

Synthesis and Catalytic Application of Ni-Supported Carbon Nanotubes for *n*-Heptane Cracking

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Abstract—Carbon nanotubes were synthesized by chemical vapor deposition and subsequently purified and oxidized by repeated treatment with nitric acid. After acid treatment the walls of carbon nanotubes became thinner and the surface area increased. The Ni-supported carbon nanotubes prepared by impregnation were applied to the cracking of *n*-heptane to show an excellent activity. This indicates that the carbon nanotubes can serve as a good catalyst support with high dispersion of metallic components. The optimum Ni loading turned out to be about 5.2 mmol/g. The cracking product was found to contain mainly small hydrocarbons; thus the Ni-supported carbon nanotubes may be applied as a potential catalyst to the cracking of heavy hydrocarbons.

Key words: Carbon Nanotubes, Ni-Loaded Catalyst, Catalytic Application, *n*-Heptane, Cracking

INTRODUCTION

Kroto et al. [1985] developed the chemistry of fullerenes in the mid 1980s. These cage-like forms of carbon have been known to exhibit exceptional material properties. Since the first discovery of carbon nanotubes with fullerenes structure a decade ago [Iijima, 1991], many researchers have reported mechanical properties that exceed those of any previously existing materials. Theoretical and experimental results have shown extremely high elastic modulus and also strengths 10 to 100 times higher than steel [Calvert, 1999; Thostenson, 2001]. They also possess superior thermal and electric properties. These exceptional properties of carbon nanotubes have been utilized for devices such as field-emission displays, scanning probe microscopy tips and micro-electronic devices [Iijima et al., 1996; Treacy et al., 1996]. With the large-scale synthesis of carbon nanotubes, attention is now being directed to their potential application in various fields of materials [Kibria et al., 2001; Lee et al., 2001].

Catalysis is a nanoscale phenomenon that has been the subject of research and development for many decades, but only recently become a nanoscale science of materials and chemistry involving more investigations on the molecular level. In the field of heterogeneous catalysis, various carbon materials have been used to disperse and stabilize metallic particles [Tans et al., 1997]. However, the carbon nanotubes, different from usual carbon materials, exhibit exceptional properties such as uniform pore diameter, high length to diameter ratio, ability of very high H₂ uptake [Dillon et al., 1997] and large specific surface area, and the hydrophobic or hydrophilic character of the surface can be controlled by chemical treatment or

modification [Fan et al., 1999]. These properties suggest an enormous potential of carbon nanotubes for application as novel materials for the catalyst carrier.

For large-scale synthesis of carbon nanotubes, the as-prepared carbon nanotubes usually contain a large amount of impurities such as metal particles, amorphous carbon and multi-shell carbon nanocapsules. These impurities make it difficult to characterize carbon nanotubes in some detail, so it is very important to purify the carbon nanotubes in order to prepare good catalysts.

In this study, we synthesized carbon nanotubes by chemical vapor deposition, purified them by different methods, characterized their properties by TEM, XRD, BET, and examined their catalytic activity for *n*-heptane cracking.

EXPERIMENTAL

1. Preparation of Carbon Nanotubes and Ni-Supported Carbon Catalyst

The multi-walled carbon nanotubes were obtained by chemical vapor deposition of acetylene over Co-La catalyst at 973 K following the procedure reported previously [Zhang et al., 1999]. A few grams of carbon nanotubes were synthesized per batch in a small reactor. The main impurities coexistent with multi-walled carbon nanotubes were metal particles and amorphous carbon. In order to remove these impurities, the as-synthesized carbon nanotubes were first suspended in concentrated HNO₃ solution with stirring and refluxing at 333 K for several hours. After filtering, washing and drying, the treatment with nitric acid was repeated twice for surface oxidation of carbon nanotubes. Subsequently, the dried oxidized carbon nanotubes were impregnated with Ni(NO₃)₂·6H₂O dissolved in alcohol with stirring for 5 h, dried at 323 K for 15 h and heated in vacuum at 409 K for 2 h. Finally, the samples were oxidized and reduced. Other samples supported on different materials were obtained by the same method.

2. Characterization

The morphology of carbon nanotubes was observed with the JEM-

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200 CX transmission electronic microscope (TEM). The specimens for TEM were first milled in an agate bowl, then dispersed in aqueous solution containing 50% alcohol by ultrasonic treatment and dropped onto holey grids. The specific surface area was measured by nitrogen physisorption at liquid nitrogen temperature using a Micromeritics ASAP 2000 apparatus. XRD patterns were taken with a D/MAX X-ray diffraction instrument by using $\text{CuK}\alpha$ in the voltage of 40 kV and current of 50 mA.

3. Activity for *n*-Heptane Cracking

Catalytic reaction of *n*-heptane cracking was carried out by using a tubular 4 mm ID flow micro-reactor at 723 K. 0.1 g of the sample with a particle size of 20/40 mesh was put into the U-shape quartz tube. Before reaction, the catalyst was pretreated by heating in nitrogen flow at a constant rate of 10 K/min to 773 K and held at this temperature for 2 h. After activation, the reactor was cooled to 723 K and held at this temperature. Then, the mixture of H_2 saturated with *n*-heptane at 298 K was passed through the reactor at a constant flow rate of 15 ml/min. Reactants and cracking products were analyzed by on-line gas chromatography with FID detector and Proparak QS column.

RESULTS AND DISCUSSION

1. Purification Treatment and Characterization of Carbon Nanotube

The TEM image of the as-synthesized carbon nanotubes is shown in Fig. 1. They are multi-walled carbon nanotubes and have outer diameter of about 20 nm, internal diameter of about 6.4 nm and length

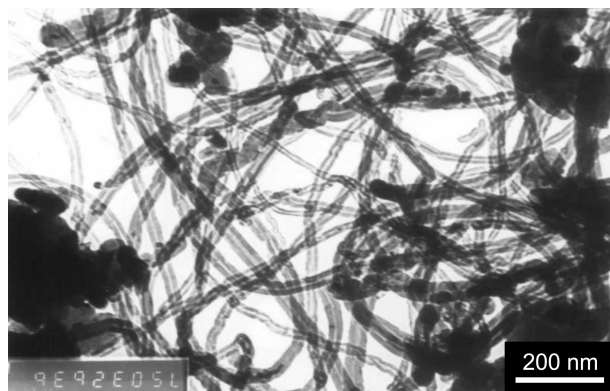


Fig. 1. TEM image of the as-synthesized carbon nanotubes.

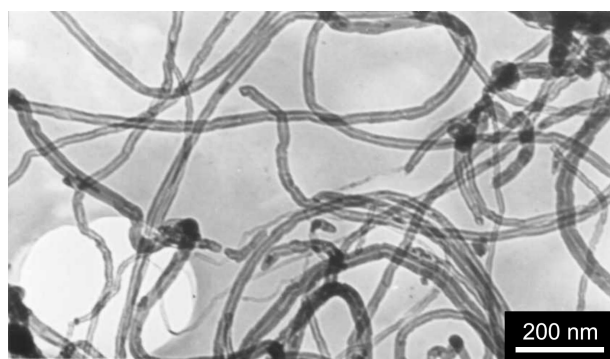


Fig. 2. TEM image of the purified carbon nanotubes.

Table 1. Diameters of carbon nanotubes before and after purification

	Outer diameter (nm)	Internal diameter (nm)	Wall thickness (nm)
Before purification	20.0	6.4	6.8
After purification	16.5	6.4	5.1

of several tens of μm . From Fig. 1, we notice that there are many dark metal agglomerates around carbon nanotubes. These dark particles contain impurities such as metal particles, amorphous carbon and bulky nanofibers. The purified carbon nanotubes after treatment with acid are shown in Fig. 2. It is observed that those dark metal agglomerates have been removed and the walls of carbon nanotubes become thinner than before. Table 1 presents the diameters of carbon nanotubes before and after purification. From these data it is noticed that the internal diameter remained unchanged while the outer diameter decreased due to the etching that occurred in the exterior of nanotubes. The wall thickness of carbon nanotubes decreased from 6.8 nm to 5.1 nm. We also find that the bulky nanofibers were not easily removed by this treatment.

In order to remove metal impurities we repeated the procedure of acid treatment until the weight loss became negligible. Concerning the thinner walls of carbon nanotube, it is considered that this is due to the oxidation of the surface of carbon nanotubes during the removal of the impurities by acid treatment. The oxidized carbon nanotubes were favored to support active metals. According to Ang et al. [2000] the groups of OH, O and COOH created on the surface of carbon nanotubes during the oxidation bring about strong interaction with the supported metals, which is favored for the dispersion of metal particles on the surface of nanotube carrier.

The specific surface area of as-prepared nanotubes was about $100 \text{ m}^2/\text{g}$, but the value was increased to about $120 \text{ m}^2/\text{g}$ after treatment with acid. This indicates that the top of some of the nanotubes was opened during this procedure. It has been reported that the top of carbon nanotubes is more easily opened than the body of tubes because the top consists of pentagon and heptagon, and thus the specific surface area increased after oxidation treatment [Tsang

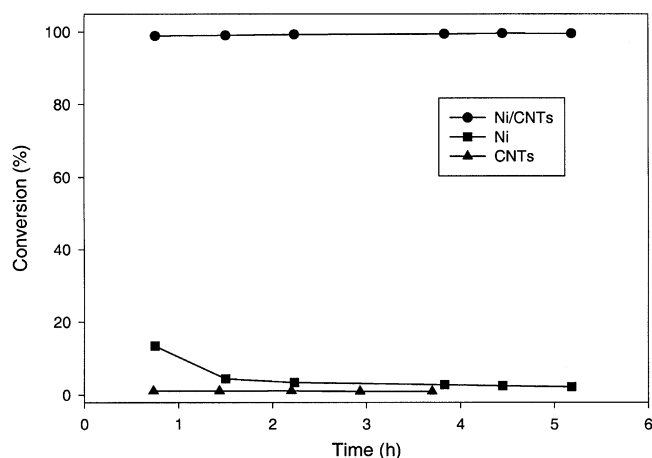


Fig. 3. Catalytic activities of three different materials for the cracking of *n*-heptane.

et al., 1993]. Therefore, one may speculate that etching of the outer surface and opening of the top of some nanotubes occurred at the same time. The XRD pattern shows one sharp peak at $2\theta=26.06$, indicating that the carbon nanotubes have a uniform pore size and graphited-wall structure and there are no impurities.

2. Activity of Ni-Supported Carbon Nanotubes for *n*-Heptane Cracking

In Fig. 3, catalytic activities of the Ni-supported carbon nanotubes (Ni/CNTs), the unsupported carbon nanotubes (CNTs) and the nickel catalyst are compared for the cracking of *n*-heptane. It is observed that neither the carbon nanotubes nor nickel alone exhibits any catalytic activity. When nickel was supported on carbon nanotubes, however, the catalyst Ni/CNTs showed a very high conversion of *n*-heptane.

Obviously, the carbon nanotube as a carrier plays a crucial role in the catalytic reaction with major contributions as follows: the high dispersion of nickel onto the carbon nanotubes having a uniform pore size, the increased acid sites on the surface of carbon nanotubes during refluxing with nitric acid, and the hydrogen spillover function of carbon nanotubes with high ability of H_2 uptake in the hydro-cracking reaction. The TEM image of Ni-supported carbon nanotubes catalyst is presented in Fig. 4, which shows that most of nickel particles are well-dispersed to form fine particles of diameter less than 20 nm. This feature must have contributed to the enhancement of the catalytic activity in the cracking reaction.

The effect of the amount of nickel loading on the activity of Ni/CNTs was examined as described in Table 2. The optimum amount of Ni loading in carbon nanotubes is about 5.2 mmol/g. This catalyst can maintain the high conversion of 99% for 15 h without show-

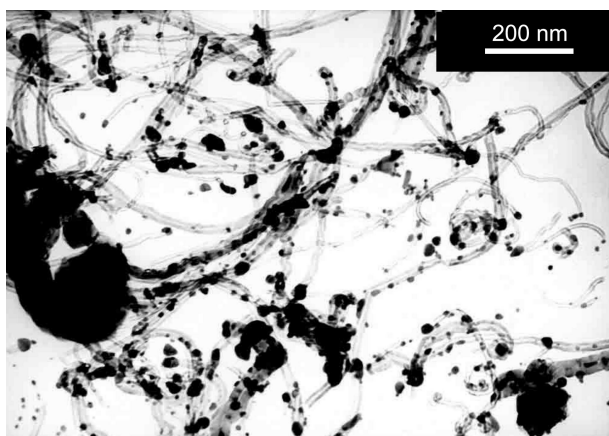


Fig. 4. TEM image of the Ni-supported carbon nanotubes.

Table 2. Effect of the amount of nickel loading on the activity and decline time

Samples	Ni-loading (mmol/g)	Conversion of <i>n</i> -heptane (%)	Decline time (h)
1	1.718	3	0
2	3.436	80	0
3	5.155	99	15
4	6.873	99	11
5	13.746	99	7

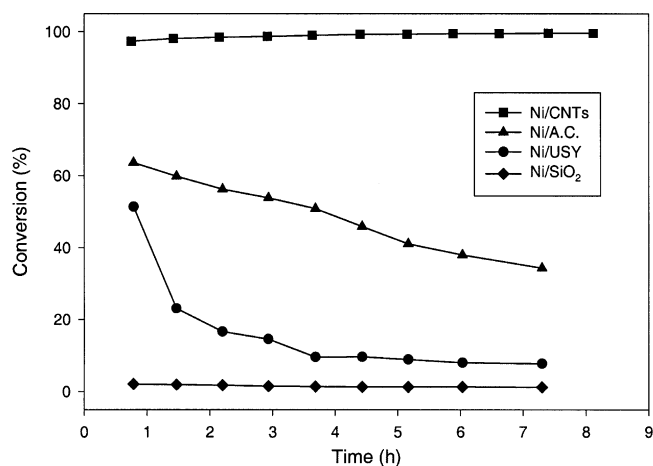


Fig. 5. Comparison of activities of Ni catalysts supported on different carriers in *n*-heptane cracking.

Table 3. Selectivities to individual products in the cracking reaction of *n*-heptane

Products	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₆ H ₁₄	Reaction time
Selectivity (%)	62.5	5.5	3.0	3.6	25.3	40 min
Selectivity (%)	63.0	7.6	7.3	0.9	13.0	150 min

ing any tendency of deactivation. If the amount of nickel loading is further increased, the cracking activity is maintained but the decline time is decreased rather rapidly because the coke deposit increases on the catalyst surface with the increase of nickel loading.

3. Role of Carbon Nanotubes in Cracking Reaction

The activity of the Ni-supported carbon nanotubes is compared with that of Ni-supported on different materials as shown in Fig. 5. While the Ni/SiO₂ catalyst showed no catalytic activity, the Ni/USY catalyst exhibited a good initial activity but the activity decreased rather rapidly. The Ni/A.C. catalyst showed a gradual decline in its activity from a conversion of 60% to 40%. Only the Ni/CNTs catalyst revealed a remarkable activity with nearly 100% conversion, which was maintained for more than 8 h without showing any tendency of deactivation.

The selectivities to individual cracking products at two different reaction times are shown in Table 3. Clearly, the main product is methane. It is also noticed that selectivities to larger molecules tended to decrease as the reaction proceeded, indicating that larger molecules were continuously cracked to low carbon molecules.

It has been a bewildering question whether the carbon in carbon nanotubes takes part in the cracking reaction in the presence of activated metal. To confirm the role of carbon nanotubes in the cracking reaction, we conducted some test reactions in the presence of hydrogen only (in the absence of *n*-heptane) over Ni, Ni/CNTs and Ni/USY, respectively. According to the reaction results, cracking products were hardly observed over these catalysts. This indicates that the resulting cracking products are formed by the cracking of *n*-heptane rather than by the decomposition of carbon nanotubes.

CONCLUSIONS

After purification and oxidation, the multi-walled carbon nano-

tubes were found to have thinner walls and an increased surface area. When impregnated with nickel, the Ni-supported carbon nanotubes exhibited a remarkable activity for the cracking of *n*-heptane with an optimal loading of about 5.2 mmol/g. The high activity may be attributed to the high dispersion of nickel on the carbon nanotubes. This indicates that the carbon nanotubes can be used as a good carrier for catalysts. Since the cracking products consist mainly of small hydrocarbons, it is expected that Ni-supported carbon nanotubes may possess a remarkable ability for the cracking of heavy hydrocarbons.

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