Research Article

A Comparative Study of the Effect of MgO and CaCO₃ as Support Materials in the Synthesis of Carbon Nanotubes with Fe/Co as Catalyst

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A comparative study of the effect of magnesium oxide and calcium carbonate as support material in the synthesis of carbon nanotubes using the catalyst Fe/Co is presented. The synthesized carbon nanotubes were characterized with Raman spectroscopy, scanning electron spectroscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction spectroscopy (XRD), and energy dispersive spectroscopy (EDS). The morphology of the carbon nanotubes synthesized with magnesium oxide as support material gives rise to carbon nanotubes with consistent and well-defined structure unlike that synthesized with calcium carbonate. The I_D/I_G ratio of synthesized carbon nanotubes (CNTs) was 0.8544 for magnesium oxide supported compared to 0.8501 for calcium carbonate supported carbon nanotube.

1. Introduction

Synthesis of carbon nanotubes (CNTs) has been extensively investigated by a number of researchers, since the first observation in 1991 [1]. Different synthetic methods such as arc discharge [2], laser vaporization [3], pyrolysis [4], plasma enhanced or thermal chemical vapor deposition [5], and catalytic chemical vapor deposition (CCVD) [6, 7] have been developed for the production of CNTs [8, 9]. The synthesis of CNTs using (CCVD) method has proved to be the most rewarding; hence, it has attracted much attention because of the advantages it has over other methods in producing high purity, high yield carbon nanotubes [8].

It is reported that the most effective catalysts for CCVD growth of CNTs are known to be iron (Fe), cobalt (Co), and Nickel (Ni) [8]. However, a comparative study of the effect of calcium carbonate and magnesium oxide as supporting material using the aforementioned catalysts has not been reported as yet. The ability of these metal catalysts in relation to their catalytic activity in the decomposition of carbon precursors or sources, the formation of metal stable carbides, the formation of graphite sheets, and the diffusion of carbons

have been reported [9, 10]. The effect of all variables and parameters on the growth of CNTs is still to be reported, and the impact of supporting material on the growth of carbon nanotubes using catalytic chemical vapor deposition reactor systems has to be studied. Precise understanding and knowledge of the catalyst on a stated supporting substance would lead to controlled growth of CNTs, which is a yardstick for various potential applications.

In this study, we report the effect of calcium carbonate and magnesium oxide as support materials in the synthesis of CNTs using Fe/Co catalysts by thermal CCVD of acetylene gas. The CNTs were grown on Fe/Co/CaCO₃ and Fe/Co/MgO under the same conditions. The morphological features were investigated using transmission electron microscopy, scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and energy dispersive spectroscopy.

2. Experimental

2.1. Materials. Iron(III) nitrate, cobaltous nitrate, magnesium oxide, calcium carbonate, and concentrated hydrochloric acid 32% were obtained from Sigma-Aldrich South Africa

FIGURE 1: Raman spectra of nanomaterial synthesized from Fe/Co on (a) magnesium oxide and (b) calcium carbonate as support material.

FIGURE 2: Scanning electron micrograph (SEM) of nanomaterial synthesized from (a) Fe/Co supported on magnesium oxide and (b) Fe/Co supported on calcium carbonate.

and used directly without further purification. Catalytic chemical vapor deposition (CCVD) reactor was obtained from Elite Thermal Systems Limited, South Africa, Mass flow meter and PowerPod 400 multichannel power supply instrument were obtained from Teledyne Hastings Instruments, USA.

2.2. Preparation of Catalyst. Iron(III) nitrate, cobaltous nitrate, and supporting materials were dissolved in 200 cm³ of distilled water in molar ratios of 2:1:2, respectively, in a beaker. The mixed dispersions were heated and evaporated with constant stirring until a paste was formed. The paste was then dried in an oven at 110°C for about 12 hours. The resulting solid material was calcined at 800°C for 5 hours.

2.3. Preparation of Nanomaterial. Carbon nanotubes were prepared in a cylindrical CCVD reactor; 40 mm o.d × 70 cm long quartz tube was heated by an electric tube furnace with a

temperature controller. Nitrogen gas was set to flow through the reactor tube at the rate of 40 mL/min. The reactor was heated at rate of 10°C and took approximately 70 min for it to reach maximum temperature of 700°C and an extra 10 min at 700°C to allow the furnace to stabilize with the flow of nitrogen at 240 mL/min. Carbon source in this case acetylene (C₂H₂) was then passed through the reactor tube at the rate of 90 mL/min for 60 min. The flow of gases was controlled by a mass flow controller (MFC). After an hour of reaction had taken place, the acetylene gas was closed and nitrogen allowed to flow at the rate of 40 mL/min until the reactor cooled to room temperature.

2.4. Characterization. The morphological features of nanomaterials were analyzed by Raman spectroscopy, FE-SEM, HR-TEM, EDS, and XRD. The Raman spectra were obtained by a Raman spectroscope, Jobin-Yvon HR800 UV-VIS-NIR Raman spectrometer equipped with an Olympus BX 40

attachment. The excitation wavelength was 514.5 nm with an energy setting of 1.2 mV from a coherent Innova model 308 argon-ion laser. The Raman spectra were collected by means of back scattering geometry with an acquisition time of 50 seconds. The surface morphology and EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope. The HR-TEM images of the sample were obtained by a CM 200 electron microscope operated at 100 kV. Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advanced diffractometer operated at 45 kV and 40 mA with monochromated copper $K\alpha_1$ radiation of wavelength ($\lambda = 1.540598$) and $K\alpha_2$ radiation of wavelength ($\lambda = 1.544426$), scan speed of 1 s/step and a step size of 0.03° .

3. Results and Discussion

Raman spectra of nanomaterial synthesized with the catalyst Fe/Co supported on magnesium oxide (MgO) and calcium carbonate (CaCO_3), respectively, are presented in Figure 1. Raman spectroscopy is a powerful nondestructive technique to study carbonaceous materials with the ability to distinguish between single and double walled carbon nanomaterials. The Raman spectrum of the carbon nanomaterial obtained with magnesium oxide as support material is presented as Figure 1(a) while the spectrum of the nanomaterial obtained with calcium carbonate as support material is presented as Figure 1(b). The Raman spectra show three major peaks: the *D* and *G* bands and their overtones in each spectrum. The *D* and *G* bands indicate the presence of crystalline graphitic carbon [11–14]. The *D* band is attributed to indicate the presence of amorphous carbon and surface defects in carbon nanotubes while the *G* band corresponds to an E_{2g} mode of graphite which is related to sp^2 bonded carbon atoms and the presence of ordered carbon nanotubes [14]. The *D* and *G* bands obtained with magnesium oxide as support material are at 1340.01 and 1568.29 cm^{-1} , respectively, with the overtone at 2678.65 cm^{-1} . The intensity ratio of the *D* and *G* bands is considered a parameter in characterizing the quality of nanomaterial. The intensity ratio of these bands in the spectrum, Figure 1(a), gives $(I_D/I_G) = 0.8544$. The *D* and *G* bands obtained with calcium carbonate as support materials are at 1342.33 and 1578.94 cm^{-1} , respectively, with the overtone at 2689.30 cm^{-1} . The intensity ratio of these bands in the spectrum, Figure 1(b), gives $(I_D/I_G) = 0.8501$. The Raman spectra obtained with these two support materials are similar and only show the presence of multiwall carbon nanotube. The high intensity of the *D* band in the spectrum of the calcium carbonate (Figure 1(b)), support material, is an indication of the presence of a large quantity of amorphous carbon in the as-prepared carbon nanomaterial compared to the carbon nanomaterial obtained from magnesium oxide support (Figure 1(a)).

The scanning electron micrograph of the nanomaterial synthesized with the catalyst Fe/Co supported on magnesium oxide and calcium carbonate are presented in Figure 2. The SEM image of the carbonaceous material obtained with magnesium oxide as support material, Figure 2(a), shows

FIGURE 3: High-resolution transmission electron micrograph (HR TEM) of nanomaterial synthesized from Fe/Co supported on magnesium oxide ((a)–(c)) and Fe/Co supported on calcium carbonate ((d)–(f)).

several carbon nanotubes of various sizes. The SEM image of the carbonaceous material obtained with calcium carbonate as support material, Figure 2(b), also shows several carbon nanotubes. The morphology of the carbon nanotubes obtained with magnesium oxide as support material have larger sizes compared to the carbon nanotubes obtained with calcium carbonate as support material. This gives the impression that the use of magnesium as support material enhances the production of larger carbon nanotubes that use calcium carbonate.

The HR-TEM micrograph of the nanomaterial synthesized with the catalyst Fe/Co with magnesium oxide and calcium carbonate supports are presented in Figure 3. The HR-TEM image of the nanomaterial obtained with magnesium oxide as support material is presented in Figures 3(a)–3(c) while that due to calcium carbonate as support material is presented in Figures 3(d)–3(f). The morphology of the

FIGURE 4: Energy dispersive spectroscopy (EDS) of nanomaterial synthesized from (a) Fe/Co supported on magnesium oxide and (b) Fe/Co supported on calcium carbonate.

FIGURE 5: X-ray diffraction spectra (XRD) of nanomaterial synthesized from (a) Fe/Co supported on magnesium oxide and (b) Fe/Co supported on calcium carbonate.

TABLE 1: Quantitative analysis of elements and atoms obtained from energy dispersive spectroscopy of Fe/Co catalyst supported on magnesium oxide and calcium carbonate.

Element	Fe/Co/MgO			Fe/Co/CaCO ₃		
	Element (% weight)	Atom (%)	Peak height (au)	Element (% weight)	Atom (%)	Peak height (au)
Carbon (C)	27.11	33.20	30326	27.15	33.25	25528
Oxygen (O)	72.46	66.61	1598	72.49	66.64	626
Magnesium (Mg)	0.22	0.13	892	—	—	—
Calcium	—	—	—	0.17	0.06	296
Iron	0.14	0.04	312	0.09	0.02	261
Cobalt	0.07	0.02	312	0.10	0.03	261
Total	100	100		100	100	

TABLE 2: Peaks obtained from X-ray diffraction of Fe/Co catalyst supported on magnesium oxide and calcium carbonate.

Support	2 Theta degrees (2θ)			
MgO	25.97	35.27	42.57	44.46
CaCO ₃	26.00	35.11	42.43	44.46

carbon nanomaterial obtained with magnesium oxide shows several carbon nanotubes which could be called multiwall carbon nanotubes (MWCNT), Figures 3(a)–3(c). This is not observed in the morphology of the carbon nanomaterial obtained with calcium carbonate as support material. With calcium carbonate as support material, we do not find well-defined multiwall carbon nanotubes. The fact that the carbon nanotube obtained with magnesium oxide as support material produces better carbon nanotube is further corroborated with SEM image as observed. HR-TEM images of the as-synthesized carbon nanotubes, Figures 3(b) and 3(e), provide the internal lattice structure of the carbon nanotubes. In Figure 3(b), a hollow midrib and walls are visible while in Figure 3(e) the lattice structure does not reveal midrib and walls.

The energy dispersive spectroscopy (EDS) analysis of the as-prepared carbon nanomaterial formed in this synthesis using magnesium oxide and calcium carbonate as support material is presented in Figure 4 and Table 1. The X-ray spectra obtained show the presence of the elements carbon, oxygen, cobalt, iron, and magnesium in Figure 4(a) and in Figure 4(b), carbon, oxygen, cobalt, iron, and calcium. The peak height and base obtained indicate that the nanomaterial produced using magnesium oxide as support material is composed of pristine graphitic carbon that the nanomaterial obtained from calcium carbonate as support material. The position of the elements magnesium and calcium in the spectral field is different in comparison to the other metals. The peak due to magnesium is at 1.35 KeV while that of calcium is at 3.7 KeV. This difference could be attributed to effect of these metals as support material. The closeness of magnesium is seen here to enhance the formation of carbon nanotubes compared to calcium, in the energy dispersive spectroscopy spectra.

The X-ray diffraction diffractograms of nanomaterial synthesized with the catalyst Fe/Co supported on magnesium oxide (MgO) and calcium carbonate (CaCO₃) are presented in Figure 5. XRD is an effective method to investigate the interlayer changes and the crystalline properties of a synthesized material. The XRD diffractograms show similar XRD patterns, Figures 5(a) and 5(b) and Table 2. Bragg diffraction peaks are observed at $2\theta = 25.97^\circ$, 35.25° , 42.57° , and 44.46° for Fe/Co/MgO and at $2\theta = 26.00^\circ$, 35.11° , 42.43° , and 44.46° for Fe/Co/CaCO₃. The strongest peaks at $2\theta = 25.97^\circ$ and 26.00° correspond to hexagonal graphite lattice of multiwalled carbon nanotubes. The low-intensity peaks at $2\theta = 35.25^\circ$, 42.57° , and 44.46° in the magnesium oxide diffractogram and at $2\theta = 35.11^\circ$, 42.43° , and 44.46° in the calcium carbonate diffractogram indicate the presence in both synthesis low-quality carbon nanomaterials.

4. Conclusion

Carbon nanotubes synthesized with the catalyst Fe/Co supported on magnesium oxide and calcium carbonate have been compared. The carbon nanotubes produced using magnesium oxide as support material show better consistency and size compared to the carbon nanotubes produced using calcium carbonate as support. Raman spectra of the as-prepared carbon nanotubes indicate the presence of higher amorphous material in the carbon nanotube prepared with calcium carbonate as support material compared to that prepared with magnesium oxide as observed in the high intensity of the *D* band. Results from TEM, SEM, and EDS were used to corroborate our observation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.
- [2] C. J. Lee, J. Park, and J. A. Yu, "Catalyst effect on carbon nanotubes synthesized by thermal chemical vapor deposition," *Chemical Physics Letters*, vol. 360, no. 3–4, pp. 250–255, 2002.
- [3] A. Thess, R. Lee, P. Nikolaev et al., "Crystalline ropes of metallic carbon nanotubes," *Science*, vol. 273, no. 5274, pp. 483–487, 1996.
- [4] M. Terrones, N. Grobert, J. Olivares et al., "Controlled production of aligned-nanotube bundles," *Nature*, vol. 388, no. 6637, pp. 52–55, 1997.
- [5] R. Sen, A. Govindaraj, and C. N. R. Rao, "Carbon nanotubes by the metallocene route," *Chemical Physics Letters*, vol. 267, no. 3–4, pp. 276–280, 1997.
- [6] Z. F. Ren, Z. P. Huang, J. W. Xu et al., "Synthesis of large arrays of well-aligned carbon nanotubes on glass," *Science*, vol. 282, no. 5391, pp. 1105–1107, 1998.
- [7] X. Ma, E. G. Wang, W. Zhou et al., "Polymerized carbon nanobells and their field-emission properties," *Applied Physical Letters*, vol. 75, p. 3105, 1999.
- [8] W. Z. Li, S. S. Xie, L. X. Qian et al., "Large-scale synthesis of aligned carbon nanotubes," *Science*, vol. 274, no. 5293, pp. 1701–1703, 1996.
- [9] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, "Self-oriented regular arrays of carbon nanotubes and their field emission properties," *Science*, vol. 283, no. 5401, pp. 512–514, 1999.
- [10] C. H. Kiang, "Carbon rings and cages in the growth of single-walled carbon nanotubes," *The Journal of Chemical Physics*, vol. 113, p. 4763, 2000.

- [11] A. N. Andriotis, M. Menon, and G. Froudakis, "Catalytic action of Ni atoms in the formation of carbon nanotubes: a molecular dynamics study," *Physical Review Letters*, vol. 85, no. 15, pp. 3193–3196, 2000.
- [12] E. D. Dikio, F. T. Thema, C. W. Dikio, and F. M. Mthunzi, "Synthesis of carbon nanotubes by catalytic decomposition of ethyne using Co-Zn-Al catalyst," *International Journal of Nanotechnology and Applications*, vol. 4, no. 2, pp. 117–124, 2010.
- [13] P. Benito, M. Herrero, F. M. Labajos et al., "Production of carbon nanotubes from methane. Use of Co-Zn-Al catalysts prepared by microwave-assisted synthesis," *Chemical Engineering Journal*, vol. 149, no. 1–3, pp. 455–462, 2009.
- [14] E. D. Dikio, "A comparative study of carbon nanotubes synthesized from Co/Zn/Al and Fe/Ni/Al catalyst," *E-Journal of Chemistry*, vol. 8, no. 3, pp. 1014–1021, 2011.