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Selective hydrogenation of citral over a novel platinum/MWNTs nanocomposites

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Pt was introduced into pure and polyacrylic acid (PAA) grafting multi-walled carbon nanotubes (MWNTs) by electroless metal deposition method and used as catalysts for hydrogenation of citral. The catalysts exhibited higher activity in the hydrogenation of citral when compared with Pt impregnated active carbon (AC) catalyst, while the selectivity of the catalysts on different MWNTs supports were quite different. The catalyst characterization results reveal that the selectivity of products is related with the morphology of the MWNTs and Pt(1 1 1) facet, functionalized carbon nanotubes will orient Pt facet and facilitate its dispersion on support.

1. Introduction

Selective catalytic hydrogenation of α,β-unsaturated aldehydes has attracted much attention in recent years, because the hydrogenation products are important intermediates of great commercial interest [1]. Many studies on hydrogenation of acrolein, crotonaldehyde, citral and cinnamaldehyde over transition metal catalysts were reported in the literature, and Pt has been proved to be one of the most effective components in these reactions [2–5]. Among all these compounds, citral is a particular attractive molecule. Three double bonds exist in citral molecule, two of which are conjugated while the third one is isolated. Reaction routes of citral hydrogenation are shown in scheme 1 [6].

Carbon materials are widely chosen as supports for hydrogenation catalysts. Various carbon materials have been used in different reactions, such as active carbon (AC) [2,4,7–9], carbon cloth [10], active carbon fiber [11–13], active carbon felts [14] and carbon nanotubes (CNTs) [15,16]. The novel CNT structures were found to have remarkable catalytic effects when used as support for selective hydrogenation reactions [17–20].

Since the surface of CNTs itself is rather inert, it is difficult to control the homogeneity of metal deposition on the surface by conventional methods. Active components can be well dispersed with grafting functional groups on the surface of CNTs, acting as specific nucleation site [21]. Generation of functional groups on the surface of CNTs can be realized by chemical oxidation treatments using HNO_3, $KMnO_4$, OsO_4, RuO_4, HNO_3–H_2SO_4, etc. [22–25]. However, some of the oxidants are known to open the tips of the tubules [22], cause damages to the tubular structure [24], or introduce contaminants [25]. In our previous work, method of large-scale functionalization of single-walled carbon nanotubes (SWNTs) has been established in polymer solvents without great change in nanotube structures [26]. The MWNTs have the similar morphology and electronic properties as SWNTs, while its price is much lower. Therefore, MWNTs is supposed to be a good support for catalysts. Herein, we try to functionalize MWNTs with polyacrylic acid (PAA) and then introduce platinum particles on the MWNTs through electroless metal deposition method. The prepared catalysts were tested in the catalytic hydrogenation of citral. The aim of this work is to check the feasibility of the new preparation method and to investigate Pt/MWNTs catalysts property as well as the relationship between activity and structure.

2. Experimental section

The MWNTs in purified form (p-MWNTs) synthesized by the chemical vapor deposition (CVD) method were purchased from Shenzhen Nanotech Port Co. Ltd., China, 2,2′-azobisisobutyronitrile (AR), acrylic acid (AR), ethylene glycol (AR), $H_2PtCl_6 \cdot 6H_2O$ and other solvents were all purchased from Shanghai Chemical Reagent Corporation.

In a typical grafting process, 1.0 g of acrylic acid was added to a three-neck round bottom flask, which was charged with 50 ml of acetone and 0.1 g of MWNTs. After 10 min of ultrasonication, the solution was purged under dry nitrogen for 30 min to remove oxygen from the flask. Then 0.05 g of 2,2′-azobisisobutyronitrile was added. The reaction was kept at 55 °C for 8 h to graft the PAA on the surfaces of MWNTs. The polymer-functionalized MWNTs, PAA-g-MWNTs, were filtered and washed by ethanol and distilled

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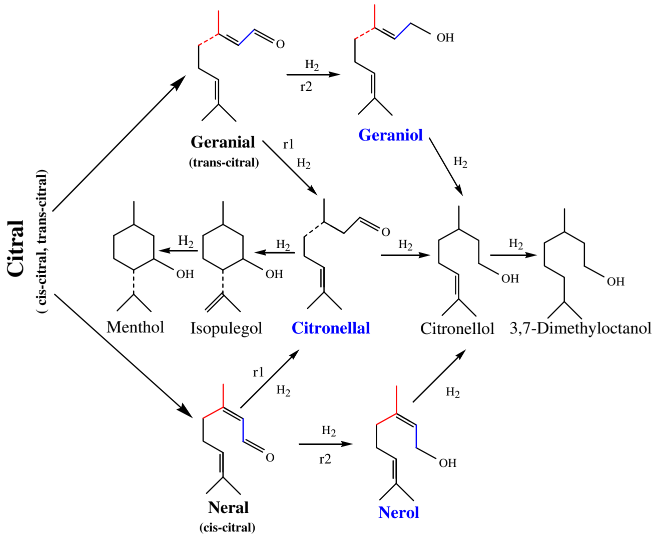

Scheme 1. Reaction routes of citral hydrogenation.

water for five times to remove the reagents residue. After that, PAA-g-MWNTs were dried in vacuum oven at 40 °C for 16 h.

The catalysts were prepared by a simple electroless metal deposition method with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$. The concentration of Pt is about 4.7 mg/ml. An appropriate volume of Pt solution and ethylene glycol were added in a flask, and then p-MWNTs or PAA-g-MWNTs were dropped into the flask. After 10 min of ultrasonication, the reaction was performed at 160 °C with magnetic stirring for 30 min. The catalysts were separated from ethylene glycol by filtration, and then dried at 120 °C for 2 h. The catalysts are denoted as Pt/p-MWNTs and Pt/PAA-g-MWNTs. For comparison, the Pt/AC catalyst was prepared by the conventional wetness impregnation method and reduced by KBH_4 aqueous solution prior to its use in the reaction.

The surface area and pore diameter of the catalysts have been measured by N_2 adsorption and desorption at 77.35 K in a Micromeritics TriStar system. The microstructures of the catalysts were observed by TEM using a JEM-2010 (HR) apparatus operated at 200 kV. XRD patterns were obtained on a Bruker D8 advance diffractometer over the 2θ range from 10° to 90°with Cu Kα radiation.

The citral hydrogenation was carried out in a well-stirred high temperature autoclave reactor. In a typical reaction, appropriate weight of citral and catalyst (10:1), mixed with 50 ml of hexane was added into the reactor. After purging with hydrogen for five times, the reaction system was pressurized with 1.0 MPa of hydrogen. The hydrogenation reaction was performed at 80 °C for 2 h. The reaction mixture was stirred at 500 rpm to eliminate the external diffusion limitations. The products were filtered and analyzed in a gas chromatograph (Trace ultra 2000, flame ionization detector with 30 m DB-5 capillary column).

3. Results and discussion

3.1. Catalyst characterization

The metal composition, specific surface areas and pore diameters of the samples are listed in Table 1. The surface area of Pt/AC catalyst is 695 m^2/g, while the pore diameter is 2.56 nm. In the case of Pt/p-MWNTs and Pt/PAA-g-MWNTs, the specific surface areas are smaller than Pt/AC, which are 103 m^2/g and 246 m^2/g, respectively. After the MWNTs were grafted with PAA, the surface area increased more than twice, while the pore diameter decreased from 15.51 nm to 11.66 nm.

Table 1
Characteristics of the catalysts

Catalyst	Pt (wt.%)	S_{BET} (m^2/g)	D_{pore} (nm)
Pt/PAA-g-MWNTs	4.96	246	11.66
Pt/p-MWNTs	5.09	103	15.51
Pt/AC	4.75	695	2.56

TEM images of the catalysts are shown in Fig. 1. In the case of the Pt/AC catalyst, the distribution of Pt nanoparticles is not uniform. Pt clusters were aggregated to large particles on AC, while in the case of the Pt/p-MWNTs and Pt/PAA-g-MWNTs catalysts, the dispersion of Pt are much better. Pt particles loaded on to the two kinds of MWNTs have similar size, which is about 2–3 nm. It was reported that the functionalization of MWNTs can facilitate the dispersion of Pt particles [21]. However, from the TEM images, the difference is not obvious between the dispersion of Pt on the two kinds of MWNTs.

XRD analysis was carried out (Fig. 2) to reveal the orientation of Pt crystal on support. The crystal structure of Pt in the catalysts is face centered cubic (fcc), confirmed by the presence of peaks at 39.6°, 46.3°, 67.4°, and 81.4° [27], assigned to Pt(111), Pt(200), Pt(220), and Pt(311), respectively. The average particle size of Pt deposited was measured by the line broadening of the Pt(220) peak using Scherrer's formula [28]. The average sizes of Pt particles were 1.92 nm, 2.85 nm, and 5.57 nm for the Pt/PAA-g-MWNTs, Pt/p-MWNTs and Pt/AC catalysts, respectively. The results indicate that Pt exhibits better dispersive property on MWNTs than that on AC. Between the two Pt/MWNTs catalysts, the XRD pattern of Pt/PAA-g-MWNTs is much more dispersive. Meanwhile, the intensity of Pt(111) in Pt/p-MWNTs is much higher than that of Pt/PAA-g-MWNTs. This indicates that the grafting of PAA on MWNTs can promote the Pt dispersion on the MWNTs. On the other hand the treatment is not in favor of the formation of Pt(111).

3.2. Hydrogenation catalytic properties

The hydrogenation of citral is a parallel and consecutive reduction of different functional groups present in the same starting substrate. The main products are citronellal (CAL), citronellol (COL), nerol (NOL), geraniol (GOL), dimethyloctanol (DMOL), isopulegol (IPOL) and menthol (MOL). The reaction routes involved in the hydrogenation of citral are shown in Scheme 1 [6]. Singh and Vannice have reported that the isolated C=C is hard to be hydrogenated under normal reaction condition [5]. However, the conjugated C=C and C=O would be hydrogenated easily. CAL, IPOL, and MOL are all formed through the hydrogenation of the conjugated C=C firstly (Scheme 1, r1). Meanwhile, the unsaturated alcohols (UCOL), NOL and GOL, are formed via C=O hydrogenation firstly (Scheme 1, r2). Both CAL and UCOL can be hydrogenated to COL and then to DMOL finally.

The catalytic results obtained on the three catalysts are listed in Table 2. The Pt/PAA-g-MWNTs catalyst shows higher activity than Pt/p-MWNTs and Pt/AC catalysts. The citral conversion reaches 87.2%, and main products are CAL, COL, and IPOL. Owing to few UCOL detected, it is suggested that the reaction follows the route 1, which is formed through conjugated C=C hydrogenation firstly. The Pt/p-MWNTs catalyst is less active for the citral hydrogenation, and the conversion of citral is about 54.5%. The UCOL is more than half in the products, which is formed through the hydrogenation of C=O. So it is suggested that the reaction follows the route 2. Pt/AC catalyst shows the lowest activity for hydrogenation of citral, the conversion is about 29.9%. The main products are CAL, which is 30.0%, UCOL, which is 26.1%, and COL, which is 18.1%.

It was reported that the larger surface area is beneficial to the higher activity. This is consistent with the case of Pt/PAA-g-