

Effect of Addition of Ni metal catalyst onto the Co and Fe supported catalysts for the formation of carbon nanotubes

Nor Aziah Buang · Zaiton Abd. Majid ·
Yusran Sulaiman · Suhaila M. Sanip ·
Ahmad Fauzi Ismail

© Springer Science + Business Media, LLC 2006

Abstract Production of novel porous material is a major target in current material science research due to its wide applications. As carbon nanotube (CNTs) is a one dimensional hollow structure it is also one of the promising materials in applications ranging from electronics to hydrogen storage medium. Catalytic chemical vapor deposition (CCVD) is a method whereby CNTs can be produced in large amount. Thus, in this work, we have synthesized CNTs via pyrolysis of acetylene using various supported transition-metal catalysts in a fixed-bed reactor. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to investigate the CNTs structure. The structures of nanotubes formed by acetylene pyrolysis were dependent on the catalysts used. It was found that alumina supported Ni/Fe catalyst inhibited the formation of CNTs growth while alumina supported Ni/Co catalyst gave high density of CNTs. However, nanotubes grown over alumina supported Ni/Fe catalyst were less dense due to the deactivation of the catalyst at the early stage of the pyrolysis process.

Keywords Carbon nanotubes · Supported catalysts · SEM · TEM

Introduction

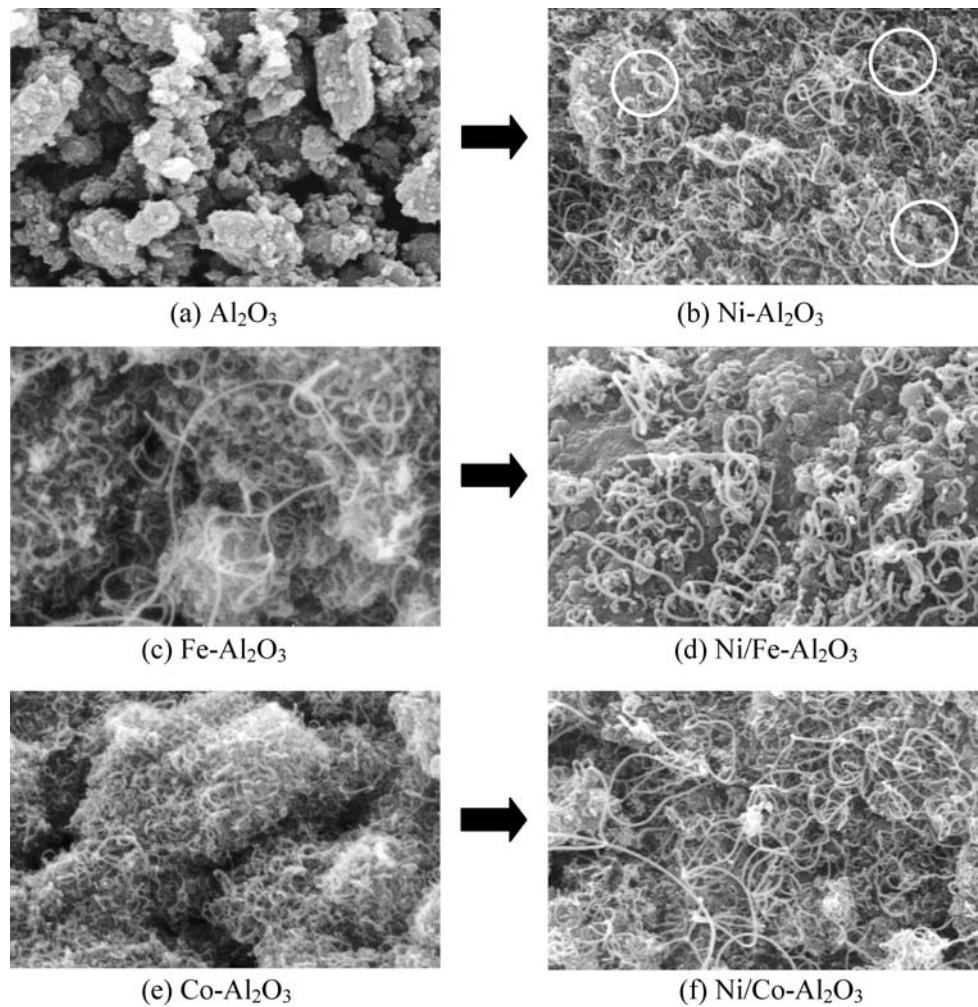
Carbon nanotubes (CNTs) are currently the focus of intense research in nanotechnology due to their unique properties and potential to impact broad areas of science and technology. Knowing its wide-ranging applications, a variety of synthesis methods have been explored. Catalytic Chemical Vapor Deposition (CCVD) has been chosen to be one of the promising methods for the synthesis of CNTs at low temperature and ambient pressure [1]. Controlled synthesis involving CCVD has been studied as an effective strategy to order or pattern CNTs on a variety of surfaces. Metal and mixture of metals supported on oxides have been found to be active as catalyst in CCVD methods [1, 2]. The role of the support materials in supported catalyst is to disperse the active phase, control the porous structure, prevent sintering, improve mechanical strength and assist catalysis.

Almost all of the supported catalyst mixtures were found to be active in the formation of different forms of CNTs. The quantity and quality of the CNTs produced over different supported catalyst were however, significantly different. Therefore, one of the active fields of research in the area of CNTs technology at present is synthesis, characterization and applications [3–5]. Several supports and transition metal/s combination have been investigated for their activity in the synthesis of CNTs under different experimental conditions [6, 7]. A wide variety of conditions have been used to condition the supported catalysts and subsequently grow CNTs. Therefore, a synthesis study on the combinations of mixed metal/s supported catalysts influences the formation CNTs was examined. In the present work, we describe the effect of monometallic and bimetallic supported catalyst on alumina towards the growth of the CNTs.

N.A. Buang (✉) · Z.A. Majid · Y. Sulaiman
Carbon Nanotube Research Group, Department of Chemistry,
Faculty of Science, Universiti Teknologi Malaysia, 81310,
Skudai, Johor, Malaysia
e-mail: noraziah@kimia.fs.utm.my

S.M. Sanip · A.F. Ismail
Carbon Nanotube Research Group, Membrane Research Unit,
Faculty of Chemical Engineering and Natural Resources,
Universiti Teknologi Malaysia, 81310, Skudai, Johor, Malaysia

Fig. 1 SEM Images of as-grown CNTs over alumina-supported catalysts (10,000 \times magnification)



Experimental

The catalysts used in this work were prepared using a wet impregnation method and the procedure is based on a previous report [8]. In this work, we used Ni, mixture of Ni-Co and Ni-Fe as catalysts instead of Co-Fe catalyst. The CVD growth of CNTs catalyzed by different catalysts was carried out using acetylene as carbon reactant. The procedure of the synthesis is described in detailed elsewhere [8]. Briefly, the catalysts were located at the center of the reactor furnace and acetylene (C_2H_2) and nitrogen (N_2) gases were introduced into the tube reactor simultaneously. The morphological structures of the products were examined by scanning electron microscope (SEM) and transmission electron microscope (TEM).

Results and discussion

Three metal species Co, Fe, and Ni were chosen in this work to explore the effect of different metal-support interactions upon the growth of CNTs. The as synthesized carbon deposit

obtained was black in colour. The SEM micrographs in Fig. 1 showed that the CNTs grown over the alumina supported catalysts were mostly in the form of tubular CNTs which grew in bundles.

The transformation of the CNTs structures were clearly seen from the SEM micrograph in Fig. 1(a)–1(f), when Ni was introduced onto the Fe-Al₂O₃ and Co-Al₂O₃ catalysts system. Comparison between micrographs of as grown CNTs over respective supported catalyst showed that CNTs bundles grown over Ni-Al₂O₃ were highly dense with many white spots at the tips of CNTs floss. These white spots originated from the metal clusters [9, 10] which indicated the occurrence of weak support-catalyst interaction. FE-SEM micrograph in Fig. 2(a) supported the occurrence of the white spots at the tip of the slightly wavy tubular CNTs which can be clearly seen in the white circled area on the SEM micrograph.

On the other hand the SEM micrograph of CNTs grown over Ni/Fe-Al₂O₃ showed less dense CNTs bundles without white spots. From this observation it can be inferred that the supported-catalyst interactions in the Ni/Fe-Al₂O₃ system were stronger. FE-SEM micrograph in Fig. 2(b) showed that

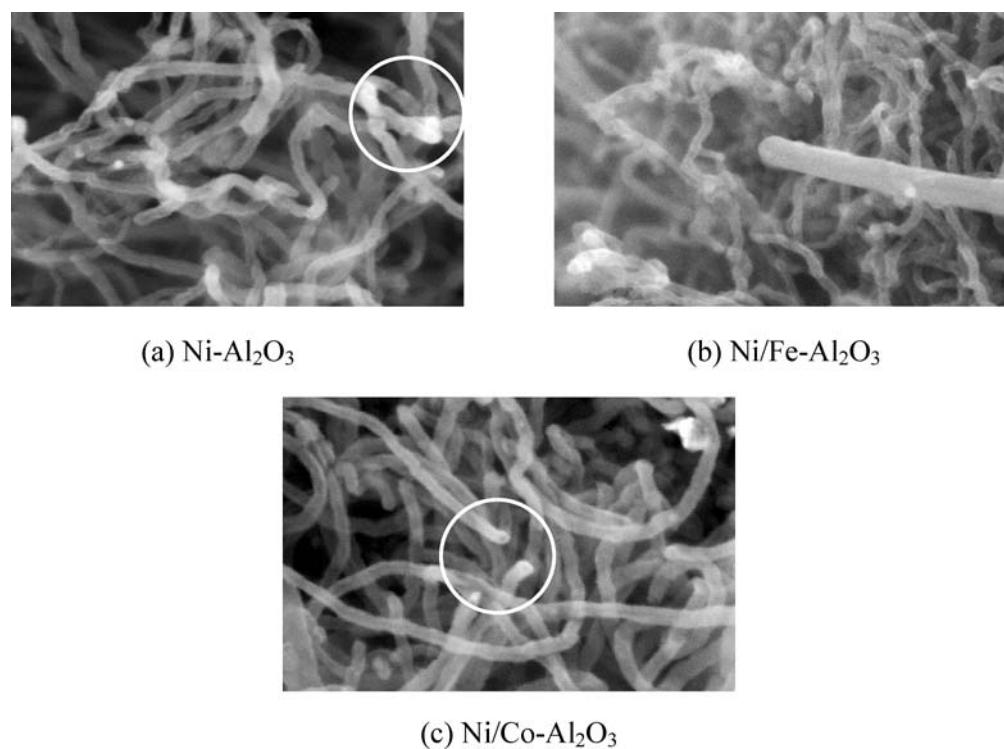


Fig. 2 FE-SEM Images of as-grown CNTs over alumina-supported catalysts

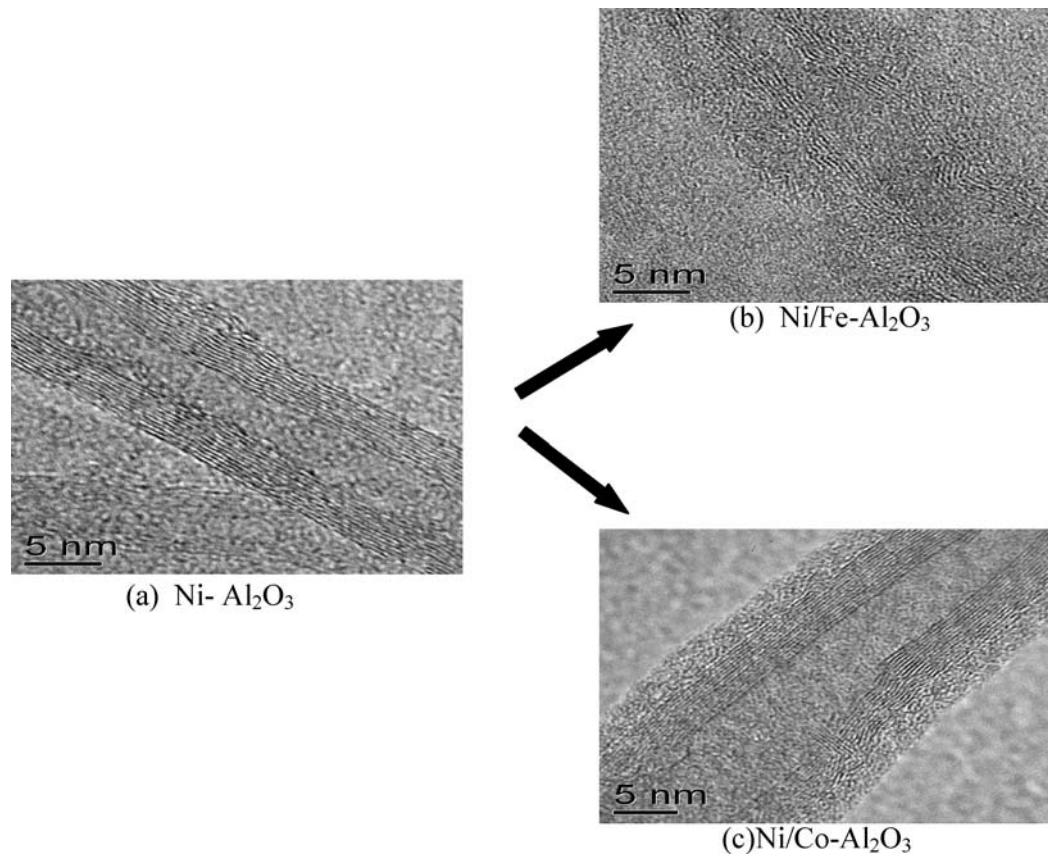


Fig. 3 TEM Images of as-grown CNTs over alumina-supported catalysts

the CNTs grown over Ni/Fe-Al₂O₃ have mixture of white spot tips and an open-end tubular structure with non uniform tubular sizes and wavier CNTs tubular structure.

However, the SEM micrograph of CNTs grown over Ni/Co-Al₂O₃ (Fig. 1(f)) revealed a highly dense CNT bundles with very little white spots. The Ni/Co-Al₂O₃ FE-SEM in Fig. 2(c) has proven that by introducing Ni, high quality and purity of as grown CNTs was produced. The FE-SEM micrograph showed uniformity of tubular sizes as well as well defined open-end CNTs tubular structure which support the statement made earlier. (Fig. 2(c), refer to the white circulated areas).

TEM analysis of all the synthesized CNTs was depicted in Fig. 3. The results showed that the as-synthesized CNTs obtained in this work are multiwalled in nature, with the number of layered walls between 10 and 12. However, the walls are not concentric. The mean inner and outer diameters of the tubes were between 4.8 nm to 8.5 nm. The interlayer spacing between the graphene sheets is ~0.34 nm, which corresponded to the actual distance between the lattice layers in the graphite structure. TEM images for as-grown CNTs over Ni/Co-Al₂O₃ appeared to be high quality MWNTs as seen in Fig. 3(c), where the occurrence of almost straight-line layered walls. It should also be noted from the TEM images the amorphous carbon deposition presence was from the early stage of the pyrolysis process. TEM results for as-grown CNTs over Ni/Fe-Al₂O₃ also revealed that the quality of the MWNT's obtained is very poor.

These results suggested that the Ni/Co-Al₂O₃ supported catalysts gave the best yield of MWNTs, showing that interaction occurred between the catalysts and the support [11]. This interaction can alter both the crystallography and electronic structures of the supported catalysts and consequently affect the yield, morphology and structure of the as-grown CNTs.

Conclusion

Combination of the metal catalyst and supporting substrate greatly affect CNTs yield, uniformity, purity and structure. In

this work, we have demonstrated that the presence of Ni in the Fe-Al₂O₃ and Co-Al₂O₃ supported catalysts systems have greatly influenced the quality and structure of as-synthesized CNTs formed. From the SEM and TEM results obtained, we can conclude that the presence of Ni onto the Co-Al₂O₃ system gave the best form of MWNTs with high purity and quality.

Acknowledgment The authors would like to thank the Ministry Of Science Technology and Innovation of Malaysia for funding this project under the IRPA mechanism of the National Fuel Cell project.

References

1. N. Nagaraju, A. Fonseca, Z. Konya, and J.B. Nagy, *Journal of Molecular Catalysis A: Chemical* **181**, 57 (2002).
2. K. Mukhopadhyay and G.N. Mathur, *International Journal of Nanoscience* **2**(3), 153 (2003).
3. M.S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* (Springer-Verlag, Germany, 2001).
4. M. Daenen, R.D. de Fouw, B. Hamers, P.G.A. Janssen, K. Schouteden, and M.A.J. Veld, *The Wondrous World of Carbon Nanotubes*. Denmark/Eindhoven University of Technology. Unpublished 2003.
5. R. Saito, G. Dresselhaus, and M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London 1998).
6. E. Flahaut, Ch. Laurent, and A. Peigney, *Carbon* **43**, 375 (2005).
7. A. Fonseca, K. Hernadi, P. Piedigrosso, L.P. Biro, S.D. Lazarescu, P. Lambin, P.A. Thiry, D. Bernaerts, and J.B. Nagy, In K.M. Kadish and R.S. Ruoff (eds.), *Fullerenes Volume IV: Recent Advances in the Physics and Chemistry of Fullerenes and Related Materials. The Electrochemical Society Inc. Proceedings Volume 97-14* (1997).
8. Tee Jia Chee, Nor Aziah Buang, Suhaila M. Sanip, and Ahmad Fauzi Ismail, *Synthesis of Carbon Nanotubes (CNTs) using supported catalysts* (2004).
9. A.K.M.F. Kibria, Y.H. Mo, and K.S. Nahm, *Catal. Lett.* **71**(3–4), 229 (2001).
10. Y.H. Mo, A.K.M.F. Kibria, and K.S. Nahm, *Synth Metals* **122**, 443 (2001).
11. P.E. Anderson and N.M. Rodríguez, *Influence of The Support on the Structural Characteristics of Carbon Nanofibers Produced from the Metal-Catalyzed Decomposition of Ethylene*. *Chem. Mater.* **12**, 823 (2000).