Pt nanoparticles deposited over carbon nanotubes for selective hydrogenation of cinnamaldehyde

Hongxia Ma *, Licheng Wang, Luyang Chen, Chao Dong, Weichao Yu,
Tao Huang, Yitai Qian

Department of Chemistry, University of Science and Technology of China, Jinzhai Road 96, Hefei, Anhui 230026, PR China

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.
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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

* Corresponding author. Tel.: +86 551 3607234; fax: +86 551 3607402.
E-mail address: mahx@ustc.edu.cn (H. Ma).

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

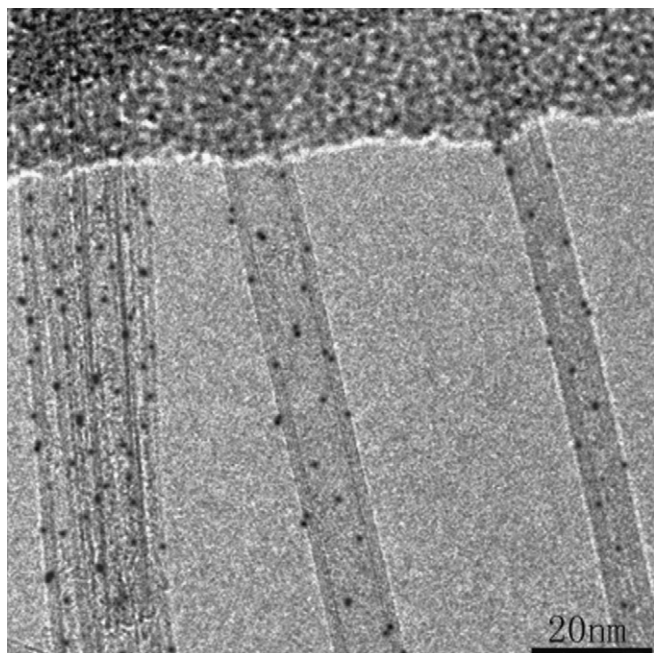| Catalyst	C/O atomic ratio	Pt/C atomic ratio	Pt $4f_{7/2}$
3%Pt/CNTs-1	90/10	0.18/100	71.2
3%Pt/CNTs-2	92/8	0.02/100	71.0

Fig. 1. HRTEM images of the catalyst 3%Pt/CNTs-1, the platinum particles are mainly deposited on the outside surface of the CNTs.
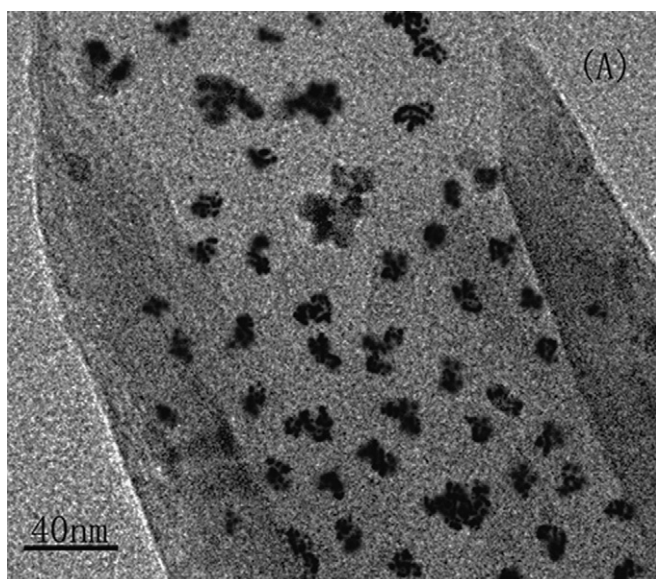

Fig. 2. TEM images of the catalyst 3%Pt/CNTs-2. The platinum particles inside the CNTs channel.

and aggregated pores (widely distributed, 20–40 nm) formed by interaction of isolated MWNT. Adsorption over CNTs can occur in the aggregated pores, inside the tube or on the external walls [21]. This could explain the difference of the two catalysts. The inner diameter of CNTs-1 was less than 10 nm, despite the platinum particles were only 2–5 nm, they were difficult deposited inside the channel. So, mainly platinum particles were adsorbed on the external walls of the CNTs. The inner diameter of CNTs-2 was between 60 and 100 nm, it was big enough for the platinum

particles deposited inside the tube. Tessonnier has easily introduced palladium particles inside the CNTs by the wet impregnation process [18].
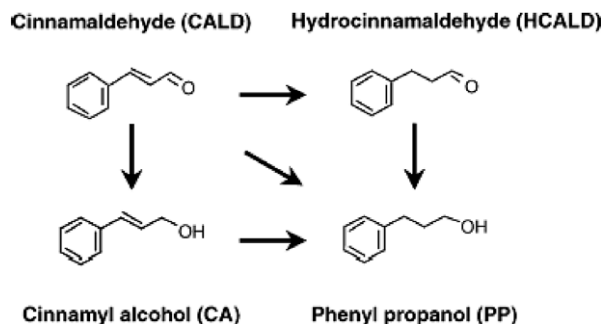
Statistical measurements performed on 400 metal particles lead to an average particle size distribution (PSD) were <2 nm for CNTs-1 (Fig. 1). However, the PSD centred at around 5 nm for CNTs-2. The preparation of the two catalysts according to the same impregnation and refluxing operation, but the average size of metal particles was quite different. This must be due to the different properties of the concave surface inside the inner tube and the convex surface of the outer surface of CNTs.

For the nanostructured carbon-supported catalysts, the different metal dispersions obtained might be explained by the different amounts of oxygen-containing surface groups; the higher this amount, the better the dispersion [22]. The oxygenated groups of CNTs-1 were a little higher than that of CNTs-2 (Table 1). The Pt particle might have a better dispersion on CNTs-1 (Fig. 1), and the particles might grow bigger due to the aggregation on CNTs-2 (Fig. 2). On the other hand, there was a strongger metal–support interaction with the inner wall surface of the CNTs, which could come from the electronic modification of the graphene planes due to the presence of curvature. Such a relatively higher interaction could affect the dispersion of the Pt particles inside the catalyst.

3.2. Hydrogenation catalytic properties

The hydrogenation of cinnamaldehyde is a parallel and consecutive reduction of different functional groups present in the same starting substrate, i.e., C=C and C=O bonds. The products obtained in the hydrogenation of cinnamaldehyde (CALD) were cinnamyl alcohol (CA), hydrocinnamaldehyde (HCALD) and phenyl propanol (PP). Other possible reaction products such as methylstyrene, phenylpropane and acetals, were not detected in the present work. Therefore, the reaction pathways involved in the hydrogenation of cinnamaldehyde are those shown in Scheme 1.

The catalytic results obtained on the two catalysts are reported in Fig. 3. The two catalysts are both very active for the hydrogenation of cinnamaldehyde, even if the full

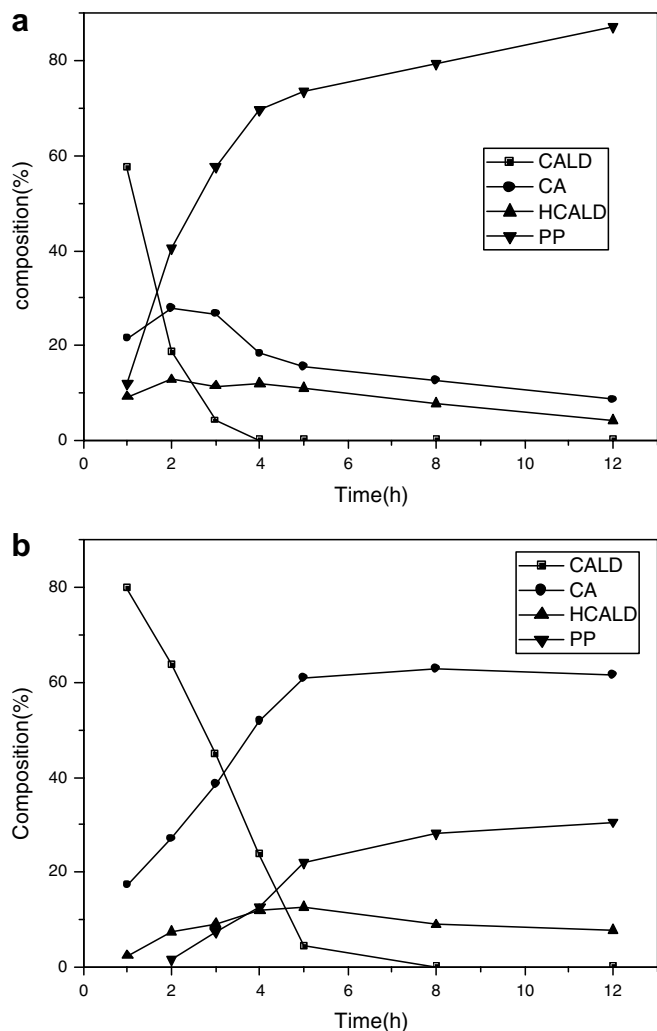Scheme 1. Reaction pathways in the hydrogenation of cinnamaldehyde.

Fig. 3. Catalytic properties for the selective hydrogenation of cinnamaldehyde over (a) 3%Pt/CNTs-1 and (b) 3%Pt/CNTs-2.

taining surface groups. It is well established that the cinnamyl alcohol selectivity increases with increasing particle size and that this effect is particularly pronounced with particles larger than 3 nm [23]. In our case, the oxygenated groups on these two catalysts were almost the same, but the size of Pt particles on CNTs-2 (about 5 nm) was larger than on CNTs-1 (<2 nm). This might be an important factor for the quite different selectivity over the two catalysts. A higher selectivity with increasing metal particle size, attributed to the lower probability of C=C bond activation compared with that of C=O bonds over larger particles, has also been reported by Gallezot and Richard [24].

It was also assumed that the observed selectivity towards the unsaturated alcohol depended on the presence of sites on the catalyst surface that can activate the carbonyl group by allowing the easy supply of hydrogen. CALD may bind to the metal particles surface via the C=O group, the C=C group, or both [25,26]. Depending on the adsorption mode, the formation of CA or HCALD may be preferred. The different adsorption modes onto the different planes of the metallic phase rely on the proportion of which varies with the particle size, and steric constraints between the phenyl group and the flat metal surface of a large particle. The particle size of CNTs-2 was larger than that of CNTs-1, and the metal crystallites on CNTs-2 might adopt morphology very different to that existing on CNTs-1, so that the adsorption of CALD on these two catalysts might very different too. For 3%Pt/CNTs-2, may be CALD can adsorb preferentially on the Pt particles surface by the C=O group, via donation of a lone pair of electrons from the oxygen atom; at the same time, hydrogen chemisorbed on Pt can attack the carbon atom in the carbonyl group.

Additional, the increased selectivity to the unsaturated alcohol is explained in terms of a transfer of the π-electrons from the graphitic planes to the metal particles. In this way the charge density on the metal increases, thus decreasing the probability for the C=C bond activation [11]. It was expected that the concave surface inside the CNTs could induce a peculiar electronic effect. The curvature of the channel could also induce modification on the molecular adsorption on the metallic phase, which in turn modifies the catalytic activity and/or selectivity of the reaction products.

4. Conclusion

In summary, the catalysts of platinum particles supported on carbon nanotubes with different inner diameter have different catalytic properties in the selective hydrogenation of cinnamaldehyde. The platinum particles can be easily supported on the surface and/or introduced inside the CNTs by a simple impregnation followed by refluxing in order to reduce Pt^{4+} to Pt^0. The platinum particles located inside the CNTs, the catalyst exhibits a high selectivity towards the C=O bond hydrogenation. Such catalyst can be readily used in several reactions, and will probably

conversion was faster obtained on the 3%Pt/CNTs-1, i.e., 100% of conversion after 4 h instead of 8 h for the 3%Pt/CNTs-2. This must be due to that the Pt particles were inside the tubes, it is difficult for the transformation of the reactants over 3%Pt/CNTs-2. Blank tests carried out over the supports alone showed no catalytic activity.

A more significant difference was observed between the two catalysts in terms of product selectivity. On the catalyst 3%Pt/CNTs-1 (Fig. 3a), the fully hydrogenated product (PP) was more than half among the products. While on 3%Pt/CNTs-2, cinnamyl alcohol (CA) was obtained about 60% under the same reaction conditions. The selective C=O bond hydrogenation was observed (Fig. 3b) over the latter. The C=C bond hydrogenation product hydrocinnamaldehyde (HCALD) was very little in both reactions.

Many explanations for the preferable selectivity to the unsaturated alcohol realized that, there were at least two factors direct the selectivity of carbon-supported catalysts, i.e., the metal particle size and the presence of oxygen-con-

open a new era in the field of nanosized catalytic materials with high selectivity.

Optimization of reaction conditions as well as the catalyst preparation procedure considerably enhanced selectivity and activity of the CNTs supported platinum catalyst. More carbon nanomaterials with various configurations and microstructures should be used as catalyst supports, and their catalytic properties should also be studied. It was expected some efficient catalysts will be found.

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