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Synthesis of Pt nanocatalysts for selective hydrogenation of *ortho*-halogenated nitrobenzene

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Monodisperse Pt nanoparticles (NPs) were prepared by reduction of platinum acetylacetonate in octadecene with the presence of $Fe(CO)_5$. The synthesized nanocatalysts presented high activity and selectively for hydrogenation of *ortho*-halogenated nitrobenzene to the corresponding *ortho*-halogenated aniline under mild reaction conditions.

nanocatalyst, platinum, selective hydrogenation

1 Introduction

Halogenated anilines, as important intermediates in the preparation of industrial dyes, herbicides, pesticides, and pharmaceuticals, are usually produced by selective hydrogenation. Although high catalytic activity in the hydrogenation reactions for halogen nitrobenzenes has been achieved over the conventional metal catalysts [1–9], the production of halogenated anilines is accompanied hydrodehalogenation, which results in the formation of undesirable by-products [10,11]. To solve this problem, several strategies have been developed that involved applications of bimetallic Pd-Ru catalyst, metallic alloy or various organic reagents to suppress dechlorination reaction in Raney-Ni systems [12].

Nanocrystalline materials, owing to their unique chemical and physical properties as compared to bulk metal, have recently received intense attention especially in catalysis [13–19]. Among various metals, platinum (Pt) with different nano-architectures or nano-morphologies exhibited excellent catalytic activities in partial oxidation, hydrogenation, and dehydrogenation of a variety of important molecules that are essential in many industrial applications [4,5,20]. Our group recently prepared a series of Pt nanoclusters as efficient catalysts for different organic synthesis. For example, highly efficient synthesis of *N*-substituted isoindolinones and phthalazinones was achieved with Pt nanowires [21]. Ultra-thin Pt nanowire catalysts with no supporting matrix resulted in hydrogenation of aromatic compounds without loss of activity after being recycled 40 time [22]. Platinum nanowire catalyst exhibited high levels of activity and selectivity toward the controlled hydrogenation of phenol [23]. Herein, we report a novel nanocatalyst based on Pt nanoparticles for selective hydrogenation of *ortho*-halogenated nitrobenzene. Compared to the conventional metal catalysts, these Pt nanocatalysts exhibit high selectivity under mild reaction conditions.

2 Experimental

2.1 Materials and instruments

Ortho-halogenated nitrobenzene, oleylamine and *o*-fluoroaniline were purchased from TCI Co., Ltd. (China). *o*-Chloroaniline was purchased from Jiecai-Trade Co., Ltd. (China) and *o*-bromoaniline was purchased from Avocado (USA). *o*-Iodoaniline was purchased from ABCR GmbH &

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Co. KG (Germany). Platinum(II) acetylacetonate was purchased from Alfa Aesar China Co., Ltd. (China). Oleic acid was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). $Fe(CO)_5$ was purchased from Jiangsu Tianyi Ultrafine metal powder Co., Ltd. (China). All materials were used without further purification. Transmission electron microscopy (TEM) measurements were conducted using a JEOL JEM-200CX instrument (Japan) at an accelerating voltage of 200 kV. The product mixtures were analyzed by GC (VARIAN CP-3800, HP-5 capillary column, FID detector, USA).

2.2 Nanocatalyst preparation

The Pt NPs were prepared according to a moficiation of a previously reported procedure with a modified procedure [24]. First, 0.1 g of platinum(II) acetylacetonate, 10 mL of octadecene, 1 mL of oleic acid and 1 mL of oleylamine were mixed under N_2 with magnetic stirring. The mixture was then heated to 70 °C to dissolve the $Pt(acac)_2$. The temperature was then raised to about 180 °C. A solution of a trace amount of $Fe(CO)_5$ in octadecene was quickly injected into the hot solution. The solution was further heated to 200 °C and kept at this temperature for 1 h before it was cooled down to room temperature. The products were precipitated by ethanol, separated via centrifugation and further purified three times by ethanol. The final product was dispersed in 10 mL of hexane for further use.

2.3 Selective hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) with different additives

First, 2 mg of nanocatalyst, 158 mg of *o*-CNB and 2 mL of methanol were loaded to the reaction tube and could be easily dispersed by a simple ultrasound. Then the tube was flushed three times with nitrogen followed by flushing with hydrogen in order to remove the air. The reaction tube was placed in an oil bath for 12 h at 50 °C with a hydrogen balloon.

2.4 Recyclability of the catalyst

After the first cycle, the reaction solution was cooled to room temperature. The used catalyst was separated from product mixtures by centrifugation and washed with methanol three times. The catalyst was then used in the next cycle. The latter processing operation for catalyst was the same as above.

3 Results and discussion

Due to the high catalytic activity exhibited by Pt nanocatalysts for hydrogenation of different aromatic compounds, we aimed to explore the potential of Pt nanoparticle catalyst for hydrogenation of *ortho*-halogenated nitrobenzene, and also examine its activity and selectivity towards the generation of halogenated anilines. In this study, we found that these nanoparticles exhibited fairly high activity and selectively for hydrogenation of *ortho*-halogenated nitrobenzene to the corresponding *o*-fluoroaniline (*o*-FAN), *o*-chloroaniline (*o*-CAN), *o*-bromoaniline (*o*-BAN) and *o*-iodoaniline (*o*-IAN) with respective conversion rates of 100%, 99.9%, 95.5% and 89.6% for *o*-fluoronitrobenzene (*o*-FNB), *o*-chloronitrobenzene (*o*-CNB), *o*-bromonitrobenzene (*o*-BNB) and *o*-iodonitrobenzene (*o*-INB).

Figure 1(a), which shows a typical TEM image of fresh Pt NPs, indicates that the Pt nanoparticles are highly dispersed and have an average size of 4.3 nm (Figure 1(b)). Figure 2 shows the XRD patterns of the fresh Pt NPs catalyst. The XRD spectrum contains five obvious peaks that are characteristics of the face-centered-cubic (fcc) crystalline Pt, corresponding to the respective planes (111), (200), (220), (311) and (222); this result is consistent with other reports [24]. The typical TEM image of the Pt NPs after the reaction was shown in the Supporting Information online.

The hydrogenation of *o*-CNB was employed as a probe reaction to test the activity and selectivity of the Pt NP

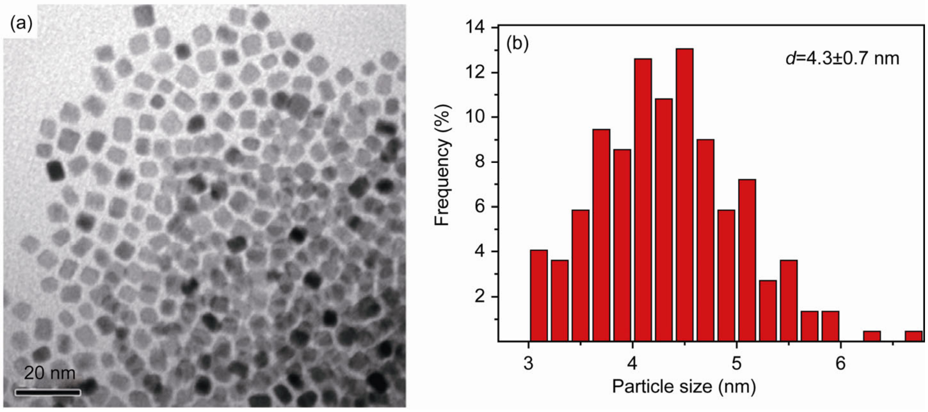


Figure 1 TEM image (a) and size distribution histogram (b) of the mono-dispersed Pt NPs.

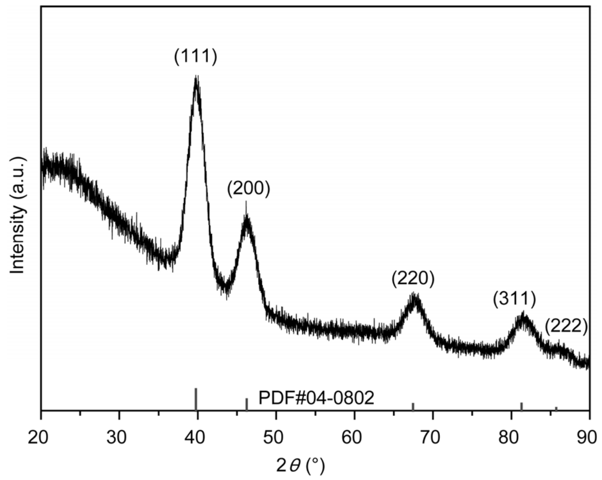


Figure 2 XRD patterns of the mono-dispersed Pt NPs.

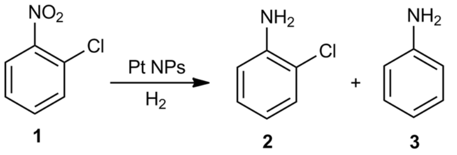
Table 1 Selective hydrogenation of *o*-CNB to *o*-CAN over mono-dispersed Pt NPs with different additives [a)]

Entry	Additive	Conv. (%)	Sel. (%)	
			2	**3**
1	none	100	89.7	0.2
2	$NH_3\cdot H_2O$	100	99.3	0.6
3	$(CH_3CH_2)_3N$	100	99.3	0.2
4	NaOH	100	92.0	0.1
5	KOH	100	78.9	0.2
6	K_2CO_3	100	91.1	0.3
7	Na_2CO_3	100	97.5	0.1
8	$NaHCO_3$	100	99.7	0.1
9	CH_3COOH	100	96.3	1.3

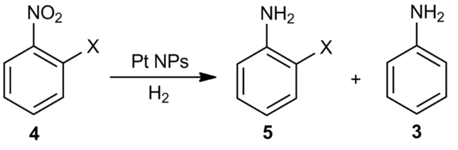
a) Reaction conditions: *o*-CNB, 158 mg; additives, 1 mmol; catalysts, 2 mg; methanol (solvent), 2 mL; hydrogen pressure, 0.1 MPa, 50 °C, 12 h.

catalysts. Initially, we conducted the screening test of different bases to find the suitable additives for the hydrogenation of *o*-CNB under this mild condition (Scheme 1). Table 1 shows the results of the hydrogenation of *o*-CNB treated by different additives, including $NH_3\cdot H_2O$, $(CH_3CH_2)_3N$, NaOH, KOH, K_2CO_3, Na_2CO_3, $NaHCO_3$, and CH_3COOH (Entries 2–9). The $NaHCO_3$ catalyst shows the highest catalytic activities. After an 8 h reaction, 100% of *o*-CNB is converted and selectively affords the target *o*-chloroaniline with a yield of 99.7 (Entry 8). Other additives, such as $NH_3\cdot H_2O$, $(CH_3CH_2)_3N$ and Na_2CO_3, also exhibit relatively high catalytic abilities for the generation of *o*-chloroaniline, with final individual yields of about 99.3%, 99.3% and 97.5% (Entries 2, 3 and 7). However, our attempts to use other metallicion agents, such as NaOH, KOH and K_2CO_3 were less successful under this condition, NaOH, KOH, and K_2CO_3 preferentially catalyzed the formation of *o*-chloroaniline, with respective yields of around 78.9, 92.0, and 91.1 (Entries 4–6). Therefore, we chose $NH_3\cdot H_2O$ and $NaHCO_3$ as the additives for further studies (Scheme 2).

Under the optimized conditions for the formation of *o*-chloroaniline from *o*-CNB, *o*-fluoro-nitrobenzene (*o*-FNB) was also tested for the generation of its corresponding fluoroaniline. Table 2 shows the results of the hydrogenation of *o*-FNB treated by $NH_3\cdot H_2O$. Here, 100% of *o*-FNB is converted and selectively affords the target *o*-fluoroaniline with yield in 99.6% (Entry 1). After the reaction was finished, the Pt nanocatalysts were collected and tested for another round of hydrogenation of *o*-FNB. After the Pt nanocatalysts were recycled 5 times, we did not observe an obvious decline of conversion and selectivity toward the generation of fluoroaniline (Entries 2–5).



Scheme 1 Selective hydrogenation of *o*-CNB to *o*-CAN over mono-dispersed Pt NPs with different additives.



Scheme 2 Selective hydrogenation of *ortho*-halogenated nitrobenzene over monodispersed Pt NPs with base.

We also tested the recyclability of Pt nanocatalysts for the formation of *o*-chloroaniline from *o*-CNB. In Table 3, which shows the results of the hydrogenation of *o*-CNB treated by $NH_3\cdot H_2O$, we see that 100% of *o*-CNB is converted and selectively affords the target *o*-fluoroaniline with a yield of 99.0% (Entry 1). After the reaction was finished, the Pt nanocatalysts were collected and tested for another round of hydrogenation of *o*-CNB. After the Pt nanocatalysts had been recycled 5 times, we did not observed an obvious decline of conversion and selectivity toward the generation of fluoroaniline (Entries 2–5).

We also tested the catalytic ability of Pt NPs for the formation of *o*-bromoaniline from *o*-bromo-nitrobenzene by using $NaHCO_3$ as additive. Table 4 shows the results of the hydrogenation of *o*-BNB treated by $NaHCO_3$. 100% of

Table 2 Selective hydrogenation of *o*-FNB to *o*-FAN over monodisperse Pt NPs with ammonia [a)]

Entry	X	Additive	Conv. (%)	Sel. (%)	
				5	**3**
1	F	$NH_3\cdot H_2O$	100	99.6	n.d. [b)]
2	F	$NH_3\cdot H_2O$	100	99.6	n.d.
3	F	$NH_3\cdot H_2O$	100	100	0
4	F	$NH_3\cdot H_2O$	100	100	0
5	F	$NH_3\cdot H_2O$	100	100	0

a) Reaction conditions: *o*-FNB,106 μL; catalysts, 2 mg; ammonia, 30 μL; methanol (solvent), 2 mL; hydrogen pressure, 0.1 MPa, 50 °C, 8 h; b) n.d.=not detected.

Table 3 Selective hydrogenation of *o*-CNB to *o*-CAN over monodispersed Pt NPs with ammonia [a)]

Entry	X	Additive	Conv. (%)	Sel. (%)	
				5	**3**
1	Cl	$NH_3 \cdot H_2O$	100	99.0	n.d. [b)]
2	Cl	$NH_3 \cdot H_2O$	100	99.6	n.d.
3	Cl	$NH_3 \cdot H_2O$	100	99.9	n.d.
4	Cl	$NH_3 \cdot H_2O$	100	99.8	0.1
5	Cl	$NH_3 \cdot H_2O$	100	99.9	0.1

a) Reaction conditions: *o*-CNB, 158 mg; catalysts, 2 mg; ammonia, 30 μL; methanol (solvent), 2 mL; hydrogen pressure, 0.1 MPa, 50 °C, 8 h; b) n.d.=not detected.

Table 4 Selective hydrogenation of *o*-BNB to *o*-BAN over monodispersed Pt NPs with sodium bicarbonate [a)]

Entry	X	Additive	Conv. (%)	Sel. (%)	
				5	**3**
1	Br	$NaHCO_3$	100	86.6	1.9
2	Br	$NaHCO_3$	100	94.3	0.6
3	Br	$NaHCO_3$	100	95.5	3.2
4	Br	$NaHCO_3$	100	94.1	4.8
5	Br	$NaHCO_3$	100	94.9	4.6

a) Reaction conditions: *o*-BNB, 202 mg; catalysts, 2 mg; sodiumbicarbonate, 84 mg; methanol (solvent), 2 mL; hydrogen pressure, 0.1 MPa, 50 °C, 8 h.

o-BNB is converted and selectively afforded the target *o*-bromoaniline with yield in 86.6% (Entry 1). After the reaction was finished, the Pt nanocatalysts were collected and tested for another round of hydrogenation of *o*-BNB. After the Pt NP catalysts were recycled 5 times, we did not observed an obvious decline of conversion and selectivity toward the generation of fluoroaniline (Entries 2–5).

Finally, we chose iodo-nitrobenzene as the substrate to test the catalytic ability of Pt nanocatalysts for the generation of iodoaniline. In Table 5, Which shows the results of the hydrogenation of *o*-INB treated by $NaHCO_3$, 100% of *o*-INB is converted and selectively affords the target *o*-iodoaniline with a yield of 80.4% (Table 5, Entry 1). After the reaction was finished, the Pt NP catalysts were collected and tested for another round of hydrogenation of *o*-INB. After the Pt nanocatalysts had been recycled 5 times, we did not observe an obvious decline of conversion and selectivity toward the generation of fluoroaniline (Entries 2, 3). However, we did find a severe decrease of efficiency of the catalyst for the generation of IAN. The final yield was about 68.0%.

Table 5 Selective hydrogenation of *o*-INB to *o*-IAN over monodispersed Pt NPs with sodium bicarbonate [a)]

Entry	X	Additive	Conv. (%)	Sel. (%)	
				5	**3**
1	I	$NaHCO_3$	100	80.4	11.1
2	I	$NaHCO_3$	100	89.6	10.5
3	I	$NaHCO_3$	100	80.5	2.8
4	I	$NaHCO_3$	100	67.3	27.3
5	I	$NaHCO_3$	100	68.0	6.3

a) Reaction conditions: *o*-INB, 249 mg; catalysts, 2 mg; sodium bicarbonate, 84 mg; methanol (solvent), 2 mL; hydrogen pressure, 0.1 MPa, 50 °C, 8 h.

4 Conclusions

We report a novel nanocatalyst based on Pt NPs for hydrogenated of *ortho*-halogenated nitrobenzene with higher selectivity and activity under mild reaction conditions than the conventional metal catalysts. The nanocatalysts were very stable and recyclable after separation from the reaction system. The results described here show that the Pt nanocatalysts are promising catalysts for industrial applications.

Supporting information

The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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