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Pt nanoparticles deposited over carbon nanotubes for selective hydrogenation of cinnamaldehyde

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Abstract

Two kinds of carbon nanotubes (CNTs) with different inner diameter (less than 10 nm: CNTs-1 and between 60 and 100 nm: CNTs-2) were used as catalyst supports. The platinum particles were simply deposited on the outside surface (CNTs-1) and inside (CNTs-2) and were easily reduced to Pt^0 by refluxing. The catalysts exhibit high activities in the selective hydrogenation of cinnamaldehyde which contains both C=C and C=O bonds. But the selectivity of these two catalysts was quite different under same reaction conditions. The high selective hydrogenation of C=O bond was observed over catalyst 3%Pt/CNTs-2, while the completely hydrogenation of both C=C and C=O bonds was found over catalyst 3%Pt/CNTs-1.

Keywords: Cinnamaldehyde hydrogenation; Carbon nanotubes (CNTs); Inner diameter; Platinum particles

1. Introduction

Selective hydrogenation of α,β-unsaturated aldehydes yields unsaturated alcohols. They are industrially valuable products and intermediates for the synthesis of fine chemicals [1–3]. The desired product in hydrogenation of cinnamaldehyde is cinnamyl alcohol, an important additive in food industry, perfumery and an intermediate in the production of certain pharmaceutics [4]. Despite economic drawbacks the conventional method used for many years for the reduction of cinnamaldehyde is based on the Meerwein–Ponndorf–Verley reaction giving the yield of cinnamyl alcohol 85–90% after purification [5]. It is apparent that the application of heterogeneous catalysis might be advantageous.

In addition, it is a suitable model reaction to investigate the effect of catalyst structure on selectivity. Many important factors can influence the activity and selectivity, such as the active metal, the catalyst support properties, the metal particle size, the solution properties and the presence of a second metal [6]. A comprehensive review of the state of the art has been published [7]. Since the reduction of the C=C bond is easier, the selectivity towards the unsaturated alcohol is generally poor. Thus, the preparation of a selective catalyst remains a challenging task. Platinum and palladium catalysts can be used. Carbon materials are among the most widely used supports for this reaction, including graphite, carbon blacks, activated carbons, fullerenes, carbon nanotubes and carbon nanofibers [8–14]. Recent results obtained in the laboratory have shown that active phase located inside the carbon nanotube cavity exhibit an extremely high activity when compared to that observed on traditional grain size catalysts [15–17]. Tessonnier et al. reported that palladium metal nanoparticles were introduced in the carbon nanotubes, and it exhibits a high selectivity towards the C=C bond hydrogenation. This result could be attributed to the peculiar morphology of the support, which in turn, significantly modified the adsorption properties of the metal surface itself [18].

It is expected that specific properties will be observed with the catalyst, which metal particles deposited on the

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different surface of the supports, i.e., inside or outside. The present article is to report the catalysts of cinnamaldehyde hydrogenation, which Pt nanoparticles supported on carbon nanotubes with different inner diameter. The X-ray photoelectron spectroscope (XPS) and transmission electron microscopy (TEM) showed that, for the CNTs with inner diameter less than 10 nm, almost all of the Pt particles were supported on the outside surface, and for the CNTs with inner diameter between 60 and 100 nm, mainly of the Pt particles were inside. These two catalysts exhibit different catalytic properties in the selective hydrogenation of cinnamaldehyde.

2. Experimental section

2.1. Materials

The carbon nanotubes (CNTs) were supplied by Shenzhen Nanotech Port Co. Ltd., China, in a purified form, and were previously treated using HNO_3 solution before used. Cinnamaldehyde, $H_2PtCl_6 \cdot 6H_2O$ and other solvents are the reagents of analytical grade. The purity of hydrogen is 99.99%.

2.2. CNTs characteristics

High-resolution TEM observations of the catalysts were conducted using the JEOL-2010 microscope, working at 200-kV accelerating voltage. The images of the starting carbon nanotubes supports showed that, the inner diameter of CNTs-1 was less than 10 nm, and the CNTs-2 displays an average inner diameter ranging between 60 and 100 nm. Both of these two supports are length up to several hundred micrometers.

The specific surface area measured by mean of the BET method, conducted with Micromeritics ASAP 2000 analyzer, using N_2 as adsorbent at the liquid nitrogen temperature, were about 400 m^2/g and 40 m^2/g for CNTs-1 and CNTs-2, respectively. The solid was essentially mesoporous with an average pore size distribution centred at around 40 nm. No trace of micropores has ever been observed.

2.3. Preparations of catalysts

The platinum salt (1.0 g of $H_2PtCl_6 \cdot 6H_2O$, 37% Pt) was dissolved in 50 mL of distilled water, and the concentration of Pt is 7.4 mg/mL. An appropriate amount of this Pt solution, ethanol, and *iso*-propanol were added in a flask, and the carbon nanotubes (2.0 g) was also dropped into the flask under vigorous stirring and a black solution was obtained. The solution was refluxed for 5 h at 130 °C and then stirred for about 12 h at room temperature.

The CNTs supported platinum nanoparticles were filtrated and washed with distilled water. Elemental analysis carried out on the filtered solution reveals no trace of platinum species, indicated that all platinum particles were adsorbed on the support. The catalyst was dried under vacuum at 80 °C, the theoretical Pt loading was set to be around 3 wt.%. The catalyst using two different CNTs as supports were abbreviated as 3% Pt/CNTs-1 and 3% Pt/CNTs-2, respectively.

2.4. Catalytic tests

The selective hydrogenation was conducted in a well-stirred high temperature high-pressure stainless steel autoclave reactor. In a typical catalytic run, the reaction mixture contains 5 ml of cinnamaldehyde, 35 ml of *iso*-propanol and 0.3 g of catalyst were added into the reactor. Then it was purged with hydrogen for three times. The reaction system was pressurized with hydrogen to 3.0 MPa and checked for leaks. The hydrogenation reaction was performed at 80 °C. Small portions of the liquid mixture were withdrawn periodically for GC analysis, in order to determine the cinnamaldehyde conversion and product distribution. The products were determined by FULI GC 9790 with FID detector and SPB™-1 capillary column (30 m × 0.25 × mm × 0.25 μm) at 120 °C.

3. Results and discussion

3.1. Catalyst characterization

The binding energies of the Pt $4f_{7/2}$ levels are collected in Table 1. The results showed that Pt^{4+} was reduced to Pt^0 in both catalysts, by using the simple refluxing method.

The relative amounts of oxygen-containing surface groups were inferred from the oxygen surface concentration determined by XPS, which was carried out in a VG Scientific ESCALAB MK II spectrometer using non-monochromatized Mg Kα radiation. The atomic ratio of C/O and Pt/C was listed in Table 1. The oxygenated groups of CNTs-1 (C/O atomic ratio = 90/10) were a little higher than that of CNTs-2 (C/O atomic ratio = 92/8) after the HNO_3 treatment.

The Pt/C atomic ratio was 0.18/100 of Pt/CNTs-1 and 0.02/100 of Pt/CNTs-2. It is showed that, almost all of the Pt particles were supported on the outside surface of 3%Pt/CNTs-1, and about 90% Pt particles were deposited inside the channel of catalyst 3%Pt/CNTs-2. The HRTEM images Figs. 1 and 2 also indicated the results.

Different studies dealing with the adsorption of nitrogen on MWNT (multi-walled carbon nanotubes) have highlighted the porous nature of these materials [19,20]. Pores in MWNT can be mainly divided into inner hollow cavities of small diameter (narrowly distributed, mainly 3–6 nm)

Table 1
The atomic ratio determined by XPS and the binding energies (eV) of the Pt $4f_{7/2}$ levels for the catalysts

Catalyst	C/O atomic ratio	Pt/C atomic ratio	Pt $4f_{7/2}$
3%Pt/CNTs-1	90/10	0.18/100	71.2
3%Pt/CNTs-2	92/8	0.02/100	71.0