

High growth of SWNTs and MWNTs from C₂H₂ decomposition over Co–Mo/MgO catalysts

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Received 20 August 2003; accepted 30 April 2004

Available online 9 June 2004

Abstract

A series of MgO supported catalysts having Co and Mo metals 5–40 wt.% in a ratio of 1:1 was prepared by impregnation method. Carbon nanotubes (CNTs) were grown over the catalysts by decomposition of C₂H₂ at 800 °C for 30 min. It was found that 5 and 10 wt.% Co–Mo/MgO catalysts produced single-wall nanotubes (SWNTs), whereas 20, 30 and 40 wt.% Co–Mo/MgO catalysts produced multi-wall nanotubes (MWNTs). The catalyst Mo/MgO was inactive in growing CNTs. In Co–Mo/MgO catalysts, however Mo generated a favorable environment to grow SWNTs. The growth of SWNTs was strongly dependent on the formation of small clusters of cobalt, which may generate from the decomposition of CoMoO₄ species during the nanotube growth. MWNTs were produced over comparatively larger cobalt clusters generated from Co₃O₄ phase during the nanotube growth stage. The yields of SWNTs were about 6% and 27% over 5 and 10 wt.% Co–Mo/MgO catalysts, respectively. MWNTs yield (576%) was observed over 40 wt.% Co–Mo/MgO catalyst. Carbon yield (%) highly varied with acetylene concentration.

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Keywords: A. Carbon nanotubes; B. Chemical vapor deposition; C. X-ray diffraction, Raman spectroscopy; D. Carbon yield

1. Introduction

Much investigation have been focused on the synthesis of carbon nanotubes (CNTs) at a low cost and, in parallel, on the characterization of CNTs in the point of industrial applications [1–3]. Among the intensively investigated synthetic methods of CNTs, the catalytic chemical vapor decomposition (CVD) of short chain hydrocarbons and CO appears to be the best method to produce CNTs in large scale at low cost [4–14]. Bimetallic supported catalysts such as Ni–Fe/Al₂O₃ [6], Co–Mo/SiO₂ [7–9] Co–Mo/MgO [10,11], Fe–Co/MgO [12,13] and Mo–Fe/Al₂O₃ [14] catalysts are found very effective to synthesize CNTs with remarkable yields. Among the bimetallic catalysts, the Mo containing catalysts showed better performance for SWNTs production, although it was believed that CVD process could

produce MWNTs only. However, the yield of SWNTs was low and in most cases it appeared with MWNTs. Further investigation was therefore necessary to scale their production up by improving catalysts and growth environment with the understanding of growth mechanism.

It was observed that the catalysts Mo/SiO₂ and Mo/MgO were inactive in growing CNTs [7–10]. The catalysts Co/SiO₂ and Co/MgO produced CNTs in small scales. However, the bimetallic Co–Mo/SiO₂ and Co–Mo/MgO catalysts yielded remarkable amounts of CNTs with high selectivity of SWNTs [7–11]. It indicates that the bimetallic catalysts prepared by Mo and Co gain some special capability to produce CNTs and specially SWNTs in a good proportion. In connection with this aspect, authors widely discussed the role of Mo in low wt.% Co–Mo/SiO₂ catalysts during CNTs growth [7,9]. It has been reported that Mo/Al₂O₃ catalyst produced SWNTs and MWNTs from the disproportionation of CO [12], whereas Mo/SiO₂ and Mo/MgO catalysts were found inactive in growing CNTs from CO and CH₄ [7–10]. This behavior indicates that supports

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play an effective role in exposing the catalyst metals in favor of CNTs production and simultaneously metals also have some degree of affinity to support to expose them over for CNTs production.

The reaction of CO over impregnated 3Co:3Mo/SiO₂ catalysts at 800 °C yielded only 1% carbon with 87% selectivity of SWNTs [7]. At 1000 °C, 1.7Co:85Mo/MgO catalyst prepared by sol-gel method produced only 2 wt.% SWNTs under controlled conditions, whereas MWNTs weighing over 15 times of the catalyst from CH₄ [11]. Impregnated 5Co:5Mo/MgO catalyst yielded 80% SWNTs and 20% MWNTs from CH₄ at 1000 °C [10]. At 850 °C, impregnated 1Mo:9Fe/SiO₂ catalyst yielded 40 wt.% carbon from CO whereas only 7 wt.% carbon containing SWNTs and MWNTs with a ratio of 3:7 from C₂H₄ [14].

From the above literature reports [7–14], it can be realized that the relative amount of SWNTs and MWNTs could be controlled by changing the support and catalyst preparation technique, varying the compositions of the catalysts, controlling the system operation conditions, and using different carbon source gases in the CVD grown reactor. It seems that the role of Mo in the bimetallic MgO catalyst needs to clear as the highest growth of SWNTs and MWNTs was achieved on Co–Mo/MgO catalyst [10,11]. Moreover, purified CNTs can easily be obtained because MgO is fully soluble in acids. On the other hand, C₂H₂ has not been employed yet to evaluate the growth of SWNTs or a mixture of SWNTs and MWNTs over Mo containing bimetallic supported catalysts. Another benefit may be achieved from C₂H₂ because it exhibits very high activity in producing Mo₂C compared to CH₄ and CO [15]. It is notable that the generation of Mo₂C may have a profound role in producing high yield of SWNTs.

In this work, we prepared a series of Co–Mo/MgO catalysts with varying wt.% and investigated their capability of growing SWNTs and MWNTs from decomposition of C₂H₂ at around 800 °C under different controlled conditions. A detailed growth mechanism of CNTs was presented in the light of the role of Mo in the catalysts in growing SWNTs and MWNTs.

2. Experiment

We prepared five Co–Mo/MgO catalysts by impregnation method. The loading ratio of Co:Mo (wt.%) was 1:1 and their total weights in the supported catalysts were 5, 10, 20, 30 and 40 wt.%. For the preparation of catalysts, Co(NO₃)₂·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O salts were used. Stoichiometric amount of MgO powders was mixed with the aqueous solution of salts and stirred at 70 °C to obtain homogeneous impregnation of salts in the support. After 4 h, the impregnate slurry was obtained and it was dried at 100 °C for 12 h in an oven.

The dried product was then calcined at 400 °C for 6 h to achieve oxide forms of metals. In this state, the catalyst product became a powder. Then, the catalyst powders were reduced at 450 °C for 4 h in 100 sccm H₂ gas flow in a reactor. These catalysts were then used for the growth of CNTs.

Approximately 20 mg catalyst powder was uniformly dispersed in the base area of a quartz plate and placed in the central region of a horizontal quartz tube reactor of diameter 4.5 cm. There, the catalyst was activated at 500 °C for 1 h in 100 sccm H₂ gas flow. Then, the growth of CNTs was performed for 30 min at 800 °C under the flow of 10/100 sccm C₂H₂/H₂ mixture. CNTs were synthesized over five catalysts at this experimental condition. Carbon yields were calculated to evaluate the activity of the catalysts. The structure and morphology of the synthesized CNTs were characterized using scanning electron microscopy (SEM), Raman spectroscopy and transmission electron microscopy (TEM). The role of Mo in the catalysts to grow SWNTs and MWNTs was evaluated by investigating X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analyses of the catalysts surfaces accompanied with Raman spectroscopy, transmission electron microscopy (TEM) and XRD findings of the grown CNTs.

3. Results and discussion

X-ray diffraction (XRD) patterns of hydrogen treated 5, 10, 20, 30 and 40 wt.% Co–Mo/MgO catalysts are shown in Fig. 1 together with that of support MgO. In

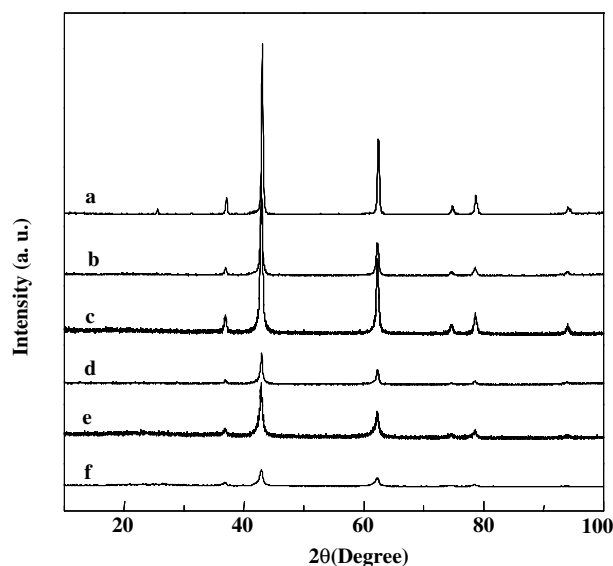


Fig. 1. XRD spectra of MgO support and Co–Mo/MgO catalysts: (a) MgO, (b) 5 wt.% Co–Mo/MgO, (c) 10 wt.% Co–Mo/MgO, (d) 20 wt.% Co–Mo/MgO, (e) 30 wt.% Co–Mo/MgO and (f) 40 wt.% Co–Mo/MgO.

the figure, a–f are the spectra for MgO and 5, 10, 20, 30 and 40 wt.% metal loaded catalysts, respectively. On comparing the spectra of the catalysts with the spectrum of MgO, it can be said that there is no difference in the peak positions of XRD spectra of the catalysts and MgO support, except very low peak intensities and peak broadening. In addition, no remarkable peaks for metallic Co and Mo appeared in the XRD spectrum of the catalysts. Formation of an ideal CoO–MgO solid solution phase in the catalysts seems responsible for the XRD reflections at the identical positions of the support MgO [16–20]. The decomposition temperature of this phase is around 900 °C [16,18,19]. It is well established that CoMoO₄ mixed species generates in Co–Mo catalysts during heat treatment [16,21,22]. Decomposition of this phase occurs at around 550 °C [9]. MoO₃ reduces at around 1000 °C. So, no peak for Mo appeared at the XRD spectrum of the catalysts. Although cobalt oxide reduces at 400 °C, it may partially consume at this temperature by interacting with MoO₃ and resulting CoMoO₄ species [16]. Moreover, very small amount of reducible Co₃O₄ species appears in Co/MgO catalyst up to 600 °C compared to unsupported Co₃O₄ [18]. It indicates that in the present catalyst system, the amount of reducible Co₃O₄ species was low. This species was highly dispersed with small sized CoMoO₄ particles over the surfaces of the catalysts. The particle size of the Co crystallite if produced any of course was small in size and dispersed well over the catalysts. So, the XRD peaks for the catalysts become broaden, their intensities decreased remarkably and concurrently no diffraction peak for Co appeared in the spectrum.

When we compile the probable oxide species found during the preparation of Co–Mo/MgO catalysts by heat treatment, these are CoO–MgO solid solution, Co₃O₄, MoO₃, Co₂MgO₄, MgMoO₄, MgMo₂O₇, CoMoO₄, etc. [11,16,21,22]. The phases present in a catalyst affect its reducibility as well as the size and morphology of the metal particles generated during reduction and hence the activity of the catalyst in practical application. Simultaneous calcination and reduction of catalysts can generate new and dispersed active species over the catalyst surfaces. In case of 6–14 wt.% Co–Mo/SiO₂ catalysts, well-dispersed CoMoO₄ species played a determinant activity and selectivity role by disproportionate it and then generating very small

Co crystallites on reduction [9]. However, in the present case, we are not sure about the fraction of the active metals dispersed over the surfaces of the Co–Mo/MgO catalysts. Measurement of the surface compositions of the catalysts should be an informative about it. In this connection, energy dispersive X-ray (EDX) analyses of the catalysts surfaces were carried out. The analytical data for the Co–Mo/MgO catalysts is summarized in Table 1.

From Table 1, it can be seen that oxygen (O) is the highest component in the surface of the catalysts. Without any exception, the differences between the surface and imposed O wt.% (O of MgO) gradually increased with increasing catalysts wt.%. It indicates that with increasing the catalysts wt.%, the oxide phases of Mo and Co are gradually increased in the surface of the catalysts. In case of 5 and 10 wt.% metal loading catalysts, 92% and 98% metals are found exposed on the catalyst surfaces. On the 5 wt.% Co–Mo/MgO catalyst, MoO₃ species seems to be dispersed over the CoO–MgO solid solution phase with an agglomeration tendency, because the surface Mo wt.% found higher than that of Co. Best dispersion of metals appeared over 10 wt.% Co–Mo/MgO catalyst. With increasing metals loading from 20–40 wt.%, the proportion of cobalt composition gradually increased on the catalyst surface than that of molybdenum. This may appear due to the high acidic nature of MoO₃ and high basic nature of MgO that may hinder the exposure of Mo species on the catalyst surface. In case of Co–Mo/SiO₂ catalysts, excess concentration of Co in the catalyst surface and that of Mo in the bulk was also reported. It was proposed that CoMoO₄ layer lies on top of MoO₃ species [9]. So, in case of 20–40 wt.% loaded catalysts, the most probable exposed phases on the solid solution are CoMoO₄ and Co₃O₄. The proportion of Co₃O₄ may increase in the surface with increasing wt.% of metal loading because no appreciable solid–solid interaction occurs between the MgO and Co₃O₄, whereas MoO₃ and MgO highly interacts and forms MgMoO₄ and MgMo₂O₇ between the temperatures 400 and 600 °C [11,16].

The SEM images of the CNTs synthesized over different Co–Mo/MgO catalysts for 30 min at 800 °C under the flow of 10/100 sccm C₂H₂/H₂ mixture are shown in Fig. 2. In the figure, a–e represents the SEM image obtained for the CNTs grown over 5, 10, 20, 30 and

Table 1
EDX analysis data for the surface compositions of various Co–Mo/MgO catalysts after treating at 450 °C in H₂ atmosphere for reduction

Metal loading (wt.%)	5.0	10.0	20.0	30.0	40.0
Surface Co (wt.%)	2.15	4.91	9.70	12.08	19.87
Surface Mo (wt.%)	2.45	4.90	8.60	10.69	14.52
Surface Mg (wt.%)	46.98	41.87	36.25	29.77	24.37
Surface O (wt.%)	48.42	48.32	45.46	47.46	41.24
Surface catalyst (%)	92.00	98.10	91.50	75.90	85.97
Imposed O (wt.%)	37.72	35.37	31.76	27.48	23.82

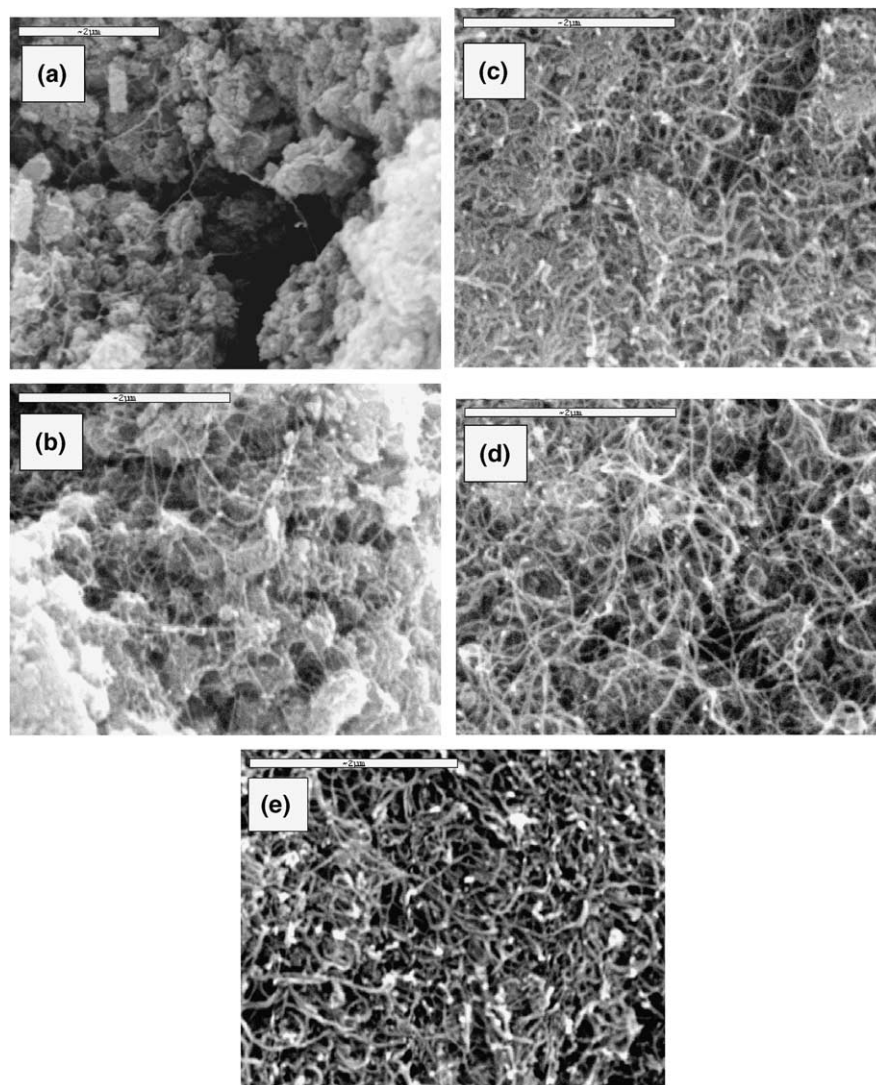


Fig. 2. SEM images of the CNTs grown over Co–Mo/MgO catalysts for 30 min at 800 °C under 10/100 sccm C_2H_2/H_2 flow: (a) 5 wt.% Co–Mo/MgO, (b) 10 wt.% Co–Mo/MgO, (c) 20 wt.% Co–Mo/MgO, (d) 30 wt.% Co–Mo/MgO and (e) 40 wt.% Co–Mo/MgO.

40 wt.% metal loaded catalysts, respectively. It can be seen that the growth density of CNTs over 5 and 10 wt.% metal loaded catalysts are poor. On the other hand, 20 wt.% and above metal loaded catalysts have grown CNTs with high densities. In these cases, the catalyst surfaces are completely covered with CNTs. The diameter of CNTs seems increased with increasing metals loading in the catalysts and lies between 10 and 20 nm.

In order to understand the structural perfection and the types of CNTs grown over the catalysts, Raman spectroscopic measurements were conducted at an excitation wavelength of 514.5 nm (Ar^+ -laser). The spectra of the CNTs are shown in Fig. 3. In the figure, a–e represents the spectra obtained for the CNTs grown over 5, 10, 20, 30 and 40 wt.% metal loaded catalysts, respectively. It can be seen that the spectra for the CNTs grown over at and above 20 wt.% metal loading cata-

lysts consist of three common peaks at 1337, 1576 and 2678 cm^{-1} , respectively. The first two peaks are associated with disordered carbonaceous products (D-band) and tangential graphitized products (G-band), characteristic peaks for MWNTs [6]. The third one is the second order Raman active combination band peak for CNTs. The spectra for the CNTs grown over 5 and 10 wt.% metal loading catalysts showed some distinct features than those appeared for 20 wt.% and above metal loading catalysts. In these cases, besides the characteristic peaks of CNTs at 1337, 1591 and 2644 cm^{-1} , pronounced radial breathing mode (RBM) peaks have appeared between 180 and 300 cm^{-1} . These RBM peaks are the characteristic peaks for the SWNTs and correspond to tube diameter of 1.2–0.8 nm [12,23]. This finding indicates that 5 and 10 wt.% metal loading catalysts synthesized SWNTs whereas catalysts containing 20 wt.% and above metal loadings grew MWNTs. Au-

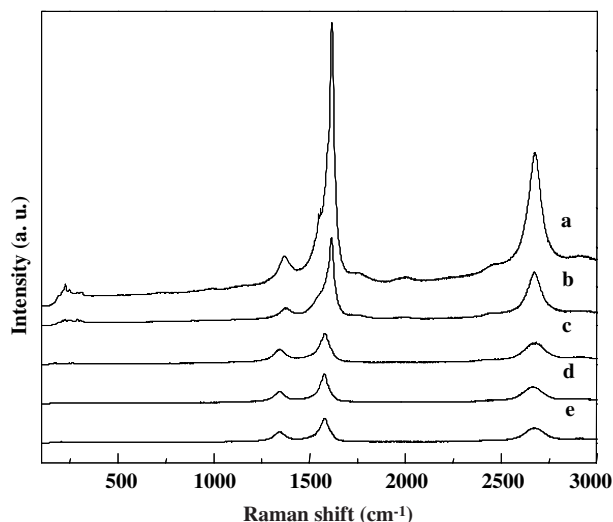


Fig. 3. Raman spectra of the CNTs grown over Co–Mo/MgO catalysts for 30 min at 800 °C under 10/100 sccm C_2H_2/H_2 flow: (a) 5 wt.% Co–Mo/MgO, (b) 10 wt.% Co–Mo/MgO, (c) 20 wt.% Co–Mo/MgO, (d) 30 wt.% Co–Mo/MgO and (e) 40 wt.% Co–Mo/MgO.

thors [7,10,14] have also found SWNTs over low wt.% catalysts such as 3Co:3Mo/SiO₂, 5Co:5Mo/MgO, 1.7Co:85Mo/MgO and 1Mo:9Fe/Al₂O₃ catalysts from

disproportionation of CO and decomposition of CH₄ and C₂H₄. However, the finding indicates that presently prepared 5 and 10 wt.% Co–Mo/MgO catalysts are active enough to synthesize SWNTs and concurrently at the set experimental condition C₂H₂ decomposition is effective to produce SWNTs as achieved by CO and CH₄.

Fig. 4 shows the transmission electron microscopy (TEM) images for the CNTs grown over 5 wt.% Co–Mo/MgO and 30 wt.% Co–Mo/MgO catalysts. The appearance of a bundle of SWNTs confirms the synthesis of SWNT over 5 wt.% Co–Mo/MgO catalyst and tube diameter is about 1 nm (Fig. 4(a)). Fig. 4(b), the low resolution TEM image, shows many individual tubes with a bundle of tube marked by an arrow grown over 30 wt.% Co–Mo/MgO catalyst. Inner hole of the tubes mostly appears as continuous white lines. Fig. 4(c) represents the growth of MWNTs of diameter 8–18 nm over this catalyst. It can be seen that some of the tubes covered by amorphous carbon layer. However, the TEM findings confirmed the Raman observations about the growth of SWNTs and MWNTs over the lower and higher Co–Mo loaded catalysts, respectively.

Raman active G-band and D-band intensity ratio (I_D/I_G) can be taken as a measure of well-structured

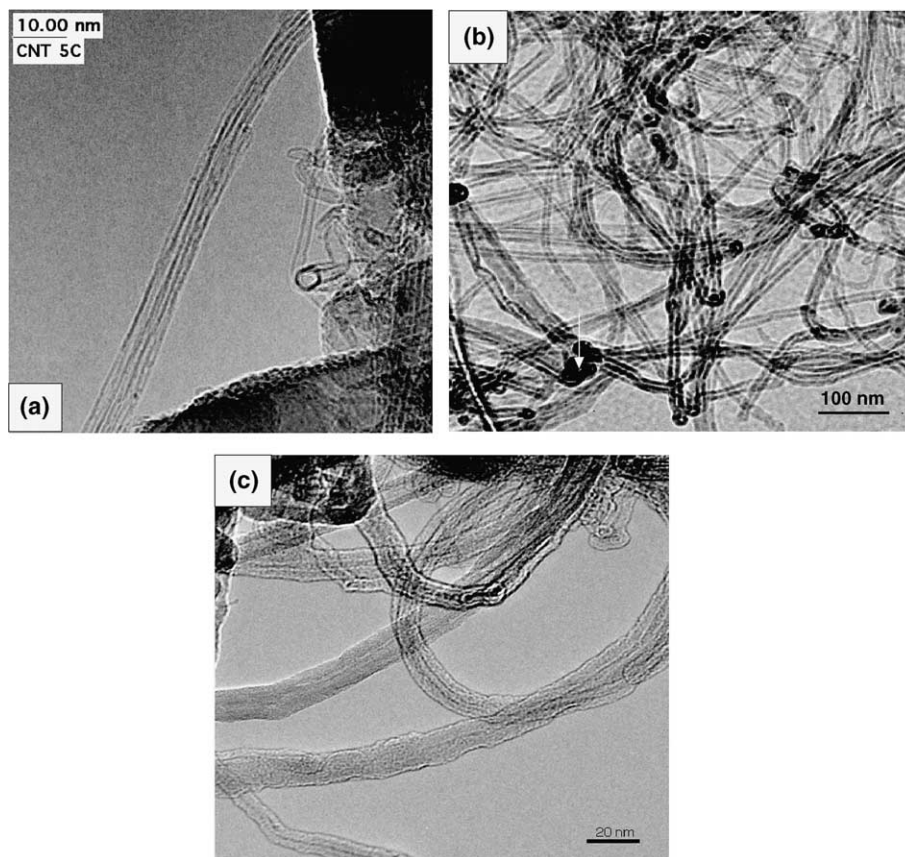


Fig. 4. TEM images of the CNTs grown over Co–Mo/MgO catalysts for 30 min at 800 °C under 10/100 sccm C_2H_2/H_2 flow: (a) 5 wt.% Co–Mo/MgO and (b, c) 30 wt.% Co–Mo/MgO.

Table 2

Raman active D and G band intensity ratio (I_D/I_G) for the CNTs grown over various Co–Mo/MgO catalysts at 800 °C for 30 min under the flow of 10/100 sccm C_2H_2/H_2 mixture

Metal loading (wt.%)	5.0	10.0	20.0	30.0	40.0
I_D/I_G value	0.15	0.17	0.48	0.40	0.44

morphology of CNTs [24]. Low I_D/I_G value represents well-graphitic structure of CNTs. In order to obtain structural information of our grown CNTs, we calculated I_D/I_G values from the Raman spectra of CNTs shown in Fig. 3 and compiled in Table 2. It can be seen that the lowest I_D/I_G value appeared for the CNTs grown over 5 wt.% Co–Mo/MgO catalyst and it is almost equal to that grown over 10 wt.% Co–Mo/MgO catalyst. The highest I_D/I_G value was obtained for the CNTs grown over 20 wt.% Co–Mo/MgO catalyst. It indicates that the quality of the SWNTs grew is better than that of MWNTs. Best quality MWNTs grew over the 30 wt.% Co–Mo/MgO catalyst.

Generally, the activity of a catalyst is evaluated by measuring the CNTs yield [7–14]. In order to understand the activity of our used catalysts, we determined the CNTs yield also. The carbon yield from our experiments is presented in Fig. 5 as a function of metal loading wt.%. This carbon yield was calculated using the formula: $[\text{carbon yield (\%)} = ((m_{\text{tot}} - m_{\text{cat}})/m_{\text{cat}}) \times 100]$ as used by the authors [25], where m_{cat} is the weight of the catalyst taken before CNTs growth and m_{tot} is the total weight of the catalyst and CNTs after the growth of CNTs. From Fig. 5, it can be seen that the carbon yield% increased more than linearly fashion with increasing metal loading up to 40 wt.%. For 5 and 10 wt.% Co–Mo/MgO catalysts, the carbon yields% are 6.1 and 27.1, respectively. On the other hand, for 40 wt.% Co–Mo/MgO catalyst, the carbon yield% reached the highest value 576.8. It indicates that we achieved very

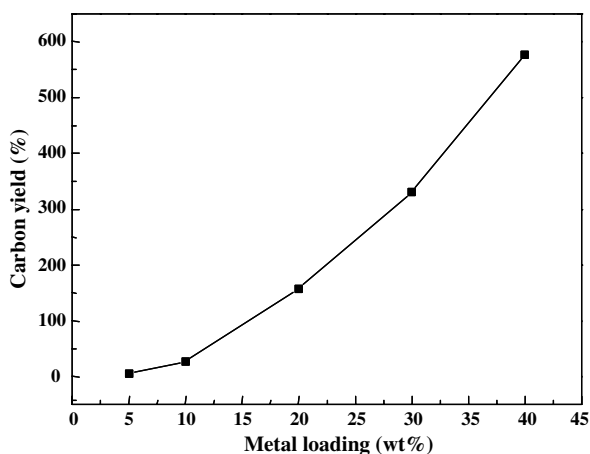


Fig. 5. Carbon yields (%) as a function of metal loadings (wt.%) in Co–Mo/MgO catalysts for 30 min growth time at 800 °C under 10/100 sccm C_2H_2/H_2 flow.

good amounts of SWNTs and MWNTs in the present study. However, we are not claiming that the total carbon yield% corresponds to CNTs only because till now the CVD process cannot produce CNTs without amorphous carbon. Amorphous carbon implies carbonaceous deposits which is not in the form of ordered nanotube and graphite. Thermogravimetric analysis (TGA) showed about 92 wt.% MWNTs in the carbon yield of 30 wt.% Co–Mo/MgO catalyst.

In order to understand the extent of positive effect of bimetallic catalysts over the monometallic catalysts in growing CNTs, we prepared 30 wt.% metal loaded Co/MgO and Mo/MgO catalysts and tried to synthesize CNTs over these catalysts by following the procedure and condition adopted for the bimetallic catalysts as described earlier. The Co/MgO catalyst produced MWNTs of carbon yield% 39.5 whereas no CNTs grew over the Mo/MgO catalyst besides amorphous carbon of yield% 1.2. It indicates that Co/MgO catalyst is not so effective and Mo/MgO catalyst is fully inactive in growing CNTs. Such an inactive behavior of Mo/SiO₂ and Mo/MgO catalysts was reported earlier also [7–10].

In order to understand the effect of C_2H_2 concentration, growth temperature and growth time on the production of MWNTs, various studies were carried out. It was found that variation of each parameter highly effect the growth of MWNTs. By maintaining a fixed flow rate 110 sccm of C_2H_2/H_2 mixture, when the flow of C_2H_2 varied from 5 to 30 sccm over 30 wt.% Co–Mo/MgO catalyst at 800 °C for 30 min, variable amounts of carbon yield were found. The variation of carbon yield% as a function of C_2H_2 flow is shown in Fig. 6. It can be seen that initially carbon yield% increased up to 10 sccm C_2H_2 flow rate. Then, the value decreased to a minimum at 20 sccm flow rate and increased with further increasing the rate of flow of C_2H_2 . This behavior indicates that equilibrium is essential between the C_2H_2 feed stock and the surface Co–Mo catalyst particles during synthesize of CNTs as observed earlier over Co–Mo/SiO₂ catalysts [7]. In the present case, such an equilibrium appeared at 10 sccm C_2H_2 flow rate. Catalyst deactivates by excess carbon when the flow rate increased up to 20 sccm and then deposits high amorphous carbon. In this case, a black shade of amorphous carbon appears in the whole focused area of the SEM image of CNTs. In our earlier CNTs growth investigations over Ni–Fe/Al₂O₃ catalysts, we also found such a behavior when we increased the C_2H_2 flow rate up to 30 sccm [6]. Alvarez et al. [7] have also ob-

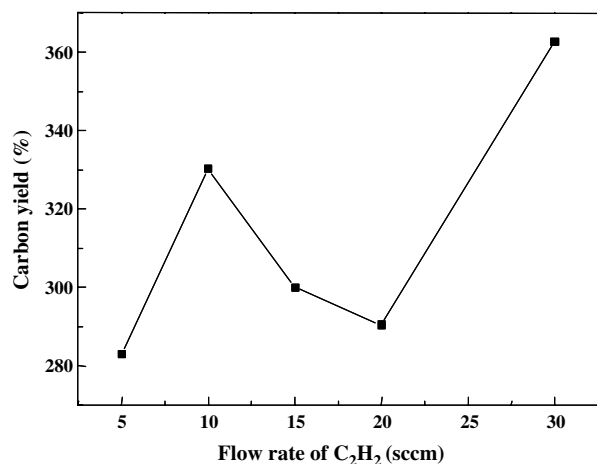


Fig. 6. Variation of carbon yields (%) as a function of C₂H₂ concentration over 30 wt.% Co–Mo/MgO catalyst for 30 min growth time at 800 °C.

served the deactivation and formation of only amorphous carbon over Co–Mo/SiO₂ catalyst at 20:80% flow of CO:He at 800 °C. The carbon yield gradually increased with increasing growth temperature from 500 to 800 °C and then decreased with increasing temperature up to 1000 °C. Longer growth time than 30 min increased carbon yield but the CNTs showed higher disordered carbon.

Fig. 7 shows the X-ray diffraction (XRD) profiles of the 30 wt.% Co–Mo/MgO catalyst accompanied with as-grown CNTs for 30 min at 800 °C. It can be seen that XRD peak for CNTs appeared at 2θ value of 26° whereas for graphite the peak appears at 26.5° [26]. The presence of a small peak at 39.2° indicates the generation of Mo₂C [15,27]. The rest part of this spectrum is analogous to that of the catalyst with comparably low peak intensities. It indicates that as-grown CNT sample

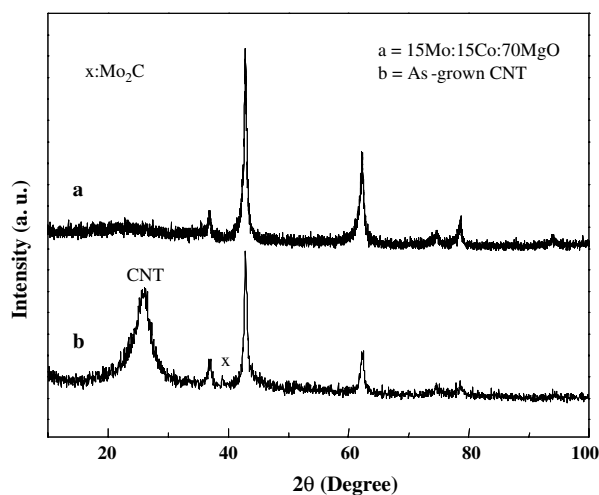


Fig. 7. XRD spectra of (a) 30 wt.% Mo–Co/MgO catalyst and (b) as-grown CNTs over the catalyst for 30 min at 800 °C under 10/100 sccm C₂H₂/H₂ flow.

consists of non-reactive catalyst still in the form of solid solution that was not decomposed at the growth temperature of 800 °C. No metal crystallites were released from solid solution to grow CNTs. It means that solid solution was not participated in the CNTs growth. It seems reasonable, because the decomposition temperature of Co containing solid solution CoO–MgO is around 900 °C [16,18,19].

Now the questions are why and how inactive Mo dramatically increased the catalytic activity of Co in bimetallic Co–Mo/MgO catalysts to grow SWNTs and MWNTs. Moreover, why the 5 and 10 wt.% Co–Mo/MgO catalysts produced SWNTs and 20–40 wt.% Co–Mo/MgO catalysts produced MWNTs. On the basis of the achieved information and literature support, we are discussing the matter below. In case of 5 and 10 wt.% Co–Mo/MgO catalysts, the key point of growing SWNTs was the CoMoO₄ species. The decomposition temperature of CoMoO₄ phase is lower than that of MoO₃ species and it is around 550 °C [9]. In the present study, CNTs were grown at 800 °C over the catalysts in C₂H₂/H₂ mixture after activating them in H₂ atmosphere for 1 h at 500 °C. Although the activation temperature was not sufficient to decompose the CoMoO₄ species, the growth temperature was high enough to decompose it into highly dispersed and very small particles of Co²⁺ and MoO₃. The H₂ gas instantly reduced Co²⁺ to metallic cobalt cluster of very small sized and it participated to the decomposition reaction of C₂H₂ to grow SWNTs. The appearance of bundles of SWNTs (Fig. 4a) indicates that each small metallic particle of cluster is participating in growing a SWNT. In the CNTs growth stage, the decomposition of CoMoO₄ species definitely enhanced from the usual characteristics of Mo to form the free species MoO₃ and to convert to the stable species Mo₂C. It has been reported that the oxide species of Mo transforms into Mo₂C during the decomposition reaction of CO, CH₄, C₂H₆ and C₂H₂ [9,15,28]. A hydrocarbon having higher number of carbon than one was found to lowers the phase transformation temperature of molybdenum oxide to its carbide. Moreover, C₂H₂ was found as a good carburizing agent for preparing Mo₂C with small crystallites. The Mo₂C synthesized by C₂H₂ decomposition showed morphology similar to that of the parent oxide [15]. It means that C₂H₂ is capable to produce Mo₂C from the CoMoO₄ phase without disturbing the size of Co cluster released from this phase. The formation of Mo₂C released extremely small sized cluster of Co²⁺ that instantly reduced to metallic cobalt cluster and participated to the decomposition reaction of C₂H₂ to grow SWNTs.

In the case of 20–40 wt.% Co–Mo/MgO catalysts, the growth of MWNTs occurred from large Co cluster. Large metallic cluster of cobalt released from the reduction of Co²⁺ and/or Co₃O₄ phase during the reaction temperature 800 °C. In these catalysts, there

also had chance to grow good amount of SWNTs from the CoMoO_4 species. But, the produced small Co clusters have high possibility to coalesce with neighboring large Co clusters due to high dispersion of Co_3O_4 phase and from intrametallic attraction. However, in case of CNTs grown over 20 wt.% Co–Mo/MgO catalyst, in the Raman spectrum (Fig. 3c), we observed RBM peaks of very low intensities in the range of frequency where RBM peaks appeared for the SWNTs grown over 5 and 10 wt.% Co–Mo/MgO catalysts (Fig. 3a and b).

When we look at the SEM images of nanotubes (Fig. 2), we see that each tube ended by showing a white spot. These white spots originated from the metal clusters [6,24]. It indicates that the CNTs were grown by tip growth mode. The necessary carbon feed stock supplied from the catalytic decomposition of acetylene dissolved in metallic Co to form cobalt carbide eutectic, i.e., metastable cobalt carbide. This cobalt carbide eutectic on dissolving more carbon became oversaturated which then precipitated graphitic carbon in forms of tubes by keeping metallic cobalt cluster at the top end of the CNTs [29,30].

4. Conclusions

Carbon nanotubes (CNTs) were grown over impregnated 5–40 wt.% Co–Mo/MgO catalysts by decomposition of C_2H_2 at 800 °C. It was observed that the production of SWNTs and MWNTs highly depends on the amount of metals loading. The Mo/MgO catalyst showed no growth of CNTs. In Co–Mo/MgO catalysts, however the inactive Mo generated CoMoO_4 species which was the main precursor for the formation of active Co cluster to grow CNTs. The produced CoO–MgO solid solution remained non-reactive in the catalyst during the CNTs growth. Small cluster of cobalt was generated from small particle of CoMoO_4 species, and grew SWNTs over 5 and 10 wt.% Co–Mo/MgO catalysts. The particle size of CoMoO_4 increased with increasing metal loading and thus the size of released cobalt cluster increased. Larger cobalt clusters are also generated from Co_3O_4 phase in case of higher metal loadings. These larger cobalt clusters grew MWNTs over 20–40 wt.% Co–Mo/MgO catalysts. The present findings can be applied to produce large amounts of SWNTs and MWNTs over Co–Mo/MgO catalysts with an understanding of the reaction mechanism.

Acknowledgements

One of the authors (A.K.M.F.K.) acknowledges the Korean Federation of Science and Technology Societies (KOFST) for granting ‘Korean Brain Pool program fellowship 2003’.

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