Investigation on Formation of Thin Carbon Nanofibers over Bimetallic Ni catalysts Non-supported and Supported on CB

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INTRODUCTION

In order to obtain uniformly thin CNFs through catalytic methods, metals or their alloys such as Ni, Fe, Co, Cu, Mo, etc. are often used in supported form on Al_2O_3, SiO_2, TiO_2, zeolite, etc [1-4]. Such metal oxides play an important role in improvement of catalytic performance for CNF synthesis. However, burdensome purification of the supports under harsh conditions is one of the major factors in CNF costs [2].

From this point of view, CB can be a good candidate as a catalyst support for CNF synthesis, because its large surface area and nano-scaled particles size not only enable high catalyst dispersion, but also can be used directly for several applications, as CB is a good conductive filler [5]. Recently, our group succeeded in the synthesis of thin fish-bone carbon nanofiber (CNF) from ethylene with high yield using CB supported Ni-Fe catalysts, and confirmed that particular CBs were superb as a support for CNF synthesis [6]. Iron shows little activity to CNF growth from ethylene [6, 7], whereas particular compositions of Ni-Fe on CB produced effectively thin herring-bone fibers of the diameters below 50 nm from ethylene [6]. Further, fine particles of catalyst, which was prepared through supporting the precursor on CB and successive combustion of the CB (CB-free catalyst), were found to exhibit a high yield of thin CNF through controlling the preparation of catalyst and conditions of the synthesis [8].

In this study, we examined the catalytic performance of various bimetallic Ni-alloy catalysts supported on CB in terms of preparation of CNFs, and investigated major factors to control the diameter and structure of CNF. CB-free catalysts (supporting and successive combustion of CB) are under examination in the synthesis of CNF.

EXPERIMENTAL

Catalysts in this were prepared as follows. Prescribed amounts of nickel nitrate and iron nitrate (or hexaammonium heptamolybdate) were dissolved in ethanol or deionized water, and then CB (Mitsubish CB #3050B: 40 nm of a mean particles size and 48 m^2/g of BET surface area, Mitsubish Chemical, Inc., Japan) was added to the solution. After

evaporation, the resulted powder was dried in a vacuum oven at 105°C overnight and stored. Combustion of CB was optimized through the TG/DTA analysis.

CNFs were prepared in a quartz flow reactor (10 cm × 45 cm) heated by a conventional horizontal tube furnace. The gas flows to the reactor are precisely monitored and regulated by MKS mass flow controllers. Powdered catalyst grains (110 ~ 130 mg) were placed in an alumina boat at the center of the reactor tube in the furnace. After reduction of the catalyst in a 20% H_2/He mixture at prescribed temperature, helium was flushed for 30 min before introduction of 200 ml/min of ethylene/hydrogen mixture over the catalyst. The total amount of carbon deposited during the time on stream was determined gravimetrically after cooling to ambient temperature.

The nanostructure and morphology of the nanofibers were observed under scanning electron microscope (JSM-6320F, JEOL) and a high resolution transmission electron microscope (JEM-100CX, JEOL).

RESULTS

The production of CNFs from ethylene/hydrogen mixture (4:1 v/v) was examined over a series of Ni-Fe and Ni-Mo catalysts in various compositions on the CB (Fig. 1). In this paper, the catalytic activity is presented as the weight of produced CNFs per the weight of alloys contained the supported catalysts, for example, the catalytic activity of 100 means the product contains 100 mg of CB, 5 mg of alloy, and 500 mg of CNFs. Ni-Fe and Ni-Mo catalysts on the CB showed a high activity (80 ~ 110) at low temperature or 480°C for 1 h. The catalytic activity of Ni-Mo catalyst for CNF growth decreased gradually as Mo content increased up to Ni-Mo (6:4 wt/wt), where the activity probably relates to Ni contents. Its behaviour differed from Ni-Fe catalysts on the CB which shows little change in the amount of carbon growth until sharp decrease at the composition of Ni-Fe (5:5 wt/wt).

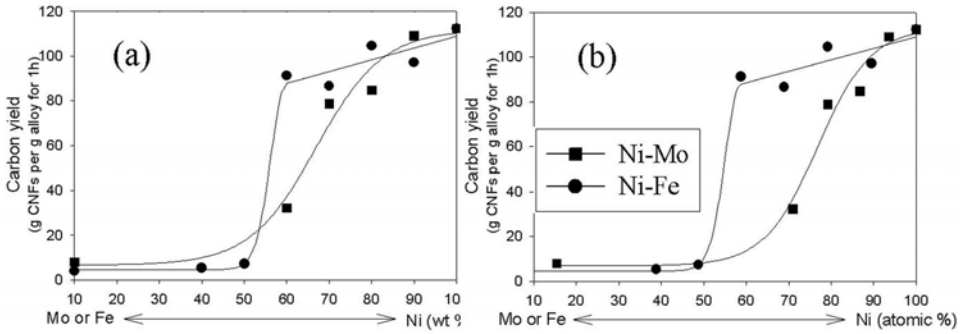

Figure 1. Catalytic activity of carbon nanofiber synthesis from ethylene/hydrogen (4:1) for 1h depending on the compositions of Ni-Mo on the CB comparing to those of Ni-Fe on the CB: (a) the metal composition is weight ratio; and (b) atomic (molar) ratio.

Figure 2 illustrates SEM features of CNFs which were produced from ethylene/hydrogen mixture (4:1 v/v) at 480°C over CB-supported nickel and various Ni-Fe catalysts. A particular alloy of Fe-Ni (1:9 wt/wt) or Fe-Ni (2:8 wt/wt) supported on the CB produced fibers of about 10~30 nm diameter under the same conditions where the thicker fibers of average 150 nm diameter were synthesized over Ni catalyst on the CB. However, a further addition of iron into Fe-Ni

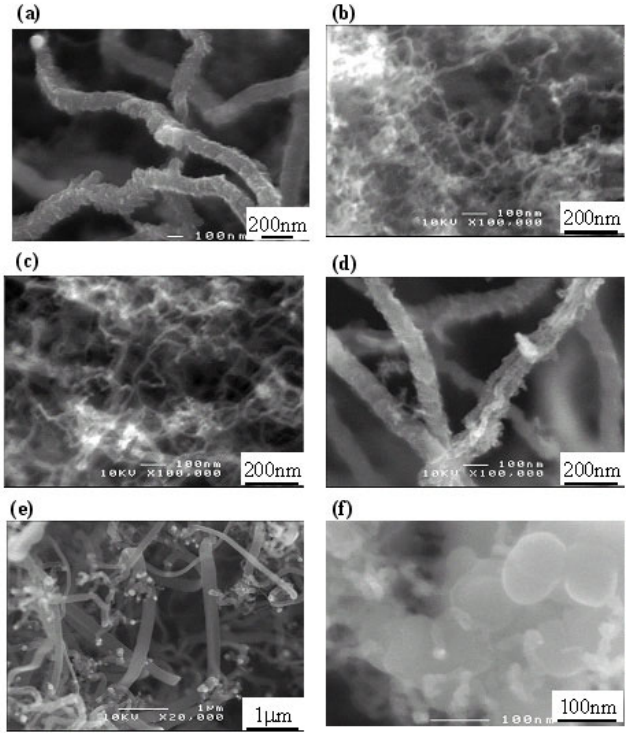

Figure 2. SEM images of products from ethylene/H2 (4:1) at 480oC for 1 h using CB-supported Fe-Ni, of which metal composition is: (a) Ni, (b) Ni-Fe (9:1), (c) Ni-Fe (8:2), (d) Ni-Fe (7:3), (e) Ni-Fe (6:4), and (f) Ni-Fe (5:5).

(2:8 wt/wt) as an alloy resulted in increase of the diameter of produced CNFs. CB-supported Fe-Ni (3:7 wt/wt) produced mainly CNFs of about 120 nm diameter.

In Figure 3, the SEM photographs of CNF produced on Ni-Mo catalyst are shown according to the metal compositions. Ni-Mo (9:1 wt/wt) produced a mixture of thick and thin CNFs of ca. 120 nm and ca. 20 nm diameters. With addition of 20 % Mo, the distribution of the fibers' diameter became more uniform to around 80 nm. Ni-Mo (7:3 wt/wt) and (6:4 wt/wt) produced mainly thin CNFs below 30 nm diameter.

DISSCUSION

Thin CNFs with herring bone structure were prepared at high yield from ethylene/hydrogen mixture using both Ni-Fe and Ni-Mo catalyst dispersed on the CB. In Ni-Fe catalyst, Ni-Fe catalysts containing 10~20 wt% iron produced thin CNFs, whereas Ni-Mo catalysts generally produced thin CNFs regardless of the metal composition. Ni-Mo (8:2) produced relatively thick CNFs of ca. 80 nm but uniformly. In the catalytic activity according to the metal composition, Ni-Fe catalysts showed sharp decrease with small addition of iron to Ni-Fe (6:4) catalyst, differing from Ni-Mo catalyst. From the aspect, Mo is probably different from Fe as a secondary metal of catalyst for

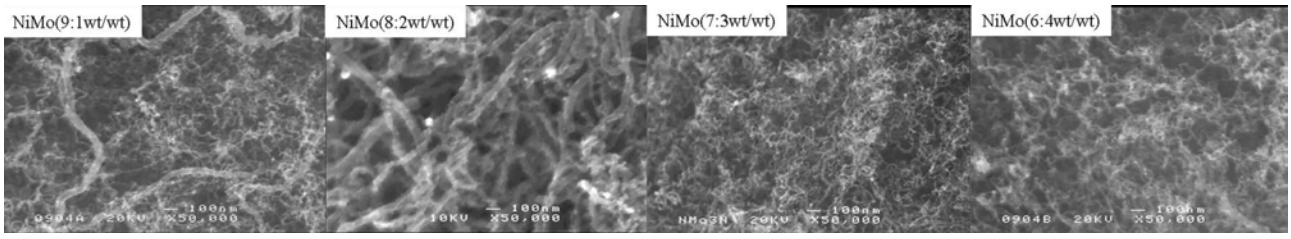

Figure 3. SEM images of products from ethylene/H2 (4:1) at 480oC for 1 h using CB-supported Ni-Fe, of which metal composition is: (a) Ni-Mo (9:1), (b) Ni-Mo (8:2), (c) Ni-Mo (7:3), and (d) Ni-Mo (6:4).

CNF synthesis. Both the sharp decrease of catalytic activity and the little relationship between Ni content and activity may mean that iron, which showed very low activity of CNF synthesis, functions as an active catalytic component when it is bimetallic in Ni-Fe catalysts. The XRD studies showed also that in Ni-Fe catalyst, the bimetallic effect appeared distinctly, where the characteristic peaks of NiO was not distinctly found in Ni-Fe (8:2) catalyst, which produced selectively thin CNFs [6]. However, the catalytic activity of

Ni-Mo catalyst certainly follows the Mo content in catalysts even though it is not linear. The diameter of CNFs became homogeneously thinner with more addition of Mo.

CONCLUSION

Thin CNFs could be obtained by using Ni alloy catalysts deposited on the CB. The CB as a catalyst support affect improvement of catalytic activity for CNF synthesis. The second metal Fe and Mo affected differently the fiber diameter, where the metal composition was important to obtain thin CNFs in high carbon yield. The difference in the structure of produced CNFs on the different Ni alloy system is now on the next research.

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