 mg of γ -Fe₂O₃-UNSSs catalyst, and 5 mL of ethanol were mixed in a 25 mL two-neck flask reactor equipped with a reflux condenser. Then the above solution was refluxed at 80 °C, followed by the addition of 4 mmol of N₂H₄·H₂O using an injection syringe. The reaction samples were collected every 10 min using an injection syringe and then filtered. The reaction conversion and yield were estimated based on the analysis of the reaction product by gas chromatography-mass spectrometry (GC-MS, Agilent 5977E).

2.3. Catalyst characterization

Powder X-ray diffraction (XRD, Rigaku D/max-2400) analysis, X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-5702), Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2010) measurements, transmission electron microscopy (TEM, FEI Tecnai G2F30, 200 kV), scanning electron microscopy (SEM, MIRA3 TESCAN), Raman spectroscopy (Jobin Yvon Lab Ram HR evolution), Fourier transform infrared (FTIR, Agilent Cary 640) spectroscopy and vibrating sample magnetometer (VSM) measurements were made to characterize the prepared samples. GC-MS (Agilent 5977E) was employed for monitoring the reaction conversion and yield as stated above.

3. Results and discussion

3.1. Characterization of catalysts

The XRD pattern recorded is shown in Fig. 1a. The different diffraction peaks observed at 30.3, 35.7, 43.4, 53.9, 57.4 and 63.0° correspond to the crystalline faces of (220), (311), (400), (422), (551) and (440), respectively, and this is consistent with the crystalline phase of γ -

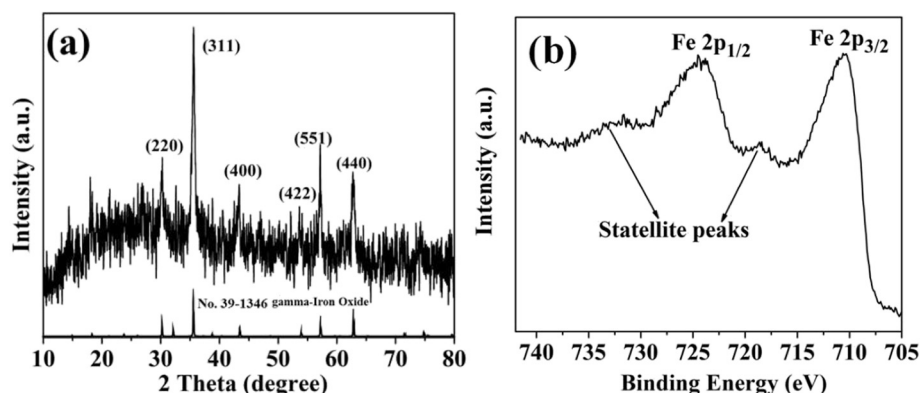


Fig. 1. (a) Powder XRD pattern of the prepared γ -Fe₂O₃-UNSSs catalyst and (b) the XPS high-resolution spectrum of Fe 2p.

Fe₂O₃ (No. 39–1346) [25]. The XPS was recorded to explore the element surface composition of γ -Fe₂O₃-UNSSs. As shown in Fig. S1, Fe and O elements signals were easily observed. The high-resolution spectrum of Fe 2p shown in Fig. 1b is characteristic for iron oxide. The Fe 2p spectrum contains Fe 2p_{1/2} (723.8 eV) and Fe 2p_{3/2} (710.3 eV) peaks, in which these two satellite peaks are important characteristic features of γ -Fe₂O₃ phase [26]. Fig. S2a shows the FTIR spectrum of the prepared catalyst. The strong and broad absorption IR bands at 700–550 cm⁻¹ are due to the multiple Fe–O stretching mode of γ -Fe₂O₃. The IR bands in the range of 3500–1100 cm⁻¹ reflect the absorbed water and CO₂ molecules in the KBr matrix [27]. Fig. S2b displays the Raman spectrum of γ -Fe₂O₃-UNSSs. The vibration characteristic peaks centered at 225, 293, 412, 613, 665 and 1320 cm⁻¹ are important characteristic peaks of γ -Fe₂O₃ phase [28]. These characteristic peaks further confirm that the prepared catalyst is γ -Fe₂O₃.

The SEM image of γ -Fe₂O₃ nanosheets shown in Fig. S3a reveals that γ -Fe₂O₃ nanosheets structure constituted by a number of nanosheets but without any obvious agglomeration to γ -Fe₂O₃ NPs. In Fig. 2a, the TEM image further confirms that the materials have ultrathin nanosheets structure. The HRTEM image of γ -Fe₂O₃-UNSSs lattice fringe is shown in Fig. S3b. It is shown that the lattice fringes of γ -Fe₂O₃ phase are observed with a d-spacing of 0.252 nm and 0.295 nm, which corresponds to the (311) and (220) lattice fringe of γ -Fe₂O₃[28]. As shown in Fig. S4, the energy dispersive X-Ray (EDX) spectrum also exhibits obvious peaks of Fe and O elements, result which is consistent with those of XPS. N₂ adsorption/desorption isotherms were also employed for investigating the textural properties of γ -Fe₂O₃-UNSSs (Fig. 2b). The N₂ adsorption/desorption isotherms of γ -Fe₂O₃-UNSSs exhibit type-IV isotherms, indicating that the catalyst has meso/macroporous structure. From the BET results, the catalyst has a large specific surface area and large pore volume of about 107.4 m² g⁻¹ and 0.30 m³ g⁻¹, respectively. Also, the catalyst exhibits pore size distribution centered between 3 and 20 nm (Fig. 2b). The large specific surface area of the prepared catalyst is obviously beneficial (concentration of active sites is proportional to BET) for enhancing its catalytic activity.

3.2. Catalytic activity of γ -Fe₂O₃-UNSSs catalyst

The prepared γ -Fe₂O₃-UNSSs solid was used in the catalytic hydrogenation of nitrobenzene using N₂H₄·H₂O as the hydrogen donor. Table 1 shows the reaction conditions screening obtained catalytic results in terms of product yield. As shown in Table 1, entries 1–5 (different solvent), the γ -Fe₂O₃-UNSSs catalyst shows an aniline yield of 100% with the solvent of ethanol and in the same reaction temperature (80 °C). When the reaction temperature was reduced to 60, 40 and 20 °C, respectively, the aniline yield was decreased accordingly (Table 1, entries 6–8). When the catalyst usage was changed, aniline yields changed accordingly (Table 1, entries 9–11).

Other iron oxides such as α -Fe₂O₃ and Fe₃O₄ NPs were also investigated. These show lower aniline yields as compared with the γ -

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