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Copper Nanoparticles Decorated Inside or Outside Carbon Nanotubes Used for Methyl Acetate Hydrogenation

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Copper nanoparticles loaded inside or outside carbon nanotubes (CNTs) were prepared by a simple wet chemistry method. The structures and physicochemical properties of the obtained materials were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Methyl acetate (MA) hydrogenation forming methanol and ethanol was chosen as the application to explore the catalytic performances of copper inside and outside CNTs. The reaction results indicated that the catalytic activity of Cu-inside-CNTs catalyst was significantly higher than that of Cu-outside-CNTs because of the space confined effects. Furthermore, the influences of Cu content on CNTs to the catalytic performance were also investigated.

Keywords: Carbon Nanotubes, Copper, Methyl Acetate, Hydrogenation, Confinement Effect.

1. INTRODUCTION

Carbon nanotubes with unique properties such as large surface area, unique hollow tubular structure, large adsorption capacity, and high chemical, thermal and mechanical stability have received considerable interest as catalyst support in heterogeneous catalysis.[1] The copper and its oxides (CuO, Cu_2O) are one of the most important catalysts since their hydrogenation property.[2] To date, copper-based catalysts also had been widely used for methanol synthesis, water gas shift reaction.[3–4] Using CNTs as catalyst support with Cu or CuO_x nanoparticles as catalytic sites, the Cu decorated CNTs catalysts had been prepared by so many physical and chemical ways: the physics methods such as arc-discharge,[5] chemical vapor deposition (CVD),[6] supercritical CO_2 fluid,[7] and the chemical methods including electrochemical co-deposition,[8] ethylene glycol reduction,[9] solution infusion.[10] All of these methods, however, are very complicated processes, expensive costs, and especially difficult to control the fixed sites of metal nanoparticles inside or outside CNTs channels. As we know, the controlled loading of Cu nanoparticles inside or outside CNTs is crucial to the study of space confined effect of CNTs to catalyst performance.

Here, we report a simple wet chemistry method which can finely regulate the loading of Cu nanoparticles inside or outside the CNTs. The Cu nanoparticles decorated CNTs were studied by TEM and XRD, indentifying the distribution of Cu on CNTs and its reductive ability. The methyl acetate (MA) hydrogenation, as one of catalytic applications of Cu decorated CNTs, was adopted to explore the confinement effect of CNTs.

2. EXPERIMENTAL DETAILS

Multi-wall CNTs (Chengdu China) are used as support materials for the preparation of Cu loaded CNTs catalyst. Prior to impregnation, the CNTs were treated with 67% HNO_3 at 393 K for 14 h, followed by washing repeatedly with deionized water until pH = 7, drying at 333 K over 12 h and then vacuum drying at 353 K for 12 h. The obtained CNTs with opened ends were used as the support for copper loading. For impregnation process on this CNTs, 0.5 g of CNTs was impregnated with 1 mL $Cu(NO_3)_2$ solution at the assistance of ultrasound. After 30 min ultrasound impregnation, another 0.5 mL

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of deionized water was orderly dropped in. Then a dry sample could be obtained after further 30 min ultrasound treatment. Subsequently, the obtained sample was dried at 373 K in air for 10 h, and calcined at 623 K under Ar atmosphere for 3 h. The final sample was defined as Cu-inside-CNTs.

The Cu-outside-CNTs was obtained by the similar impregnation method to that of Cu-inside-CNTs, but having a specific pre-filling procedure on CNTs. Here, the pre-filling way used on CNTs by filling xylene in its channels are similar to the precursor report.[11] Briefly, before the $Cu(NO_3)_2$ solution impregnation process, the acid treated CNTs with opened ends were first pre-impregnated with 1ml xylene at the assistance of ultrasound, inhibiting the entrance of $Cu(NO_3)_2$ solution into its inner wall. After that, the CNTs were impregnated with $Cu(NO_3)_2$ solution, following by drying at 353 K in air for 2 h and calcining at 623 K in Ar atmosphere for 3 h. The final samples were defined as Cu-outside-CNTs. Both of these two types of Cu loaded CNTs, Cu-outside-CNTs and Cu-inside-CNTs, have the same Cu-content of 10 wt%. Moreover, another two samples with higher Cu loading amount, 20 wt% and 40 wt%, as reference, were also prepared by the same method to that of 10 wt% Cu-inside-CNTs.

The microstructures of carbon nanotubes samples were characterized with transmission electron microscopy (TOPCON EM-002B working at 120 kV). The crystal structure of the materials was confirmed by X-ray diffraction (XRD) with a Rigaku D/max-2550 V diffractometer employing Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å).

All the catalytic reactions were conducted with a fixed-bed stainless steel reactor (9.5 mm OD). 0.5 g catalyst was loaded into the reactor. Before the reaction, the catalysts were reduced *in situ* by a flow of pure hydrogen at 573 K for 10 h. After being cooled to the reaction temperature, the flow rate of pure hydrogen was changed to 80 $ml \cdot min^{-1}$ and the reaction pressure were maintained at 3 MPa. Then, the MA was injected by a pump with the flow rate of 0.9 $g \cdot h^{-1}$. The liquid MA was evaporated to MA gas by heater band, and carried into the reactor by the hydrogen flow. The CO, CH_4, CO_2 and Ar were analyzed online by the gas chromatograph equipped with TCD detector. The liquid products after catalytic reaction were collected with an ice water trap using 1-butanol as solvent, and analyzed by another gas chromatograph with flame-ionization detector (FID), in which 1-propanol was employed as the internal standard.

3. RESULTS AND DISCUSSION

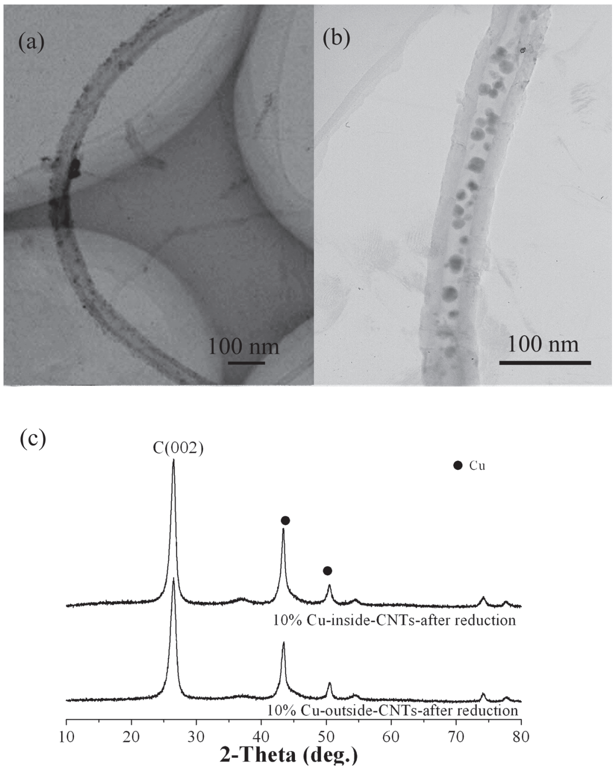

Fig. 1. TEM photos of (a) Cu-outside-CNTs after reduction, (b) Cu-inside-CNTs after reduction and (c) XRD patterns of Cu-outside-CNTs after reduction and Cu-inside-CNTs after reduction. (Reduction with 100% H_2 at 573 K for 10 h).

Figures 1(a) and (b) exhibit TEM images of Cu-outside-CNTs and Cu-inside-CNTs catalysts after reduction at 573 K with 100% H_2 for 10 h, respectively. For Cu-outside-CNTs catalyst, Cu nanoparticles with the size from 10 to 15 nm had been deposited evenly on the outer surface of CNTs, as shown in Figures 1(a). The schematic illustration of the preparation process of Cu-outside-CNTs was showed in Figure 2. The xylene, here, was used to lock the CNTs channels temporarily before the decoration of the exterior CNTs surface with Cu clusters, which can effectively prevent the access of $Cu(NO_3)_2$ solution infiltrating into CNTs channels.[11] Furthermore, the higher boiling point of xylene than that of water can also allows the preferential evaporation of water on the outside of nanotubes, leading to the unique copper loading only on the external surfaces of CNTs. Different from Cu-outside-CNTs, almost all of the Cu nanoparticles of Cu-inside-CNTs were filled inside the channel of CNTs shown in Figure 1(b). The formation of Cu nanoparticles inside CNTs should be attributed to the following reasons: First, the bigger size of CNTs channels was beneficial for solution entering to the inner cavities of CNTs. Second, most of the ends of CNTs have been opened after the concentrated nitric acid treatment. Relatively low surface tension of water and the capillary force donated by CNTs channels ensured that an equal volume liquid can be sucked by CNTs channels entirely. Third, the additional water added in the second step for Cu-inside-CNTs preparation shown in Figure 2 helped to wash the residual copper salt, shifting them into CNTs channels. For these two type catalysts, Cu-outside-CNTs and Cu-inside-CNTs, their Cu nanoparticles size are in the range from 10 to 18 nm

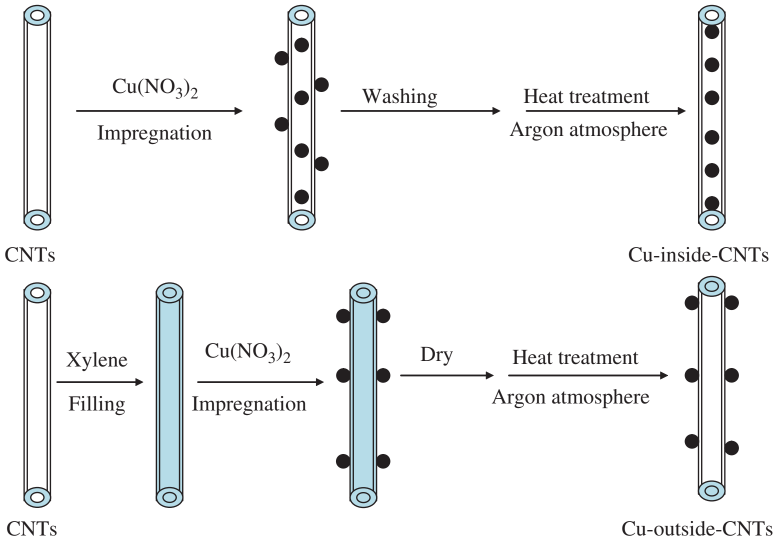

Fig. 2. Schematic illustration of the formation process of Cu-inside-CNTs and Cu-outside-CNTs.

according to the TEM images in Figures 1(a) and (b). The average Cu crystallite sizes of these two catalysts after reduction had also been estimated according to their XRD patterns shown in Figure 1(c). The values of Cu-outside-CNTs and Cu-inside-CNTs after reduction were 14.3 nm and 15.1 nm respectively, which are in good agreement with the values obtained from their TEM images.

Figure 3 presents the XRD profiles of 10 wt% Cu-outside-CNTs, 10 wt% Cu-inside-CNTs, 20 wt% Cu-inside-CNTs and 40 wt% Cu-inside-CNTs catalysts only after calcination in Ar atmosphere without further reduction by hydrogen. During the oxygen-free calcination of Cu loaded CNTs, auto-reduction of copper oxide using CNTs as reductant may be happen. Comparing the XRD pattern of 10 wt% Cu-inside-CNTs with that 10 wt% Cu-outside-CNTs, more metallic Cu can be detected on the Cu-inside-CNTs than Cu-outside-CNTs, indicating that the Cu loaded inside CNTs channels is better to be auto-reduced than outside of CNTs channels. The similar results for other different metal oxides had also been found by other researchers.[12] Furthermore, the XRD patterns also prove that the valence state change of Cu from $Cu + Cu_2O$ in 10% Cu-inside-CNTs to $CuO + Cu_2O$ in 40% Cu-inside-CNTs, which means the reducibility of catalysts decrease with the increase of Cu loading amount. And the average crystallite size of 20% Cu-inside-CNTs and 40% Cu-inside-CNTs were about 16.4 nm and 22.3 nm, respectively.

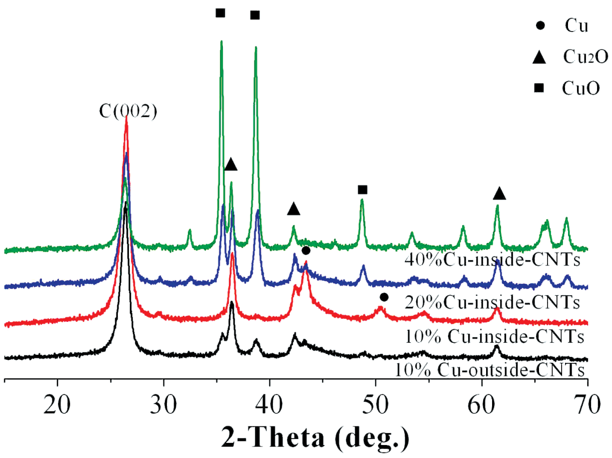

Fig. 3. XRD profiles of 10% Cu-outside-CNTs, 10% Cu-inside-CNTs, 20% Cu-inside- CNTs and 40% Cu-inside-CNTs.

The catalytic performances of catalysts in MA hydrogenation reaction were compared in Table I. Clearly, the catalysts with Cu nanoparticles inside CNTs channels have better activity than that the Cu nanoparticles outside CNTs channels even under the same reaction conditions. Although the same Cu loading amount, MA conversion on 10 wt% Cu-inside-CNTs catalyst is 13.9%, about 3 times bigger than that of 10 wt% Cu-outside-CNTs. This result should be attributed to the space confined effect of CNTs, which make Cu clusters inside CNTs channels

Table I. Methyl acetate hydrogenation reaction performances over various catalysts.

	Coversion (%)	Molecular selectivity (mol%)					
Catalysts	MA	MeOH	EtOH	EA	CO	CH_4	CO_2
10% Cu-outside-CNTs	4.8	49.8	43.7	4.1	2.4	0	0
10% Cu-inside-CNTs	13.9	55.3	31.9	12.8	0	0	0
20% Cu-inside-CNTs	35.0	54.7	32.5	11.9	0.8	0.1	0
40% Cu-inside-CNTs	10.6	52.4	37.4	8.3	1.9	0	0

Notes: Reaction conditions: 493 K; 3 MPa; 2 h; catalysts weight = 0.5 g; $F(H_2) =$ 80 ml/min; $F(MA) =$ 0.9 g/h; MA = methyl acetate; EA = ethyl acetate; MeOH = methanol; EtOH = ethanol.

more reducible than outside, resulting to the same Cu content but different active pure Cu sites of these two catalysts for MA hydrogenation. Ethyl acetate (EA) was from the secondary reaction of the ethanol product, via its trans-esterification with methyl acetate, consequently lowering the apparent ethanol selectivity. Different Cu loading content inside CNTs channels can obviously effects the conversion speed of methyl acetate, as shown in Table I. Increasing the Cu content inside CNTs channels from 10 wt% to 20 wt% effectively improve the MA conversion from 13.9% to 35.0%, which should only be attributed to the increase of active Cu content inside CNTs channels. However, when the Cu content reached up to 40 wt%, the catalyst activity of Cu-inside-CNTs does not increase as we expected. Conversely, it decreases sharply. It seems that the Cu clusters size of this 40 wt% Cu-inside-CNTs, about 22.3 nm similar to the aperture of CNTs channels, is too bigger that most of the CNTs channels are blocked, inhibiting the access of reactants into CNTs channels and then decreasing the efficiency of this catalysts.

4. CONCLUSIONS

In this work, the Cu nanoparticles loaded inside or outside CNTs were prepared by a simple wet chemistry method. Methyl acetate hydrogenation was selected as the application to investigate the confinement effect of the copper clusters within the channels of CNTs. Reaction results indicated that the catalytic activity of Cu-inside-CNTs catalyst was significantly higher than that of Cu-outside-CNTs. Furthermore, the effects of Cu content inside CNTs channels on catalyst activity had also investigated, in which 20 wt% Cu-inside-CNTs showed the highest catalytic activity.

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