



**Laporan Akhir Projek Penyelidikan
Jangka Pendek**

**A Novel Production of Single-walled
Carbon Nanotubes and Hydrogen via
Single-step Conversion of Natural Gas**

by

Prof. Dr. Abdul Rahman Mohamed

Dr. Sharif Hussein Sharif Zein

Dr. Chai Siang Pio

Assoc. Prof. Dr. Jamil Ismail

Prof. Dr. Kouichi Miura

Prof. Dr. Koichi Equchi

2008



Final Report

SAGA END OF PROJECT REPORT – To be filled by principal Investigator

Date of this report: 8 July 2008

A. DETAILS OF THE SAGA PROJECT

Principal Investigator : Prof. Dr. Abdul Rahman Mohamed

Co-researcher : i) Dr. Sharif Hussein Sharif Zein
(**Please state names of additional co-researchers involved since project started [if any]) ii) Dr. Chai Siang Piao
iii) Associate Prof. Dr. Jamil Ismail
iv) Prof. Dr. Kouichi Miura
v) Prof. Dr. Koichi Equchi

SAGA Fund Reference No. : C49

Title : A Novel Production of Single-walled Carbon Nanotubes and Hydrogen via Single-step Conversion of Natural Gas

Grant Approved : RM 159,000.00

1st Disbursement : RM 82,000.00

2nd Disbursement : RM 77,000.00

Project Duration : 36 months.

Start Date: 7 July 2005 End Date: 7 July 2008

This project was completed : a within the period originally proposed; or
b extended beyond the proposed period

How many man-months did the project involve?
 Man-months

What were the total project expenses? RM 159,000.00

input
etc.

B. OBJECTIVES ACHIEVEMENT

- i) Original project objectives (please state the specific project objectives as described in the application form)

1. To develop effective catalysts for synthesizing single-walled carbon nanotubes
2. To study the properties of the catalyst that enhance the formation of single-walled carbon nanotubes
3. To study the formation mechanism of carbon nanotubes, and the influence of the process parameters on the morphology of carbon nanotubes
4. To investigate the type and the properties of the produced carbon nanotubes

- ii) Objectives Achieved (Please state the extent to which the project objectives was achieved)

All the grant objectives have been successfully achieved.

- iii) Objectives not achieved (Please identify the objectives that were not achieved and give reasons)

None

- C. **Assessment of Research Approach** (Please highlight the main steps actually performed and indicate any major departure from the planned approach or any difficulty encountered)

The main step performed was the development of catalyst to synthesize single-walled carbon nanotubes, whereas, the major departure from the planned approach was the investigations of the properties of produced carbon nanotubes. Certain properties characterizations require the use of sophisticated equipment such as high-resolution transmission electron microscopy which is not available in Malaysia.

- D. **Assessment of the Project Schedule** (Please make any relevant comment regarding the actual duration of the project and highlight any significant variation from plan)

This project has been extended for another 12 months from the original plan. It has been reported in the 20th month progress report that almost all the objectives proposed in the grant had been achieved in 20th month time except objective 4 (partly achieved) which required third parties to perform the analysis for the samples. Till 31 May 2007 (20th month of progress), there was unspent amount of RM 47,602.89. Therefore, we extended the project to 36 months mainly due to the delay in the sample characterizations and to fully utilize the remaining allocation to produce an excellent output. This characterization problem has been solved by performing the in Kyoto University.

- E. **Assessment of Project Costs** (Please comment on the appropriateness of the original budget and highlight any major departure from the planned budget)

There is a slight variation of RM 1021.88 between the total expenses and the allocated funding. Corrective action has been taken. The overdraft was overruled from the allocation in other grants.

F. Benefits of the Project

i. Technical contribution of the project :

a. What was the achieved direct output of the project :

Basic Research Project

- Algorithm
- Structure
- Data
- Other, please specify : **Technology and science**

b. How would you characterize the quality of this output?

- Significant breakthrough
- Major Improvement
- Minor Improvement

ii. Contribution of the project to knowledge

a. How has the output of the project been documented?

- Detailed project report
- Product/process specification documents
- Other, please specify: **Scientific paper publications**

ii) How significant are citations of the results?

- Citations in national publications
- Citations in international publications
- None yet
- Not known

G. REPORTS, PAPERS AND PUBLICATIONS

i. List of reports and conference/seminar papers written:

1. Sharif Hussein Sharif Zein, Abdul Rahman Mohamed and Siang-Piao Chai (2005). The screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane. *Proceedings of the 4th Asia-Pacific Chemical Reaction Engineering Symposium (APCRE 2005)*, 12-15 June, Gyeongju, Korea, 545-546.
2. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). Dependence of the formation of carbon nanotubes on CoO and NiO supported on Al₂O₃ and SiO₂ nanoparticles. *Proceedings of the International Conference on MEMs and Nanotechnology (ICMN 2006)*, 14-15 March, Kuala Lumpur, 145-151.
3. Abdul Rahman Mohamed, Siang-Piao Chai and Sharif Hussein Sharif Zein (2006). Effect of CoO-MoO/Al₂O₃ catalyst calcination temperature on the uniformity of the synthesized carbon nanotubes diameters. *Proceedings of the Seventh International Conference on the Science and Application of Nanotubes (NT 2006)*, 18-23 June, Nagano, Japan, 28.
4. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). The production of CO_x-free hydrogen and carbon nanofibers from direct catalytic decomposition of methane. *Proceedings of the 1st International Conference on Natural Resources Engineering and Technology (INRET 2006)*, 24-26 July, Putrajaya, 37-44.
5. Abdul Rahman Mohamed, Siang-Piao Chai and Sharif Hussein Sharif Zein (2006). Production of carbon nanotubes from catalytic decomposition of methane. *Proceedings of International Forum on Research & Development and Innovation in Oil, Gas & Petrochemical Industry*, 6-7 December, Kuala Lumpur.
6. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). Formation of Carbon Nanotubes on Co-Mo/Al₂O₃ Catalyst from Methane Decomposition: The effect of catalyst reduction temperature. *Proceeding of Materials Today Asia 2007 (MTAS 2007)*, Beijing, China, 3-5 September, P1.44.

ii. List of scientific publications (including name(s) of co-author(s), date of publication, location and name of publisher. Please attach pre-print copies of the publications)

7. Sharif Hussein Sharif Zein, Abdul Rahman Mohamed and Siang-Piao Chai (2006). The screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane, *Studies in Surface Science and Catalysis*, 159, 725-728. (Elsevier)
8. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). Preparation of carbon nanotubes over cobalt-containing catalysts via catalytic decomposition of methane. *Chemical Physics Letters*, 426, 345-350. (Elsevier)
(Impact factor: 2.207)
9. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). Formation of Y-junction carbon nanotubes by catalytic CVD of methane. *Solid State Communications*, 140, 248-250. (Elsevier)
(Impact factor: 1.535)
10. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). CO_x-free hydrogen and carbon nanofibers produced from direct decomposition of methane on nickel-based catalysts. *Journal of Natural Gas Chemistry*, 15, 253-258. (Elsevier)
11. Kong Bee Hong, Aidawati Azlin Binti Ismail, Mohamed Ezzaham Bin Mohd Mahayuddin, Abdul Rahman Mohamed and Sharif Hussein Sharif Zein (2006). Production of high purity multi-walled carbon nanotubes from catalytic decomposition of methane. *Journal of Natural Gas Chemistry*, 15, 266-227. (Elsevier)

12. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). Moderate temperature synthesis of single-walled carbon nanotubes on alumina supported nickel oxide catalyst. *Materials Letters*, 61(16), 3519-3521. **(Elsevier)**
(Impact factor: 1.625)
13. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). Synthesizing carbon nanotubes and carbon nanofibers over supported-nickel oxide catalysts via catalytic decomposition of methane. *Diamond & Related Materials*, 16(8), 1656-1664. **(Elsevier)**
(Impact factor: 1.788)
14. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). The effect of catalyst calcination temperature on the diameter of carbon nanotubes synthesized by the decomposition of methane. *Carbon*, 45, 1535-1541. **(Elsevier)**
(Impact factor: 4.260)
15. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). The effect of reduction temperature on Co-Mo/Al₂O₃ catalysts for carbon nanotubes formation. *Applied Catalysis A: General*, 326, 173-179. **(Elsevier)**
(Impact factor: 3.166)
16. Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2008). Production of carbon nanotubes via catalytic decomposition of methane. *ASM Science Journal* (Accepted). **(Akademi Sains Malaysia)**

H. FINANCIAL REPORT

i) Please report the expenditure of the project so far:

Vote	Project Cost Component	Expenditure RM	
		Allocated	Expended
Vote 11000	Salary and wage	40,000	91,266.25
Vote 14000	Overtime	-	-
Vote 21000	Traveling expenses and subsistence	15,000	26,226.90
Vote 22000	Transportation of goods	-	-
Vote 23000	Communication and utilities i.e. Phone, fax, postage etc	0	321.20
Vote 24000	Rental	-	-
Vote 26000	Supply of raw materials & materials for repair & maintenance	10,000	273.29
Vote 27000	Research materials & supplies including animals, disposables etc.	29,000	1,6478.39
Vote 28000	Maintenance and minor repair services	0	150.00
Vote 29000	Professional services & other services including printing & hospitality, registration fees	25,000	22,845.85
Vote 35000	Equipment (Justification and quotation of each equipment to be purchased should be provided)	40,000	2,460.00
Total		159,000	160,021.88

- Please attach financial statement/ breakdown from bursary of institution.
- If there is amount transferred to another institution for use of co-researchers, please ensure financial statement/ breakdown is provided for that amount.

ii) If there is/are variation(s) between the proposed and actual expenditure, please provide the reasons:

There is an overdraft of total RM 1021.88 in this project.

iii) If there is/are variation(s) between the proposed and actual expenditure, please indicate the corrective action you plan to take:

The overdraft of RM 1021.88 has been overruled using the allocation from other grants.

Final Report

I. KEY PERFORMANCE INDICATORS ACHIEVEMENT

i) Scientific Knowledge Creation

No. of Publications (with impact factors)

(*Please list down all related publications since project started and attach the hardcopy)

No	Type of Publication	No. of publications	Title	Impact factor 2007
1	Journal i) International [High impact or cited in Science Citation index (SCI) or Current Contents (CC)]	9	Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). Preparation of carbon nanotubes over cobalt-containing catalysts via catalytic decomposition of methane. <i>Chemical Physics Letters</i> , 426, 345-350.	2.207
			Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). Formation of Y-junction carbon nanotubes by catalytic CVD of methane. <i>Solid State Communications</i> , 140, 248-250.	1.535
			Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). CO _x -free hydrogen and carbon nanofibers produced from direct decomposition of methane on nickel-based catalysts. <i>Journal of Natural Gas Chemistry</i> , 15, 253-258.	
			Kong Bee Hong, Aidawati Azlin Binti Ismail, Mohamed Ezzaham Bin Mohd Mahayuddin, Abdul Rahman Mohamed and Sharif Hussein Sharif Zein (2006). Production of high purity multi-walled carbon nanotubes from catalytic decomposition of methane. <i>Journal of Natural Gas Chemistry</i> , 15, 266-227.	
			Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). Moderate temperature synthesis of single-walled carbon nanotubes on alumina supported nickel oxide catalyst. <i>Materials Letters</i> , 61(16), 3519-3521.	1.625
			Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). Synthesizing carbon nanotubes and carbon nanofibers over supported-nickel oxide catalysts via catalytic decomposition of methane. <i>Diamond & Related Materials</i> , 16(8), 1656-1664.	1.788

	ii) Local		<p>Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). The effect of catalyst calcination temperature on the diameter of carbon nanotubes synthesized by the decomposition of methane. <i>Carbon</i>, 45, 1535-1541.</p> <p>Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). The effect of reduction temperature on Co-Mo/Al₂O₃ catalysts for carbon nanotubes formation. <i>Applied Catalysis A: General</i>, 326, 173-179.</p> <p>Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2008). Production of carbon nanotubes via catalytic decomposition of methane. <i>ASM Science Journal</i> (Accepted).</p>	<p>4.260</p> <p>3.166</p> <p>-</p>
2	<p>Papers (seminar/ conference/ workshop/Inaugural Lecture/Keynote)</p> <p>i) International</p>	6	<p>Sharif Hussein Sharif Zein, Abdul Rahman Mohamed and Siang-Piao Chai (2005). The screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane. <i>Proceedings of the 4th Asia-Pacific Chemical Reaction Engineering Symposium (APCRE 2005)</i>, 12-15 June, Gyeongju, Korea, 545-546.</p> <p>Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). Dependence of the formation of carbon nanotubes on CoO and NiO supported on Al₂O₃ and SiO₂ nanoparticles. <i>Proceedings of the International Conference on MEMs and Nanotechnology (ICMN 2006)</i>, 14-15 March, Kuala Lumpur, 145-151.</p> <p>Abdul Rahman Mohamed, Siang-Piao Chai and Sharif Hussein Sharif Zein (2006). Effect of CoO-MoO/Al₂O₃ catalyst calcination temperature on the uniformity of the synthesized carbon nanotubes diameters. <i>Proceedings of the Seventh International Conference on the Science and Application of Nanotubes (NT 2006)</i>, 18-23 June, Nagano, Japan, 28.</p> <p>Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2006). The production of CO_x-free hydrogen and carbon nanofibers from direct catalytic decomposition of methane. <i>Proceedings of the 1st International Conference on Natural Resources Engineering and Technology (INRET 2006)</i>, 24-26 July, Putrajaya, 37-44.</p>	

	ii) Local		<p>Abdul Rahman Mohamed, Siang-Piao Chai and Sharif Hussein Sharif Zein (2006). Production of carbon nanotubes from catalytic decomposition of methane. <i>Proceedings of International Forum on Research & Development and Innovation in Oil, Gas & Petrochemical Industry</i>, 6–7 December, Kuala Lumpur.</p> <p>Siang-Piao Chai, Sharif Hussein Sharif Zein and Abdul Rahman Mohamed (2007). Formation of Carbon Nanotubes on Co-Mo/Al₂O₃ Catalyst from Methane Decomposition: The effect of catalyst reduction temperature. <i>Proceeding of Materials Today Asia 2007 (MTAS 2007)</i>, Beijing, China, 3-5 September, P1.44.</p>	
3	<p>Chapter in Scientific books/ Monographs</p> <p>i) International</p> <p>ii) Local</p>	2	<p>Sharif Hussein Sharif Zein, Abdul Rahman Mohamed and Siang-Piao Chai (2006). The screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane, <i>Studies in Surface Science and Catalysis</i>, 159, 725-728.</p> <p>Mohamed, A.R., <i>Nanotub Karbon: Penemuan Sains yang Merevolusikan Nanoteknologi</i>, Pulau Pinang: Universiti Sains Malaysia, 2006.</p>	
4	<p>Electronic Journal (Peer reviewed/ with impact factors)</p> <p>i) International</p> <p>ii) Local</p>			

ii) Technology Creation

(Relevant documents to be attached)

No	Technology creation
1	<p data-bbox="289 827 791 851">Major scientific discoveries & new inventions</p> <p data-bbox="887 417 1212 440">Major scientific discoveries</p> <ul style="list-style-type: none"> <li data-bbox="931 448 1970 584">i) Achieving a simple approach to produce multi-walled carbon nanotubes (MWNTs) with nearly uniform diameter through proper calcination of the catalyst at optimum temperature. In the past, complicated catalyst preparation procedures are required to develop the catalyst to produce CNTs with nearly uniform diameter. These findings have been reported in journals of Carbon and Applied Catalysis A. <li data-bbox="931 592 1970 812">ii) Achieving the way to produce single-walled carbon nanotubes (SWNTs) at moderate temperature. Commonly, SWNTs can only be produced at high reaction temperatures, such as at 1000°C and above. With this new catalyst developed in this project, SWNTs can be grown at the temperature as low as 700°C. These findings have been reported in Materials Letters and Diamond and Related Materials. Recently, we have achieved the synthesis of SWNTs with nearly uniform diameter. The finding has been reported in scientific paper and sent to high impact factor journal (under review). <li data-bbox="931 820 1970 976">iii) Achieving the way to produce Y-junction CNTs. Y-junction CNTs possess unique structure that makes them difficult to be produced at all times. In this study, Y-junction CNTs are successfully grown using trimetallic catalysts (NiO-CuO-MoO/SiO₂) at the temperature of 700°C. This finding is exceptional because this is the first time the synthesis of Y-junction CNTs from trimetallic catalysts is reported. This finding has been reported in Solid State Communications. <p data-bbox="887 1016 1063 1039">New inventions</p> <ul style="list-style-type: none"> <li data-bbox="931 1070 1970 1125">iv) Achieving the ways of tailor making the types of CNTs, including MWNTs with nearly uniform diameter, thin-walled CNTs, Y-junction CNTs and carbon nanofibers. <li data-bbox="931 1133 1970 1235">v) This process is simpler and cheaper involving a single step approach to produce CNTs from methane gas. Methane is the major composition of natural gas and Malaysia is one of the largest natural gas exporters in the world. Therefore, methane gas is highly abundant at low cost in Malaysia.

2	No. of patents filed	i) In the process of patent filing ii) iii)
3	No. of patents attained	i) ii) iii)
4	No. of technology platforms created and transferred	i) In the process of signing NDA with SGL Carbon GmbH ii) iii)
5	No. of technology platforms acquired & applied	i) ii) iii)

Final Report

J. ORGANISATIONAL OUTCOMES OF THE PROJECT ((Please describe as specifically as possible the organizational benefits arising from the project and provide an assessment of their significance)

i. Contribution of the project to expertise development			
a. How did the project contribute to expertise?			
<input checked="" type="checkbox"/>	PhD degrees	How many:	1 _____
<input checked="" type="checkbox"/>	MSc degrees	How many:	1 _____
<input type="checkbox"/>	Research staff with new specialty	How many:	_____
<input checked="" type="checkbox"/>	Other, please specify: _____		Undergraduate students (Final year) _____
b. How significant is this expertise?			
<input checked="" type="checkbox"/>	One of the key areas of priority for Malaysia (Nanotechnology)		
ii. Economic contribution of the project? (only fill if relevant)			
a. How has the economic contribution of the project materialized?			
<input checked="" type="checkbox"/>	Cost savings		
<input checked="" type="checkbox"/>	Time savings		
<input type="checkbox"/>	Other, please specify: _____		
b. How important is this economic contribution?			
<input type="checkbox"/>	High economic contribution	Value: RM	_____
<input type="checkbox"/>	Medium economic contribution	Value: RM	_____
<input type="checkbox"/>	Low economic contribution	Value: RM	_____
c. When has this economic contribution materialized?			
<input type="checkbox"/>	Already materialized		
<input type="checkbox"/>	Within months of project completion		
<input type="checkbox"/>	Within three years of project completion		
<input checked="" type="checkbox"/>	Expected in three years or more		
<input type="checkbox"/>	Unknown		

iii. Infrastructural contribution of the project

a. What infrastructural contribution has the project had?

- New equipment Value: RM _____
- New/improved facility Investment: RM - _____
- New information networks
- Other, please specify: _____

b. How significant is this infrastructural contribution for the organization?

- Not significant/does not leverage other projects
- Moderately significant
- Very significant/significantly leverages other projects

iv. Contribution of the project to the organization's reputation

a. How has the project contributed to increasing the reputation of the organization

- Recognition as a Center of Excellence
- National award
- International award
- Demand for advisory services
- Invitations to give speeches on conferences
- Visits from other organizations
- Other, please specify: _____

b. How important is the project's contribution to the organization's reputation?

- Not significant
- Moderately significant
- Very significant

K) Human Capacity Building

i) No. of researchers in the team (since project started)

(Professor/Assoc. Prof./Lecturers (Dr.)/PhD student/Masters student/Research officer/ Research Assistant)

Age and gender		No. of Researchers															
		<20		21-30		31-40		41-50		51-60		61-70		71-80		81-90	
		Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Research member																	
1) Professor							1		2								
2) Assoc. Professor									1								
3) Lecturer (Dr.)						1											
4) PhD students			1														
5) Masters student				1													
6) Research officer																	
6a) No. of PhD level =																	
6b) No. of Master's level =																	
6c) No. of Undergraduate level =																	
6d) Others (please state [if any]) =																	
7) Research assistant																	
7a) No. of Undergraduate level =				1													
7b) No. of diploma level =																	
7c) Others (please state [if any]) =																	

ii) Disciplines of researchers within team :

- 1) Prof. Abdul Rahman Mohamed (Project leader)
To coordinate and to lead the research group as well as to plan for the research direction.
- 2) Dr. Sharif Hussein Sharif Zein (Co-researcher)
To guide the postgraduate and undergraduate students for developing the catalyst and studying the process for carbon nanotubes production.
- 3) Assoc. Prof. Dr. Jamil Ismail (Co-researcher)
To assist in catalyst development for the chemistry point of view.
- 4) Prof. Dr. Kouichi Miura (Co-researcher) and Prof. Dr. Koichi Eguchi (Co-researcher)
To provide the HRTEM facility to analyze the carbon nanotubes products.
- 5) Mr. Chai Siang Piao (PhD student)
To conduct the research works for catalyst development and carbon nanotubes production.
- 6) Ms. Kong Bee Hong (Master student)
To purify the carbon nanotubes produced in this work.
- 7) Ms. Tan Shwu Miin (Final year student)
To develop the efficient catalysts for synthesizing SWNTs at large quantity.

L. NATIONAL IMPACTS OF THE PROJECT

i. Contribution of the project to organizational linkages

a. Which kinds of linkages did the project create?

- Domestic industry linkages
- International industry linkages
- Linkages with domestic research institutions, universities
- Linkages with international research institutions, universities

b. What is the nature of the linkages?

- Staff exchanges
- Inter-organizational project team
- Research contract with a commercial client (SGL Carbon GmbH)
- Informal consultation
- Other, please specify: _____

ii. Social-economic contribution of the project

a. Who are the direct customer/beneficiaries of the project output?

Customers/beneficiaries: _____ Number: _____

b. How has/will the socio-economic contribution of the project materialized?

- Improvements in health
- Improvements in safety
- Improvements in the environment
- Improvements in energy consumption/supply
- Improvements in international relations
- Other, please specify: _____

iii. How important is this socio-economic contribution?

- High social contribution
 Medium social contribution
 Low social contribution

iv. When has/will this social contribution materialized?

- Already materialized
 Within three years of project completion
 Expected in three years or more
 Unknown

Signature:

ARahman

Date:

10/07/08

Official Stamp:

Dimajukan

Endorsed by:
Research Management Centre
Official Stamp:

An 20/7/09

PROFESSOR ASMA ISMAIL

Deputy Vice Chancellor
(Research & Innovation)
Chancellory
Universiti Sains Malaysia
11800 USM, Penang.

PROFESOR ABDUL RAHMAN MOHAMED

304.PJKIMIA.6053001

JUMLAH GERAN : 159,000.00

NO PROJEK :-

PANEL - SAGA

PENAJA - AKADEMIK SAINS MAL

JABATAN BENDAHARI
UNIT KUMPULAN WANG AMANAH
UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN

PENYATA KUMPULAN WANG

TEMPOH BERAKHIR 30/06/2008

Tempoh Projek:01/08/2005 - 31/07/2007

A NOVEL PRODUCTION OF SINGLET-WALLET CARBON NANOTUBES & HYDROGEN

<u>Vot</u>	<u>Peruntukan</u> (a)	<u>Perbelanjaan sehingga 31/12/2007</u> (b)	<u>Tanggung semasa 2008</u> (c)	<u>Perbelanjaan Semasa 2008</u> (d)	<u>Jumlah Perbelanjaan 2008</u> (c + d)	<u>Jumlah Perbelanjaan Terkumpul</u> (b+c+d)	<u>Baki Peruntukan Semasa 2008</u> (a-(b+c+d))
11000 GAJI KAKITANGAN AWAM	40,000.00	91,266.25	0.00	0.00	0.00	91,266.25	(51,266.25)
21000 PERBELANJAAN PERJALANAN DAN SARAH	15,000.00	26,171.90	0.00	55.00	55.00	26,226.90	(11,226.90)
23000 PERHUBUNGAN DAN UTILITI	0.00	321.20	0.00	0.00	0.00	321.20	(321.20)
26000 BAHAN MENTAH & BAHAN UNTUK PENYELE	10,000.00	273.29	0.00	0.00	0.00	273.29	9,726.71
27000 BEKALAN DAN ALAT PAKAI HABIS	29,000.00	16,340.39	0.00	(883.88)	(883.88)	15,456.51	13,543.49
28000 PENYELENGGARAAN & PEMBAIKAN KECIL	0.00	150.00	0.00	0.00	0.00	150.00	(150.00)
29000 PERKHIDMATAN IKTISAS & HOSPITALITI	25,000.00	22,845.85	0.00	0.00	0.00	22,845.85	2,154.15
35000 HARTA-HARTA MODAL LAIN	40,000.00	2,460.00	0.00	0.00	0.00	2,460.00	37,540.00
	<u>159,000.00</u>	<u>159,828.88</u>	<u>0.00</u>	<u>(828.88)</u>	<u>(828.88)</u>	<u>159,000.00</u>	<u>0.00</u>
Jumlah Besar	<u>159,000.00</u>	<u>159,828.88</u>	<u>0.00</u>	<u>(828.88)</u>	<u>(828.88)</u>	<u>159,000.00</u>	<u>0.00</u>

**RESEARCH
PUBLICATIONS**

Screening of metal oxide catalysts for carbon nanotubes and hydrogen production via catalytic decomposition of methane

S.H.S. Zein*, A.R. Mohamed and S.P. Chai

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

A number of catalysts prepared from transition metals such as copper (Cu), iron (Fe), nickel (Ni), cobalt (Co) and manganese (Mn) on TiO₂ support were tested for the decomposition of methane into hydrogen and carbon. These catalysts were used in the experiments without any pretreatment. The experimental results show that the activities of the metal-TiO₂ catalysts decreased in the order of NiO/TiO₂ > CoO/TiO₂ > MnO_x/TiO₂ ≈ FeO/TiO₂ ≈ CuO/TiO₂. NiO/TiO₂ catalyst exhibited extremely high initial activity in the decomposition of methane. The optimum NiO doping on TiO₂ for the decomposition of methane were obtained at 20mol% NiO. The effective promoters for the catalyst was investigated using 15mol%M/20mol%NiO/TiO₂ catalysts (where M = MnO_x, FeO, CoO and CuO). 15mol%MnO_x/20mol%NiO/TiO₂ was found to be an effective bimetallic catalyst for the catalytic decomposition of methane into hydrogen and carbon, giving higher catalytic activity, attractive carbon nanotube formed as well as longer catalytic lifetime.

1. INTRODUCTION

Carbon nanotubes are one of the most innovative material technologies of the twenty first century, because of their many desirable material properties [1-5]. For the synthesis of carbon nanotubes, several methods have been developed (mainly arc discharge, laser ablation, and chemical vapor deposition). The development of a reliable source of large quantities of carbon nanotubes is dependent on better production methods. The abundance of natural gas, which contains primarily methane, can be better utilized by increasing its use as a source of chemicals in place of its predominant use as a fuel. The decomposition of methane to hydrogen and carbon nanotube is of current interest as it is an alternative route to the production of carbon nanotubes from natural gas. The decomposition of methane at higher temperature attracts considerable interest today because the conversion of methane at this condition is higher [6-8]. However, at higher temperature, the catalyst deactivates very fast due to the formation of encapsulating type carbon on the catalyst. Thus, in order to put this process into practice, a catalyst with high activity without any treatment prior to its use becomes necessary.

2. EXPERIMENTAL PROCEDURE

All the catalysts used in this work were prepared by conventional impregnation method. The selected dopant concentrations were actually relative to the molar quantity of the TiO₂ support.

* E-mail: chhussein@eng.usm.my

3.2. The effect of NiO loading on TiO₂ support

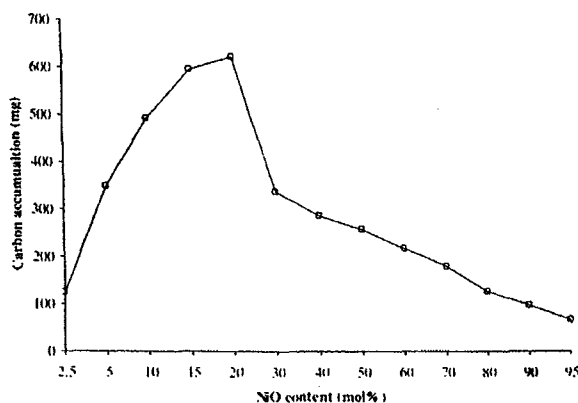


Fig. 1. The relationship between the carbon accumulation and the NiO doping on TiO₂ support in the methane decomposition at 998 K and GHSV of 2700 h⁻¹ at steady state.

NiO concentration was varied from 2.5 to 95 mol% on TiO₂ support as shown in Fig. 1. The optimum NiO doping on TiO₂ for decomposition of methane obtained was at 20 mol%NiO. Further increase the NiO content on TiO₂ support leads to lower the carbon accumulation. NiO/TiO₂ catalysts with different NiO doping were investigated using XRD as to reveal the reason of lower carbon accumulation being observed over high-loaded NiO catalysts. The XRD results obtained indicated that as the amount of NiO loaded increased, the number of Ni⁰ sites were also increased and sintered to form larger NiO particles which lead to a catalyst deactivation.

3.3 The effect of promoter on 20 mol% NiO/TiO₂ catalyst

Table 3 shows the performance of the promoted-catalysts for the decomposition of methane to hydrogen at 5, 60, 120 and 180 min of time on stream. The results in Table 3 revealed that the activity of the parent catalyst and MnO_x-doped catalyst remained almost constant until 120 min of time on stream. The activity of the other promoted-catalysts, on the other hand, decreased with an increase in the time on stream. The data for the CoO-doped catalyst and 20 mol%NiO/TiO₂ could not be recorded at 120 min and 180 min, respectively because of the pressure build-up in the reactor. This finding indicates that adding MnO_x enhances the stability and the resistibility of the NiO/TiO₂ catalyst towards its deactivation.

Table 3

The performance of the catalysts doped with transition metals on 20 mol% NiO/TiO₂ catalyst for hydrogen production at 998 K and GHSV of 2700 h⁻¹ at steady state.

Catalyst	H ₂ Concentration (%)			
	5 min	60 min	120 min	180 min
20 mol% NiO/TiO ₂	61	62	61	-
15 mol% CuO/20 mol% NiO/TiO ₂	61	67	46	34
15 mol% MnO _x /20 mol% NiO/TiO ₂	59	58	56	48
15 mol% FeO/20 mol% NiO/TiO ₂	57	50	44	27
15 mol% CoO/20 mol% NiO/TiO ₂	66	59	-	-



Preparation of carbon nanotubes over cobalt-containing catalysts via catalytic decomposition of methane

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S. Pulau Pinang, Malaysia

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Abstract

Decomposition of methane into carbon nanotubes over CoO catalysts supported on various catalyst supports at 550 °C and 700 °C was investigated. The effect of catalyst promoters on the supported CoO catalysts at 700 °C was also examined. Electron microscope observations showed that among the various catalyst supports tested, alumina was found to be the most appropriate for CoO that CoO/Al₂O₃ catalyst grew carbon nanotubes with significant hollow cores. Experimental results further revealed that introducing FeO into CoO/Al₂O₃ catalyst resulted in the formation of carbon nanotubes with thin wall structure. Introducing MoO into CoO/Al₂O₃ catalyst increased the carbon capacity and the selectivity of CoO/Al₂O₃ catalyst in growing better quality carbon nanotubes.

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1. Introduction

Since their discovery in 1991 by Iijima [1], carbon nanotubes have been the object of intense scientific study. Carbon nanotubes, possessing extraordinary properties [2], have the potential applications in the areas of electronic, energy storage, catalysis, and nanocomposites [3–7]. Carbon nanotubes have been synthesized by electric-arc-discharge [8], laser-ablation [9], and chemical vapor deposition (CVD) of hydrocarbon gases over catalytic materials [10]. Arc discharge and laser ablation can produce high quality carbon nanotubes, but both have significant limitation in mass production of carbon nanotubes and are not adaptable to industrial production. By comparison, the CVD method is the most promising route for a large-scale production of carbon nanotubes. Moreover, CVD method allows the growth of large amounts of carbon nanotubes at a lower cost because it can proceed at lower reaction temperature (below 1000 °C).

In the CVD method, hydrocarbons such as methane, ethylene, acetylene, or benzene are dominantly used

[11,12]. Supported transition metals, most frequently supported Fe, Ni, or Co, are used as the catalysts precursors in the CVD method [13–15]. However, based on the literature [11,16,17], Co is of more importance than Fe and Ni in forming better quality carbon nanotubes. The commonly used catalyst supports are alumina, silica, titania, and zeolites [18–21]. Catalyst supports are also reported to have great determination on the catalytic activity of a catalyst and the morphology of the produced carbon nanotubes. Therefore, choosing the proper support for the catalyst is needed for selectively controlling the morphology and the yields of carbon nanotubes. Sometimes, a catalyst promoter, such as Co, Cu, Fe, Mn, Mo, or Ni [22–25], is added into the supported catalysts. The alloy phase formed from the catalyst promoter can further enhance the activity, stability, and selectivity of the bimetallic catalysts in the carbon nanotubes production.

In this study, methane is used as a carbon source for the preparation of carbon nanotubes. Methane, a major component of natural gas, is abundantly available at relatively very low cost. It is also stable at elevated temperature. These two reasons have attracted our interest in producing carbon nanotubes via catalytic decomposition of methane. Recently, our group had succeeded in obtaining high yield

* Corresponding author. Fax: +604 5941013.

E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

bon deposited on the catalyst over the weight of the metal oxide portion of the catalyst after its complete deactivation. The selectivity of the carbon nanotubes formation was estimated by TEM. For those catalysts which possessed initial methane conversion of above 1%, the methane decomposition reaction was brought to a halt when the conversion of methane was attained below 1%. For the remaining catalysts that possessed initial methane conversion of below 1%, the reaction was allowed to continue in the reactor for another 30 min so as to confirm that the catalysts were completely deactivated. The catalytic properties of the tested catalysts are tabulated in Tables 1–3, respectively. The outer diameters of the carbon nanotubes were measured from the TEM images. The corresponding data was used to calculate their average diameters and standard deviations and these results are reported in Table 4.

Table 1
Catalytic properties of supported CoO catalysts for methane decomposition at 550 °C

Catalysts	Methane conversion ^a (%)	Duration (h)	Carbon capacity (gC/gCoO) (%)
CoO/Al ₂ O ₃	9.3	1.5	710
CoO/CaO	0.1	0.5	2.7
CoO/CeO ₂	3.0	0.5	70
CoO/H-ZSM-5	8.3	2	1254
CoO/MgO	0.2	0.5	4.1
CoO/SiO ₂	12.5	2	1337
CoO/TiO ₂	0.2	0.5	7.0

^a Initial methane conversion.

Table 2
Catalytic properties of supported CoO catalysts for methane decomposition at 700 °C

Catalysts	Methane conversion ^a (%)	Duration (h)	Carbon capacity (gC/gCoO) (%)
CoO/Al ₂ O ₃	6.5	1	223
CoO/CaO	0.7	0.5	14
CoO/CeO ₂	5.1	0.5	131
CoO/H-ZSM-5	4.7	0.5	122
CoO/MgO	0.4	0.5	13
CoO/SiO ₂	3.3	0.5	109
CoO/TiO ₂	1.4	0.5	45

^a Initial methane conversion.

Table 3
Catalytic properties of promoted supported CoO catalysts for methane decomposition at 700 °C

Catalysts	Methane conversion ^a (%)	Duration (h)	Carbon capacity (gC/gCoO-M) (%)
8CoO-2CuO/Al ₂ O ₃	2.9	0.5	77
8CoO-2FeO/Al ₂ O ₃	5.2	0.5	134
8CoO-2MoO/Al ₂ O ₃	6.3	1.5	281
8CoO-2NiO/Al ₂ O ₃	5.3	0.5	142

^a Initial methane conversion.

Table 4
Average diameters and standard deviations of carbon nanotubes produced over various CoO-containing catalysts at 550 °C and 700 °C

Catalysts	Reaction temperature (°C)	Average diameter (nm)	Standard deviation (nm)	Number of nanotubes counted
CoO/SiO ₂	550	27.0	5.8	78
CoO/H-ZSM-5	550	27.5	8.2	131
CoO/Al ₂ O ₃	550	14.6	4.5	133
CoO/Al ₂ O ₃	700	9.4	3.6	101
8CoO-2NiO/Al ₂ O ₃	700	8.9	3.5	148
8CoO-2FeO/Al ₂ O ₃	700	7.3	3.7	123
8CoO-2MoO/Al ₂ O ₃	700	10.7	3.2	220

3.1. Catalytic performance of supported CoO catalysts at 550 °C

Experimental data obtained in the decomposition of methane over the supported CoO catalysts at 550 °C are summarized in Table 1. The inspection of the data obtained reveals that the amount of carbon deposited on CoO/SiO₂, CoO/H-ZSM-5, and CoO/Al₂O₃ catalysts were higher than those for the other tested catalysts. On the other hand, CoO/CaO, CoO/MgO, and CoO/TiO₂ catalysts possessed initial methane conversion of below 1%, revealing that these catalysts are not active in the decomposition of methane. The carbon capacity over the supported CoO catalysts, as shown in Table 1, was found to decrease in the order of silica > zeolite > alumina > ceria > titania > magnesia > calcium oxide. The best catalytic performance was that of CoO/SiO₂ catalyst, giving the highest carbon capacity of 1337%. The used CoO/SiO₂, CoO/H-ZSM-5, and CoO/Al₂O₃ catalysts were analyzed using TEM. The TEM images of the carbons deposited on the CoO/SiO₂, CoO/H-ZSM-5, and CoO/Al₂O₃ catalysts are shown in Fig. 2a,b and c, respectively. One can observe that carbon nanotubes were grown on the surfaces of these catalysts. Generally, carbon nanotubes formed on these catalysts exhibited hollow cores morphology. However, the hollow cores of the carbon nanotubes grown on the CoO/SiO₂ and CoO/H-ZSM-5 catalysts were narrow and insignificant in low TEM magnification. On the other hand, CoO/Al₂O₃ catalyst grew carbon nanotubes with significant hollow cores as can be seen in Fig. 2c. The diameters of carbon nanotubes formed on CoO/SiO₂ and CoO/H-ZSM-5 catalysts were roughly the same, i.e., 27.0 ± 5.8 nm and 27.5 ± 8.2 nm, respectively, whereas the diameter of carbon nanotubes on CoO/Al₂O₃ catalyst was 14.6 ± 4.5 nm, obviously smaller than those formed on the other catalysts. In addition, some of the carbon nanotubes formed on CoO/Al₂O₃ catalyst had open-end structure, meaning that no catalyst particles were present at the tips of the carbon nanotubes. The growth mechanisms of carbon nanotubes by catalytic growth have been proposed as either tips or base-growth on catalysts [27–29]. According to the TEM results in Fig. 2, the catalyst particles were seldom found at the tips of the carbon nanotubes grown on alumina supported CoO catalyst, which implies that the

alysts are denoted as CoO-M/Al₂O₃ hereafter in this Letter, where M = CuO, FeO, MoO, and NiO. The weight ratio of CoO to M was set at 8:2. The results in Table 3 indicate that the addition of metal oxide species into CoO/Al₂O₃ catalyst brought about a slight decrease in the methane conversion at the initial period, irrespective of the kind of added metal oxides. The addition of CuO, FeO, and NiO shortened the catalytic lifetime and reduced the carbon capacity of CoO/Al₂O₃ catalyst in the methane decomposition. In contrast, the addition of MoO increased the catalytic lifetime and the carbon capacity of CoO/Al₂O₃ catalyst to 1.5 h and 281%, respectively. As shown in Table 3, the carbon capacity of the promoted catalysts decreased in the following order 8CoO-2MoO/Al₂O₃ > 8CoO-2NiO/Al₂O₃ > 8CoO-2FeO/Al₂O₃ > 8CoO-2CuO/Al₂O₃.

The morphology of the carbon nanotubes produced on the promoted CoO/Al₂O₃ catalysts was examined in TEM and their images are shown in Fig. 3. From the TEM images, we can deduce that the influence of the promoters is great in controlling the morphology of the carbon nanotubes formed. Fig. 3a shows the TEM image of the carbon nanotubes deposited on 8CoO-2NiO/Al₂O₃ catalyst. TEM observations indicate that two types of carbon nanotubes were formed on the NiO promoted catalyst, including long carbon nanotubes with a diameter of ca. 15.8 nm and short carbon nanotubes with smaller diameters of ca. 5.3 nm. The average diameter of the grown carbon nanotubes

was 8.9 nm. Fig. 3b shows the TEM image of thin wall carbon nanotubes deposited on the 8CoO-2FeO/Al₂O₃ catalyst. Owing to the very thin wall structure of the carbon nanotubes, the inner cores of the nanotubes were clearly seen. These formed carbon nanotubes were smaller in size with a diameter of 7.3 ± 3.7 nm. This also shows that FeO is of importance in assisting the formation of carbon nanotubes with thin wall structure. TEM image in Fig. 3c indicates that dense carbon nanotubes were grown on the surface of 8CoO-2MoO/Al₂O₃ catalyst. Adding MoO into CoO/Al₂O₃ catalyst enhanced the formation of longer carbon nanotubes. In addition, the produced carbon nanotubes were quite straight with the inner cores axis parallel to the wall of nanotubes. The diameters of the carbon nanotubes produced over this catalyst were relatively uniform. The average diameter calculated was 10.7 nm with a standard deviation of 3.2 nm. The formation of cobalt-molybdenum alloys seemed to stabilize the catalyst in the methane decomposition reaction, giving higher carbon capacity and catalytic lifetime as aforementioned and forming better quality carbon nanotubes. It is widely known that copper is an efficient promoter for supported Ni catalysts [22] for enhancing longer catalytic lifetime. However, adding copper into CoO/Al₂O₃ catalyst reduced its catalytic activity. No carbon nanotubes were observed on the used 8CoO-2CuO/Al₂O₃ catalyst and the TEM image shown in Fig. 3d was mainly the catalyst particles

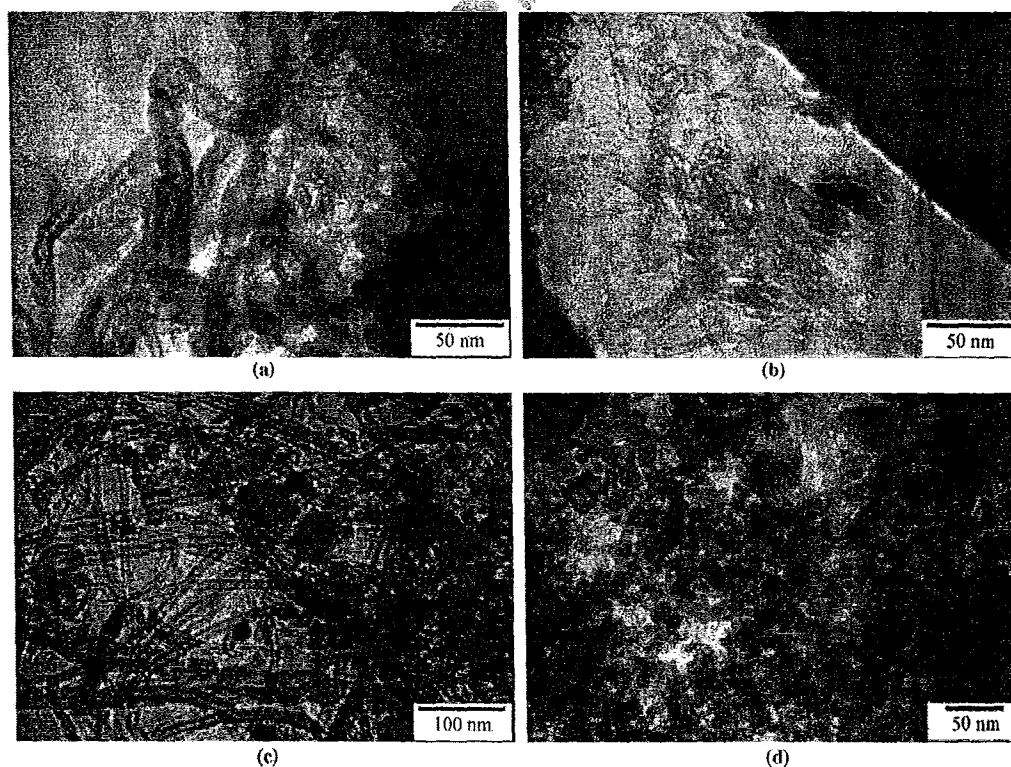


Fig. 3. TEM images of carbon nanotubes grown from methane decomposition over the bimetallic catalysts at 700 °C. (a) 8CoO-2NiO/Al₂O₃; (b) 8CoO-2FeO/Al₂O₃; (c) 8CoO-2MoO/Al₂O₃; and (d) 8CoO-2CuO/Al₂O₃.



Formation of Y-junction carbon nanotubes by catalytic CVD of methane

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, SPS Pulau Pinang, Malaysia

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Abstract

Y-junction carbon nanotubes were grown by catalytic CVD of methane at 700 °C on NiO–CuO–MoO(7:2:1)(w/w/w)/SiO₂ catalyst. For comparison, NiO–CuO(8:2)(w/w)/SiO₂ and NiO–MoO(8:2)(w/w)/SiO₂ catalysts were tested for carbon nanotube formation. TEM analysis indicates that no Y-junction structures were formed with the latter two catalysts. This finding elucidates why the addition of a small amount of MoO to NiO–CuO/SiO₂ catalyst is crucial for enhancing the formation of Y-junction carbon nanotubes.

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Keywords: A. Y-junction carbon nanotubes; A. Supported metal catalysts; B. Chemical vapor deposition; C. Transmission electron microscopy

1. Introduction

Ever since their discovery by Sumio Iijima in 1991 [1], carbon nanotubes have been one of the most actively studied materials in research. Carbon nanotubes, possessing many unique structural, mechanical, and electrical properties [2], are considered promising building blocks for nanoscale devices such as quantum wires, field-effect transistors, electron emitters, diodes, and so on [3]. In 1995, Y-junction carbon nanotubes, structures comprising three joining tubes, were first observed in the carbon soot produced from an arc-discharge method [4]. The discovery of Y-junction carbon nanotubes brings new hope for the development of carbon nanotube-based nanoscale devices, especially nanoscale three-terminal devices such as three-terminal transistors, amplifiers and switches. Since this type of carbon nanotube is newly found, its growth mechanism remains controversial. The main focus of current research is on finding a suitable way of synthesizing Y-junction carbon nanotubes. In fact, many methods have been proposed for growing this structure, including arc discharge, template growth, and chemical vapor deposition (CVD) [5–8]. Among these, CVD is widely recognized as an attractive method due to its potential for large-scale production of carbon

nanotubes. In this communication, we report the synthesis of Y-junction carbon nanotubes from catalytic CVD of methane over supported trimetallic catalyst.

2. Experimental

For studying the formation of Y-junction carbon nanotubes, catalysts of three types, i.e. NiO–CuO–MoO(7:2:1)(w/w/w)/SiO₂, NiO–CuO(8:2)(w/w)/SiO₂, and NiO–MoO(8:2)(w/w)/SiO₂, were prepared using a conventional impregnation method. Ni(NO₃)₂·6H₂O (supplied by Aldrich), (NH₄)₆Mo₇O₂₄·4H₂O (supplied by Fischer), and Cu(NO₃)₂·3H₂O (supplied by Merck) were used as the metal sources for the preparation of NiO, MoO, and CuO. Silica (Cab-osil, supplied by RhD) was used as a catalyst support. The impregnated samples were dried at 105 °C for 12 h and calcined in air at 600 °C for 5 h. The catalysts were then sieved to a size of 425–600 μm. The catalysts were used without prior reduction in the hydrogen flow since the metal in oxide form will be readily reduced in the reaction environment by means of methane and the hydrogen gas produced. 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 detailed experimental set-up and catalyst preparation procedures have been reported previously [9,10]. The carbons deposited on the catalysts were analyzed using a transmission electron microscopy (TEM) system (Philips, model CM12).

* Corresponding author. Tel.: +60 4599 5999x6410; fax: +60 4594 1013.
E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

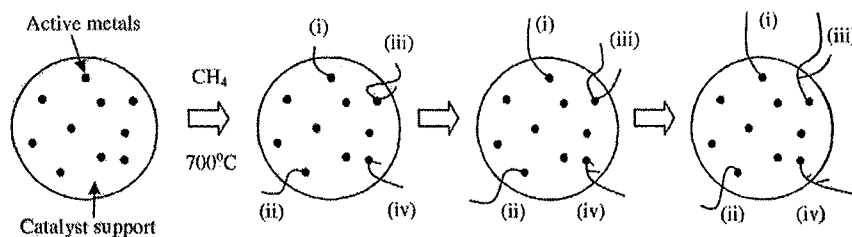


Fig. 2. Schematic diagrams showing the proposed sequential growth mechanism of straight ((i), (ii)) and Y-junction ((iii), (iv)) tabular carbon structures.

by (iii), (iv) in Fig. 2. It is likely that the addition of a small amount of MoO to NiO–CuO acts as nucleation sites, seeding the growth of carbon nanotube branches. We believe that, after some time, the surface carbons deposited on the active metals will join the graphitic layers for both carbon nanotube stems and branches, forming a poorly graphitized junction part. This is evident when most of the junction parts observed under the TEM exhibit poor crystalline wall structure. The continuous growth of a carbon nanotube stem forms the Y-junction structure. In the process that follows, other branches could also be formed on the Y-junction carbon nanotube stem. The growth mechanism of a second carbon nanotube branch is represented by (iv) in Fig. 2 and the arrows indicated in Fig. 1(a) show clearly the other short carbon nanotube branches. Y-junction carbon nanotubes without short branches (Fig. 1(b)) were grown on the catalyst, following the mechanism represented by (iii) in Fig. 2.

4. Conclusions

Y-junction carbon nanotubes were synthesized over a complex NiO–CuO–MoO/SiO₂ catalyst. Straight tubular carbon structures were formed by NiO–CuO and NiO–MoO supported on SiO₂ catalysts. Adding a small amount of MoO to NiO–CuO sees the formation of Y-junction carbon nanotubes. This shows that Mo plays a role in inducing the formation of carbon nanotube branches. However, the yield of Y-junction carbon nanotubes obtained in this study is still low, as they are

only a by-product of the CVD process. We believe that through appropriate adjustment of the ratio of NiO, CuO and MoO, it will be possible to increase the selectivity of the catalyst towards the formation of Y-junction carbon nanotubes.

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Article

CO_x-Free Hydrogen and Carbon Nanofibers Produced from Direct Decomposition of Methane on Nickel-Based Catalysts

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed*

*School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan,
14300 Nibong Tebal, SPS Penang, Malaysia*

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Abstract: Direct decomposition of methane was carried out using a fixed-bed reactor at 700 °C for the production of CO_x-free hydrogen and carbon nanofibers. The catalytic performance of NiO-M/SiO₂ catalysts (where M=AgO, CoO, CuO, FeO, MnO_x and MoO) in methane decomposition was investigated. The experimental results indicate that among the tested catalysts, NiO/SiO₂ promoted with CuO give the highest hydrogen yield. In addition, the examination of the most suitable catalyst support, including Al₂O₃, CeO₂, La₂O₃, SiO₂, and TiO₂, shows that the decomposition of methane over NiO-CuO favors SiO₂ support. Furthermore, the optimum ratio of NiO to CuO on SiO₂ support for methane decomposition was determined. The experimental results show that the optimum weight ratio of NiO to CuO fell at 8:2 (w/w) since the highest yield of hydrogen was obtained over this catalyst.

Key words: methane decomposition; hydrogen; carbon nanofibers; supported catalyst

1. Introduction

The utilization of natural gas, one of the world's abundant resources, to produce valuable chemicals is one of the desirable goals in the current natural gas processing industry. In this regard, the production of hydrogen from natural gas has attracted the interest of industrialists and researchers. The conventional options of hydrogen production from natural gas, such as steam reforming, partial oxidation, and autothermal reforming [1], involve CO_x production at some point in the technological chain of the process. Thus, the gas needs further treatment to separate hydrogen from the other gases such as CO and CO₂. Hence, it is of importance to develop a simpler and less energy intensive method to produce hydrogen, which is free of CO_x formation as this can reduce the capital cost in comparison to the conventional method. One way to reach this objective is to use direct decomposition of methane over catalytic materials for the production of hydrogen [2–4].

Direct catalytic decomposition of methane, the main constituent of natural gas, offers the possibility of producing two valuable chemical commodities: pure hydrogen and carbon nanofibers. It is a technologically simple one-step process without energy and material intensive gas separation stages and shows the potential to be a CO_x-free hydrogen production process. The hydrogen produced from methane decomposition does not contain CO_x impurities. Undoubtedly, the produced hydrogen can be used directly without any removal of CO_x. Carbon nanofibers, a by-product, which are produced from methane decomposition, are predominant mesoporous materials with high surface area [4]. Such properties make these promising materials for applications in the areas of catalysis, adsorption, and nanocomposites [5–7].

Recently, direct catalytic decomposition of methane at lower temperature has received attention as an alternative route to the production of hydrogen. Several groups have studied methane decomposition

* Corresponding author. E-mail: chrahman@eng.usm.my

High purity methane (99.999% supplied by Malaysian Oxygen Sdn. Bhd.) was mixed with argon (99.999% purity, supplied by Sitt Tatt Industrial Gases Sdn. Bhd.) before entering the reactor and 0.2 g of catalyst was put in the middle part of the reactor for each run. The flow of methane was regulated using a mass flow controller (MKS) and the argon flow was regulated using mass flow controllers (Brooks, model 5850E). The product gases were analyzed using an on-line gas chromatograph (Hewlett-

Packard Series 6890, USA). The schematic diagram of the experimental apparatus is shown in Figure 1. The carbon nanofibers deposited on the catalysts were analyzed using a transmission electron microscope (TEM) (Philips, CM12). During preparation for the TEM experiments, a few samples of the spent catalyst were dispersed in acetone (99.8% purity), and then a drop was deposited on a coated copper grid. The conversion of methane, and the hydrogen yield are defined as follows:

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

$$\text{Hydrogen yield} = \frac{\text{Mole of hydrogen produced}}{\text{Mole of metal oxide in a fresh catalyst}} \quad (2)$$

3. Results and discussion

3.1. Effect of catalyst promoters

Table 1 shows the catalytic performance of the NiO/SiO₂ catalyst promoted with different metal oxide species for methane decomposition at 700 °C. The promoted catalysts are denoted as NiO-M/SiO₂ in this article (where, M=AgO, CoO, CuO, FeO, MnO_x, and MoO). The loadings of NiO-M were adjusted to 10 wt.% with respect to the weight of the catalyst and the weight ratio of NiO to M was set as 9:1. For all catalysts, the methane decomposition proceeded selectively to form hydrogen as the only gaseous product. Methane conversion over the NiO/SiO₂ catalyst was high during the initial reaction. The conversion decreased remarkably with time on stream, possessing conversion of below 1% after 30 min of time on stream. The addition of CoO and MoO slightly improved the catalytic lifetime of NiO/SiO₂ for the methane decomposition. In contrast, the addition of AgO, FeO, and MnO_x shortened the catalytic lifetime of NiO/SiO₂. It was noticed that NiO/SiO₂ promoted with CuO showed significant increase in the catalytic activity and the lifetime in methane decomposition. In the

presence of CuO as the promoter for NiO/SiO₂, the stability and activity of the catalyst were enhanced markedly.

Figure 2 shows the hydrogen yields over the tested catalysts for 90 min of reaction. The yields were estimated from the obtained methane conversion, assuming that the methane conversion to hydrogen and carbon proceeded stoichiometrically (CH₄→C+2H₂). The hydrogen yield for NiO/SiO₂ was evaluated as 140 mol_{H₂}/mol_{NiO₂}. The hydrogen yields for 9NiO-1CoO, 9NiO-1FeO, and 9NiO-1MoO/SiO₂ were 157 mol_{H₂}/mol_(NiO-CoO), 134 mol_{H₂}/mol_(NiO-FeO), and 161 mol_{H₂}/mol_(NiO-MoO), respectively. However, NiO/SiO₂ promoted with AgO and MnO_x were less active in methane decomposition, giving hydrogen yields of 19 mol_{H₂}/mol_(NiO-AgO) and 14 mol_{H₂}/mol_(NiO-MnO_x), respectively. According to

Table 1. Methane conversions up to 90 min reaction over 9NiO-1M catalysts supported on SiO₂ at 700 °C

Catalyst	Methane conversion (%)			
	5 min	30 min	60 min	90 min
NiO/SiO ₂	47.6	0.8	0.7	0.5
9NiO-1AgO/SiO ₂	1.7	0.9	0.9	0.7
9NiO-1CoO/SiO ₂	48.8	3.5	1.6	1.4
9NiO-1CuO/SiO ₂	51.5	43.0	26.2	1.5
9NiO-1FeO/SiO ₂	44.1	1.0	0.7	0.6
9NiO-1MnO _x /SiO ₂	3.2	0.7	0.5	0.4
9NiO-1MoO/SiO ₂	47.8	2.1	1.6	1.4

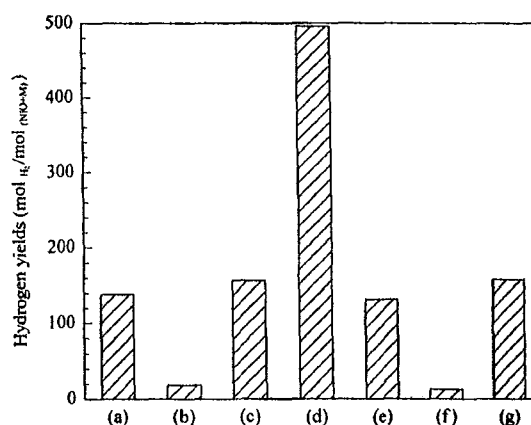


Figure 2. Hydrogen yields in the methane decomposition over NiO/SiO₂ and 9NiO-1M/SiO₂ catalysts at 700 °C

(a) NiO/SiO₂; (b) 9NiO-1AgO/SiO₂; (c) 9NiO-1CoO/SiO₂; (d) 9NiO-1CuO/SiO₂; (e) 9NiO-1FeO/SiO₂; (f) 9NiO-1MnO_x/SiO₂; (g) 9NiO-1MoO/SiO₂

from 9:1 to 5:5 remarkably prolonged the catalytic lifetime. However, the addition of excess amounts of CuO (weight ratio NiO:CuO<4:6) decreased the catalytic lifetime for the methane decomposition. As shown in Figure 5, the hydrogen yield increased significantly with an increase in CuO loading into the NiO/SiO₂ catalyst and the yield attained the maximum at NiO:CuO=8:2. The maximum hydrogen yield was 536, which was about 4 times greater than that of the NiO/SiO₂ catalyst. The hydrogen yields obtained for the catalysts with the weight ratio of NiO:CuO as 9:1, 7:3, 6:4, 5:5, and 4:6 are 494, 452, 272, 208, and 128 mol_{H₂}/mol_(NiO-CuO), respectively. This shows that the increase of copper content improved the catalyst stability, but the continual increase of copper content resulted in a great decrease of the catalyst stability.

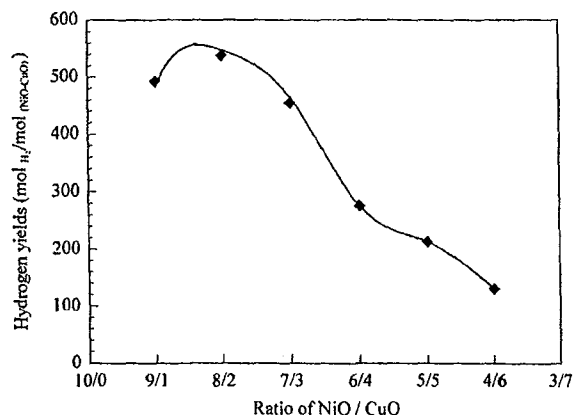


Figure 5. Hydrogen yields in the methane decomposition over NiO-CuO/SiO₂ catalysts with different weight ratios of NiO to CuO at 700 °C

3.4. Characterization of used catalysts

Figure 6 shows the TEM images of carbon deposited by the methane decomposition over NiO/SiO₂ and 8NiO-2CuO/SiO₂ catalysts. It was found that carbon nanofibers were formed on the surfaces of both catalysts. However, there are differences in the morphology of the grown carbon nanofibers. It was noticed that the average diameter of the carbon nanofibers grown on the 8NiO-2CuO/SiO₂ catalyst were clearly larger than those on the NiO/SiO₂ catalyst. Furthermore, carbon nanofibers on the 8NiO-2CuO/SiO₂ catalyst seem more fragile when compared to those formed on the NiO/SiO₂ catalyst. This reveals that the carbon nanofibers grown on the NiO/SiO₂ catalyst have a higher degree of graphi-

tization than those on the 8NiO-2CuO/SiO₂ catalyst. Owing to the high activity and stability of the 8NiO-2CuO/SiO₂ catalyst in methane decomposition, the grown carbon nanofibers are denser, forming an interwoven coverage under TEM observation. It is important to note that catalyst particles were present on the tips of carbon nanofiber grown on the NiO/SiO₂ catalyst, whereas no catalyst particles were observed on the tips of carbon nanotubes formed by the 8NiO-2CuO/SiO₂ catalyst. This shows that the growth model of carbon nanofibers on these two catalysts was different. It is deduced that the carbon nanofiber grown by the NiO/SiO₂ catalyst followed the tips-growth model where the catalyst particles located on the tips of the carbon nanofibers were active for methane decomposition. On the other hand, the based-growth model was used for growing carbon nanofibers on the 8NiO-2CuO/SiO₂ catalyst, where the catalyst particles attached on the SiO₂ support were active for methane decomposition.

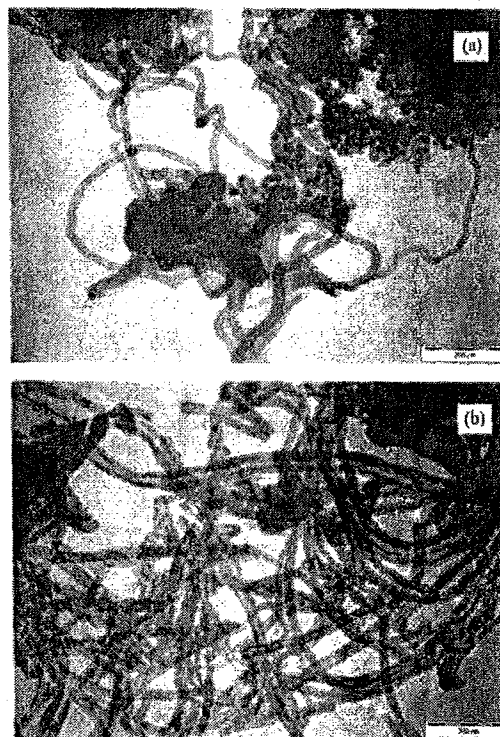
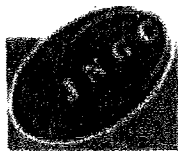


Figure 6. TEM image of carbon nanofibers produced on (a) NiO/SiO₂, and (b) 8NiO-2CuO/SiO₂, in methane decomposition at 700 °C

4. Conclusions

A comparison of the catalytic properties of the NiO/SiO₂ catalyst promoted with AgO, CoO, CuO,



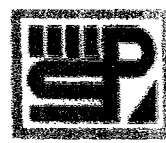
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Article

Production of High Purity Multi-Walled Carbon Nanotubes from Catalytic Decomposition of Methane

Kong Bee Hong, Aidawati Azlin Binti Ismail, Mohamed Ezzaham Bin Mohd Mahayuddin, Abdul Rahman Mohamed, Sharif Hussein Sharif Zein*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

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Abstract: Acid-based purification process of multi-walled carbon nanotubes (MWNTs) produced *via* catalytic decomposition of methane with NiO/TiO₂ as a catalyst is described. By combining the oxidation in air and the acid refluxes, the impurities, such as amorphous carbon, carbon nanoparticles, and the NiO/TiO₂ catalyst, are eliminated. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirm the removal of the impurities. The percentage of the carbon nanotubes purity was analyzed using thermal gravimetric analysis (TGA). Using this process, 99.9 wt% purity of MWNTs was obtained.

Key words: multi-walled carbon nanotubes; purification; acid refluxes; oxidation; methane; decomposition

1. Introduction

Since their discovery by Iijima in 1991 [1], carbon nanotubes have been extensively researched and have resulted in various potential applications [2–4], thus opening a new chapter in nanoscale materials science. However, a major issue that remains unresolved is its purification. Most synthesis methods of the carbon nanotubes are based on the use of the catalyst and the as-synthesized carbon nanotubes are then contaminated with metal catalyst and other carbonaceous materials such as amorphous carbon and carbon nanoparticles [5]. These impurities are closely entangled with the carbon nanotubes and hence influence the carbon nanotubes structural and electronic properties and thereby limit their applications [6]. Therefore, it is necessary to purify the as-synthesized carbon nanotubes to enable their application in many areas.

Several purification processes have been reported.

For example, Wiltshire *et al.* [7] used magnet to separate ferromagnetic catalyst particles from an aqueous surfactant solution of carbon nanotubes. The residual quantity of the Fe catalyst was 3 wt%. Moon *et al.* [8] used a two step process of thermal annealing in air and acid treatment to purify single-walled carbon nanotubes. This process provided carbon nanotubes with metal catalysts less than 1%. Strong *et al.* [9] used a combination of oxidation followed by acid washing and provided residue mass as low as 0.73 wt%. A microwave-assisted digestion system was used to dissolve the metal catalyst in organic acid followed by filtration [10,11]. This method provided 99.9 wt% purity of the carbon nanotubes.

Although various purification methods have been reported by researchers, which have shown high purity, no effective common method has yet been found for the removal of impurities for all types of as-synthesized carbon nanotubes. Therefore, the purification method depends on the specific type of cat-

* Corresponding author. Tel: 6045996442; Fax: 604-5941013; E-mail: chhussein@eng.usm.my

as-synthesized MWNTs (500 °C). This is because of the metal catalysts that still remained in the MWNTs and enhanced the combustion rate of the MWNTs and thus reduced the combustion temperature [15]. Figure 1(c) shows the TGA graph of MWNTs that were purified using nitric acid refluxes followed by oxidation in air. There was no weight loss between 0 °C and 400 °C, which indicates that these MWNTs are free of amorphous carbon. The MWNTs started burning at approximately 500 °C and completed at 700 °C. Thus, the purified MWNTs have purity of 84 wt%. The metal catalysts that still exist were of 16 wt%. Therefore, in this purification process, oxidation in air is more suitable than chemical oxidation.

To remove the end caps of the multi-walled carbon nanotubes and to expose the metal oxides for further acid dissolving, oxidation in air was introduced prior to acid refluxes. Figure 1(d) shows the TGA graph of the MWNTs after purification using oxidation in air followed by nitric acid refluxes and then re-oxidation in air. There was no mass loss between the temperature ranges of 300 °C and 400 °C, which indicates that the purified MWNTs are free of amorphous carbon. The MWNTs started burning at 500 °C and stopped at 835 °C. The residue at 835 °C amounted to 8 wt% of the original mass and was attributed to the NiO/TiO₂ catalyst. The total mass loss of this sample was 92 wt%.

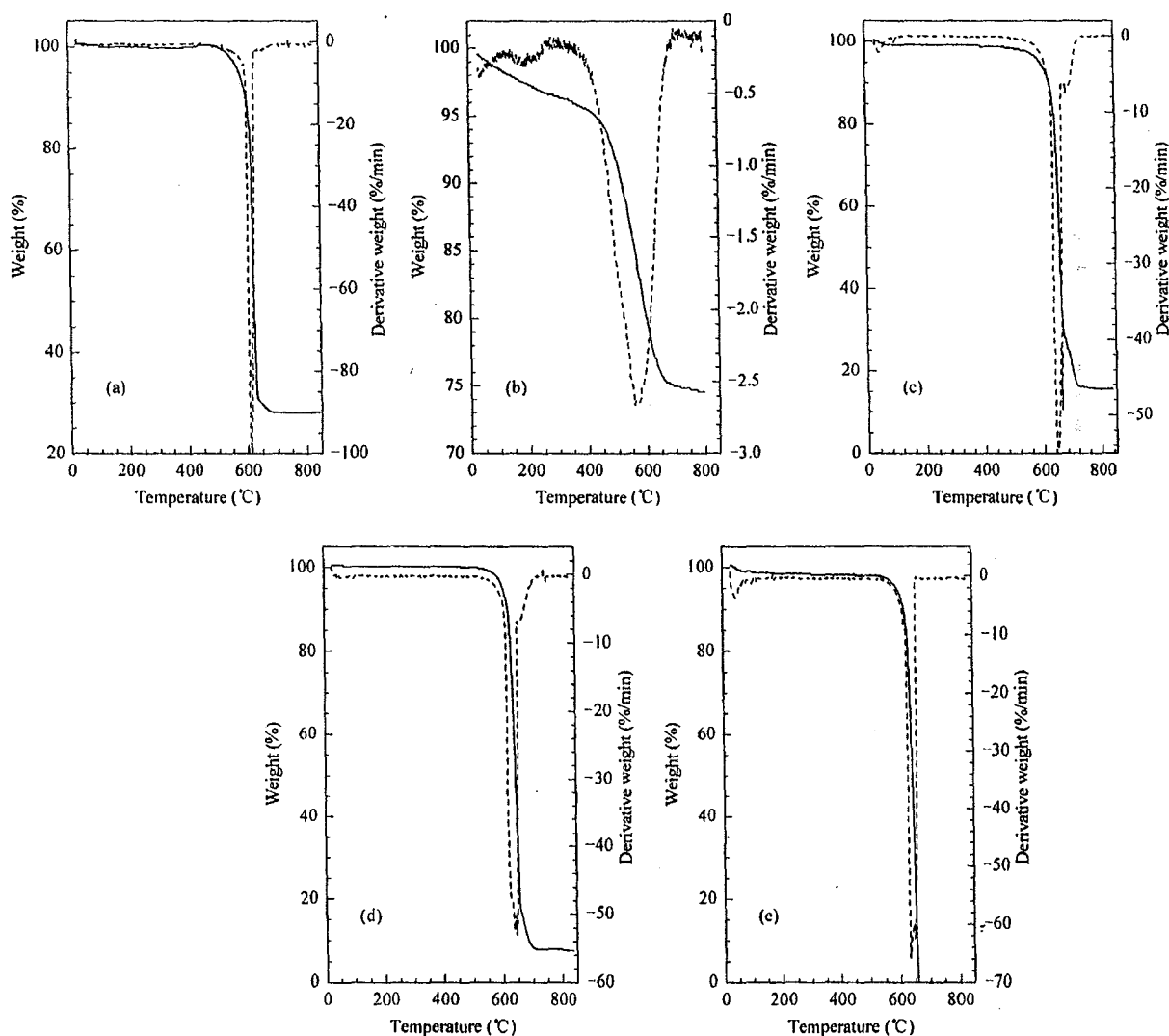


Figure 1. TGA graphs of: (a) as-synthesized MWNTs, (b) MWNTs after purification using nitric acid refluxes/chemical oxidation, (c) MWNTs after purification using nitric acid refluxes/oxidation in air, (d) MWNTs after purification using oxidation in air followed by nitric acid refluxes and then re-oxidation in air, (e) MWNTs after purification using oxidation in air followed by sulfuric acid refluxes and then re-oxidation in air

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Moderate temperature synthesis of single-walled carbon nanotubes on alumina supported nickel oxide catalyst

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S. Pulau Pinang, Malaysia

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Abstract

A simple nickel oxide catalyst has been developed in synthesizing single-walled carbon nanotubes (SWNTs) at moderate temperature. The catalyst used in the experiment was without a preceding reduction in hydrogen flow. The synthesis of SWNTs was performed at a temperature of 700 °C, which represents a moderate reaction temperature. The presence of SWNTs on the catalyst was confirmed by transmission electron microscope (TEM) and Raman spectroscopy. The Raman spectrum shows a strong intensity at the radial breathing mode, indicating that the occurrence of SWNTs was dominant. Raman data further reveals that the synthesized SWNTs had the diameters in the range from 0.58 to 2.02 nm. © 2006 Elsevier B.V. All rights reserved.

Keywords: Single-walled carbon nanotubes; Catalyst; Nanomaterials; Electron microscopy; Raman spectroscopy

1. Introduction

The remarkable electronic and mechanical properties of single-walled carbon nanotubes (SWNTs) have generated an intense interest in searching for better synthesis ways to grow them. In this regard, arc-discharge, laser ablation and catalytic growth methods have been developed to produce these one-dimensional structures. However, arc-discharge and laser ablation methods, which require very high temperature (≥ 3000 °C) [1], are not economical for producing SWNTs in a large quantity. By comparison, the catalytic growth method, involving the decomposition of hydrocarbons catalyzed by supported transition metals, has been appreciated as the most promising method for producing SWNTs on a large scale [2]. Unfortunately, most of the catalytic growth methods favor higher reaction temperatures (900–1200 °C) in synthesizing SWNTs [3–5], which is a major drawback. According to Ando et al. [4], higher energy is required to form SWNTs due to the high strain energy, resulting from the smaller diameter and high curvature of these one-dimensional structures. It is important to note that higher reaction temperature increases the cost of production and enhances the deposition of undesirable carbonaceous materials

which resulted from the thermal-pyrolysis of hydrocarbons. On the other hand, reducing the reaction temperature favors the formation of multi-walled carbon nanotubes (MWNTs) and carbon nanofibers [4–7]. Therefore, synthesizing SWNTs at lower reaction temperature is of difficulty and truly a challenge. As a consequence of this, many works have been done to reduce the temperature in synthesizing SWNTs, such as using microwave plasma enhanced chemical vapor deposition (MPCVD) [8,9] and alcohol CVD [10]. Both methods are efficient in reducing the temperature synthesis of SWNTs.

As our research interest, here we report a single-step process to synthesize SWNTs at a reaction temperature of 700 °C via catalytic decomposition of methane using unreduced NiO/Al₂O₃ catalyst. This setup is less sophisticated than the MPCVD. In addition, the use of methane, a low cost hydrocarbon feedstock, can reduce the cost of SWNTs production. Reduction of catalyst is avoided in this study because this could increase the complexity of catalyst synthetic procedure and the cost of catalyst used on a large scale production of SWNTs [11,12].

2. Experimental

In this study, the synthesis of SWNTs was carried out at atmospheric pressure in a fixed bed reactor (length and diameter of the reactor were 600 and 20 mm, respectively). The detailed

* Corresponding author. Tel.: +60 4 599 6410; fax: +60 4 594 1013.

E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

SWNTs, was mainly induced by the strong metal-support interaction (MSI) between the NiO nanoparticles and the Al₂O₃ support. Strong MSI of NiO/Al₂O₃ catalyst allowed high NiO dispersion and prevented NiO species from aggregating and forming larger clusters. However, some of the adjacent NiO nanoparticles might agglomerate during calcination, forming larger NiO particles that led to the formation of MWNTs as observed in the TEM image.

4. Conclusions

A simple nickel oxide based catalyst has been developed in synthesizing SWNTs at moderate temperature. The TEM images of the used catalyst reveal the presence of SWNTs and MWNTs. The Raman spectrum shows strong intensity at radial breathing mode, indicating that the occurrence of SWNTs was dominant. As confirmed by Raman spectroscopy, the synthesized SWNTs have a diameter in the range from 0.58 to 2.02 nm. However, the broad radial breathing mode discloses that the synthesized SWNTs were not mono-dispersed in diameter. Further studies will be conducted to control the distribution and the size of NiO nanoparticles on Al₂O₃ support for enhancing the selectivity and the attainability in producing SWNTs with narrower diameter distribution at this reaction condition.

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Synthesizing carbon nanotubes and carbon nanofibers over supported-nickel oxide catalysts via catalytic decomposition of methane

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

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Abstract

Supported-NiO catalysts were tested in the synthesis of carbon nanotubes and carbon nanofibers by catalytic decomposition of methane at 550 °C and 700 °C. Catalytic activity was characterized by the conversion levels of methane and the amount of carbons accumulated on the catalysts. Selectivity of carbon nanotubes and carbon nanofiber formation were determined using transmission electron microscopy (TEM). The catalytic performance of the supported-NiO catalysts and the types of filamentous carbons produced were discussed based on the X-ray diffraction (XRD) results and the TEM images of the used catalysts. The experimental results show that the catalytic performance of supported-NiO catalysts decreased in the order of NiO/SiO₂ > NiO/HZSM-5 > NiO/CeO₂ > NiO/Al₂O₃ at both reaction temperatures. The structures of the carbons formed by decomposition of methane were dependent on the types of catalyst supports used and the reaction temperatures conducted. It was found that Al₂O₃ was crucial to the dispersion of smaller NiO crystallites, which gave rise to the formation of multi-walled carbon nanotubes at the reaction temperature of 550 °C and a mixture of multi-walled carbon nanotubes and single-walled carbon nanotubes at 700 °C. Other than NiO/Al₂O₃ catalyst, all the tested supported-NiO catalysts formed carbon nanofibers at 550 °C and multi-walled carbon nanotubes at 700 °C except for NiO/HZSM-5 catalyst, which grew carbon nanofibers at both 550 °C and 700 °C.

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Keywords: Carbon nanotubes; Carbon nanofibers; Catalytic process; Electron microscopy

1. Introduction

Very small diameter filamentous carbons had been successfully synthesized by decomposition of hydrocarbon over transition metal catalysts prior to the discovery of fullerene in 1985 [1]. However, the synthesis of filamentous carbons did not attract the attention of scientists in those early years. The extensive research in this field only started after the discovery of multi-walled carbon nanotubes by Sumio Iijima in 1991 [2]. This discovery was a real breakthrough on filamentous carbon research and had attracted a great number of researchers in exploring deeper into understanding the synthesis mechanism, the properties of carbon nanotubes and their potential applications. The synthesis of carbon nanotubes before 1993 was carried out mainly by using the electric-arc-discharge method, which had limitation in the high yield

production of carbon nanotubes. In 1993, catalytic approach was first used by Yacaman et al. [3] in synthesizing carbon nanotubes and this method has potentiality to be scaled up to industrial production. There are still vast amounts of work to be done to improve the said production method in order to produce carbon nanotubes on a large scale and with desirable morphology. In addition, extensive research has been carried out to reduce the cost of carbon nanotubes production. One of the main approaches for reducing the cost of production is to lower the reaction temperature. Such a condition is advantageous, as most of the catalysts do not deactivate rapidly at lower reaction temperature, i.e. below 700 °C [4–6]. However, production of carbon nanotubes still favors higher reaction temperature due to the fact that lower reaction temperature leads to the formation of carbon nanofibers as has been identified by several authors [4,7,8].

In this study, methane was used as a carbon source. This is due to the fact that methane, a major component of natural gas, is highly abundant at low cost. Furthermore, it is stable at elevated temperatures. For this reason, catalytic decomposition

* Corresponding author. Tel.: +60 4 599 5999x6410; fax: +60 4 594 1013.
E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

conversions and percentage of carbon deposition. The percentage of carbon deposition is defined as follows:

$$\text{Carbon deposition (\%)} = 100 \frac{\text{weight of carbon deposited on the catalyst}}{\text{weight of NiO portion of the catalyst}}$$

2.3. Characterization

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 fresh catalysts and the deposited carbons were analyzed via a transmission electron microscopy (TEM) system (Philips, model CM12). X-ray diffraction (XRD) patterns of the fresh catalysts were measured by Siemen D-5000 diffractometer, using Cu K α 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. The average NiO crystallites size was obtained by the Scherrer equation based on the half-width of diffraction lines assigned to NiO(111).

$$D_{\text{NiO}(111)} = \frac{0.89\lambda}{\beta_d \cos\theta} \times \frac{180^\circ}{\pi}$$

where D is the average NiO crystallite size, λ is the peak length (1.54056 Å), β_d is the corrected half peak width of NiO from 37.4°

3. Results

3.1. Methane decomposition on supported-NiO catalysts

Fig. 2 depicts the kinetic curves of methane conversions with time on stream of methane over different supported-NiO

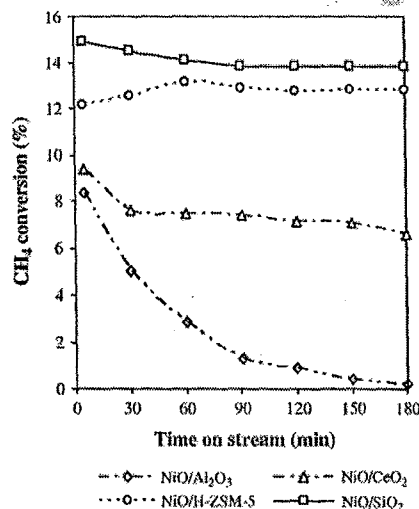


Fig. 2. Kinetic curves of methane conversion as a function of time over supported-NiO catalysts. Reaction temperature=550 °C.

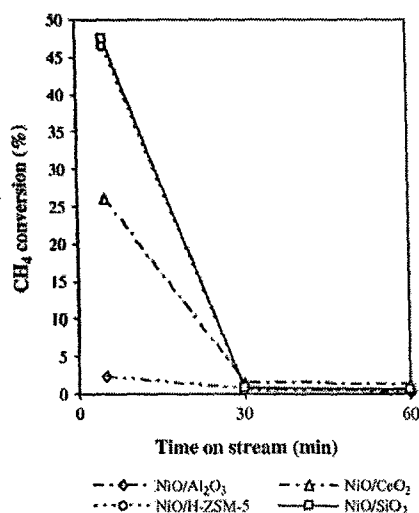


Fig. 3. Kinetic curves of methane conversion as a function of time over supported-NiO catalysts. Reaction temperature=700 °C.

catalysts at 550 °C. Fig. 2 shows that the methane conversion for NiO/SiO₂ catalyst was the highest among the catalysts tested, followed by NiO/HZSM-5, NiO/CeO₂ and NiO/Al₂O₃ catalysts. NiO/Al₂O₃ catalyst was not efficient in methane decomposition where the catalytic activity obtained declined gradually with time on stream and complete deactivation was observed at 180 min. Fig. 3 shows the kinetic curves of methane conversions as a function of time on stream in methane decomposition at 700 °C. It can be seen that the initial methane conversions over NiO/SiO₂, NiO/HZSM-5 and NiO/CeO₂ catalysts increased when the reaction temperature was raised from 550 °C to 700 °C. However, the stability of these catalysts became weak. It is noteworthy that the catalytic activity dropped rapidly after methane came into contact with the catalysts and the reaction was stopped after 1 h reaction as the methane conversions recorded for all tested catalysts were below 2%. The carbon deposition is estimated from the kinetic curves of methane conversions and the amounts of carbon produced after 3 h reaction at 550 °C and 1 h reaction at 700 °C are summarized in Table 1. Among the supported-NiO catalysts tested, the NiO/SiO₂ catalyst yielded the highest amount of carbon in methane decomposition, giving the percentage of carbon deposition of 3451% and 1032% at 550 °C and 700 °C, respectively. As a whole, the

Table 1

The amount of carbon deposited on 10 wt.% NiO catalysts supported on different catalyst supports at 550 °C and 700 °C, respectively

Catalysts	550 °C		700 °C	
	Carbon deposition (%)	Duration (h)	Carbon deposition (%)	Duration (h)
NiO/SiO ₂	3451	3	1032	1
NiO/HZSM-5	3130	3	981	1
NiO/CeO ₂	1824	3	649	1
NiO/Al ₂ O ₃	599	3	69	1

Table 2
The average NiO crystallite size for supported-NiO catalysts

Catalysts	D, average NiO crystallite size (nm)
NiO/SiO ₂	39.6
NiO/HZSM-5	20.8
NiO/CeO ₂	57.9
NiO/Al ₂ O ₃	3.1

on Al₂O₃ support were very small and highly dispersed [23]. This is in agreement with the results obtained from the TEM analysis, which suggested that Al₂O₃ give the formation of very small NiO crystallites. The average diameter of NiO crystallites on different catalyst supports as estimated from the XRD patterns is summarized in Table 2. The data in Table 2 show that the average diameter of NiO crystallites decreased in the order of NiO/CeO₂ (57.9 nm) > NiO/SiO₂ (39.6 nm) > NiO/HZSM-5 (20.8 nm) > NiO/Al₂O₃ (3.1 nm).

3.3. Characterizations of deposited carbons

Fig. 6 shows the TEM images of NiO/SiO₂, NiO/HZSM-5, NiO/CeO₂ and NiO/Al₂O₃ catalysts after 3 h reaction in methane decomposition at 550 °C. All the TEM images show that the carbons deposited on the catalysts from methane

decomposition had filamentous structures. In detail, the TEM investigation made clear that there was a big difference in the morphology of deposited carbons produced over these tested supported-NiO catalysts. The filamentous carbons grown on NiO supported on SiO₂, HZSM-5 and CeO₂ catalysts were in the form of carbon nanofibers, whereas multi-walled carbon nanotubes were grown on the surface of NiO/Al₂O₃ catalyst at the reaction temperature of 550 °C. In Fig. 6d, we can notice that the inner core of the multi-walled carbon nanotubes produced over NiO/Al₂O₃ catalyst is significant even at low magnification. Fig. 7 shows the TEM images of the supported-NiO catalysts after 1 h reaction with methane at 700 °C. As can be seen in Fig. 7a, multi-walled carbon nanotubes were produced on NiO/SiO₂ catalyst, whereas a mixture of carbon nanofibers and carbon nanotubes with thick wall and small cavity (Fig. 7c) were grown on the surface of NiO/CeO₂ catalyst. As can be observed in Fig. 7b, carbon nanofibers were grown on the surface of NiO/HZSM-5 catalyst. Interestingly, the TEM image (Fig. 7d) shows that a mixture of multi-walled carbon nanotubes and single-walled carbon nanotubes were grown on NiO/Al₂O₃ catalyst at 700 °C.

More than 50 filamentous carbons per sample were taken into account for measuring their outer diameters. The corresponding histograms were drawn and presented in Figs. 8 and 9, which

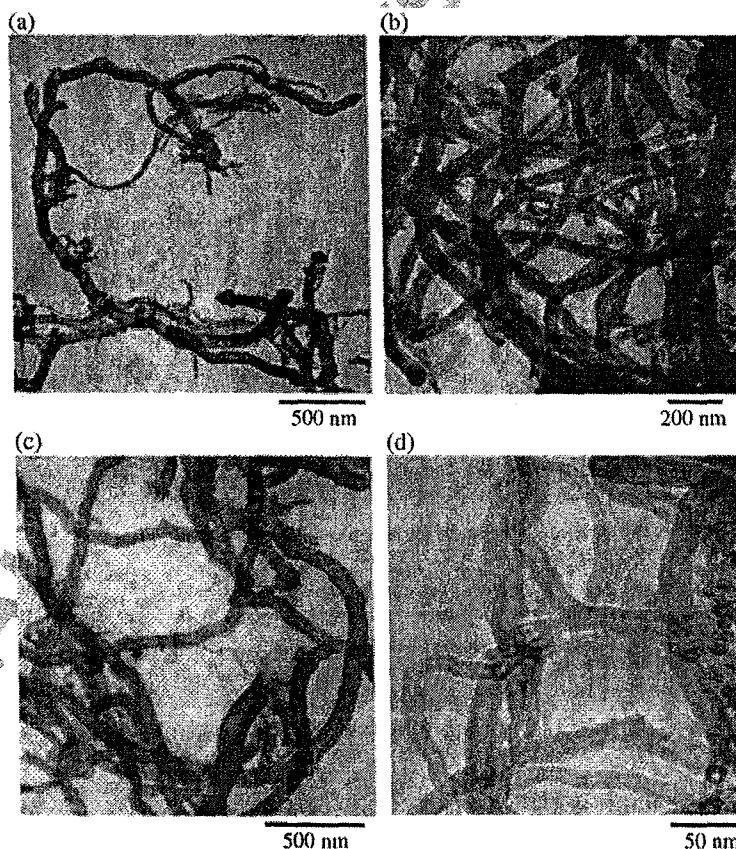


Fig. 6. TEM images of filamentous carbons produced on (a) NiO/SiO₂; (b) NiO/HZSM-5; (c) NiO/CeO₂; (d) NiO/Al₂O₃ at 550 °C.

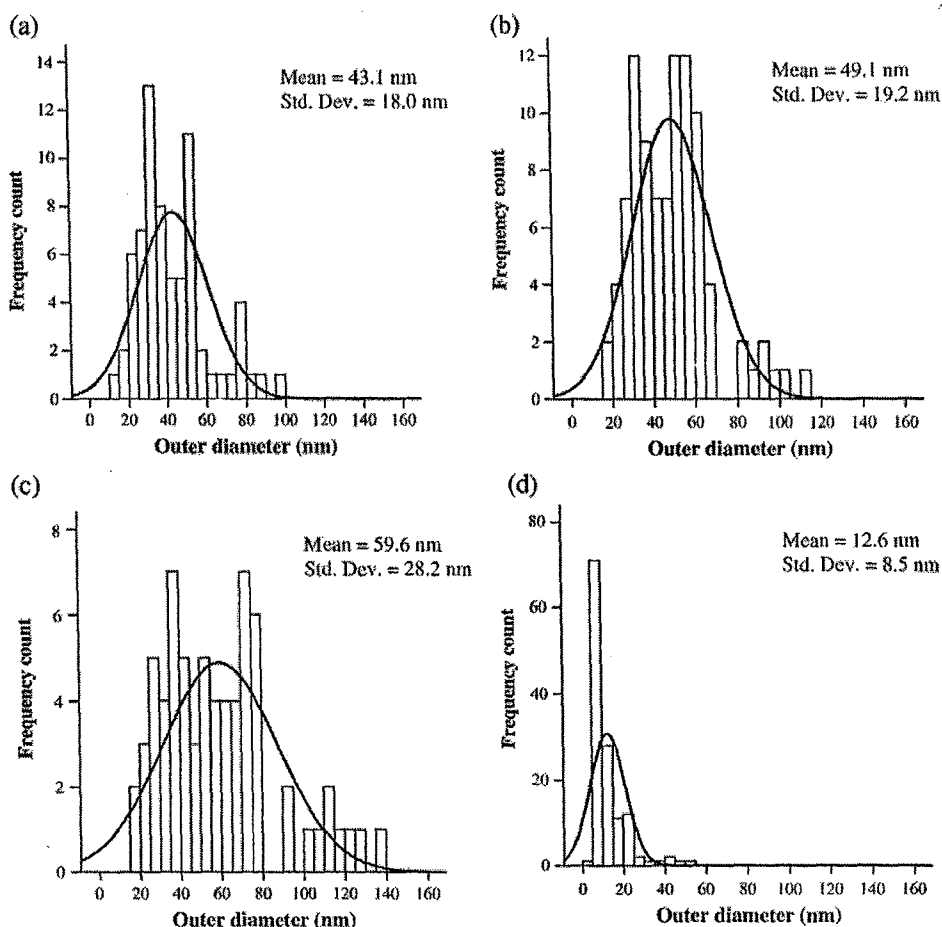


Fig. 8. Outer diameter distribution histograms of filamentous carbons synthesized over (a) NiO/SiO₂; (b) NiO/HZSM-5; (c) NiO/CeO₂; (d) NiO/Al₂O₃ catalysts at 550 °C.

resulted in a sudden surface carbon buildup on the catalysts surface. This can be seen from the initial methane conversions obtained over the catalysts tested at 700 °C which were higher than those at 550 °C. The rate of surface carbon formation was inherently much higher than the rate of carbon removal from the active surface in this condition, resulting in the accumulation of surface carbons which finally encapsulated the active site of the catalyst. This is the reason why all the tested catalysts were deactivated rapidly at 700 °C, whereas at 550 °C, they were more resistant towards catalyst deactivation.

Filamentous carbons with different morphologies were grown on these catalysts in methane decomposition. In Fig. 6, carbon nanofibers were grown on NiO supported on SiO₂, HZSM-5 and CeO₂ catalysts, and likewise carbon nanotubes on NiO/Al₂O₃ catalyst at the reaction temperature of 550 °C. To find the cause of this, we have to understand the catalyst structure. For NiO/Al₂O₃ catalyst, the Al₂O₃ support exhibited a strong interaction with NiO which dispersed NiO crystallites and formed smaller NiO crystallites. A strong metal interaction with support prevented the occurrence of the sintering process for forming larger NiO clusters. As shown in Table 2, the

average size of NiO crystallite on Al₂O₃ support was only 3.1 nm. This is the reason for the formation of smaller carbon nanotubes on NiO/Al₂O₃ catalyst. In addition, smaller sized NiO crystallites seemed to be the contributing factor in the formation of carbon nanotubes with hollow cores. On the contrary, bigger sized NiO crystallites such as those formed on NiO/SiO₂, NiO/HZSM-5 and NiO/CeO₂ catalysts contributed towards growing carbon nanofibers with solid cores as can be observed on the used catalysts at 550 °C. We believe that NiO supported on SiO₂, HZSM-5 and CeO₂ possessed weak MSI effect compared to that on Al₂O₃. The catalysts with weak MSI were easily sintered during the catalyst calcination and formed larger NiO clusters with random sizes. This led to the formation of carbon nanofibers with larger outer diameters and of highly non-uniform sizes.

When comparing the average outer diameters of filamentous carbons produced (Fig. 6) with the average NiO crystallites size of supported-NiO catalysts (Table 2), we can notice that the filamentous carbons formed possessed larger diameters than the average NiO crystallite sizes. The larger sized filamentous carbon observed on the supported-

is of importance in synthesizing carbon nanotubes with narrower diameter range.

5. Conclusions

The physical properties of the catalyst supports have a great effect on determining the state of NiO species. The catalysts presented with sharper NiO peaks in the XRD patterns seem to be active in methane decomposition and favor the formation of carbon nanofibers at lower reaction temperature. It can be seen that carbon nanofibers were grown on the surface of NiO/SiO₂, NiO/HZSM-5 and NiO/CeO₂ catalysts at 550 °C. Among the tested catalyst supports, Al₂O₃ seems to be the most suitable to support NiO crystallites in growing carbon nanotubes. Albeit NiO/Al₂O₃ catalyst showed less catalytic activity in methane decomposition, it grew carbon nanotubes at lower reaction temperature. The broad NiO peaks for NiO/Al₂O₃ catalyst observed in the XRD patterns strongly suggest that small NiO crystallites were well-dispersed on Al₂O₃ support and this is more likely the reason for the enhanced formation of multi-walled carbon nanotubes at 550 °C and single-walled carbon nanotubes at 700 °C. On the other hand, increasing the reaction temperature to 700 °C increased the initial methane conversions of the catalysts but the catalysts deactivated rapidly with time on stream. However, the TEM analysis discloses that 700 °C is the preferred temperature for the formation of carbon nanotubes on the supported-NiO catalysts. Further experimental data analysis reveals that higher reaction temperature is needed to grow carbon nanotubes with hollow cores, narrower diameter range and of smaller sizes.

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The effect of catalyst calcination temperature on the diameter of carbon nanotubes synthesized by the decomposition of methane

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S. Pulau Pinang, Malaysia

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Abstract

The effect of catalyst calcination temperature on the uniformity of carbon nanotubes (CNTs) diameter synthesized by the decomposition of methane was studied. The catalysts used were CoO–MoO/Al₂O₃ without prior reduction in hydrogen. The results show that the catalyst calcination temperature greatly affects the uniformity of the diameter. The CNTs obtained from CoO–MoO/Al₂O₃ catalysts, calcined at 300 °C, 450 °C, 600 °C, and 700 °C had diameters of 13.4 ± 8.4, 12.6 ± 5.1, 10.7 ± 3.2, and 9.0 ± 1.4 nm, respectively, showing that an increase in catalyst calcination temperature produces a smaller diameter and narrower diameter distribution. The catalyst calcined at 750 °C was inactive in methane decomposition. Transmission electron microscopy (TEM) studies showed that CNTs grown on the catalyst calcined at 700 °C were of uniform diameter and formed a dense interwoven covering. High-resolution TEM shows that these CNTs had walls of highly graphitized parallel graphenes.

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1. Introduction

Carbon nanotubes (CNTs) are a new form of carbon molecules with many outstanding properties [1]. These properties make them potentially useful in various applications, including in the areas of electronic, mechanical, composite, etc. [2–4]. In order to put these potential applications into practice, CNTs with uniform diameters are required. This is attributable to the properties of CNTs: their metallic, semiconducting and mechanical properties, which depend strongly on their chirality and diameter [5–7]. Both distinctive characteristics of CNTs have a great impact on their many important applications. Chirality has a close correlation with CNTs diameter. Therefore, by controlling the uniformity of CNTs, one can also control their chirality.

There are many production methods which have been developed to produce CNTs, including laser ablation, electric-arc-discharge and chemical vapor deposition (CVD) [8–10]. Among these, CVD shows clear advantages in synthesizing CNTs with uniform diameter. It is widely accepted that the size of metallic particles in the catalytic materials determines the diameter of the produced CNTs [11,12]. Consequently, by narrowing the size distribution of the metallic particles of catalysts used in CVD, CNTs with uniform diameters can be synthesized.

Many groups of researchers have successfully produced CNTs with nearly uniform diameters [13–19]. However, some of these involve complicated catalyst preparation procedures. In this paper, we demonstrate a simple catalyst preparation method in synthesizing catalyst which is effective in growing CNTs with nearly uniform diameter. In this regard, a series of CoO–MoO/Al₂O₃ catalysts were prepared and calcined at temperatures ranging from 300 °C to 750 °C. The effect of the catalyst calcination temperature on the diameter of CNTs was investigated. The study of the

* Corresponding author. Fax: +60 45941013.

E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

yields slightly increased from 196% to 205% over the catalysts calcined at 300 °C and 450 °C, respectively. The highest carbon yield, being 245%, was obtained for the catalyst calcined at 600 °C. Nevertheless, the carbon yields declined gradually to 240% and then to 226% for the catalysts calcined at 650 °C and 700 °C, respectively. The catalyst that calcined at 750 °C was completely inactive in methane decomposition and no deposited carbon was observed on the catalyst surfaces.

3.2. Characterization of CNTs

The morphologies of the deposited carbons were analyzed using TEM and the outer diameters of the produced CNTs measured from the respective TEM pictures. More than 100 CNTs per sample were taken into account for measuring their diameters and studying their morphologies.

The average diameter and standard deviation of the produced CNTs with respect to the catalyst calcination temperatures were calculated and shown in Fig. 2. The results show that CNTs with smaller diameters and narrower diameter distributions were grown on the catalysts calcined at higher temperatures. The CNTs obtained from the CoO–MoO₃/Al₂O₃ catalyst that calcined at 300 °C, 450 °C, 600 °C, and 700 °C demonstrated diameters of 13.4 ± 8.4 , 12.6 ± 5.1 , 10.7 ± 3.2 , and 9.0 ± 1.4 nm, respectively.

The histogram of the produced CNTs diameters were drawn and presented in Fig. 3a–d. The solid lines correspond to the Gaussian fits. In Fig. 3a, one can notice that the diameter distribution of the CNTs grown on the catalyst calcined at 300 °C was relatively broad. These CNTs had diameters distributed over a wide range from 3 to 47 nm and with an average diameter of 13.4 nm. The corresponding TEM image shows that the diameter distribution of

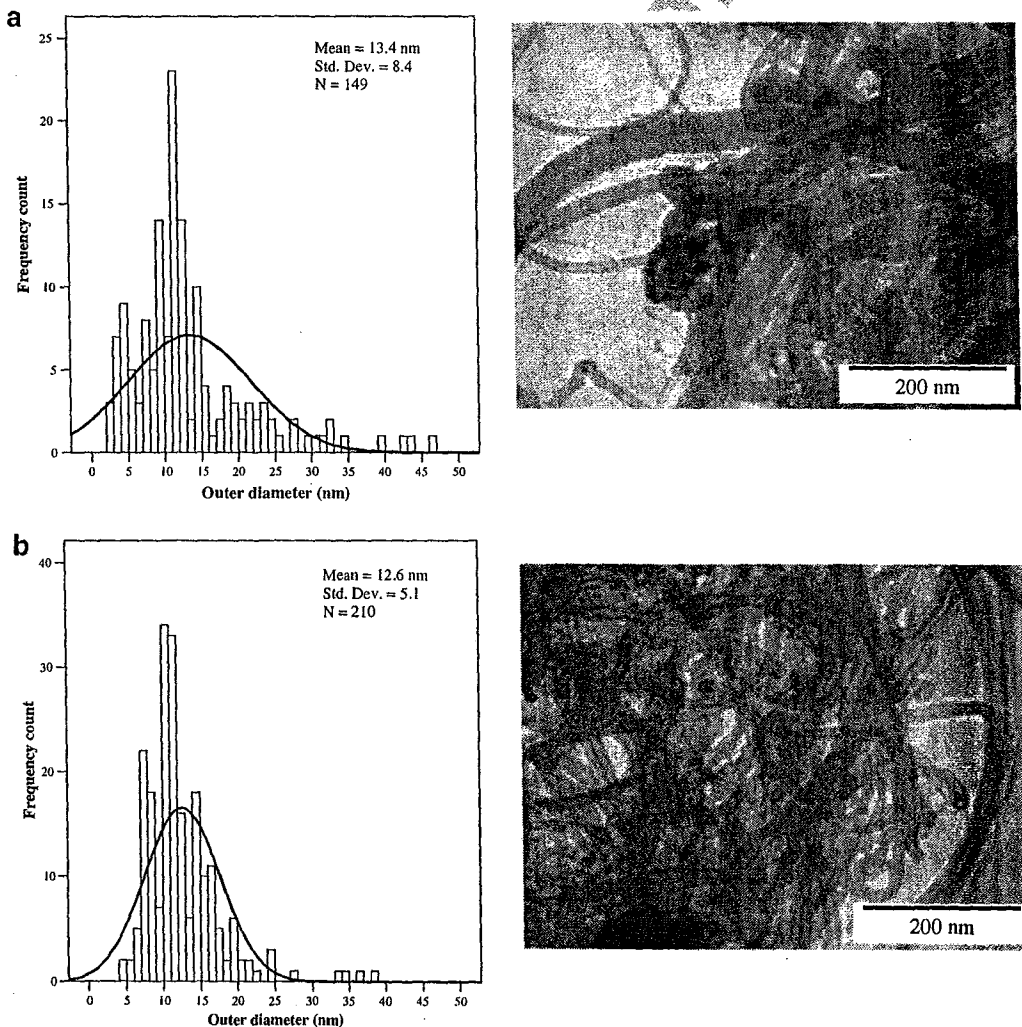


Fig. 3. (Left) Histogram of CNTs diameter distributions; (Right) TEM images of CNTs grown on CoO–MoO₃/Al₂O₃ catalysts, calcined at (a) 300 °C, (b) 450 °C, (c) 600 °C, and (d) 700 °C, respectively.

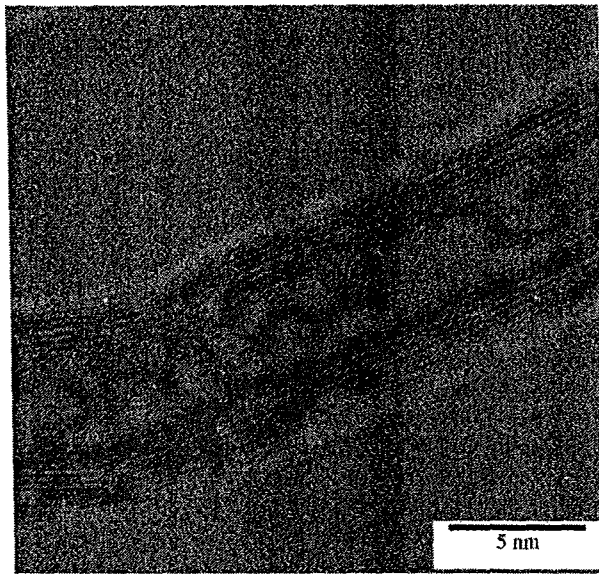


Fig. 4. HRTEM image of CNTs grown on CoO-MoO/Al₂O₃ catalyst, calcined at 700 °C.

temperatures ranging from 300 °C to 750 °C. The representative peaks for Co₃O₄/CoAl₂O₄, Al₂O₃, and CoMoO₄ are denoted in the XRD spectra. It is important to note that the diffraction peaks at 31.3°, 36.9°, and 65.2° could be assigned to Co₃O₄ and/or CoAl₂O₄ phases. It is difficult to distinguish between Co₃O₄ and CoAl₂O₄ phases from the XRD patterns shown as both have cubic spinel-like structure, showing identical diffraction peaks [26,27]. However, the change in color observed for the catalyst samples calcined at different temperatures could provide useful information for differentiating between Co₃O₄ and

CoAl₂O₄ phases [28–30]. The gray color observed for the catalysts calcined at 300 °C, 450 °C, and 600 °C suggests that Co₃O₄ was formed as the major phase [30]. The catalyst calcined at 700 °C was teal in color which indicates the possible coexistence of Co₃O₄ and CoAl₂O₄ in the sample. The color of the catalyst calcined at 750 °C was observed to change from teal to blue which suggests that CoAl₂O₄ was generated as the major cobalt phase [28–30]. This is in good agreement with the finding reported by Chokkaram et al. [31] that the increase of calcination temperature increases the quantity of the generated CoAl₂O₄ phase. CoMoO₄ phase is identified in the bimetallic CoO-MoO/Al₂O₃ catalysts, suggesting that the small amount of molybdenum oxide was well mixed with the cobalt oxide. The presence of CoMoO₄ is important as it stabilizes the cobalt species, preventing them from agglomerating to form larger clusters of inconsistent sizes [32]. Owing to the strong interaction between cobalt and alumina, it is reasonable to speculate that cobalt oxide was well dispersed on alumina support. The observation of broad peak at $2\theta = 36.9^\circ$ for the shown five spectra indicates that the cobalt species was well dispersed and formed smaller cobalt oxide crystallites on alumina support [33].

The change of catalyst calcination temperature resulted in slight changes in the XRD patterns. It is noticeable that the width of the diffraction peak at 36.9° (Fig. 5a–e) increased with increasing catalyst calcination temperatures from 300 °C to 750 °C. This shows that higher calcination temperature resulted in the formation of smaller cobalt oxide crystallites. The average sizes of cobalt oxide crystallites for the catalysts calcined at different temperatures are tabulated in Table 1. Indirectly, this also tells us that cobalt oxide and alumina interaction became stronger with increasing calcination temperatures [30,34].

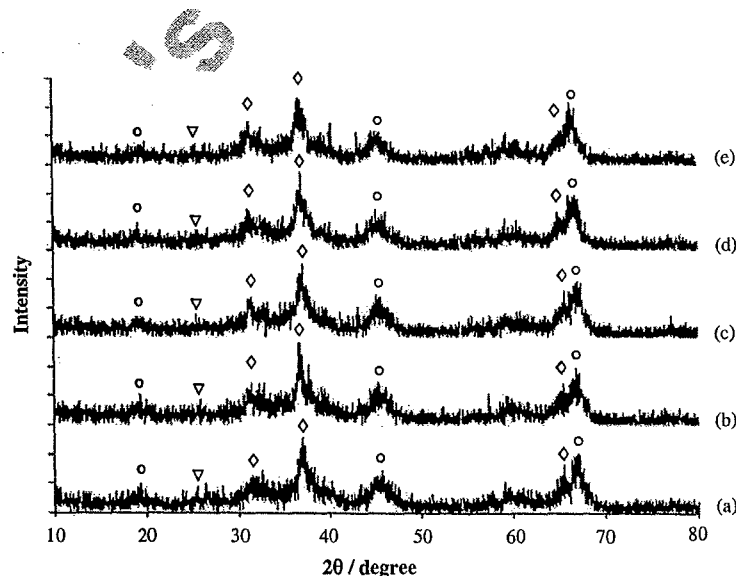


Fig. 5. XRD patterns of CoO-MoO/Al₂O₃ catalysts calcined at (a) 300 °C, (b) 450 °C, (c) 600 °C, (d) 700 °C, and (e) 750 °C. (◇) Co₃O₄ or CoAl₂O₄; (○) Al₂O₃; (▽) CoMoO₄.

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The effect of reduction temperature on Co-Mo/Al₂O₃ catalysts for carbon nanotubes formation

Siang-Piao Chai, Sharif Hussein Sharif Zein, Abdul Rahman Mohamed*

*School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan,
14300 Nibong Tebal, S.P.S. Pulau Pinang, Malaysia*

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Abstract

Catalyst reduction temperature was observed to affect the yield and diameter uniformity of carbon nanotubes (CNTs) produced on Co-Mo/Al₂O₃ catalysts. The results show that on the whole, the reduced catalysts gave higher carbon yield. The CNTs obtained from the unreduced catalyst and the catalysts reduced at 400, 550, and 700 °C had diameters of 9.0 ± 1.4 , 11.0 ± 1.8 , 11.2 ± 1.8 , and 12.1 ± 2.7 nm, respectively, showing that an increase in catalyst reduction temperature produced a slightly larger average diameter and wider diameter distribution. Raman spectra further elucidate that better-graphitized CNTs were produced on the catalysts reduced with increasing reduction temperatures.

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Keywords: Carbon nanotubes; Methane decomposition; Catalyst reduction; Co-Mo/Al₂O₃ catalysts

1. Introduction

Carbon nanotubes (CNTs), demonstrating unique structural, mechanical, and electrical properties [1], possess many new important applications such as the quantum wires, field-effect transistors, field emitters, diodes, gas sensor, electric power storage, targeted drug delivery, catalyst support, reinforcing elements in composites, etc. [2–4]. Their great future prospects have driven the development of various effective ways to produce them. In this regard, arc-discharge, laser ablation and catalytic chemical vapor deposition (CVD) [5–7] arise as the three most popular methods for producing CNTs. Among the said methods, catalytic CVD has received great interest from researchers, industrialists and scientists today due to its capability in not only producing CNTs in large quantities, but also tailor-making CNTs with desirable morphologies.

Catalysts such as supported-cobalt, -iron, and -nickel are commonly used to catalyze the growth of CNTs [8–10]. In most cases, catalysts are reduced in hydrogen flow prior to being used in CNTs production [11–15]. However, hydrogen reduction of metal oxides at times is not essential since the

hydrocarbon atmosphere is able to reduce the catalyst under the reaction conditions [16,17]. Anyway, the reduction of metal oxide for a catalyst with strong metal-support interaction in hydrocarbon atmosphere is complicated. Therefore, hydrogen pre-reduction is preferred. According to Chen et al., hydrogen reduction makes the catalyst more vulnerable and it will be further reduced during the CNTs synthesis process in hydrocarbon environment. It was also reported that complete reduction of catalyst should be avoided because it will generate metallic particles which are feasible to agglomerate to form larger metallic clusters under the synthesis condition [18]. This tends to grow CNTs with larger diameter distribution and of poorer quality [11,19]. Therefore, the investigation on the effect of catalyst reduction on the catalyst used for CNTs production is essential.

Our previous studies of CNTs growth by methane decomposition showed that CNTs of better morphology and narrower diameter distribution were grown on unreduced Co-Mo/Al₂O₃ catalyst [20]. We also reported that CNTs yield and diameter uniformity can be strongly influenced by the catalyst calcination temperatures [21]. In the present study, the influence of catalyst reduction on the yield, degree of graphitization and the diameter uniformity of produced CNTs is investigated. The carbon yields are calculated based on the degree of methane conversion and the produced CNTs are

* Corresponding author. Tel.: +6 4 599 6410; fax: +6 4 594 1013.

E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

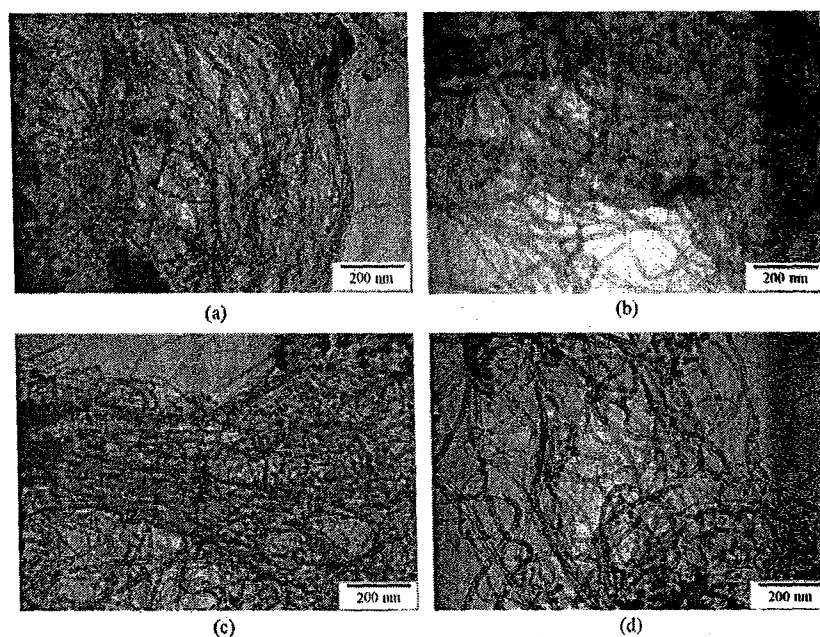


Fig. 2. Low magnified-TEM images of CNTs grown on (a) unreduced catalyst, and catalysts reduced at (b) 400, (c) 550, and (d) 700 °C, respectively.

formation of encapsulated surface carbon from methane decomposition, which in turn de-activated the catalyst.

3.2. TEM characterization

Fig. 2 shows the TEM images of CNTs grown on unreduced and reduced Co-Mo/Al₂O₃ catalysts. It was observed that CNTs were grown densely on the surfaces of all the tested catalysts, forming an interwoven covering. We also could notice that all the CNTs produced on Co-Mo/Al₂O₃ catalysts have nearly uniform diameter. Fig. 3 shows the higher magnified TEM images of the CNTs produced on the unreduced catalyst and catalyst reduced at 550 °C. Significant hollow cores could be observed for the produced CNTs. Furthermore, no catalyst particles were present at the tips of the CNTs. This indicates that the CNTs were grown following the base-growth model on Co-Mo/Al₂O₃ catalyst, where the cobalt particles attached on alumina support were active in growing them. In most cases, opening at the tips was observed. CNTs with open-tips have

more advantages than the enclosed-tips CNTs because the former provides the hollow parts which can be readily utilized for filling and adsorption purposes.

For obtaining the CNTs diameter distributions, more than 100 CNTs per sample were taken into account for measuring their outer diameters from the respective TEM pictures. The histogram of the produced CNTs diameters were drawn and presented in Fig. 4a–d. The solid lines correspond to the Gaussian fits. The results show that the unreduced catalyst grew CNTs with smaller diameters and narrower diameters distribution. The increase in catalyst reduction temperature grew CNTs with slightly larger diameters and wider diameter distributions. This is principally due to the agglomeration of the metallic cobalt in the reduced catalysts to form larger and non-uniform metallic cluster. The summary of the average diameters and standard deviations of the CNTs produced were presented in Fig. 5. The CNTs obtained from the unreduced Co-Mo/Al₂O₃ catalyst and those reduced at 400, 550, and 700 °C demonstrated the diameters of 9.0 ± 1.4 , 11.0 ± 1.8 ,

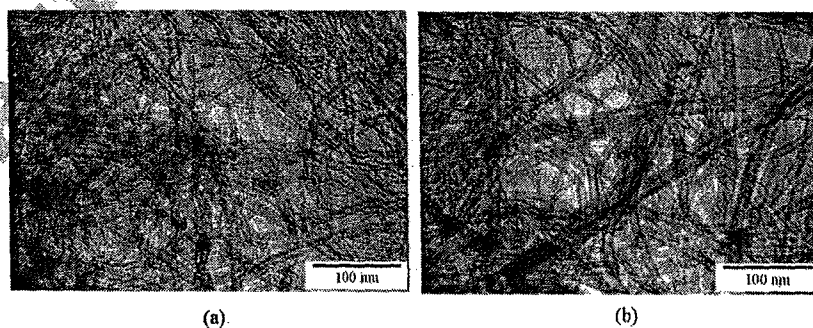


Fig. 3. High-magnified TEM images of CNTs grown on (a) unreduced catalyst, and (b) catalyst reduced at 550 °C.

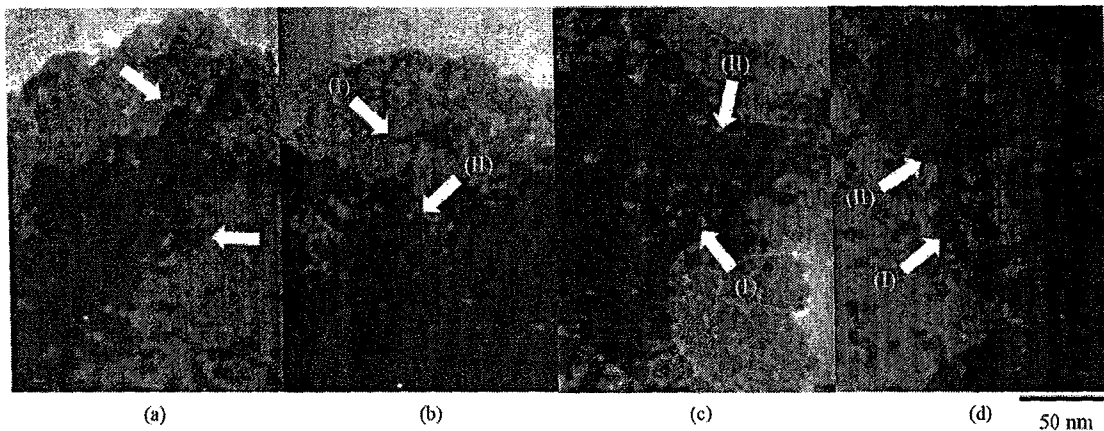


Fig. 6. TEM images of Co-Mo/Al₂O₃ catalysts: (a) unreduced catalyst, and catalysts reduced at (b) 400, (c) 550, and (d) 700 °C, respectively. All figures are on the same scale.

3.3. Raman characterization

Raman spectroscopy was employed to analyze the degree of graphitization of the produced CNTs. Fig. 7 shows the Raman spectra of CNTs produced by methane decomposition on the unreduced and reduced catalysts. For all the Raman spectra, two major bands were observed, representing D- and G-bands. The D-band, observed at 1350 cm⁻¹, is known as either the disorder induced due to the wall disorder or the presence of amorphous carbon deposited on the outer surface of nanotubes. The G-band (observed at 1590 cm⁻¹) can be attributed to the degree of graphitization of CNTs. The ratio of I_D/I_G of the D- and G-band can be regarded as an index for the crystalline order of CNTs [26]. To estimate the value of I_D/I_G , each Raman

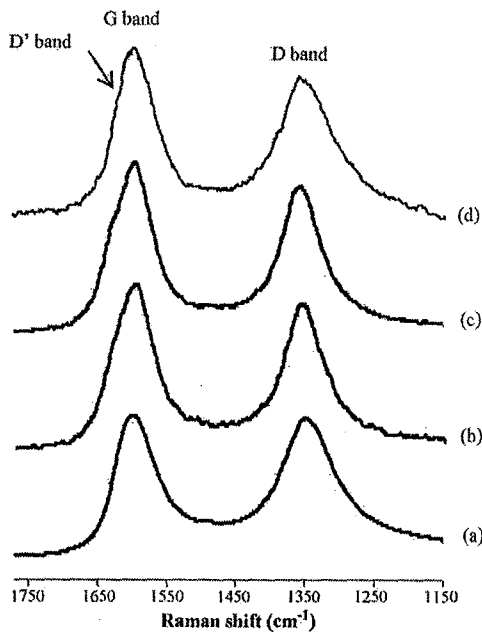


Fig. 7. Raman spectra for CNTs grown on (a) unreduced catalyst, and catalysts reduced at (b) 400, (c) 550, and (d) 700 °C, respectively.

spectrum shown in Fig. 7 was performed the curve fittings using Lorentzian function for three bands (D, D', and G band). D' band was assigned to the imperfect graphite or disordered carbons [27]. The I_D/I_G results for all the samples are shown in Fig. 8.

In Fig. 8, it was noted that the obtained I_D/I_G ratio for CNTs produced on unreduced catalyst is less than unity, indicating good crystallinity of the graphite sheets. Interestingly, after reducing the catalyst with hydrogen, all the CNTs deposited on reduced catalysts showed much smaller I_D/I_G ratios as compared to those produced on unreduced catalysts. This reveals that the reduced catalysts provoked the formation of better-graphitized CNTs. For the unreduced catalysts, excessive methane was needed to reduce the oxide of cobalt to a metal phase, an active catalyst for growing CNTs. Subsequently, methane would react with the reduced cobalt for growing CNTs. Probably, the reduction and subsequent reaction by methane, occurring almost concurrently on a catalytic site, induced the formation of CNTs with higher defects level or disorder structure. Consequently, the CNTs produced on the unreduced catalyst possessed higher I_D/I_G ratio. Thus, it appears that the reduced catalyst provides a more suitable nucleation site for growing CNTs with fewer defects

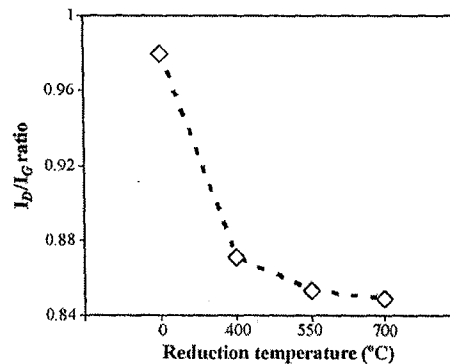


Fig. 8. Changes in the I_D/I_G ratio for CNTs as a function of reduction temperature.

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Production of Carbon Nanotubes via Catalytic Decomposition of Methane

SIANG-PIAO CHAI, SHARIF HUSSEIN SHARIF ZEIN AND ABDUL RAHMAN MOHAMED*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S. Pulau Pinang, Malaysia.

* Corresponding author (email: chrahman@eng.usm.my)

KEYWORDS: Carbon nanotubes, Carbon nanostructures, Catalytic Decomposition of Methane, Supported Catalysts, Morphology

Abstract

Since the discovery of carbon nanotubes (CNTs) in 1991, a fundamental question remains after this 17-year experience: How to control morphologically the synthesis of CNTs. This effort has always been a challenge. In this paper, we report the results that we published previously with the aims at sharing the possible controlled synthesis approach via this novel production method. In our findings, we demonstrated that various CNTs could be synthesized by using specially developed supported catalysts from catalytic decomposition of methane. These synthesized CNTs include carbon nanofibers (CNFs), single-walled and multi-walled CNTs, Y-junction CNTs, and CNTs with special morphologies. From the results presented in this paper, it can be known that catalyst composition and reaction parameters play important factors in controlling the morphology and type of CNTs formed. The synthesis of CNTs with various morphologies is important because this could enrich the nanostructures of carbon family. This finding also provides useful data for better understanding on the parameters that govern the growth mechanism of CNTs which may be required in the near future for enhanced controlled synthesis of CNTs.

1. Introduction

In the early 90s, tubular carbon structure with a diameter in the range order of the nanometer was first observed and then has been called carbon nanotubes (CNTs) (Iijima, 1991). The first observed CNTs were multi-walled carbon nanotubes (MWNTs). Two years later, single-walled carbon nanotubes (SWNTs) were successfully synthesized (Iijima and Ichihashi, 1993). In general, CNTs are unique nanostructures possessing extraordinary mechanical, electrical and thermal properties with providing strong, light and high toughness characteristics (Lau and Hui, 2002; Reich et al., 2004). It is of importance to note that the most striking part of this material is the properties could be either semiconducting or metallic depending on their geometrical characteristics. This uniqueness leads CNTs to a variety of new important applications such as the quantum wires, field-effect transistors, field emitters, diodes, gas sensor, electric power storage, etc (Baughman *et al.*, 2002).

To date, many methods for CNTs synthesis have been developed. Among them, laser ablation, electric-arc-discharge and catalytic growth are the most three popular methods which are widely being used. Arc-discharge and laser ablation methods are efficient in synthesizing SWNTs. However, both methods require very high temperature (> 3000°C) and subject to lower CNTs yield (Dai, 2001) which limit the possibility from up-scaling both to industrial scale production. By comparison, catalytic growth method has been appreciated as the best method to produce CNTs at a lower synthesis temperature, high yield and at relatively low cost (Yacaman *et al.*, 1993; Ivanov *et al.*, 1994). Consequently, this method has attracted the immense attention of scientists around the world in studying and developing high-selectivity catalytic materials in growing CNTs with

3. Results and Discussion

3.1 Formation of carbon nanofibers

Fig. 2 shows the TEM images of typical carbon nanofilaments with solid cores or with insignificant hollow core, known as carbon nanofibers (CNFs). This type of carbon nanostructures has great potential applications as catalyst support and reinforcement materials. CNFs as shown in Figs. 2a and 2b were grown from methane decomposition at 550°C on $\text{CoO}_x/\text{SiO}_2$ and NiO/SiO_2 catalysts, respectively (Chai *et al.*, 2006a; Chai *et al.*, 2007d). The diameter distribution of CNFs grown on $\text{CoO}_x/\text{SiO}_2$ catalyst was 27.0 ± 5.8 nm and 44.4 ± 18.4 nm for those grown on NiO/SiO_2 catalyst. In Fig. 2a, one can notice that the diameter of CNFs grown on $\text{CoO}_x/\text{SiO}_2$ catalyst was more uniform as compared to those shown in Fig. 2b. To explain why $\text{CoO}_x/\text{SiO}_2$ catalyst grew CNFs with narrower diameter distribution than those on NiO/SiO_2 catalyst, we have to comprehend the effect of metal-support interaction (MSI) of a catalyst. In the case of NiO/SiO_2 catalyst, NiO particles attached weakly on SiO_2 support. Under the reaction condition, NiO migrated and recombined with the adjacent NiO particles, agglomerating to form larger non-uniform NiO clusters. These clusters led to the growth of CNFs of larger and non-uniform diameters. On the other hand, the $\text{CoO}_x/\text{SiO}_2$ catalyst possesses stronger MSI effect than that of NiO/SiO_2 catalyst. The stronger MSI of $\text{CoO}_x/\text{SiO}_2$ catalyst assisted the formation of CoO_x with more uniform size and of smaller size on SiO_2 support and these CoO_x particles played a significant role in growing CNFs with comparatively uniform diameter and of smaller size (Chai *et al.*, 2007d).

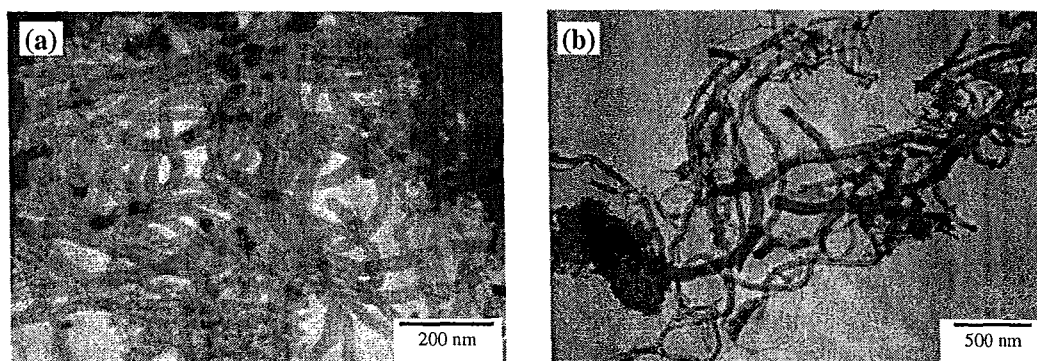


Fig. 2. TEM images of CNFs grown on (a) $\text{CoO}_x/\text{SiO}_2$, and (b) NiO/SiO_2 catalysts.

3.2 Formation of multi-walled carbon nanotubes

Figs. 3a and 3b show the TEM images of MWNTs grown on $\text{CoO}_x\text{-MoO}_x(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst via decomposition of methane at 700°C (Chai *et al.*, 2007a; Chai *et al.*, 2007b). The high degree of diameter control and uniformity of the synthesized MWNTs can be seen clearly in the TEM images. The TEM analysis shows that out of total 156 MWNTs measured, more than 98% had diameters ranging from 6 nm to 12 nm. The calculated average diameter and standard deviation were 9.0 nm and 1.4 nm, respectively. The formation of MWNTs with nearly uniform diameters on $\text{CoO}_x\text{-MoO}_x(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ is principally due to the added molybdenum which stabilizes the cobalt species and Al_2O_3 that provides a suitable support for better dispersion of both cobalt and molybdenum particles (Chai *et al.*, 2006c; Chai *et al.*, 2007a). The ultimate goal for both catalyst components subject to preventing the intense agglomeration of cobalt particles from forming larger clusters under the reaction conditions, in which these clusters will lead to the formation of CNTs of larger and non-uniformity diameter. It was also noted that the MWNTs were grown densely on all surfaces of the catalyst particles, forming an interwoven covering. Fig. 3b shows the high-magnified TEM image of the produced CNTs. Significant hollow cores could be observed for the produced

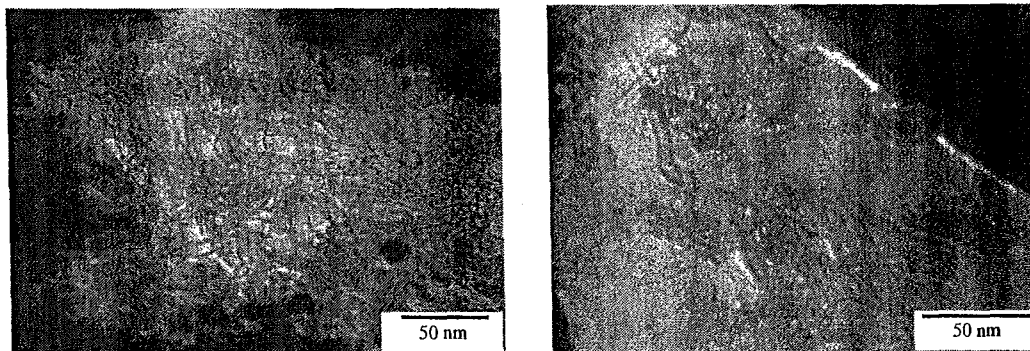


Fig. 4. TEM images of thin-walled CNTs grown on $\text{CoO}_x\text{-Fe}_2\text{O}_3(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst.

3.3 Formation of single-walled carbon nanotubes

Figs. 5a and 5b show the high-magnified and low-magnified TEM images of CNTs grown on $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst via decomposition of methane at 700°C (Chai *et al.*, 2007c). Two types of CNTs were grown on the said catalyst, i.e. SWNTs and MWNTs, as indicated by arrow A and arrow B, respectively. From the TEM analysis, we could notice that the synthesized SWNTs appeared in two forms, i.e. isolated (arrow A1) and bundles (arrow A2). The Raman spectrum (not shown in this paper) shows strong intensity at radial breathing mode (RBM), indicating that the occurrence of SWNTs was dominant. The RBM in the low frequency region shows five components at 123, 188 and 260 cm^{-1} . The frequency of these modes is known to be inversely proportional to the diameter of SWNTs. For calculating the diameter of SWNTs, we adopted the dependence of the RBM frequency on the diameter proposed by Bachilo *et al.* (2002):

$$\omega_{\text{RBM}} = 12.5 + \frac{223.5}{d} \quad (2)$$

Based on this equation, the diameters of SWNTs were calculated as $d = 2.02, 1.27$ and 0.90 nm ; respectively (Chai *et al.*, 2007c). Nevertheless, the RMB also discloses that the synthesized SWNTs were not mono-dispersed in diameter. To arrive at the understanding why SWNTs were formed on $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst, we have to know the nature of the catalyst structure. It is well accepted that the formation of CNTs is governed by the size of the metallic catalyst particles. In this case, if we are able to reduce the size of NiO particles to an extent, SWNTs can be grown. The formation of SWNTs on $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst did reveal that very small sized NiO were formed on Al_2O_3 support and this size was small enough for growing SWNTs. As what we believe, the formation of these ultra-small NiO nanoparticles was mainly induced by the strong MSI effect between the NiO and the Al_2O_3 support. The catalyst with strong MSI allowed high NiO dispersion and prevented NiO from agglomerating and forming larger clusters. Probably, some adjacent NiO particles might combine/sinter during the calcination and reaction stages to form larger NiO particles and these particles led to the formation of MWNTs as indicated by arrow B in the TEM image.

3.5 Formation of carbon nanotubes of special morphologies

In addition to the ordinary morphology, several unique ones have been observed in our research works (Mohamed, 2006). Some morphologies are very attractive which may have some special advantages in certain applications. Fig. 7a shows the bamboo-like CNTs. These nanostructures were grown on NiO/CeO₂ catalyst at 700°C. Several compartments can be observed along the nanotubes axis, providing many unique chambers for gas storage when they are used as a gas sensor. Another type CNTs were grown from methane decomposition at 800°C on NiO/CeO₂ catalyst and their respective TEM image was shown in Fig. 7b. These carbon nanostructures were named as encapsulated type CNTs. One can observe that the metallic parts of the catalyst were encapsulated within the tubes, as indicated by an arrow. We believe that nickel was in quasi-liquid state at 800°C. This condition allowed them to be elongated and segregated during the growth of CNTs, and finally it trapped within the nanotubes, forming an encapsulated structure. Figs. 7c and 7d show the helix-shaped CNTs and chain-like CNTs, respectively. Both nanostructures were observed on the CoO_x-MoO_x(8:2)(w/w)/Al₂O₃ and CoO_x/Al₂O₃ catalysts after methane decomposition at 800°C. The formation of helix-shaped CNTs had been reported by Amelinckx et al. (1994). According to the authors, helix-shape is formed due to the eclipse shaped active sites of cobalt which determine the initial geometry of this structure. In details, this may be due to the violation of the continuity condition for growing straight nanotubes because of the disparity of the carbon extrusion velocity and the rate of carbon deposition (Amelinckx et al., 1994). In most cases, only a mixture of CNTs with unique morphologies was obtained. The study describes the production of various structures of CNTs through selection of the catalyst components and reaction parameters.

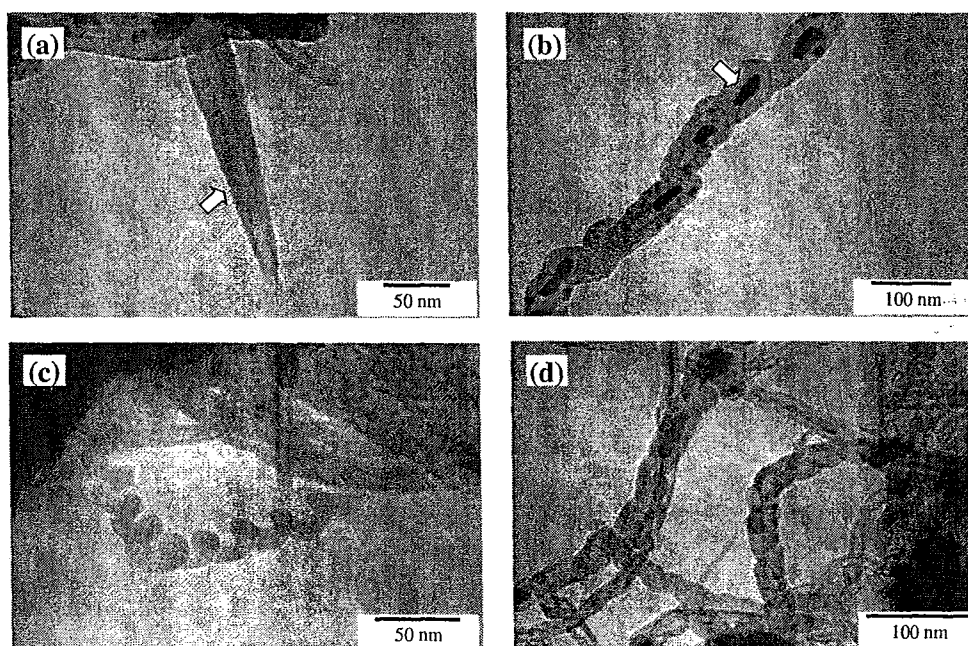


Fig. 7. TEM images of carbon nanostructures synthesized over various supported catalysts via decomposition of methane: (a) bamboo-like CNTs; (b) encapsulated type CNTs; (c) helix-shaped CNTs; (d) chain-like CNTs.

4. Conclusions

Various types of filamentous carbons, including CNFs, MWNTs, SWNTs, Y-junction CNTs and others with special morphologies, have been catalytically grown by supported catalysts via catalytic decomposition of methane. The types of filamentous carbons formed with respective to the catalysts

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A Novel Production of Carbon Nanotubes via Catalytic Decomposition of Methane

SIANG-PIAO CHAI, SHARIF HUSSEIN SHARIF ZEIN AND ABDUL RAHMAN MOHAMED*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S. Pulau Pinang, Malaysia.

* Corresponding author (email: chrahman@eng.usm.my)

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Abstract

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is adopting the principle of decomposition of carbon-containing gases over catalytic materials. In this aspect, supported transition metals, especially metals from group VIII (Fe, Co, Ni) in the periodic table, are extensively being used (Chai *et al.*, 2006c; Zein *et al.*, 2006). The main challenge of catalytic method is on how to control the type and morphology of CNTs synthesized. To date, no one has successfully achieved the controlled synthesis of CNTs. Thus, we intend to report in this paper the findings that we published in the scientific literature, disclosing the factor and the criteria that govern the formation of CNTs of different type and morphology.

2. Materials and methods

All the catalysts tested in this study were prepared using conventional impregnation method as reported elsewhere (Mohamed, 2006). Metals in nitrate form were used as a precursor for preparing monometallic, bimetallic and trimetallic catalysts. The total metals loading was adjusted to be 10 wt% for all catalysts. The desired amounts of the metal nitrate were first dissolved in distilled water and then impregnated on the support powder. The resulting paste was dried at 105°C for 12 h, calcined at 600°C or 700°C for 5 h, followed by sieving into 425 – 600 µm particles. The synthesis of CNTs were carried out at atmospheric pressure in a stainless-steel fixed-bed reactor (length and diameter of the reactor were 600 and 20 mm, respectively) as shown in Fig. 1, using methane as carbon feedstock. High purity methane (99.999% supplied by Malaysian Oxygen Bhd.) was mixed with nitrogen (99.999% purity, supplied by Sitt Tatt Industrial Gases Sdn. Bhd.) with ratio 1:1 (v/v) before entering the reactor. For synthesizing nanotubes materials, 200 mg of catalyst was distributed in the middle part of the reactor for each run and the reaction temperature was varied from 550°C to 800°C. The carbon deposited on the catalysts were analyzed using a transmission electron microscope (TEM) (Philips, CM12). In preparation for TEM analysis, a few samples of the used catalyst were dispersed in acetone (99.9% purity), and then a drop was deposited on a coated copper grid.

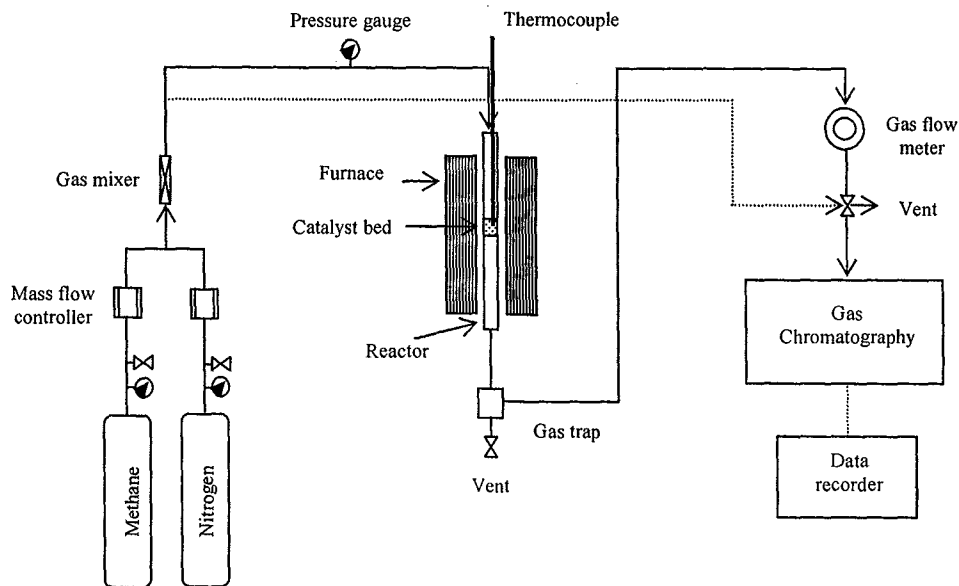


Fig. 1. Schematic diagram of the experimental setup.

3. Results and Discussion

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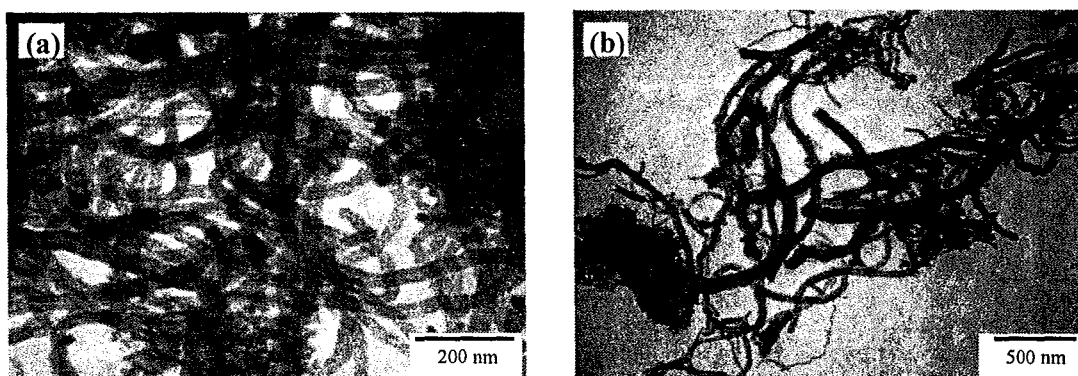


Fig. 2. TEM images of CNFs grown on (a) $\text{CoO}_x/\text{SiO}_2$, and (b) NiO/SiO_2 catalysts.

3.2 Formation of multi-walled carbon nanotubes

Figs. 3a and 3b show the TEM images of MWNTs grown on $\text{CoO}_x\text{-MoO}_x(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst via decomposition of methane at 700°C (Chai *et al.*, 2007a; Chai *et al.*, 2007b). The high degree of diameter control and uniformity of the synthesized MWNTs can be seen clearly in the TEM images. The TEM analysis shows that out of total 156 MWNTs measured, more than 98% had diameters ranging from 6 nm to 12 nm. The calculated average diameter and standard deviation were 9.0 nm and 1.4 nm, respectively. The formation of MWNTs with nearly uniform diameters on $\text{CoO}_x\text{-MoO}_x(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ is principally due to the added molybdenum which stabilizes the cobalt species and Al_2O_3 that provides a suitable support for better dispersion of both cobalt and molybdenum particles (Chai *et al.*, 2006c; Chai *et al.*, 2007a). The ultimate goal for both catalyst components subject to preventing the intense agglomeration of cobalt particles from forming larger clusters under the reaction conditions, in which these clusters will lead to the formation of CNTs of larger and non-uniformity diameter. It was also noted that the MWNTs were grown densely on all surfaces of the catalyst particles, forming an interwoven covering. Fig. 3b shows the high-magnified TEM image of the produced CNTs. Significant hollow cores could be observed for the produced

MWNTs. Furthermore, no catalyst particles were present at the tips of the nanotubes. This indicates that the nanotubes were grown following the base-growth model on $\text{CoO}_x\text{-MoO}_x(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst, where the cobalt particles attached on alumina support were active in growing them. In most cases, opening at the tips, marked by arrows, were observed. CNTs with open-tips have more advantages than the enclosed-tips CNTs because the former provides the hollow parts which can be readily utilized for filling and adsorption purposes. Although many effective ways in producing CNTs with nearly uniform diameters have been suggested in the literature, this study represents a simple and convenient way to achieve this objective. This also reflects a real possibility to produce CNTs with uniform diameter by means of a simpler and cheaper approach in the near future (Chai *et al.*, 2007a).

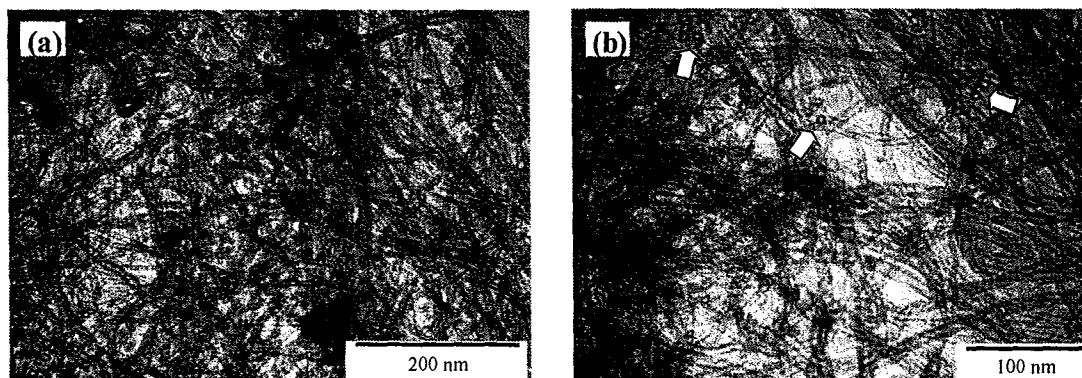


Fig. 3. (a) Low-magnified, and (b) high-magnified TEM images of MWNTs grown on $\text{CoO}_x\text{-MoO}_x(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst.

The physical and chemical properties of MWNTs are sophisticated especially for those CNTs with thicker wall structure. This is due to the coupling effect between the constituent graphene layers. As a consequence, MWNTs with a smaller diameter and thinner wall structure are needed in the miniaturization electronic applications because of their better electronic and electrical properties. In this study, thin-walled CNTs were synthesized using $\text{CoO}_x\text{-Fe}_2\text{O}_3(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst in methane decomposition at 700°C , shown in Fig. 4 (Chai *et al.*, 2006d). We believe that the growth of thin-walled CNTs on $\text{CoO}_x\text{-Fe}_2\text{O}_3$ based catalysts was mainly induced by the $\text{CoO}_x\text{-Fe}_2\text{O}_3$ alloy formed on Al_2O_3 support. This conclusion was made after considering the findings which showed that CoO_x supported on Al_2O_3 could not grow CNTs with thin-walled structure, whereas Fe_2O_3 supported on Al_2O_3 was not active in methane decomposition at 700°C . By taking the thickness of each graphene layer and the spacing of the graphitic interplanar to be 0.1421 nm and 0.3354 nm, respectively (Liu *et al.*, 2003), the number of graphene layers can be estimated using the following equation:

$$\tau = 0.1421 n + 0.3354 (n - 1)$$

Based on this equation, we could estimate that the produced thin-walled CNTs consisted of the graphene layers of only 2 – 4. However, the detailed wall structure of nanotubes still needs further characterization using high-resolution TEM (HRTEM) as to confirm the number of graphene layers.

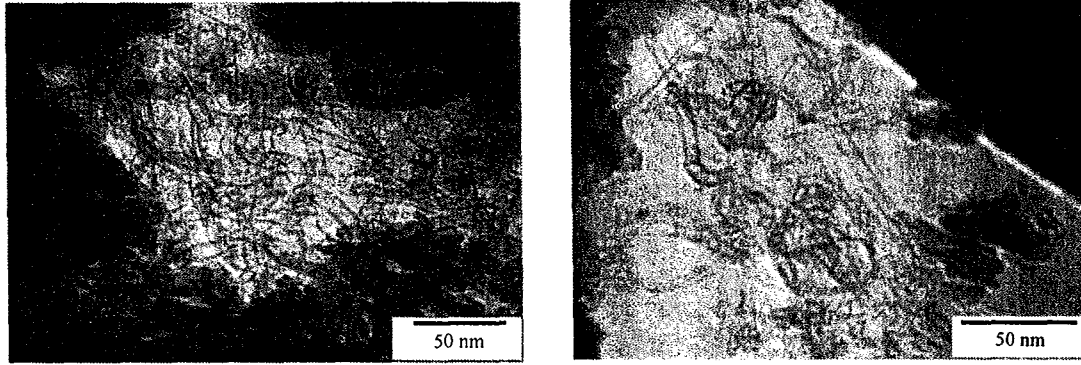


Fig. 4. TEM images of thin-walled CNTs grown on $\text{CoO}_x\text{-Fe}_2\text{O}_3(8:2)(\text{w/w})/\text{Al}_2\text{O}_3$ catalyst.

3.3 Formation of single-walled carbon nanotubes

Figs. 5a and 5b show the high-magnified and low-magnified TEM images of CNTs grown on $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst via decomposition of methane at 700°C (Chai *et al.*, 2007c). Two types of CNTs were grown on the said catalyst, i.e. SWNTs and MWNTs, as indicated by arrow A and arrow B, respectively. From the TEM analysis, we could notice that the synthesized SWNTs appeared in two forms, i.e. isolated (arrow A1) and bundles (arrow A2). The Raman spectrum (not shown in this paper) shows strong intensity at radial breathing mode (RBM), indicating that the occurrence of SWNTs was dominant. The RBM in the low frequency region shows five components at 123, 188, 260, 356 and 395 cm^{-1} . The frequency of these modes is known to be inversely proportional to the diameter of SWNTs. For calculating the diameter of SWNTs, we adopted the dependence of the RBM frequency on the diameter proposed by Bachilo *et al.* (2002):

$$\omega_{RBM} = 12.5 + \frac{223.5}{d} \quad (2)$$

Based on this equation, the diameters of SWNTs were calculated as $d = 2.02, 1.27, 0.90, 0.65$ and 0.58 nm , respectively (Chai *et al.*, 2007c). Nevertheless, the RMB also discloses that the synthesized SWNTs were not mono-dispersed in diameter. To arrive at the understanding why SWNTs were formed on $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst, we have to know the nature of the catalyst structure. It is well accepted that the formation of CNTs is governed by the size of the metallic catalyst particles. In this case, if we are able to reduce the size of NiO particles to an extent, SWNTs can be grown. The formation of SWNTs on $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst did reveal that very small sized NiO were formed on Al_2O_3 support and this size was small enough for growing SWNTs. As what we believe, the formation of these ultra-small NiO nanoparticles was mainly induced by the strong MSI effect between the NiO and the Al_2O_3 support. The catalyst with strong MSI allowed high NiO dispersion and prevented NiO from agglomerating and forming larger clusters. Probably, some adjacent NiO particles might combine/sinter during the calcination and reaction stages to form larger NiO particles and these particles led to the formation of MWNTs as indicated by arrow B in the TEM image.

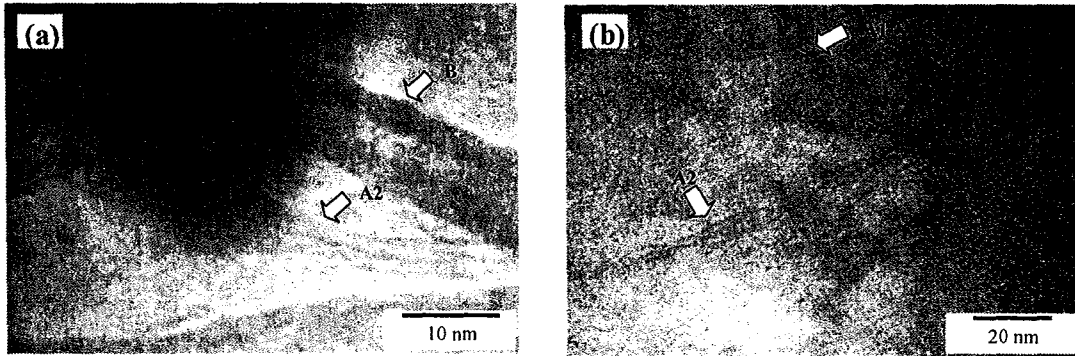


Fig. 5. (a) High-magnified, and (b) low-magnified TEM images of SWNTs grown on NiO/Al₂O₃ catalyst.

3.4 Formation of Y-junction carbon nanotubes

Fig. 6 shows the TEM images of Y-junction CNTs grown on NiO-CuO-MoO_x(7:2:1)(w/w/w)/SiO₂ catalyst from methane decomposition at 700°C. The joints of the branches were marked by arrows in the TEM image. Y-junction CNTs, a structure composing three joining tubes, were first observed in the carbon soot produced from arc-discharge method (Zhou and Seraphin, 1995). The discovery of Y-junction CNTs brings a new hope to the development of CNTs-based nanoscale devices, especially nanoscale three-terminal devices such as three-terminal transistors, amplifiers and switches. In this study, it was found that SiO₂ supported NiO, CuO and NiO-CuO catalysts grew only straight CNTs, and none of Y-junction structure was observed on these catalysts. However, by adding a small amount of MoO_x to NiO-CuO, Y-junction CNTs were grown. It seems that molybdenum species acted as the nucleation sites in this case, seeding the growth of Y-junction CNTs. The detailed growth mechanism for this structure has been reported previously (Chai *et al.*, 2006b). However, the yield of Y-junction CNTs obtained in this study is still low as they are only the by-product obtained from this process. We believe that through proper adjustment of the ratio of NiO, CuO and MoO_x, it is possible to increase the selectivity of the catalyst towards the formation of Y-junction CNTs.

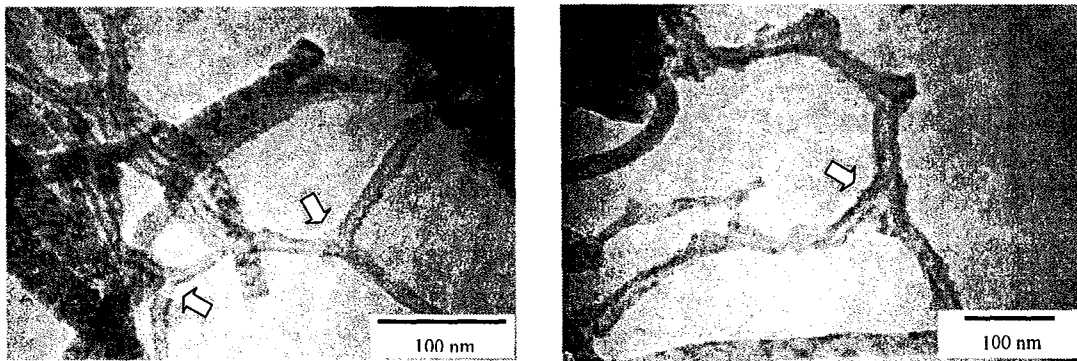


Fig. 6. TEM images of Y-junction CNTs grown on NiO-CuO-MoO_x(7:2:1)(w/w/w)/SiO₂ catalyst.

3.5 Formation of carbon nanotubes of special morphologies

In addition to the ordinary morphology, several unique ones have been observed in our research works (Mohamed, 2006). Some morphologies are very attractive which may have some special advantages in certain applications. Fig. 7a shows the bamboo-like CNTs. These nanostructures were grown on NiO/CeO₂ catalyst at 700°C. Several compartments can be observed along the nanotubes axis, providing many unique chambers for gas storage when they are used as a gas sensor. Another type CNTs were grown from methane decomposition at 800°C on NiO/CeO₂ catalyst and their respective TEM image was shown in Fig. 7b. These carbon nanostructures were named as encapsulated type CNTs. One can observe that the metallic parts of the catalyst were encapsulated within the tubes, as indicated by an arrow. We believe that nickel was in quasi-liquid state at 800°C. This condition allowed them to be elongated and segregated during the growth of CNTs, and finally it trapped within the nanotubes, forming an encapsulated structure. Figs. 7c and 7d show the helix-shaped CNTs and chain-like CNTs, respectively. Both nanostructures were observed on the CoO_x-MoO_x(8:2)(w/w)/Al₂O₃ and CoO_x/Al₂O₃ catalysts after methane decomposition at 800°C. In most cases, only a mixture of CNTs with unique morphologies was obtained. Nonetheless, this is a preliminary study, which pictures the controllable growth of CNTs through manipulating the catalyst components and reaction parameters.

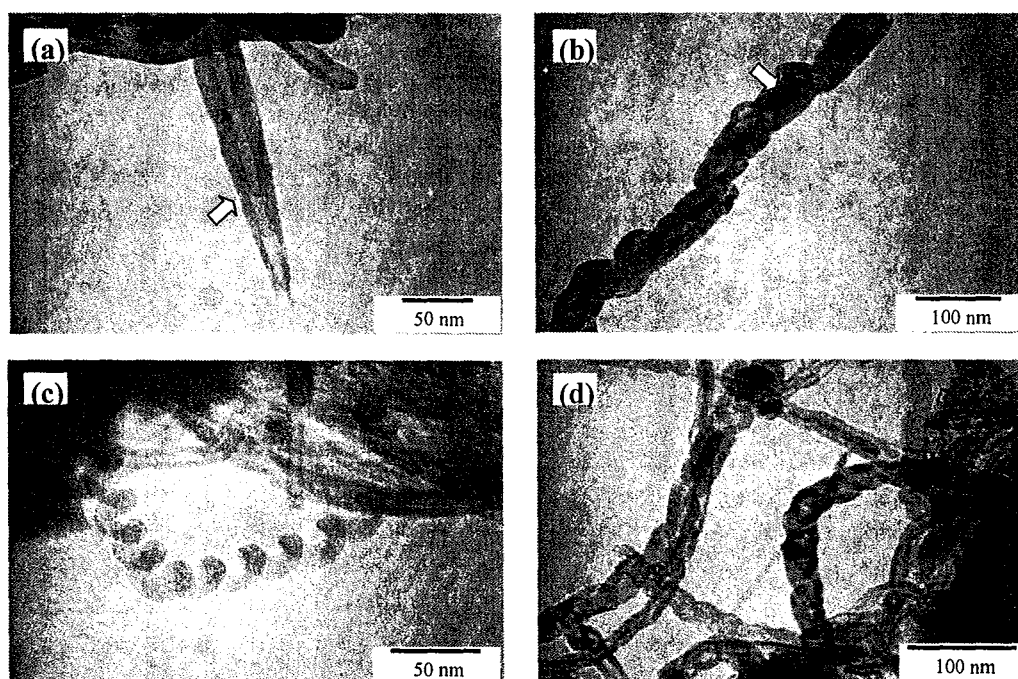


Fig. 7. TEM images of carbon nanostructures synthesized over various supported catalysts via decomposition of methane: (a) bamboo-like CNTs; (b) encapsulated type CNTs; (c) helix-shaped CNTs; (d) chain-like CNTs.

4. Conclusions

Various CNTs, including CNFs, MWNTs, SWNTs, Y-junction CNTs and others with special morphologies have been catalytically grown by supported catalysts via catalytic decomposition of methane. Various CNTs synthesized in this study have enriched the nanostructures of carbon family, providing more unique materials which may be needed in future applications. Furthermore, this finding is important because it shows that synthesizing CNTs with desirable morphologies could be achieved through manipulating the catalyst components and reaction parameters. This does provide useful information to the next level for controlled synthesis of CNTs for the need of the markets.

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Notations

n number of graphene layers
 d diameter of SWNTs, nm

Greek letters

τ thickness of nanotube wall (each side), nm
 ω peak position in the RBM region, cm^{-1}

Subscript

RBM radial breathing mode

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