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The Examination of NiO and CoO_x Catalysts Supported on Al₂O₃ and SiO₂ for Carbon Nanotubes Production by Catalytic Chemical Vapor Deposition of Methane

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The effects of catalyst components on the synthesis of carbon nanotubes (CNTs) are always the concern of many. The aim of this work is to examine the dependence of the morphology of CNTs formed on the nature of NiO and CoO_x catalysts supported on Al₂O₃ and SiO₂ at two different synthesis temperatures, i.e. 550°C and 700°C, respectively. Catalytic chemical vapor deposition (CCVD) of methane was adopted for synthesizing the nanotubes materials. The developed catalysts were characterized by X-ray diffraction (XRD) and temperature programmed reduction (TPR). The morphology of the produced carbon nanostructures was analyzed by transmission electron microscopy (TEM). The experimental result shows that CNTs were present on the surfaces of most of the tested catalysts. The yield of the CNTs produced over these catalysts was calculated. It was found that the yield decreased in the order of NiO/SiO₂>CoO_x/SiO₂>CoO_x/Al₂O₃>NiO/Al₂O₃ for the reaction at 550°C and in the order of NiO/SiO₂>CoO_x/Al₂O₃>CoO_x/SiO₂>NiO/Al₂O₃ at 700°C. The morphological analysis reveals that the structure of the CNTs depends upon the effects of metal-support interaction (MSI) and the synthesis temperature.

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1. Introduction :

Carbon nanotubes (CNTs), exhibiting superior unique structural, mechanical, optical and electrical properties [1], have great potential applications in advance technologies, such as quantum wires, field-effect transistors, field emitters, diodes, etc. [2-5]. Since their discovery in 1991 [6], research in the field of CNTs has undergone an exponential growth. In general, there are three principal methods adopted in producing CNTs : laser ablation, electric-arc-discharge and catalytic chemical vapor deposition (CCVD). By comparison, CCVD method is of great interest since it produces CNTs at a lower temperature, higher yield and at relatively low cost.

Different carbon-containing molecules, including methane, acetylene, ethylene, propylene, benzene, toluene, hexane, alcohol and acetone have been used as carbon feedstock in synthesizing CNTs [7, 8]. Among these hydrocarbons, methane is used in this study, concerning methane is the primary composition of natural gas which is cheap and highly abundant worldwide. Furthermore, methane has high stability at elevated temperatures in preventing self-pyrolysis [9, 10]. Self-pyrolysis of hydrocarbons will lead to the formation of amorphous carbon which is the impurity of the nanotubes product.

Previously, we have reported that TiO₂ supported NiO catalyst records the lowest activation energy in methane decomposition into CNTs and hydrogen [11]. In this paper, we will further examine the roles of metal oxides (CoO_x and NiO) and catalyst supports (alumina and silica) as well as the effect of synthesis temperatures on the morphologies and the yield of the CNTs produced via CCVD of methane.

2. Experimental :

2.1 Preparation of supported catalysts :

All the catalysts used in this study were prepared by conventional impregnation method. Ni(NO₃)₂.6H₂O (supplied by Aldrich) and Co(NO₃)₂.6H₂O (supplied by Aldrich) were used as the metal sources of NiO and CoO_x with each loading amount adjusted to 10 wt % for all the prepared catalyst samples. Both metals in nitrate form were first dissolved in distilled water and then impregnated onto SiO₂ powders (Cab-osil, supplied by RdH) and Al₂O₃ (supplied by Ajax), respectively. The impregnated samples were dried at 105 °C for 12 hours and calcined in air at 600 °C for 5 hours. The catalysts were then sieved to a size of 425 - 600 μm. The synthesized catalysts were tested in the reaction without a preceding reduction in hydrogen flow.

2.2 Synthesis of CNTs :

CNTs were synthesized via CCVD of methane at atmospheric pressure in a stainless-steel fixed-bed reactor (length and diameter of the reactor were 600 and 20 mm, respectively). High purity methane (99.999 % purity, supplied by Malaysian Oxygen Bhd.) was mixed with high purity nitrogen (99.999 % purity, supplied by Sitt Tatt Industrial Gases Sdn. Bhd.) with ratio 1:1 (v/v) before entering the reactor. The detailed experimental setup and procedure were reported previously [11 - 13]. For synthesizing nanotubes materials, 200 mg of catalyst was distributed in the middle part of the reactor for each run. The reactor was then mounted in an electrical furnace and heated to 550 °C or 700 °C in nitrogen flow. The efficiency of these catalysts were reported in carbon yield. The percentage of carbon yield is defined as follows:

$$\text{Carbon yield (\%)} = \frac{\text{weight of carbon deposited on a catalyst}}{\text{weight of CoO}_x \text{ or NiO portion of a catalyst}} \times 100$$

2.3 Characterizations :

The product gases were analyzed using an on-line gas chromatograph (Hewlett-Packard Series 6890, USA). The gas chromatograph was controlled on-line, using HP ChemStation Revision A. 06.01. [403] software. The conversions of methane recorded by on-line gas chromatograph were used to calculate the percentage of carbon yield. In this study, the methane decomposition reaction was stopped when the conversion of methane attains below 1 % for all the tested catalysts. The carbons deposited on the catalysts were analyzed using a transmission electron microscope (TEM) system (Philips, model CM12) that used an accelerating voltage of 80 kV to extract electrons and Soft Imaging System model SIS 3.0. X-ray diffraction (XRD) patterns of the fresh catalysts were measured by Siemens D-5000 diffractometer, using $\text{CuK}\alpha$ radiation and a graphite secondary beam monochromator. Intensity was measured by step scanning in the 2θ range of 10° - 75° with a step of 0.02° and a measuring time of 2 s per point. Temperature programmed reduction (TPR) was performed to determine the reducibilities of the catalyst samples. TPR studies were carried out on a Thermofinnigan TPDRO 1100 instrument. About 25 mg of fresh catalyst was placed in a U-tube quartz reactor. Prior to the reduction, the catalyst samples were pretreated in nitrogen flow (20 ml/min). The temperature was raised to 100°C from room temperature at a heating rate of $5^\circ\text{C}/\text{min}$, and held at 100°C for 10 min. After the pretreatment, the sample was cooled to room temperature and the carrier gas consisting of 5 % hydrogen balance nitrogen (20 ml/min) was allowed to pass over the samples. Subsequently, the temperature was increased from ambient to 1000°C at a heating rate of $5^\circ\text{C}/\text{min}$. The reduction was measured by monitoring the hydrogen consumption with the TCD detector.

3. Results :

3.1 XRD characterization :

The fresh catalysts were characterized using XRD as to understand the structures of NiO and CoO_x supported on

Al_2O_3 and SiO_2 , respectively. Figure (1) shows the XRD patterns of the four catalysts samples tested in this work. The representative peaks of NiO, Co_3O_4 , Al_2O_3 and SiO_2 are denoted in the XRD spectra. One can clearly observe that the peak of NiO ($2\theta = 37.4^\circ$) and Co_3O_4 ($2\theta = 36.9^\circ$) supported on SiO_2 are sharp and narrow which disclosed that both metal oxides were well crystallized on the SiO_2 support. The characteristics of these peaks also tell us that both NiO and Co_3O_4 crystallites on SiO_2 appeared in a larger size. On the other hand, broad peak observed for NiO ($2\theta = 37.4^\circ$) and Co_3O_4 ($2\theta = 36.9^\circ$) on Al_2O_3 support shows that NiO and Co_3O_4 were well dispersed on Al_2O_3 support and formed smaller crystallites [14].

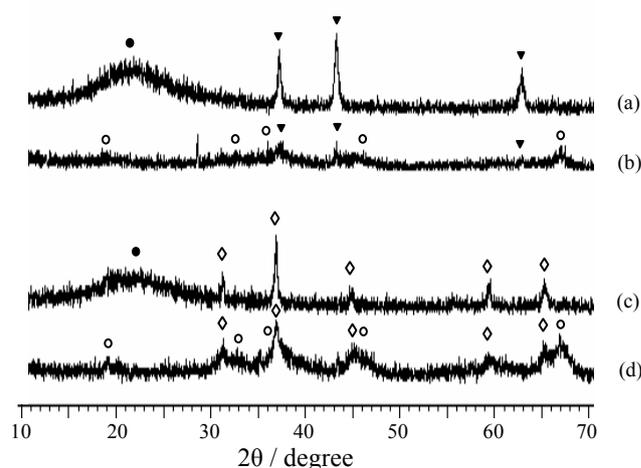


Figure (1) : XRD patterns of catalysts (a) NiO/ SiO_2 ; (b) NiO/ Al_2O_3 ; (c) CoO_x / SiO_2 ; and (d) CoO_x / Al_2O_3 . (▼) NiO; (◇) Co_3O_4 ; (●) SiO_2 ; (○) Al_2O_3 .

3.2 TPR characterization :

Metal-support interaction (MSI) effects are known to influence the reduction and dispersion of metal oxide of supported metal catalysts. A catalyst with strong MSI increases the difficulty in the reduction of the precursor oxide by increasing the reduction temperature. To determine the MSI effect of the catalysts, these samples were characterized by TPR. Figures (2a - d) illustrate the TPR profiles of NiO/ SiO_2 , NiO/ Al_2O_3 , CoO_x / SiO_2 , and CoO_x / Al_2O_3 catalysts, respectively. For NiO/ Al_2O_3 catalyst, two broad peaks were observed in the TPR profile. The first peak ($380 - 600^\circ\text{C}$) is assigned to the reduction of dispersed NiO, which was interacted with Al_2O_3 support, to form Ni. Another peak ($700 - 830^\circ\text{C}$) is associated with the reduction of NiAl_2O_4 to form Ni [15]. Broad reduction peaks shown in the TPR profile of NiO/ Al_2O_3 catalyst indicates the presence of highly dispersed NiO [16]. This is in agreement with the results obtained by the XRD studies. For CoO_x / SiO_2 catalyst, a major reduction peak centered at 320°C was observed. This peak is assigned to the reduction of Co_3O_4 to CoO , followed by reduction of CoO to Co . Small bumps noticed at ca. 400°C and 900°C are associated to the reduction of CoO residual and reduction of Co_2SiO_4 to Co , respectively [17, 18]. The TPR profile of CoO_x / Al_2O_3 catalyst possessed a major peak at ca. 430°C and a shoulder at ca. 520°C , corresponding to the reduction of Co_3O_4 to CoO and CoO to Co , respectively. Since none hydrogen

consumption was observed above 900 °C, it can be concluded that CoAl_2O_4 are not present in the catalyst in significant amount [19]. In general, it was observed that alumina-based catalysts possessed higher reduction temperatures than the silica-based catalysts. This reveals that alumina associated strongly with CoO_x and NiO. Comparatively, the interaction between CoO_x and NiO with silica is slightly weaker.

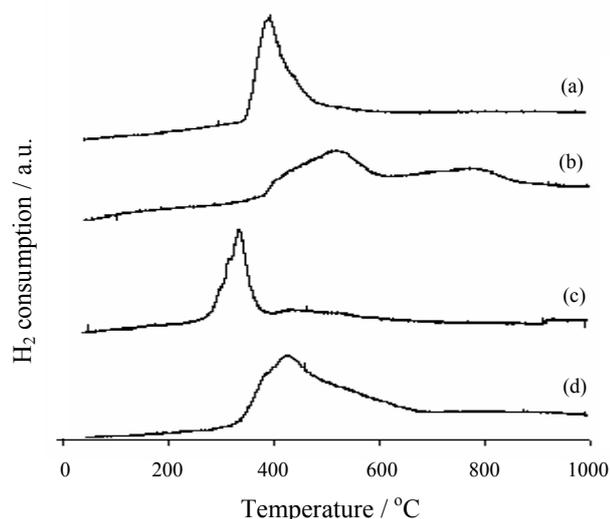


Figure (2) : TPR profiles of catalysts (a) NiO/SiO₂; (b) NiO/Al₂O₃; (c) CoO_x/SiO₂; and (d) CoO_x/Al₂O₃.

3.3 Carbon yield :

The activities of the catalysts in methane decomposition were studied at two synthesis temperatures, i.e. 550 °C and 700 °C, which represent mild and moderate temperatures. The amounts of CNTs deposited on these catalysts were calculated and shown in Table (1). Duration represents the catalytic lifetime where the tested catalysts were deactivated in the reaction except for NiO/SiO₂ that was still active after the duration. One can observe that carbon yield for these catalysts were higher at 550 °C than that at 700 °C. This was due to the shorter catalytic lifetime recorded for the catalysts reacted at the temperature of 700 °C. As shown in Table (1), the carbon yield decreased in the order of NiO/SiO₂ > CoO_x/SiO₂ > CoO_x/Al₂O₃ > NiO/Al₂O₃ for the reaction at 550 °C and in the order of NiO/SiO₂ > CoO_x/Al₂O₃ > CoO_x/SiO₂ > NiO/Al₂O₃ at 700 °C.

Table (1) : The amount of CNTs produced in methane CCVD at 550°C and 700°C, respectively.

Temperatures	Catalysts	Carbon yield	Duration
550°C	CoO _x /Al ₂ O ₃	710 %	1.5 h
	CoO _x /SiO ₂	1337 %	2.0 h
	NiO/Al ₂ O ₃	543 %	1.5 h
	NiO/SiO ₂	3451 %	3.0 h
700°C	CoO _x /Al ₂ O ₃	223 %	1 h
	CoO _x /SiO ₂	109 %	1 h
	NiO/Al ₂ O ₃	69 %	1 h
	NiO/SiO ₂	1032 %	1 h

3.4 Electron microscopy characterization :

TEM images of the carbon nanofilaments produced at 550 °C were shown in Figure (3). In Figure (3a) it can be noted that carbon nanofilaments deposited on NiO/SiO₂ at 550 °C exhibited solid cores and highly non-uniform diameters. Carbon nanofilaments grown on CoO_x/SiO₂ at 550 °C, shown in Figure (3b), appeared to have relatively uniform diameters and under the high TEM magnification, the narrow cavities could be clearly seen. The TEM examination further revealed that in most cases carbon nanofilaments with significant hollow cores were formed on the alumina-based catalysts (NiO/Al₂O₃ and CoO_x/Al₂O₃) at 550 °C, shown in Figure (3c) and Figure (3d). The synthesized nanofilaments on this type catalyst had smaller diameters compared to those deposited on silica-based catalysts (NiO/SiO₂ and CoO_x/SiO₂) at the similar reaction conditions. We define the carbon nanofilaments with such structure (significant hollow cores) as CNTs hereafter in this paper.

The morphology of the carbons synthesized at 700 °C was also characterized using TEM and the TEM images of these samples were shown in Figure (4). The analysis indicated that CNTs were grown on the surfaces of NiO/SiO₂, NiO/Al₂O₃, and CoO_x/Al₂O₃ catalysts after CCVD of methane. However, we could not observe any carbon nanofilaments grown on the surface of CoO_x/SiO₂ at 700 °C and the TEM image shown in Figure (4b) are mainly the catalyst particles of CoO_x/SiO₂. It was also found that the effect of reaction temperature was very momentous as the diameter of the CNTs formed were of smaller and their hollow cores clearly seen when they were produced at 700 °C. It was also noted that CoO_x assisted the formation of CNTs with narrower diameter distribution as the CNTs synthesized over supported CoO_x catalysts possessed smaller standard deviation compared to supported NiO catalysts. Table (2) summarizes the average diameters and standard deviations of the CNTs synthesized over these different catalytic materials at 550 °C and 700 °C.

Table (2) : Average diameters and standard deviations of CNTs synthesized over various catalysts at 550 °C and 700 °C.

Temperatures	Catalysts	Average diameters (nm)	Standard deviations (nm)
550°C	CoO _x /Al ₂ O ₃	14.6	4.5
	CoO _x /SiO ₂	27.0	5.8
	NiO/Al ₂ O ₃	12.6	8.5
	NiO/SiO ₂	43.1	18.0
700°C	CoO _x /Al ₂ O ₃	9.4	3.6
	CoO _x /SiO ₂	-	-
	NiO/Al ₂ O ₃	7.8	4.5
	NiO/SiO ₂	23.4	8.0

4. Discussion :

The XRD patterns of NiO/SiO₂ show strong and narrow NiO peak at $2\theta = 37.4^\circ$, suggesting that larger NiO crystallites were formed. Furthermore, the TPR studies revealed that NiO supported on silica has weak MSI. This suggests that NiO has great mobility on silica surface. NiO

in this condition did not incorporate strongly with the silica during the calcination step, thus formed larger sized NiO crystallites. Also, based on the XRD results, smaller sized NiO crystallites were formed and well distributed on

the NiO attached on the alumina support was active in growing CNTs. This model is known as base growth model [21, 22].

As shown in Figure (1) for the XRD patterns, broader

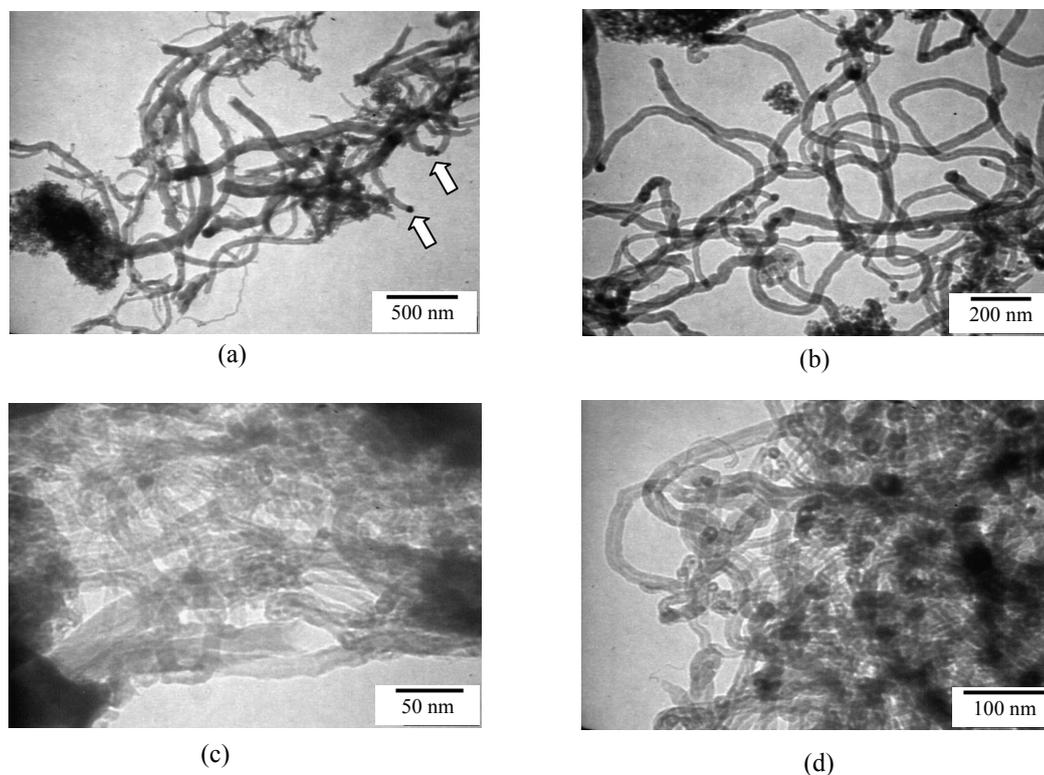


Figure (3) : TEM images of CNTs produced on (a) NiO/SiO₂; (b) CoO_x/SiO₂; (c) NiO/Al₂O₃; and (d) CoO_x/Al₂O₃ at 550°C.

alumina support. The TPR analysis disclosed that this phenomenon was mainly due to the strong interaction of NiO with alumina, preventing the sintering of adjacent NiO crystallites to form larger NiO clusters.

Comparing the TEM images shown in Figure (3) and Figure (4), we could see that the diameter of CNTs grown on NiO/Al₂O₃ were comparatively narrower than those grown on NiO/SiO₂. It is worthwhile to state that the NiO crystallites sizes on silica were not expected to be uniform because the sintering of NiO could occur randomly with any adjacent NiO crystallites. This was the reason why carbon nanofilaments of non-uniform diameters were produced on NiO/SiO₂. As previously mentioned, the interaction between NiO and silica is weak. This causes NiO particles to be detached easily from silica support during the growth of carbon nanofilaments. For this reason, most of the carbon nanofilaments synthesized on NiO/SiO₂ catalyst were with the presence of catalyst particles at their tips as indicated by arrows in Figure (3a) and Figure (4a). This growth model is widely referred to as tip growth model [20]. Comparatively, NiO sintered firmly with the alumina support and this restricted the detachment of NiO from alumina support during the growth of CNTs. This can be known when some of the CNTs observed showed none metal catalyst particles at the tips of the CNTs. In this case,

peak at $2\theta = 36.9^\circ$ was observed for CoO_x/Al₂O₃. In addition, the TPR profiles showed that CoO_x/Al₂O₃ possessed higher reduction temperature than CoO_x/SiO₂. These once again show us that CoO_x interacted strongly with alumina than silica. Investigating the produced CNTs on CoO_x/Al₂O₃ catalyst indicates that most of the CNTs formed had tips with open ends, suggesting that no catalyst particles were present at the tips of the nanotubes. This observation is evidence for the base growth model to take place in growing CNTs. On the other hand, the carbon nanofilaments formed on CoO_x supported on silica follows the tips growth model as it was observed that the catalyst particles were present at the tips of nanofilaments.

The effect of synthesis temperature in CCVD of methane influenced enormously the morphologies of the CNTs formed and the total carbon yield. At 550 °C, the tested catalysts were stable where the catalysts exhibited longer catalytic lifetime in producing CNTs. When the reaction temperature was increased to 700 °C, the catalysts were more active but unstable as the catalysts deactivated rapidly with the time on stream. These catalysts deactivated after one-hour reaction at 700 °C as shown in Table (1). In addition, the carbon yield recorded over these catalysts was greater at 550 °C than that at 700 °C. Therefore, lower reaction temperature (550 °C) seemed preferable for

obtaining greater carbon yield. However, higher reaction temperature (700 °C) is needed to obtain better CNTs which are well-graphitized and of smaller size. Comparing the morphologies of produced carbon nanofilaments shown in Figure (3) and Figure (4), we could notice that higher temperature is vital in realizing the formation of CNTs with significant hollow cores and of smaller diameters.

After comparing the effect of the catalyst supports, i.e. silica and alumina, on the morphologies of the produced CNTs, we can conclude that alumina provides a better template to support the metal oxides (NiO and CoO_x) for better dispersing and forming smaller metal oxide catalyst particles. These factors induce the formation of smaller diameter CNTs with hollow cores although the synthesis temperature was low. However, if considering the yield of carbon produced, regardless of the quality of CNTs, silica support is a better choice. This may be due to the silica has a weak interaction with both NiO and CoO_x. This finding concludes that the role of support is very important in CNTs production and choosing the right support should be considered for selectively producing CNTs with desirable morphology. When we examined CoO_x on two different supports, i.e. silica and alumina, in CCVD of methane, we observed that relatively uniform diameter CNTs were grown on both catalysts (Table 2). The diameter

agglomeration of CoO_x to form larger clusters seemed not to occur.

5. Conclusions :

Interaction between metal oxide and catalyst support, as well as the CNTs synthesis temperature greatly affect the yield, uniformity and morphology of the CNTs formed. Supported-CoO_x catalysts (CoO_x/SiO₂ and CoO_x/Al₂O₃) were of prime importance in producing CNTs with uniform diameters. On the contrary, supported-NiO catalysts (NiO/SiO₂ and NiO/Al₂O₃) produced CNTs with non-uniform diameters. The role played by the support can be understood on the basis of the interaction of the metal oxide particles. Alumina is a better support than silica for CoO_x and NiO due to its strong MSI effect, which allows high metal oxides dispersion. Such interactions prevent metal species from aggregating and forming unwanted large clusters that lead to producing larger and non-uniform diameter CNTs. Catalysts with strong MSI, such as alumina-based catalysts, grew easily smaller diameter CNTs with significant hollow cores at both 550 °C and 700 °C. This work further discloses that higher synthesis temperature is needed for producing CNTs with the following properties : i) higher graphitization; ii) smaller diameter; iii) narrower diameter distribution; and iv)

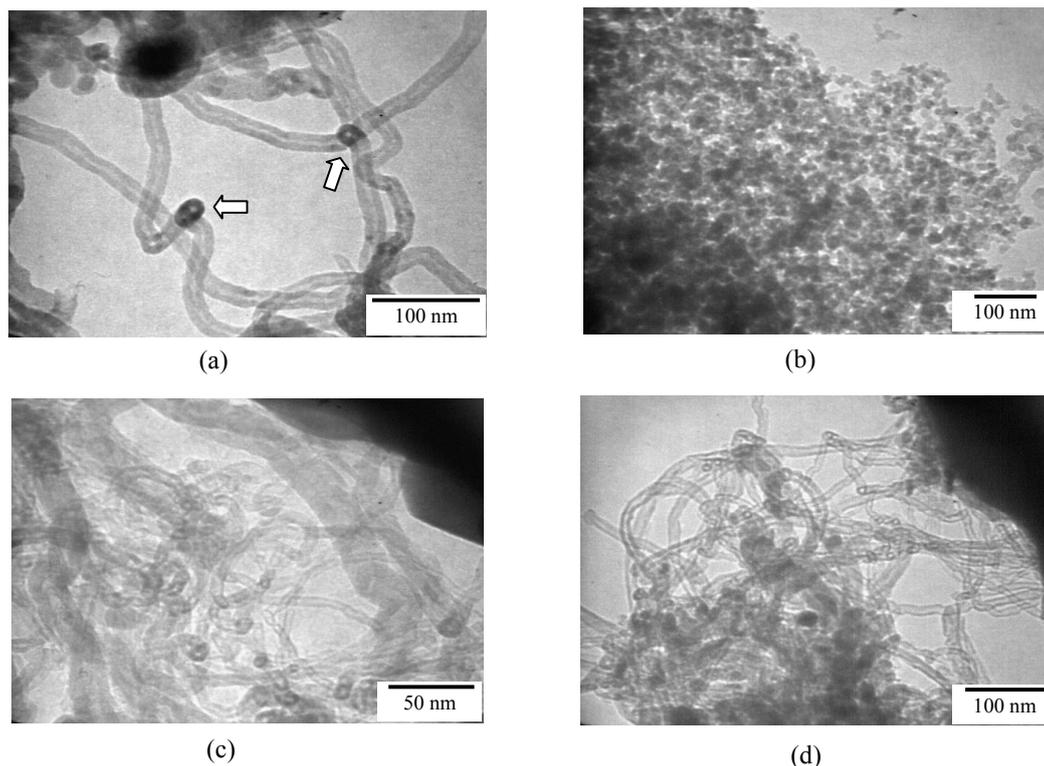


Figure (4) : TEM images of CNTs produced on (a) NiO/SiO₂; (b) CoO_x/SiO₂; (c) NiO/Al₂O₃; and (d) CoO_x/Al₂O₃ at 700°C.

distributions of the produced CNTs were narrower compared to those grown on the silica-based catalysts. We believe this is due to the nature of CoO_x which formed more uniform crystallites that led to growing CNTs with uniform diameters and it is also speculated that intense

obvious hollow core.

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