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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.

Keywords: Carbon nanotubes; Pt supported catalyst; Nitrobenzene hydrogenation; Catalytic activity

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 HNO_3–H_2SO_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 ($Na_2S_2O_4$) 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 Kα 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

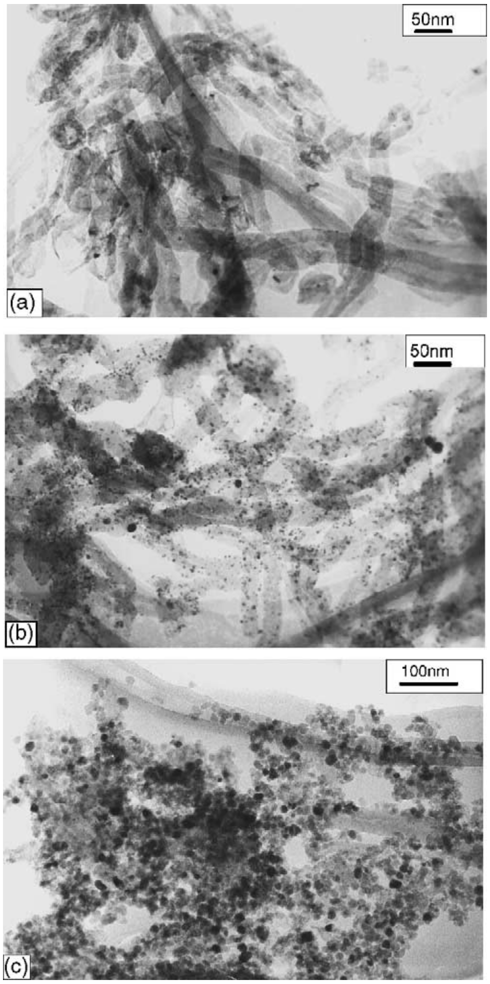

Fig. 1. TEM images of calcinated (a) 1Pt/CNT, (b) 3Pt/CNT and (c) 3Pt/AC catalyst.