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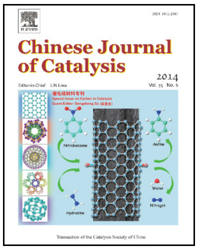

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Reduction of nitrobenzene catalyzed by carbon materials

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ABSTRACT

The reduction of nitrobenzene catalyzed by different carbon materials (mainly carbon nanotubes) was studied. TGA, TPD, TEM, N_2 adsorption-desorption, and Raman spectroscopy were used to show that it was oxygenated groups that gave catalytic activity, while the surface area, pore structure, morphology, structural defects and Fe impurities in the catalysts did not have a significant influence on the activity. The carbonyl group played an important role, but the carboxylic group and anhydride adversely affected the reaction. The conjugated π system, which was necessary for electron transfer and nitrobenzene adsorption, was another critical factor. The reaction proceeded through the direct route in which the intermediate nitrosobenzene was converted directly to aniline quickly.

1. Introduction

The selective reduction of nitroarenes is an important process because aromatic amines are used in producing agrochemicals, pharmaceuticals, dyes and pigments, to name just a few of their applications [1–3] and continuous efforts have been devoted to developing efficient production techniques. Since the traditional non-catalytic methods that use either the Fe/HCl system (Bechamp procedure) or metal sulfides inevitably generate large amounts of wastes [3], green and environmentally friendly selective reduction routes are urgently sought. Various kinds of noble metals [4–7] such as Au, Pd, Pt, and Ru have been reported to be highly effective catalysts. However, the high price and scarcity of these precious metals are main drawbacks that hindered their large scale industrial application. Besides, these metals are sensitive to air and moisture when they are in metal complex forms [8]. As an alternative, a number of cost-effective metals [9–11] including Fe, Ni and Cu are attracting increasing attention, but their metal and metal oxide nanoparticles often have issues such as agglomeration that lead to deactivation.

The direct use of carbon materials as the catalyst is an interesting topic attracting more attention. Carbon, especially nanocarbons, can be used as an efficient catalyst for many gas phase and liquid phase reactions [12–17]. As a matter of fact, carbon is also active in the reduction of nitrobenzene [18–21]. One major problem with carbon-catalyzed reactions is that the activity may be due to metal impurities that remained in the carbon materials. However, we have found that nitrobenzene reduction can proceed without a metal catalyst by using model

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catalysts [22]. Here, we studied systematically the reduction of nitrobenzene catalyzed by carbon materials, mainly carbon nanotubes (CNTs) and found that carbon indeed was an efficient catalyst for this reaction. The carbonyl group was one important active site, while the carboxylic and anhydride groups played an adverse role. The operating conditions and reaction pathway were also studied.

2. Experimental

2.1. Chemicals

The CNTs were bought from CNano Technology Ltd. (Flotube 9000). Graphite flake, nitrobenzene (99%), azoxybenzene (98%), azobenzene (97%), and hydrazobenzene (90%) were purchased from Alfa Aesar. Hydroxylamine (97%) and nitrosobenzene (97%) were obtained from Sigma-Aldrich. Granular activated carbon and hydrazine monohydrate were supplied by China Medicine Group Shanghai Chemical Reagent Company. Nanodiamond synthesized by the detonation method followed by acid washing was bought from Beijing Grish Hitech Co. (China). All reagents except the carbon catalysts were used without further purification.

2.2. Preparation of carbon materials

The CNTs were treated with concentrated HCl (rCNT) before use. Then, rCNT was dispersed in concentrated HNO_3 and treated at 120 °C (temperature of the oil bath) for 2 h after ultrasonication. After filtration and washing with distilled water, the oCNT obtained was dried at 110 °C. For the thermal treatment, aliquots of oCNTs were calcined in a quartz tube under flowing helium at the set temperature for 2 h, and the samples were cooled under helium to room temperature. The annealed samples were designated as oCNT-*X* (*X* was the annealing temperature).

Graphite oxide (GO) was synthesized by Hummers' method with some modification [23]. Concentrated H_2SO_4 (230 mL) was added to a mixture containing graphite flakes (10.0 g) and $NaNO_3$ (5.0 g). The mixture was stirred by a mechanical agitator in an ice bath. Next, $KMnO_4$ (30 g) was added to the slurry within 1 h. After 2 h, the mixture was heated to 35 °C, and kept for another 2 h, followed by the slow addition of deionized water (500 mL). Subsequently, the slurry was heated to 90 °C. After 40 min, H_2O_2 (30%) was dropped into the mixture until its color turned to light yellow. Finally, the product was washed first with HCl (2 mol/L), and then deionized water. The GO obtained was dried in an oven at 60 °C.

Graphene was prepared using the method in a previous report [24]. GO (1.0 g) was dispersed in 600 mL of deionized water. After 5 mL of ammonia was added, the mixture was ultrasonicated for 2 h. Then 4 mL of hydrazine monohydrate (85%) was added, and the flask that contained the solution was immersed in an oil bath at 90 °C for 4 h. The solution was filtrated and the product reduced graphene oxide (RGO) was washed with water, followed by drying in an oven at 60 °C. In addition, graphene was also prepared by the thermal exfoliation method. Typically, 1.0 g of GO was heated quickly (15 °C/min) to a set temperature and kept for 2 h, followed by cooling to room temperature under a noble gas.

2.3. Sample characterization

The morphology of samples was observed by transmission electron microscope (TEM, Tecnai G2 F20). Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449 F3 apparatus under argon flow (50 mL/min) with a heating rate of 10 °C/min from 35 to 950 °C. The specific surface area was measured by the BET method using nitrogen adsorption isotherms obtained on a Micrometrics ASAP 2020 system. Pore size distributions were estimated from the desorption branch of the isotherm using the BJH method. The total pore volume (V_t) was estimated from the amount adsorbed at the relative pressure of 0.988. Raman spectroscopy was performed by a LabRam HR 800 using 633 nm laser.

2.4. Catalytic test

Nitrobenzene reduction was studied using the above materials as catalyst with hydrazine monohydrate as the reducing reagent. Typically, a set amount of catalyst, 1.2 g of nitrobenzene and 6.0 equivalent of hydrazine monohydrate were added into a 25 ml round-bottom flask. The mixture was heated in an oil bath for a set period of time using a water-cooled condenser. When the reaction was completed, a methanol/water (volume ratio 75:25) solution was added and the mixture was diluted to exactly 50 mL in a volumetric flask. The products were analyzed by HPLC (Elite, UV detector, mobile phase: 75/25 (*v*/*v*) methanol/water) with a SinoChrom ODS-BP column. Unless otherwise noted, the reaction temperature was the temperature of the oil bath.

3. Results and discussion

3.1. Catalytic performance of oCNT under different conditions

We firstly used oCNT as an example to evaluate the catalytic activity of carbon materials for nitrobenzene reduction. The conversion was quite low without a catalyst, but it increased notably to 43.9% when only 2 mg of oCNT was added, indicating the crucial role of the catalyst (Table 1). The conversion increased as more catalyst was added from 2 to 20 mg, but a

Table 1
Effect of catalyst loading on nitrobenzene reduction.

Catalyst loading (mg)	*X*(Nitrobenzene)/(%)	*S*(Aniline)/(%)
0	21.8	98.8
2	43.9	93.5
8	69.4	96.7
15	92.7	93.1
20	97.2	95.2
25	99.7	93.5

Reaction conditions: a set amount of oCNT, 1.2 g of nitrobenzene, 6.0 equiv of hydrazine monohydrate, 100 °C, 4 h.