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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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## Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> Catalyst with Excellent Catalytic Performance for Hydrogenation of Nitroarenes in Aqueous Medium

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## Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> Catalyst with Excellent Catalytic Performance for Hydrogenation of Nitroarenes in Aqueous Medium

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Catalytic hydrogenation of aromatic nitro compounds was carried out in neat water with Pt nanoparticles deposited on surface amine-functionalized magnetite. The hydrophilic Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst exhibited excellent activity as well as superior selectivity to the corresponding amines. 99.9% yield of *p*-chloroaniline (*p*-CAN) was obtained at 303 K under an H<sub>2</sub> atmosphere in aqueous media; the turnover frequency value reached 500 h<sup>-1</sup> in the absence of any additives or promoters. Furthermore, the novel nanocomposites can be readily isolated from the reaction system by a magnet and recycled at least six times without any loss in activity.

Keywords amine, hydrogenation, nitroarene, platinum catalyst, water

#### INTRODUCTION

Aromatic amines are considered as versatile compounds and have been used in many commercial applications in the chemistry of organic fine chemicals, such as the synthesis of dyes, drugs, herbicides, and pesticides.<sup>[1]</sup> Many commonly used routes are still based on stoichiometric reduction which produce large amounts of wastes such as acid effluents or metal oxides residue.<sup>[2,3]</sup> The environmentally benign synthesis of amines facilitated by catalytic hydrogenation is attracting increasing attention in recent years, a variety of precious metals such as Pd,<sup>[4–6]</sup> Pt,<sup>[7–20]</sup> Rh,<sup>[21]</sup> Ru<sup>[22–24]</sup>, and non-noble metals such as nickel<sup>[25–29]</sup> are investigated either in bulk or supported forms for the catalytic reduction of aromatic nitro-compound into the corresponding amine. However, one critical limitation with the catalytic hydrogenation is that the co-occurrence of the hydrodechlorination in chlorinated aromatic compounds, which significantly limits the selectivity to chloroanilines, and that the formation of hydrogen chloride from this process is likely adsorbed on the active sites causing deactivation of the catalyst or corrosive to the reactor.<sup>[14]</sup> Therefore, great efforts have been paid to overcome this problem, such as introducing special promoters or inhibitors<sup>[13,16,30]</sup> and modifying the properties of the catalysts. However, the use of inhibitors and modifiers brings about impurities in the final product, and they must be eliminated after processing for further applications. Thus, it is highly desirable to develop simpler hydrogenation processes operating at mild conditions without hydrodechlorination. Recently, it was reported that gold<sup>[31,32]</sup> and silver<sup>[33–35]</sup> deposited on SiO<sub>2</sub> or ZrO<sub>2</sub> could completely inhibit hydrodechlorination reaction and had the excellent selectivity to chloroaniline in the liquid hydrogenation of chloronitrobenzene, however, present reaction systems suffered from relatively high temperature and pressure  $(T > 373 \text{ K and } P > 1.0 \text{ MPa H}_2).$ 

In recent years, supported Pt catalysts have been found to be among the most promising ones owing to their high selectivity to the formation of the desired amines. Especially, Pt nanoparticles based on special materials, including iron oxides<sup>[36-39]</sup> and PICP<sup>[40]</sup> have revealed that Pt catalysts are also highly selective for the hydrogenation of chloronitrobenzene under mild condition. However, these Pt-based hydrogenation procedures are subjected to some general insufficiencies, including the use of hazardous organic solvents as the reaction media and form of a non-negligible amount of the condensation by-product between amines and alcohols (served as solvents).<sup>[32]</sup> Subsequent studies<sup>[41,42]</sup> revealed that the addition of adequate amount of water into organic solvents (alcohols) could improve the activity and selectivity of the catalysts, but it was hard to completely overcome the condensation of by-products because of the present of alcohols. Therefore, some researchers try to perform the hydrogenation of nitro group in neat water. In such scenarios, water, the most benign, abundant, and inexpensive solvent would lead to a particularly green process in the view of green chemistry. However, only one successful example of the use of water as reaction media was reported in the liquid hydrogenation of nitro compound.<sup>[43]</sup> It was found that the Pt/GA (gum acacia)

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catalyst could catalyze hydrogenation of nitroarenes to arylamines in aqueous medium with a nitroarenes/catalyst molar ratio of 416 in time of 6–8 h, however, the activity and yield of chlorinated amine were not satisfied enough. In this sense, there is a strong incentive to develop new simple, efficient, easily handled procedures that can allow the highly active and selective reduction of the nitro group in water under mild conditions.

In the present study, we prepared amine-functionalized  $Fe_3O_4$  stabilized Pt nanoparticles for the selective hydrogenation of nitroarenes in aqueous medium. With a nitroarenes/catalyst molar ratio of 1500, the complete conversion was achieved at 303 K under an H<sub>2</sub> atmosphere; the turnover frequency (TOF) was reached about 500 h<sup>-1</sup>. To the best of our knowledge, this excellent catalytic property for the hydrogenation of chloroni-trobenzene over Pt-based catalysts under milder conditions has not been reported. The Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst could reuse six times and conveniently separated from the reaction system by a magnet.

#### **EXPERIMENTAL**

#### Synthesis of Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>

The Fe<sub>3</sub>O<sub>4</sub>–NH<sub>2</sub> stabilized Pt nanoparticles (Pt–NH<sub>2</sub>– Fe<sub>3</sub>O<sub>4</sub>) were synthesized as follows: 0.5 g of Fe<sub>3</sub>O<sub>4</sub>–NH<sub>2</sub> and 50 mL ethanol were mixed into a 100 mL round bottom and were under ultrasonication for 30 min using an ultrasonic cleaning bath. Then 1.0 mL of the aqueous H<sub>2</sub>PtCl<sub>6</sub>· 6H<sub>2</sub>O (32.1 mM) solution was dropped into flask and maintained under ultrasonication for 2 h. Afterward, the flask was put into an ice–water bath, an excessive NaBH<sub>4</sub> solution was slowly added into the above mixture within 15 min under vigorous stirring. After stirring for 3 h, the black solid was collected with a magnet, washed with deionized water for several times, and finally dried under vacuum at room temperature overnight, The weight percentage of Pt in the catalyst was determined by ICP analysis (1.3 wt% Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub>).

#### Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> for Hydrogenation

The reaction was carried out in a 25 mL round-bottom flask. A typical procedure for the hydrogenation of nitroarenes is as follows: the desired amounts of catalyst (5 mg), nitroarenes (0.5 mmoL), and solvent (7.0 mL) were charged to the flask equipped with a balloon. The reactor was vacuumized and flushed with pure hydrogen. When the designated reaction temperature was reached, the stirring rate was adjusted to 1500 rpm, and reaction time was accounted. Many experimental data were obtained by repeating the reaction two or three times and they had the good repeatability.

#### **Catalyst Characterization**

Transmission electron microscopy (TEM) measurements were carried out on a JEOL model 2010 instrument operated at an accelerating voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on carbon-coated copper grid and dried at room temperature. The X-ray diffraction (XRD) patterns were obtained using a modern multipurpose theta/theta powder X-ray diffraction system, equipped with a fast linear detector. X-ray photoelectron spectroscopy (XPS, Kratos XSAM800) spectra was obtained by using Al K $\alpha$  radiation (12 kV and 15 mA) as an excitation source (hv = 1486.6 eV) and Au (BE Au4f = 84.0 eV) and Ag (BE Ag3d = 386.3 eV) as reference. All binding energy (BE) values were referenced to C 1s peak of contaminant carbon at 284.6 eV. Brunauer–Emmett–Teller (BET) surface areas were measured by nitrogen adsorption at 77.05 K on an ASAP-2020 adsorption apparatus. A Fourier transform infrared (FT-IR) spectrum was recorded with a Nicolet 6700 (resolution 0.4 cm<sup>-1</sup>) infrared spectrometer and samples were dispersed in potassium bromide and compressed into pellets.

#### **Catalyst Recycles**

The catalyst was recycled as following procedures, at the end of one hydrogenation run, the catalyst was separated from the reaction system by using a magnet, and the supernatant liquid was removed from the flask. The black solid catalyst was thoroughly washed three times with ethanol to remove the adsorbed species, and then fresh substrate and solvent were added into for next runs. All liquid samples were analyzed by gas chromatography (Agilent GC-7890) with an FID detector and HP-5 supelco column (30 m × 0.25 mm, 0.25  $\mu$ m film) and nitrogen as a carrier gas.

#### **RESULTS AND DISCUSSION**

The synthesis of the Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst is described in Scheme 1. Amine functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by a one-pot solvethermal method at 473 K in a reaction time of 6 h at the first step. Then, Pt ionic coordinated with amine on the surface of the Fe<sub>3</sub>O<sub>4</sub> and reduced with NaBH<sub>4</sub> aqueous solution with vigorous stirring, at last, Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst was obtained with the help of a magnet. The amine group on the surface of Fe<sub>3</sub>O<sub>4</sub> acts as a stabilizer and plays an important role in avoiding the leaching of Pt nanoparticles.

Figure 1 shows the XRD analysis patterns of  $Fe_3O_4-NH_2$ and  $Pt-NH_2-Fe_3O_4$ . The XRD pattern of  $Fe_3O_4-NH_2$  shows that the sharp and strong peaks are corresponding to the characteristic peaks of magnetite nanoparticles, which indicates the products are well crystallized<sup>[5]</sup> and are the exactly same results as that reported by Li et al.<sup>[44]</sup> and Ma et al.<sup>[5]</sup> Furthermore, compared with  $Fe_3O_4-NH_2$ , an almost identical XRD pattern was observed after immobilization of Pt on the magnetite (Figure 1b), indicating the crystalline structure and the average size of the crystalline domain of the support were well maintained in the Pt samples. No peaks toward metallic Pt were detected owing to the fact that the Pt particle sizes were very small, indicating that the Pt particles are highly dispersed on the surface of the amine functionalized  $Fe_3O_4$ .

The BET surface area, average pore diameter, and total pore volume of support and catalyst are listed in Table 1.

NH2

NH<sub>2</sub> NH<sub>2</sub>

H2PtCl6· 6H2O

NH<sub>2</sub>

Fe3O4-NH2-Pt4+

SCH. 1. Schematic process for loading Pt particles onto the surface of aminefunctionalized magnetite composite. (1) Synthesis of  $Fe_3O_4$ – $NH_2$ . (2) Pt ionic coordinates with  $Fe_3O_4$ – $NH_2$ . (3) Reduction and the form of loading Pt particles.

NaBH4

ultrasonic,3 h

473 K

6 h

H<sub>2</sub>N

H<sub>2</sub>N

ultrasonic

Characterization results showed that BET surface area, average pore diameter, and total pore volume of  $Pt-NH_2-Fe_3O_4$ catalyst were higher than those of support. These changes are mainly due to dispersion property caused by the addition of Pt particles. TEM experiments have been carried out to detect a possible structure of the metallic Pt particles (Figure 2). These images show that the  $Fe_3O_4$  support has the average particle size of about 15 nm. However, the identification of the small Pt particles was unsuccessful, possibly due to the poor contrast between Pt and  $Fe_3O_4$  support.

The FT-IR spectra of  $Fe_3O_4$ – $NH_2$  and Pt– $NH_2$ – $Fe_3O_4$  were also investigated. Figure 3a shows the FT-IR spectrum of  $Fe_3O_4$ – $NH_2$ . The peaks at 1055, 1629, 3426, and around 2846–2923 cm<sup>-1</sup> correspond to C–N stretching, N–H deformation and C–H stretching models of the alkyl chain,<sup>[45]</sup> indicating that large amount of 1,6-hexanediamine molecules are

FIG. 1. XRD patterns of (a) Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> and (b) Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> catalysts.

TABLE 1 BET surface area, average pore diameter and total pore volume of support and catalyst

Sample	BET specific surface area (m <sup>2</sup> /g)	Average pore diameter (nm)	Total pore volume (cm <sup>3</sup> /g)
Fe <sub>3</sub> O <sub>4</sub> -NH <sub>2</sub> Pt-NH <sub>2</sub> -Fe <sub>3</sub> O <sub>4</sub>	23.43 51.74	8.24 18.92	0.0483 0.2447

immobilized on the surface of the nanoparticles.<sup>[46]</sup> Furthermore, compared with  $Fe_3O_4$ – $NH_2$ , an almost identical FT-IR pattern was observed after immobilization of Pt on the magnetite (Figure 3b), indicating that almost no change occurs after immobilization of Pt on the magnetite nanoparticles surface.

XPS survey scan of the surface of the Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> particles showed the presence of oxygen, carbon, platinum, Pt<sub>4f</sub>, and iron (Figure 4A). To ascertain the oxidation state of the Pt, high-resolution narrow scan was carried out (Figure 4B). According to the previous research, the Pt 4f<sub>7/2</sub> and 4f<sub>5/2</sub> peaks found at BE = 71.4 and 74.4 eV, respectively, have been attributed to metallic platinum which was well consistent with the binding energy of Pt (0).<sup>[7]</sup> The second set of peaks for Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> observed at BE = 74.7 and 77.7 eV, respectively, occurring at higher BE values can be attributed to Pt atoms with lower charge density. However, under the reaction conditions most of the unreduced catalyst also gets reduced and contribute to high yields of the desired product.

The catalytic activity of Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> sample is measured by using a model reaction of the catalytic reduction of *p*chloronitrobenzene (*p*-CNB) into *p*-CAN with hydrogen, which has been demonstrated to be an effective way to evaluate the catalytic capability of noble metal nanocatalysts.<sup>[4,23]</sup> Table 2 shows the conversion and selectivity to *p*-CAN for *p*-CNB hydrogenation at 303 K under an H<sub>2</sub> atmosphere over Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> in aqueous media. No conversion was discovered in the absence of catalysts or in the presence of pure Fe<sub>3</sub>O<sub>4</sub>–NH<sub>2</sub> under the same reaction conditions, which clearly proved that platinum particles

FIG. 2. Typical TEM images of  $Pt-NH_2-Fe_3O_4$  (A and B) at different magnifications.







FeCl<sub>3</sub>·6H<sub>2</sub>O

H<sub>2</sub>N(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>

Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub>-Pt



FIG. 3. FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> and (b) Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>.

were the indispensable component in the hydrogenation p-CNB to the corresponding amines. The data showed that the conversion of p-CNB reached 100% with the reaction time increased from 1 to 3 h. Moreover, the high selectivity (>99.9%) for p-CAN maintained even at 100% p-CNB conversion, and this phenomenon most probably attributed to the intermediates produced in the reaction process being further hydrogenated to the desired product *p*-CAN and the undesired hydrodechlorination reaction of p-CNB molecule was inhibited during the reaction. In addition, a complete conversion was detected within 25 min when the reaction was performed under the hydrogen pressure of 1 MPa H<sub>2</sub> (the reaction was carried out in a 60 mL Parr stainless-steel reactor). It also could be seen that the selectivity to p-CAN maintained when the reaction was conducted at 1 MPa H<sub>2</sub>. These data show that the undesired hydrodechlorination can be avoided over the Pt-NH2-Fe3O4 catalyst even at higher H2 pressure, indicating that Pt-NH2-Fe3O4 was an excellent catalyst for selective hydrogenation of p-CNB to p-chloroaniline in aqueous media.

Table 2 also presents the activities and selectivities for *p*-CNB hydrogenation at 303 K and an H<sub>2</sub> balloon over Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> in a range of organic solvents. Special attention was made to distinguish the by-products in the reduction of *p*-CNB in different solvents (with GC-MS). Aniline (AN), *p*-chloronitrosobenzene (*p*-CNSB), and the condensation product between amines and alcohols were detected as the by-products in the investigated solvents. When methanol and *n*-propanol were used as the solvents, the catalyst Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> could catalyze the *p*-CNB to *p*-CAN with conversions of 44.7% and 61.1%, and the



FIG. 4. (A) The wide survey XPS spectrum and (B) Pt  $_{\rm 4f}$  peaks of Pt–NH2–Fe3O4 catalyst.

TABLE 2 Hydrogenation of *p*-CNB over Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst in different solvents<sup>a</sup>

		Sel. (%)			
Solvent	Conv. (%)	p-CAN	AN	<i>p</i> -CNSB	Others
H <sub>2</sub> O <sup>b</sup>	_		_		_
H <sub>2</sub> O	61.2	>99.9	0.0	0.0	$n.d^{f}$
$H_2O^c$	93.3	>99.9	0.0	0.0	n.d
$H_2O^d$	100	>99.9	0.0	0.0	n.d
$H_2O^e$	100	>99.9	0.0	0.0	n.d
Methanol	44.7	87.3	0.2	12.2	0.3
<i>n</i> -Propanol	61.1	93.4	1.2	5.1	0.3
1,4-Dioxane	25.7	78.3	0.0	15.8	5.9
Hexane	29.6	96.2	0.0	1.4	2.4

Notes. <sup>a</sup>Reaction conditions: *p*-chloronitrobenzene (0.5 mmol), 5 mg Pt (1.3 wt%)–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst in different solvents (7 mL) at temperature of 303 K with an H<sub>2</sub> balloon in 1 h.

<sup>b</sup>5 mg pure Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub>.

<sup>c</sup>Reaction time: 2 h.

<sup>d</sup>Reaction time: 3 h.

<sup>e</sup>Reaction time: 25 min; P = 1 MPa.

<sup>f</sup>Not detected.

selectivities to *p*-CAN could reach 87.3% and 93.4%, respectively. As for the by-products, small amount of AN (ca. 0.2% and 1.2%) and condensation product (both are 0.3%) as well as large amount of the intermediate *p*-CNSB (ca. 12.2% and 5.1%) were detected. However, the use of other organic solvents such as 1,4-dioxane and hexane resulted in low conversion of p-CNB (below 30%) under identical reaction conditions. Although the hydrodechlorination product of AN could be completely inhibited, increased unknown by-products was detected. Amazingly, *p*-CNB possesses very little solubility in neat water, but a comparable *p*-CNB conversion of 61.2% was obtained with the highest selectivity (>99.9%) for *p*-CAN during the reaction process. The results indicate that the catalytic activity for the *p*-CNB hydrogenation is closely related with the solvent polarity.

We also compared the activity and selectivity of  $Pt-NH_2-Fe_3O_4$  with those of Pt deposited on  $Al_2O_3$ ,  $TiO_2$ , AC, MCM-41, MWCNTs, and  $Fe_3O_4$  in aqueous medium. The results in Table 3 indicated that both the  $Pt-NH_2-Fe_3O_4$  and Pt/MWCNTs showed the highest activity for the hydrogenation of *p*-CNB to *p*-CAN, but the catalyst  $Pt-NH_2-Fe_3O_4$  exhibited higher selectivity (>99.9%) than the catalyst Pt/MWCNTs (93.6%). In addition, the poor activity of 30.7% was obtained by the catalyst Pt/MCM-41 and the lowest selectivity of 23.6% toward p-CAN was detected by the catalyst  $Pt/Al_2O_3$  as a result of the severe side reaction of hydrodechlorination under identical reaction. These data show that the choice of the solid support has a significant influence on the catalytic activity and selectivity.

for hydrogenation of aromatic nitro compounds <sup>a</sup>					
		6)			
Catalyst	Conv. (%)	p-CAN	<i>p</i> -CNSB	AN	Others
Pt/Al <sub>2</sub> O <sub>3</sub>	99.0	23.6	0	76.4	n.d
Pt/TiO <sub>2</sub>	95.5	96.1	0	3.4	n.d
Pt/MCM-41	30.7	97.7	0	0.9	1.4
Pt/AC	82.3	98.9	0	1.1	n.d
Pt-NH <sub>2</sub> -Fe <sub>3</sub> O <sub>4</sub>	100	>99.9	0	0.0	n.d
Pt/MWCNTs	100	93.6	0	6.4	n.d
Pt-Fe <sub>3</sub> O <sub>4</sub>	81.1	>99.9	0	0.0	n.d

TABLE 3 Comparative study of different supported platinum catalysts for hydrogenation of aromatic nitro compounds<sup>a</sup>

Note. <sup>a</sup>Reaction conditions: *p*-chloronitrobenzene (0.5 mmol), 5 mg of catalyst in 7 mL water at temperature of 303 K with an  $H_2$  balloon in 3 h.

Compared with the reported Pt-based catalytic systems, which are highly selective to hydrogenation of haloaromatic nitro compounds, the catalytic performance of this catalytic system composed of Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> and the solvent of water is the best one. Such as Zhang et al.<sup>[36]</sup> obtained 100% yield of *p*-CAN over Pt–Fe<sub>3</sub>O<sub>4</sub> catalyst at 333 K and 1 atm hydrogen pressure, however, the TOF was only 19 h<sup>-1</sup>. Sreedhar et al.<sup>[43]</sup> only obtained 88% yield with a TOF of 52 h<sup>-1</sup> with catalyst Pt/GA at room temperature under atmospheric pressure in water. In the present work, more than 99.9% yield of *p*-CAN was observed at 303 K and a hydrogen balloon pressure in aqueous media; the TOF value reached 500 h<sup>-1</sup> with *p*-CNB/catalyst molar ratio of 1500 in the absence of any additives or promoters. The comparison the activity and selectivity with those reported under similar conditions was summarized in Table 4.

The catalytic hydrogenation of a variety of aromatic nitro compounds over  $Pt-NH_2-Fe_3O_4$  catalyst was carried out in aqueous media at 303 K under a hydrogen balloon pressure of  $H_2$  and the results are shown in Table 5. The results indicated that the catalyst  $Pt-NH_2-Fe_3O_4$  could afford a rapid conversion



FIG. 5. Recycling of Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> for the hydrogenation of *p*-CNB.

of the aromatic nitro compounds to the corresponding amines with a substrates/catalyst ratio of 1500. The reduction of *p*-CNB and nitrobenzene could be accomplished within 3 h and 3.5 h, respectively. Other aromatic nitro-compound required a reaction time of 4 h for the complete hydrogenation, which is probably due to the relatively large steric hindrance or the low solubility of the reactants in water. Especially, nearly complete yield (>99.9%) of *p*-CAN was observed when the catalyst was reused six times. Moreover, no hydrodechlorination product was detected in each runs as shown in Figure 5. The high dispersed and stable immobilized active Pt species by the amine groups on the surface of the catalyst was responsible for the excellent reusability. The magnetic property of the catalyst facilitated the separation and redispersion of the nanoparticles after completion of each run.

Although it was difficult to give the exact reaction mechanism of the present  $Pt-NH_2-Fe_3O_4$  system catalyzed hydrogenation of nitro aromatics, some useful information was achieved through analysis of the reaction results. The results indicate that

TABLE 4
Comparison of previous study of different supported platinum catalysts for hydrogenation of o- and p-CNB in similar conditions

Catalyst	Substrate	Conditions	Conv. (Yield) (%)	Sel. (%)	TOF $(h^{-1})$	Ref.
GA-Pt	p-CNB	r.t., 1 atm $H_2$ , $H_2O$	(88)		52	[43]
Pt-PICP	<i>p</i> -CNB	r.t., 1 atm $H_2$ , THF	(96)		200	[40]
Pt/Al <sub>2</sub> O <sub>3</sub>	<i>p</i> -CNB	$303 \text{ K}, 1 \text{ atm H}_2$ , ethanol	99.0	80.9	266	[47]
$Pt/ZrO_2$	<i>p</i> -CNB	$303 \text{ K}, 1 \text{ atm H}_2, \text{ ethanol}$	99.4	90.4	432	[47]
Pt/TiO <sub>2</sub>	<i>p</i> -CNB	$303 \text{ K}, 1 \text{ atm H}_2, \text{ ethanol}$	99.5	92.8	2304	[47]
Pt/Fe <sub>3</sub> O <sub>4</sub>	o-CNB	333 K, 1 atm $H_2$ , methanol	100	(>99.9)	19	[36]
$Pt-Fe_3O_4-Fe^{3+}$	o-CNB	$303 \text{ K}, 1 \text{ atm H}_2, \text{ methanol}$	100	(83.4)	21	[11]
Pt/Fe <sub>2</sub> O <sub>3</sub>	o-CNB	333 K, 1 atm $H_2$ , methanol	100	(>99.9)	805	[36]
Pt–NH <sub>2</sub> –Fe <sub>3</sub> O <sub>4</sub>	p-CNB	$303 \text{ K}, 1 \text{ atm } \text{H}_2, \text{H}_2\text{O}$	100	>99.9	500	This work

TABLE 5 Hydrogenation of different substrates over Pt–NH<sub>2</sub>–Fe<sub>3</sub>O<sub>4</sub> catalyst

Entry	Nitro-aromatic	Product	Time (h)	Yield (%)
1	NO <sub>2</sub>	NH <sub>2</sub>	3.5	97.6
2	CT NO <sub>2</sub>	Ct NH <sub>2</sub>	3	>99.9
3		NH <sub>2</sub>	4	98.7
4			4	>99.9
5	NO <sub>2</sub> Br	NH <sub>2</sub> Br	4	97.0
6	H <sub>3</sub> C NO <sub>2</sub>	H <sub>3</sub> C NH <sub>2</sub>	4	>99.6
7	NO <sub>2</sub> CH <sub>3</sub>	NH <sub>2</sub> CH <sub>3</sub>	4	99.9
8	HO NO <sub>2</sub>	HO NH2	4	95.1
9	H <sub>3</sub> C <sub>1</sub> NO <sub>2</sub> NO <sub>2</sub>	H <sub>3</sub> C <sub>O</sub> NH <sub>2</sub>	4	93

Note. Reaction conditions: 0.5 mmol of substrates, 5 mg of catalyst in 7 mL water at temperature of 303 K with an  $H_2$  balloon.

a number of factors such as the reaction conditions and support nature as well as the solvents that can influence the catalytic performance of the Pt-hydrogenation system. It can be seen that except the target product p-CAN, no other product was detected when the reduction was preceded in aqueous medium owing to the side reaction of hydrodechlorination and condensation could be entirely eliminated (Table 2). However, when the hydrogenation was performed in methanol and n-propanol medium, aniline, p-CNSB, and the condensation products were detected as the main by-product due to the presence of the competition adsorption on the surface of the catalyst.<sup>[41]</sup> The intermediate p-CNSB can be further hydrogenated to p-CAN with the extension of reaction time; but the other two by-products cannot be catalyzed to the desired product, which resulted in lower selectivity. In order to investigate the role of NH<sub>2</sub> group on the catalytic of the catalyst, for comparison, we prepared the Pt-Fe<sub>3</sub>O<sub>4</sub> for the hydrogenation of p-CNB at the same conditions. The results indicated that the Pt-Fe<sub>3</sub>O<sub>4</sub> led to low activity (ca. 81.9%) while Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> was the most active and selective catalyst for p-CNB the hydrogenation to p-CAN, suggesting amine groups of the support have a positive influence on the catalytic properties. Combined with these results, we propose that the suppression

of hydrodechlorination activity and the absence of condensation reaction between amines and alcohols are responsible for complete selectivity to the corresponding amine.

#### CONCLUSIONS

In summarization, the hydrophilic Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> catalyst was prepared by deposited Pt particles onto the surface of the amine-functionalized magnetite nanoparticles through liquidphase reductive process. The Pt-NH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> showed high efficiency for the clean reduction of a variety of aromatic nitro compounds at 303 K under an H<sub>2</sub> atmosphere in water. The unprecedented high activity and selectivity achieved for the clean synthesis of amine via aqueous Pt-catalyzed hydrogenation is preliminarily attributed to a significant beneficial effect of water as a solvent. The side reaction of hydrodechlorination and the condensation could be entirely eliminated in the presence of water. In addition, the Pt-NH2-Fe3O4 catalyst was quite stable and could be reused several times without significant deactivation. Therefore, the results provide a kind of more robust and ecofriendly catalytical system for the development of a sustainable catalytic route for the production of aromatic amines.

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