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## Efficient chemoselective hydrogenation of halogenated nitrobenzenes over an easily prepared $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-modified mesoporous carbon catalyst

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### Abstract

Efficient chemoselective hydrogenation of halogenated nitrobenzenes using low-cost catalysts is an important research area for applied catalysis. In this work, a Fe metal organic gel (Fe-MOG) which was prepared via metal coordination interaction between Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 1,4-naphthalenedicarboxylic acid. Fe-MOG was used as the precursor for the fabrication of a low-cost  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-modified mesoporous carbon catalyst ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC) through carbonization under an N<sub>2</sub> atmosphere at high temperature. The obtained  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst had high catalytic activity and selectivity for the hydrogenation of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> functionalized nitrobenzenes without obvious dehalogenation. The hydrogenation reactions had product yield and selectivity for the corresponding halogenated aniline of 100% when using hydrazine hydrate as the reducing agent. The whole hydrogenation reaction process was environmentally friendly because of its harmless byproducts (H<sub>2</sub>O and N<sub>2</sub>). In addition, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst was recyclable because of the magnetism of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> active sites. The catalytic activity of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst was not obviously decreased after being recycled five times. Therefore, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst has a great potential for future applications in the chemoselective hydrogenation of halogenated nitrobenzenes.

## Introduction

Halogenated anilines are a series of crucial intermediates and raw materials for the synthesis of fine chemicals, such as pesticides, medicines, dyes, and photosensitive materials.<sup>1</sup> Thus the synthesis of halogenated anilines has attracted increasing attention. At present, halogenated anilines are mainly obtained by the hydrogenation of the corresponding halogenated nitrobenzenes.<sup>2, 3</sup> Methods for the hydrogenation of halogenated nitrobenzenes in industry mainly include metal/acid reduction, sulfide reduction, and catalytic hydrogenation. However, production processes of the first two methods can generate hazardous substances, including iron slag and sulfur-containing wastewater.<sup>4, 5</sup> Catalytic hydrogenation is an environmentally friendly method for the preparation of halogenated anilines.<sup>6</sup> Until now, the catalysts that have been investigated for the hydrogenation of halogenated nitrobenzenes have been mainly noble metal-based catalysts, such as Pd-on-Si catalysts,<sup>7</sup> Ru-Pt bimetallic nanocatalysts,<sup>8</sup> Pd/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>9</sup> Pt-B/Al<sub>2</sub>O<sub>3</sub>,<sup>10</sup> Pd-NiO@SiO<sub>2</sub>,<sup>11</sup> and Ru/NPC.<sup>12</sup> However, there are still some limitations that prevent large-scale application of such catalysts. These include the slight dehalogenation phenomenon that frequently occurs in the reaction when using noble metal-based catalysts and the scarcity and high cost of noble metals.<sup>9</sup>

To design of low-cost catalysts for the chemoselective hydrogenation of halogenated nitrobenzenes, the use of non-noble metal-based catalysts with high catalytic activity that are eco-friendly and easily recyclable is desirable. In this respect, the most widely used Raney Ni catalyst has been used in the chemoselective hydrogenation of halogenated nitrobenzenes, but inhibitors must be introduced into the reaction mixture to prevent the dehalogenation phenomenon and to maintain the selectivity of the hydrogenation reaction.<sup>13</sup> On the other hand, non-precious metals supported on nanostructured porous materials for the catalytic hydrogenation of halogenated nitrobenzenes can enhance the catalytic activity to some extent because the nanostructured porous materials exhibit unique chemical, physical, and electrical properties. Most recently, Hua Song *et al.* prepared carbon nanotube-supported Co-B amorphous alloy catalysts for the hydrogenation of *m*-chloronitrobenzene (*m*-CNB) to *m*-chloroaniline (*m*-CA) with high chemoselectivity under the reaction conditions of 413 K and 2.0 MPa H<sub>2</sub>.<sup>14</sup> The Ni-supported catalyst CN/Ni/Al<sub>2</sub>O<sub>3</sub> has high chemoselectivity for *p*-CNB under 1.0 MPa H<sub>2</sub> and 393 K.<sup>15</sup> Ni/TiO<sub>2</sub> catalyst has also been used in the

hydrogenation of halogenated nitrobenzenes with excellent catalytic performance.<sup>16</sup> A MOF-derived Co-CoO@N-doped porous carbon catalyst was reported by Jiang *et al.* for the hydrogenation of nitro compounds with halogenated groups.<sup>17</sup> The work of Lykakis *et al.* proved that the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) can catalyze the hydrogenation of nitro compounds with reducing functional groups.<sup>18</sup> The above reported non-noble metal-based catalysts are indeed low-cost and have excellent chemoselectivity for the hydrogenation of nitroaromatic compounds with or without halogenated groups. However, there are still some drawbacks. In particular, the preparation processes of the reported catalysts were complicated, the precursors acting as catalyst support sources were expensive, and most of the catalysis processes required harsh conditions, including high H<sub>2</sub> pressure.

Based on the above considerations and to address the limitations, we reported a simple one-pot pyrolysis method to fabricate a novel catalyst for the hydrogenation of a variety of halogenated nitrobenzenes. First, a Fe metal-organic gel (Fe-MOG) was prepared through coordination interaction between Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 1,4-naphthalenedicarboxylic acid (NDC) in ethanol in a simple method. Then the Fe-MOG was carbonized under an inert atmosphere at 500 °C to synthesize the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP-supported mesoporous carbon catalyst ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC). The active sites on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were inlaid uniformly in porous carbon. At atmospheric pressure, this catalyst exhibited high yield and excellent chemoselectivity (typically 100%) for the hydrogenation of halogenated nitrobenzenes to the corresponding halogenated anilines using N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O as the reductant. The whole reaction system did not generate byproducts or harmful products. Moreover, the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst exhibited superior recyclability and excellent stability after being reused at least five times. This work may promote the investigation of low-cost  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-based catalysts for the highly chemoselective hydrogenation of halogenated nitrobenzenes in the chemical industry.

## Experiment

### Materials

NDC and halogenated nitrobenzenes were purchased from Tianjin Heowns Biochem.. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (80 wt %) were supplied by Sinopharm Chemical Reagent Co.

Ltd (China). All other reagents used in this work were of analytical grade and did not require further purification.

### Catalyst preparation

Based on recent research,<sup>19</sup> we prepared the Fe-MOG by coordination interaction of iron and NDC. 5 mmol of NDC was dissolved in 50 mL of ethanol at 343 K. Then, 100 mL of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution (75 mM) was added to the hot solution. The mixture was stirred at ambient temperature for 48 h. The Fe-MOG was obtained by suction filtration, washed with ethanol, and dried in a vacuum oven at 40 °C overnight. The product was then calcined at a certain high temperature (400 °C, 500 °C, 600 °C or 700 °C) for 30 min with a heating rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. Finally, the 0.75-X- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst was prepared (X represents the carbonization temperature).

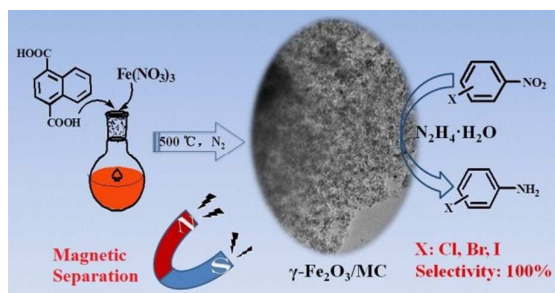
### Hydrogenation of halogenated nitrobenzenes

In a typical experiment, 0.5 mmol of halogenated nitrobenzenes, 15 mg of 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst, and 5 mL of ethanol were ultrasonically dispersed in a 25 mL two-neck round-bottom flask. Then 2 mmol of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was added to the reaction system, and the mixture was stirred vigorously at 80 °C for approximately one hour with a reflux condenser. The reaction products were analyzed by gas chromatography-mass spectroscopy (GC-MS, Agilent 5977E).

### Catalyst characterization

Transmission electron microscopy (TEM, Tecnai G20 F30) was used to characterize the morphology of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalysts. Powder X-ray diffraction (PXRD) was recorded with a Rigaku D/max-2400 diffractometer using Cu-K $\alpha$  radiation. This was used for investigating the physical properties of the catalyst. X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-5702) was used to measure the electronic states of the surface of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalysts. The Fe content of the prepared nanocatalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). A Quantum Design Vibrating sample magnetometer (VSM) was employed for measuring the magnetism of the catalyst. FTIR spectra of the Fe-MOG and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC were obtained on a Fourier transform infrared spectrometer (FTIR). Raman spectroscopy (Jobin Yvon Lab Ram HR evolution) and

a micromeritics ASAP 2010 (USA) were used to observe the physical properties of the catalyst. Elemental composition of  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  was performed using energy dispersive X-ray spectroscopy (EDS). The conversion and chemoselectivity of the hydrogenation reactions were investigated by GC-MS (Agilent 5977E).



**Scheme 1.** Schematic illustration of the synthesis and application of  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst.

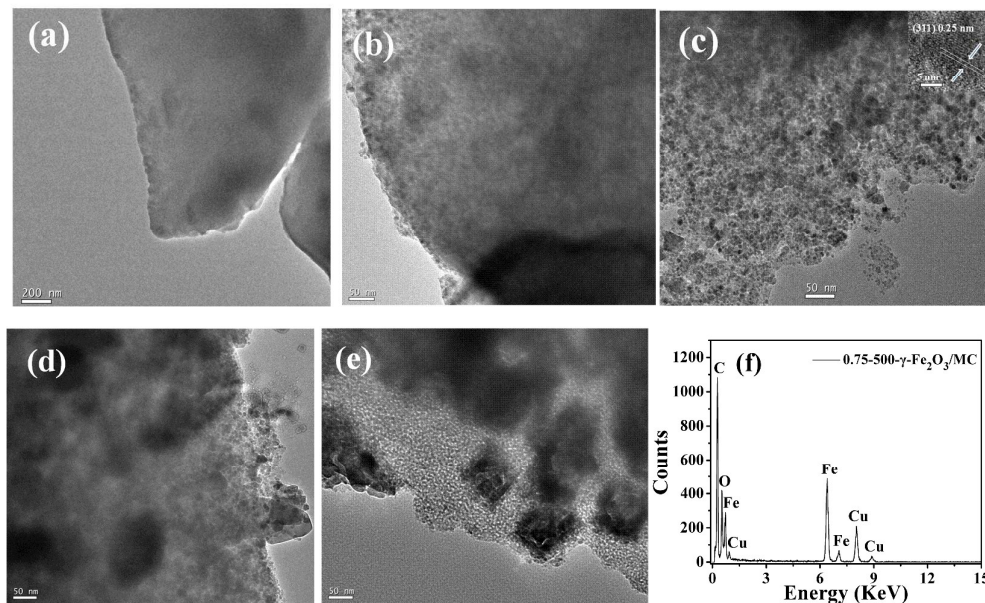
## Results and Discussion

### Characterization of the catalyst

The catalyst precursor Fe-MOG was synthesized by the simple mixing of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and NDC in ethanol solution, and the  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst was prepared by carbonization of the Fe-MOG under a nitrogen atmosphere. The preparation process of the catalyst  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  is illustrated in scheme 1. The morphologies of all the prepared samples characterized using TEM are shown in Fig. 1. Fig. 1a shows the sheet structure of the Fe-MOG. When the Fe-MOG was carbonized in different annealing temperatures (400 °C, 500 °C, 600 °C, and 700 °C), the obtained materials showed slight differences in morphology. For example, the porous structure was more evident, and the  $\gamma\text{-Fe}_2\text{O}_3$  NPs were uniformly dispersed in the carbon framework after calcination at 500 °C, and the lamellar structure of the 0.75-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst was almost unchanged (Fig. 1c). It can be seen from the lattice that the interplanar spacing of 0.25 nm can be attributed to the (311) crystal face of  $\gamma\text{-Fe}_2\text{O}_3$  (Fig. 1c insert).<sup>20</sup> However, in the sample of 0.75-400- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$ , the  $\gamma\text{-Fe}_2\text{O}_3$  NPs did not form inside of the porous carbon under the insufficient temperature of 400 °C (Fig. 1b). In contrast, at high annealing temperatures (600 °C and 700 °C), the 0.75-600- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  (Fig. 1d) and 0.75-700- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  (Fig. 1e) catalysts, had obviously larger  $\gamma\text{-Fe}_2\text{O}_3$  NPs due to agglomeration at high temperature. The  $\gamma\text{-Fe}_2\text{O}_3$  particle size may influence the catalytic



activity of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalysts. The EDS spectrum shows that  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst was composed of carbon, oxygen, and iron (Fig. 1f).



**Fig. 1.** TEM images of Fe-MOG (a), 0.75-400- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (b), 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (c), 0.75-600- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (d) and 0.75-700- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (e). EDS spectrum of the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (f).

In order to study the thermal stability and composition of the sample, the TGA curve was recorded in a nitrogen atmosphere, and the temperature control program was set to rise from 25 °C to 900 °C at a heating rate of 10 °C min<sup>-1</sup> (Fig. 2a). The TGA curve of the Fe-MOG sample during annealing shows a gentle incline corresponding to weight loss between 25 °C and 380 °C resulting from the removal of micromolecules. When the calcination temperature reached 380 °C, the weight of the sample began to decrease abruptly, probably because of pyrolysis of the organic framework. The curve tended to be stable between 480 °C and 635 °C, and the target catalyst sample was successfully obtained. The weight again sharply dropped in the range from 635 °C to 680 °C due to the loss of carbon and oxygen, which could be caused by the reduction reaction of the structure carbon and iron oxide.

XRD spectra of the prepared catalysts were used to further investigate the crystalline phases and structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC. Fig. 2b shows the XRD spectra of 0.75-400- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC, 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC, 0.75-600- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC, 0.75-700- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC, 0.5-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (prepared using 5 mmol of NDC and 5 mmol of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), and the reused catalyst of 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC. The characteristic peaks of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were clearly observed, and

corresponded to the (220), (311), (400), (511), and (440) crystal faces (JCPDS No. 39-1346).<sup>21</sup> However, the spectrum of 0.75-700- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC is different from the others, and a new diffraction peak at 44.7° was observed, indicating the formation of Fe(0) (JCPDS No. 6-696).<sup>22</sup> This is because the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were reduced by the structure carbon of the MC in the high temperature range (635 °C to 680 °C), which is consistent with the results from the TGA analysis.

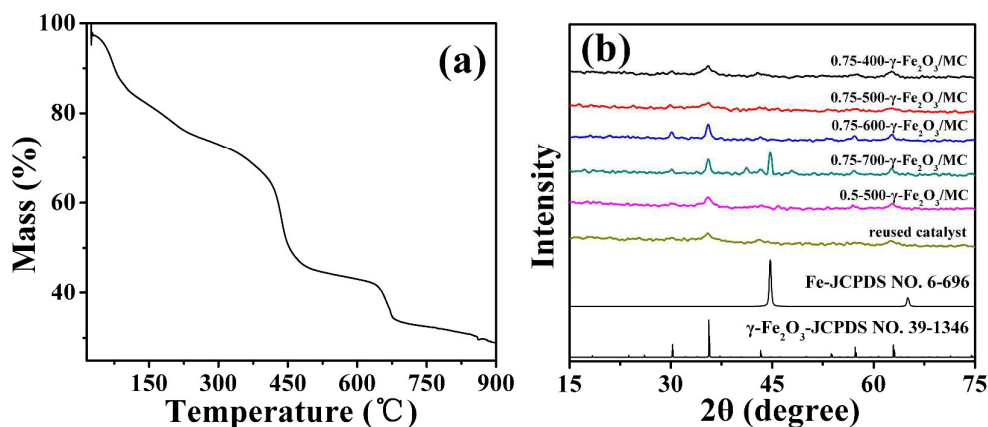


Fig. 2. TGA curve of 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (a), XRD patterns for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (b).

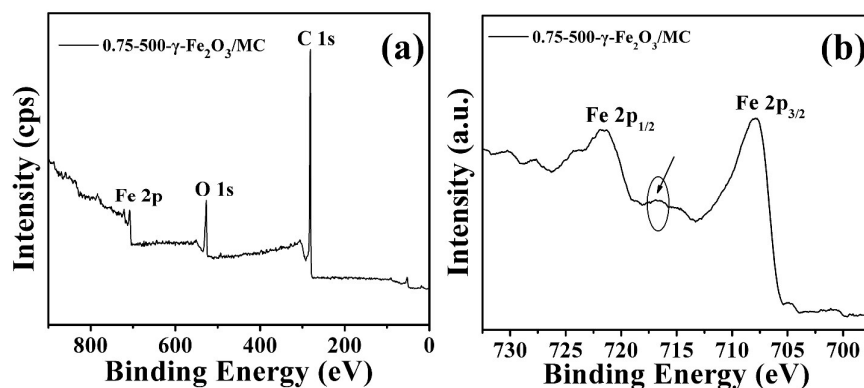


Fig. 3. XPS wide-scan spectrum of the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (a), XPS spectrum of Fe 2p (b).

The XPS wide-scan spectrum of the catalyst also shows the existence of iron (Fig. 3a). To further understand the valence information of the iron element, the fine spectrum of Fe 2p was investigated. As shown in Fig. 3b, two broad peaks were observed at 721.5 eV and 707.9 eV, and these corresponded to the Fe 2p<sub>1/2</sub> and Fe 2p<sub>3/2</sub>, respectively. Furthermore, the satellite peak between 721.5 eV and 707.9 eV suggests that the iron oxide is  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs.<sup>20, 23</sup> The XPS results demonstrate the existence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and agree with the XRD analysis. Additionally, there are almost no other crystal forms of iron oxides.



The Raman spectrum of the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst is shown in Fig. S1. The D band and G band appearing in the Raman spectrum are the characteristic peaks of the carbon crystal. The peak at 1336 cm<sup>-1</sup> is the D band, indicating a lattice defect of the carbon crystal, while the G band located at 1581 cm<sup>-1</sup> represents an in-plane stretching vibration of sp<sup>2</sup> hybrid carbon atoms.<sup>24</sup> Generally, the degree of disorder of the carbon material is measured by the intensity ratio of the D-peak to G-peak ( $I_D/I_G$ ). The value of  $I_D/I_G$  of 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC is 0.87, indicating that the carbon crystal has fewer defect sites and tends to be ordered. From the FTIR spectra of the Fe-MOG and 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC (Fig. S2), it can be seen that the annealed catalyst undergoes a significant change in structure compared to before the heat treatment (Fig. S2a). As shown in Fig. S2b, a prominent peak appears at 592 cm<sup>-1</sup>, which is the characteristic absorption peak of the iron-oxygen bond. Furthermore, from the ICP-AES results, the Fe content of the prepared 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst is 30.33%. The mesoporous material  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC exhibits the typical IV type isotherm, due to the presence of mesoporous structure. The surface area of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC is 223 m<sup>2</sup> g<sup>-1</sup> and average pore size of is 5 nm as can be seen from the Fig. S3. Fig. S4 shows the magnetization curves of 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC. The magnetic hysteresis loop was clearly observed, which indicated the magnetic nature of the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst. The saturation magnetization was approximately 14.9 emu g<sup>-1</sup>, and the catalyst was easily adsorbed on the centrifuge tube wall by a magnet (Fig. S4, *insert*). Therefore, the desirable magnetic properties of the catalyst are favorable for the recycling and reuse of the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst.

### Hydrogenation of halogenated nitrobenzenes

The prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalysts were studied for the liquid-phase hydrogenation of halogenated nitrobenzenes to the corresponding halogenated anilines. The main side reaction is dehydrohalogenation, which leads to aniline as the byproduct.<sup>25</sup> As shown in Table 1, the reaction conditions and catalyst were screened using the hydrogenation of *p*-CNB to *p*-CA as the model reaction. Initially, the catalysts were prepared by calcination at 400 °C, 500 °C, 600 °C, and 700 °C, and the catalytic performance was investigated at the optimal reaction

conditions (using 4 equivalents of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  as the reducing agent, ethanol as the solvent, atmospheric pressure, and  $80^\circ\text{C}$  for the reaction temperature). The results show that excellent yield and selectivity of reaction reach up to 100% in one hour by using 0.75-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  as the catalyst. However, other catalysts did not afford the desired catalytic effect (Table 1, entries 1-4). This was probably because the active sites  $\gamma\text{-Fe}_2\text{O}_3$  had almost not been formed when annealed at  $400^\circ\text{C}$ . In contrast, annealing at higher temperatures of  $600^\circ\text{C}$  and  $700^\circ\text{C}$ , the  $\gamma\text{-Fe}_2\text{O}_3$  NPs tended to aggregate and were further reduced to Fe NPs. Low loading of the catalyst (0.5-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$ ) exhibited 97.4% conversion and 100% selectivity at two hours (Table 1, entry 5). Table 1, entries 6-8 shows that the conversion of *p*-CNB to *p*-CA decreased when the reaction temperature decreased to 60, 40, and  $25^\circ\text{C}$ . The reaction has almost no yield when  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  was not added or when  $\text{H}_2$  was used as the reducing agent (Table 1, entries 9, 12). Furthermore, the reaction effect was undesirable when using two or one equivalents of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  as the reducing agent (Table 1, entries 10, 11). The reaction yield was only 67.3% when water was used as a solvent, mainly because the *p*-CNB is insoluble in water (Table 1, entry 13). The use of the Pd/C catalyst for the reaction resulted in poor selectivity for the hydrogenation of *p*-CNB to *p*-CA, and a high proportion of dechlorinated aniline product was produced (Table 1, entry 14). Thus, it can be seen that the  $\gamma\text{-Fe}_2\text{O}_3$ -based  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalysts exhibit much more excellent chemoselectivity for the hydrogenation of *p*-CNB to *p*-CA than the noble metal-based catalyst (Pd/C). Furthermore, the reaction system was investigated without a catalyst, and the yield was only 1.23% (Table 1, entry 15). As shown in entry 16, using a non-heat treated iron gel (Fe-MOG) as the catalyst, the conversion of the *p*-CNB was 8.8% under the same reaction conditions. In addition, the Fe/MC obtained by the hydrogenation of the  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst was also investigated for the hydrogenation of *p*-CNB, the yield of *p*-CA was found to be 32.3% (Table 1, entry 17). The XRD spectrum of the Fe/MC catalyst consisted with the spectrum of the 0.75-700- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  is displayed in Fig. S5, which was contained a little iron oxide. From the above results, the 0.75-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst showed good catalytic activity and selectivity for the hydrogenation of *p*-CNB to *p*-CA at the optimized reaction conditions.

**Table 1.** Screening the reaction conditions using the catalytic hydrogenation of *p*-CNB to *p*-CA as the probe reaction.<sup>a</sup>

Entry	Catalyst	Temperature (°C)	Time (min)	Conv. (%)	Sel. (%)
1	0.75-400- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	180	23.3	100
2	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	60	100	100
3	0.75-600- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	120	13.9	100
4	0.75-700- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	120	27.2	100
5	0.5-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	120	97.4	100
6	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	60	180	66.7	100
7	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	40	300	26.5	100
8	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	25	300	13.1	100
9 <sup>b</sup>	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	300	0.2	100
10 <sup>c</sup>	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	60	49.1	100
11 <sup>d</sup>	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	60	72.6	100
12 <sup>e</sup>	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	60	0.2	100
13 <sup>f</sup>	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC	80	60	67.3	100
14	Pd/C	25	40	99.6	34.7
15	None	80	300	1.23	100
16	Fe-MOG	80	60	8.8	100
17	Fe/MC	80	60	32.3	100

**Reaction conditions:** <sup>a</sup> *p*-CNB (0.5 mmol), catalyst (15 mg), 2 mmol of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, ethanol (5 mL).

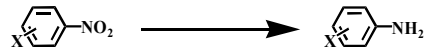
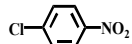
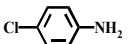
<sup>b</sup> Without reductant. <sup>c</sup> 1 mmol of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O. <sup>d</sup> 0.5 mmol of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O. <sup>e</sup> Using H<sub>2</sub> as the reductant. <sup>f</sup>



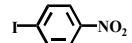
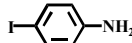


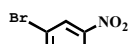
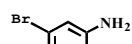
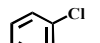
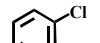
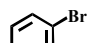
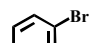
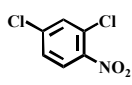
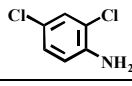
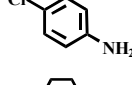
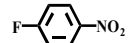
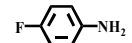
Using water as solvent.

To investigate the general applicability of the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst, the hydrogenation of a variety of halogenated nitrobenzenes was carried out. As shown in Table 2, the hydrogenation of *o* (*m*, *p*)-CNB, *o* (*m*, *p*)-bromonitrobenzene, and 1-iodo-4-nitrobenzene (*p*-INB) were all fully converted to the corresponding haloanilines using the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst. Both the yield and selectivity reached 100% in an hour or in 70 minutes (entries 1-7). Hydrogenation of 1-nitro-2,4-dichlorobenzene still achieved a high selectivity of 98.3%, while only 1.7% of *m*-CNB was formed because of the dehalogenation of the *o*-position Cl (Table 2, entry 8). Besides, the hydrogenation of *p*-fluoronitrobenzene (*p*-FNB) has been investigated using 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst. As can be seen from the entry 9, the reaction has the conversion of 82% and selectivity of 96.6% in the 3 h. Substrate

and product concentration ratio curves for the hydrogenation of *p*-CNB, *p*-bromonitrobenzene (*p*-BNB), and *p*-INB are shown in Fig. S6. The conversion for the reduction of *p*-CNB to *p*-CA and *p*-INB to *p*-iodoaniline (*p*-IA) increased linearly for the first 40 min of reaction, and then the curves increased gradually up to 60 min. The figures only have two curves of substrates and target products, which implies that there were almost no byproducts formed in the whole reaction process (Figs. S6a and c). This was also confirmed by the GC-MS monitoring process. Similarly, the reduction of *p*-BNB had the same reaction system with a reaction time that was only ten minutes longer (Fig. S6b). The comparison of the reaction conditions, conversions and selectivity in the hydrogenation of *p*-CNB to *p*-CA using 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst and other reported noble metals and non-precious metal-based catalysts were listed in Table 3. The noble metals based catalysts 0.12Pd-Si<sup>7</sup> and Ru5/NPC(NB)<sup>12</sup> can hydrogenate the *p*-CNB to *p*-CA with high selectivity of 99.9% and 98%, respectively, but they need high H<sub>2</sub> pressure and reaction temperatures. The Pd-NiO@SiO<sub>2</sub><sup>11</sup> and Pd@Pt-1/0.25/Al<sub>2</sub>O<sub>3</sub><sup>26</sup> catalysts although can catalyze hydrogenation of *p*-CNB under mild reaction conditions, the selectivity of *p*-CA is low. Other reported non-precious metal-based catalysts CN/Ni/Al<sub>2</sub>O<sub>3</sub><sup>15</sup> and 12% Ni/Al-SBA-15<sup>27</sup> also need high H<sub>2</sub> pressure for hydrogenating the *p*-CNB to *p*-CA with selectivity lower than 100%. The reported Co<sub>0.2</sub>Fe<sub>2.8</sub>O<sub>4</sub> catalyst with the same reaction conditions of this work, has a *p*-CA selectivity of 99.6%.<sup>28</sup> Although the reported 5wt% Pt/CMK-3<sup>29</sup> and 5wt% Ru/CMK-3<sup>30</sup> have very high selective hydrogenation to *p*-CNB, the 5wt% Pt/CMK-3 also need high H<sub>2</sub> pressure and the 5wt% Ru/CMK-3 has only 49.9% of conversion in 1 h. Thus, it was concluded that the 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst exhibited excellent catalytic activity for the hydrogenation of a variety of halogenated nitrobenzenes with almost 100% yield and selectivity.

**Table 2.** Hydrogenation of various halogenated nitrobenzenes to corresponding halogenated aniline using 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst.

Entry			Time (min)	Yield (%)	Sel. (%)
	Substrate	Product			
1			60	100	100

2			70	100	100
3			60	100	100
4			70	100	100
5			60	100	100
6			70	100	100
7			60	100	100
8			180	98.3	98.3
				1.7	
9			180	82	96.6

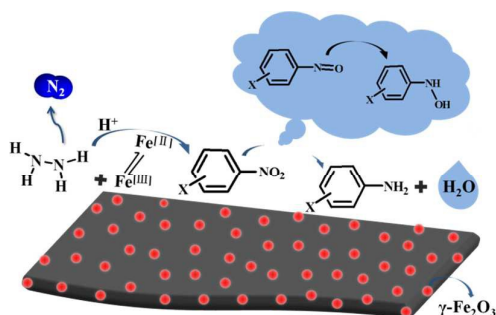
**Reaction conditions:** substrate (0.5 mmol), 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC nanocatalyst (15 mg), N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (2 mmol), solvent (5 mL), reaction temperature (80 °C). Yield

**Table 3.** The comparison of the catalytic performance over different catalysts in the catalytic hydrogenation of *p*-CNB to *p*-CA.

Entry	Catalyst & Dosage	Substrates Dosage	Active Sites Loading	Time	T/ °C	P/MPa	Conv. (%)	Sel. (%)	Ref.
1	0.12Pd-Si 50 mg	2 mmol	Pd/0.12wt%	36 h	100	P <sub>H2</sub> =1	>99.9	>99.9	7
2	Ru5/NPC(NB) 10 mg	1 mmol	Ru/4.4wt%	2.5 h	140	P <sub>H2</sub> =1.5	98	98	12
3	Pd-NiO@SiO <sub>2</sub> 0.19 g	1 g	Pd/0.36wt%	2.5 h	30	P <sub>H2</sub> =0.1	100	82.7	11
4	Pd@Pt-1/0.25/Al <sub>2</sub> O <sub>3</sub> 0.1 g	2 g	Pt/0.25wt%	3 h	45	P <sub>H2</sub> =0.1	98.5	82.1	26
5	CN/Ni/Al <sub>2</sub> O <sub>3</sub> 50 mg	50 mg	/	10 h	120	P <sub>H2</sub> =1	96.8	>99.9	15
6	12%Ni/Al-SBA-15 15mg	1 mmol	Ni/12wt%	7.5 h	110	P <sub>H2</sub> =2.5	100	97	27
7	Co <sub>0.2</sub> Fe <sub>2.8</sub> O <sub>4</sub> 0.1 mmol	10 mmol	/	20 min	80	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	100	99.6	28
8	5wt% Pt/CMK-3 25 mg	21 mmol	Pt/5wt%	10 min	25	P <sub>H2</sub> =4	77.7	>99	29
9	5wt% Ru/CMK-3 20.9 mg	8.1 mmol	Ru/5wt%	1 h	30	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	49.9	>99	30
10	0.75-500- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /MC 15 mg	0.5 mmol	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /43 wt%	1 h	80	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	100	100	This work

Scheme 2 shows the mechanism for the hydrogenation of halogenated nitrobenzenes to

halogenated anilines using the  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst. First,  $\text{Fe}^{3+}$  was reduced to  $\text{Fe}^{2+}$  by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  and released nitrogen and the hydrogen ion. Subsequently, the nitroso compound was generated by the reduction of the nitro compound in which  $\text{Fe}^{2+}$  supplied electrons and was oxidized to  $\text{Fe}^{3+}$ . Then the nitroso compound reacted with  $\text{Fe}^{2+}$  to form phenylhydroxylamine.<sup>18, 31</sup> Finally, phenylhydroxylamine was further reduced to the arylamine compound. During the reaction procedure, negligible halogenated phenylhydroxylamine has been detected by the GC-MS. However, the halogenated phenylhydroxylamine should be quickly transformed into halogenated anilines, thus the final products are the halogenated anilines,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ .



Scheme 2. Mechanism for hydrogenation of halogenated nitrobenzenes over 0.75-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst.

The stability and recyclability of catalysts are of great importance in practical application. In this work, to further explore the lifetime and stability of the catalyst, the conversion rate of each reused reaction was recorded at 15 minute intervals. The catalyst can be separated from the reaction system using an external magnetic field because of the magnetic property of  $\gamma\text{-Fe}_2\text{O}_3$ . Fig. 4 shows that the catalyst still maintained excellent catalytic activity after five repetitions. The reused catalyst was further characterized. As shown in Fig. 2b, the XRD result revealed that the crystalline phase and structure of the reused 0.75-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst did not change as compared with the fresh prepared catalysts. The FTIR and TEM results (Fig. S2b, Fig. S7, respectively) also shows that the morphology and the structure of the catalyst had no obvious changes. Therefore, the 0.75-500- $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst exhibit superior reusability and stability.



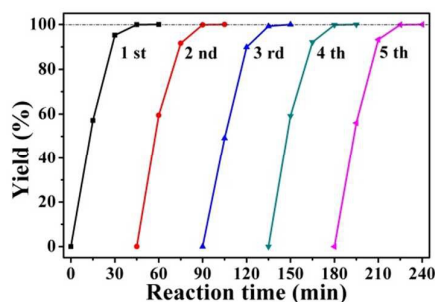


Fig. 4. Recyclability tests of 0.75-500- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst for hydrogenation of *p*-CNB to *p*-CA.

## Conclusions

In conclusion, we have demonstrated a concise and efficient method to synthesize the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/MC catalyst for the hydrogenation of halogenated nitrobenzenes. The catalysts were prepared by an accurate annealing procedure of Fe-MOG which was generated by the mixing of ferric nitrate and NDC. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were uniformly encapsulated in a carbon structure, which exhibited dramatically high catalytic activity and specific selectivity for the hydrogenation of a variety of halogenated nitrobenzenes to the corresponding halogenated anilines. The obtained catalyst was readily recycled because of its intrinsic magnetic property and could be reused at least five times without decrease of catalytic activity and selectivity. Therefore, such a highly efficient, low-cost, strongly stable, and eco-friendly catalyst provides a versatile platform and has potential application in other catalytic reduction reactions.

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## Notes and references

Supplementary data associated with this article can be found, in the online version.

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## Graphical Abstract

The easily prepared cost-effective  $\gamma\text{-Fe}_2\text{O}_3/\text{MC}$  catalyst was used for the hydrogenation of halogenated nitrobenzenes with 100% selectivity for the corresponding halogenated anilines.

