Carbon supported Pt colloid as effective catalyst for selective hydrogenation of nitroarenes to arylhydroxylamines[†]

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The Pt colloid supported on carbon is an active and selective catalyst for the partial hydrogenation of nitroaromatics with electron-withdrawing substituents to the corresponding *N*-arylhydroxylamine, indicating an additive-free green catalytic approach for arylhydroxylamine synthesis.

N-Arylhydroxylamine (HA) usually exists as an intermediate during catalytic hydrogenation of various nitroarenes (NA) to aromatic amines.¹ The amount of HA accumulated in the hydrogenation process changes dramatically according to the properties of substrates, reaction conditions and different catalyst systems. Since HA is generally very active and can be converted to many high-valued fine chemicals,^{2,3} the direct synthesis of HA has been an attractive topic to synthetic chemists for decades.⁴ However, it is extremely difficult to get high HA yield by conventional catalytic hydrogenation techniques.

HA has been synthesized from NA by chemical reduction using Zn/NH₄Cl(HCOONH₄) in aqueous suspension,⁵ biocatalytic reduction using baker's yeast or plant cells,⁶ and selective hydrogenation using noble metal catalysts with a large amount of organic additives. Typical additives are DMSO,⁷ divalent sulfur compounds,⁸ organic bases (monoamine, pyrrolidine, piperidine, pyridine)⁹ and organic phosphorus compounds.¹⁰ However, the conventional chemical reduction method has been challenged due to serious pollution, and the biological reduction has the shortcoming of low efficiency with long reaction time using a large quantity of biocatalyst. The selective catalytic hydrogenation reduction seems to be a better choice for HA preparation, which is environmentally benign and offers several advantages over chemical and biochemical reductions. However, the knowledge on the chemoselective catalytic hydrogenation of NA to HA has been so far very limited. Only some patents claimed Pd/C and Pt/C as catalyst with the help of a large amount of selectivity-improving organic additives. Despite the serious shortcoming of separation, purification and further application of HA in the additive-containing system as reported in patents, the HA yield is still low and far from ideal.

There have been some publications concerning the organic additive-free hydrogenation of NA. Neri *et al.* studied the

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reaction kinetics of 2,4-dinitrotoluene over Pd/C¹¹ and found that during the reaction the yield of intermediate arylhydroxylamine was about 82%. Oemer et al. studied the hydrogenation kinetics of 2,6-dinitrotoluene using Pt/C and Pt/Al₂O₃ as catalysts and got 2-amino-6-nitrotoluene as the main intermediate.¹² Westerterp et al. studied the kinetics of the catalytic hydrogenation of 2,4-dinitrotoluene over a 5 wt% Pd/C using methanol as solvent. The reaction was conducted in a batch slurry reactor under the conditions of 2 MPa and 308 K, and the maximum selectivity of 4-hydroxylamino-2nitrotoluene was 79.3%.13 It is obvious that the direct synthesis of HA through selective catalytic hydrogenation of NA is a difficult task. Therefore, it is important to have a deep understanding of the reaction mechanism and to design an active, selective and additive-free hydrogenation catalyst system for the clean and efficient synthesis of HA.

Pt/C is a well-known catalyst material and a solid knowledge has been accumulated on it as a mild selective hydrogenation catalyst and effective electrocatalyst. It has been well accepted that the preparation method and the dispersion of Pt particle on C play very important roles in its catalytic performance. Pt colloid has recently become attractive.^{14–16} The Pt/C prepared from colloid method showed unique properties and excellent electrocatalytic activity.¹⁶

In this communication, we report at the first time a green and highly efficient catalytic methodology for chemoselective hydrogenation of various nitroaromatic compounds into the corresponding HA using Pt colloid on carbon as catalyst. The catalyst is especially effective for those NA containing electron-withdrawing substituents. Without adding any chemical promoters, high HA selectivity (maximum 96.5%) and almost 100% NA conversion were obtained, indicating a general catalytic methodology for HA production.

The catalytic hydrogenation reaction was carried out in a 70 ml stainless-steel autoclave. All products were analyzed by HPLC and LC-MS. The Pt colloid on carbon catalyst was prepared according to the literature.¹⁶ Briefly, H₂PtCl₆ was quantitatively dissolved in deionized H₂O containing Tween-20 and Brij-35. Aqueous NaBH₄ was added dropwise to the solution which soon turned into a dark black stable colloid solution. Under vigorous stirring, active carbon was added to the colloid solution. The Pt/C catalyst was obtained by filtration, washing with hot H₂O to remove the surfactant from the carbon surface. The particle size of Pt is about 3 nm. The surface morphology and structural characteristics of the Pt/C as well as experimental details are described in the supporting information (ESI)[†] and in the literature.¹⁶

Table 1 summarizes the results of the catalytic hydrogenation of several substituted NA to the corresponding HA over

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[†] Electronic supplementary information (ESI) available: Catalytic hydrogenation experiment, analytical and spectral characterization data, preparation and characterization of catalyst. See DOI: 10.1039/b916686f

Entry	Substrate	Product	t/ min	Conv./ %	Sel./ %
1 ^{<i>a</i>}		O ₂ N NHOH	190	100	92.3
2 ^{<i>b</i>}		NO2 NHOH	170	100	91.9
3 ^b		02N	115	100	86.3
4 ^{<i>b</i>}		с	65	100	86.3
5 ^c	HOC ₂ H ₄ O ₂ S	HOC ₂ H ₄ O ₂ S	210	100	93.4
6 ^{<i>c</i>}		Соон	120	100	90.7
7 ^a	HOOC-	HOOC	120	100	96.5
8 ^a	NO ₂	HOHN CI	115	100	51.1
U	O ₂ N-CI		115	100	38.2
	NO	№НОН			

 Table 1
 Chemoselective hydrogenation of different NA to HA over carbon supported Pt colloid



Scheme 1 Reaction pathway for the hydrogenation of *m*-DNB.

unchanged. Di- and tri-substituted NA were also investigated. 3,5-Dinitrobenzoic acid (entry 7) gave the highest selectivity of 96.5% at 100% conversion. The hydrogenation of 1-chloro-2,4-dinitrobenzene (entry 8) resulted in two isomeric HA products. The *para*-nitro group in 1-chloro-2,4-dinitrobenzene is easier to be hydrogenated than the *ortho*-nitro group due to a steric effect.

We have recently reported the highly selective partial hydrogenation of *m*-dinitrobenzene (*m*-DNB) to *m*-nitroaniline (c2) over Ru/C.¹⁷ In order to explore the hydrogenation reaction mechanism for the formation of *N*-(3-nitrophenyl)hydroxylamine (b), *m*-DNB was chosen as a model substrate. The whole reaction pathway is illustrated simply in Scheme 1.

The hydrogenation of *m*-DNB should be practically more complicated, nitroso compounds and trace amounts of dimer may also exist in the reaction system. However, only the compounds illustrated in Scheme 1 were detected by HPLC and GC. The material balance was good, indicating that other impurities were negligible. Effects of different catalyst and reaction parameters were studied. It was proven that mild reaction conditions favour the formation of HA (b) and THF is a suitable solvent with better effect than ethanol and methanol. Table 2 showed the typical comparison results of different catalysts and solvents. Under the reaction conditions, the maximum HA (b) yield over colloid Pt/C is 92.3% at 100% conversion, while the maximum yield over Ru, Pd and Ni catalysts were notably lower than Pt. Though we tried to increase the performance of Ru, Pd and Ni catalysts by optimizing the reaction parameters, the HA (b) yield could not be further increased. For all the catalyst systems, different amount of byproducts *m*-dihydroxylaminobenzene (c1), m-nitroaniline (c2), m-hydroxylaminoaniline (d) and complete hydrogenation product m-diaminobenzene (e) were observed. Several commercial Pt/C and Pt/Al2O3 catalysts were also tested and typical results are listed in Table 2. It is obvious that our colloid Pt/C showed the highest yield of HA.

 Table 2
 Chemoselective hydrogenation of m-DNB to m-hydroxylaminonitrobenzene over different catalyst and solvent

Catalyst	Weight (g)	Solvent	t/ min	Maximum yield/%
3.5 wt% Ru/C	0.5	THF	475	66.6
3.5 wt% Pd/C	0.2	THF	80	86.7
RANEY [®] Ni	0.5	THF	180	86.4
$2 \text{ wt\% Pt/Al}_2 \text{O}_3^a$	0.2	THF	150	90.7
2 wt% Pt/C ^{\bar{b}}	0.2	THF	240	90.9
2 wt% Pt/C	0.05	THF	190	92.3
2 wt% Pt/C	0.05	Ethanol	160	78.3
2 wt% Pt/C	0.05	Methanol	73	91.0

Reaction conditions: 283.15 K, 0.1 MPa, 10 mmol substrate, 30 ml solvent. ^{*a*} Commercial Pt/Al₂O₃ from Dalian Tongyong Chemicals, China. ^{*b*} Commercial Pt/C from Donggang Chemicals, China.

Reaction conditions: 283.15 K, 0.1 MPa. ^{*a*} 10 mmol substrate, 30 ml THF, 50 mg 2 wt% Pt/C. ^{*b*} 2 mmol substrate, 10 ml THF, 10 mg 2 wt% Pt/C. ^{*c*} 10 mmol substrate, 30 ml THF, 100 mg 2 wt% Pt/C. The conversion and selectivity were determined by HPLC.

135 100

NO

93.7

carbon supported Pt colloid catalyst. Since HA was generally unstable and can be easily further hydrogenated to aromatic amine, mild reaction conditions of 283.15 K and 0.1 MPa were adopted in this study to retard the formation of amine. The Pt/C prepared from the colloid route showed excellent activity and selectivity under mild conditions. As a contrast, several commercial Pt/C samples prepared by the impregnation method by different makers showed lower selectivity under the same reaction conditions. It is reasonable to infer that the excellent catalytic performance of colloid Pt/C is due to the function of finely dispersed and unformed Pt nano particle on carbon. Nine kinds of NA with different substituents including nitryl, carbonyl, ester and carboxyl were investigated. As shown in entries 1-3, the complete reduction of *m*-, *o*and p-dinitrobenzene gave the HA yield of 92.3%, 91.9% and 86.3%, respectively. The selectivity for the partial reduction of 1-(4-nitrophenyl)ethanone (entry 4) was 86.3% at 100% conversion and the reducible carbonyl group remains



Fig. 1 The concentration-time plots for the selective hydrogenation of *m*-DNB to HA over Pt/C. Reaction conditions: 283.15 K, 0.1 MPa, 10 mmol *m*-dinitrobenzene, 30 ml THF, 50 mg 2wt% Pt/C. The conversion and selectivity were determined by HPLC.

The relationships of component concentration versus reaction time are shown in Fig. 1. The concentration of m-DNB decreased almost linearly with reaction time, suggesting that the reaction has dynamically pseudo-zero order dependence with m-DNB. At the early stage of the reaction, the selectivity to N-(3-nitrophenyl)hydroxylamine (b) was very high only with a trace amount of byproducts, c2. As the reaction time increase, c1 gradually appeared and accumulated, then d and e were formed in sequence. During the whole hydrogenation course, c2 was the main byproduct and the total amount of c1, d and e was much lower than c2. As the concentration of m-DNB decrease, the amount of b increases almost linearly and its yield reaches the highest value of 92.3% at 100% m-DNB conversion.

The hydrogenation of NA is a typical consecutive reaction with HA as the first intermediate and amine as the final product. Pt colloid on carbon is very active and can catalyze the hydrogenation under very mild conditions, which consequently stop the consecutive hydrogenation reaction in the middle and accumulates the intermediate HA to be the main product. In addition, when NA has electron-withdrawing substituent in the phenyl ring, the N-O bond in the hydroxylamino group was strengthened by the electron-withdrawing groups through the π -conjugation of the phenyl ring,¹⁸ which effectively stabilize the HA and retard its further converting. As a matter of fact, the formation rate of HA in the reaction system is much higher than its disappearing. The reaction termination for HA production can be easily observed from the H₂ up-taking rate. When NA was completely converted, the H₂ up-taking rate changed to be obviously slow.

In summary, this communication provides an effective method to obtain HA by the partial hydrogenation of NA over carbon supported Pt colloid catalyst without using any chemical promoters. Very good results were obtained with NA bearing electron-withdrawing substituents. Since NA can be further converted to highly valuable compounds through several reactions like Bamberger rearrangement, this result will generally contribute to the synthetic methodology of NA derivatives. We are grateful to the National High Technology Research and Development Program of China (863 Program, Grant No 2007AA03Z345) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT0711).

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