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Effect of FeO_x loaded on CoO_x/Al_2O_3 catalyst for the formation of thin-walled carbon nanotubes

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ABSTRACT

Effects of FeO_x loaded on CoO_x/Al_2O_3 catalyst on the yield and morphology of the produced carbon nanotubes were studied. The findings showed that the addition of a small amount of FeO_x on the CoO_x/Al_2O_3 catalyst provoked the formation of carbon nanotubes with a thin wall structure. The results also revealed that an increase in FeO_x content decreased the yield of carbon nanotubes. An optimized weight ratio of CoO_x to FeO_x was found to be 8:2 (w/w) whereby the catalyst of this composition grew carbon nanotubes with a thin wall structure and not of diminutive carbon yield.

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1. Introduction

Carbon nanotubes have created an active area of current research because of their unique structural, mechanical, and electrical properties [1]. They are generally considered as promising building blocks for nanoscale devices. Several nanoelectronics devices based on carbon nanotubes such as quantum wires, field effect transistors, field emitters and diodes have been demonstrated [2–5]. It is well accepted that the properties of carbon nanotubes, including electrical and mechanical properties depend strongly on their chirality, diameter, and wall thickness [6–8]. The interaction or coupling between the constituent graphene layers for carbon nanotubes with thick walls results in their physical and chemical properties being more complicated. On the other hand, carbon nanotubes with smaller diameters and thinner walls are much needed in the miniaturization of electronic applications due to their excellent electronic and electrical properties.

Our previous results showed that the NiO/TiO_2 catalyst was effective in producing carbon nanotubes from methane and the activation energy for the process was one of the lowest ever reported in the literature [9]. However, the produced carbon nanotubes possessed a larger diameter (~40 nm) and a thick wall morphology. We had also demonstrated that FeO_x might induce the formation of carbon nanotubes with a thin wall structure [10]. Nevertheless, no further study was carried out to investigate the influence of FeO_x on the morphology of nanotubes grown. Hence, this letter is aimed at reporting the effect of FeO_x loaded on the CoO_x/Al_2O_3 catalyst on carbon yield and morphology of the carbon nanotubes synthesized via methane decomposition.

2. Experimental

$Co(NO_3)_2.6H_2O$ (supplied by Aldrich) and $Fe(NO_3)_2.9H_2O$ (supplied by Merck) were used as metal sources for the preparation of CoO_x and FeO_x. Alumina (supplied by Ajax) was used as a catalyst support. All the catalysts used in this study were prepared using a conventional impregnation method. The experimental setup and the catalyst preparation procedures had been reported previously [10–12]. The synthesis of carbon nanotubes was carried out at atmospheric pressure in a stainless steel fixed-bed reactor at a temperature of 700 °C. The product gases were analyzed using on-line gas chromatography (Hewlett-Packard Series 6890, USA). Carbon nanotubes deposited on the catalysts were analyzed using a transmission electron microscope (TEM) (Philips, CM12) and a scanning electron microscopy (SEM) image of the catalyst particles was taken using LEO Supra 50 VP FESEM. An X-ray diffraction (XRD) pattern of the catalyst after reaction was measured by Bruker D8 Advance Powder Diffractometer. Intensity was measured by step scanning in the 2θ range of 20–70° with a step of 0.02° and a measuring time of 2 s/point.

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Table 1
Carbon yields of CoO_x/Al_2O_3, CoO_x–FeO_x/Al_2O_3 and FeO_x/Al_2O_3 catalysts in methane decomposition at 700 °C.

Catalysts	Carbon yield (%)
CoO_x/Al_2O_3	187
$8CoO_x$–$2FeO_x/Al_2O_3$	134
$6CoO_x$–$4FeO_x/Al_2O_3$	104
$4CoO_x$–$6FeO_x/Al_2O_3$	66
$2CoO_x$–$8FeO_x/Al_2O_3$	25
FeO_x/Al_2O_3	–

Carbon yields (%) as defined below were evaluated for CoO_x/Al_2O_3, CoO_x–FeO_x/Al_2O_3 and FeO_x/Al_2O_3 catalysts after 30 min of reaction.

$$\text{Carbon yield}(\%) = \frac{\text{Weight of carbon deposited on catalyst}}{\text{Weight of alloy portion of catalyst}} \times 100.$$

3. Results and discussion

Table 1 shows the yields of carbon obtained for CoO_x/Al_2O_3, CoO_x–FeO_x/Al_2O_3 and FeO_x/Al_2O_3 catalysts from methane decomposition at 700 °C. The results showed that carbon yield decreased with an increase in FeO_x loading on the CoO_x/Al_2O_3 catalyst. The yields recorded for the catalysts with weight ratios of CoO_x to FeO_x of 10:0, 8:2, 6:4, 4:6, and 2:8 were 187, 134, 104, 66, and 25%, respectively. This shows that the continual increase in FeO_x content led to a decrease in the catalyst activity. As shown in Table 1, FeO_x supported on Al_2O_3 was not active in methane decomposition at 700 °C. As a consequence, incorporating a large quantity of FeO_x with CoO_x/Al_2O_3 reduced catalytic activity in methane decomposition markedly. For studying the effect of FeO_x loading on the morphology of the grown carbon nanotubes, TEM was used to examine the reacted catalysts.

Fig. 1 shows the TEM images of carbon nanotubes deposited on CoO_x/Al_2O_3, $8CoO_x$–$2FeO_x/Al_2O_3$, $6CoO_x$–$4FeO_x/Al_2O_3$, and $4CoO_x$–$6FeO_x/Al_2O_3$ catalysts from methane decomposition at 700 °C. In Fig. 1a, carbon nanotubes grown on the CoO_x/Al_2O_3 catalyst possessed significant hollow cores and the average diameter calculated was ca. 9.4 nm. It was found that adding a small amount of FeO_x on CoO_x/Al_2O_3 saw the growth of carbon nanotubes of comparatively smaller in diameter. Moreover, it can be seen in Fig. 1b that carbon nanotubes grown on the $8CoO_x$–$2FeO_x/Al_2O_3$ catalyst had thinner walls compared to those grown on the CoO_x/Al_2O_3 catalyst. These grown nanotubes had an average diameter of ca. 7.3 nm. Carbon nanotubes with a thin wall structure were also grown on the $6CoO_x$–$4FeO_x/Al_2O_3$ catalyst as shown in Fig. 1c and the measured average diameter of the nanotubes was ca. 6.8 nm. Fig. 1d shows the TEM image of carbon nanotubes grown after methane decomposition over the $4CoO_x$–$6FeO_x/Al_2O_3$ catalyst. As expected, thin-walled carbon nanotubes were formed on the catalyst. The average diameter of the nanotubes measured was 7.1 nm, almost similar to the nanotubes grown on other FeO_x-promoted catalysts. However, the length of the grown nanotubes was obviously shorter for a catalyst with high loaded FeO_x. An explanation for this was that the length of carbon nanotubes is directly dependent on the activity and deactivation rate of the catalyst. The greater the deactivation rate is, the shorter the grown carbon nanotubes are. For this reason, the formation of shorter carbon nanotubes on high loaded FeO_x catalysts is mainly caused by the reduced catalytic activity and the greater deactivation rate of these catalysts.

As shown in Table 1, the FeO_x/Al_2O_3 catalyst was not active in methane decomposition at 700 °C. Thus, no carbon nanotubes could be grown from the said catalyst. Differently, the CoO_x/Al_2O_3 catalyst was active in methane decomposition and gave the growth of carbon nanotubes but with a thicker wall structure. Therefore, it can be speculated that the formation of thin-walled carbon nanotubes on FeO_x-promoted catalysts was induced by the formation of the CoO_x–FeO_x alloy on Al_2O_3 support and we believe that this alloy possessed the selectivity in growing carbon nanotubes with a thinner wall structure. The TEM studies of the used catalysts showed that FeO_x loaded catalysts grew carbon nanotubes with almost consistent diameter and wall thickness,

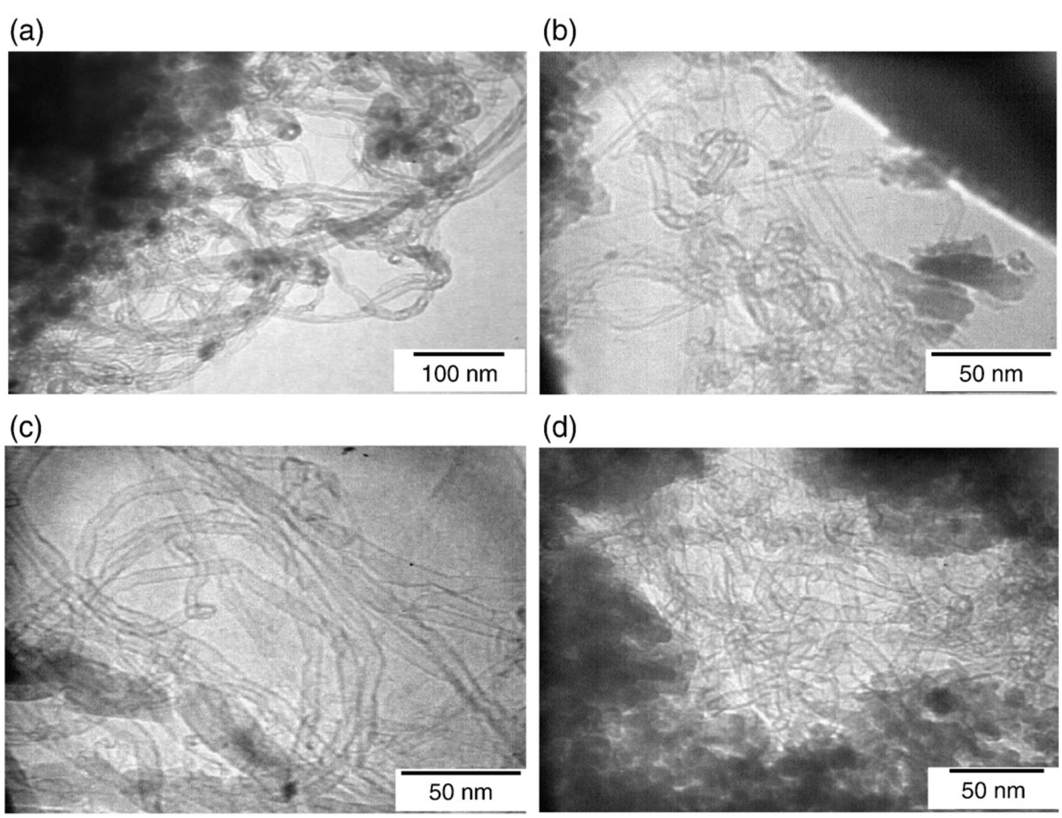

Fig. 1. TEM micrographs of carbon nanotubes grown on (a) CoO_x/Al_2O_3, (b) $8CoO_x$–$2FeO_x/Al_2O_3$, (c) $6CoO_x$–$4FeO_x/Al_2O_3$ and (d) $4CoO_x$–$6FeO_x/Al_2O_3$ at 700 °C.

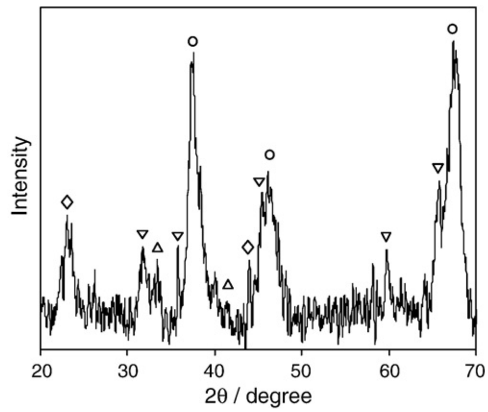

Fig. 2. XRD pattern of the $8CoO_x$–$2FeO_x/Al_2O_3$ catalyst after methane decomposition at 700 °C. (▽) Co_3O_4, (△) Fe_2O_3, (○) Al_2O_3, (◇) graphite.

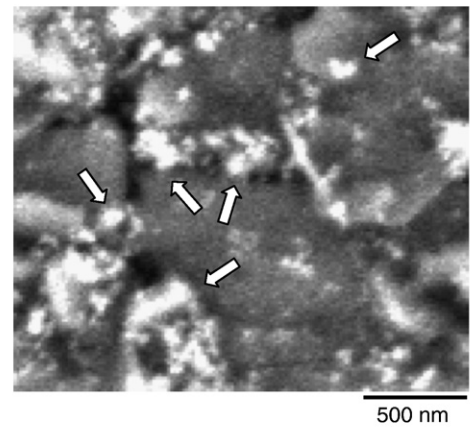

Fig. 4. SEM micrograph of the $8CoO_x$–$2FeO_x/Al_2O_3$ catalyst.

regardless of the percentage of FeO_x loading. The XRD pattern of the $8CoO_x$–$2FeO_x/Al_2O_3$ catalyst after the reaction is shown in Fig. 2. The diffraction peaks due to Co_3O_4, Fe_2O_3, Al_2O_3 and graphite were noted in the XRD pattern. The diffraction peaks at 23° and 44°, corresponding to (002) and (100) reflections of the graphite, indicated that the carbon deposited on the catalyst has a graphite-like structure. The graphitic interplanar distance d_{002} was determined from Bragg's law. The calculated interplanar distance is 0.378 nm. By taking the thickness of each graphene layer and the spacing of the graphitic interplanar as 0.142 nm [13] and 0.378 nm respectively, the number of the graphene layers can be estimated from the equation: $\tau = 0.142 + 0.378\ (n-1)$, where τ represents the thickness of the nanotube wall (each side, nm) and n the number of graphene layers. Based on this equation, it can be estimated that the majority of thin-walled carbon nanotubes grown on the CoO_x–FeO_x/Al_2O_3 catalysts consisted of only 2–4 graphene layers. However, the detailed wall structure of the nanotubes still needs to be further characterized by high-resolution TEM (HRTEM).

Fig. 3 shows the summary of carbon yields, average diameters and average number of graphene layers ($\acute{n}$) of carbon nanotubes synthesized over CoO_x/Al_2O_3, $8CoO_x$–$2FeO_x/Al_2O_3$, $6CoO_x$–$4FeO_x/Al_2O_3$ and $4CoO_x$–$6FeO_x/Al_2O_3$ catalysts. Concerning the yield and structure of the nanotubes produced over these catalysts, it can be accentuated that $8CoO_x$–$2FeO_x/Al_2O_3$ is the most suitable catalyst in growing these thin-walled nanotubes. Undeniably, the higher loaded FeO_x catalyst is not appropriate because of lower carbon yield and the formation of shorter carbon nanotubes. The SEM micrograph of the $8CoO_x$–$2FeO_x/Al_2O_3$ catalyst is shown in Fig. 4 so as to divulge the morphology of the catalyst particles. The SEM micrograph reveals bright and dark contrast under a quantum back scattered electron detector (QBSD). The bright spots in the QBSD image represent the metal-rich regions (CoO_x–FeO_x) (indicated by arrows) and the darker areas are assigned to the alumina support. As shown in the micrograph, the metal oxide crystallites distributed on the surface of alumina were irregularly shaped. It is important to point out that no catalyst particles were present at the tips of carbon nanotubes grown on CoO_x–FeO_x/Al_2O_3 catalysts, as shown in the TEM images of Fig. 1. This reveals that carbon nanotubes grown on the CoO_x–FeO_x/Al_2O_3 catalysts followed the based-growth model, in which CoO_x–FeO_x crystallites positioned on the alumina surface were responsible for the growth of carbon nanotubes from the methane decomposition.

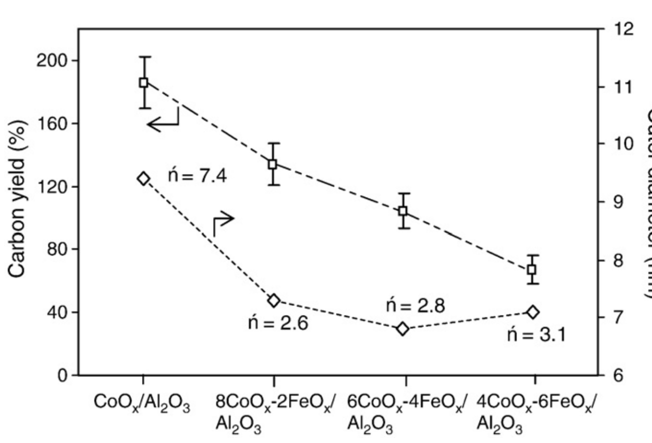

Fig. 3. A summary of carbon yields, average outer diameters and average number of graphene layers ($\acute{n}$) of carbon nanotubes grown over CoO_x/Al_2O_3, $8CoO_x$–$2FeO_x/Al_2O_3$, $6CoO_x$–$4FeO_x/Al_2O_3$ and $4CoO_x$–$6FeO_x/Al_2O_3$ catalysts at 700 °C.

4. Conclusions

Thin-walled carbon nanotubes were synthesized over the CoO_x–FeO_x/Al_2O_3 catalyst from methane decomposition at 700 °C. It was found that FeO_x was the main promoter that provoked the formation of thin-walled carbon nanotubes. The examination of the carbon morphology and carbon yield revealed that the high loaded FeO_x catalyst resulted in a lowered carbon yield and formation of shorter tubes. The desirable CoO_x to FeO_x weight ratio was found at 8:2 (w/w) as the catalyst of this composition showed its ability to produce carbon nanotubes with a thin wall structure and not of diminutive carbon yield.

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