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# THE SYNTHESIS OF THIN-WALLED CARBON NANOTUBES OVER $CoO-Fe_2O_3$ BASED CATALYSTS

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**Abstract** Thin-walled carbon nanotubes were produced from methane decomposition at 700°C over $CoO-Fe_2O_3/Al_2O_3$ catalysts. The effects of $Fe_2O_3$ loading on $CoO/Al_2O_3$ catalyst towards catalytic activity and morphology of produced carbon nanotubes were studied. The results show that the addition of a small amount of $Fe_2O_3$ into $CoO/Al_2O_3$ catalyst grew carbon nanotubes having thin wall structure. The increase of $Fe_2O_3$ content decreased the carbon nanotubes yield. Concerning the yield and the morphology of carbon nanotubes produced the appropriate weight ratio of CoO to $Fe_2O_3$ in growing thin-walled carbon nanotubes fell at 8:2.

## Introduction

Carbon nanotubes have created an active area of research because of their unique structural, mechanical, and electrical properties (Dresselhaus *et al.*, 2001). 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 (Tans *et al.*, 1998; Fuhrer *et al.*, 2000; Baughman *et al.*, 2002; Zhou *et al.*, 2002). In this study, carbon nanotubes were synthesized via catalytic decomposition of methane. The use of methane as carbon source is due to the fact that methane is the primary composition of natural gas which is cheap and highly abundant in Malaysia. Our previous results show that $NiO/TiO_2$ catalyst is effective in producing carbon nanotubes with the lowest activation (Zein *et al.*, 2004). However, the produced carbon nanotubes possessed larger diameter (~ 40 nm) and thicker wall morphology.

The physical and chemical properties of carbon nanotubes are more complicated for carbon nanotubes with thicker wall due to the interaction or coupling between the constituent graphene layers. Carbon nanotubes with smaller diameter and thinner wall are much needed in the miniaturization electronic applications due to their excellent electronic and electrical properties. Recently, we have reported that carbon nanotubes with improved quality were produced over $CoO-MoO/Al_2O_3$ catalyst and thin-walled carbon nanotubes over $CoO-Fe_2O_3/Al_2O_3$ catalyst (Chai *et al.*, 2006). Carbon nanotubes synthesized from both the catalysts had average diameters of below 10 nm. In this study, further works were carried out in investigating the effect of $Fe_2O_3$ loading on $CoO/Al_2O_3$ catalyst on the catalytic activity and the morphology of grown carbon nanotubes with the aims of obtaining the desirable CoO to $Fe_2O_3$ weight ratio in growing thin-walled carbon nanotubes.

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## Material and Methods

$Co(NO_3)_2.6H_2O$ (supplied by Aldrich) and $Fe(NO_3)_2.9H_2O$ (supplied by Merck) were used as metal sources for the preparation of CoO and $Fe_2O_3$. Alumina (supplied by Ajax) was used as a catalysts support. All the catalysts tested in this study were prepared using conventional impregnation method.

The detailed experimental setup and catalyst preparation procedures have been reported previously (Chai *et al.*, 2006). 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 an on-line gas chromatograph (Hewlett-Packard Series 6890, USA) and the carbon nanotubes deposited on the catalysts were analyzed using a transmission electron microscope (TEM) (Philips, CM12). The catalytic performance of $CoO/Al_2O_3$, $CoO\text{-}Fe_2O_3/Al_2O_3$ and $Fe_2O_3/Al_2O_3$ catalysts were evaluated in terms of methane conversion (%), carbon yield (%) and catalytic duration (h) and these variables are defined as follows:

$$\text{Methane conversion (\%)} = \frac{\text{Mole of methane reacted}}{\text{Mole of methane input}} \times 100 \quad \text{....(1)}$$

$$\text{Carbon yield (\%)} = \frac{\text{Weight of carbon depoited on catalyst}}{\text{Weight of alloy portion of catalyst}} \times 100 \quad \text{....(2)}$$

Catalytic duration (time) = time taken for the conversion of methane attaining below 1%...........(3)

**Results and Discussion**

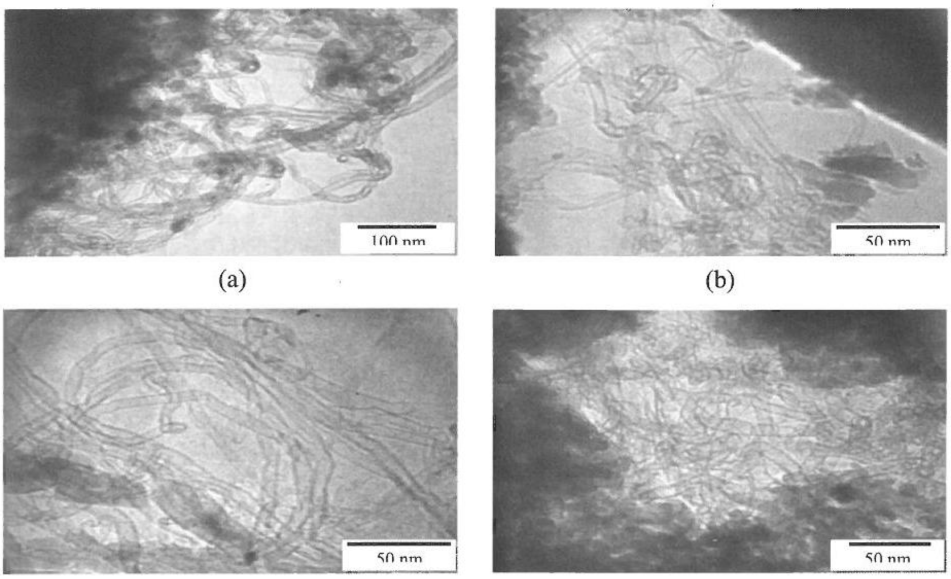
Table 1 shows the catalytic properties of $CoO/Al_2O_3$, $CoO\text{-}Fe_2O_3/Al_2O_3$ and $Fe_2O_3/Al_2O_3$ catalysts. The results showed that carbon yield decreased with an increase of $Fe_2O_3$ loading on $CoO/Al_2O_3$ catalyst in methane decomposition. The carbon yields obtained for the catalysts with the weight ratio $CoO:Fe_2O_3$ of 10:0, 8:2, 6:4, 4:6, and 2:8 were 223, 134, 104, 66, and 25%, respectively. This shows that the continual increase of $Fe_2O_3$ content led to a great decrease in the catalyst activity. The reduced activity of high loaded $Fe_2O_3$ catalyst is because of $Fe_2O_3$ on $Al_2O_3$ support was not active for methane decomposition at a reaction temperature of 700°C. As a consequence of this, incorporating $Fe_2O_3$ into $CoO/Al_2O_3$ catalysts reduced its catalytic activity markedly. For studying the effect of $Fe_2O_3$ loading on the morphology of the grown carbon nanotubes, TEM was used to analyze the used catalysts.

**Table 1.** Catalytic properties of tested catalysts for methane decomposition at 700°C

| Catalysts | Methane Conversion* (%) | Duration (h) | Carbon Yield ($g_C/g_{alloy}$), % |
|---|---|---|---|
| $CoO/Al_2O_3$ | 6.4 | 1 | 223 |
| $8CoO\text{-}2Fe_2O_3/Al_2O_3$ | 5.2 | 0.5 | 134 |
| $6CoO\text{-}4Fe_2O_3/Al_2O_3$ | 3.4 | 0.5 | 104 |
| $4CoO\text{-}6Fe_2O_3/Al_2O_3$ | 2.8 | 0.5 | 66 |
| $2CoO\text{-}8Fe_2O_3/Al_2O_3$ | 0.6 | 0.5 | 25 |
| $Fe_2O_3/Al_2O_3$ | - | - | - |

*Methane conversion after 5 minutes reaction

Figure 1 shows the TEM images of carbon nanotubes deposited on $CoO/Al_2O_3$, $8CoO\text{-}2Fe_2O_3/Al_2O_3$, $6CoO\text{-}4Fe_2O_3/Al_2O_3$, and $4CoO\text{-}6Fe_2O_3/Al_2O_3$ catalysts from methane decomposition at 700°C. In Figure 1a, it is shown that carbon nanotubes that grow on $CoO/Al_2O_3$ catalyst. These formed nanotubes possessed significant hollow cores with diameter of ca. 9.4 nm. The addition of a small amount of $Fe_2O_3$ into $CoO/Al_2O_3$ catalyst grew carbon nanotubes with comparatively thinner wall structure and smaller in diameter. As shown in Fig. 1b carbon nanotubes grow on $8CoO\text{-}2Fe_2O_3/Al_2O_3$ câtalysts have thinner wall structure compared to those formed on $CoO/Al_2O_3$ catalyst. These grown nanotubes had diameter of ca. 7.3 nm. Carbon nanotubes with similar structure were grown as well on $6CoO\text{-}4Fe_2O_3/Al_2O_3$ catalysts. As shown in Fig. 1c the calculated diameter for those nanotubes was ca. 6.8 nm. Figure 1d shows the TEM image of the used $4CoO\text{-}6Fe_2O_3/Al_2O_3$ catalysts. As expected, thin-walled carbon nanotubes were formed on the catalyst. The diameter of the nanotubes was almost similar to those grown on the previously mentioned $Fe_2O_3$ loaded catalyst, i.e. with diameter of ca. 7.1 nm. However, the length of the grown nanotubes was obviously shorter. This is expected since the growth rate of carbon nanotubes is directly dependent on the catalyst activity and catalyst deactivation rate. The higher the deactivation rate is, the shorter carbon nanotubes are grown. For this reason, the formation of shorter carbon nanotubes in this case is due to the reduced catalytic activity and fast deactivation rate of high loaded $Fe_2O_3$ catalysts.




(a) (b)

(c) (d)

**Figure 1.** TEM images of carbon nanotubes grown on (a) $CoO/Al_2O_3$; (b) $8CoO\text{-}2Fe_2O_3/Al_2O_3$; (c) $6CoO\text{-}4Fe_2O_3/Al_2O_3$; (d) $4CoO\text{-}6Fe_2O_3/Al_2O_3$ at 700°C

In this study, it was found that $Fe_2O_3/Al_2O_3$ catalyst was not active in the methane decomposition at 700°C. Thus, no carbon nanotubes were grown on the said catalyst. On the other hand, $CoO/Al_2O_3$ catalyst was active in methane decomposition and activate the growth of carbon nanotubes but with thicker wall structure. Therefore, the growth of thin-walled carbon nanotubes over $CoO\text{-}Fe_2O_3$ based catalysts was mainly induced by the $CoO\text{-}Fe_2O_3$ alloy formed on $Al_2O_3$ support and we believe that this alloy possessed the selectivity in growing carbon nanotubes with thinner wall structure. The TEM studies of the used catalysts showed that $Fe_2O_3$ loaded catalysts gave the formation of carbon nanotubes with almost consistent in diameter and wall thickness, regardless of the percentage of $Fe_2O_3$ loading. Owing to the very thin wall structure of the produced carbon nanotubes, we expected that they might have wall thickness of only 2 – 4 graphene layers. However, the detailed wall structure of carbon nanotubes needs further characterization using high-resolution TEM (HRTEM).

It is important to point out that no catalyst particles were present at the tips of carbon nanotubes formed. This reveals that carbon nanotubes grown on the $CoO\text{-}Fe_2O_3/Al_2O_3$ catalyst followed the mechanism of based-growth model, where the $CoO\text{-}Fe_2O_3$ alloy supported on $Al_2O_3$ subjected to the growth of carbon nanotubes. As regards to the yield and the morphology of the produced carbon nanotubes, $8CoO\text{-}2Fe_2O_3/Al_2O_3$ catalysts is the most suitable catalyst in growing this thin-walled structure. Undeniable, higher loaded $Fe_2O_3$ catalyst is not appropriate because of lower carbon yield and forming shorter carbon nanotubes. On the other hand, without the addition of $Fe_2O_3$, thicker wall carbon nanotubes were grown on $CoO/Al_2O_3$ catalyst. Therefore, $Fe_2O_3$ is the main promoter provokes the formation of thin-walled carbon nanotubes on $CoO/Al_2O_3$ catalyst.

## Conclusions

Thin-walled carbon nanotubes were synthesized using $CoO\text{-}Fe_2O_3/Al_2O_3$ catalyst in methane decomposition at 700°C. The examination of carbon morphology and carbon yield revealed that high loaded $Fe_2O_3$ catalyst in growing thin-walled carbon nanotubes is not encouraged as it reduced the catalytic activity and formed shorter carbon nanotubes. The desirable CoO to $Fe_2O_3$ weight ratio is at 8:2 (w/w) that the catalyst with this composition is able to grow carbon nanotubes with thin wall structure and is not subjected to intense diminution in the carbon yield.

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