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A novel approach to Co/CNTs catalyst *via* chemical vapor deposition of organometallic compounds

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A novel approach for attaching well-dispersed cobalt nanoparticles homogeneously onto carbon nanotubes *via* metal organic chemical vapor deposition technique is reported. The obtained Co/CNTs catalysts feature a narrow size distribution of Co particles centering around 7.5 nm, and show high activity and regioselectivity for hydroformylation of 1-octene.

KEY WORDS: carbon nanotubes; MOCVD; cobalt; hydroformylation.

1. Introduction

After the discovery of carbon nanotubes (CNTs) [1], much attention has been focused on their potential as supports for heterogeneous catalysts [2–14] because of their unique structure and properties [15] as well as good hydrogen storage capacity [16]. Some studies have shown that CNTs are suitable for supporting many types of metal [2–8] or active complex species in various amount [4], especially for catalysts used in liquid-phase reactions in which the CNT-supported catalysts show high conversion and high selectivity [10]. For heterogeneous catalysis, one of the key issues is to prepare homogeneous and highly active metal catalysts supported on CNTs. Up to now, most of the research about CNT-supported catalysts have adopted the conventional approaches to prepare catalysts that include impregnation, ion-exchange and co-precipitation methods, in which several steps are normally involved, including adsorption/loading, drying, calcination and reduction steps. Because of these, the catalyst structure and morphology would change significantly, which results in the inhomogeneous dispersion of metal particles on CNTs [3–9]. This is the case especially for the cheap but widely used iron group catalysts (Fe, Co and Ni). Metal organic chemical vapor deposition (MOCVD) is a potential alternative for making stable and active catalysts with well-developed structure [17–19], but till now little work has been done about making CNT-supported catalysts by the MOCVD method. Here we report for the first time that uniform cobalt nanoparticles with the diameter centering around 7.5 nm supported on CNTs can be prepared *via* the MOCVD method. The catalytic performance tests show that the CNT-supported catalysts made by the MOCVD method are active for hydroformylation of 1-octene.

2. Experimental

CNTs used in this study was supplied by Shenzhen Nanotech Port Co., Ltd. (NTP) in China. The CNTs and activated carbon (AC) were pre-treated by refluxing in 4.0 N HNO_3 at 120 °C for 4 h before loading catalyst. The Co/CNTs catalysts prepared *via* the MOCVD method with $Co_2(CO)_8$ as precursor were termed as CoM hereafter. For a typical run, the CNT support and $Co_2(CO)_8$ were first mixed in a mortar for 0.5 h, then the mixture was transferred into a quartz tube, which was ramped under vacuum conditions following a multi-stage temperature program (2 °C/min up to 40 °C, held for 1 h; 0.25 °C/min up to 70 °C, held for 1 h; 0.25 °C/min up to 120 °C, held for 1 h; 0.5 °C/min up to 450 °C, held for 2 h before cooling back to room temperature). For comparison, the Co/CNTs catalyst made *via* traditional impregnation method (termed as CoI hereafter) and Co/AC made *via* the MOCVD method (termed as CoA hereafter) were also prepared and tested under the same conditions for 1-octene hydroformylation. All catalysts were examined using transmission electron microscopy (TEM, JEOL JEM-2000EX operated at 100 kV and Philips Tecnai G^2 20 operated at 200 kV) and XRD (D/max-2400 operated at 40 kV and 100 mA, CuK? radiation). Micro-FT-IR spectra were recorded on a Nicolet Magna-750 FT-IR spectrometer. The

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hydroformylation of 1-octene was conducted at 130 °C and 5 MPa in a fixed-bed reactor in flowing gas of H_2:CO (50:50 in volume) with a space velocity of 0.1716 h^{-1}, 1-octene mixed with cyclohexane in a volume ratio of 5:95 was continuously injected into the reactor using high pressure liquid pump. Before the reaction the catalyst was reduced in flowing hydrogen, during which the reactor was first ramped at 2 °C/min to 350 °C, then was kept at 350 °C for 2 h. After reduction the catalyst bed was cooled down to reaction temperature. For each run, 500 mg of catalyst was used. The reactants and products were analyzed using GC–MS equipped with a HP-INNOWAX capillary column and FID detector (Agilent 6890N GC/5973MSD). The Co content in catalyst was analyzed using inductively coupled plasma emission spectrometry (ICP-OES).

3. Results and discussion

The typical TEM image of the CNT material after refluxing treatment in HNO_3 is shown in figure 1a. It has been found that after HNO_3 oxidation treatment, the CNT sample does not contain residues such as Ni catalyst and its support, and carbonaceous impurity agglomerate, as can be seen in figure 1a. The outer diameters of the CNTs are in a range of 20–60 nm with the inner diameters being in a range of 5–10 nm. The BET surface area of the CNTs, determined by nitrogen adsorption at 77 K, is ca. 140 m^2/g.

The typical TEM image of the CoM sample is shown in figure 2a, from which it can be seen that the spherical cobalt particles on CNTs are quite uniform and distributed homogeneously. The HRTEM examination reveals that these CNT-supported cobalt nanoparticles are nano-sized single crystals, of which the well-developed (111) planes can be clearly seen, as shown in the inset in figure 2a. The measured lattice constant of these nano-sized Co crystals is ca. 0.228 nm. The XRD study further confirms that these nanoparticles are featured with crystalline structure. Figure 3 shows the XRD pattern of Co/CNTs, from which it can be seen that the (111) diffraction peak of the fcc cobalt phase is weak and wide, implying the size of cobalt particles on CNTs is quite small. The (311) peak of Co_3O_4 is also visible in figure 3, implying that some partly oxidized cobalt particles are present. Based on the TEM measurement of about 300 particles in random regions, the average size of cobalt particles is estimated to be around 7.5 nm. The size distribution of CNT-supported cobalt particles is rather narrow and features in a log-normal distribution, as shown in figure 2b. The average diameter of the Co° crystallites calculated by the Scherrer equation is 7.3 nm, which is in good agreement with the TEM result of 7.5 nm discussed above.

It has been reported that the oxygen-containing groups on the carbon supports may function as the anchoring sites for the metallic precursors and/or metals, in other words, the metal particle size and distribution are strongly dependent on the surface chemical properties of the support, especially on the concentration and the type of the various oxygen-containing groups [20, 21]. In our case, the CNT supports were pretreated in HNO_3under fluxing conditions, resulting in a large amount of oxygen-containing groups on the nanotube surfaces such as hydroxyl, carboxyl, and carbonyl groups, which is confirmed by FT-IR studies (figure 4). In the case of MOCVD process in which it is easy for the catalyst precursor to get access to the functional groups on the CNT support [17], these oxygen-containing groups act as nucleation sites for metal complex [20]. This makes it possible to tune the size and distribution of the catalyst particles by tailoring the amount of oxygen-containing functional groups and the loading amount of metal cobalt catalyst.

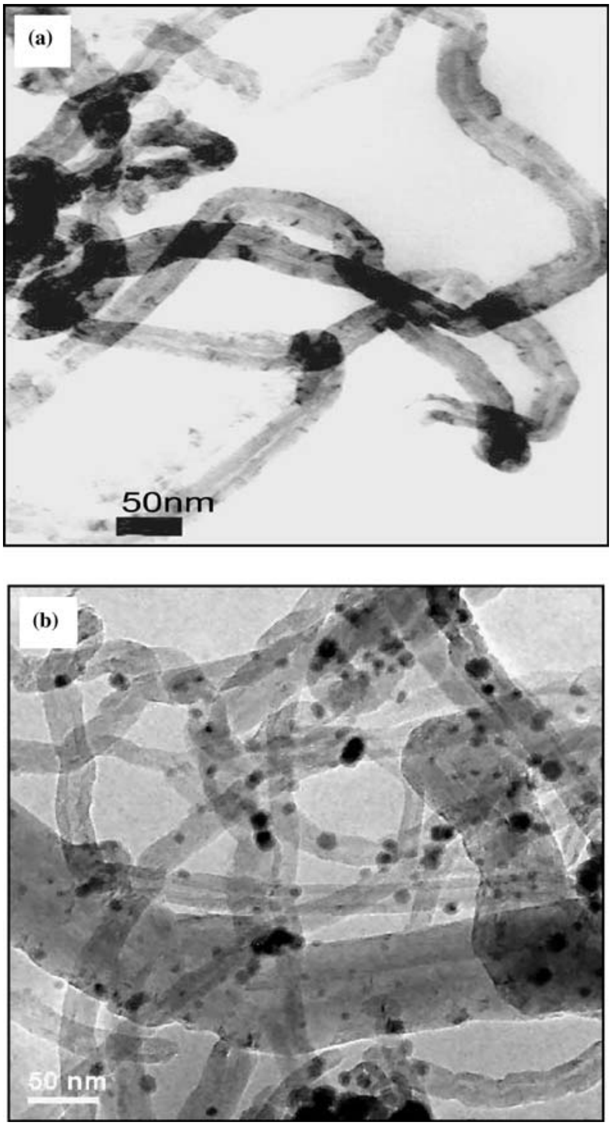

Figure 1. TEM images of the CNT samples (a) and the used CoM catalyst (b) in the 1-octene hydroformylation.

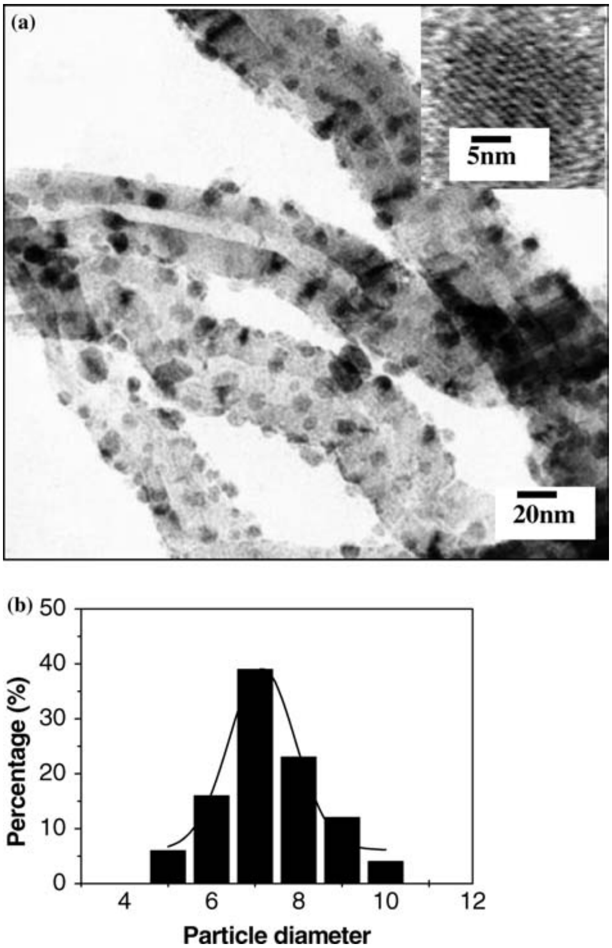

Figure 2. TEM analysis of the Co/CNTs catalyst (CoM): (a) HRTEM image, the inset shows an individual Co particle in which well-developed (111) planes can be clearly seen ($d_{(111)}$ = 0.226 nm); (b) the size distribution of Co particles on CNTs (based on the measurement of about 300 particles).

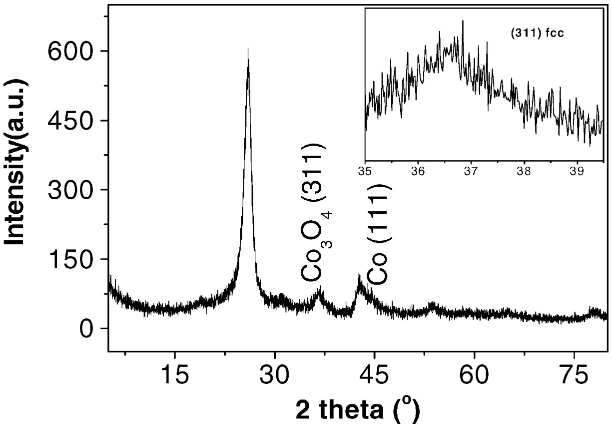

Figure 3. XRD pattern of the Co/CNTs catalyst (CoM).

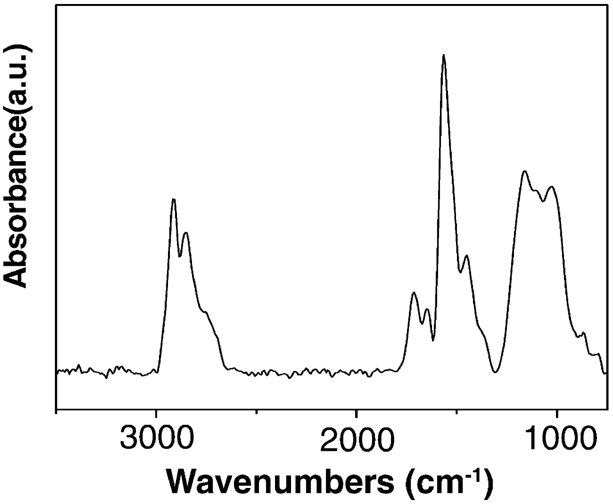

Figure 4. The Micro-FTIR spectrum of CNTs after HNO_3 oxidation treatment.

The catalytic performance of CNT-supported Co particles in the hydroformylation of 1-octene has been tested in a fixed-bed reactor at 130 °C and 5.0 MPa of syngas pressure, of which the results in the steady state after 20 h are shown in table 1. It has been found that for the 1-octene hydroformylation, the CoM catalysts made *via* the MOCVD approach show better activity and excellent regioselectivity. Under the conditions adopted in the present study, the 1-octene conversion and the selectivity to C^9-aldehyde can reach 65.4% and 81.23%, respectively, with the *n*/*i* ratio being at 1.53, which are consistently higher than in the case of CoI catalysts made *via* the traditional approach. It is assumed that the higher catalytic performance of CoM catalysts for 1-octene hydroformylation are due to the high dispersion of cobalt particles on CNTs, implying that the homogeneous distribution of cobalt metal particles on CNTs plays a key role for the better performance of CoM catalysts. The activity of the Co/CNTs catalyst is remarkably higher than that of the Co/AC catalysts under the same conditions. Similar phenomenon has been observed by Baker and his colleagues [3], in their case carbon nanofiber supported palladium catalysts were tested. In our case, the excellent regioselectivity and catalytic activities might be attributed to the unique structure, electrical properties, and the high external surface of CNTs. To clarify this point, more work is still needed.

Figure 5 illustrates the results of the stability test of CoM catalyst during 36 h of hydroformylation operation. It can be seen that the conversion of 1-octene first increases very quickly with time in the initial reaction stage, and reaches a maximum at about 10 h, and then the conversion levels off after about 20 h. No obvious deactivation is observed under the reaction conditions adopted. Figure 1b is the representative TEM image of Co/CNTs catalyst after being used for 36 h at 130 °C and 5 MPa. It can be seen that Co crystals are about 5–12 nm and anchored primarily on the outer surface of the CNTs. It should be noted that the particles become bigger after reaction, probably because the Co crystals

Table 1

Catalytic performance of cobalt catalysts in 1-octene hydroformylation

Catalyst	Loading of Cobalt (wt%)	Conversion of 1-Octene (%)	Selectivity to C^9-aldehyde (%)	*n*/*i*[a]
CoM	5.8	65.4	81.23	1.53
CoI	8.7	58.7	71.56	1.46
CoA	10.6	68.2	62.1	1.26

[a] Ratio of normal C^9-aldehyde to isomer-C^9-aldehyde.

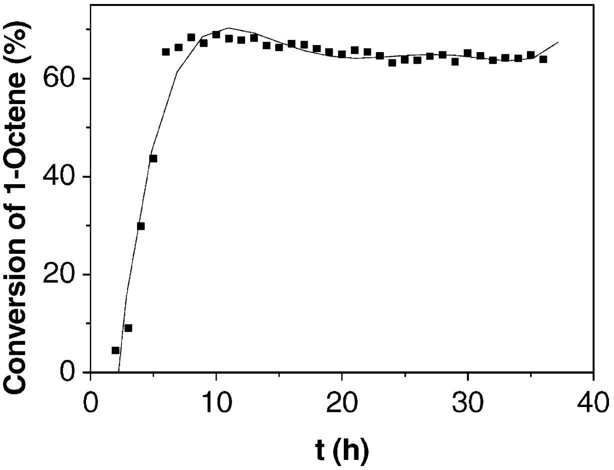

Figure 5. Stability test of CoM (cobalt loading of 5.8 wt%) for 1-octene hydroformylation.

are completely covered by support materials, and/or sintered.

In summary, we have demonstrated for the first time that a highly dispersed Co/CNTs catalyst with a narrow size distribution of the active metal species can be produced *via* a simple solvent-free MOCVD approach. The as-synthesized Co/CNTs catalysts show good activity and regioselectivity for the 1-octene hydroformylation. It can be expected that this work will lead to a new approach for making carbon nanotube-supported metals that are of great potential as catalyst for the hydroformylation of olefins.

Acknowledgments

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