Synthesis of multi-walled carbon nanotubes using CoMnMgO catalysts through catalytic chemical vapor deposition*

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The CoMgO and CoMnMgO catalysts are prepared by a co-precipitation method and used as the catalysts for the synthesis of carbon nanotubes (CNTs) through the catalytic chemical vapor deposition (CCVD). The effects of Mn addition on the carbon yield and structure are investigated. The catalysts are characterized by temperature programmed reduction (TPR) and X-ray diffraction (XRD) techniques, and the synthesized carbon materials are characterized by transmission electron microscopy (TEM) and thermo gravimetric analysis (TG). TEM measurement indicates that the catalyst CoMgO enclosed completely in the produced graphite layer results in the deactivation of the catalyst. TG results suggest that the CoMnMgO catalyst has a higher selectivity for CNTs than CoMgO. Meanwhile, different diameters of CNTs are synthesized by CoMnMgO catalysts with various amounts of Co content, and the results show that the addition of Mn avoids forming the enclosed catalyst, prevents the formation of amorphous carbon, subsequently promotes the growth of CNTs, and the catalyst with decreased Co content is favorable for the synthesis of CNTs with a narrow diameter distribution. The CoMnMgO catalyst with 40% Co content has superior catalytic activity for the growth of carbon nanotubes.

Keywords: CoMnMgO catalyst, carbon nanotubes, chemical vapor deposition, methane decomposition

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1. Introduction

Carbon nanotubes (CNTs) can be used in various fields, such as electronics, medicine, and catalysis.[1–3] Therefore, intense research efforts have been made to produce CNTs at a reasonable cost. To date, the most widely used method of synthesizing CNTs is the catalytic chemical vapor deposition (CCVD) method,[4] which appears to be the most promising way for large scale production at low cost and a relatively low temperature with cheap apparatus.

In the CCVD synthesis of CNTs, Fe, Co, and Ni nanoparticles supported on oxides, such as Al_2O_3,[5] SiO_2,[6] and MgO,[7] are usually used as catalysts. After the synthesis of CNTs, removal of the catalyst is required. It has been demonstrated that MgO could be dissolved from the synthesized carbon materials by simple and mild purification procedures without destroying the structure of CNTs. The structure and yield of CNTs are dependent on the catalyst type and size.[8] Especially, the catalyst size is directly proportional to the diameter of synthesized CNTs.[9]

Moreover, it has been found that the bimetallic catalyst can improve the yield of CNTs compared with the monometallic catalyst.[10,11] Since the monometallic catalyst is easily enclosed by the produced graphite layer, thus resulting in the deactivation of the catalyst, the addition of a promoter is needed for further improving the yield and quantity of the CNTs.

Hence, in the present study, the CNTs are synthesized using CoMnMgO containing three different amounts of Co, 60%, 40%, and 20% (mass percentage), and four catalysts 60CoMgO, 60CoMnMgO, 40CoMnMgO, and 20CoMnMgO are chosen to investigate the role of Mn in yielding the CNTs and the effect of the Co content on the diameter of the produced CNTs. The as-produced carbon products are characterized by TEM and TG analysis.

2. Experiment

2.1. Catalysts preparation

The Co, Mn and Mg nitrates (with a total metal concentration of 0.5 mol/L) were co-precipitated at PH 10 by sodium hydroxide. The precipitate was then filtered and thoroughly washed about six times with warm distilled water to eliminate sodium and nitrate ions. The precipitates were dried at 100 °C overnight and calcined at 400 °C for 4 h. The Mn content was 20% (mass fraction) in the CoMnMgO catalysts.

2.2. Synthesis of CNTs

100 mg of the catalyst powder was dispersed on a ceramic boat, and then placed in a horizontal quartz reactor (inner diameter = 3.5 cm) to grow CNTs. Firstly, the catalyst powder was reduced *in situ* in H_2 at 650 °C for 1 h. Subsequently, the system was switched to high purity methane (100 mL/min) for the methane cracking reaction for 1 h. After the reaction, the as-grown CNTs were cooled to room temperature in N_2 atmosphere.[4]

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2.3. Characterization

Temperature-programmed reduction (TPR) measurements were carried out at atmospheric pressure in a fixed-bed reactor. A 50-mg sample was loaded, and the reduction agent of 5% H_2/95% N_2 was introduced with a flow rate of 30 mL/min. The temperature of the reactor was increased linearly from 50 °C to 850 °C at a rate of 5 °C/min and kept at 850°C for 30 min. Subsequently, the effluent stream was analyzed for hydrogen by a thermal conductivity detector (TCD).[4]

Phase analysis was performed by power X-ray diffraction (XRD) through using a D/MAX-2500 (Rigaku Company) diffractometer with Cu Kα radiation. The scans were made over a range of 2θ values of 10 °C∼ 90°C.

Thermo gravimetric experiments (TGA Q500) for the samples were carried out under the flowing air, and heated up to the prescribed temperature 1000 °C with a heating rate of 10 °C/min.

Transmission electron microscopy (TEM) was taken on a Tecnai G2 F20 S-Twin microscope at an accelerating voltage of 200 kV.

3. Results and discussion

Temperature programmed reduction of H_2 (H_2-TPR) as displayed in Fig. 1 is usually employed for estimating the catalyst reducibility. The catalyst 60CoMgO presents two reduction peaks, one is centered at 270 °C and the other at around 450 °C∼850 °C. The first peak can be attributed to the reduction of Co^{3+} into Co^{2+}, and the second reduction is due to the reduction of Co^{2+} into metallic Co. For the CoMnMgO catalysts, the area of the first peak remarkably increases, and the maximum temperatures of the second peak are 690 °C, 750 °C, and 850 °C for 60CoMnMgO, 40CoMnMgO, and 20CoMnMgO, respectively. The increase of temperature indicates the stronger interaction among Co, Mn and Mg species as Co content decreases. Additionally, H_2 consumption of the second reduction peak decreases with the decrease of Co content, which is due to the reduction of the low Co amount.

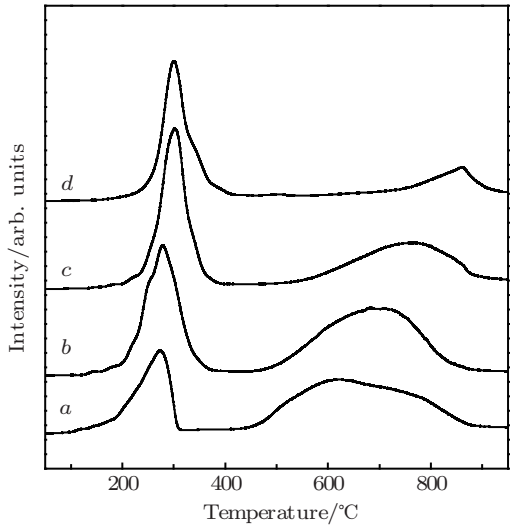


Fig. 1. H_2-TPR profiles for catalysts of curve *a* 60CoMgO, curve *b* 60CoMnMgO, curve *c* 40CoMnMgO, and curve *d* 20CoMnMgO.

The XRD profiles of the oxide catalysts are shown in Fig. 2. All the catalysts exhibit similar diffraction peaks, which can be attributed to spinel phase (Co_3O_4, JCPDS 42-1467; $MgCo_2O_4$, JCPDS 02-1073; $MnCo_2O_4$, JCPDS 23-1237). However, it is hard to distinguish between them because their diffractions are very similar.

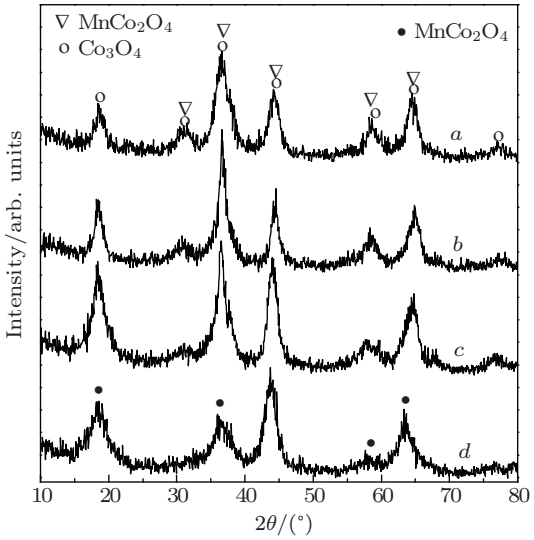


Fig. 2. XRD patterns of the catalysts of curve *a* 60CoMgO, curve *b* 60CoMnMgO, curve *c* 40CoMnMgO, and curve *d* 20CoMnMgO.

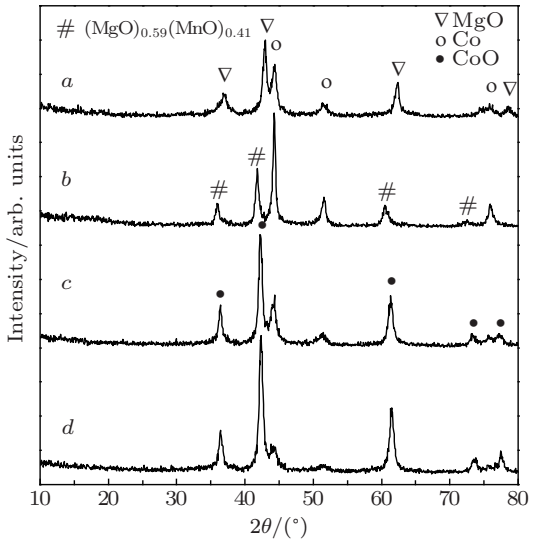


Fig. 3. Powder XRD patterns of the catalysts of curve *a* 60CoMgO, curve *b* 60CoMnMgO, curve *c* 40CoMnMgO, and curve *d* 20CoMnMgO, reduced in H_2 at 650 °C for 1 h.

The XRD profiles of the reduced catalysts are shown in Fig. 3. All the catalysts exhibit three peaks at 44.21°, 51.52°, and 75.85°, corresponding to the planes (111), (200), and

(220) of metallic Co (JCPDS15-0806), respectively. The crystallites sizes of the peak at $2\theta = 44.21^\circ$ are calculated based on Scherrer's equation for metallic Co, and the average crystallite sizes are estimated to be 14 nm for 60CoMgO, 17.9 nm for 60CoMnMgO, 13.5 nm for 40CoMnMgO, and 9.9 nm for 20CoMnMgO, respectively. The results show that compared with the CoMgO catalyst with the same Co content, the addition of Mn is conducible to the formation of large Co particles. Jiang *et al*.[12] also found that the sizes of the formed metallic Co particles in the reduced CoMn catalyst were larger than in the Co catalyst, which is consistent with our results. Furthermore, the particle size of metallic Co decreases as the Co content is reduced in the CoMnMgO sample. Additionally, $(MgO)_{0.59}(MnO)_{0.41}$ (JCPDS77-2379) is formed in the 60CoMnMgO catalyst. For 40CoMnMgO and 20CoMnMgO catalysts, the peaks at 36.5°, 42.4°, 61.5°, 73.7°, and 77.5°, correspond to the planes (111), (200), (220), (311), and (222) of CoO (JCPDS15-0806), respectively, accounting for the partial reduction of Co species and suggesting H_2 consumption of the second peak in the H_2-TPR is due to the reduction of CoO.

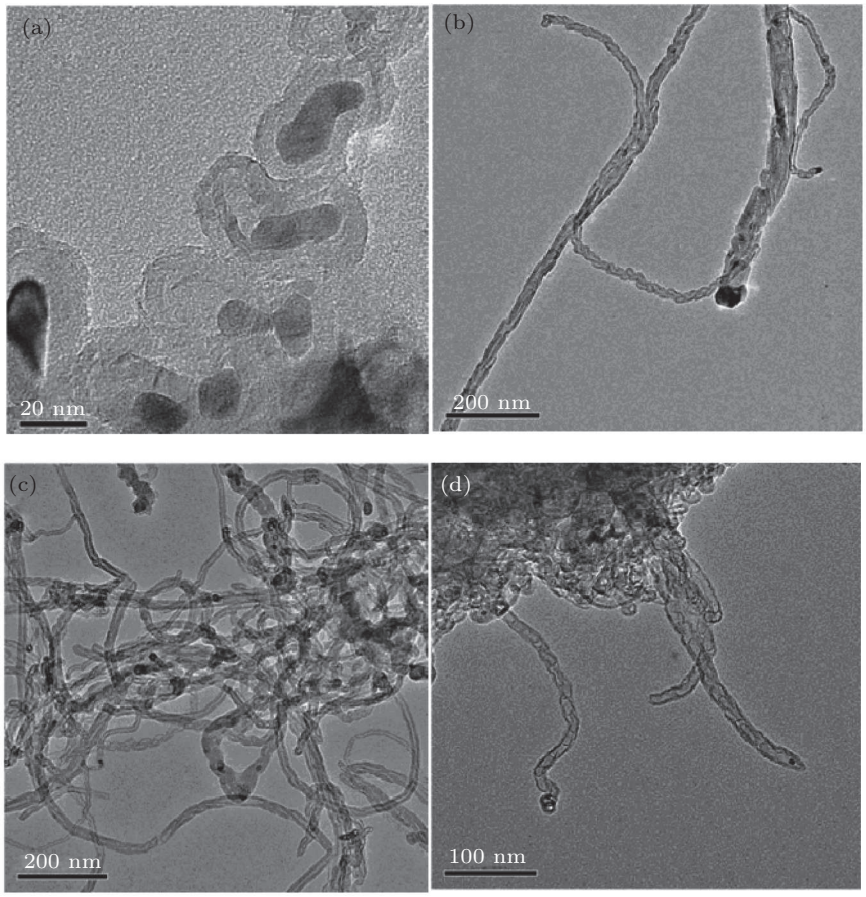


Fig. 4. TEM images of as-produced materials grown with catalysts of (a) 60CoMgO, (b) 60CoMnMgO, (c) 40CoMnMgO, and (d) 20CoMnMgO.

The 60CoMgO catalyst and CoMnMgO catalysts with various amounts of Co content are used for synthesizing the CNTs. For 60CoMgO catalyst, carbon onions are observed in the TEM image, as shown in Fig. 4(a). Numerous spherical-shape graphite covered catalyst particles are obtained, and some elongated catalyst particles are found inside the CNTs and carbon onions. The particles change in a similar manner to those found by Rümmeli's and Behr's groups.[13,14] In fact, CNTs and carbon onions could exert an internal pressure in a range of 10 GPa–30 GPa, which could result in the deformation of nanocrystal.[15] In this case, the graphite walls form a diffusion barrier around the catalyst particle and prevent the contact of CH_4 with the catalyst. Therefore, the catalyst particles are enclosed completely in the graphite layer, leading to the deactivation of the catalyst and an inability to participate in the CNTs growth.[16,17] On the contrary, all the CoMnMgO catalysts are active in the formation of CNTs. The catalyst particles (shown in Fig. 4(b)) are detected on the tips of CNTs by the TEM method, which is accessible to the carbon precursor. The addition of Mn prevents the formation of enclosed catalysts and subsequently promotes the formation of CNTs. Furthermore, some bamboo-like nanotubes are grown with using

the catalyst 20CoMnMgO, as displayed in Fig. 4(d).

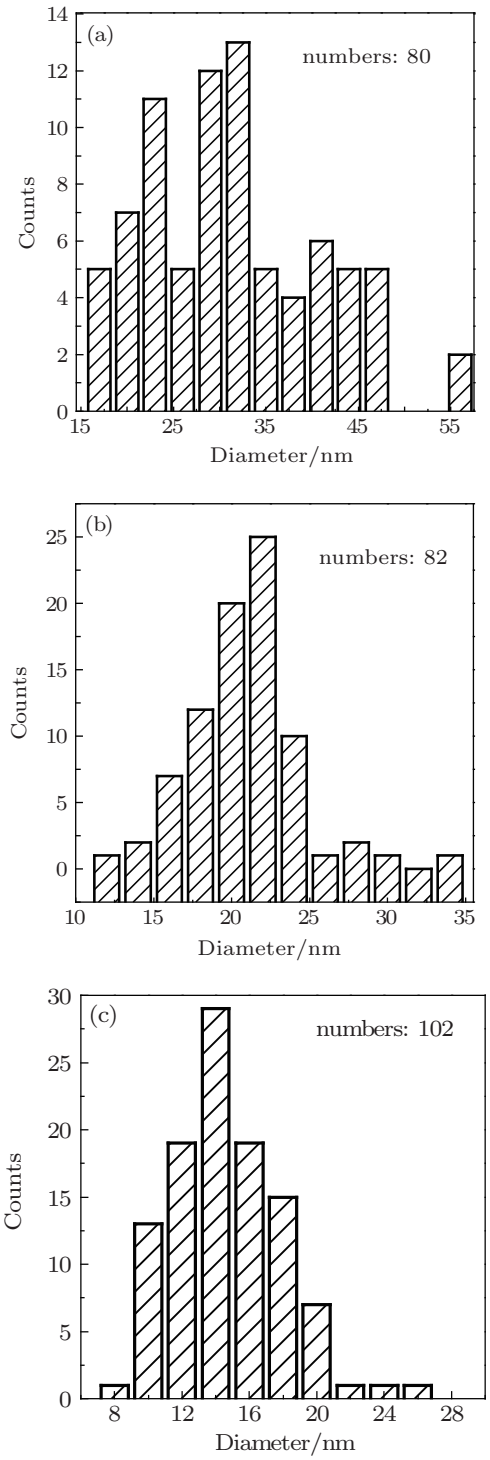


Fig. 5. External diameter distributions of CNTs grown with using the catalyats of (a) 60CoMnMgO, (b) 40CoMnMgO, and (c) 20CoMnMgO.

Figure 5 shows the outer diameter distributions of CNTs, determined by TEM. The average diameter of CNTs shows a decreasing trend in the sequence of catalysts: 60CoMnMgO > 40CoMnMgO > 20CoMnMgO. The variation trend may arise from the decrease of metallic Co particle sizes as shown in XRD results. A low Co content is conducible to a narrow diameter distribution. A possible reason is that a high Co content tends towards agglomeration, resulting in non-uniform diameter distribution of Co particles.

Table 1 shows the yields of carbon materials using different catalysts. The yields are 6.7%, 1040.0%, 1116.7%, and 70.0% for 60CoMgO, 60CoMnMgO, 40CoMnMgO, and 20CoMnMgO, respectively. It could be noted that the 60CoMgO exhibits very poor activity in the decomposition of CH_4 and growth of carbon material. The catalyst CoMgO is enclosed completely in the graphite layer in the early stage of reaction and does not participate in the further growth of CNTs, which should be responsible for the low yield of carbon nanomaterial. The addition of Mn into CoMgO dramatically improves the growth of carbon nanomaterial. Decomposed carbon species from CH_4 over CoMnMgO catalyst tend to grow CNTs continuously rather than to cover the catalyst. The 40CoMnMgO catalyst possesses a superior catalytic activity compared with the other three catalysts. Higher metal loadings could lead to the agglomeration of metal nanoparticles, resulting in large and non-uniform catalyst particles, thus the yield of CNTs on 60CoMnMgO decreases. On the other hand, lower metal loadings also reduce the yield of CNTs remarkably when the Co content is 20%. A possible reason is that Co metal nanoparticles serve as the catalytic sites for the growth of CNTs, and 20CoMnMgO could not provide adequate catalytic sites due to the low amount and difficulty in reducing Co species as represented in the H_2-TPR results.

Table 1. Yields of carbon materials with different catalysts.

Catalyst	60CoMgO	60CoMnMgO	40CoMnMgO	20CoMnMgO
Yield/%	6.7	1040.0	1116.7	70.0

Thermo gravimetric (TG) analysis is a widely employed method of estimating the carbon yield, the degree of crystallinity and the selectivity of catalysts for carbon nanotubes.[18–20] In general, those losses are attributed to the removal of amorphous carbon (300 °C∼400 °C), CNTs (400 °C∼700 °C) and massive graphite carbon (> 700 °C) at the different oxidation temperatures.[21–27] Figure 6 presents the weight losses of these products during heating in air. For the products grown with using 60CoMgO catalyst, three major weight losses are recorded, indicating that three types of carbon deposits are formed in the synthesized materials. As observed from TG analyses, most of the weight loss is associated with CNTs for the products grown with using the CoMnMgO catalysts, indicating high selectivity to the growth of CNTs, and the weight losses are 23.4%, 91.7%, 92.1%, and 50.9% for 60CoMgO, 60CoMnMgO, 40CoMnMgO, and 20CoMnMgO, respectively, consistent with the yields of carbon materials.

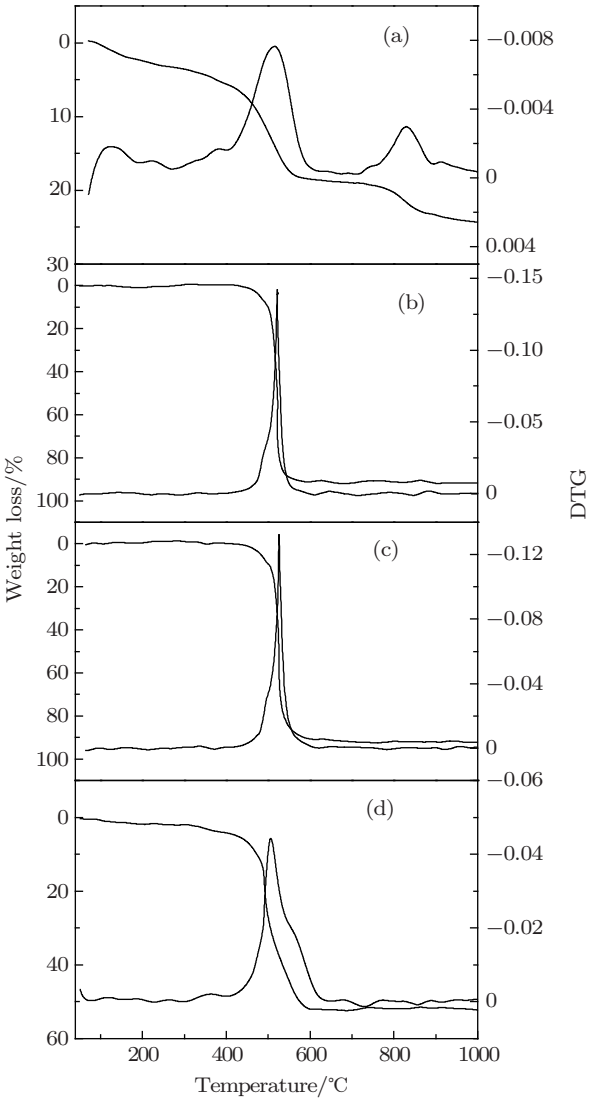


Fig. 6. TG and DTA curves of the obtained products from catalysts of (a) 60CoMgO, (b) 60CoMnMgO, (c) 40CoMnMgO, and (d) 20CoMnMgO.

4. Conclusions

The synthesis of CNTs using CoMgO and CoMnMgO catalysts are studied, and the effects of Mn addition on the carbon yield and structure are also investigated. The addition of Mn can change the morphology of carbon material grown on the catalysts and avoid forming the enclosed catalysts in the graphite layer, subsequently promote the growth and yield of CNTs. The diameter of CNTs decreases with the Co content decreasing for CoMnMgO catalyst series. A low Co content was beneficial for CNTs with a narrow diameter distribution and the 40CoMnMgO catalyst has superior catalytic activity for CNTs growth.

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