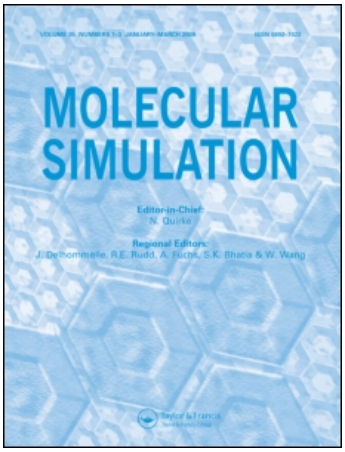

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Effect of Catalyst Preparation on Carbon Nanotube Growth

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A highly dispersed Ni–Fe/Al_2O_3 catalyst was prepared by glow discharge plasma treatment followed by thermal calcinations. With this plasma prepared catalyst, carbon nanotubes encapsulated with metal particle or filled with nickel nano-wire were produced. This is very different from the conventional catalyst, with which the normal multi-wall carbon nanotubes or nano-capsule chains were synthesized. The plasma preparation leads to a significant change in the interaction between metal and the support.

Keywords: Carbon nano-tubes; Plasma preparation; Thermal calcinations; Ni-based catalyst

INTRODUCTION

Since Iijima discovered carbon-nanotubes (CNTs) in 1991 [1], more and more attentions have been paid worldwide to this field because of the distinct properties of CNTs, such as its high mechanical strength [2]. Some applications including electron emission [3], hydrogen storage [4] and transistor [5] have been reported. CNTs were prepared by several methods including laser ablation [6], pyrolysis [7], arc discharge [8] and catalytic chemical vapor deposition [9–12]. Among all these methods, catalytic conversion can be used for the mass production of CNTs at relatively low cost [11,12]. The type and the morphology of CNTs were affected by many parameters that were involved in catalytic chemical vapor deposition. One of the important factors is the catalyst structure. In order to control the CNTs growth toward what we expect, it is very important to investigate the relationship between the CNTs growth and the catalyst structure (e.g. catalyst particle size [13], metal supported [12] and the type of support [10,14]). In this regard, Kukovitsky [13] studied the dependence of diameter of CNTs upon the size of nickel particles supported on amorphous carbon films. The relation between the diameter of CNTs and the size of initial catalytic particles is very complicated. The study showed [13] that the distribution of diameter of CNTs and the particle size distribution were similar when starting particles are immobile and the reaction temperature is set at 700°C. The universal Gaussian nanotube diameter distribution is observed in the temperature range of 700–800°C. In this case, the growth of CNTs followed the vapour–liquid–solid (VLS) growth mechanism. Kukovitsky did not find CNTs filled with diameters less than 10 nm in their experiments. Sinha [14] reported the formation of CNTs filled with metal particles and metal nano-wire over Co/aluminophoshate (AIPO-5) catalysts and metal free CNTs on Co/zeolite (Na-Y) catalyst. The difference between these two catalysts may be from the different metal-support interaction.

The catalyst prepared by plasmas has some typical advantages over the conventional catalyst. For examples, high dispersion of catalytic active species, ultra-fine catalyst particle and uniform particle size can be achieved using plasma preparation [15]. In this work, we prepared Ni–Fe/Al_2O_3 catalysts for CNTs production using plasma preparation and the conventional preparation. CNTs with different morphology were obtained. It confirms that the catalyst preparation has an important effect on CNTs formation.

EXPERIMENT

The conventional preparation and plasma preparation have been used to prepare the catalyst for

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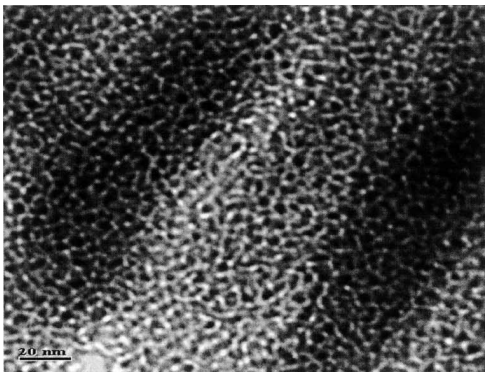

FIGURE 1 TEM image of the fresh Ni–Fe/Al_2O_3 (C).

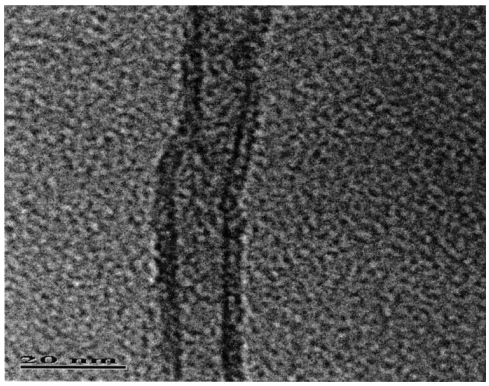

FIGURE 3 The carbon nano-tube produced on Ni–Fe/Al_2O_3 (C) catalyst.

the formation of CNTs. First, alumina was impregnated by a $Ni(NO_3)_2$ and $Fe(NO_3)_3$ aqueous solution for about 6 h. The precursors of the catalysts were then dried at 90°C for 16 h. The conventional Ni–Fe/Al_2O_3 catalyst was attained by calcining the obtained sample for another 6 h for 600°C (the catalyst is referred as Ni–Fe/Al_2O_3 (C)). For plasma preparation, the dried sample was treated by glow discharge plasma before further calcinations (the catalyst is referred as Ni–Fe/Al_2O_3 (P)). Both catalysts were reduced in a flowing hydrogen for 1 h at 650°C with a flow rate of 50 cm^3/min before the catalytic reaction.

The formation of CNTs was carried out in an 8 mm i.d. quartz-tube fixed-bed reactor. Around 70 mg catalyst was placed into the reactor. After reduction using hydrogen, argon was used to purge the system. Then the feed gases, methane and argon, were introduced into the reactor when the temperature reached 750°C. The total flow rate of the feed gas was 80 ml min^{-1} with a CH_4/Ar feed ratio of 3/5. The reaction time was 15 min for each catalyst. The reactor was cooled down slowly to room temperature with the flowing argon after reaction.

The morphology of catalysts and CNTs were observed by transmission electron microscopy (TEM). The samples for TEM analyses were dispersed in ethanol solution with ultrasonic treatment for around 20 min and then transferred to a copper grid with a polymer membrane. All the analyses were carried out with a JEOL JEM-100CXII transmission electron microscope.

RESULTS AND DISCUSSION

Morphology of the Catalyst

Figures 1 and 2 showed the TEM images of the fresh Ni–Fe/Al_2O_3 (C) and Ni–Fe/Al_2O_3 (P) catalysts. Comparing Fig. 2 with Fig. 1, it can be seen that the active species (Ni) over Ni–Fe/Al_2O_3 (P) are highly dispersed on Al_2O_3 support and it is much better than that over Ni–Fe/Al_2O_3 (C). The size of the catalytically active species of Ni–Fe/Al_2O_3 (P) is mainly in the range of 4–10 nm. For the Ni–Fe/Al_2O_3 (C) catalyst, the catalyst particles are bigger and the catalytically active species are aggregated in

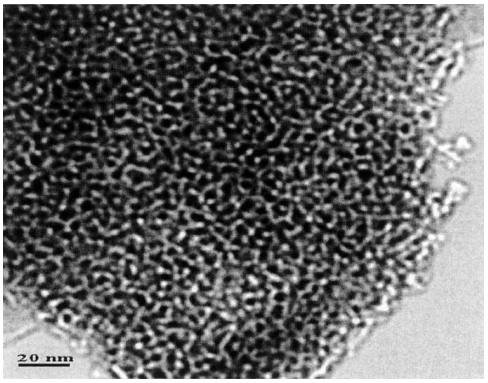

FIGURE 2 TEM image of the fresh Ni–Fe/Al_2O_3 (P).

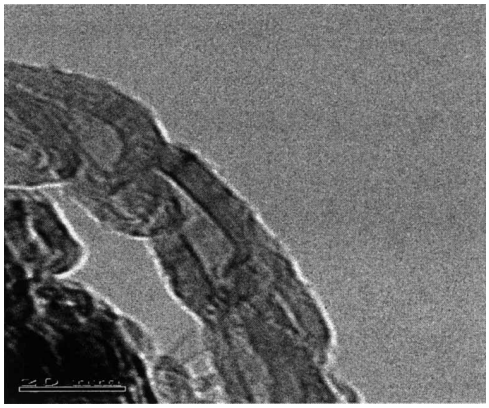

FIGURE 4 Carbon nano-chain produced on Ni–Fe/Al_2O_3 (C) catalyst.

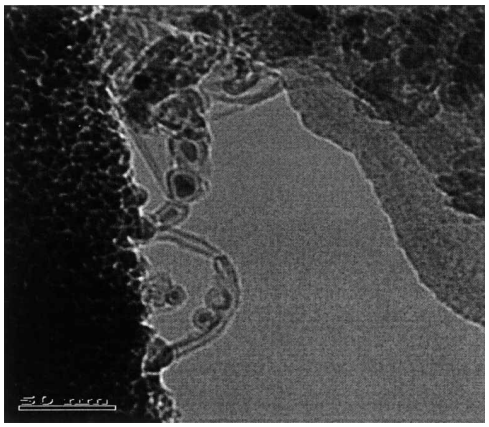

FIGURE 5 Carbon nano-tubes with encapsulated metal particle produced on Ni–Fe/Al_2O_3 (P) catalyst.

strips. The difference could be induced from the interaction between the catalyst powder and the excited atoms or molecules, radicals, especially, electrons within plasmas [15,16].

Morphology of the CNTs

Several typical TEM images of CNTs obtained on Ni–Fe/Al_2O_3 (C) were shown in Figs. 3 and 4. Figure 3 showed that the diameter of CNTs was about 10 nm. And there are no metal particles enclosed in CNTs. Some empty carbon nano-chains were also observed, as shown in Fig. 4.

Figures 5 and 6 present some typical TEM images of CNTs obtained over Ni–Fe/Al_2O_3(P). CNTs with encapsulated metal were observed. The enclosed metal presents as nano-particle or as nano-wire, as shown in Figs. 5 and 6.

The TEM images showed different CNTs can be synthesized on Ni–Fe/Al_2O_3(C) and Ni–Fe/Al_2O_3 (P). CNTs obtained on Ni–Fe/Al_2O_3(C) are metal free. Metal particles encapsulated inside the CNTs are observed with Ni–Fe/Al_2O_3(P). Even the nickel nano-wire as long as 70 nm was formed inside the CNTs obtained. It suggests that the catalyst prepared by plasmas may be suitable to produce the CNTs with encapsulated metal particle or nano-wire. Such CNTs could have a potential application in the field of nano-technology with their novel magnetic properties [14].

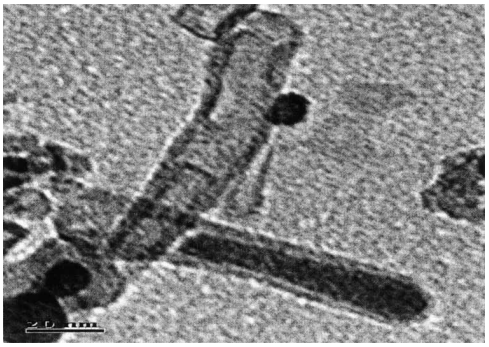

FIGURE 6 Carbon nano-tubes with encapsulated metal wire produced on Ni–Fe/Al_2O_3 (P) catalyst.

CONCLUSION

The present investigation confirms that the catalyst preparation has an important effect on the production of CNTs. The catalyst prepared by plasmas leads to a formation of CNTs with encapsulated metal. Even the metal nano-wire as long as 70 nm was formed inside the CNTs obtained. However, the catalyst prepared conventionally induces CNTs without such encapsulated metal. Therefore, the plasma preparation must induce some significant change in the interaction between metal active species and the support. Further investigation is being conducted for a better understanding.

Acknowledgements

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