



Carbon nanotubes supported Pt catalysts for phenylacetylene hydrogenation: effects of oxygen containing surface groups on Pt dispersion and catalytic performance

Chuang Li^a, Zhengfeng Shao^a, Min Pang^a, Christopher T. Williams^b, Changhai Liang^{a,*}

^a Laboratory of Advanced Materials and Catalytic Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

^b Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia, SC 29208, USA

ARTICLE INFO

Article history:

Received 25 May 2011

Received in revised form 20 July 2011

Accepted 7 September 2011

Available online 28 September 2011

Keywords:

Carbon nanotubes

Oxygen-containing groups

Pt catalysts

Hydrogenation

Phenylacetylene

ABSTRACT

Carbon nanotubes with different surface groups were achieved by oxidative treatments with $\text{HNO}_3\text{--H}_2\text{SO}_4$ and followed thermal treatments. Deposition of Pt particles onto carbon nanotubes was achieved through chemical reduction of $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ by ethylene glycol in the presence of NaOH. The as-prepared samples were characterized by temperature programmed desorption, Fourier transform infrared spectroscopy, X-ray diffraction and high resolution transmission electron microscopy. The type and amount of surface oxygen functional groups on the carbon nanotubes can be regulated by thermal treatments at different temperatures in an inert atmosphere. Both dispersion and sintering resistance of Pt nanoparticles were found to be a function of amount of oxygen surface groups on the carbon nanotubes, however, the amount of oxygen surface groups apparently did not affect the Pt loading on the carbon nanotubes. The Pt nanoparticles supported on the functionalized carbon nanotubes by oxidation treatment gave superior catalytic activity for the phenylacetylene hydrogenation, which phenylacetylene conversion and selectivity to styrene are 99% and 88%, respectively. This may be due to the higher dispersion (i.e., smaller particle size) of the Pt nanoparticles, which is beneficial for the hydrogenation of phenylacetylene.

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1. Introduction

Phenylacetylene (PA) removal from styrene (ST) by selective hydrogenation is a process of great industrial importance [1,2], because PA, an impurity in ST, poisons and deactivates the catalysts for ST polymerization. The PA concentration in ST is required to be decreased to below 10 ppm. The PA hydrogenation proceeds under relatively mild condition, and the desired product is the intermediate (i.e., ST), making it very convenient for the evaluation of process designs [2] and testing of hydrogenation catalysts [3–6]. In this sense, there is a substantial amount of literature (both homogeneous [7–9] and heterogeneous [10–16] catalysts) exploring highly selective processes toward the selective hydrogenation of alkynes.

It is noted that the supports are of great importance in the supported metallic catalysts, since their interaction with the metallic phases can greatly influence the catalytic properties of the resulting materials. The effect of metal particle size on the catalytic properties of supported catalysts is still an important problem in heterogeneous metal catalysis. Changing the dispersion (i.e., the

metal particle size) may affect both specific activity and selectivity. These changes are believed to be brought about by electronic and geometric effects. For the nanostructured carbon supported catalysts, the metal dispersions obtained might be explained by the varying amounts of oxygen-containing surface groups. Carbon nanotubes (CNTs) are promising materials for numerous applications because of their unique mechanical, chemical, and electrochemical properties. The surface defects and functional groups created under the strongly oxidizing conditions can be used effectively as anchors for metal species. For the chemically inert CNTs, it is necessary to modify the surface groups in order to anchor metallic nanoparticles into their structure. Oxidation method has been widely used to create oxygen-containing groups in carbon materials. Meanwhile, it is an efficient way to remove amorphous carbon in CNTs [17] and to create some functional surface groups on CNTs to favor the anchorage of metallic nanoparticles [18]. Chemical treatment of CNTs is expected to create more anchored sites for metal anchoring, avoiding agglomeration problems. However, well-dispersed metal particles on CNTs are challenging as there are still relatively few sites available for anchoring the metal particles.

The acidic surface groups on CNTs play an especially important role in adsorption and catalysis. The oxygen-containing surface groups on CNTs have received more and more attention, but only

* Corresponding author. Fax: +86 411 84986056.

E-mail address: changhai@dlut.edu.cn (C. Liang).

a few studies have been directed at elucidating the influence of the surface oxygen groups on the catalytic behavior of the CNTs-supported catalysts. Several groups have reported [19–22] that oxygen-containing surface groups changed metal dispersion on CNTs, furthermore affected the catalytic performance of the resulted catalysts. However, it is not clear about effects of amount and type of oxygen-containing groups on the metal dispersion. To the best of our knowledge, no report is found on the functionalized CNTs with different oxygen-containing groups obtained by oxidative treatments with $\text{HNO}_3\text{--H}_2\text{SO}_4$ and followed thermal treatments. Herein, we have obtained the oxidized CNTs with different amount of surface oxygen groups, and systematically studied effects of oxygen-containing surface groups of CNTs on dispersion of Pt nanoparticles and on the catalytic performance of the resulting catalysts.

2. Experimental

2.1. Preparation

Commercial multi-walled CNTs (above 95% purity) with the diameter of 20–40 nm and the length of 1–2 μm were obtained from Shenzhen Nanotech. Port. Co. Ltd. The CNTs were synthesized by a chemical vapor deposition method using nickel as catalysts, and the amorphous carbon content is no more than 3%. All the reagents used for the experiments were of analytical grade.

The CNT (1.0 g) was refluxed in 100 mL of 0.2 M HNO_3 and 0.6 M H_2SO_4 mixture for 4 h. After refluxing, the mixture was cooled to room temperature, and filtered. Then the CNTs were washed repeatedly using distilled water and dried at 120 $^\circ\text{C}$ for 24 h [23,24]. The oxidized CNTs were marked as oCNTs.

In order to investigate the influence of heat treatment on the surface properties and catalytic performance of CNTs, about 3 g of oCNTs sample was treated in an Ar stream (100 $\text{cm}^3 \text{min}^{-1}$) for 2 h at 300, 500 and 700 $^\circ\text{C}$, respectively. The resulting samples were labeled as oCNTs-3, oCNTs-5, and oCNTs-7, respectively.

Pt nanoparticles were synthesized from the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ by using modified procedures published in reference [25,26]. Typically, the oCNTs were firstly added in Pt colloidal solution. An amount of diluted hydrochloric acid was added to adjust the pH value to below 3 when the above solution was cooled to 80 $^\circ\text{C}$. This can remove partly glycolate as a stabilizer for the colloid. Then the mixture was heated to 140 $^\circ\text{C}$, and stirred for 1 h. After cooled to room temperature, the obtained black sample was filtered, washed by ethanol and dried at 70 $^\circ\text{C}$ in air. All catalysts were prepared with 1.0 wt% Pt loading.

2.2. Characterization

Fourier transform infrared (FT-IR) spectra were collected at room temperature on a Nicolet Impact 410 with a resolution of 4 cm^{-1} . Samples were first dried for 24 h at a temperature of 383 K. The dried samples were mixed with KBr in a mass ratio of 1:300.

X-ray diffraction analysis of the samples was carried out using a Rigaku D/Max-RB diffractometer with $\text{Cu K}\alpha$ monochromatized radiation source, operated at 40 kV and 100 mA.

The Pt content was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The samples were treated with sodium peroxide solution and then nitric acid solution, and the solution was filtered and analyzed by ICP-OES.

The oxidized CNTs were dried in an oven at 70 $^\circ\text{C}$ for 2 h under dynamic air before further measurements. Temperature-programmed desorption (TPD) was carried out in a horizontal quartz tube reactor with an inner diameter of 10 mm. Helium (99.9999%, 30 sccm) was used as carrier gas. An on-line infra-red

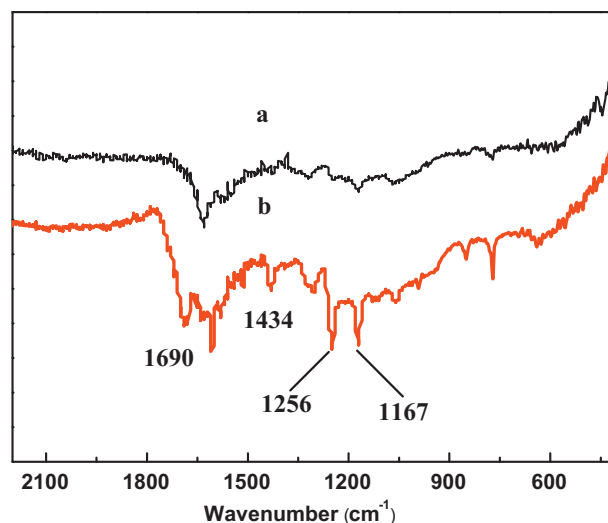


Fig. 1. FT-IR spectra of the CNTs (a) and oCNTs (b) samples.

detector (Binos) was used to detect CO and CO_2 . The Binos was calibrated and the measurement range is 0–4000 ppm for both gases. Typically, about 200 mg was used for each TPD measurement. The sample was heated from room temperature to 1100 $^\circ\text{C}$ at a heating rate of 2 $^\circ\text{C min}^{-1}$, and then held at that temperature for 1 h before cooling down to room temperature.

The particle size and distribution of the samples were analyzed by transmission electron microscopy (TEM) (Philips CM200, 200 kV). Powder samples were ultrasonicated in ethanol and dispersed on copper grids covered with a porous carbon film.

2.3. Phenylacetylene hydrogenation

Selective hydrogenation of PA was carried out in a 50 cm^3 closed vessel at the controlled temperature. The catalyst was activated in hydrogen stream at 300 $^\circ\text{C}$ for 2 h, followed by cooling to room temperature. About 0.10 g of the catalyst was placed in the reactor with 10 mL ethanol and 0.534 g PA. The substrate/Pt mole ratio was kept in 1250. The vessel was filled with H_2 to 0.40 MPa and vented three times to remove the air, finally filled with H_2 to 0.40 MPa. The reaction was carried out at 50 $^\circ\text{C}$ for 1 h with stirring. The temperature from 40 to 70 $^\circ\text{C}$ and the pressure from 0.40 to 0.80 MPa were examined to investigate their influences on the catalytic performance. The products were analyzed by a 7890 II gas chromatograph using an FID detector with a SE-54/52 capillary column. A known amount of n-octane solution was used as the internal standard.

3. Results and discussion

CNTs tend to aggregate in polar solvent due to hydrophobic nature of surface. It is necessary to modify the CNT surface in order to deposit a large surface density of Pt nanoparticles with uniform distribution. Oxidation treatment is one of the common surface modification methods for CNTs. Fig. 1 shows FT-IR spectra of CNTs and oCNTs. After oxidation in $\text{HNO}_3\text{--H}_2\text{SO}_4$, some additional bands appear at 1690, 1434, 1256 and 1167 cm^{-1} . The peak at 1690 cm^{-1} can be assigned to C=O stretching vibration of carboxy or carbonyl groups [27]. The bands at 1434 cm^{-1} and 1170 cm^{-1} are associated with $-\text{NO}_2-$ [28] and a C–O stretching vibration [29], respectively. The 1256 cm^{-1} band due to C–O groups is also significantly enhanced in the oxidized sample. Obviously, $\text{HNO}_3\text{--H}_2\text{SO}_4$ treatment introduces oxygen-containing groups.

TPD is becoming popular for characterization of oxygen-containing groups on the surface of carbon materials. In this

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