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Shunsuke Kurasawa [a], Shinji Iwamoto [a] & Masashi Inoue [a]

[a] Graduate School of Engineering, Kyoto University, Yoshida, Kyoto, 606-8501, Japan

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SYNTHESIS OF CARBON NANOTUBES BY THE CATALYTIC DECOMPOSITION OF METHANE ON Ni-BASED CATALYSTS

Shunsuke Kurasawa, Shinji Iwamoto, and Masashi Inoue
Graduate School of Engineering, Kyoto University, Yoshida, Kyoto, 606-8501, Japan

Catalytic decomposition of methane into carbon and hydrogen was examined on Ni-based catalysts. The Ni catalyst supported on zirconia that was synthesized by the glycothermal method showed the highest carbon yield. TEM observation revealed that multi-walled carbon nanotubes with an average diameter of ~30 nm were formed on this catalyst. Effects of the modification of the Ni/zirconia catalyst with other metal elements were also examined. The products formed on the Ni-Cu catalysts contained carbon filaments with the graphite sheets oriented at a certain angle with respect to the growth axis of the filament. The carbon nanotubes formed on the Ni-Co, Ni-Fe and Ni-Mo catalysts had the narrow distributions of tube diameter as compared with those formed on the Ni catalysts. Although the Ni-Mn catalyst exhibited a very low yield of carbon nanotubes, they had smaller populations of bends than the carbon nanotubes formed on the other Ni-based catalysts.

Keywords: carbon nanotubes; methane; Ni; zirconia; multi-walled; glycothermal method

INTRODUCTION

Since the discovery of the carbon nanotubes in 1991 [1], they have attracted much attention because of their electric properties and mechanical strength. There have been many researches about synthetic methods [2] and potential applications to electron field emitter, advanced composites and so on. Among the synthetic methods such as catalytic decomposition of hydrocarbon on metal particle, laser ablation and arc discharge method, catalytic decomposition of methane seems to be efficient for the large-scale and low-cost synthesis because methane is extremely abundant. Although there have been many researches about the catalytic synthesis of carbon nanotubes using alumina, silica and zeolite

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as catalyst supports [2,3], catalysts supported on zirconia were scarcely investigated. In this paper, we examined the catalytic decomposition of methane yielding multi-walled carbon nanotubes using zirconia as a catalyst support and the synthesis of carbon nanotubes with various diameters is described.

EXPERIMENTAL

Catalyst Preparation

Zirconia (150 m^2/g surface area) was prepared by the glycothermal (GT) method [4] and used as a catalyst support. Alumina (JRC-ALO-3, 123 m^2/g surface area), zirconia (JRC-ZRO-1, 15.1 m^2/g surface area), titania (JRC-TIO-4, 50 m^2/g surface area) and silica (Kieselgel 60, Merck, 435 m^2/g surface area) were also used as catalyst supports.

Catalysts were prepared by the impregnation method using an aqueous solution of appropriate metal salts (nickel nitrate, cupric formate, cobalt nitrate, iron nitrate, ammonium molybdate and manganese chloride) with the total metal content of 10 wt%, and calcined at 400°C for 30 min before use.

Synthesis of Carbon Nanotubes

The reactions for the synthesis of carbon nanotubes were carried out in a thermogravimetric apparatus (RIGAKU, TAS8110). The catalysts (20 mg) without pre-reduction was heated in an argon flow (10 ml/min) to the reaction temperature, and the gas flow was replaced with a methane stream (40 ml/min). The weight gain due to the carbon formation was monitored against the reaction time, and the reaction was continued until the weight gain ceased. The reaction rate was calculated from the initial slope of the weight gain-vs.-time curve, and the carbon yield was directly obtained by the weight gain at the end of the reaction.

Characterization

The carbons formed by the reaction were observed on a transmission electron microscope (TEM; Hitachi H-800) operated at 200 kV. Raman spectra were recorded on a Jobin-Yvon T64000 at room temperature using a 514.5 nm line of an argon laser. The X-ray powder diffraction patterns were recorded on a Shimadzu XD-D1 diffractometer using CuKα radiation.

RESULTS AND DISCUSSION

Effects of the Catalyst Supports

Among the Ni catalysts supported on various carriers, the Ni catalyst supported on zirconia (GT) showed the highest carbon yield (3.47 g/g-cat) (Fig. 1). TEM observation revealed that multi-walled carbon nanotubes with an average diameter of ~30 nm were formed on this catalyst, and sinuousness were characteristic of these carbon nanotubes. As can be seen in Figure 2, no other type of carbon products was observed by TEM. Carbon nanotubes were also formed on the Ni catalysts supported on the commercial alumina, silica and zirconia although the yields were low. Encapsulating carbons were formed on the Ni/titania catalyst. XRD pattern of the product formed on Ni/zirconia(GT) exhibited a strong peak at $2\theta = 26.0$ deg, which was assigned to CNTs, and indicated that NiO was reduced to Ni metal. Thermal oxidation of carbon formed on these catalysts was examined by TG-DTA. Weight loss at 400–500°C, due to the combustion of amorphous carbon, was 1.9 wt% for carbon formed on Ni/zirconia (GT), although 5.4 wt% and 32 wt% of weight loss were observed for carbon formed on Ni/silica and Ni/zirconia, respectively.

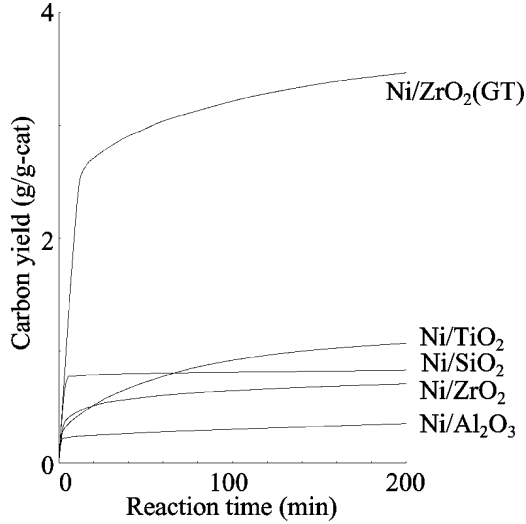

FIGURE 1 Weight gain due to carbon formation on 10 wt% Ni catalysts at 650°C.

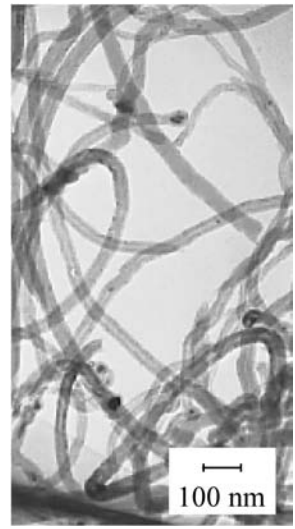

FIGURE 2 TEM image of carbon nanotubes formed on 10 wt% Ni/ZrO_2(GT).

Bimetallic Catalysts

Effects of the modification of the Ni/zirconia (GT) catalyst with other metal elements were examined. For the Ni-Cu catalysts, the reaction rate decreased with increasing the Cu content. However, the lifetime of the catalyst was prolonged, and as a consequence, the highest carbon yield (6.89 g/g-cat) was attained on the 8 wt% Ni-2 wt% Cu catalyst. The products formed on the Ni-Cu catalysts were composed of carbon fibers with 50–100 nm diameters together with carbon filaments with the graphite sheets oriented at a certain angle with respect to the growth axis of the filament. The relative intensity ratio (I_D/I_G) of the D band to the G band in Raman spectra increased with the addition of Cu (Fig. 3). The XRD patterns of the catalysts (Fig. 4) revealed that the peaks assigned to Ni metal shifted to the lower angle side, indicating the formation of Ni-Cu alloy. This seems to be the cause of the structural changes of carbon fibers.

The Ni-Co, Ni-Fe and Ni-Mo catalysts yielded carbon nanotubes with smaller diameters and narrower distributions as compared with the Ni catalysts (Table 1). Carbon nanotubes formed on the Ni-Fe catalysts had the morphology similar to that of the carbon nanotubes formed on the Ni catalyst and showed low I_D/I_G ratio, whereas those formed on the Ni-Co and Ni-Mo catalysts were sinuous and showed high I_D/I_G ratios. The Ni-Mn catalyst exhibited a very low yield of carbon nanotubes, but they had smaller population of bends than the nanotubes formed on the other

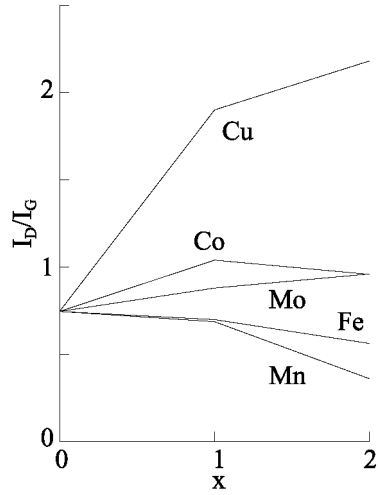

FIGURE 3 The I_D/I_G ratio of carbon formed on $(10-x)$ wt% Ni-x wt% metal catalysts.

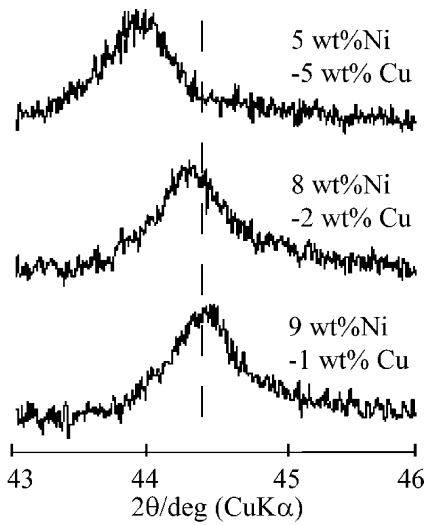

FIGURE 4 XRD patterns of the Ni-Cu catalysts redused at 650°C: dotted line is the peak positon of Ni.

TABLE 1 Characteristics of NiO and Carbon Nanotubes Formed at 650°C

	10 wt% Ni	9 wt% Ni −1 wt% Co	9 wt% Ni −1 wt% Fe	9 wt% Ni −1 wt% Mo
Average outer diameter (nm)	32	24	29	23
Average inner diameter (nm)	8.5	5.3	7.0	6.2
Average wall thickness (nm)	12	9.4	11	8.4
Crystallite size of NiO* (nm)	31	21	20	20

*calculated by Scherrer's equation.

Ni-based catalysts. This result was in good agreement with the low I_D/I_G ratio of the product.

CONCLUSION

Ni catalyst supported on zirconia prepared by the glycothermal method showed high activity for carbon nanotube synthesis. Carbon nanotubes formed on this catalyst were multi-walled with an average diameter of 30 nm. Carbon fibers formed on the Ni-Cu catalysts possessed large diameters as compared with the pure Ni catalyst and showed the low degree of graphitization, which seems to be related with the formation of Ni-Cu alloys. Ni-Co and Ni-Mo catalysts yielded carbon nanotubes with small diameters. Carbon nanotubes formed on the Ni-Mn catalyst had smaller populations of the bends and showed high crystallinity.

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