

Nitrobenzene hydrogenation with carbon nanotube-supported platinum catalyst under mild conditions

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Abstract

Carbon nanotube (CNT)-supported Pt catalysts have been prepared by impregnation and reduction–precipitation method using chloroplatinic acid as metal precursor. The structure of the catalysts has been characterised using TEM, BET and XPS. The catalytic performance for nitrobenzene hydrogenation was evaluated under atmospheric pressure and ambient temperature. The results show that the catalysts, both of low and higher Pt loading, show high activity for nitrobenzene directly hydrogenating to aniline under mild conditions. The highly dispersed Pt and mesoporosity structure of acid-oxidized CNT-supported Pt catalyst are responsible for the extraordinary activity.

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1. Introduction

Aniline as an important chemical raw material is mainly used for production of methylene diphenyl diisocyanate (MDI), and also used as additive for rubber process, intermediates dyes and pigments, pesticides and herbicides. About 85% of global aniline is produced by catalytic hydrogenation of nitrobenzene. Both liquid phase and vapor phase hydrogenation methods are employed, but the common question is that severe reaction conditions are required, i.e., higher reaction temperature and pressure. So it is more interesting to ameliorate the reaction condition under mild reaction condition maintaining the high catalytic activity.

It is noted that metal nanoclusters are attractive catalysts and show high activity and selectivity due to the surface effect. To keep the dispersion of active component under

reaction condition, substrates are often used. Carbon nanotubes (CNTs), as a kind of carbon materials, have been used as supports for depositing metal nanoparticles. Many kinds of methods of depositing nanosized metal particles on CNTs have been developed. For example, Dai and co-workers decorate Ti, Ni, Pd, Au, Al and Fe on single-walled CNTs through electron-beam deposition [1]. Rh nanoparticles (1.5–2.5 nm) are loaded on CNTs by surface-mediated organometallic reaction [2]. The metal nanoparticles on CNTs substrates perform some unusual catalytic properties. Ni and Pd particles supported by CNTs show excellent selective hydrogenation capacity for crotonaldehyde [3] and cinnamaldehyde [4]. Rh nanoparticles on CNTs are highly active in the liquid-phase hydrogenation of cyclohexene [5].

In this contribution, CNT-supported Pt nanoclusters (designated as Pt/CNT hereafter) are produced by impregnation with 1% Pt loading (1Pt/CNT) and reduction method with 3% Pt loading (3Pt/CNTs) and their catalytic activities are investigated for nitrobenzene hydrogenation under ambient temperature and atmospheric pressure.

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2. Experimental procedure

2.1. Preparation of catalysts

The CNTs used as catalyst support are prepared by pyrolyzing propylene and hydrogen over diatomite-supported Ni catalyst. The as-grown CNTs are 20–40 nm in diameter, several microns in length. CNTs are first pre-oxidized. They are doused in hydrofluoric acid to remove diatomite, followed by $\text{HNO}_3\text{--H}_2\text{SO}_4$ refluxing to create surface complexes on CNTs surfaces to improve the surface hydrophilicity. At the same time, the Ni catalysts are almost excluded except that the Ni particles enwrapped by graphite lattice remain intact. The residue Ni detected by X-ray fluorescence spectroscopy is about 0.8 wt%.

Two kinds of methods are used to prepare the CNTs-supported Pt catalysts: one with 1 wt% Pt loading is prepared by incipient wetness method, the other with 3 wt% Pt loading by reduction–precipitation method. Pre-oxidized CNTs are dispersed in the solution of hexachloroplatinic acid, and then the suspension is sonicated for 30 min and dried at 110 °C overnight. Before use, the catalyst is calcinated at 500 °C for 3 h under nitrogen. 3Pt/CNTs catalyst is produced by reduction hexachloroplatinic acid (0.02 M) with sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) solution (0.32 M) under some pH value [6]. CNTs are first dispersed in the hexachloroplatinic acid solution, and then sodium hydrosulfite solution is dropped under strong stirring. The pH value of the solution is adjusted by adding some drops of aqueous concentrated NH_3 solution. The Pt loading is related with the pH value of the slurry. The as-made precipitate is watered, filtered, dried at 110 °C. Then, calcination is conducted at 500 °C for 1 h under nitrogen gas.

AC-supported Pt catalyst is prepared according to the reduction–precipitation method for comparison. The same pretreatment of AC is made. The Pt loading is 3 wt%.

2.2. Nitrobenzene hydrogenation

The nitrobenzene hydrogenation is operated at ambient temperature and atmospheric pressure. Before reaction, the catalyst is in situ reduced at 50 °C for 3 h. 0.25 ml nitrobenzene and 25 ml alcohol are injected into a three-necked bottle with 0.025 g catalyst. Hydrogen flow is set 50 ml/min. Samples are withdrawn intermittently.

2.3. Characterisation

The dissolved Pt by enough aqua regia is analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry using ICP-AES LEEMAN PRODIGY. The chemical analysis of the products is performed by gas chromatography (GC/GC-MS TURBOMASS HP5973). The specific surface area and pore distribution are carried out by physical adsorption of nitrogen at 77 K by using a Sorptomatic 1990 apparatus. The transmission electron microscopy (TEM) of a JEOL 200CX is used to characterise the prepared catalysts. X-ray

photoelectron spectra (XPS) are obtained by using KRATOS spectrometer fitted with an Al $\text{K}\alpha$ source. The binding energy (BE) is calibrated by setting the Au 4f spectra at 84.0 eV.

3. Results and discussion

3.1. Characterisation of Pt/CNT catalysts

3.1.1. Transmission electron microscopy

The TEM images of 1Pt/CNT, 3Pt/CNT and 3Pt/AC after calcination are shown in Fig. 1. Pt particles located on CNTs by impregnation have a wide range size of 5–10 nm, and some have congregated into large particles; the distribution on the outer surfaces of CNT is not so homogeneous. But Pt clusters produced by reduction method extensively cover CNTs, and the average particle diameter is generally about 3 nm. Different preparing methods result in different dispersion of Pt over CNT, since different surface property of oxidized CNT is resulted. It is reported that HNO_3 -oxidized CNT is negative net surface charge [7], which decides that

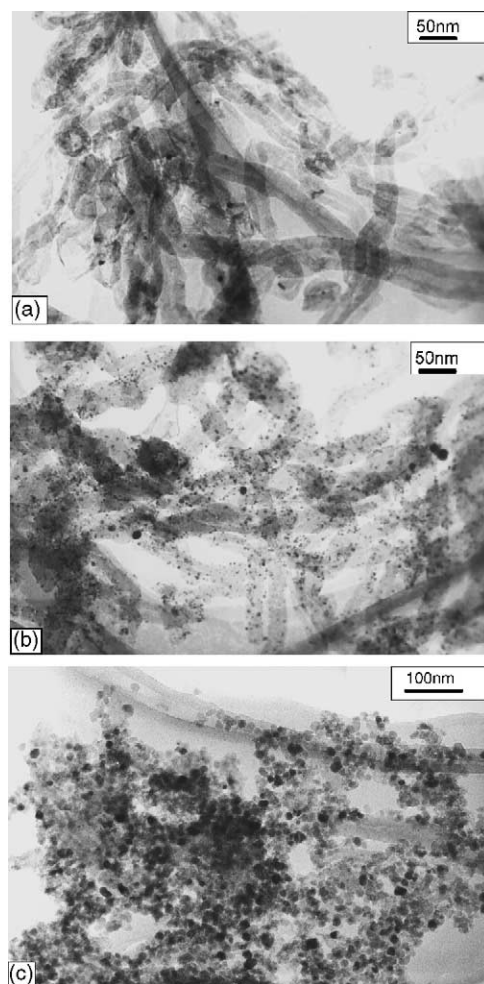


Fig. 1. TEM images of calcinated (a) 1Pt/CNT, (b) 3Pt/CNT and (c) 3Pt/AC catalyst.

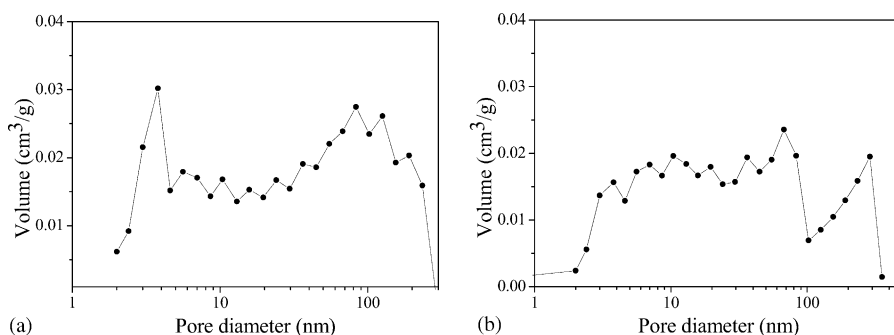


Fig. 2. The pore distributions of (a) support CNTs and (b) Pt/CNT catalyst.

CNTs will adsorb cations in the solution. When H_2PtCl_6 is used as precursor, adsorption of PtCl_4^{2-} anions is weak, leading to a very poor dispersion. Moreover, upon calcination, Pt will further agglomerate into fewer larger particles [8]. But for loading Pt by reduction–deposition method, PtCl_4^{2-} ions are reduced to ions with low valence or metallic state by reducing agent; Pt with positive or zero charge will nucleate and grow at acidic sites under electrostatic attraction [9]. A great many of adsorption sites homogeneously disperse on the surfaces of the oxidized-CNT supports, to which transition metal nanoparticles attach [10], so Pt particles decrease their sizes even though Pt loading increases.

Pt clusters on AC are larger than those on CNT. They are 8–10 nm in size. Most of Pt particles are located on the outer surfaces and aggregate larger particles. Because AC has a developed microporous structure, Pt first aggregates on the outer surfaces of micropores, causing blocking of the mouth of micropores, so Pt particles on AC are denser and larger.

3.1.2. Volumetric adsorption apparatus

Specific surface area of 1Pt/CNT and 3Pt/CNT is $156 \text{ m}^2/\text{g}$ and $170 \text{ m}^2/\text{g}$, respectively. The increase of SSA of 3Pt/CNT is due to the decrease of Pt particle size and increase of Pt particle number in comparison with 1Pt/CNT.

The pore distribution curve of support CNTs (Fig. 2) shows that the pore size mainly ranges from 2 nm to 100 nm, which is formed by entangling of CNTs [11]. The mesoporous structure of Pt/CNT catalyst favors all active sites accessible for catalyst precursor during preparing process and decreases the diffusion limit of reactant and product during reaction. When Pt particles are densely coated on CNT, Pt particles occlude a fraction of micropores with width less than 2 nm; at the same time, some pores with 100–300 nm have been formed. The modification is advantageous to the decrease of the steric hindrance during reaction.

3.1.3. X-ray photoelectron spectroscopy (XPS)

According to the XPS spectra as shown in Fig. 3, the peak of Pt in the 4f binding energy region can be curve fitted with doublet peaks: one at about 71.5 eV can be attributed to metallic Pt, and the other at about 73.6 eV can be assigned to Pt^{2+} species [12]. The slightly higher BE of metallic Pt is probably due to its small particle size. The peak sites give an inconsiderable shift after the catalyst is reduced, but the ratio of area of metallic Pt and oxidized Pt appreciably increases prior to the calcinated sample. Pt/CNT can be further reduced at such low temperature, and the easiness of reducibility is related to the concentration of surface groups and the presence of ultrafine Pt particles. According to the study on Pt supported

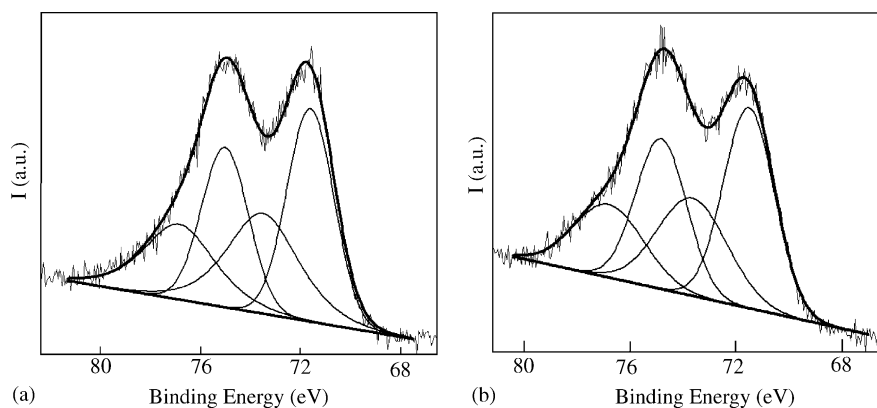


Fig. 3. The XPS spectra of Pt for (a) calcinated catalyst and (b) reduced catalyst.

by carbon black, chemical groups hinder reduction process [13]. CNTs have turbostratic graphite structure that is inert. Oxidization treatment introduces a certain amount of groups that is necessary for preparing catalyst, and the amount is not so large that reduction is prohibited. Pt particles have larger surface energy due to size effect, leading to their easy reducibility.

3.2. Catalytic activity

The distribution of reactant and products is shown in Fig. 4.

Activated carbon (AC) or activated carbon cloth (ACC)-supported Pt catalysts are ever reported for nitrobenzene hydrogenation [14,15]. The activities and reaction conditions are compared in Table 1.

The home-made AC-supported catalyst shows no activity in the nitrobenzene hydrogenation process under mild reaction condition. It should be attributed to the heterogeneously distribution and the larger size of Pt particles (see Fig. 1c).

The distinction between activity and intermediate type for CNT- and AC-supported Pt catalysts can be drawn from Table 1. The activity of 1Pt/CNTs catalyst increases by two times than that of Pt/AC and Pt/ACC under similar reaction condition, and the activity of 3Pt/CNT is about three times that of 1Pt/CNTs. The intermediates are different, leading to different conversion rates to aniline.

The excellent activity of Pt/CNT catalyst is mainly related to the homogeneous distribution of ultrafine metallic platinum particles over CNT, and the structure characteristics of the support are also favorable. It has been reported that Pt with 3 nm diameter shows the highest mass activity or specific activity [16]. Hence, CNT-supported Pt catalysts exhibit extraordinary activity even under mild reaction condition. The aggregated pores between entangled CNTs with radius of 2–100 nm take the most fraction of the pores, which would not prevent reactant diffusing to the surface of active component, so almost all Pt particles are accessible for reactant. The combination of support structure and the distribution and the size of the active phase are responsible for the catalytic behavior.

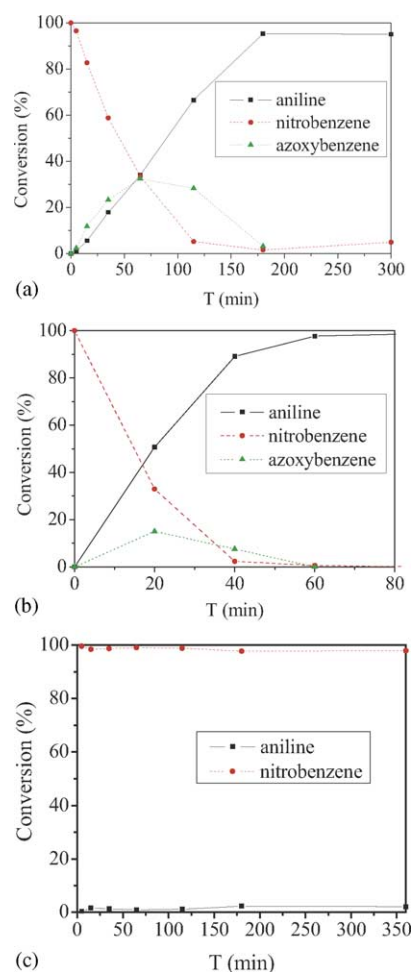


Fig. 4. Catalytic behaviors of (a) 1Pt/CNT, (b) 3Pt/CNT and (c) 3Pt/AC catalyst.

For Pt/AC or Pt/ACC catalysts, nitrobenzene (Ph-NO₂) first swiftly hydrate into phenylhydroxylamine (Ph-NHOH), and then the intermediate slowly transforms into aniline. But for Pt/CNT catalyst, neither nitrosobenzene nor phenylhydroxylamine is detected, azoxybenzene occurs as the only detected intermediate. This excludes that azoxybenzene is

Table 1
Comparison of catalytic activities

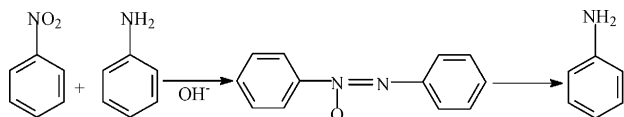
	Reaction conditions						Activity			Note
	Loading (%)	T_{red}/t_{red} (°C/h)	T_{react} (°C)	F_{H_2} (sccm)	M_{cat} (g)	V_{Ph-NO_2} (ml)	t_1^a (min)	t_2^b (min)	Intermediate	
Pt/CNT	1	50/1	A.T. ^c	50	0.025	0.25	180	180	<chem>O=C1N=CN=C1</chem>	This work
Pt/CNT	3	50/1	A.T.	50	0.025	0.25	40	40	<chem>O=C1N=CN=C1</chem>	This work
Pt/AC	3	50/1	A.T.	50	0.025	0.25	–	–	–	This work
Pt/AC	1	100/3	25	50	0.025	0.25	300	600	<chem>O=C1N=CN=C1</chem>	[14]
Pt/ACC	1	50/1	0	50	0.1	0.49	100	600	<chem>O=C1N=CN=C1</chem>	[15]

^a Conversion time of nitrobenzene.

^b Time for 90% aniline.

^c Ambient temperature.

the product of reaction between nitrosobenzene and phenylhydroxylamine. We believe that azoxybenzene is the outcome of nitrobenzene condensation with aniline as shown in formula (1-1).



Nitrobenzene is directly hydrogenated to aniline due to the unusual catalytic property of Pt/CNT, and then nitrobenzene condenses with the product aniline to produce azoxybenzene, which will convert into aniline rapidly. The different mechanisms of nitrobenzene hydrogenation are resulted from the high activity of Pt/CNTs catalyst.

Generally, the liquid-phase catalytic hydrogenation reaction on fixed bed needs 150–250 °C and 0.15–1.0 MPa. But for CNT-supported Pt catalyst with 3 wt% Pt loading, the aniline yield reaches to 90% after 40 min even at ambient temperature and atmospheric pressure. Using the reduction method, Pt loading, keeping average diameter of 3–5 nm, can be increased to 20 wt% [6]. Then, reaction rate can be expected to further improve when the catalyst with higher Pt loading is employed. Such high reaction rate under mild condition acquired with CNT-supported Pt catalyst indicates that CNTs are a very promising support materials of catalysts in practical application.

4. Conclusions

Pt/CNTs catalysts show extraordinary activity for nitrobenzene hydrogenation even at ambient temperature and atmospheric pressure. The 90% yield of aniline needs 240 min and 40 min for Pt/CNTs catalyst with Pt loading of 1 wt% and 3 wt%. Nitrobenzene is directly hydrogenated to aniline; at the same time, nitrobenzene also condenses with aniline to produce azoxybenzene, which hydrates to aniline rapidly.

CNTs are appropriate support for platinum catalysts. Homogeneously distributed ultrafine platinum particles can be deposited on CNTs. The size effect of Pt particles results in low reduction temperature needed for the CNT-supported Pt catalyst and their high catalytic activity at mild reaction condition. Aggregated pores between entangled CNTs reduce the mass transfer limit of the reactant

and the product during the reaction, resulting in excellent activity.

(1-1)

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