Catalysis of Nano Particles Confined inside the Channels of CNTs

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Introduction

Carbon nanotubes (CNTs) have well defined hollow interiors and exhibit unusual mechanical and thermal stability as well as electron conductivity. This opens intriguing possibilities to introduce other matter into the cavities, which may lead to nanocomposite materials with interesting properties or behavior different from the bulk. For example, CNTs have been studied as supports dispersing transition metals for hydrogen involving reactions such as hydrogenation and dehydrogenation of hydrocarbons, and fuel cell electrode reactions [1-4]. In addition, the well-defined tubular structure of CNTs enables the encapsulation of catalysts and chemical reactions in the interior channels. The presentation will be focused on the application of nano-related science and technology in the fields of catalysis, with an emphasis on the electron properties of the confined systems and the synergetic confinement effects between the encapsulated metallic nanoparticle and carbon nanotubes.

Materials and Methods

The preparation procedures have been reported previously for the CNT-encapsulated metal and metal oxide particles dispersed on the CNT outer walls [5]. Briefly, raw CNTs were first opened up and cut into segments of 200~500 nm long by refluxing in concentrated HNO_3 (68 wt.%) at 140 °C for 14 h. The resulting CNTs have an inner and outer diameter of 4~8 and 10~20 nm, respectively. Aqueous solutions with certain concentration of the target components were introduced into the CNT channels utilizing the capillary forces of CNTs aided by ultrasonication and stirring. The following drying and heat treatment at 350 °C in Ar resulted in CNT-encapsulated nano-particles. Before catalysis test, the catalyst was normally activated by reduction in a pure H_2 stream at 350 °C for 5 h (standard activation conditions unless otherwise stated). The activated catalysts with the nano-particles outside the tubes were prepared by impregnating CNTs with closed caps in the certain aqueous solution, followed by the same drying, heat-treatment and reduction procedures. The catalysis test were carried out in a fixed bed reactor under the conditions described in our previous publications.

Results and Discussion

Two unique properties concerning the redox and catalysis of the CNT-encapsulated metals and metal oxides will be reported [6-8]. The auto-reduction of the encapsulated Fe_2O_3 is significantly facilitated inside CNTs with respect to the outside nanoparticles, and it becomes more facile with decreasing CNT channel diameter as evidenced by temperature programmed reaction, in situ XRD and Raman spectroscopy. The oxidation of encapsulated metallic Fe nanoparticles on the other hand is retarded in comparison to that of the outside Fe particles as shown by in situ XRD and gravimetrical measurements with an online microbalance. A striking enhancement of the catalytic activity of Rh particles confined inside nanotubes for the conversion of CO and H_2 to ethanol has been found. The overall formation rate of ethanol inside nanotubes exceeds that on the outside of the nanotubes by more than an order of magnitude, although the latter is much better accessible. We attribute these unique behaviors' of transition metal nanoparticles inside CNTs to a particular electronic interaction of the encapsulates with the interior CNT surface.

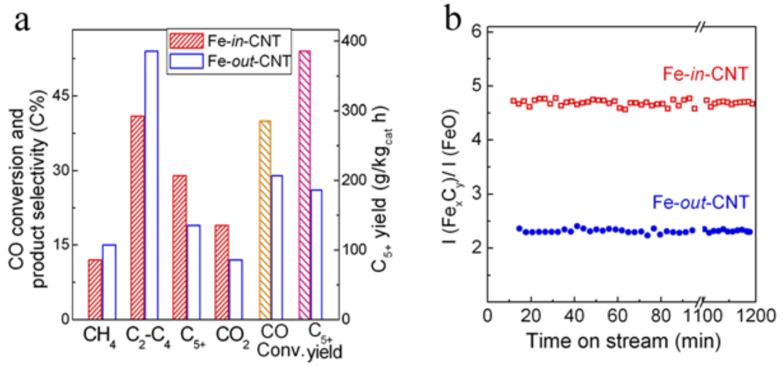

Figure 1. (a) FTS activity of Fe-*in*-CNT and Fe-*out*-CNT at 280 °C and 50 bar; (b) comparison of the iron carbide/iron oxide ratio at 9 bar [6].

Significance

Our findings indicate that CNT-confined metal nanoparticles exhibit an enhanced activity in syngas conversion due to the improved reducibility with respect to the metal particles dispersed on the CNT exterior surfaces. This provides a novel approach to tune the catalytic behavior of metal catalysts for many reactions, which are sensitive to the electronic state of the active components, e.g. syngas conversion, hydrogenation/dehydrogenation of hydrocarbons, ammonia synthesis and catalysis in fuel cell. These findings will also stimulate further experimental and theoretical studies on the CNT confinement effect.

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