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Selective hydrogenation of cinnamaldehyde to cinnamyl alcohol with carbon nanotubes supported Pt-Co catalysts

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Abstract

The Pt-Co catalysts supported on carbon nanotubes (CNTs) have been prepared by wet impregnation and the selective hydrogenation of cinnamaldehyde (CMA) to the corresponding cinnamyl alcohol (CMO) over the catalysts has been studied in ethanol at different reaction conditions. The results show that Pt-0.17 wt%Co/CNTs catalyst exhibits the highest activity and selectivity at a reaction temperature of 60 °C under a pressure of around 2.5 MPa, and 92.4% for the conversion of CMA and 93.6% for the selectivity of CMA to CMO, respectively. The selective hydrogenation for the C=O double bond in CMA would be improved as increasing the H_2 pressure, and the selective hydrogenation for the C=C double bond in CMA is enhanced as increasing the reaction temperature. In addition, these catalysts have also been characterized using transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), H_2-temperature programmed reduction (H_2-TPR) and H_2-temperature programmed desorption (H_2-TPD) techniques. The results show that Pt particles are dispersed more homogeneously on the outer surface of the nanotubes, while the strong interaction between Pt and Co would improve the increasing of activated hydrogen number because of the hydrogen spillover from reduced Pt^0 onto CNTs and increase the catalytic activity and selectivity of CMA to CMO.

Keywords: Cinnamaldehyde (CMA); Cinnamyl alcohol (CMO); Pt-Co/CNTs catalyst; Selective hydrogenation

1. Introduction

Catalytic hydrogenation of α, β-unsaturated aldehydes (UAL) to unsaturated alcohols (UOL) is a reaction of industrial importance [1–4]. The hydrogenation of α, β-unsaturated aldehyde to give selectively saturated aldehyde or unsaturated alcohols, could be achieved by choosing suitable metal complex catalyst [5–9]. So the selection of promoters, supports and reduction conditions is important for the selective formation of UOL. Carbon nanotubes (CNTs) have developed entirely new field in many natural science since their discovery at the beginning of the last decade [10]. The unique physical and chemical properties make them potential and promising applications in various areas like reinforcement materials and microelectronics devices. Recently, there has been great interest to use CNTs as catalyst supports. Such structures can display unusual behaviors compared to classical supports, especially for liquid-phase reactions and some meaningful results have been obtained [11–13].

A typical example of α, β-unsaturated aldehydes (UAL) to unsaturated alcohols (UOL) is the hydrogenation of cinnamaldehyde (CMA) to cinnamyl alcohol (CMO), one of the important starting materials for production of perfumes, flavorings, pharmaceuticals, and other fine chemicals. However, it is a challenging task to accomplish selective hydrogenation of the C=O double bond since the hydrogenation of the C=C double bond is thermodynamically more favorable than the C=O hydrogenation, and low yields of the desired product are obtained with the conventional hydrogenation catalysts [14]. Only a few catalysts suitable for that purpose have been reported hitherto, most of them are Pt- and Co-based catalysts [15–19].

The aim of the present work is to report the preparation and the characterization of a platinum and cobalt-decorated carbon nanotubes catalyst and its implication in hydrogenation reactions. The catalytic activity is investigated for the liquid-phase selective hydrogenation of CMA into the corresponding unsaturated alcohol (CMO) in mild reaction conditions.

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Comparison is made with Graphite supported Pt-Co catalysts in terms of activity, expressed as conversion, and selectivity towards the C=C double bond and the C=O double bond hydrogenation. The microstructure, H_2 reduction and desorption properties of the catalysts are also studied using transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), H_2-temperature programmed reduction (H_2-TPR) and H_2-temperature programmed desorption (H_2-TPD) techniques, respectively.

2. Experimental

2.1. Catalyst preparation

CNTs are prepared according to method described in Ref. [20]. The surface area of CNTs is 110 m^2/g and the average pore diameter value is 22 nm, the pore volume is 0.311 ml/g. The as-prepared carbon nanotubes are subsequently purified by thick nitric acid treatment at 80 °C for16 h in order to dissolve the residual catalyst which could be contained in their structure during the synthesis process and decorate the surface before used as catalyst carrier. The solid is filtered and washed several times with distilled water until the pH reached 7 and then dried overnight at 110 °C. The surface area of commercial Graphite is 16 m^2/g and the average pore diameter value is 21 nm, the pore volume is 0.0344 ml/g. The Graphite is purified by thick nitric acid treatment also before used as catalyst carrier.

Pt/CNTs and Pt/Graphite catalysts are prepared by conventional impregnation with an aqueous solution of $Pt(NH_3)_4Cl_2$. The sample impregnated is reduced by KBH_4, filtered and washed with large amount of water, dried at 110 °C overnight before use. The content of platinum is 0.50 wt%. Pt-Co/CNTs and Pt-Co/Graphite catalysts are prepared by co-impregnation with aqueous solutions of $Pt(NH_3)_4Cl_2$ and $Co(NH_3)_4Cl_2$ with a weight of Pt 0.50 wt% and Co 0.17 wt% (unless otherwise stated). The bimetallic catalyst preparation process is similar to monometallic Pt/CNTs and Pt/Graphite catalysts.

2.2. Catalyst characterization electron microscopy

Transmission electron microscopy (TEM) is a conventional method to give detailed information about the shapes, mean size and size distribution of metallic dispersions. The microstructure of the carbon nanotubes supported platinum material is observed by TEM using a JEM-2010 (HR) apparatus operated at 200 kV. The bulk composition of the samples is determined by energy dispersive X-ray spectrometry (EDS).

2.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements are performed on a VG ESCALAB 2201-XL spectrometer. Non-monochro Mg Kα radiation are used as a primary excitation. The binding energies are calibrated with the C1s level of adventitious carbon (284.6 eV) as the internal standard reference.

2.4. Temperature programmed reduction (H_2-TPR) and desorption (H_2-TPD)

The reduction properties of the supported Pt catalysts are measured by means of H_2-TPR. Prior to experiments, 50 mg of the catalysts are pre-treated in a He flow at 200 °C for 15 min. Then the sample is cooled to −50 °C in flowing He. The feed is then switched to 5 vol.% H_2 in He, the reduction gas which is purified with deoxidizer and silica gel. The reaction temperature is programmed to rise at a constant rate of 10 °C/min up to 300 °C and the flow-rate is 30 ml/min. Amount of H_2 consumption during the H_2-TPR is measured by a thermal conductivity detector (TCD), and the effluent H_2O formed during H_2-TPR is adsorbed with a 5A molecular sieve. The hydrogen uptakes are quantified using CuO as a standard.

H_2-TPD experiments are carried out over the same equipment of TPR studies. Prior to experiments, 50 mg of the catalysts are pre-treated in a 5 vol.% H_2 in He flow at 200 °C for 15 min. Then the sample is cooled to −30 °C in flowing 5 vol.% H_2 in He. The feed is then switched to He, which is purified with deoxidizer and silica gel. The reaction temperature is programmed to rise at a constant rate of 10 °C/min up to 300 °C and the flow-rate is 30 ml/min. Amount of H_2 desorption during H_2-TPD is measured by a thermal conductivity detector (TCD).

2.5. Catalytic properties measurement

The hydrogenation reaction of CMA is carried out at low pressure and low temperature, in a stainless steel reactor equipped with a hydrogen inlet, a teflon vessel and a muphet stirrer. A mixture of 0.36 g catalyst, 8.0 mmol CMA and 19.0 ml C_2H_5OH is placed in the reactor. The reaction temperature is maintained by water bath.

Chemical analysis of the products is performed by gas chromatography Perkin-XL equipped with a FID detector and SE-30 capillary column. Reactants and products are identified by comparison with authentic samples. Biphenyl is used as internal standard.

3. Results and discussion

3.1. Electron microscopy

The TEM images and EDS patterns of Pt/CNTs and Pt-Co/CNTs are shown in Fig. 1. Fig. 1(A) shows that most of the Pt particles over Pt/CNTs are dispersed more homogeneously on the outer surface of the nanotubes, leading to small diameters on the whole, and Pt particles have a wide range size of 2–5 nm. Different preparing methods result in different dispersion of Pt particles over CNTs, since different surface property of oxidized CNTs is resulted. It is reported that HNO_3-oxidized CNTs is negative net surface charge [21,22], which decides that CNTs will adsorb cations in the solution and favor their homogeneous dispersion on the outer surface. The TEM image of Pt-Co/CNTs catalyst is similar to that of Pt/CNTs.