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# **Convenient and Selective Hydrogenation of Nitro Aromatics with a Platinum Nanocatalyst under Ambient Pressure**

Kunling Xu,<sup>a</sup> Yuan Zhang,<sup>a</sup> Xiaorong Chen,<sup>a</sup> Lei Huang,<sup>a</sup> Rui Zhang,<sup>a</sup> and Jun Huang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China Fax: (+86) 25-8317-2261; e-mail: junhuang@njut.edu.cn

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**Abstract:** A convenient and highly selective platinum nanocatalyst was developed for the hydrogenation of nitro aromatics into the corresponding anilines at room temperature under ambient pressure. The platinum catalyst was highly active and selective for the hydrogenation of nitro aromatic compounds. Reducible groups such as aldehyde, ketone and nitrile were untouched during the hydrogenation of the corresponding nitro compounds, and the corresponding anilines were obtained quantitatively.

**Keywords:** anilines; hydrogenation; nanocatalyst; nitro aromatics; platinum

Functionalized anilines are industrially important intermediates for fine chemicals such as agrochemicals, pharmaceuticals and dyestuffs.<sup>[1]</sup> Most of the aniline is produced from the catalytic hydrogenation of nitrobenzene, but the selective reduction of a nitro group with H<sub>2</sub> is not easy when other reducible groups are present in the same molecule.<sup>[2]</sup> Moreover, a vast number of nitro aromatics are commercially available or easily prepared, so it is highly desirable to develop highly active and selective catalysts for the reduction of nitro groups. A number of transition metal catalysts (based on Pt, Pd, Ru etc.) were reported to be highly efficient for the hydrogenation of nitrobenzene.<sup>[3]</sup> However, it is difficult to avoid side reactions with these highly active metal (Pt, Pd or Ru) catalysts when applied to nitro substrates with other reducible groups. To solve the problem, other metal catalysts (such as Au, Ag and Cu) were developed for the selective hydrogenation of nitro groups, but the activities were always not high, and the reaction conditions were harsh (for example, T > 100 °C and P > 1.0 atm  $H_2$ ).<sup>[2,4]</sup> In addition, some other hydrogen sources were used for the catalytic hydrogenation of nitro compounds as stoichiometric reducing agents, and a high selectivity was obtained.<sup>[2g,h,j]</sup> From a sustainable chemistry viewpoint, the direct hydrogenation of nitro compounds using  $H_2$  with a highly active catalyst was favorable, as the related process will be more efficient and green. And herein we reported a Pt nanocatalyst, which is highly selective and efficient for the hydrogenation of functionalized nitro aromatics to the corresponding anilines under mild conditions (Scheme 1).

Ionic liquids based on 1,1,3,3-tetramethylguanidinium (TMG) were reported and used in nanocatalysis extensively.<sup>[5]</sup> Moreover, in order to minimize the amount of utilized IL and increase the contact surface in related reactions, supported ionic liquid systems were studied for some reaction systems.<sup>[6]</sup> Additionally, polymer-supported ionic liquid systems (ionic polymeric materials) were developed and employed in transition metal catalysis.<sup>[7]</sup> Although these ionic polymeric materials are recyclable easily, mass transfer was limited as the materials are non-porous and insoluble in the reaction systems. Therefore, we recently reported a highly porous ionic copolymer (PICP) material based on TMG with the  $CO_3^{2-}$  anion and the related CuO nanocatalyst for C-O coupling reactions, and the PICP was shown as an excellent support for CuO nanoparticles.<sup>[8]</sup> Thereafter, PICP material based



R= F, Cl, Br, I, CHO, CN, NH<sub>2</sub>, CH<sub>3</sub>CO, OH etc.

**Scheme 1.** Pt-catalyzed selective hydrogenation of nitro aromatics.



**Figure 1.** TEM images of the Pt nanoparticles on the porous ionic polymer material. The fresh Pt nanocatalyst (*left*), the 5<sup>th</sup> time recovered Pt nanocatalyst (*right*), scale bar for both pictures 20 nm.

on TMG with the Cl<sup>-</sup> anion was applied as a support for Pt nanoparticles and the related Pt/PICP was used as a catalyst for hydrogenation of nitro aromatics (the catalyst preparation is presented in the Supporting Information).

As shown in Figure 1, the Pt particles were highly dispersed on the PICP, and the mean diameter of the nanoparticles is around 2-4 nm (Figure 1, left). Hydrogenation of nitrobenzene was performed as the model reaction with our Pt/PICP nanocatalyst, and the results are listed in Table 1. We were delighted to find that the Pt/PICP nanocatalyst was highly active and selective. The hydrogenation of nitrobenzene by the Pt/PICP gave aniline quantitatively in THF, diethyl ether, ethyl acetate or solvent-less at room temperature under ambient pressure (with an  $H_2$  balloon) with  $0.5 \mod \%$  Pt loading (Table 1, entries 1, 4, 6, 7). Ethanol, toluene and hexane were also good solvents for the hydrogenation of nitrobenzene (Table 1, entries 3, 5, 8). The PICP with the  $CO_3^{2-}$  anion was a poorer support than the PICP with the Cl- anion (Table 1, entries 1, 2). It is well known that some byproducts, including nitrosobenzene, N-phenylhydroxylamine, azoxybenzene, azobenzene and hydrazobenzene are formed in the transformation. But our Pt/ PICP nanocatalyst exhibited an extremely high selectivity for aniline, even at low conversion (Table 1, entries 5, 7, 10). It should be mentioned that hydrogenation of nitrobenzene with a very low Pt loading (10 ppm Pt/PICP nanocatalyst) gave aniline in 83% yield (Table 1, entry 11), which showed the potential for practical application. For comparison, commercial Pt/C and Pd/C were tested under similar reaction conditions, lower activities and selectivities were obtained

**Table 1.** Pt-catalyzed hydrogenation of nitrobenzene to aniline. $^{[a]}$ 

Entry	Time [min] <b>60</b>	Solvent	Conv./Yield [%]	
1		THF	100/99	
2 <sup>[b]</sup>	60	THF	95/93	
3	60	ethanol	100/95	
4	60	diethyl ether	100/99	
5	60	toluene	80/80	
6	60	ethyl acetate	100/99	
7	10	solvent-free	100/99	
8	60	hexane	85/85	
9 <sup>[c]</sup>	60	THF	99/99	
10 <sup>[d]</sup>	60	THF	99/99	
11 <sup>[e]</sup>	360	THF	84/83	
12 <sup>[f]</sup>	60	solvent-free	93/86 <sup>[h]</sup>	
13 <sup>[g]</sup>	60	solvent-free	89/81 <sup>[h]</sup>	

<sup>[a]</sup> *Reaction conditions:* nitrobenzene, 1.0 mmol; Pt/PICP 0.5 mol%; with an  $H_2$  balloon; at room temperature; the conversions and yields were determined by GC ( $C_{16}H_{34}$  used as internal standard).

- <sup>[b]</sup> PICP with  $CO_3^{2-}$  anion used as support.
- <sup>[c]</sup> The first time recycled Pt/PICP.
- <sup>[d]</sup> The fifth time recycled Pt/PICP.
- <sup>[e]</sup> Pt/PICP (0.001 mol%) 100 °C, 1.5 MPa  $H_2$  in an autoclave.
- <sup>[f]</sup> 2 mol% Pt/C as catalyst.
- [g] 2 mol% Pd/C as catalyst.
- <sup>[h]</sup> Some azoxybenzene formed as by-product detected by GC-MS.

1261

even with high catalyst loadings (Pt/C and Pd/C, 2 mol%) (Table 1, entries 12, 13). The Pt/PICP nanocatalyst was recovered easily by filtration without any loss of efficiency, a quantitative yield of aniline was obtained with the recycled Pt/PICP nanocatalyst (Table 1, entries 9, 10). After removal of the Pt/PICP nanocatalys by filtration, the filtrate was investigated by ICP-OES (inductively coupled plasma optical emission spectroscopy), and no Pt was detected (below the detection limitation of 7 ppb). The filtrate was inactive towards further hydrogenation of nitrobenzene. A TEM image showed the structure of the recovered Pt nanocatalyst (5th time recovered). Although the mean diameter of the recovered Pt nanoparticles was slightly increased to about 3-6 nm (Figure 1, right), the Pt nanocatalyst was still active for the hydrogenation of nitrobenzene.

It is much more important to prepare functionalized anilines by hydrogenation of the corresponding nitro aromatics, especially when other reducible groups are present in the same molecules. Therefore, various functional nitro aromatic compounds were employed for the hydrogenation (Table 2). Interestingly, nitro aromatics with halides (F, Cl, Br and I) were hydrogenated selectively to the corresponding anilines, only a very small amount of aniline (dehalogenation side reaction) by-product was observed (Table 2, entries 2-7). The hydrogenation of 3-iodonitrobenzene required a higher temperature (50°C) and more Pt catalyst (2 mol%). It could be that the  $I^$ anion is formed and slightly deactivates the Pt nanocatalyst, as the hydrogenation of nitrobenzene gave aniline in 24% yield only (24% conversion also) when 10% KI was added to the reaction mixture (the same reaction conditions used as Table 1, entry 1 except for KI added). Hydroxy and amine groups were well tolerated for the hydrogenation of the corresponding nitro compounds with Pt/PICP, and the products were obtained quantitatively (Table 2, entries 8-12). It is important that reducible groups such as aldehyde, ketone and nitrile were untouched during the hydrogenation of the corresponding nitro compounds, and quantitative products were obtained (Table 2, entries 13–15). The hydrogenation of 2,6-dimethylnitrobenzene required harsher reaction conditions, which showed the steric effect of the two methyl groups (Table 2, entry 16).

To investigate the hydrogenation's selectivity for nitro and olefin groups, the hydrogenation of 3-nitrostyrene was performed under the same reaction conditions (0.5 mol% Pt/PICP, at room temperature, with an H<sub>2</sub> balloon), and the results are shown in Figure 2. The hydrogenation of nitro and olefin groups occurred at the same time, although the ethyl group was formed faster than the NH<sub>2</sub> group at first. And 3-nitrostyrene was hydrogenated into 3-ethylaniline completely after 3 h. The Pt/PICP nanocatalyst showed

**Table 2.** Selective hydrogenation of nitro aromatics with Pt nanocatalyst.<sup>[a]</sup>

Entry	ArNO <sub>2</sub>	Time [h]	ArNH <sub>2</sub>	Yield [%] <sup>[b]</sup>
1		1		99
2		1	F	98 <sup>[c]</sup>
3		1		99
4		1		96 <sup>[c]</sup>
5		3	CI NH <sub>2</sub>	96 <sup>[c]</sup>
6	Br NO <sub>2</sub>	6	Br NH <sub>2</sub>	96 <sup>[c]</sup>
7		10	I NH <sub>2</sub>	92 <sup>[c,d,e]</sup>
8		10		99
9	H <sub>2</sub> N-NO <sub>2</sub>	10	H <sub>2</sub> N-NH <sub>2</sub>	99
10		3		99
11		3		99
12		3		99
13		3		99
14		5		99 <sup>[f]</sup>
15		10	NC-NH2	99 <sup>[d,e]</sup>
16		10		99 <sup>[d,f]</sup>

<sup>[a]</sup> *Reaction conditions:* nitro compound, 1.0 mmol; Pt/PICP 0.5 mol%; with an H<sub>2</sub> balloon; at room temperature.

<sup>[b]</sup> Yields determined by GC.

- <sup>[c]</sup> The by-product is aniline.
- <sup>[d]</sup> At 50 °C.
- <sup>[e]</sup> 2 mol% Pt/PICP used.
- <sup>[f]</sup> 1 mol% Pt/PICP used.



**Figure 2.** Hydrogenation of 3-nitrostyrene with Pt/PICP. *Reaction conditions:* 3-nitrostyrene, 1.0 mmol; THF, 1.0 mL as solvent; Pt/PICP 0.5 mol%; with a  $H_2$  balloon; at room temperature.

low selectivity for the hydrogenation of olefin and nitro groups, although the  $Pt/TiO_2$  was reported to exhibit selectively for the hydrogenation of 3-nitrosty-rene.<sup>[2e]</sup> Moreover, the hydrogenation of a mixture of styrene and nitrobenzene was performed also, and similar results were obtained (see Supporting Information, Figure S3).

It is generally accepted that aniline derivatives were formed with Pt catalysts though both direct route and condensation routes.<sup>[4e,9]</sup> Although it was difficult to give the exact reaction mechanism of our Pt/PICP-catalyzed hydrogenation of nitro aromatics, some useful information was achieved through analysis of the reaction results. Polar solvents were usually used for the hydrogenation of nitro aromatics as some intermediates (for example, azoxybenzene and azobenzene though the condensation route) were polar compounds and poorly soluble in a non-polar solvent. Therefore, the hydrogenation of nitro aromatics was not easily completed in non-polar solvents. But in our Pt/PICP catalyst system, the nitrobenzene was converted only into aniline even at low conversion in non-polar solvents (Table 1, entries 4, 7), which indicated that the reaction pathway was mostly though the direct route. Moreover, the selectivity was kept up to 99%, and nearly no by-product was detected at conversion from 0 to 68% (see Supporting Information, Figure S3), which is also consistent with the direct route, and no condensation intermediate was found. In our catalyst system, the PICP support is a highly porous ionic material with the flexible 1,1,3,3tetramethylguanadinium cation and Cl<sup>-</sup> anion anchored on the rigid DVB polymer, and the Cl<sup>-</sup> anion may help the hydrogenation of N-phenylhydroxylamine into aniline through the dehydration pathway. Based on these results, we propose that the nitrobenzene was adsorbed strongly onto the surface of the porous support firstly, and then nitrobenzene was hydrogenated directly to aniline before being desorbed from the support. The highly porous ionic material PICP was an excellent support for Pt nanoparticles, and Pt/PICP exhibited high activity and selectivity for the hydrogenation of nitro aromatics under mild conditions.

In conclusion, we have demonstrated a convenient and highly selective Pt nanocatalyst for the hydrogenation of nitro aromatics into the corresponding anilines. The PICP material was an excellent support for Pt nanoparticles, and Pt/PICP exhibited high activity and selectivity for the hydrogenation of nitro aromatics under mild conditions. The hydrogenation of nitrobenzene over Pt/PICP gave aniline quantitatively under mild conditions, and no by-product was detected for the hydrogenation of nitrobenzene even at low conversion in polar or non-polar solvents, which indicated that the nitrobenzene was converted directly into aniline. Nitro aromatics with halides (F, Cl, Br and I) were hydrogenated selectively to the corresponding anilines. Reducible groups such as aldehyde, ketone and nitrile were untouched during the hydrogenation of the corresponding nitro compounds, and the corresponding anilines were obtained quantitatively.

### **Experimental Section**

#### **Preparation of the Pt/PICP**

The catalyst Pt/PICP was synthesized by a one-pot procedure. In a typical experiment, 100 mg of PICP were initially dispersed in 20 mL of  $H_2PtCl_6 \cdot 6H_2O$  (14.1 mg/0.027 mmol) solution for 6 h with stirring. Then, 2 mL of NaBH<sub>4</sub> solution (10.2 mg/0.27 mmol NaBH<sub>4</sub> used) were added into the suspension within 2 min with stirring. Subsequently, the solid was filtered and washed with water. And then the Pt/PICP catalyst was obtained after being dried under vacuum at room temperature for 1 day. The Pt/PICP catalyst was characterized by ICP-OES (inductively coupled plasma optical emission spectroscopy) analysis and 4.9 wt% of Pt was found for the Pt/PICP catalyst.

# Typical Procedure for the Hydrogenation of Nitro Compounds

A nitro aromatic (1.0 mmol) and THF (2.0 mL) were added to a Schlenk tube which contained Pt/PICP (Pt: 0.5– 2.0 mol%) catalyst and a stir bar under argon. And then a balloon of H<sub>2</sub> was connected to the Schlenk tube. The reaction mixture was stirred for 1 hour at 25 °C under 1 atm of H<sub>2</sub> (with a balloon). After the reaction was completed, the Pt/PICP was separated by filtration, and the products (in the filtrate mixture) were analyzed by GC.

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1264