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STUDIES ON CARBON NANOTUBE SYNTHESIS *via* METHANE CVD PROCESS USING CoO_X AS CATALYST ON CARBON SUPPORTS

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In this work, influence of CoO_x concentrations (5, 10, 15 and 20 wt%) over activated carbon (AC) support with respect to methane chemical vapour decomposition (m-CVD) was studied by taking into consideration the parameters like catalyst calcination temperature, reduction temperature and reaction temperature. On-line gas chromatography data showed that catalytic activity of reduced CoO_x catalyst was much higher than that of unreduced catalyst irrespective of its reaction temperatures. Maximum CH_4 conversion of 85% was obtained for 15 wt% catalyst at a calcination temperature of 350 ^oC, reduction temperature of 450 ^oC and reaction temperature of 850 ^oC. For higher reduction temperature at 550 ^oC, catalyst activity was found to be lower (~ 50.2%) as compared to other reaction conditions. Reaction temperatures at 650 and 750 ^oC gave very low CH_4 conversions and poor carbon nanotubes (CNTs) formations. TEM images illustrated that *twisted ribbon* like multi-walled carbon nanotubes (MWNTs) with an average internal diameter of ~16 nm and wall thickness ~ 2.5 nm were obtained over reduced CoO_x/AC catalyst at a reaction temperature of 850 ^oC. However, broader diameter and non-graphitized filamentous nanostructures were observed for the catalyst reduced at higher temperature.

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1. Introduction

The fascinating properties of carbon nanotubes (CNTs) have brought an enormous interest to this new field of nanotechnology, which created high expectations for applications in various fields of science and technology [1-3]. In spite of great progress in the synthesis of different types of CNTs, one of the key problems that still persist is the availability of large quantities of CNTs with well defined structures to meet the global demands. One of the most promising ways for large scale CNTs synthesis is chemical vapour deposition (CVD) [4]. In recent years, it has been shown that the parameters like metal catalyst concentration [5], pre-treatment conditions [6] and reaction atmospheres [7] play a crucial role in CNTs synthesis. Our research group has previously reported on aforementioned parameters in methane CVD process using traditional support materials like alumina [8-10] silica [11-13] and MgO [14]. Higher production cost and purification of CNTs are some of the setbacks in using traditional supports. In order to overcome all these constraints, it is necessary to identify a readily available, cheaper material that can be separated from the as-synthesized products.

Nowadays, AC is one of the most easily available and potentially significant materials for industrial applications because of its higher surface area and porosity as compared to other traditional supports. It has the advantage of decomposing hydrocarbon gases like methane at even

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*Corresponding author: chrahman@eng.usm.my lower temperature [15-17]. In this study, cobalt oxide (CoO_x) catalysts supported on activated carbon (labelled as CoO_x/AC) was prepared by wet impregnation method. Previous studies by our group showed the significance of CoO/Al_2O_3 catalyst over CoO/SiO_2, CoO/CaO, CoO/CeO_2, CoO/H-ZSM-5, CoO/MgO, and CoO/TiO_2 in CNTs formation [18-19]. The main purpose of this work is to investigate the CoO_x/AC catalyst in methane CVD for synthesizing CNTs. The effects of catalyst preparation conditions such as metal loading, calcination and reduction temperatures on the morphology and the quality of CNTs formed were investigated.

2. Experimental

2.1 Preparation of supported catalysts

CoO_x/AC catalysts were prepared by dissolving the calculated amount of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (supplied by Aldrich) in acetone and the solution was impregnated onto the AC powders (supplied by Century chemicals Sdn. Bhd). The catalyst samples were prepared with 5, 10, 15 and 20 wt% of cobalt oxide over the AC support. The impregnated samples were dried at 105 ^oC for 12 h and calcined in N_2 at 350/450 ^oC for 3 h. The catalysts were then sieved using a standard set of Taylor sieves in a sieve shaker and the particles that passed through 53 μm sieves and retained upon 45 μm sieves were taken. The calcined samples were further subjected to reduction under H_2 atmosphere in a tubular quartz reactor at two different temperatures of 450 and 550 ^oC for 3 h.

2.2 Preparation of carbon nanotubes

The synthesis of CNTs was carried out in a horizontal quartz tube fixed-bed reactor (length and diameter of the reactor were 1050 mm and 60 mm, respectively) at atmospheric pressure via catalytic decomposition of methane. The Schematic diagram is described elsewhere [20]. High purity methane (99.99 % supplied by Malaysian Oxygen Bhd) was mixed with nitrogen (99.99 % purity, supplied by Sitt Tatt Industrial Gases Sdn Bhd) with a flow rate ratio of 1: 2 (CH_4 : N_2 = 120 ml/min : 240 ml/min) before entering the reactor. The flow of gases was controlled using respective mass flow controllers (supplied by MKS Instruments, Singapore). For synthesizing nanotube materials, 0.2 g of CoO_x/AC catalyst was placed on a quartz boat at the middle part of the reactor for each run. The reactor was then mounted in an electrical furnace and heated under N_2 flow to the desired temperatures of 750 ^oC and 850 ^oC. All of the experiments were carried out for a period of 2 h time to study the CoOx/AC catalyst activity and its performance in methane CVD.

2.3 Characterization

The calcined catalyst samples were subjected to temperature programmed reduction (TPR) studies using Micromeritics Autochem II chemisorption analyzer. In the TPR studies, all catalyst samples were first pre-treated under Argon atmosphere from 30 to 150 ^oC to remove any volatile organic impurities. In the second step, catalyst reduction was carried out in presence of 10 % H_2 /Ar gas mixtures at a ramping rate of 10 ^oC/min from 30–900 ^oC. The product gases from the reactor were analyzed using an on-line gas chromatography (GC) (Agilent Technologies 7890, USA). The GC was controlled on-line, using ChemStation B.02.01 software. The carbons deposited on the catalyst were analyzed using a transmission electron microscope (TEM) system (Philips, model CM12). The thermal stability analysis of product samples was carried out in the presence of purified air mixtures using thermogravimetric analyzer (TGA) (TA Instruments, SDT Q600) with Universal Analysis 2000 software. In TGA analysis, the purified air was set at a gauge pressure of 1 bar and the flow rate was set at 100 ml/min with a temperature ramping rate of 10 ^oC / min. All our samples were analyzed with in the temperature range of 30–900 ^oC.

3. Results and discussion

3.1 Effect of catalyst calcination temperature on CH_4 conversion

The prepared CoO_x/AC catalysts were calcined at 350 and 450 °C. It was then subjected to TPR analysis to study the CoO_x transformation profiles of Co_3O_4, CoO and finally to metallic Co. It was noticed from Fig.1 that catalysts calcined at 350 and 450 °C displayed an identical pattern of TCD signal with respect to the reduction temperatures. Various reduced phases of CoO_x were witnessed. TPR profiles in Fig.1 showed a wide hump at 250 °C in the initial stages, which was due to the reductive decomposition of the cobalt precursor attached to the surface of the AC support. At the second stage, a sharper peak observed at about 400 °C corresponds to the reduction of Co_3O_4 to CoO. A broad peak at 600 °C was due to the reduction of CoO to Co and the peak at 825 °C corresponds to the catalyzed gasification of the carbonaceous support. This observation was earlier reported by Huertemendia et al [21]. The reduction profile of cobalt oxides depends mainly on the nature of support materials and its metal - support interaction phenomena [22].

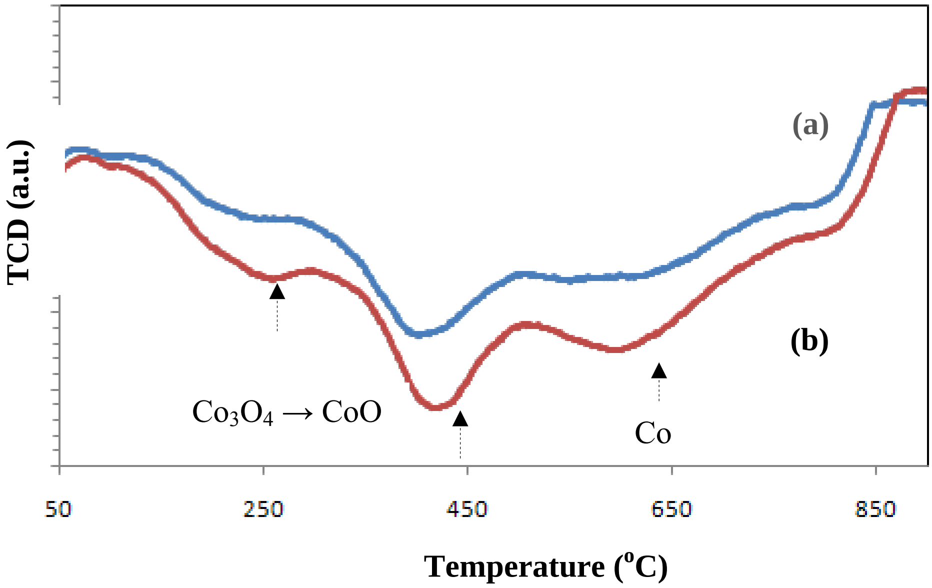

Fig. 1. TPR profiles of CoO_x/AC catalyst calcined at 350 °C and 450 °C temperatures

TPR profiles as observed in Fig. 1 did not show any major discrepancy in the metal-support interaction (MSI) for the catalysts calcined at different temperatures of 350 and 450 °C respectively.

3.2 Effect of reaction temperature and CoO_x loading on CH_4 conversion

It is well known that the rate of methane decomposition depends entirely upon the parameters like reaction temperature, time, etc. As it was also previously reported that cobalt oxide distribution over the support determines the catalytic activity as well as the quality of CNTs formed. Catalyst samples with varied concentrations of 5, 10, 15 and 20 wt% were prepared for the study of its influence on methane decomposition and the nanotube formation. In order to maintain the uniformity in reaction parameter studies, all the catalysts were calcined at 350 °C and reduced at 450 °C. Initially, methane decomposition studies were carried out at the reaction temperatures of 650, 750 and 850 °C for a specific period of 60 min. Reaction temperature of 650 °C gave very low methane conversions as shown in Table 1. It was seen that the catalyst with 15 wt% CoO_x concentration was more efficient when compared to other concentrations such as 5, 10 and 20 wt%. It was revealed that by increasing the CoO_x loading over the AC support, availability of catalytic active sites on the AC surface was also increased. However, it attained a saturation level at 15 wt% CoO_x loading, after which further metal oxide loading led to bulk deposition of accumulated CoO_x thereby hindering the effective catalyst sites and thus reducing the CH_4 conversion efficiency. From the methane conversions data, it was observed that rate of methane conversion was drastically changed at 750 and 850 ^oC. The catalyst activity seemed to be higher at 750 ^oC at the very first instant, after that a steep fall was noticed with rapid deactivation of catalyst. This showed that the cobalt particles were available at much active state, thereby m-CVD occurred at a faster rate. The catalyst activity could not be maintained for a longer duration because of rapid bulk deposition of carbon from methane over the active sites during CVD at 750 ^oC. There was a gradual raise in methane conversions at 850 ^oC for the first 10 min irrespective of their metal concentrations, indicating that the catalytic activity was higher and could yield a maximum conversion of around 85% for a catalyst concentration of 15 wt%. Among all of the synthesized catalysts, the best catalytic activity was identified for a CoO_x loading of 15 wt% at a reaction temperature of 850 ^oC.

Table 1. Effect of CoO_x (5,10,15 and 20 wt %) loading and reaction temperatures (650/750 and 850 ^oC) on CH_4 conversions.

CoO_x loading	**Reaction Temperature**	**Methane Conversion**	**At CVD time**
wt (%)	(^oC)	(%)	(min)
5	650	4.3	10
	750	9.8	10
	850	18.7	10
10	650	8.1	10
	750	42	10
	850	39.5	10
15	650	8.3	10
	750	17	10
	850	89	10
20	650	7.9	10
	750	16.5	10
	850	41.4	10

3.3 Effect of catalyst reduction temperatures during m-CVD reaction

Catalyst reduction studies were performed over the catalysts with CoO_x loading at 15 wt% and calcined at 350 ^oC. Methane CVD studies over the catalyts reduced at different temperatures of 350, 450 and 550 ^oC were conducted. In general, reduction of CoO_x catalyst would make ease the availability of reduced Co species to decompose CH_4 as well as to grow CNTs. As noticed in Fig. 2, **f**rom the methane conversion curves, it was observed that the catalyst reduced at 450 ^oC performed better than other reduced catalysts in m-CVD reactions. The catalyst reduced at this temperature were found to possess more CoO particles as can be observed from the TPR curve in Fig.1. These CoO particles were found to contribute towrads methane decomposition. It was believed that at higher reduction temperature of 550 ^oC, more metallic Co^o would be prevalent over the support surface. It seems that the presence of such metallic Co^o would not be efficient in CH_4 decomposition as compared to CoO. For all other cases, the conversion pattern showed a decreasing trend in catalytic activity after initial 10 min of reaction time.

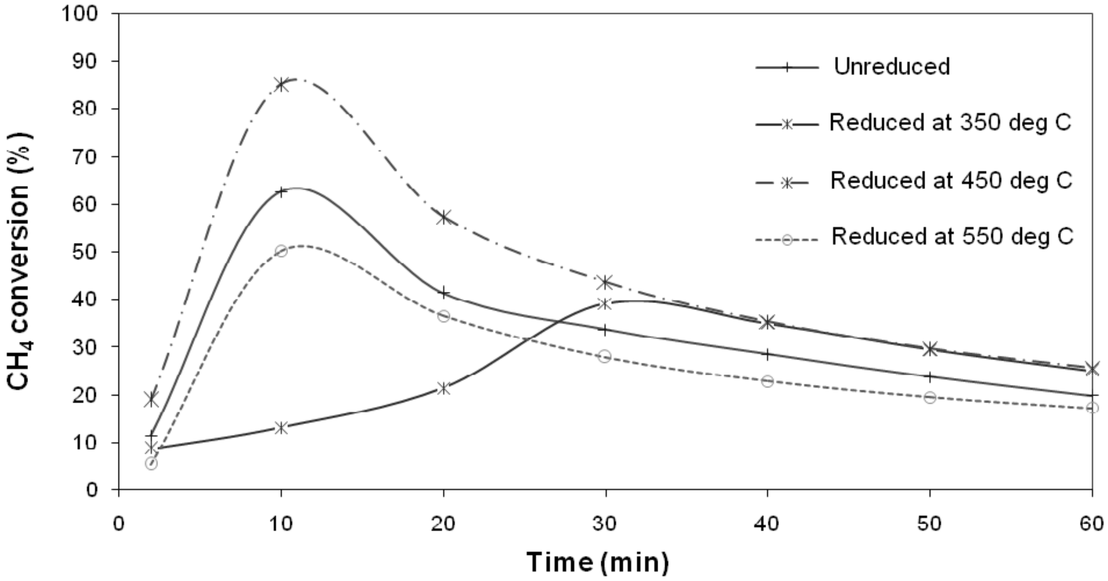

Fig. 2. Effect of reduction temperatures on 15 wt% CoO_x/AC catalysts calcined at 350 °C in methane conversion at a reaction temperature of 850 °C

3.4 TEM Characterization

After m-CVD reaction, the carbon deposits were subjected to surface morphological studies. Fig. 3(a) shows the TEM results of carbon deposits obtained from unreduced catalyst. It was observed that the unreduced CoO_x/AC catalyst performed better in methane decomposition than that of catalysts reduced at 350 and 550 °C (Fig. 2). Moreover at 350 °C reduced environment, the catalysts particle size seemed to be much smaller than that of the particles obtained from 550 °C. This was evident from the Fig. 3(b) and (d). Further, the catalyst calcined at 350 °C, reduced at 350/450 °C and reacted at 850 °C formed *twisted ribbon* like MWNTs (avg. dia ~ 16 nm and wall thickness ~ 2.5 nm). In both cases, as in Fig .3 (b) and (d), *tip-growth mechanism* of CNTs were observed as a result of weak metal-support interaction (MSI) of the catalysts. When m-CVD was carried out at a lower reaction temperature of 750 °C over the reduced CoO_x/AC catalyst, no CNTs were found to grow (Fig. 3c). This may be due to the rapid methane decomposition at 750 °C, with simultaneous deposition of carbon over the active catalytic surface thereby suppressing the development of carbon nuclei to further develop into CNTs.

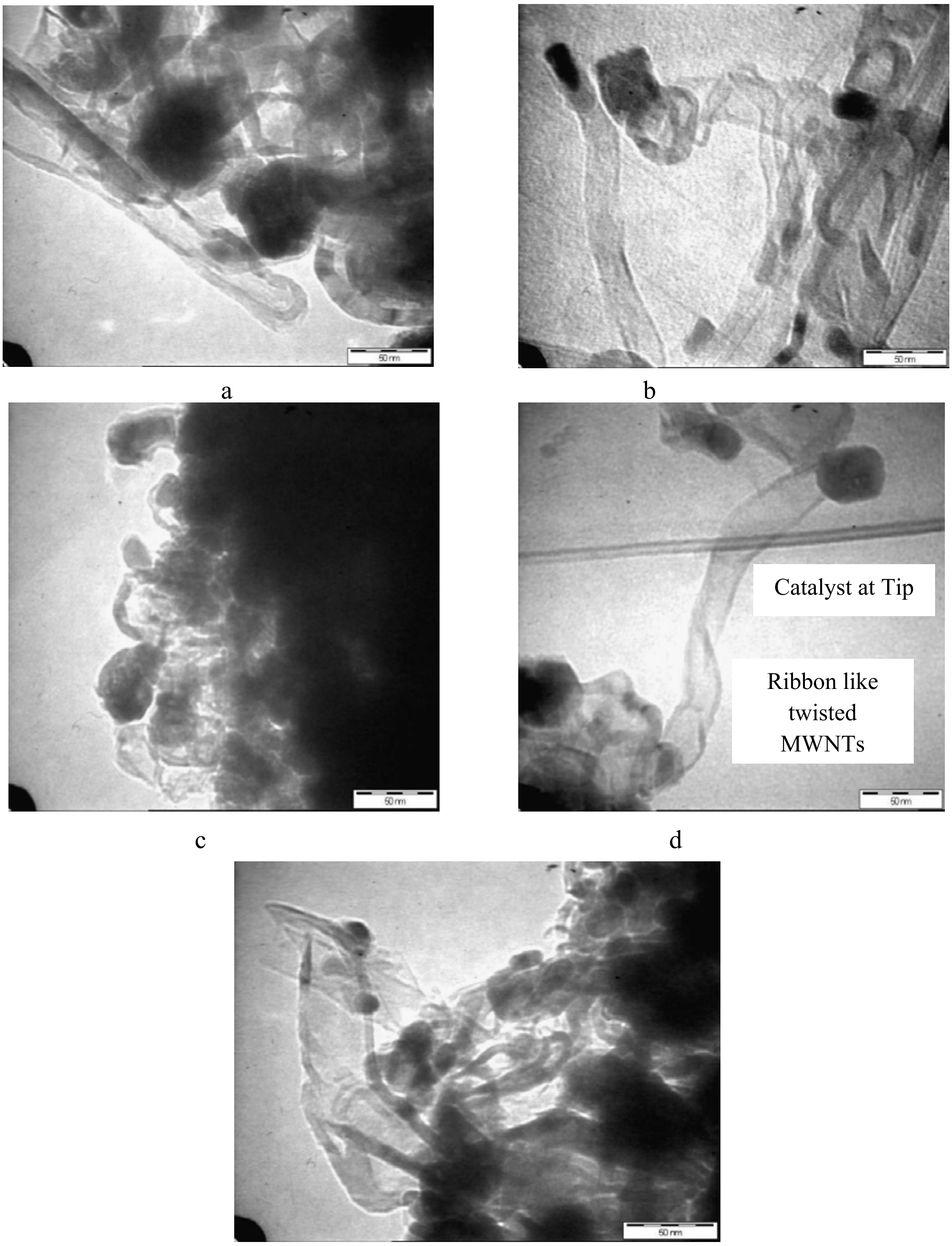

Fig. 3.TEM images of carbon deposits from 15 wt% CoO_x/AC catalyst, calcined (350 °C); reaction (850 °C) (a) Unreduced ;(b) reduction (350 °C) ;(c)reduction (350 °C) and reaction (750 °C); (d) reduction (450 °C) and reaction (850 °C); (e)reduction (550 °C) and reaction (850 °C)

It was also observed from Fig. 3(e) that the catalyst particle size has developed much bigger diameter filamentous nanostructures. Also, seldom the catalyst could be seen at the tip of these poorly developed morphologies. This may be due to availability of agglomerated metallic Co^o particles (as witness from Fig. 1) at higher reduction temperature of 550 °C. It was also confirmed from Fig. 4, that synthesized CoO_x catalyst could with stand thermally upto a temperature of 560 °C, whereas the MWNTs synthesized after m-CVD reaction had a thermal stability temperature of 635 °C. The secondary peak in the derivative curve of TGA plot confirmed the multi-walled nanotubes formed over the CoO_x catalyst at optimized conditions.

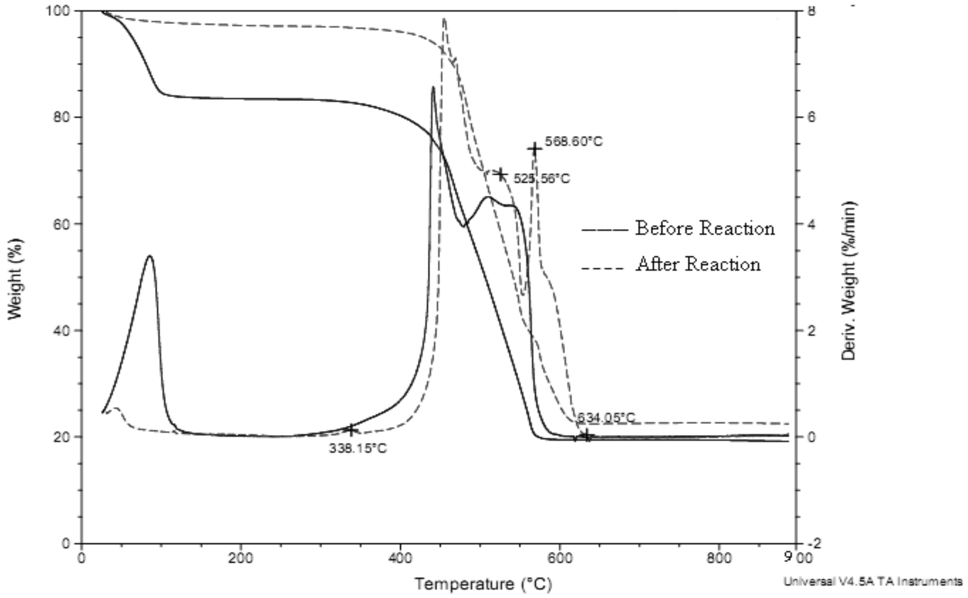

Fig. 4. TGA plot of pre-treated CoO_x/AC catalyst samples calcined at 350 °C and reduced at 450 °C showing (——) before reaction and (- - - -) after reaction conditions.

4. Conclusions

Cobalt oxide catalysts were synthesized successfully over low-cost activated carbon support to synthesize CNTs by m-CVD method. 15 wt% CoO_x catalysts over AC support, calcined in N_2 atmosphere at 350 °C and reduced at 450 °C under H_2 atmospheres achieved a maximum methane conversion of 85 % at the initial 10 min of reaction time. MWNTs with *twisted ribbon* like structures with an average diameter of 16 nm were reported. The nanotubes were grown followed the *tip-growth mechanism* that depicted a weak interaction between Cobalt oxide and carbon supports. Both unreduced catalyst and the one subjected to reduction at 550 °C gave low CH_4 conversions. It was inferred that CoO_x/AC catalyst reduced at 550 °C produced broad nanofilamentous structures but without well defined graphitized walls. Further in-depth study is being conducted to know the growth kinetics and mechanism.

Acknowledgments

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References

[1] V.N. Popov, Mater. Sci. Eng., R **43**, 61 (2004).
[2] Q.Zeng, Z.Li, Y.Zhou, J. Nat. Gas Chem. **15**, 235 (2006).
[3] M.Paradise, T.Goswami, Mater. Des. **28**, 1477 (2007).
[4] C.E.Baddour, C.Briens, Int. J. Chem. Reactor Eng. **3**, 1 (2005).
[5] M.P.Mendoza, C.Valles, W.K.Maser, M.T.Martınez, A.M.Benito, Nanotechnol. **16**, 224 (2005).
[6] Z.Yu, D.Chen, B.Totdal, A.Holmen, Catal. Today **100**, 261 (2005).
[7] H.Yu, Q.Zhang, Q.Zhang, Q.Wang, G.Ning, G.Luo, F.Wei, Carbon **44**, 1706 (2006).
[8] D.Mehn, A.Fonseca, G.Bister, J.B.Nagy, Chem. Phys. Lett. **393**, 378 (2004).
[9] S.P.Chai, S.H.S.Zein, A.R.Mohamed, Appl. Catal., A **326**, 173 (2007).
[10] S.P.Chai, S.H.S.Zein, A.R.Mohamed, Carbon **45**, 1535 (2007).
[11] S.P.Chai, S.H.S.Zein, A.R.Mohamed, Chem. Phys. Lett. **426**, 345 (2006).
[12] R.E.Herbert, H.Pforte, T.Hesjedal, Mater. Lett. **61**, 2589 (2007).
[13] S.Takenaka, H.Umebayashi, E.Tanabe, H.Matsune, M.Kishida, J. Catal. **245**, 392 (2007).
[14] L.Ni, K.Kuroda, L.P.Zhou, T.Kizuka, K.Ohta, K.Matsuishi, J.Nakamura, Carbon **44**, 2265 (2006).
[15] N. Muradov, Catal. Commun. **2**, 89 (2001).
[16] E.K.Lee, S.Y.Lee, G.Y.Han, B.K.Lee, T.J.Lee, J.H.Jun, K.J.Yoon, Carbon **42**, 2641 (2004).
[17] B.Fidalgo, Y.Ferna´ndez, L.Zubizarreta, A.Arenillas, A.Domı´nguez, J.J.Pis, J.A. Mene´ndez, Appl. Surf. Sci. **254**, 3553 (2008).
[18] W.M.Yeoh, K.Y.Lee, S.P.Chai, K.T.Lee, A.R.Mohamed, New Carbon Mater. **24**, 119 (2009).
[19] S.P.Chai, S.H.S.Zein, A.R.Mohamed, Solid State Commun. **140**, 248 (2006).
[20] V.M.Sivakumar, A.R.Mohamed, A.Z.Abdullah, S.P.Chai, J. Nanomat. Article ID 395191, 11 pages, doi:10.1155/2010/395191, (2010).
[21] M. Huertemendia, F. Coloma, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso, presented at the 23rd Biennial Conference, July 18-23, 1997, Pennsylvania State University, University Park, PA.
[22] S.P.Chai, V.M.Sivakumar, S.H.S.Zein, A.R.Mohamed, Carbon Sci. Tech. **1**, 24, (2008).