An investigation into the production of hydrogen and carbon nanomaterials by the thermocatalytic decomposition of methane

Wang, Hongyan

2013

Wang, H. (2013). An investigation into the production of hydrogen and carbon nanomaterials by the thermocatalytic decomposition of methane. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/53652>

<https://doi.org/10.32657/10356/53652>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**AN INVESTIGATION INTO THE PRODUCTION OF
HYDROGEN AND CARBON NANOMATERIALS BY
THE THERMOCATALYTIC DECOMPOSITION OF
METHANE**

WANG HONGYAN

School of Mechanical and Aerospace Engineering

2013

**AN INVESTIGATION INTO THE PRODUCTION OF
HYDROGEN AND CARBON NANOMATERIALS BY THE
THERMOCATALYTIC DECOMPOSITION OF METHANE**

WANG HONGYAN

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University

in partial fulfillment of the requirement for the degree of

Doctor of Philosophy

2013

Abstract

Hydrogen is widely considered to be one of the most promising alternative energy carriers and clean fuels. Hence, much effort has been directed in developing efficient, economic and environmental friendly approaches for the production of hydrogen. Among the many hydrogen production reactions, the catalytic decomposition of methane (CDM) over supported nickel catalysts has generated much interest. The major driving factor for the research activities on catalytic methane decomposition is the highly desirable products- CO_x -free hydrogen and carbon nanotubes (CNTs) or carbon nanofibres (CNFs) instead of gaseous CO_x . This reaction will eliminate the need for CO_x separation and sequestration processes altogether. The main objective of this research project is to produce hydrogen by thermal decomposition of methane over pure metallic catalysts and to optimize the process by developing high efficiency and long active-life catalysts. In this thesis, a comprehensive study on a series of unsupported nano-particle catalysts such as Ni, Ni-Cu and Ni-Cu-Co was presented. These unsupported catalysts prepared in a facile method showed comparable catalytic activity as the supported catalysts, and offered two major advantages by (1) providing easy recovery of the catalyst and a convenient way for the purification of the CNFs by leaching the metal catalyst with a mild acid solution and (2) preventing the formation of traceable CO which may be generated in supported (SiO_2 and Al_2O_3) catalysts. To the best knowledge of the author, this study was the first time that investigated the catalytic activities and deactivation mechanisms of Ni, Ni-Cu and Ni-Cu-Co alloy particles towards CDM systematically. The thesis consisted mainly of the following five parts:

(1) Unsupported NiO and NiO-CuO nano-particles were prepared by a facile method and these nano-particles showed promising catalytic activity towards CDM. Unlike the supported catalysts, it was necessary to introduce methane to the reactor at lower temperatures to avoid catalyst particles sintering into bigger ones during the reaction. The textural and micro-structural properties of the deposited carbon were also characterized in detail. This work provided helpful guidance on the direct preparation of active metallic catalysts in the next chapters.

(2) Metallic nickel nano-particles were prepared primarily as catalysts for CDM. Nickel particle aggregates with controlled crystalline size and primary particle size were prepared firstly by the precipitation of nickel nitrate and oxalic acid in ethanol solution, followed by the thermal decomposition of nickel oxalate dihydrate under oxygen-free atmosphere. A series of decomposition atmospheres ($\text{CH}_4\text{-N}_2$ in different ratios) were used to investigate their effects on the morphology and crystalline size of the metallic nickel particles. The effects of ramp-up rate and reaction temperatures on the catalytic activity were also studied.

(3) A series of Ni-Cu alloy particles with different atomic ratios of Ni/Cu were prepared by the thermal decomposition of fibrous Ni-Cu oxalate precursors in methane atmosphere. The resulting porous aggregates of Ni-Cu alloy particles showed promising catalytic activities for methane decomposition at temperatures of 700 and 750 °C. The stability of the catalysts was discussed and the deactivation mechanism was proposed.

(4) A series of unsupported Ni-Cu-Co alloy particles with promising catalytic activity were prepared by thermal decomposition of Ni-Cu-Co oxalates in methane atmosphere. The addition of cobalt led to the formation of alloy particles with smaller crystalline size and particle size than those of Ni-Cu alloy or pure Ni particles. The objective of this part of the project was to investigate the genesis of the phase composition and properties of Ni-Cu-Co alloy catalyst. The effect of the addition of cobalt to the Ni-Cu catalyst on the stability of the catalyst was studied.

(5) In this chapter, a detailed catalytic deactivation study was carried out. A series of kinetic experiments had been conducted using two types of catalysts (Ni and Ni-Cu-Co alloy). The effects of methane partial pressure and reaction temperatures on the maximal hydrogen formation rate were studied. The reaction order and activation energy of pure Ni and Ni-Cu-Co catalyst were calculated. Two models including the empirical model (General Power Law Equation) and a phenomenal model (Exponential Decay Model) were used to fit the experimental results of Ni catalysts. Different deactivation mechanisms of pure Ni and Ni-Cu-Co catalyst were proposed and discussed.

Acknowledgements

Firstly and foremost, I would like to express my sincere gratitude to my supervisor, Prof Lua Aik Chong, for his invaluable guidance and constant encouragement during the past five years.

Next, I would like to offer my thanks to Mr Yuan Kee Hock, Higher laboratory Executive in the Thermal and Fluids Research Laboratory, MAE, for his invaluable assistance. I would also like to thank my friends for their help and encouragement whenever needed.

Last but not the least, I wish to acknowledge my family for their moral support and blessing, which always cheer me up and keep me going on.

Table of Contents

Abstract	1
Acknowledgements	IV
Table of Contents	V
List of Figures	X
List of Tables	XX
List of Symbols	XXI
List of Abbreviations	XXII
Chapter 1 Introduction	1
1.1 Introduction	1
1.2 Objectives and scope	5
Chapter 2 Literature Review	9
2.1 Methods for hydrogen production from natural gas	9
2.1.1 Steam reforming of methane (SRM)	9
2.1.2 Partial oxidation of methane (POM)	10
2.1.3 Autothermal reforming of methane (ARM)	11
2.1.4 CO ₂ (Dry) reforming	12
2.1.5 Thermal (catalytic) decomposition methane (TDM/CDM)	13
2.2 Comparison between TDM /CDM and SRM	15
2.3 CO _x free hydrogen production	19
2.4 History background of CDM	21
2.5 CDM reaction process	22

Table of contents

2.5.1 Methane activation on metal surface	24
2.5.2 Carbon atoms migration and CNTs/CNFs growth.....	25
2.5.3 Catalyst state in reaction	27
2.5.4 Catalyst deactivation.....	29
2.6 Catalysts for the CDM	31
2.6.1 Active phase	31
2.6.2 Effect of the catalysts crystallite size	33
2.6.3 Effect of support	35
2.6.4 Effect of promoters	39
2.7 Reaction mechanism and kinetic studies	48
2.7.1 Mechanism rate equations.....	48
2.7.2 Deactivation kinetic studies	53
2.8 Summary	57
Chapter 3 Experimental Set-up and Procedures for Catalysts Preparation and Characterisation	59
3.1 Chemicals.....	59
3.2 Catalytic activity evaluation setup	60
3.3 Catalyst preparation procedures.....	63
3.3.1. Preparation of Ni and Ni-Cu catalysts and evaluation of their catalytic activities	63
3.3.2 Systematic preparation of metallic nickel particles and evaluation of their catalytic activity	64
3.3.3 Preparation of metallic Ni-Cu alloy and evaluation of its catalytic activity....	66

3.3.4 Preparation of metallic Ni-Cu-Co alloy and evaluation of its catalytic activity	68
3.3.5 Experiments for kinetic studies.....	69
3.4 Characterization of the catalysts and carbon deposits	70
Chapter 4 Preparation and Characterization of Ni and Ni-Cu Nano-Particles and Evaluation of Their Catalytic Activities.....	73
4.1 Introduction.....	73
4.2 Results and discussion	74
4.2.1 Characterization of the precursors and catalysts.....	74
4.2.2 Catalytic activity	82
4.2.3 Characterization of the deposited carbon.....	85
4.3 Summary	92
Chapter 5 Systematic Preparation of Metallic Nickel Particles and Evaluation of Their Catalytic Activity	94
5.1 Introduction.....	94
5.2 Results and discussion	94
5.2.1 Effect of reactant concentration	94
5.2.2 Effect of atmosphere	102
5.2.3 Effect of ramp-up rate	112
5.2.4 Effect of reaction temperature.....	113
5.3 Lifetime tests of the catalysts.....	115
5.4 Summary	117
Chapter 6 Systematic Preparation of Ni-Cu Alloy Particles and Evaluation of Their	

Catalytic Activity	120
6.1 Introduction.....	120
6.2. Results and discussion	120
6.2.1 Characterization of the catalysts	120
6.2.2 Catalytic activity	127
6.2.3 Stability and deactivation mechanism of the catalysts	137
6.3 Summary	141
Chapter 7 Systematic Preparation of Ni-Cu-Co Alloy Particles and Evaluation of Their Catalytic Activity	143
7.1 Introduction.....	143
7.2 Experiment results	143
7.2.1 Characterization of the catalysts	143
7.2.2 Catalytic activity	147
7.3 Discussion.....	157
7.4 Summary	160
Chapter 8 Kinetic Studies and Modelling Work	161
8.1 Introduction.....	161
8.2 Reaction rate kinetic studies	161
8.3 Deactivation analysis and modelling work of based on Ni catalyst	170
8.4 Deactivation mechanism of Ni-Cu-Co alloy catalysts.....	188
8.5 Summary	190
Chapter 9 Conclusions	192
Chapter 10 Future studies	196

Table of contents

References	197
Publications	219

List of Figures

Fig. 1.1 Global energy systems transition [13].....	3
Fig. 2.1 Illustration of an ATR reactor.....	12
Fig. 2.2 Equilibrium conversion of methane under different pressures and temperatures [8].....	15
Fig. 2.3 Economics of hydrogen production by CDM (A) hydrogen selling price as a function of carbon-selling price; and (B) selling price of different carbon products [6].....	19
Fig. 2.4 Schematic pictures of the formation of a CNF (left) and CNT (right) [81]	22
Fig. 2.5 TEM micrographs of the nickel catalyst and the generated CNT, (a) Ni nanocrystal supported on MgAl_2O_4 , acquired <i>in situ</i> (3.5 mbar H_2 , 430 °C); and(b) A multi-walled CNT; scale bars, 5 nm [53].....	23
Fig. 2.6 Image sequence of a growing carbon nanofiber. Images a-h illustrate the elongation/contraction process. Drawings are included to guide the reader in locating the positions of mono-atomic Ni step edges at C-Ni interface. The images are acquired in situ with $\text{CH}_4:\text{H}_2$ -1:1 at a total pressure of 2.1 mbar with the sample heated to 809K [53].	24
Fig. 2.7 Schematic of three carbon diffusion mechanisms in CDM (solid black circle: carbon atoms), adapted from [94].....	26
Fig. 2.8 FIM images (left) and corresponding ball model (right) of the a) the staring clean Ni crystal ($T=61\text{K}$), b) after exposure to H_2 (600 °C), and c) after exposure to C_2H_2 [98]	28
Fig. 2.9 Graphical representation of the bulk of literature data on catalysts, preferred temperature range and carbon products related to catalytic methane decomposition reaction. Catalysts: 1- Ni-based, 2-Fe-based, 3-carbon-based, 4-summary of data related to Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, W catalysts, 5-non-catalytic decomposition. Carbon products: CF-carbon filaments, TC-turbostratic carbon, GC-graphitic carbon, AmC-amorphous carbon [113]	32

Fig. 2.10 Effects of NiO crystal size on the growth rate (left) and the final carbon yield (right) of CNF. Reaction conditions: $T=580\text{ }^{\circ}\text{C}$, $P_{\text{tot}}=100\text{ kPa}$, $P_{\text{CH}_4}=80\text{ kPa}$, $P_{\text{H}_2}=5.5\text{ kPa}$. Total flow: 50ml/min [118]	33
Fig. 2.11 Methane conversion over Ni catalysts supported on different supports at $500\text{ }^{\circ}\text{C}$ [122]	36
Fig. 2.12 Change of the methane conversion as a function of time on a stream of methane in CDM at 773 K over Co catalysts supported on different supports. Catalysts: 0.06g, loading of Co: 20%wt.%, $P(\text{CH}_4):101\text{ kPa}$, and flow rate:50 ml/min [123].....	37
Fig. 2.13 Hydrogen (●) and carbon (○) yields as a function of Cu:Ni molar ratio during methane decomposition over the $\text{Ni}_x\text{Cu}_y\text{Mg}_z\text{O}$ ($x:z=2.4:1$) catalysts at $665\text{ }^{\circ}\text{C}$ ($T_{\text{reduction}}=850\text{ }^{\circ}\text{C}$) [133]	40
Fig. 2.14 TEM pictures of $82\text{ Ni}-8\text{ Cu}-\text{Al}_2\text{O}_3$ after 2 h of methane decomposition at $650\text{ }^{\circ}\text{C}$ [139]	42
Fig. 2.15 Change of methane conversion as a function of time on stream of methane in the CDM over Ni/SiO_2 modified with different metal species (Cu, Rh, Pd, Ir and Pt) Reaction temperature $=550\text{ }^{\circ}\text{C}$, catalysts $=0.040\text{ g}$, $\text{CH}_4=101\text{ kPa}$ and 40ml/min [120]	45
Fig. 2.16 Rates of carbon formation on Ni-Cu/ SiO_2 alloy catalysts by decomposition of methane at different partial pressure of methane or hydrogen (a) 1% Cu catalyst, (b) 10% Cu catalyst. Points are experimental values, Curves are calculated using model equation[170]	52
Fig. 2.17 Methane cracking: parity diagram based on the results for the sequential experiments on used catalysts samples[167].....	52
Fig. 2.18 Plot of activity expression in relation to time ($d=2$) at $650\text{ }^{\circ}\text{C}$ [169].....	54
Fig. 2.19 Experimental (points) and calculated (lines) time dependencies of specific carbon content on the catalyst in a perfect-mixing reactor at $550\text{ }^{\circ}\text{C}$ [107].	55
Fig. 2.20 Predicted and experimental change in carbon specific weight with time. Reaction conditions: $T=500\text{ }^{\circ}\text{C}$; Total reaction gas flow rate $=120\text{ ml/min}$ with 10 mg of catalyst: (a) $P_{\text{total}}=10\text{ bar}$, 10 vol% H_2 and balance CH_4 ; (b) $P_{\text{total}}=1\text{ bar}$, 5 % H_2 and balance CH_4 [173].	56

Fig. 3.1 Schematic diagram of experimental setup	61
Fig. 3.2 Photograph of experimental setup.....	62
Fig. 4.1 XRD patterns of the samples Nioxa, Nioxa-Cuoxa, NiO and NiO-CuO. (The crystal sizes of the metal oxides were calculated from the most intense peak at around 43 °)	74
Fig. 4.2 XRD patterns of the Ni and Ni-Cu samples after reduction in H ₂ . The crystal sizes were calculated from the most intense peak of metallic Ni or Ni-Cu alloy. The bottom graph (b) shows the expanded region corresponding to the most intense peaks of the Ni and Ni-Cu alloy along with the positions expected for the pure metals.	75
Fig. 4.3 Temperature-programmed reduction curves of NiO and NiO-CuO	77
Fig. 4.4 FESEM micrographs of catalyst precursors and reduced catalysts: (a) Nioxa, (b) Nioxa-Cuoxa, (c) NiO (inset), (d) NiO-CuO (inset), (e) Ni, (f) Ni-Cu alloy and TEM micrographs of (c) NiO and (d) NiO-CuO.....	79
Fig. 4.5 Particle size distributions (a, b) and pore size distributions (c, d) of NiO and NiO-CuO	80
Fig. 4.6 Catalytic activity tests of Ni catalysts using (a) route I and (b) route II (Reaction conditions: 0.05g NiO, methane 20% balanced by nitrogen, flow rate = 25ml/min)	82
Fig. 4.7 Catalytic activity tests of Ni-Cu catalysts using (a) route I and (b) route II (Reaction conditions: 0.05g NiO-CuO, methane 20% balanced by nitrogen, flow rate = 25ml/min) ..	82
Fig. 4.8 TEM micrographs of metallic Ni-Cu alloy at the initial stage at 600 °C using (a) route I, inset (FESEM micrograph), and (b) route II. TEM micrograph (c) of the deposited carbon after the decomposition reaction using route I.....	84
Fig. 4.9 TEM micrographs of carbon deposits on the Ni catalysts using route II at a reaction temperature of (i) 500 °C at (a) low magnification, and (b) high magnification; and (ii) 550 °C for (c) fine carbon fibres, and (d) lumps of carbon fibres. All the pictures presented are representative of the whole samples.	85
Fig. 4.10 TEM micrographs of carbon deposits on the Ni-Cu catalysts using route II at a reaction	

temperature of (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C, (e) 700 °C, and (f) (g) (h) 750 °C.	
All the pictures presented are representative of the whole samples.	87
Fig. 4.11 XRD patterns of spent catalysts using route II under different reaction temperatures...	91
Fig. 5.1 XRD patterns of nickel oxalate dihydrate	95
Fig. 5.2 FESEM and TEM (insets) micrographs of nickel oxalate dihydrates (a) Nioxa-C1, (b) Nioxa-C2, (c) Nioxa-C3, (d) Nioxa-C4, and (e) Nioxa-C5	96
Fig. 5.3 Schematic molecular structure of nickel oxalate dihydrate ribbons.....	97
Fig. 5.4 FESEM micrographs of metallic nickel particles (a): Ni-C1-M0.2, (b): Ni-C2-M0.2, (c): Ni-C3-M0.2, (d): Ni-C4-M0.2, and (e): Ni-C5-M0.2.....	98
Fig. 5.5 XRD patterns of metallic nickel particles obtained by reduction in methane gas stream	99
Fig. 5.6 Methane conversion and hydrogen formation rate over nickel catalysts prepared from different nickel oxalate concentrations (Reaction conditions: 0.15g nickel oxalate dihydrate, 20% methane balanced by nitrogen, methane-nitrogen combined flow rate = 25ml/min, reaction temperature = 550 °C).....	100
Fig. 5.7 TEM micrographs of catalysts and deposited carbons after > 8 hours of decomposition reaction (a) Ni-C1-M0.2, (b) Ni-C2-M0.2, (c) Ni-C3-M0.2, (d) Ni-C4-M0.2, (e) Ni-C5-M0.2, and (f) Ni-C1-M0.2 (high magnification)	101
Fig. 5.8 Methane conversion for nickel catalysts originating from nickel oxalate reduced in different atmospheres (Reaction conditions: 0.15g nickel oxalate dihydrate, methane 20% balanced by nitrogen, flow rate = 25ml/min, reaction temperature = 550 °C).	103
Fig. 5.9 TGA graph of nickel oxalate dihydrate in N ₂ atmosphere	104
Fig. 5.10 TEM micrographs (a), (b), (c), (d) ,(e) ,(f) and FESEM micrographs (g), (h) of the products resulting from nickel oxalate decomposition at different temperatures and atmospheres	106
Fig. 5.11 XRD patterns of the resulting products of nickel oxalate decomposition in N ₂ and CH ₄	

atmospheres	108
Fig. 5.12 TEM micrographs of catalysts and deposited carbon after > 8 hours of catalytic decomposition reaction (a) Ni-C4-M0.2, (b) Ni-C4-M0, and (c) Ni-C4-M0	111
Fig. 5.13 Methane conversion for nickel catalysts at different temperature ramp-up rate (Reaction conditions: 0.15g nickel oxalate, methane 20% balanced by nitrogen, flow rate = 25ml/min, reaction temperature=550 °C)	112
Fig.5.14 Methane conversion for nickel catalysts at different reaction temperatures (Reaction conditions: 0.15g nickel oxalate, methane 20% balanced by nitrogen, flow rate = 25ml/min)	113
Fig. 5.15 Morphology of carbon formed at different temperatures (a) 525 °C, (b) 550 °C, and (c) 575 °C	114
Fig. 5.16 Kinetic curves of methane conversions during methane decomposition over Ni catalysts at different temperatures. (Reaction conditions: 0.015 g nickel oxalate dihydrate, methane 100%, flow rate = 20 ml/min).....	116
Fig. 5.17 Morphology of carbon formed after complete deactivation at different temperatures (a) 500 °C, (b) 525 °C, and (c) 550 °C.....	116
Fig. 6.1 XRD patterns of (a) copper oxalate and nickel oxalate hydrates reference and (b) Ni-Cu oxalates with different Ni/(Ni+Cu) ratios (Ni content: Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3: 75%; Ni-Cu-4: 62.5%; Ni-Cu-5: 50%; Ni-Cu-6 43.75%; Ni-Cu-7: 37.5%)	121
Fig. 6.2 TEM micrographs of Ni-Cu oxalates and pure copper oxalate: (a) Ni-Cu-1, (b) Ni-Cu-2, (c) Ni-Cu-3, (d) Ni-Cu-4, (e) Ni-Cu-5, (f) Ni-Cu-6, (g) Ni-Cu-7, (h) and (i) copper oxalate	122
Fig. 6.3 XRD patterns of reference (a) and Ni-Cu alloy (b) with different Ni/(Ni+Cu) ratios obtained by reduction in methane gas stream. (Ni content: Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3: 75%; Ni-Cu-4: 62.5%; Ni-Cu-5: 50%; Ni-Cu-6 43.75%; Ni-Cu-7: 37.5%,	

reduction temperature: 450 °C)	124
Fig. 6.4 FESEM micrographs of Ni-Cu alloy with different Ni/(Ni+Cu) ratios: (a) Ni-Cu-1, (b) Ni-Cu-2, (c) Ni-Cu-3, (d) Ni-Cu-4, (e) Ni-Cu-5, (f) Ni-Cu-6 and (g) Ni-Cu-7 obtained by reduction in methane gas stream.....	126
Fig. 6.5 (a) Methane conversions during step-wise rising temperature reaction and (b) average methane conversion values, over Ni-Cu alloy catalysts of different Ni/Cu ratios (Reaction conditions: 0.15g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, test duration: 30min at each reaction temperature, Ni content: Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3: 75%; Ni-Cu-4: 62.5%; Ni-Cu-5: 50%; Ni-Cu-6 43.75%; Ni-Cu-7: 37.5%)	127
Fig. 6.6 Methane conversions using different catalysts with varying Ni/(Cu+Ni) ratios at (a) 700 °C and (b) 750 °C reaction temperatures (Reaction conditions: 0.15g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min).....	128
Fig. 6.7 Methane conversions using different catalysts for various different samples (a) pure Ni, (b) Ni-Cu-1, (c) Ni-Cu-2, (d) Ni-Cu-3 and (e) Ni-Cu-5 (Reaction conditions: 0.15g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, Ni content: Pure Ni:100%, Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3:75%; Ni-Cu-5: 50%)	130
Fig. 6.8 XRD patterns of spent catalysts under different reaction temperatures: (a) 700 °C and (b) 750 °C	131
Fig. 6.9 TEM micrographs of carbon deposits on different Ni-Cu catalysts: (a) Ni-Cu-1, (b) Ni-Cu-2, (c)(d) Ni-Cu-3, (e) Ni-Cu-4, (f) Ni-Cu-5, (g) Ni-Cu-6 and (h), (i) Ni-Cu-7, at a reaction temperature of 700 °C	133
Fig. 6.10 TEM micrographs of carbon deposits on different Ni-Cu catalysts: (a),(b)Ni-Cu-3, (c) Ni-Cu-4, (d) Ni-Cu-5, (e) Ni-Cu-6, and (f) Ni-Cu-7, at a reaction temperature of 750 °C .	135
Fig. 6.11 Methane conversions using different catalysts at 700 °C for complete catalyst	

deactivation. (Reaction conditions: 0.015g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=20 ml/min).....	137
Fig. 6.12 TEM micrographs of carbon deposits on the different Ni-Cu catalysts after total deactivation: (a),(b) Ni-Cu-3, (c),(d) Ni-Cu-4, and (e),(f) Ni-Cu-7 (Reaction conditions: 0.015g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=20 ml/min, reaction temperature :700 °C).....	138
Fig. 6.13 Postulated model of the arrangements of nickel and copper atoms and the selective carbon diffusion path in the surface of (a), (c) Ni/Cu (7:3) and (b), (d) Ni/Cu (3:7) alloys [131].....	140
Fig. 7.1 TEM micrographs of Ni-Cu-Co oxalates, Co-Cu oxalate and pure cobalt oxalate: (a) Ni-Cu-Co-1, (b) Ni-Cu-Co-2, (c) Ni-Cu-Co-3, (d) Ni-Cu-Co-4, (e) Ni-Cu-Co-5, (f) Co-Cu and (g) Co (Ni/Co/Cu ratios: Ni-Cu-Co-1(0.7/0.05/0.25), Ni-Cu-Co-2(0.625/0.125/0.25), Ni-Cu-Co-3(0.5/0.25/0.25), Ni-Cu-Co-4(0.375/0.375/0.25), Ni-Cu-Co-5(0.25/0.5/0.25), Co-Cu(0/0.75/0.25))	144
Fig. 7.2 FESEM micrographs of Ni-Cu, Co-Cu and Ni-Cu-Co alloys: (a) Ni-Cu-3, (b) Ni-Cu-Co-1, (c) Ni-Cu-Co-2, (d) Ni-Cu-Co-3, (e) Ni-Cu-Co-4, (f) Ni-Cu-Co-5, (g) Co-Cu	145
Fig. 7.3 XRD patterns of (a) reference and (b) Ni-Cu-Co alloys by reduction in methane.....	146
Fig. 7.4 Methane conversions during step-wise rising temperature reaction for Ni-Cu-Co alloy catalysts (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, test duration: 30min at each reaction temperature, Ni/Co/Cu ratios: Ni-Cu-Co-1(0.7/0.05/0.25), Ni-Cu-Co-2(0.625/0.125/0.25), Ni-Cu-Co-3(0.5/0.25/0.25), Ni-Cu-Co-4(0.375/0.375/0.25), Ni-Cu-Co-5(0.25/0.5/0.25), Co-Cu(0/0.75/0.25)).....	148
Fig. 7.5 Methane conversions using different catalysts at 700 °C (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min).....	149
Fig. 7.6 Methane conversions using different catalysts at 750 °C (Reaction conditions: 0.15g Ni-	

Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min).....	150
Fig. 7.7 Methane conversions using Ni-Cu-Co-1 at various reaction temperatures (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)	150
Fig. 7.8 Methane conversions using Ni-Cu-Co-3 at various reaction temperatures (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)	151
Fig. 7.9 XRD patterns of spent catalysts at different reaction temperatures: (a) 700 °C and (b) 750 °C	153
Fig. 7.10 TEM micrographs of spent catalysts: (a) Ni-Cu-3, (b) Ni-Cu-Co-1, (c) Ni-Cu-Co-2, (d) (h) Ni-Cu-Co-3, (e) Ni-Cu-Co-4, (f) Ni-Cu-Co-5, (g) Co-Cu at a reaction temperature of 700 °C.	154
Fig. 7.11 TEM micrographs of spent catalyst Ni-Cu-Co-1 at a reaction temperature of 750 °C .	155
Fig. 7.12 TEM micrographs of spent catalysts: (a) Ni-Cu-Co-2, (b) Ni-Cu-Co-3, and (c) Ni-Cu-Co-4 at a reaction temperature of 750 °C	156
Fig. 7.13 TEM micrographs of spent catalysts: Ni-Cu-Co-2 at different reaction temperature of (a) 775 °C and (b), (c) 800 °C	156
Fig. 7.14 Methane conversions during step-wise rising temperature reaction using Ni-Cu-Co and Ni-Cu alloy catalysts (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, test duration: 30min at each reaction temperature)	159
Fig 8.1 Influence of gas liner velocity on the conversion of methane (Reaction conditions: total flow rate/amount of nickel oxalate =10ml /0.0075g, 20ml/0.015g, 30ml/0.0225g, 40ml/0.03g, methane 20% balanced by nitrogen, reaction temperature =525 °C)	162
Fig. 8.2 H ₂ formation rate versus reaction time for Ni catalyst under different methane partial pressures (P _{CH₄}) and different reaction temperatures: (a) 575 °C, (b) 550 °C, and (c) 525 °C	

(Reaction conditions: 0.015 g nickel oxalate dihydrate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).....	164
Fig. 8.3 Dependence of the maximal hydrogen formation rate $r_{\max}$ versus partial pressure of methane P_{CH_4} at different temperatures for reaction under Ni catalyst (Reaction conditions: 0.015 g nickel oxalate dihydrate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min)	165
Fig. 8.4 Arrhenius plot $\ln k$ vs. $(1/T)$ (Reaction conditions: 0.015 g nickel oxalate dihydrate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min)	166
Fig. 8.5 H_2 formation rate versus reaction time for 2Ni-1Cu-1Co catalyst under different methane partial pressures (P_{CH_4}) and different reaction temperatures: (a) 750 °C, (b) 700 °C, and (c) 650 °C (Reaction conditions: 0.015 g 2Ni-1Cu-1Co oxalate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).....	168
Fig. 8.6 Dependence of the maximal hydrogen formation rate $r_{\max}$ versus partial pressure of methane P_{CH_4} at different temperatures for reaction under 2Ni-1Cu-1Co catalyst (Reaction conditions: 0.015 g 2Ni-1Cu-1Co oxalate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).	169
Fig. 8.7 Arrhenius plot $\ln k$ vs. $(1/T)$ (Reaction conditions: 0.015 g 2Ni-1Cu-1Co oxalate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).	170
Fig. 8.8 TEM micrographs of Ni catalyst after 10 min of reaction under different methane partial pressures at 525 °C (a) P_{CH_4} = 0.2 (b) P_{CH_4} = 0.4, and (c) P_{CH_4} = 0.8	172
Fig. 8.9 Spent Ni catalyst after complete deactivation with P_{CH_4} = 0.2 for different reaction temperatures (a) 525 °C, (b) 550 °C, and (c) 575 °C.....	173
Fig. 8.10 Activity versus time at 525 °C for different methane partial pressures (a) 0.8 atm, (b) 0.6	

atm, (c) 0.4 atm, and (d) 0.2 atm.....	176
Fig. 8.11 Activity versus time at 550 °C for different methane partial pressures (a) 0.8 atm, (b) 0.6 atm, (c) 0.4 atm, and (d) 0.2 atm.....	178
Fig. 8.12 Activity versus time at 575 °C for different methane partial pressures (a) 0.8 atm, (b) 0.6 atm, (c) 0.4 atm, and (d) 0.2 atm.....	180
Fig. 8.13 Logarithmic decay amplitude A versus logarithmic methane partial pressure at different reaction temperatures.....	184
Fig. 8.14 Logarithmic decay constant t^* versus logarithmic methane partial pressure at different reaction temperatures.....	184
Fig. 8.15 Hydrogen formation rate versus reaction time for different methane partial pressures at reaction temperatures of (a) 525 °C, (b) 550 °C, and (c) 575 °C: solid line – experimental data; dash line – activity calculated from Eq. 8.13.....	187
Fig. 8.16 Spent 2Ni-1Cu-1Co catalysts after complete deactivation for $P_{CH_4} = 0.2$ under different reaction temperatures of (a) 650 °C, (b) 700 °C, and (c) 750 °C (insets: high magnification).....	189
Fig. 8.17 TEM micrographs of 2Ni-1Cu-1Co catalysts after reaction for 10 min for $P_{CH_4} = 0.2$ at different reaction temperatures of (a) 650 °C, (b) 700 °C, and (c) 750 °C.....	189

List of Tables

Table 1.1 Heat of combustion of various fuels	4
Table 2.1 Comparison of SRM and TDM for hydrogen production[42].....	17
Table 2.2 Different methods to produce CO _x -free hydrogen	20
Table 2.3 Selected performance results of catalysts for CDM	47
Table 2.4 Reaction steps of methane cracking starting with two adsorption mechanisms [22]	49
Table 2.5 Summary of mechanistic rate equations on supported metal catalysts.....	50
Table 3.1 List of chemicals.....	59
Table 3.2 Experimental conditions for kinetic studies.....	70
Table 4.1 Textural and structural characteristics of catalyst and carbon nano-fibres obtained from route II	89
Table 6.1 Compositions of different Ni-Cu alloy samples	125
Table 7.1 Compositions of different Ni-Cu-Co alloy samples	147
Table 7.2 Physico-chemical properties of selected transition metals. NA = data not available[74]	157
Table 8.1 Decay amplitude, decay constant and coefficient of determination R^2 for the Exponential Decay Model at different temperatures and methane partial pressures	181
Table 8.2 Deactivation order, deactivation function and coefficient of determination R^2 for the General Power law Equation ($d \neq 1$) at different temperatures and methane partial pressures	182
Table 8.3. Mean deviation between the experimental and model results of catalyst hydrogen formation rate under different operating conditions	188

List of Symbols

A	Decay amplitude	dimensionless
a	Normalized catalyst activity factor : $r(t)/r_{\max}$	dimensionless
d	Deactivation order	dimensionless
E_a	Activation energy	kJ/mol
ΔH	Heat of adsorption	J/mol
k	Rate constant	mol/(g _{cat} min atm ⁿ)
n	Reaction order	dimensionless
p_i	Partial pressure of component i	atm
$r(t)$	Reaction rate at a give time	mol/g _{cat} min
r_o	Initial reaction rate	mol/g _{cat} min
$r_{\max}$	Maximum reaction rate	mol/g _{cat} min
r_d	Deactivation function	min ⁻¹
R	Gas constant: 8.31	J/Kmol
t	Reaction time	min
t^*	Decay constant	min
v	Pre-exponential factor	mol/(g _{cat} min atm ⁿ)
R	Gas constant: 8.31	J/Kmol
S_{BET}	Surface area derived by BET method	m ² /g
V_p	Total pore volume from N ₂ adsorption at p/p ₀ =0.99	cm ³ /g
d_{002}	interplanar distance of (002) planes	nm
L_c	Domain crystalline size along the c-axis direction	nm

List of Abbreviations

ARM	Autothermal reforming of methane
BET	Brunauer-Emmett-Teller Surface Area Analysis
BJH	Barrett-Joyner-Halenda Pore Size and Volume Analysis
CCS	Carbon capture and sequestration
CDM	Catalytic decomposition of methane
CNFs	Carbon nanofibres
CNMs	Carbon nanomaterials
CNTs	Carbon nano-tubes
DRM	Dry reforming of methane
FESEM	Field emission scanning electron microscope
NG	Natural gas
PEMFC	Proton exchange membrane fuel cells
POM	Partial oxidation of methane
SRM	Steam reforming of methane
TDM	Thermal decomposition of methane
TEM	Transmission electron microscope
TGA	Thermogravimetric analyzer
TPR	Temperature programmed reduction
WGS	Water-gas shift reaction
XRD	Powder X-ray diffractometer
WGS	Water-gas shift reaction
PSA	Pressure swing adsorption

Chapter 1 Introduction

1.1 Introduction

Energy forms a very important growth engine for the economic development of a nation and its social progress and well being. During the last century, cheap and abundant fossil fuel energy has taken the most important role in the industrialization process in many countries. Accordingly, the living standards of mankind have been greatly enhanced. However, in this century, it is generally realized that the fossil fuel-based energy system is facing two major challenges: gradual depletion of energy resources accelerated by an rising energy demand and the global environmental deterioration caused by the inappropriate energy use, in the form of global warming, ozone layer depletion, acid rains, air pollution and so on [1-4]. The fossil fuel greenhouse effect has become more credible as observations and studies accumulate. The more these fossil fuels are burnt in a conventional way, the more will be the pollution added to our environment and hence the poorer will be the quality of life on earth.

Currently, intense efforts have been made to establish an environmentally sustainable energy future based on renewable energy sources such as wind, solar and biomass. However, in the short term, their contributions to electricity generation remains low due to the generally high cost and immature technology [5]. Nuclear energy is another seemingly promising power source and nuclear power production is a mature technology widely used in many countries [6]. Nonetheless, taking into account the limited uranium

reserves and safety concerns, the utilization of nuclear power is still very controversial [5-8]. Therefore, it is generally believed that, for the foreseeable future, fossil fuels will still continue to be the world's major energy source due to its reliability and low cost. Technological advances and challenges to increase the efficiency and decrease the negative effects of fossil fuel consumption have become a very urgent and real issue [4, 9-11].

Hydrogen is forecasted to be the most promising, alternative energy carriers and clean fuels in the near future [12-14]. In fact, from the historical perspective of energy development, the eventual transition to hydrogen energy is inevitable [13]. As shown in Fig. 1.1[13], since the mid 19th century, the form of energy has been shifted from solids (woods and coal) to liquids (oil) and then to gases (methane and hydrogen). If one takes an atomic view of the transition, it turns out that the ratio of hydrogen (H) to carbon(C) in the molecule of each form of energy has increased. In other words, the evolution of energy systems is a “decarbonization” process. The future hydrogen energy age will eventually realize the carbon free energy systems.

Hydrogen is an environmental friendly fuel which can be converted to electricity efficiently via fuel cells with zero emissions of greenhouse gases or hazardous species such as volatile organic compounds[15]. Until now, hydrogen has been used in a number of industrial applications, like ammonia production, oil refineries and methanol production plants[14].

Fig. 1.1 Global energy systems transition [13].

There are several reasons for the great potential in the use of hydrogen[16]:

- (i) Most abundant element in the universe.
- (ii) Lightest existing gas (14 times less dense than air).
- (iii) Efficient fuel source (capable of producing more energy per pound of fuel than gasoline)
- (iv) Environmentally friendly (zero-emission) fuel

Table 1.1 shows the heat of combustion for a variety of fuels [15]. Hydrogen possesses the highest energy content per unit mass as compared to any of the known fuels and burns cleanly. Although, hydrogen is the most abundant element in the universe, it rarely exists as free molecular hydrogen. Hence, intensive research is being pursued to obtain it from

primary energy sources such as biomass [17] and fossil fuels [6].

Table 1.1 Heat of combustion of various fuels

Fuel	Energy(kcal/g)
Hydrogen	34.0
Petroleum	10.3-8.4
Paraffin	10.3-9.8
Graphite(Coal)	7.8
Castor oil	9.4
Wood	4.2

Worldwide statistics show that nearly 48% hydrogen is produced from natural gas (NG), 30% from petroleum, and 18% from coal, while only 4% hydrogen produced is obtained through water electrolysis [18]. This high contribution of natural gas is due to the economic feasibility technology [19-21]. Currently, the refinery industry is facing problems associated with increasing environmental regulations. In order to overcome these restrictions, there is an increasing demand for clean hydrogen production [8, 22]. Further, at present, there is an increasing interest in fuel cells as a source of energy. Fuel cells are highly efficient devices that produce electricity and heat by electrochemical oxidation of hydrogen and it is believed that in the near future, mass production of hydrogen will be possible in a large scale. However, the hydrogen used in the fuel cells cannot be contaminated by CO and CO₂. This requires a method to produce hydrogen cleanly without carbon capture and sequestration processes.

It is generally believed that in the near to medium term, future hydrogen production will

continue to rely on fossil fuels, primarily natural gas. However, the industry method of hydrogen production will generate large quantities of CO₂ and CO. This necessitates the removal of greenhouse gases known for contributing to global warming effect, and CO concentrations must be reduced to a few ppm to prevent poisoning of the electrocatalysts used in fuel cells. So, in recent years, efficient and environmentally friendly production of hydrogen has received more and more attention.

1.2 Objectives and scope

Supported nickel catalyst has been the most commonly used for methane decomposition due to its higher catalytic activity and stability as compared with unsupported nickel catalyst [8, 23, 24]. It has been demonstrated from previous studies that without supports, the pure nickel catalyst prepared by the conventional method would suffer severe aggregation and lose catalytic activity very rapidly even under mild reaction conditions [25-27]. Therefore, very few attempts to synthesize unsupported nickel catalyst for the methane decomposition reaction have been reported [8, 28, 29]. However, it was found that the thermal decomposition of methane over supported catalysts might lead to the formation of traceable CO via the reaction of the carbonaceous residues with the oxygen in the support, like SiO₂ and Al₂O₃ [30-32]. Phosphoric acid fuel cells, which are the most commercially developed fuel cells, do not tolerate CO concentrations above 1.5% [32]. The CO-free requirement of the hydrogen stream is even more stringent (ppm level) for the proton exchange membrane fuel cells (PEMFC). Furthermore, with a supported catalyst, the strong binding of the catalyst and the carbon nano-tubes (CNTs) to the support material, like SiO₂ and Al₂O₃, causes difficulties in cleaning the CNTs to make

them a practical by-product. Usually, sodium hydroxide or hydrofluoric acid (HF) solution is utilized to dissolve the silica support [33, 34]. HF is the most effective chemical to dissolve silica, however, it is extremely dangerous and difficult to handle [34]. Therefore, the bulk nickel catalyst could provide easy recovery of the catalyst and a convenient way for the purification of the CNTs or carbon nanofibres (CNFs) by leaching the bulk metal catalyst with a mild acid solution [28].

The main objectives of this research project are to develop unsupported metallic catalysts with excellent catalytic activity towards CDM, to study the mechanism of catalyst deactivation process and to develop theoretical models for CDM. The scope of this work covers the following areas:

1. To prepare NiO and NiO-CuO nano-particle catalysts by Ni or Ni-Cu oxalate decomposition in air

Unsupported NiO and NiO-CuO nano-particles are to be prepared by a facile method and evaluated for their catalytic activities towards methane decomposition. The decomposition of fibrous nickel (or mixed) oxalate precursors will lead to the formation of porous oxide aggregates. The effect of the solvent and preparation conditions on the oxide morphology will be studied. In order to stabilize these unsupported catalysts, the reduction and pre-reaction conditions will be investigated.

2. To prepare unsupported metallic nickel catalyst directly without a hydrogen reduction

step

Metallic nickel particle aggregates with controlled crystalline size and primary particle size are to be prepared by direct decomposition of nickel oxalate. The effects of the concentration of the reactants on the morphology and crystalline size of the nickel oxalate will be discussed. A series of decomposition atmospheres ($\text{CH}_4\text{-N}_2$ in different ratios) will be used to investigate their effects on the morphology and crystalline size of the metallic nickel particles. The reaction conditions (e.g. temperature ramp-up rate, reaction temperature) will be discussed and optimized.

3. To prepare unsupported Ni-Cu and Ni-Cu-Co alloy catalysts by decomposition of mixed oxalate in methane atmosphere

A series of Ni-Cu alloy and Ni-Cu-Co alloy particles with different Ni/Cu/Co ratios are to be prepared by the thermal decomposition of oxalate precursors under methane atmosphere. Different reaction temperatures will be used to investigate the optimum temperature for each of the catalysts. The quasi-liquid phenomena occurring in the reaction will be discussed in detail, based on the catalyst composition, morphology and particle size.

4. To develop theoretical models for the thermocatalytic decomposition process and provide a reasonable explanation on the mechanism of catalyst deactivation based on the catalysts performance and phenomena in the reaction.

The reactions underlying the decomposition process will be analyzed by theoretical models. Such predictions will be compared with experimental results. The deactivation mechanisms of different catalyst systems will be proposed.

Chapter 2 Literature Review

2.1 Methods for hydrogen production from natural gas

The current methods of hydrogen production are mainly based on steam reforming and catalytic partial oxidation of hydrocarbons and carbons containing feedstocks such as natural gas, coal and petroleum fractions[35-37]. Compared with other fossil fuels feed, natural gas is a better choice for hydrogen production [38, 39]. It is widely distributed and easy to handle. It has a large reserve and the growth of proven reserve is increasing steadily and even larger than that of oil [39]. Moreover, it has the highest hydrogen to carbon ratio. Generally, there are several catalytic processes for the production of hydrogen from methane as follows:

- (1) Steam Reforming of Methane(SRM)
- (2) Partial Oxidation of Methane (POM)
- (3) Autothermal Reforming of Methane (ARM)
- (4) Dry (CO₂) Reforming of Methane (DRM)
- (5) Thermal/catalytic decomposition of Methane (TDM/CDM)

2.1.1 Steam reforming of methane (SRM)

SRM is a well known and dominated industrial process used for hydrogen production and it is a highly optimized reaction. This process basically involves a catalytic conversion of methane and steam to hydrogen and carbon oxides. The process consists of three main steps [40, 41]: (1) synthesis gas generation, (2) water-gas shift, and (3) gas purification.

To protect the catalysts in the hydrogen plant, methane has to be desulphurized before being fed to the reformer. The desulphurized feedstock is then mixed with the process steam and the reaction (Eq. 2.1) usually takes place over a nickel catalyst in a metal alloy tube at a temperature in the range of 700-1000 °C with steam partial pressure of up to 30 bar [14, 41, 42]. This reaction is equilibrium limited and highly endothermic:

Then, the resulting syngas is cooled down and sent to shift reactors, where the exothermic water-gas shift reaction (WGS) occurs and extra hydrogen is produced.

This reaction occurs in two steps: the first is conducted at 400-500 °C to reduce CO concentration to 2-5%, and the second stage is to carried out at (177-257 °C) to reduce CO to 1% [22]. Finally, CO₂ can be separated from H₂ by chemical absorption unit or pressure swing adsorption (PSA) which is widely used in modern plants. The degree of purification depends on the application. In order to meet the requirement of commercial applications, further purification such as palladium membrane, selective methanation may also be needed [41, 43].

2.1.2 Partial oxidation of methane (POM)

As stated above, steam reforming method is a very energy intensive process which requires a large amount of superheated steam. Then, an alternative process - partial oxidation of methane at lower energy costs, was developed. Partial oxidation involves [44] the reaction of oxygen with fuel to produce H₂ and CO when the oxygen-to-fuel ratio is less than that required for total combustion. Partial oxidation can be conducted with a

catalyst (catalytic partial oxidation) or without a catalyst (non-catalytic partial oxidation).

For methane partial oxidation, the process can be represented by equation (2.3):

Similarly, after reforming, a shift reactor and hydrogen purification equipment are also indispensable. Unlike SRM, this reaction is mildly exothermic and hence no external heating energy is required. However, additional oxygen input is necessary, which drastically increases the reforming costs. Therefore, the industrial application of POM is still limited [45].

2.1.3 Autothermal reforming of methane (ARM)

Recently, hydrogen production by autothermal reforming of methane (ARM) has received considerable attention due to its high energy efficiency with low investment cost. ARM is actually a combination of homogeneous partial oxidation with steam reforming process. The overall chemical reactions taking place in the ARM include partial oxidation, steam reforming, and water gas shift. The partial oxidation step can supply enough heat for the steam reforming step.

There are three zones in the ARM reactor: (1) combustion zone, (2) thermal zone, and (3) catalytic zone, as shown in Fig. 2.1 [14]. The combustion zone is a turbulent diffusion flame where methane and oxygen are gradually mixed and combusted. In the thermal zone above the catalyst bed, homogenous gas phase reactions occur, including homogeneous steam methane reforming and WGS reactions. In the catalytic zone, with the aid of catalysts, further conversion of methane is achieved through heterogeneous

catalytic reactions at 927-1127 °C.

Compared with steam reforming, the main advantages of this system consist of (1) economics of scale, (2) more compact unit and (3) much large single-stream units are possible. The major disadvantage is the same as POM- an oxygen source is needed.

Fig. 2.1 Illustration of an ATR reactor

2.1.4 CO_2 (Dry) reforming

In the last decade, special attention has been paid on the production of synthesis gas by dry reforming of hydrocarbons like methane and propane [46-51]. The chemical reactions taking place are shown in equations (2.4) and (2.5). CO_2 reforming (Eq. 2.4) is typically

influenced by the simultaneous occurrence of the reverse water gas shift (Eq. 2.5), which results in CO/H₂ ratios of more than 1.

This reaction is more endothermic than SRM, so it must be carried out at a higher temperature (above 1120K) to achieve optimum conversion. The original ideas of many dry reforming researchers aim to decrease CO₂ in order to solve the global warming problem. However, after scrutinization, this is not reasonable because at the end, after the shift reaction, 1 mole of CO₂ consumed yields 2 moles of CO (Eq. 2.4). The major difficulty with the commercial application of dry reforming is the thermodynamically favoured formation of coke, which leads to the catalyst deactivation via either CH₄ decomposition or CO disproportionation [14]

2.1.5 Thermal (catalytic) decomposition methane (TDM/CDM)

In view of long-term environmental uncertainties of the CO₂ sequestration approach, there have been proposals to decarbonize fossil fuels by recovering and sequestering solid carbon instead of gaseous CO₂ [42, 52]. This alternative method is based on the decomposition of hydrocarbons (mainly methane) to hydrogen and elemental carbon in an air-water free environment. In this method, methane is thermally decomposed into solid carbon and hydrogen. It is a moderately endothermic process:

Methane is one of the most stable organic molecules. The dissociation energy for C-H

bond in methane ($E=436$ kJ/mol) is one of the highest among all organic compounds. So, non-catalytic thermal decomposition of methane (TDM) requires high temperature. Since the 1950s, TDM has been applied for the production of carbon black with hydrogen as a by-product and supplemental fuel for the process which is called thermal black process [53]. This process was operated in a semi-continuous mode using two tandem reactors at high operational temperatures (1400 °C). The mechanism of TDM has been extensively studied [54, 55]. According to Holmen *et al.* [56], the overall process of TDM at (1200 - 1500 °C) has been described as a stepwise dehydrogenation as follows:

It is explained by the free radical mechanism, where the following equations can describe the initiation step:

As can be seen from the above reactions, the homogenous dissociation of methane is the only primary source of free radicals and it controls the reaction rate of the overall process. This reaction is followed by a series of consecutive and parallel reactions with relatively much lower activation energies and the solid carbon is the final product. [57].

Fig. 2.2 depicts the equilibrium conversion of methane and as a function of reaction temperature and pressure. It is obvious high conversion is favored by high temperature and low pressure (1atm). The major problem with the TDM is the high reaction

temperature (above 1400 °C). Therefore, in the past decades, intensive research has been focused on the development of efficient catalysts to reduce the reaction temperature which is called catalytic decomposition of methane (CDM) [8, 22, 58, 59].

Fig. 2.2 Equilibrium conversion of methane under different pressures and temperatures [8]

2.2 Comparison between TDM /CDM and SRM

It is obvious to find that, except for the last method, the first four methods all involve large emissions of greenhouse gases and H₂ purification process. At present, SRM is the most popular and frequently used method which contributes about 48% of the world

production of hydrogen [36]. However, this method causes relatively high emissions of CO₂ which is the main greenhouse gas. In view of the gloomy prospects of a global climate change associated with enormous volumes of fossil-derived CO₂ emissions, the concept of decarbonization of fossil fuel is proposed [6, 42]. In terms of hydrogen production, decarbonization can be realized by the way of sequestration of carbon either as CO₂ or elemental carbon (e.g. TDM). The carbon (in the form of CO₂) capture and sequestration (CCS) consists of several steps including CO₂ capture, pressurization, liquefaction, transportation and final disposal, through the injection of liquid CO₂ into geologic formations or in aquifers [6]. However, it was estimated that the CCS would add about 25-30% to the cost of hydrogen production [60]. Besides, much applied research and field-testing is required to prove the environmental safety of this CO₂ disposal method [6]. However, in the TDM process, the solid carbon can be utilized in a variety of traditional and modern application areas or can be securely stored [6].

In the SRM, the hydrogen produced needs to be further purified and even after the purification, it may not achieve 100% pure hydrogen. In this case, hydrogen cannot be used in some applications, such as hydrogen fuel-cell which is the most widely hydrogen-used device. In fact, for proton exchange membrane fuel cells (PEMFC), CO is a strong poison even when its concentration is very low (20ppm) [15], whereas for alkaline fuel cells, besides CO, ppm levels of CO₂ are also poisonous. Removal of CO and CO₂ to ppm levels from the hydrogen stream makes this process complex and expensive [61].

Table 2.1 Comparison of SRM and TDM for hydrogen production[42]

Item	SRM	TDM
Reaction chemistry	$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$	$\text{CH}_4 = \text{C} + 2\text{H}_2$
Mols H_2 per mol CH_4	4	2
Endothermic heat of reaction (kcal/mol CH_4)	60	18
Process heat in kcal/mol H_2 (at 80% thermal efficiency)	18.8	11.3
Process Thermal Efficiency for H_2 production (%)	75	58
CO_2 Emission Mols CO_2 /mol H_2	0.43	0.05
Process Unit Operations	1. Reformer 2. Shift 3. CO_2 separation	1. Pyrolyzer 2. CH_4 separation if needed
Sequestration net energy reduction (%)	Liquid CO_2 , in ocean, gas wells, aquifers ~ 15%	Solid C, in land fill, mines or market ~0%
Net Energy Efficiency %	75-15=60%	58%
By-product value	Low	High materials potential
Uncertainties	Possible Hazardous Environmental Effects	Minimal
Process development	Well developed	Needs development

Steinberg [42] made a comparison of the parameters of the SRM and TDM process as shown in Table 2.1. Due to the involvement of H_2O molecules, SRM produces twice amount of H_2 per mol natural gas than TDM. However, SRM requires much more heat of

reaction than TDM. Assuming that methane is used to supply the energy for the processes, then SRM produces almost 9 times amount of CO₂ than TDM (If H₂ were used as the energy source, then TDM will be a 100% CO and CO₂ free process). The overall process thermal efficiencies for SRM and TDM are estimated to be 75% and 58%, respectively. But after taking into account of the CO and CO₂ sequestration process, the net energy efficiency will be almost the same. Furthermore, the value of the solid carbon by-product from TDM has a current market value and more potential applications may be explored which will significantly reduce the overall cost of hydrogen production from the TDM process.

The pioneer researcher Muradov [6] had evaluated the feasibility of hydrogen production from CDM from the economy point of view. As shown in Fig. 2.3 (A), if considering the market value of the by-product, the CDM process becomes competitive in comparison with the SRM process once the carbon can be sold at a price of US\$ 0.34/kg. Fig. 2.3 (B) summarizes the data of the selling prices of different potential carbon products from CDM. It should be noted that the by-product carbon could become a credit to CDM only if a large enough market for the consumption of the carbon produced from CDM is developed.

Fig. 2.3 Economics of hydrogen production by CDM (A) hydrogen selling price as a function of carbon-selling price; and (B) selling price of different carbon products [6]

2.3 CO_x free hydrogen production

Due to the long-term environmental problems and uncertainties associated with SRM and CCS, new methods for the direct production of pure hydrogen are being considered. Several technologies for directly producing CO_x–free hydrogen are summarized in Table

2.2 [8].

Table 2.2 Different methods to produce CO_x-free hydrogen

Process	$\Delta H_{773}(\text{kJ/mol H}_2)$	Reaction temperature	Cost	Co-product
H ₂ O electrolysis	246.35	Room temperature	High	O ₂
NH ₃ decomposition	35.57	698-798K	Low	N ₂
Catalytic decomposition of CH ₄	43.23	Above 773K	Medium	C
Step-wise reforming of CH ₄	43.23	723-873K	Medium	Trace CO _x

Water electrolysis is often considered as it is the only process that does not rely on fossil fuels, and its product is in high purity. However, at present, the widespread use of this process is still limited due to its high cost. In recent years, ammonia catalytic decomposition has been proposed and investigated to produce CO_x-free hydrogen [62-65]. With the aid of catalyst (Ru-, Ni-based), the conversion of ammonium can approach nearly 100% at 873K [64]. However, it is necessary to mention that ammonium is not a type of energy source and is synthesized from hydrogen whose production technology is critical for this ammonia route to be environmental friendly and economically competitive [8]. Besides, ammonia itself is a severe poison to the catalyst of PEMFC [66, 67]. Stepwise steam reforming is also employed to produce CO-free hydrogen for use in fuel cells and other processes that are sensitive to CO poisoning. The process consists of two steps involving the decomposition of methane in a first step followed by steam gasification of the surface carbon in the second step [57, 68]. This is actually a combination of methane decomposition and catalyst regeneration process. The temperature in step I needs to be delicately controlled to facilitate the removal of the surface carbon in step II. However, the hydrogen produced in step II still contains trace

CO (<0.5%) [57]. CDM is another alternative method to produce CO_x free hydrogen which will be experimentally and theoretically studied in this thesis.

2.4 History background of CDM

Catalytic decomposition of hydrocarbon first attracted the public attention back in the late 19th century. It was reported in a patent published in 1889 [69] that carbon filaments were obtained in a metallic crucible while heating carbon-containing gases. The morphology of the carbon nanofibers was clearly observed until after the invention of the transmission electron microscope (TEM) in 1993 [8]. Radushkevich and Lukyanovich [70] presented the first TEM micrographs of carbon fibers in 1952. The pioneering work during the 1950s discovered that carbon filament could grow by the interaction of a series of carbon containing gases (e.g, hydrocarbons, CO) with metals [71]. The most active metals consist of iron, cobalt and nickel. The detailed studies in this area in the period 1950-1970s were focused on suppressing the undesirable formation of carbon deposits on the surface of industrial catalysts or metallic steam cracker tubes [72]. In the last 20 years, with the development of advanced characterization techniques, the unique structure of the carbon materials triggered an outburst of research interest. The growth mechanism of carbon nanomaterials (CNM) including carbon nanotubes (CNTs), carbon nanofibers (CNFs) on transition metal catalysts, has been explored extensively [71, 73-76]. CDM is a special case which focused on the production of hydrogen with CNM as by-products. The idea of “simultaneous production of hydrogen and nanocarbon from methane decomposition” has aroused great interest and a great cumulative effort is underway to investigate this process [8, 58, 59, 77]. However, several major challenges, such as

reaction mechanism, design of catalyst and optimization of the process and reactor ,still remain unresolved [8].

2.5 CDM reaction process

In early 1970s, Baker and co-workers studied the formation of filamentous carbon from the decomposition of acetylene catalyzed by nickel, cobalt and iron and developed a model for the growth of carbon nanofibres [78-80]. This model is generally accepted by the later researchers. In the case of CDM, it can be simplified as three successive steps: firstly, methane molecules adsorb and dissociate on the surface to form elementary carbon atoms and molecular hydrogen. Subsequently, carbon atoms diffuse on the surface (subsurface) or through the bulk of catalyst particle to a proper area for the growth of the CNT or CNF. Fig. 2.4 depicts the formation process of CNF and CNT growth based on a bulk diffusion mechanism proposed by Snoeck *et al* [81].

Fig. 2.4 Schematic pictures of the formation of a CNF (left) and CNT (right) [81]

Recent advances in in-situ techniques allow researchers to observe this reaction at the atomic level. Helveg *et al.* [82, 83] studied the formation of CNTs from methane decomposition over supported nickel nanocrystals and presented time resolved, high-resolution in-situ TEM observations of the CNTs growth process. Fig. 2.5 shows the fresh metallic catalyst and the growing CNT during reaction. The nickel nanocrystal possesses a faceted equilibrium shape in H_2 atmosphere (Fig. 2.5a). The lattice fringes correspond to the (111) and (200) lattice planes in metallic Ni. After the addition of methane, a graphitic multi-walled CNT grows with an elongated Ni particle located at the end (Fig. 2.5b).

Fig. 2.5 TEM micrographs of the nickel catalyst and the generated CNT, (a) Ni nanocrystal supported on $MgAl_2O_4$, acquired *in situ* (3.5 mbar H_2 , 430 $^{\circ}C$); and (b) A multi-walled CNT; scale bars, 5 nm [53].

With a camcorder, Helveg *et al.* [82, 83] recorded the CNT growth process as shown in Fig. 2.6. It shows that in the very beginning, the initial faceted Ni particle transforms into highly elongated shape and the graphene sheets grow in a direction parallel to the nickel surface. Soon afterwards, the elongated particle quickly contracts into a spherical shape.

They proposed that the monatomic steps emerging at the Ni surface are the nucleation sites for growing new graphene layers. Besides, during the whole process, the catalyst stays in crystalline state.

Fig. 2.6 Image sequence of a growing carbon nanofiber. Images a-h illustrate the elongation/contraction process. Drawings are included to guide the reader in locating the positions of mono-atomic Ni step edges at C-Ni interface. The images are acquired in situ with $\text{CH}_4:\text{H}_2$ -1:1 at a total pressure of 2.1 mbar with the sample heated to 809K [53].

2.5.1 Methane activation on metal surface

The activation process begins with adsorbing methane at the surface of catalyst. The catalytic ability of transition metals can be linked to their electronic structure. Transition metals have non-filled 3d-orbitals. The adsorbed methane interacts with the catalyst particles by transferring an amount of its electron density to the catalyst [84] like a “donor” and “acceptor”. The interaction of methane with Ni (111), (100), (110) planes were extensively studied both experimentally and theoretically to decide which is most

active to activate methane. Yang and Chen [85] examined the catalyst crystallographic planes during carbon filament growth using in-situ TEM equipped with selected area electron diffraction (SAD). Based on TEM-SAD results and extended Hückel molecular orbital calculations (EHMO), they suggested that Ni (100) and Ni (110) surfaces are the gas/metal interfaces, while Ni (111) and (311) are the graphite/metal interfaces. Based on bulb experiment, Beebe *et al.* [86] found that Ni (110) was the most reactive surface and Ni(111) was the least reactive for methane activation. Some activation energies on low index faces had also been derived based on simulations. It was reported that the dissociation of methane on Ni (100) plane had activation energy in the range of 50-70 kJ/mol while in the range of 50-130 kJ/mol for Ni (111) plane [86-93]. As discussed above, it seems that the more open plane (100) is more active for chemisorption of methane.

2.5.2 Carbon atoms migration and CNTs/CNFs growth

In order to keep the active surface clean and the reaction to proceed continuously, the carbon atoms released from methane dissociation need to migrate to appropriate areas to nucleate into CNTs/CNFs. So far, there are still controversies about the carbon diffusion paths: bulk diffusion, surface diffusion or sub-surface diffusion as illustrated in Fig. 2.7 [94]. Bulk diffusion was first proposed by Baker [79] who determined the activation energies of acetylene decomposition on different metals in in-situ TEM. A very good agreement between the measured activation energy and the activation energy for the diffusion of carbon in bulk metal phase was observed, which was an indirect evidence for carbon bulk diffusion mechanism. Another strong evidence was provided by Avdeeva *et*

al.[26] who investigated CDM on a nickel catalyst using in-situ XRD. During the reaction, they observed a diffraction peak shifting to a smaller angle by 0.3° which was ascribed to an increase of the lattice parameter of Ni by $0.014\text{\AA}$. It was attributed to carbon dissolution in the bulk nickel with a concentration of 2%. The various morphologies of carbon products (CNTs/CNFs) were also used to imply the bulk diffusion mechanism. Snoeck *et al.* [81] proposed that at lower temperatures, the diffusion rate was faster than the nucleation rate. So, carbon atoms diffuse in the bulk uniformly and nucleate on the entire back surface of the catalyst particles. Therefore, carbon filaments without hollow cores were observed. However, at a higher temperature, in order to keep up with the higher nucleation rates, the short diffusion path is preferentially adopted and the long one is neglected, which lead to the formation of CNTs (See Fig. 2.4).

Fig. 2.7 Schematic of three carbon diffusion mechanisms in CDM (solid black circle: carbon atoms), adapted from [94]

With the development of computer simulations, surface diffusion mechanism is proposed and supported by several research groups. A much lower activation energy for surface diffusion is usually obtained when compared with that of bulk diffusion through ab initio plane wave density functional calculations or density functional calculations [82, 83, 95]. Zhu *et al.* [96] simulated two different carbon concentrations and found that the bulk diffusion energy barrier could be substantially lowered by increasing the carbon concentration in bulk, which suggested that surface diffusion can be replaced by bulk diffusion when the decomposition rate is higher than the surface diffusion rate.

Recently, it was reported that sub-surface diffusion was energetically more favorable than surface or bulk diffusion [73, 97, 98]. By diffusing into the sub-surfaces (one layer below the surface) of both Ni (100) and Ni (111), the carbon p states were more stabilized [97]. Combining the DFT calculations and in-situ XRD and XPS experimental results, the mechanism proposed that after dissociation, the carbon atoms penetrated into the Ni (111) and Ni (100) planes to form a surface carbide layer and migrated to octahedral subsurface sites through subsurface diffusion path.

However, the driving force for carbon migration is still unclear [73]. The most prevailing statement is that the carbon concentration gradient between the gas/metal interface and metal/carbon interface is the driving force for carbon diffusion [99, 100].

2.5.3 Catalyst state in reaction

.

Fig. 2.8 FIM images (left) and corresponding ball model (right) of the a) the starting clean Ni crystal ($T=61K$), b) after exposure to H_2 (600 °C), and c) after exposure to C_2H_2 [98]

Moors *et al.* [98] observed the chemical state of catalyst particles during the carbon nanotube nucleation using field ion/electron microscopy with in-situ local chemical probing of a single nanosized nickel crystal. As illustrated in Fig. 2.8, heat treatment in H_2 will induce a major transformation of the Ni particles, from a clean and well-

characterized hemispherically shaped catalyst (Fig. 2.8 (a)) to a particle with polyhedral morphology whose surface is dominated by large areas of (001) top and {111}/{011} side planes. A thin rim of stepped plane {113} facets was formed between the low miller index planes. Then, after the acetylene introduction for 11s, another significant reconstruction occurred, which proceeded via the shrinking to the central (001) and the surrounding {111} side planes. Meanwhile, a large extension of the stepped rim {113} was observed. These experimental observations as well as theoretical simulations, indicated that the carbon atoms induced step edges {113} play as nucleation sites for the graphene sheet formation. The particle shape changes again after the catalyst was cooled in inert gas which made it impossible to capture these successive transformations by post reaction characterization

2.5.4 Catalyst deactivation

In a CDM process, carbon deposits form on the surface of catalysts continuously until complete deactivation. This deactivation process varies under different reaction conditions. It could be a long or very short period. In a CDM process, the released carbon should be removed and transferred to the precipitating sites for CNTs/CNFs growth as well as for keeping the catalytic active surface clean. So, in the steady state, the rate of methane dissociation, carbon diffusion and CNF growth should be almost at the same level [8]. If the diffusion rate cannot keep up with decomposition rate, the carbon will accumulate at the catalytic active face and prevent methane dissociation. The most common observation in the deactivated catalyst is catalyst particles at the tips of CNFs which are covered with carbon layers on the active surface for methane activation [82,

101, 102]. Takenaka *et al.* [103, 104] proposed that the changes in the Ni catalyst structure led to the catalyst deactivation. They found nickel carbide species (not Ni_3C) gradually formed after a long reaction time which was subsequently followed by a complete deactivation. The collision between carbon fibers or coating of carbon on the metal surface was suggested as the reason behind the formation of nickel carbide.

Space limitation is also proposed as a reason for deactivation since the formed filaments could interfere with each other, inhibiting the CNFs growth [105]. Avdeeva *et al.* [26] reported a similar conclusion that the Ni particle on the tip of a filament would stop moving when the porous CNFs granules achieved near close-packed structure which would lead to nickel encapsulation by carbon.

For the Ni-Cu catalyst, atomic erosion of the catalyst was postulated to be the deactivation reason [26]. Another deactivation mechanism suggested was that catalyst particles would be fragmented and drawn into the hollow core of the CNFs/CNTs, which usually occurs at higher temperature ($>700\text{ }^{\circ}\text{C}$) when catalyst particles are in a quasi liquid state [106, 107].

Salmones *et al.* [108] studied the catalytic activity and life time of Ni-Mg-Al catalyst with different Ni contents, i.e. 15 wt.% , 25 wt.%, and 50 wt.%. It was found that the catalyst with high Ni content deactivates much faster than that of with lower Ni content and postulated that it was related to the pore geometry of the catalyst. The high Ni content results in catalyst having pores with ink-bottle shape which are easily embedded by the

produced carbon materials in a short period. However, the Ni particles in the catalysts with low Ni content are mainly located on the pore openings and situated on the tip of the produced carbon, retaining its high accessibility for continuous reaction.

Italiano [109-112] studied the Ni and Co supported catalysts and found that sintering of the catalyst particles and filamentous carbon formation with metal particle at tip lead to the destruction and deactivation of catalyst. It seems that the addition of Mg and La species prevent the Ni sintering more efficiently than K and Cl. Co based catalysts, mainly when Al_2O_3 is used as support, are characterized by a strong metal support interaction which lead to a base growth of carbon filaments. This peculiarity of “base mechanism” was proposed to be the reason to avoid the catalyst deactivation during cyclic process based on reaction and air regeneration.

2.6 Catalysts for the CDM

2.6.1 Active phase

Iron group (Ni, Co, Fe) metals are the most widely used catalysts in CDM. In general, Ni and Co-based catalysts show sufficient catalytic activity for CDM reactions in the temperature range 500-800 °C. To obtain the equivalent conversion rate, Fe-based catalysts usually need high reaction temperature (>800 °C) [8]. Fig. 2.9 summarizes the recent literature data on the catalysts, temperature range studied and type of carbon products of CDM [113]. It is established that the catalytic activity and carbon yield of the metal catalysts in CDM decrease in the following order: $\text{Ni} > \text{Co} > \text{Fe}$ [101, 114, 115]. It

was explained that this was correlated to the affinity of carbon and metal. The enthalpy of surface carbide formation is -117kJ/mol for Fe, -50 kJ/mol for Co, 4kJ/mol for Ni. Only the decomposition of unstable “virtual” metal carbide-like phase results in the formation of filamentous carbon [114]. Besides, it was found that the activity order for Fe/Al₂O₃, Co/Al₂O₃ and Ni/Al₂O₃ catalysts was a reverse of that for their initial temperatures for the deactivation[116].

Fig. 2.9 Graphical representation of the bulk of literature data on catalysts, preferred temperature range and carbon products related to catalytic methane decomposition reaction. Catalysts: 1-Ni-based, 2-Fe-based, 3-carbon-based, 4-summary of data related to Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, W catalysts, 5-non-catalytic decomposition. Carbon products: CF-carbon filaments, TC-turbostratic carbon, GC-graphitic carbon, AmC-amorphous carbon [113]

2.6.2 Effect of the catalysts crystallite size

Nickel-based catalysts have drawn the most attention based on research studies [8, 22]. This is because supported nickel particles are always capable, in a more or less successful manner, of catalyzing CDM. But it has a narrow operable temperature range of 500 to 550 °C, above which, an abrupt deactivation usually occurs due to the fast methane dissociation rate [117].

Fig. 2.10 Effects of NiO crystal size on the growth rate (left) and the final carbon yield (right) of CNF. Reaction conditions: $T=580\text{ }^{\circ}\text{C}$, $P_{\text{tot}}=100\text{ kPa}$, $P_{\text{CH}_4}=80\text{ kPa}$, $P_{\text{H}_2}=5.5\text{ kPa}$. Total flow: 50ml/min [118]

Due to the nature of the reaction mechanism, the crystallite size of the catalyst plays a critical role in this process. From previous studies in the literature, it was found that there was an optimum size range for continuous CNF growth. Outside of this range (too large or too small), catalyst particles were adverse to CNF growth. Chen et al .[118] prepared a variety of nickel catalysts with different particle sizes by using different support materials

and sintering at various temperatures. Their studies clearly showed that the highest carbon yield and initial CNF growth rate were obtained based on a Ni (NiO) catalyst with a crystallite size of about 34 nm. It was explained that a small Ni crystal led to a high saturation concentration of CNF, resulting in a lower concentration gradient within the nickel particles while a larger particle possessed a lower surface area which resulted in both a slower decomposition rate and lesser carbon yield. Ermakova et al. [117, 119] reported a similar conclusion that the optimal average particle size for producing CNFs ranged from 30 to 40 nm. They examined a series of supported nickel catalysts for different reaction times. It was found that after 1 h, different catalysts with various initial nickel particle sizes actively aligned to achieve the same thermodynamic size through merger or dispersion (e.g 30-40 nm under 550 °C). Takenaka et al. [120] obtained the dominant size of nickel particles supported on SiO₂ during the reaction indirectly through visual observation and a statistical analysis of the diameter distribution of the CNFs formed in CDM. Nickel particles with sizes ranging from 60 to 100 nm showed the longest catalytic life for reactions under 500 °C. Pinilla et al. [121] investigated the catalytic activity of Ni supported on Al₂O₃ and MgO for the temperature range of 500 to 700 °C. Crystallite sizes ranging from 10 to 20 nm showed better performance than the other sizes, notably for higher reaction temperatures (600-700 °C).

Based on the afore-mentioned published results, it could be deduced that, with increasing temperature (e.g. 500°C→550°C→580°C→700°C), the optimal particle domain size decreased (e.g. 60-100nm→30-40nm→34nm→10-20 nm). This is probably attributed to the delicate balance between the methane decomposition rate and the carbon diffusion

rate. Particle size has a major influence on both processes. It is likely that a self-organizing system exists whereby it can regulate the appropriate particle size to adapt to the reaction conditions.

2.6.3 Effect of support

Usually, the catalyst matrix consists of active metal particles and support materials. Support plays a crucial role in every catalyst, which can influence the particle size, dispersion and stabilization of the metallic catalyst particles through the interaction between the metal catalyst and support material, which is usually called metal-support interaction (MSI). The MSI may be different depending on the different preparation methods and catalyst composition. Therefore, there is no a consensus on which is the best support material.

Takenaka *et al.* [122] prepared a series of nickel catalysts supported on different supports (SiO_2 , graphite, TiO_2 , ZrO_2 , SiO_2 , Al_2O_3 , MgO/SiO_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$) using the impregnation method. The catalysts supported on TiO_2 , SiO_2 and graphite showed higher catalytic activity and stability while the ones supported on Al_2O_3 or MgO showed negligible activity as shown in Fig. 2.11. Mixed oxide compounds of Ni and support component ($-\text{O}-\text{Ni}-\text{O}-\text{M}$; $\text{M}=\text{Mg}$, Al and Si) were observed to be inactive catalysts indicating that Ni was not completely reduced due to strong MSI. As an active catalyst, the nickel existed in a metallic state, supporting the conclusion that only the metallic nickel was active for this reaction.

Fig. 2.11 Methane conversion over Ni catalysts supported on different supports at 500 °C [122]

Ermakova *et al.* [117] arrived at a similar conclusion that the best activity was observed on the catalyst with minimal interaction between the active component and support. They compared a number of nickel catalysts supported on different support materials (Al_2O_3 , SiO_2 , ZrO_2 , MgO , $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{ZrO}_2/\text{SiO}_2$ and MgO/SiO_2). The total carbon yield decreased with the various catalyst supports in the order: $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{MgO} > \text{ZrO}_2/\text{SiO}_2 > \text{Al}_2\text{O}_3/\text{SiO}_2 > \text{MgO}/\text{SiO}_2$. The highest carbon yield was obtained for Ni/SiO_2 , which possessed an appropriate nickel crystal size of 30 nm and larger amount of operable catalyst particles. For those catalysts that exhibited lower activities, such as Ni-MgO , it was explained that stable solid solutions (support and catalyst) were usually formed, which would decrease a proportion of the operable metal and induce distortions in its crystal lattice. In contrast to the results in reference [117], $\text{Ni}/\text{Al}_2\text{O}_3$ prepared using

fusing method in this study, exhibited considerable catalytic activity, suggesting the importance of the preparation method, which could influence the interaction between the metal catalyst and support.

Suelves [121] also prepared a series of nickel supported catalysts by fusing precursors of nickel and support together under a moderate temperature (450 °C). Good results were obtained by using Al_2O_3 and MgO as support which led to form smaller Ni crystallites (10-30nm). Ni catalyst supported on SiO_2 and TiO_2 showed poor catalytic performance due to a larger nickel crystal domain size (>50nm).

Fig. 2.12 Change of the methane conversion as a function of time on a stream of methane in CDM at 773K over Co catalysts supported on different supports. Catalysts: 0.06g, loading of Co: 20% wt.%, $\text{P}(\text{CH}_4)$:101kPa, and flow rate:50 ml/min [123].

The effect of support was also evaluated based on the catalytic activity over Co catalysts

supported on different oxide materials which were prepared using the impregnation method [123]. As shown in Fig. 2.12, Al_2O_3 was the most effective support followed by MgO , TiO_2 and SiO_2 , which were seemingly contradictory to the results in reference [117]. In this case, the size of Co crystallites took the critical role. Co particles with sizes ranging from 10 to 30 nm showed higher activity and longer life. The stronger MSI in the $\text{Ni}/\text{Al}_2\text{O}_3$ led to smaller crystal size and K-edge XANES and EXAFS techniques confirmed that in all the catalysts, Co presented as a metallic state during the reaction.

Based on the above discussions, it can be seen that the preparation methods strongly influence the MSI. Among the different methods for catalyst preparation, co-precipitation and impregnation are most widely used. The first method involves the precipitation of precursors of both active metals and support, followed by calcination. In the second method, the solution of active metal ions is impregnated into the support which is usually porous oxide (SiO_2 , AlO_3 , ZrO_2) following by calcination. In recent years, it was reported that fusing the precursors of active metal and support directly resulted in effective catalysts, similar to the ones prepared by co-precipitation or impregnation method [124, 125]. In general, catalysts prepared by impregnation or fusing method have a weak interaction between metal and support. Catalysts prepared from co-precipitation possess strongest MSI and this will facilitate the formation of smaller metal catalyst crystallites. However, a strong MSI will sometimes lead to the formation of spinal phases such as NiAl_2O_4 due to preparation conditions such as high calcination temperature [126, 127]. In this case, a part of Ni existing in NiAl_2O_4 cannot participate in the CDM process.

Normally, supported nickel catalysts show considerable catalytic activity in most cases while pure NiO prepared by conventional methods is inactive due to the formation of overly large particle size [27, 128]. But, the Raney-type catalyst prepared from Me-Al (Me=Fe, Co or Ni) alloys by leaching out aluminum with NaOH solution showed reasonably good catalytic activity in CDM [29, 129, 130]. This is probably ascribed to the porous structure with high surface area which facilitates a continuous supply of fresh metal crystallites. Li *et al.*[28] prepared NiO with a fibrous structure through precipitation of α -Ni(OH)₂ in ethylene glycol at 393K. The unique structure of NiO led to fibrous metallic Ni with a small crystal size of 10 nm, which then rapidly stabilized to the size of 17-18 nm during the reaction.

2.6.4 Effect of promoters

Due to the endothermic nature of CDM, higher methane conversion is favored by high reaction temperature (Fig. 2.2). However, supported nickel catalyst has a optimum reaction temperature of less than 600 °C [77]. In order to improve the high temperature activity and stability, adding promoters such as copper, are investigated.

Copper, as a non-transition metal with its 3d shell completely filled, is reported to be inert to the CDM reaction. However, it is an effective promoter which can form alloys with iron group metals and increase the stability of the catalysts. In the last century, Baker *et al.* [131, 132] carried out a comprehensive investigation of the interaction between the selected hydrocarbons and unsupported Ni-Cu alloy or Ni catalysts. They found that those catalysts showed no tendency to decompose methane at temperatures below 900 °C.

In 2004, Baker *et al.* [133] prepared a series of Ni-Cu-MgO catalysts with high catalytic activity and stability at 665 to 725 °C. In contrast, Ni-MgO exhibited negligible activity at temperatures greater than 650 °C. Ni_{2.4}Cu_{0.6}MgO was found to be the best catalyst being capable of generating large amount of CO free H₂ and solid carbon up to 38 mol/g_{cat} as shown in Fig. 2.13. It was explained that, in Ni-Cu-MgO system, copper tends to segregate on the surface of the Ni-Cu alloy particle [131]. As the methane is being introduced, there is an enhancement in the number of surface Ni⁰ sites due to the selective and strong interaction between methane and nickel. Then, a balance is established between the carbon growth and its bulk diffusion at the regions. The existence of a large number of exposed Ni⁰ sites was indicated as the reason behind the fast deactivation in Ni-MgO.

Fig. 2.13 Hydrogen (●) and carbon (○) yields as a function of Cu:Ni molar ratio during methane decomposition over the Ni_xCu_yMg_zO (x:z=2.4:1) catalysts at 665 °C ($T_{\text{reduction}} = 850$ °C) [133]

The copper effect was intensively studied by Chen *et al.* [77, 134-136] through comparing the activities of catalysts Ni/Al₂O₃ and Ni-Cu/Al₂O₃. It was revealed that the promotion effect was actually achieved by lowering the intrinsic activity of nickel, thus moderating the deactivation rate and shifting to a higher working temperature as compared to the Ni/Al₂O₃. The catalyst with a composition of Ni:Cu:Al =15:3:2 (mole ratio) showed a moderate catalytic activity by good stability (80 h), generating about 600 g carbon per gram of nickel at 600 °C [77].

Avdeeva *et al.* [137-139] studied Ni-Cu-Al₂O₃ catalysts and found that the addition of copper greatly increased their lifetime and efficiency in CDM reaction at 625-675 °C. The effects of copper concentration, reaction temperature and methane concentration were investigated. “Octopus-type” carbon was formed when the concentration of Cu was more than 15wt.% as shown in Fig. 2.14. A high carbon yield (700g/g_{Ni}) was obtained under optimal conditions. They ascribed the high carbon capacity to the increasing number of (111) planes due to the enrichment of the catalyst particle surface with Cu. This was confirmed by the observation of the growth of several filaments from one plane [139].

Fig. 2.14 TEM pictures of 82Ni-8Cu-Al₂O₃ after 2 h of methane decomposition at 650 °C [139]

Monzon *et al.* [140, 141] prepared Ni_xCu_{1-x}MgAl catalysts and tested their activity for CDM. After calcination at 800 °C and reduction at 750 °C, Ni-Cu alloy nanoparticles over a mixed MgO-MgAl₂O₄-NiAl₂O₄ support were observed. Their results showed that low proportions of Cu ($x \leq 0.2$) lead to high stability as compared with that of the NiMgAl catalyst.

Suelves *et al.* [121, 124, 125, 127, 142] extensively investigated Ni and Ni-Cu catalysts supported on Al₂O₃, SiO₂, MgO, or TiO₂ prepared by co-precipitation, fusion and impregnation techniques and concluded that the presence of copper would greatly improve the Ni dispersion and increase the conversion rate. After adding copper, the catalytic activity of the catalysts only depended on catalyst composition, irrespective of the preparation methods. NiCuMgO with an optimized composition (78:6:16) showed the

best performance, whereby it approached the equilibrium conversion at 700 °C and maintained a stable activity for at least 8 hours.

Cunha *et al.* [129, 130] studied the copper effect in Raney-type Ni and Fe catalysts and stated that the formation of encapsulating carbon on nickel or iron can be prevented by “ensemble control”. This involved diluting the active metal phase with an inactive one (Cu), separating the active Ni sites from each other and thereby decreasing the formation rate of encapsulation carbon.

Several conclusions concerning the effects of copper can be drawn based on the literature data in references [8, 135].

1. Cu is much more easily reduced than Ni, Co and Fe. In the reduction process, Cu is reduced at low temperature and acts as the centre for H₂ activation and facilitates the reduction of NiO, so as to promote the release of Ni from mixed oxide, even the spinel-like phases (NiAl₂O₄), thereby increasing the operable amount of Ni sites.
2. Metallic Ni diluted with Cu is less active than pure Ni for methane dissociation. Cu, a non-transition metal with its 3d shell completely filled, may exert electronic effects on Ni, thereby weakening the catalytic efficiency of Ni.
3. Ni and Cu form alloy over a wide range of composition and the surface segregation of Cu was often observed. This so-called “ensemble effect” favours the formation of “octopus-like” carbon filaments and stabilizes the catalyst performance.

4. Doping of copper could lead the catalyst particle into quasi-liquid state at above 700 °C, which will disintegrate the catalyst particle into small particles and be encapsulated into the interior of the carbon filaments. The tendency increases with increasing the content of Cu.

ZnO was also used as a promoter to increase the activity and stability of Ni/Al₂O₃[143]. It was reported that doping the ZnO could delay the appearance of the quasi-liquid state of the Ni particles to 750 °C and weaken the wetting effect of the metallic particles on the growing carbon layers, thereby delaying the encapsulation and deactivation of the catalyst. This was attributed to the formation of ZnAl₂O₄ spinel-like structure.

Shah *et al.* [144-146] investigated the catalytic decomposition of hydrocarbons (methane, ethane, propane) over binary Fe-M/Al₂O₃ (M= Pd, Mo, Ni) catalysts. The results demonstrated that bimetallic supported catalysts were more active than monometallic catalysts (Fe/Al₂O₃ and Pd/Al₂O₃), with hydrogen concentration peaking at around 80 vol% in the reaction temperature range of 700-800 °C. Ni/Al₂O₃ exhibited the highest initial conversion rate below 700 °C but was deactivated substantially with increasing temperature. Combinations of different active metal elements with varied optimum working temperatures seem to suppress the deactivation and improve the overall performance.

The doping effects of different metals (Cu, Rh, Pd, Ir, and Pt) into supported Ni catalysts were studied by Takenaka *et al.* [147, 148]. It was found that the addition of other metals

into Ni led to a reduction of the total H₂ yields as compared with Ni/SiO₂, except for Pd as shown in Fig. 2.15. Actually, doping Pd and Cu prolonged the catalytic life of the catalysts. The highest yield of carbon of 1170 gC/g (Pd+Ni) was obtained with the optimized catalyst Pd_{0.5}Ni_{0.5}/CNF. The formation of Pd-Ni alloy with appropriate Pd/Ni played a major role in improving the catalyst performance.

Fig. 2.15 Change of methane conversion as a function of time on stream of methane in the CDM over Ni/SiO₂ modified with different metal species (Cu, Rh, Pd, Ir and Pt) Reaction temperature =550 °C, catalysts =0.040 g, CH₄=101 kPa and 40ml/min [120]

Chesnokov and Chichkan [149] prepared Ni/Al₂O₃, Ni-Cu/Al₂O₃ and Ni-Cu-Fe/Al₂O₃ by mechanochemical activation of a mixture of transition metal oxides (Fe₂O₃, NiO, CuO) with aluminum hydroxide using mill cylinders. The combination of Ni, Cu and

Fe brought much higher carbon yields and stability at 700 °C than Ni or Ni-Cu catalyst, which was attributed to the formation of finely dispersed Ni-Cu-Fe alloy particles. Based on the carbide cycle mechanism, they proposed that the large carbon concentration gradient and oversaturation at the gas-metal interface led to the catalyst deactivation. This could be prevented or suppressed by doping with iron, leading to the decrease in methane decomposition rate and accelerating the carbon diffusion rate. It is indicated that the diffusion coefficient of carbon atoms through iron is three orders magnitude higher than through nickel.

Based on different experimental conditions, such as catalyst composition, preparation method, support, promoter, reaction conditions (temperature, pressure, etc), the catalytic activity and stability could be distinct from each other. Selected results for the catalytic decomposition of methane over different catalysts are summarized in Table 2.3. The experimental conditions are listed, together with the equilibrium methane conversion (X_{eq}), the maximum conversion reached (X_{max}), the final conversion after testing for t hours (X_t) and the total carbon yield. The equilibrium methane conversion was calculated using HSC chemistry 6.0 software. The calculations were made for temperatures ranging from 25 to 1000 °C and different methane partial pressures. In general, Ni-based catalysts can produce a high carbon yield. The high conversion rate is usually favored by high catalyst load, high temperature and lower methane partial pressures.

Table 2.3 Selected performance results of catalysts for CDM

Catalyst [reference]	m _{cat} (mg)	Tem (° C)	Flow rate (ml/min)	Conc. CH ₄ %	X _{eq} (%)	X _{max} (%)	X _t (%)	t (h)	Carbon yield
90Ni-Al ₂ O ₃ [77]	0.1	500	68	60	37.6	20	6	80	344g/gNi
2Ni-1Cu-1 Al ₂ O ₃ [77]	0.1	750	68	37	92.4	70	2	17	191 g/gNi
15Ni-3Cu-2Al ₂ O ₃ [77]	0.1	600	68	100	58.4	20	0	50	585 g/gNi
Ni[26]	0.1	550	120	100	44.8	5	0	1	10 g/gNi
Ni[28]	0.04	500	60	100	31.6	10	0	75	398 g/gNi
90Ni-10Al ₂ O ₃ [26]	0.1	550	120	100	44.8	16	0	15.5	161 g/gNi
87Ni-3Cu-10Al ₂ O ₃ [26]	0.1	550	120	100	44.8	12	0	28	276 g/gNi
60Ni-25Cu-15SiO ₂ [150]	0.02	650	60	50	78	60	5	30	801 g/gNi
23Ni-77La ₂ O ₃ [151]	0.05	700	15	100	80.2	75	30	22	73.9 g/gNi
15Ni-85CNF[152]	0.1	525	75	100	38	8.5	0	20	268 g/gNi
65Ni25Cu10Nb ₂ O ₅ [153]	0.05	600	40	100	58.4	43	3	45	743 g/gNi
2.4Ni-0.6Cu-MgO[133]	0.05	665	60	100	73.8	30	0	45	456 g/gNi
2Ni-1Al ₂ O ₃ [154]	0.3	700	20	100	80.8	67	60	8	N.A.
78Ni-6Cu-16Al ₂ O ₃ [154]	0.3	700	20	100	80.8	65	65	8	N.A
2Ni-1MgO[127]	0.3	700	20	100	80.8	67	50	8	N.A.
78Ni-6Cu-16MgO[127]	0.3	700	20	100	80.8	67	67	8	N.A
2Ni-1SiO ₂ [155]	0.3	700	20	100	80.8	52	45	8	N.A.
78Ni-6Cu-16SiO ₂ [155]	0.3	700	20	100	80.8	71	65	8	N.A
Raney Ni30 [29]	2.5	700	110	10	95.9	95	89	5	N.A
Raney Ni30 [29]	2.5	600	110	10	88	83	80	12	N.A.
Raney Ni30 [29]	0.5	600	110	10	88	73	33	5	N.A
1Co/4Al ₂ O ₃ [123]	0.06	500	50	100	31.6	9	0	6	56.4 g/gCo
1Co/4MgO[123]	0.06	500	50	100	31.6	7	0	4	28.3 g/gCo
3Co/1 Al ₂ O ₃ [156]	0.1	500	75	100	31.6	7.5	0	15	63 g/gCo

3Co/1 Al ₂ O ₃ [156]	0.1	600	75	100	58.4	17	0	3.5	34 g/gCo
9Co/91Al ₂ O ₃ [157]	0.05	700	35	14.3	94.1	32	23	4	N.A
Raney Co30[29]	2.5	700	110	10	95.9	90	89	5	N.A
85Fe/15SiO ₂ [158]	0.015	700	12	100	80.2	N.A.	N.A.	N.A	45 g/gFe
Fe/SiO ₂ [115]	0.015	700	12	100	80.2	N.A.	N.A.	N.A	16.5 g/gFe
Fe/Al ₂ O ₃ [159]	0.1	625	75	100	64.9	4	0	23	26.5 g/gFe
Fe (Fe ₃ O ₄)[18]	2	800	5	100	91.3	97	95	83	N.A.
Fe50 Raney [29]	2.5	700	110	10	95.9	91	91	12	N.A.
Fe50Cu50 Raney[130]	1.25	600	110	10	88	51	32	6	N.A.
85Fe-5Co-Al ₂ O ₃ [159]	0.1	625	75	100	64.9	7.9	0	16.5	16 g/gFe
50Fe-6Co- Al ₂ O ₃ [159]	0.1	625	75	100	64.9	8	0	40	52.4 g/gFe
70Ni-10Cu-10Fe-Al ₂ O ₃ [149]	1.5	700	71.7	100	80.8	62	55	14	12g/gCat
37(Pd-Ni)/CNF [148]	0.02	550	50	100	44.8	13	4	30	1170g/gPd+Ni

2.7 Reaction mechanism and kinetic studies

Different kinetic models in the literature had been proposed to describe the CNT growth process from methane decomposition. In general, the deduced rate equations can be roughly classified into two categories: detailed mechanism rate equations and mathematically fitted deactivation rate equations.

2.7.1 Mechanism rate equations

The reaction starts with methane adsorption on the metal surface. Generally, the dissociation of methane on the metal surface is proposed to follow two pathways: non-dissociative methane adsorption (N-DMA) [86, 160] and dissociative methane adsorption (DMA) [92, 161-164]. For the N-DMA, the methane molecule is adsorbed

(molecular adsorption) and transformed to an intermediated state which can either be desorbed or move forward to dissociation.

Table 2.4 Reaction steps of methane cracking starting with two adsorption mechanisms [22]

Mechanism of N-DMA		Mechanism of DMA	
$\text{CH}_4 + \text{S}(\text{vacant site}) = \text{CH}_4(\text{ad})$	N-(1)	$\text{CH}_4 + \text{S}(\text{vacant site}) = \text{CH}_3(\text{ad}) + \text{H}(\text{ad})$	D-(1)
$\text{CH}_4(\text{ad}) = \text{CH}_3(\text{ad}) + \text{H}(\text{ad})$	N-(2)	$\text{CH}_3(\text{ad}) = \text{CH}_2(\text{ad}) + \text{H}(\text{ad})$	D-(2)
$\text{CH}_3(\text{ad}) = \text{CH}_2(\text{ad}) + \text{H}(\text{ad})$	N-(3)	$\text{CH}_2(\text{ad}) = \text{CH}(\text{ad}) + \text{H}(\text{ad})$	D-(3)
$\text{CH}_2(\text{ad}) = \text{CH}(\text{ad}) + \text{H}(\text{ad})$	N-(4)	$\text{CH}(\text{ad}) = \text{C}(\text{ad}) + \text{H}(\text{ad})$	D-(4)
$\text{CH}(\text{ad}) = \text{C}(\text{ad}) + \text{H}(\text{ad})$	N-(5)	$\text{C}(\text{ad}) = \text{C}(\text{dissolved})$	D-(5)
$\text{C}(\text{ad}) = \text{C}(\text{dissolved})$	N-(6)	$2\text{H}(\text{ad}) = \text{H}_2 + 2\text{S}$	D-(6)
$2\text{H}(\text{ad}) = \text{H}_2 + 2\text{S}$	N-(7)		
Carbon diffusion and precipitation or encapsulation on Ni			
Diffusion in Ni phase: $\text{C}(\text{dissolved}) = \text{C}(\text{nickel rear})$			C-(1)
Precipitation from Ni phase: $\text{C}(\text{nickel rear}) = \text{C}(\text{carbon filaments})$			C-(2)
Formation of encapsulation carbon: $\text{C}(\text{ad}) = \text{C}(\text{encapsulation})$			C-(3)

In the DMA, the methane is adsorbed and dissociated concomitantly. The reaction steps of these two mechanisms are summarized in Table 2.4. In a continual process of CDM, several more steps will follow the methane adsorption and dissociation. The dissolved carbon will diffuse in the bulk or surface and precipitate at the rear of the Ni particles in the form of CNTs/CNFs (Eqs. C-(1) and C-(2)). Alternatively, encapsulation carbon will form in the case of deactivation (Eq. C-(3)).

The kinetics of CDM based on different proposed mechanisms had been extensively studied. The main studies are summarized in Table 2.5, which list the reaction conditions,

the deduced reaction rate equations and the proposed rate limiting steps. All the studies investigated the relationship between the partial pressure of CH₄ or H₂ and the reaction rate r , which is usually the initial reaction rate $r_{\max}$ or a constant rate in certain reaction condition. Figs. 2.16 and 2.17 are examples for the comparison of the predicted model and the experimental results.

Table 2.5 Summary of mechanistic rate equations on supported metal catalysts

Reference	Reaction condition	Reaction rate equation	Rate-limiting step
Bernardo <i>et al.</i> [165]	Ni-Cu/SiO ₂ Microbalance 525-575 °C CH ₄ -H ₂	$r = (kP_{CH_4} - k'P_{H_2}^2)/P_{H_2}^\alpha \quad (2.11)$ <p> k: forward specific reaction constants for N-(1) step. ((kPa)^(α-1)s⁻¹) N-(1). k': reverse specific reaction constants for N-(1) step ((kPa)^(α-2)s⁻¹) α : representing the inhibiting influence of H₂ ($\alpha < 0.5$) r: carbon deposition rate (s⁻¹) P : partial pressure of component (kPa) </p>	N-(1)
Demicheli <i>et al.</i> [166]	Ni/Al ₂ O ₃ -CaO Microbalance 565-665 °C CH ₄ -H ₂ -N ₂ Activation energy :88kJ/mol	$r_{\max} = k(P_{CH_4} - P_{H_2}^2/K_e)/(1 + K_H P_{H_2}^{0.5})^n \quad (2.12)$ <p> $r_{\max}$: first reaction rate without deactivation (g(g cat)⁻¹ h⁻¹) k : the specific constant for carbon deposition reaction rate (g(g cat)⁻¹ h⁻¹kPa⁻¹) K_H : hydrogen adsorption constant (kPa^{-0.5}) K_e : equilibrium constant (kPa) k_d : deactivation rate constant (h⁻¹) n: number of active sites involved in controlling step </p>	N-(1)
Snoeck <i>et al.</i> [167]	ICI 46-9P steam Reforming catalyst micro balance 500-550 °C CH ₄ -H ₂ Activation energy:59 kJ/mol	$r = \frac{k_M^+ K_{CH_4} \cdot (P_{CH_4} - \frac{1}{K_M^*} P_{H_2}^2)}{(1 + \frac{1}{K_T^*} P_{H_2}^2 + K_{CH_4} \cdot P_{CH_4})^2} \quad (2.13)$ <p> k_M^+ : specific rate constant of rate limiting step molC/g_{cat} h K_{CH_4} : equilibrium constant for methane adsorption (kPa⁻¹) K_M^* : experimentally determined threshold </p>	N-(2)

		constant for methane cracking (kPa) K_r'' : incorporated coefficient (kPa ^{-1.5})	
Alstrup and Taveres [168]	Ni/SiO ₂ Microbalance 450-550 °C CH ₄ -H ₂ Activation energy:90 kJ/mol	$r_1 = k_1(P_{CH_4}S^2 - \frac{S_{CH_3}S_H}{K_1}) \quad (2.14)$ $r_2 = k_2(S_{CH_3}S - \frac{S_{CH_2}S_H}{K_2}) \quad (2.15)$ <p> k_1 forward rate constant for reaction step (1) gC/(g_{cat} atm s)) k_2 forward rate constant for reaction step (2) gC/(g_{cat} s)) K_1 equilibrium constant for step (1) K_2 equilibrium constant for step (2) S: the concentration of unoccupied sites S_i :is the concentration of sites occupied by species i (e.g H, CH) $S = 1 - S_H - S_{CH} - S_{CH_2} - S_{CH_3} - S_c$ </p>	D-(1) D-(2)
Zavarukhin and Kuvshinov [107]	Ni/Al ₂ O ₃ Fluidized bed 490-590 °C CH ₄ -H ₂	$r_{max} = k \frac{P_{CH_4} \frac{P_{H_2}^2}{K_p}}{(1 + K_H P_{H_2}^{0.5})^2} \quad (2.16)$ <p> k :specific rate constant for carbon deposition rate (g/(g_{cat}h kPa)) K_p: equilibrium of constant (kPa) K_H: equilibrium constant for hydrogen adsorption (kPa^{-0.5}) C:specific weight of carbon deposited on catalyst (g/g_{cat}) k_a: deactivation rate constant (g_{cat})³h/g³ a: activity coefficient </p>	D-(1)
Borghei <i>et al</i> [169]	Ni-Cu/MgO Fixed bed 550-650 °C CH ₄ -H ₂ Activation energy:50 kJ/mol	$r_{max} = \frac{k^+ P_{CH_4} - \frac{k^-}{k_r} P_{H_2}^2}{(1 + \frac{1}{k_r} P_{H_2}^{1.5})^2} \quad (2.17)$ <p> k^+: rate constant of the forward reaction of the rate-limiting step mol/(g_{cat} h atm) k^-: rate constant of the reverse reaction of the rate-limiting step (mol/(g_{cat} h atm^{0.5})) k_r : atm^{-1.5} </p>	D-(1)

Fig. 2.16 Rates of carbon formation on Ni-Cu/SiO₂ alloy catalysts by decomposition of methane at different partial pressure of methane or hydrogen (a) 1% Cu catalyst, (b) 10% Cu catalyst. Points are experimental values, Curves are calculated using model equation[170]

Fig. 2.17 Methane cracking: parity diagram based on the results for the sequential experiments on used catalysts samples[167].

2.7.2 Deactivation kinetic studies

Studies had been conducted on the deactivation kinetic models to measure the deactivation rate, which is usually a function of reaction variables such as reactant concentrations and temperature [166] [107] [169, 171]. The normalized activity factor “ a ” is introduced and defined by the expression

$$a = \frac{\text{reaction rate over time on stream}}{\text{reaction rate with fresh catalyst}} = \frac{r}{r_{max}} \quad (2.18)$$

where “ r ” is the reaction rate at any time t and r_{max} is the initial reaction rate. The decrease in normalized activity can generally be related to catalyst deactivation. The following equation is considered as a general form for the determination of activity factor:

$$\frac{da}{dt} = r_d a^d \quad (2.19)$$

where “ d ” is called the order of deactivation and “ r_d ” is a function of temperature methane and hydrogen partial pressure.

Demicheli *et al.*[166] studied the catalyst performance over time during the reaction. After processing and plotting the data, it was found that it was a first order deactivation for catalyst Ni/CaO-Al₂O₃ ($d = 1$) and the deactivation rate increased with the reaction temperature and was proportional to P_{CH_4}/P_{H_2} . The following expression for activity factor was obtained:

$$a = \exp \left[-\frac{k_d P_{CH_4} (t - t^*)}{P_{H_2}} \right] \quad (2.20)$$

where, k_d is deactivation rate constant (h^{-1}), t^* is the time at which the deactivation process begins ($a=1$ for $t = t^*$).

Borghei *et al.* [169] followed the general form of activity factor “ a ” and calculated it from Eq. 2.19 with “ d ” as an unknown parameter. Different “ d ” values had been tried to achieve the best fit for the data. Fig. 2.18 shows the correlation between “ a ” and “ t ” when “ d ” equals to “2”. “2.11” was found to be the optimum value using the F-test method and hence the deactivation of the catalyst was determined to be a second order reaction. It was shown that methane and hydrogen composition had a parabolic effect $(P_{CH_4}/P_{H_2})^2$ on the reaction of the catalyst and a higher temperature caused faster deactivation of the catalysts ($E_d=178\text{KJ/mol}$)

$$a = \frac{1}{[1 + (d - 1)r_d t]^{1/(d-1)}} \quad (2.21)$$

Fig. 2.18 Plot of activity expression in relation to time ($d=2$) at 650 °C [169]

Phenomenological approaches[172] [107] were used to quantitatively describe the process of the catalyst deactivation due to its complexity. A parabolic relationship was observed between “ a ” and “ $c/c_{\max}$ ” which could be approximately formulated into a parabolic dependence relationship:

$$a = 1 - \left(\frac{c}{c_{max}} \right)^2 \quad (2.22)$$

$$\frac{dc}{dt} = r_{max} \quad (2.23)$$

Where “ c ” is the specific weight of carbon deposited on the catalyst (g/g_{cat}), c_{max} is the total weight of carbon deposition after the complete deactivation of the catalyst (g/g_{cat}).

The analytic solution of the equation set gives.

$$a = \frac{1}{ch^2 \left(\left(\frac{r_{max}}{c_{max}} \right) t \right)} \quad (2.24)$$

$$c_{max} = \sqrt{\frac{2}{k_a r_{max}}} \quad (2.25)$$

Where the coefficient k_a is determined as a function of the temperature based on the experimental data on the dependence of maximal carbon content on the temperature and hydrogen partial pressure. The model equations accurately predicted the specific carbon content at 550 °C for 15 h as shown in Fig. 2.19. The discrepancy between the calculated and experiment data was no more than 10% [107].

Fig. 2.19 Experimental (points) and calculated (lines) time dependencies of specific carbon content on the catalyst in a perfect-mixing reactor at 550 °C [107].

Hazra *et al.*[173] conducted CDM over Ni/Al₂O₃ using thermo-balance at 500 °C at a pressure range from 1 to 10 bar. They assumed that the decomposition rate was controlled by the deposition of carbon and the formation of carbon fibres. They also assumed that the number of adsorption sites (active sites) decreased due to the encapsulation of the Ni surfaces by carbon. Based on Langmuir-Hinshelwood formulations [174], they developed a system of six non-linear differential equations and two algebraic equations which were integrated using MATLAB. 12 parameters were contained in their models, some of which were obtained from the literature. The weight change curve of the catalyst during the reaction was compared with the model as a function of time, as shown in Fig. 2.20.

Fig. 2.20 Predicted and experimental change in carbon specific weight with time. Reaction conditions: T=500 °C; Total reaction gas flow rate =120 ml/min with 10 mg of catalyst: (a) P_{total}=10 bar, 10 vol% H₂ and balance CH₄; (b) P_{total}=1 bar, 5 %H₂ and balance CH₄ [173].

2.8 Summary

Hydrogen production from fossil fuels such as natural gas, which can be free CO/CO₂ emissions, is an environmentally attractive approach and favourable for PEM fuel cell applications. This review shows that CDM is cost competitive when compared with conventional hydrogen production process such as SRM. Iron group (Ni,Co,Fe) metals are the most widely used catalysts in CDM. In general, Ni-based catalysts show best catalytic activity for CDM reactions at moderate temperatures (500-600 °C). In order to achieve high methane conversions, Ni catalysts have been doped with metals such as Cu, Pd or Fe to increase their stability at higher temperature. The catalyst crystallite size plays a critical role in the process and support materials such as Al₂O₃ SiO₂ are indispensable which can influence the particle size, dispersion and stabilization of the metallic catalyst thorough metal-support interaction (MSI). There is no a consensus on which is the best support materials due to the different reaction conditions. Several different mechanisms of catalyst deactivation have been proposed.

The magnetic property of Ni nanostructures has been extensively examined in terms of size and shape but its catalytic property is less understood. This is probably due to the insufficient thermal stability of these nickel nanomaterials under the reaction conditions.

It is apparent from the literature survey that few studies have focused on the catalytic activity of unsupported catalyst for the CDM although bulk catalyst may offer some advantages over supported catalyst. Unsupported catalyst, for instance, may prevent the formation of traceable CO via the reaction of the carbonaceous residues with the oxygen

in the support, like SiO_2 and Al_2O_3 . Moreover, the bulk nickel catalyst could provide easy recovery of the catalyst and a convenient way for the purification of the CNFs by leaching the bulk metal catalyst with a mild acid solution or simply using a magnetic field. Therefore, it would be very interesting and promising to develop unsupported Ni based catalyst with good catalytic activity towards CDM.

While, the CDM reaction has been extensively studied, unfortunately less attention has been given to modelling catalyst deactivation, optimization and regeneration issues of the process. More efforts focusing on simulating the kinetics of metal catalyst deactivation and modelling of the carbon deposition need to be studied..

Chapter 3 Experimental Set-up and Procedures

for Catalysts Preparation and Characterisation

This chapter described the catalyst preparation methods, characterisation methods and catalytic activity evaluation process. Unsupported metal oxides (NiO and NiO-CuO), and metallic Ni, Ni-Cu, and Ni-Cu-Co alloys were prepared. The various catalysts used and the methane decomposition reaction conditions were elaborated in detail.

3.1 Chemicals

The chemicals that were used in this project are listed in Table 3.1. The chemical name, chemical structure and suppliers are given as well.

Table 3.1 List of chemicals

Name	Structure	Company and Purity
Nickel nitrate hexahydrate	$(\text{Ni}(\text{NO}_3)_2) \cdot 6\text{H}_2\text{O}$	Purity $\geq 98.5\%$ Sigma-Aldrich, Singapore
Copper nitrate trihydrate	$(\text{Cu}(\text{NO}_3)_2) \cdot 3\text{H}_2\text{O}$	Purity $\geq 99\%$ Sigma-Aldrich, Singapore
Cobalt nitrate hexahydrate	$(\text{Co}(\text{NO}_3)_2) \cdot 6\text{H}_2\text{O}$	Purity $\geq 98\%$ Sigma-Aldrich, Singapore
Oxalic acid	HOCCOOH	Purity $\geq 99\%$ Sigma-Aldrich, Singapore
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	Purity $\geq 99\%$ Sigma-Aldrich, Singapore
Deionized water	H_2O	In-house
Methane	CH_4	99.999%

Nitrogen	N ₂	99.999%
hydrogen	H ₂	99.999%
Diluted oxygen	5%O ₂ /95%N ₂	99.999%

3.2 Catalytic activity evaluation setup

Fig. 3.1 and Fig. 3.2 show the schematic and photograph of the catalytic activity evaluation set-up respectively. The test rig in Fig. 3.2 consisted of gas sources (N₂, Methane, diluted H₂ and diluted O₂), flow controllers, gas mixers, reactor, tube furnace with temperature controls, gas chromatograph and exhaust systems with fume hood. Diluted H₂ was used for the metal oxide reduction and diluted oxygen was used for the passivation of the reduced catalyst particles which were used for other characterizations. Methane was used as the reacting gas and N₂ was used as a diluting gas. The gas mixer was filled with small ceramic rings to form a porous structure which would help the gases to be well mixed. In order to eliminate the possible catalytic effect of the reactor, quartz was chosen as the material for the reactor. In this experiment, a long quartz tube (i.d. 10 mm, length 800 mm) was inserted into the tube furnace for the methane decomposition process. Teflon ferrules and stainless steel fittings were used to connect the reactor ends to ensure air-tightness. The reactor was placed in a tube furnace (Lenton, LTF/12/28/500) which was controlled by a temperature programmer. Typically, a certain amount of catalyst supported by quartz wool was placed in the mid-length of the reactor. A K-type thermocouple, placed near the catalyst bed, was used to detect the temperature of the catalyst bed. Another K-type thermocouple, placed on the outer reactor, was used to control the temperature of the furnace through the temperature controller. The reacting

gases were controlled by mass flow controllers (Alicat Scientific, MC-100SCCM-D/5M) and then introduced into the reactor system. The outlet gas after the reactor was analyzed by a gas chromatograph (Agilent 6890-5973 GC-MS network system) equipped with a

1. Gas cylinder (N_2)	6. One-way valve	11. Thermocouple	16. Quartz tube reactor
2. Gas cylinder (CH_4)	7. Pressure gauge	12. Indicator	17. GC-MS detector system
3. Pressure gauge	8. Relief valve	13. Catalyst	18. Temperature controller
4. Regulating valve	9. Gas mixer	14. Quartz basket	19. Gas clean filter
5. Mass flow controller	10. Thermowell	15. Tube furnace	20. Gas cylinder (H_2-N_2)
21. Gas cylinder (O_2-N_2)	22. Drying tube		

Fig. 3.1 Schematic diagram of experimental setup

Fig. 3.2 Photograph of experimental setup

HP-molesieve column and a thermal conductivity detector (TCD) using helium as carrier. A six-way valve was used to sample the gas every 5 min. Before the data analysis, the GC was well calibrated against fixed compositions of CH_4 , H_2 , N_2 certified gas mixtures with expanded uncertainty of 0.1%-1%. The concentrations of hydrogen and methane were determined using the calibrated data and then the methane conversion (defined as the number of moles of consumed methane divided by the initial number of moles of methane.) was calculated.

3.3 Catalyst preparation procedures

3.3.1. Preparation of Ni and Ni-Cu catalysts and evaluation of their catalytic activities

3.3.1.1 Preparation of NiO and NiO-CuO

In a typical procedure for preparing nickel oxide or nickel oxide-cupric oxide, 2.6 g of Ni (NO₃)₂·6H₂O (or 2.6 g of Ni (NO₃)₂·6H₂O and 0.72 g of Cu(NO₃)₂·3H₂O) was dissolved into 30 ml of pure ethanol. A stoichiometric amount of oxalic acid, dissolved in 30 ml pure ethanol, was added into the above solution using a burette under magnetic stirring for 30 mins. The light blue suspension was transferred into a 100 ml capacity Teflon-lined stainless steel autoclave and kept at 120 °C for 12h. After cooling to room temperature, a bluish solid precipitate was obtained by filtration and then thoroughly washed with distilled water. The resulting precipitate was dried at 80 °C under vacuum. The dried sample was calcined under 500 °C for 2 h under oxygen flow to obtain the final product of metal oxide (NiO or NiO-CuO).

3.3.1.2 Procedures of catalyst reduction and catalytic activity evaluation

Methane decomposition experiments were conducted in a long quartz tube reactor (i.d. 10 mm, length 800 mm) which was heated by an electric tube furnace (Lenton, LTF/12/28/500) under atmospheric pressure. 50 mg of NiO or NiO-CuO was placed in the centre of the quartz tube reactor and the sample was supported on quartz wool. A K-type thermocouple covered with a quartz thermo-well was placed near the catalyst bed to detect the temperature of the catalyst bed. The reactor was vertically fitted in the electric

furnace. Before the reaction, a reduction treatment of the catalysts was performed – the reactor temperature was first increased to 400 °C under N₂ flow of 50 ml min⁻¹. Then, 5 % H₂ in N₂ was introduced to the reactor and the temperature was kept at 400 °C for 1 h. Subsequently, the temperature was increased to the reaction temperature (500 to 750 °C) under N₂ gas (route I) or CH₄-N₂ gas (route II). For route I, methane was only introduced to the reactor when it had reached the desired reaction temperature. N₂ was used as the gas atmosphere during the temperature-rise period. In route II, methane was introduced to the reactor immediately after the reduction reaction and continued to flow throughout the subsequent temperature ramp-up period and the decomposition reaction. The reaction conditions for all the catalysts were as follows: a catalyst charge of 50 mg and a total flow rate of 25 ml/min with methane concentration of 20 % for a range of reaction temperatures from 500 to 750 °C. The outlet gas after the reactor was analyzed by a gas chromatograph (Agilent 6890-5973 GC-MS network system) equipped with a HP-molesieve column and a TCD detector using helium as carrier.

3.3.2 Systematic preparation of metallic nickel particles and evaluation of their catalytic activity

3.3.2.1 Preparation of nickel oxalate

Nickel oxalate was used as the metallic nickel catalyst precursor. A series of nickel oxalates have been prepared by a precipitation method, followed by a hydrothermal process. In a typical procedure, a certain amount of Ni (NO₃)₂·6H₂O was dissolved into 30 ml of pure ethanol. Then, a stoichiometric amount of oxalic acid, dissolved in 30 ml

pure ethanol, was added into the above solution using a burette under magnetic stirring for 30 mins. Then, the light blue suspension was transferred into a 100 ml capacity Telfon-lined stainless steel autoclave and kept at 120 °C for 12h. After cooling to room temperature, a bluish solid precipitate was obtained by filtration and then thoroughly washed with distilled water. The resulting precipitate was dried at 80 °C in a vacuum oven. Five nickel oxalate dihydrate samples (Nioxa-Ct) were obtained by changing the concentration of the reactant: Nioxa-C1: $C(\text{reactant})=2.25 \text{ mmol/L}$; Nioxa-C2: $C(\text{reactant})=4.5 \text{ mmol/L}$; Nioxa-C3: $C(\text{reactant})=6.75 \text{ mmol/L}$; Nioxa-C4: $C(\text{reactant})=9 \text{ mmol/L}$; and Nioxa-C5 $C(\text{reactant})=18 \text{ mmol/L}$, where “Nioxa” denotes nickel oxalate dihydrate, the suffix number “t=1-5” represents the level of concentration of reactant, and C refers to the concentration of reactant $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$.

3.3.2.2 Preparation of metallic nickel particles

Metallic nickel particles were synthesized by heating the prepared nickel oxalate samples in a $\text{CH}_4\text{-N}_2$ mixture stream with varying methane concentrations. In all cases, 0.15g nickel oxalate dihydrate was placed in the centre of a quartz tube reactor (i.d. 10 mm, length 800 mm) and the sample was supported on quartz wool. Nickel oxalates were dehydrated and decomposed into metallic nickel by heating up to 450 °C. The resulting metallic Ni can be represented as Ni-Ct-Mi, where “t” denotes the level of concentration (C) of precursor, and “i” denotes the volume flow rate ratio of methane (M) to the total flow rate of the gas mixture.

3.3.2.3 Optimization of methane decomposition process

After the formation of metallic nickel catalyst, the methane decomposition reaction was carried out thereafter by increasing the furnace temperature to the desired reaction temperature (525, 540, 550, 560 and 575 °C) with a ramp-up rate of 5 °C/min and held for a long time (>8 hours) for the reaction. Besides, different ramp-up rates (2, 5, 7, 10 and 15 °C/min) were also used in another experiment to optimize the reaction condition. Methane gas diluted with N₂ (the mixture consisting of 20% methane and 80% of N₂) was used as the reacting gas with a total flow rate of 25 ml/min. The resulting gas after the reactor was analyzed by a gas chromatograph (Agilent 6890 GC) equipped with a HP-mole sieve column and a TCD detector using helium as the carrier gas.

3.3.3 Preparation of metallic Ni-Cu alloy and evaluation of its catalytic activity

3.3.3.1 Preparation of Ni-Cu mixed oxalates

Ni-Cu mixed oxalates were used as precursors for preparing the Ni-Cu alloy particles. A series of mixed oxalates with different atomic proportions of Ni/Cu had been prepared using the same precipitation method, followed by a hydrothermal process. In a typical procedure, a certain mass of Ni (NO₃)₂·6H₂O and Cu (NO₃)₂·3H₂O with a total metal ions of 9 mmol was dissolved into 30 ml of pure ethanol. A stoichiometric mass of oxalic acid, dissolved in 30 ml pure ethanol, was added into to the above solution using a burette under magnetic stirring for 30 mins. The light blue suspension was transferred into a 100 ml capacity Teflon-lined stainless steel autoclave and kept at 120 °C for 12 h. After

cooling to room temperature, a bluish solid precipitate was obtained by filtration and then thoroughly washed with distilled water. The resulting precipitate was dried at 80 °C in a vacuum oven.

Seven Ni-Cu oxalate samples, were obtained by changing the Ni/Cu atomic proportions: Ni-Cu-1: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.9375$; Ni-Cu-2: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.875$; Ni-Cu-3: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.75$; Ni-Cu-4: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.625$; Ni-Cu-5: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.5$; Ni-Cu-6: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.4375$; Ni-Cu-7: $\text{Ni}/(\text{Ni}+\text{Cu}) = 0.375$. Pure copper oxalate and nickel oxalate were also prepared for comparison purposes using the same procedures.

3.3.3.2 Preparation of Ni-Cu alloy catalyst

Ni-Cu alloy particles were synthesized by heating the prepared Ni-Cu oxalate samples in a $\text{CH}_4\text{-N}_2$ mixture stream ($\text{CH}_4/\text{N}_2=1$) with a total flow rate of 25 ml/min. In all cases, a certain amount of Ni-Cu oxalate (typically, 0.15g) was placed in the centre of a quartz tube reactor (i.d. 10 mm, length 800 mm) and the sample was supported on quartz wool. Nickel-copper oxalates were dehydrated and decomposed into Ni-Cu alloy by heating up to 450 °C.

3.3.3.3 Methane decomposition reaction over Ni-Cu alloy catalysts

After the formation of the metallic catalyst, the methane decomposition reaction was carried out thereafter by increasing the furnace temperature to the desired reaction temperature and held for a certain period. $\text{CH}_4\text{-N}_2$ ($\text{CH}_4/\text{N}_2=0.25$) was used as the reacting gas with a total flow rate of 25 ml/min. The resulting gas after the reactor was analyzed by a gas chromatograph (Agilent 6890 GC) equipped with a HP-molesieve

column and a TCD detector using helium as the carrier gas. For all the samples, a series of reactions were carried out with a stepwise heating mode to get the general workable reaction temperature range. Several temperatures were selected: 500 and 600, 650, 700, 750, 800 and 850 °C. The reaction started at 500 °C and after a period of time (30 min), the temperature was increased at 10 °C/min to the next higher temperature. The stepwise heating was continued until the conversion of methane was lower than that of the starting temperature.

3.3.4 Preparation of metallic Ni-Cu-Co alloy and evaluation of its catalytic activity

3.3.4.1 Preparation of Ni-Cu-Co oxalate

Ni-Cu-Co mixed oxalates were used as precursors for preparing the Ni-Cu-Co alloy particles. A series of mixed oxalates with different Ni/Cu/Co proportions had been prepared by a precipitation method, followed by a hydrothermal process. In a typical procedure, a certain amount of Ni (NO₃)₂·6H₂O, Cu (NO₃)₂·3H₂O Co (NO₃)₂·6H₂O with a total metal ions of 9 mmol were dissolved into 30 ml of pure ethanol. A stoichiometric amount of oxalic acid, dissolved in 30 ml pure ethanol, was added into the above solution using a burette under magnetic stirring for 30 mins. The light pink suspension was transferred into a 100 ml capacity Teflon-lined stainless steel autoclave and kept at 120 °C for 12 h. After cooling to room temperature, a purple solid precipitate was obtained by filtration and then thoroughly washed with distilled water. The resulting precipitate was dried at 80 °C in a vacuum oven.

Six Ni-Cu-Co oxalate samples were obtained by changing the Ni/Co/Cu atomic

proportions: Ni-Cu-Co-1(0.7/0.05/0.25), Ni-Cu-Co-2(0.625/0.125/0.25), Ni-Cu-Co-3(0.5/0.25/0.25), Ni-Cu-Co-4(0.375/0.375/0.25), Ni-Cu-Co-5(0.25/0.5/0.25), Co-Cu(0/0.75/0.25). The content of the copper in all the catalysts was kept 25% which was the same as the Ni-Cu-3 sample.

3.3.4.2 Preparation of Ni-Cu-Co alloy catalyst

The procedures for the preparation of Ni-Cu-Co alloy followed exactly those of Ni-Cu, which had been described in Section 3.3.3.2.

3.3.4.3 Methane decomposition reaction over Ni-Cu-Co alloy catalysts

The procedures for methane decomposition using Ni-Cu-Co catalysts followed exactly those of Ni-Cu, which had been described in Section 3.3.3.3

3.3.5 Experiments for kinetic studies

The general process of CDM using the two types of catalysts was carried out which were similar to the procedures described in Chapters 5 and 7. In order to evaluate the catalyst full performance including the whole deactivation process, small amount of catalyst was used. Typically, 0.015g of the catalyst (oxalate) was loaded in the middle of the reactor and decomposed into metallic catalyst in a 25 ml/min flow of CH₄-N₂ mixture (CH₄:50%) with increasing temperature to 450 °C. The exhausted gas flowed through a water trap and discharged to the exhausting system. Then the temperature continued to increase to the desired reaction temperature in a 25 ml/min diluted CH₄-N₂ flow (CH₄: 20%). After reaching the desired reaction temperature, a 20 ml/min of flow with different CH₄ partial

pressures (20, 40, 60, 80 %) was used. The composition of the exhausted gas mixture was detected by GC-TCD and the methane conversion was calculated. The reaction would continue at the constant temperature until the catalyst was deactivated completely. The typical experimental conditions used in this study are presented in Table 3.2.

Table 3.2 Experimental conditions for kinetic studies

Catalyst	In-situ catalyst preparation		Reaction conditions in CDM		
	Temperature	Atmosphere	Temperature ramp-up conditions	CDM reaction at desired temperature	
				Temperature	Feed composition
Ni	Room temperature to 450 °C Heating rate: 5 °C/min	Flow rate: 25 ml/min Feed: CH ₄ - N ₂ (CH ₄ :50%)	Heating rate: 5 °C/min	525 °C, 550 °C, 575 °C	Flow rate: 20 ml/min
Ni-Cu-Co-3			Flow rate: 20 ml/min Feed: CH ₄ -N ₂ (CH ₄ :20%)	650 °C, 700 °C, 750 °C	Feed : CH ₄ -N ₂ , CH ₄ concentration: 20%, 40%, 60%, 80% in volume

3.4 Characterization of the catalysts and carbon deposits

In order to characterize the freshly prepared reactive nickel catalyst, a passivation treatment was conducted to avoid self-ignition of the nickel catalyst. After the nickel oxide particles were reduced in the quartz tube reactor, it was subsequently cooled down to ambient temperature in a nitrogen atmosphere. Then, a slightly oxidizing O₂-N₂ mixture stream consisting of 0.5% O₂ was allowed to flow through the prepared metallic nickel particles for 1 h at room temperature before the sample was removed from the reactor.

Powder X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (Philips, PW1830) using $\text{CuK}\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation at 40 kV and 30 mA and operated on a continuous scan mode. The X-ray diffraction patterns were recorded in the scan range of $2\theta = 10\text{-}90^\circ$ at a scan rate of $1^\circ/\text{min}$. The mean crystallite sizes of nickel and nickel oxalate were calculated from the Scherrer equation, where the particle shape factor of 0.9 was used.

Nitrogen adsorption-desorption isotherms of the catalysts were determined at 77 K using a volumetric adsorption analyzer (Micromeritics, ASAP 2020). The surface area of the catalyst particles was calculated using the multipoint Brunauer-Emmett-Teller (BET) equation. Pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method using the adsorption branch of the isotherms.

Field emission scanning electron microscopy (FESEM) was used to study the morphology and the physical characteristics of the catalyst particles and the deposited carbons using a field emission scanning electron microscope (JEOL JSM-7600F) equipped with an energy dispersive X-ray spectroscopy (EDX).

Transmission electron microscopy (TEM) micrographs were obtained using a transmission electron microscope (JEOL JEM 2010) at an operating voltage of 200 kV. Samples for the TEM analysis were prepared by drying the catalyst particles in ethanol on carbon-coated copper grids.

Temperature-programmed reduction (TPR) measurements were carried out using a TPR system (Quantachrome ChemBET 3000). Typically, about 0.03g of the catalyst sample (NiO or NiO-CuO) was placed in a U-tube holder and the sample was first degassed at 300 °C for 2 hours by flushing with N₂ gas. Upon degassing, the reductive gas mixture consisting of 5% H₂/N₂ at a flow rate of 50 ml/min flowed through the sample. The sample was heated from ambient conditions to 1000 °C to obtain the TPR profiles of the sample

Chapter 4 Preparation and Characterization of Ni and Ni-Cu Nano-Particles and Evaluation of Their Catalytic Activities

4.1 Introduction

Few studies have focused on the catalytic activity of unsupported catalyst for the CDM although bulk catalyst may offer some advantages over supported catalyst. Unsupported catalyst, for instance, may prevent the formation of traceable CO via the reaction of the carbonaceous residues with the oxygen in the support, like SiO_2 and Al_2O_3 [30-32]. Moreover, the bulk nickel catalyst could provide easy recovery of the catalyst and a convenient way for the purification of the CNFs by leaching the bulk metal catalyst with a mild acid solution [28] or simply using a magnetic field [175]. The magnetic property of Ni nanostructures has been extensively examined in terms of size and shape but its catalytic property is less understood. This is probably due to the insufficient thermal stability of these nickel nanomaterials under the reaction conditions [176]. In this chapter, the application of porous metal oxide (NiO or NiO-CuO) as catalyst for methane decomposition is studied. For detailed description of experimental procedures, please refer to section 3.3.1.

4.2 Results and discussion

4.2.1 Characterization of the precursors and catalysts

Nickel and copper oxalates were used as precursors for producing nickel and copper oxides, respectively. Nickel oxalate dihydrate ($\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) belongs to the magnesium series (Mg, Mn, Fe, Co, Ni and Zn) which can crystallize into the α form (monoclinic) or β form (orthorhombic) depending on the preparation conditions [177]. Usually, the oxalates contain two structural water molecules, for instance, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Copper oxalate hydrate does not belong to the magnesium series and different water contents are proposed in the published articles ($\text{CuC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, $0 < x < 1$, e.g. $x=1/3$, $1/2$) [178-180].

Fig. 4.1 XRD patterns of the samples Nioxa, Nioxa-Cuoxa, NiO and NiO-CuO. (The crystal sizes of the metal oxides were calculated from the most intense peak at around 43°)

Fig. 4.2 XRD patterns of the Ni and Ni-Cu samples after reduction in H_2 . The crystal sizes were calculated from the most intense peak of metallic Ni or Ni-Cu alloy. The bottom graph (b) shows the expanded region corresponding to the most intense peaks of the Ni and Ni-Cu alloy along with the positions expected for the pure metals.

Fig. 4.1 shows the XRD patterns of the prepared catalyst precursors before and after calcination. All the diffraction peaks of the nickel oxalate or nickel-copper oxalate precursors showed the characteristics of the nickel oxalate hydrate phase which could be indexed to the orthorhombic phase of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS 25-0582). After calcination in air, a series of distinct diffraction peaks at $2\theta=37, 44, 62, 75$ and 79° were also observed which corresponded to NiO (JCPDS 44-1159). CuO reflections were also observed in the NiO-CuO sample indicating that the solid solution of NiO and CuO was not formed completely, leaving remnant CuO particle inclusions intact.

XRD patterns of the samples after reduction treatment under 5% H_2 -95% N_2 flow at 400°C are shown in Fig. 4.2. Three prominent reflections which could be assigned to metallic Ni planes (111), (200) and (220) were evident in the pure nickel catalyst. In the Cu containing sample, Ni-Cu alloy was formed from the evidence of a slight shift in the position of the metallic Ni peaks which were located between the positions of pure metallic nickel and metallic copper as shown in Fig. 4.2 (b). The lattice parameter of Ni-Cu alloy was $3.556 \text{ \AA}$ which corresponded to a Ni:Cu atomic composition close to 2.33:1 [181]. However, the atomic ratio of Ni/Cu as determined by EDX was about 2.95:1, which was closer to the nominal ratio of 3:1. The slight enrichment in the Cu as determined from lattice parameter was in agreement with a slightly later reduction of nickel as shown in the TPR test in Fig. 4.3 Martinez-Arias et al [182] proposed that in the reduction process of supported NiO-CuO, the later reduction of the nickel (a higher reduction temperature) compared with copper probably led to the formation of a core

slightly enriched in Cu and a surface enriched in nickel.

Fig. 4.3 Temperature-programmed reduction curves of NiO and NiO-CuO

To be active in the decomposition reaction, catalysts must be in the metallic state. The reduction characteristics of NiO and NiO-CuO were studied by TPR as shown in Fig. 4.3. The reduction curve of pure NiO had one peak and it commenced to be reduced at about 390-450 °C. The curve of NiO-CuO shows two peaks – a small sharp one centred at 230 °C and a large one with its maximum reduction peak rate at round 340 °C. An in-situ study [183] reported that CuO could be rapidly reduced and the presence of metallic Cu could greatly enhance the reducibility of the Ni species. It was proposed [184] that metallic copper can dissociate the hydrogen molecule into hydrogen atoms which can be

spilled over to the surface of the neighbouring NiO. This led to a lower NiO reduction temperature as compared with that of pure NiO. Therefore, in the curve of NiO-CuO, the first one peak at the lower temperature was attributed to the reduction of Cu ($\text{Cu}^{\text{II}} \rightarrow \text{Cu}^0$) while the other one was the reduction of NiO [134, 185]. In addition, the reduction temperature was dependent on the particle size. For bulk NiO or Co_3O_4 , it was reported that for smaller particle size, initial reduction temperature would be lower. [186, 187]. So, the lower reduction temperature of NiO-CuO might be attributed to its smaller particle sizes (Fig. 4.4 (c) (d)) or the crystallite size (9.2 nm for NiO-CuO in comparison to 14.1 nm for NiO). In the case of the NiO-CuO, the complete reduction to the metallic alloy was accomplished at a temperature of about 400 °C while for the NiO, the complete reduction to nickel was achieved at a temperature of about 500 °C. In the supported nickel based catalyst systems, such as Ni-Cu/ Al_2O_3 , Ni-Cu/MgO, high reduction temperature, typically about 700 °C is needed because of the strong interaction between nickel and its support [140, 141]. In this study, with unsupported catalyst, a much lower reduction temperature was (400 °C) was sufficient.

Fig. 4.4 FESEM micrographs of catalyst precursors and reduced catalysts: (a) Nioxa, (b) Nioxa-Cuoxa, (c) NiO (inset), (d) NiO-CuO (inset), (e) Ni, (f) Ni-Cu alloy and TEM micrographs of (c) NiO and (d) NiO-CuO

Fig. 4.5 Particle size distributions (a, b) and pore size distributions (c, d) of NiO and NiO-CuO

Fig. 4.4 shows the morphologies and particle sizes of the oxalate precursors, metal oxides and metallic nickel and alloy. Fig. 4.4 (a) and (b) shows that the nickel oxalate and nickel-copper oxalate respectively have rod-like morphology. The fibre-like oxalate structures were decomposed into aggregates of spherically shaped particles of NiO and NiO-CuO in the presence of oxygen as shown in Fig. 4.4 (c) and (d) respectively. Fig. 4.5 (a) and (b) compares the particle size distributions of NiO and NiO-CuO which were based on the TEM micrographs by counting about 100 primary particles. The pore size

distributions of NiO and NiO-CuO aggregates are shown in Fig. 4.5 (c) and (d) which were based on N₂ adsorption isotherms at 77K. As shown in Fig. 4.5, both NiO and NiO-CuO had wide particle size and wide pore size distributions. However, for NiO-CuO, the particle size distribution was more normal with a distinct dominant size centering at around 9.5-11 nm (Fig. 4.5 (b)) as compared with that of NiO, with sizes ranging from 13.6 to 17.8 nm (Fig. 5 (a)). The particle size ranges of NiO-CuO and NiO as determined by TEM were in good agreement with the crystal sizes as derived from the XRD patterns which were 9.2 and 14.1 nm respectively (Fig. 4.1). A bimodal pore size distribution was observed for both NiO and NiO-CuO particles. The first peak probably corresponded to the size of cavities between adjacent primary particles as deduced from Fig. 4.4 (c) and (d). The second peak corresponded to the mesopores and macropores existing in the NiO or NiO-CuO aggregates. The surface areas of NiO and NiO-CuO were 60 and 40 cm³/g respectively.

After reduction of NiO and NiO-CuO by H₂, the primary small nickel and nickel-copper crystallites tended to coalesce and agglomerate together, resulting in large nickel and nickel-copper particle aggregates. As shown in Fig. 4.4 (e) and (f), the metallic nickel or Ni-Cu particles were joined together and grown into bigger particles. In comparison with the metallic Ni, the reduced Ni-Cu alloy would tend to form continuous networks as shown in Fig. 4.4 (e), which was probably due to the linking of the agglomerates of Ni-Cu particles.

4.2.2 Catalytic activity

Fig. 4.6 Catalytic activity tests of Ni catalysts using (a) route I and (b) route II (Reaction conditions: 0.05g NiO, methane 20% balanced by nitrogen, flow rate = 25ml/min)

Fig. 4.7 Catalytic activity tests of Ni-Cu catalysts using (a) route I and (b) route II (Reaction conditions: 0.05g NiO-CuO, methane 20% balanced by nitrogen, flow rate = 25ml/min)

Usually, in this reaction, supported catalyst was first reduced into its metallic state in H₂ atmosphere at a certain temperature and then heated up to the temperature for decomposition reaction in N₂ atmosphere (route I). After that, methane was introduced to

start the hydrogen production process. However, for unsupported catalyst, the catalyst particles may be sintered or coalesced into bigger particles in the heating process before it reaches the reaction temperature especially if it can be reduced at a lower temperature as compared with the reaction temperature. In the tests, methane was introduced immediately after reduction phase and the temperature would continue to increase up to the reaction temperature (route II). The carbon produced was proposed to play the role as “support” to stabilize the catalyst particles. For both routes, the resulting gas mixtures were analyzed after the introduction of methane. Fig. 4.6 (a) and (b) shows the methane conversion and hydrogen formation rate over nickel catalysts as a function of reaction time using routes I and II respectively. It appeared that both routes resulted in the same trend: at 500 °C, the nickel catalyst yielded stable catalytic activity which was relatively higher for route II. However, the catalyst lost its activity when the decomposition temperature was increased to 550 °C. At this reaction temperature of 550 °C, the Ni catalyst deactivated faster using route I than route II with the deactivation durations lasting about 125 min and 275 min respectively.

The catalytic activity of methane decomposition over unsupported Ni-Cu catalyst was studied for varying reaction temperatures. Similar to the reactions with Ni catalyst, two reaction processes, i.e., routes I and II were studied. Fig. 4.7 (a) and (b) shows the methane conversion and hydrogen formation rate over Ni-Cu catalysts as a function of reaction time using routes I and II respectively. Comparing Ni-Cu catalyst with nickel catalyst at 500 °C reaction temperature, the hydrogen formation rate was lower due to the reduction of active sites on the particle surface. However, the reaction temperature had

increased to study higher temperatures than those for Ni catalyst. Fig. 4.7 (b) shows that increasing reaction temperature greatly increased the methane conversion rate as the reaction is endothermic. However, for reaction temperature above 750 °C, the Ni-Cu catalyst deactivated rapidly probably due to the breakdown of the catalyst to a quasi-liquid state as evidenced by the TEM micrographs which would be discussed in the next section. Due to pressure buildup, the tests for 700 and 750 °C reaction temperatures were carried out for shorter durations as shown in Fig. 4.7 (b). At a reaction temperature of 600 °C in Fig. 4.7 (a), the Ni-Cu catalyst subjected to route I was deactivated and lost its catalytic activity completely after a short duration as compared with those at 500 and 550 °C. However, for the Ni-Cu catalyst prepared using route II, the catalyst remained active even up to 750 °C with a highest methane conversion of 85%.

Fig. 4.8 TEM micrographs of metallic Ni-Cu alloy at the initial stage at 600 °C using (a) route I, inset (FESEM micrograph), and (b) route II. TEM micrograph (c) of the deposited carbon after the decomposition reaction using route I

Fig. 4.8 (a) and (b) shows the TEM micrographs of Ni-Cu catalyst at the initial stage at 600 °C using routes I and II respectively. It clearly showed that the Ni-Cu particles prepared using route I sintered and coalesced into much larger particles when compared

with catalyst using route II. The initial resulting carbons produced are surmised to play the role of “supports” to stabilize and disperse the catalyst particles as shown in Fig. 4.8 (b). Fig. 4.8 (c) shows the same catalyst using route I after the reaction at 600 °C. The catalyst was deactivated which could be attributed to the carbon deposits on the catalyst surfaces. A comparison of this morphology with that of the catalyst at the initial stage in Fig. 4.8 (a) showed that the deposited carbon covering the catalyst surface in Fig. 4.8 (c).

4.2.3 Characterization of the deposited carbon

Fig. 4.9 TEM micrographs of carbon deposits on the Ni catalysts using route II at a reaction temperature of (i) 500 °C at (a) low magnification, and (b) high magnification; and (ii) 550 °C for (c) fine carbon fibres, and (d) lumps of carbon fibres. All the pictures presented are representative of the whole samples.

Fig. 4.9 shows the used Ni catalysts using route II at reaction temperatures of 500 °C and 550 °C. At a reaction temperature of 500 °C, fibre-like carbons were produced with faceted Ni particles on the tips. One Ni particle gave rise to one smooth and regular shaped carbon filament with a diameter of about 100 nm. However, at 550 °C, two types of carbon co-existed. One type consisted of very fine carbon fibre with diameters of about 10-50 nm (Fig. 4.9 (c)). Another type appeared as large lumps of carbon fibres with

large nickel particles of 100 to 200 nm embedded inside (Fig. 4.9 (d)).

The commonly accepted model of methane decomposition and carbon growth on nickel catalysts consists of three stages: (1) activation and decomposition of methane on Ni(100) and Ni(110) planes, (2) carbon dissolution and diffusion through the catalyst particle, (3) carbon segregation in the form of CNFs or CNTs on Ni (111) planes due to the coincidental symmetry between the Ni (111) and graphite (002) [8, 84]. To maintain the continuous growth of CNFs, the balance among the methane decomposition rate, the carbon diffusion rate and the precipitation rate has to be achieved by using appropriate catalyst particle size [188]. At higher temperature, the decomposition rate is higher due to the endothermic nature of the reaction. At the same time, the unsupported nickel particles may be sintered into bigger particles. The balance is broken when the dissociation rate is much faster than the carbon diffusion rate and subsequently carbon layers will be formed on the active surfaces of the catalysts, resulting in the so-called deactivation process. Only small catalyst particles can be active for this higher temperature reaction as shown in Fig. 4.9 (c). It also can be explained that although the catalyst particles in Fig. 4.9 (b) and (d) had comparable sizes (100 to 150 nm), the catalyst particles in Fig. 4.9 (d) became deactivated due to carbon capsulation at a higher temperature of 550 °C.

In the case of the Ni-Cu catalyst, the range of the reaction temperatures had been extended up to 750 °C, i.e. from 500 °C to 750 °C as shown in Fig. 4.7(b). The TEM micrographs of the used Ni-Cu catalysts are shown in Fig. 4.10. During the reaction as shown in Fig. 4.10 (a) to (e), all the Ni-Cu catalysts had been sintered into quasi-

octahedral particles whose particle size could reach up to 300 to 400 nm. Several filaments grew from one particle to form the “octopus” structure which was fully consistent with the observations on supported Ni-Cu catalysts [26, 106].

Fig. 4.10 TEM micrographs of carbon deposits on the Ni-Cu catalysts using route II at a reaction temperature of (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C, (e) 700 °C, and (f) (g) (h) 750 °C. All the pictures presented are representative of the whole samples.

The doping effect of copper has been studied and can be summarized into two aspects: diluting the active sites of nickel (100 and 110) for dissociation of methane and promoting more precipitation sites (111) for carbon filament formation [8, 26, 139]. The dilution effect means that after Cu is rich with d electrons, which may exert electronic effect on Ni. Metallic Ni diluted by Cu is less active than pure Ni for methane dissociation so that it retards the accumulation of carbon atoms. Baker *et al*[131] studied the surface composition of Ni-Cu alloy under ethylene or hydrogen atmospheres. Based on the results of in situ electron diffraction analysis, controlled atmosphere electron microscopy, physical and chemisorption studies, the authors suggested that the metals in an alloy tend to collect up in the form of clusters rather than being uniformly dispersed. Copper itself is inactive for methane decomposition. Introducing copper to nickel will definitely decrease methane decomposition rate. Copper segregation on the alloy surface into island-like sectors is characteristic for the Ni-Cu system [131, 189]. The copper segregation on the Ni (111) planes results in the formation of several carbon filaments growing from one particle which facilitates carbon transportation. In moderate temperature range, for instance from 500 to 700 °C in the tests in Fig. 4.10 (a)-(e), the carbon diffusion and precipitation rates are able to keep pace with the methane decomposition rate. However, in the Ni-Cu system, a temperature limit exists, above which, some of the Ni-Cu alloy particles would become a quasi-liquid state and part of the catalyst particles might be sucked deep into the interior of the carbon filament or bamboo-shaped CNT such as those shown in Fig. 4.10 (f) and (h) (see the circled areas). This migration is apparently due to the so-called catalyst periodical jumping mechanism. In this action, the quasi-liquid catalyst particle can be easily split into smaller particles

and lose its catalytic activity. The reaction temperature used was much lower than the metal melting points. Bulk copper has a melting point of 1083 °C, which is much lower than that of nickel (1453 °C) [74]. The melting point of Ni-Cu alloy usually falls between their respective individual melting values. Therefore, the existence of the metal in a quasi-liquid state at about 750 °C is probably attributed to the size effect of nano-metal particles [76, 106] and the interfacial effect between nano-carbon and nano-metal [106, 143]. Therefore, the occurrence of a quasi-liquid state of the catalyst depends on the particle size, composition, metal support interaction [143], and the interfacial wetting effect by the carbon during reaction. Hence, some of the larger particles can still be rigid and less of a liquid state as shown in Fig. 4.10 (g) and (h) (see square area).

Table 4.1 Textural and structural characteristics of catalyst and carbon nano-fibres obtained from route II

Sample	*S _{BET} (m ² /g)	Temp. (°C)	S _{BET} (m ² /g)	V _{pore} (cm ³ /g)	d ₀₀₂ (nm)	L _c (nm)
	catalyst			Carbon		
Ni	18.4	500	33.3	0.078	0.3410	6.1
Ni		550	45.2	0.135	0.3417	5.8
Ni-Cu	12.6	500	176.8	0.24	0.3413	5.3
Ni-Cu		550	171.6	0.294	0.3402	6.3
Ni-Cu		600	170.6	0.251	0.3393	7.4
Ni-Cu		650	107.8	0.169	0.3384	8.6
Ni-Cu		700	104.5	0.201	0.3387	9.5
Ni-Cu		750	108.4	0.289	0.3389	10.3

*S_{BET}(m²/g): surface area of the catalyst after reduction in hydrogen.

Upon careful examination, it was revealed that the microstructure and textural characteristics of the carbon deposit depended on the constituents of the catalyst and the reaction temperature. The CNFs generated using pure nickel in Fig. 4.9 showed ordered and smooth structure whose surface area was also relatively lower than that of Ni-Cu catalyst as shown in Table 4.1. The addition of copper in the Ni-Cu catalyst led to CNFs with disordered and coarse structure, having a great number of mesopores on the surface (Fig. 4.10 (a)-(d)). However, when the reaction temperature was increased to 700 or 750 °C, the surface of the CNFs turned out to be smooth which seems to relate to the surface composition of the catalyst. Baker *et al* [133] prepared a series of Ni-Cu-MgO catalysts with high catalytic activity and stability at 665 to 725 °C. In contrast, Ni-MgO exhibited negligible activity at temperatures greater than 650 °C. In an earlier study [131], it was found that, in Ni-Cu system, copper could tend to segregate on the surface of the Ni-Cu alloy particle. As the methane was being introduced, there was an enhancement in the number of surface Ni⁰ sites due to the selective and strong interaction between methane and nickel. Then, a balance was established between the carbon growth and its bulk diffusion at the regions. The existence of excessive number of exposed Ni⁰ sites was indicated as the reason behind the fast deactivation in Ni-MgO. Metallic Ni diluted with Cu is less active than pure Ni for methane dissociation under a lower temperature range (e.g. 500 °C). Besides, different from active Ni with half filled 3d shell, Cu, a non-transition metal with its 3d shell completely filled, may exert electronic effects on Ni, thereby weakening the catalytic efficiency of the segregated nickel in alloy. In terms of carbon nucleation, it is likely that the presence of copper which can be uniformly dispersed or in the form of clusters in the bulk and on the surface of the catalyst particle,

may influence the nucleation of the CNFs by blocking carbon dissolution in nickel [170]. Therefore, every nucleated carbon fibre possesses a porous structure with interstices in the bulk of the fibre. However, at high reaction temperature such as 750 °C, the copper and nickel may undergo a phase separation. The copper element dispersed on the catalyst particle surface could reduce or become negligible, resulting in the formation of the carbon becoming uniform and smooth on the surface, similar to those generated from pure nickel.

Fig. 4.11 XRD patterns of spent catalysts using route II under different reaction temperatures

The structural and textural properties of CNFs formed on Ni and Ni-Cu catalysts at 500-750 °C were studied using nitrogen adsorption and XRD analysis. XRD patterns of the selected carbon deposits revealed the presence of graphitic carbon, metallic Ni or Ni-Cu alloy as shown in Fig. 4.11. The results had been analyzed and summarized in Table 4.1. It could be seen that the introduction of copper essentially influenced the texture of the

CNFs as exhibited by increases in the BET surface area and pore volume as compared with CNFs formed on the Ni catalyst [139, 190]. The surface area of the CNF produced by the Ni-Cu catalyst at the lower temperatures of 500 to 600 °C had the highest value of about 170 m²/g. However, further increase in the reaction temperature decreased the surface area of the resulting CNF.

Interplanar distance d_{002} and the domain crystalline size L_c (along the c-axis which is directed perpendicular to the graphite plane (002)) of the CNFs were determined from XRD data. Table 4.1 shows that the structural parameters of CNFs depended on the temperature of methane decomposition. Generally, increasing in the reaction temperature from 500 °C to 750 °C decreased the value of d_{002} from 0.341 to 0.338 nm which was approaching to that of perfect graphite ($d_{002} = 0.3354\text{nm}$). However, the crystalline size L_c increased with increasing reaction temperature for CNFs produced using Ni-Cu catalyst.

4.3 Summary

Unsupported NiO and NiO-CuO particles with promising catalytic activity for methane decomposition were prepared by a facile method. Without support, the decomposition of fibrous oxalate precursors resulted in the formation of porous oxide aggregates (surface area of 40 to 60 m²/g) with small primary particles (8-20 nm). These porous oxide aggregates required significant lower temperature in the reduction to become metallic state as compared with that of the supported ones as observed from the TPR results. After reduction, the porous metallic Ni or Ni-Cu alloy could become an effective catalyst for

methane decomposition to produce hydrogen.

After the reduction of the metallic oxide to its metallic state at 400 °C, two process routes were investigated and the results showed that for the unsupported catalyst, it was vital to introduce methane to the reactor at lower temperature to avoid the catalysts from sintering into bigger particles. The initial CNFs acted as transporting agents and supports to take individual catalyst particles away and prevent them from sintering with adjacent particles. The unsupported Ni catalyst showed stable activity at a reaction temperature of 500 °C whereas the unsupported Ni-Cu catalyst exhibited stable activity for a wider temperature range of 500 to 750 °C. Like the supported catalyst, the addition of copper could shift the optimum temperature to 700 °C for the Ni-Cu catalyst due to the diluting effect to the active nickel sites although the particle size had increased as compared with the Ni catalyst. “Doping” copper led to the formation of “octopus” and porous CNFs, whose surface area was much higher than the one produced from pure Ni catalyst. However, at higher temperatures of 650 to 750 °C, the porous texture of CNFs was depressed probably due to the Ni-Cu alloy undergoing phase separation with increasing temperature. The XRD showed that increasing reaction temperature resulted in decreasing d_{002} and increasing average coherent scattering region directly perpendicular to the graphite plane (002) (L_c) of CNFs

Chapter 5 Systematic Preparation of Metallic Nickel Particles and Evaluation of Their Catalytic Activity

5.1 Introduction

In this chapter, active metallic nickel particles can be readily obtained under mild reaction condition (around 400 °C). Furthermore, the conventional H₂ reduction process is avoided which will also simplify this reaction process by eliminating the H₂ source. The influence of the preparation conditions of the nickel nano-particle aggregates on the methane cracking performance as well as the mechanism of deactivation of the catalyst were studied. For detailed description of experimental procedures, please refer to section 3.3.2.

5.2 Results and discussion

5.2.1 Effect of reactant concentration

The crystalline structure of the as-synthesized nickel oxalate powders was characterized by XRD analysis as shown in Fig. 5.1. All the diffraction peaks showed the characteristics of the nickel oxalate hydrate phase which could be indexed to the orthorhombic phase of NiC₂O₄·2H₂O (JCPDS 25-0582). The crystalline size was calculated which was based on the data of the (202) peak. With increasing solution

concentration of the reactant, the resulting nickel oxalate clearly showed increasing crystalline size.

Fig. 5.1 XRD patterns of nickel oxalate dihydrate

Fig. 5.2 shows the morphology and particle size of the nickel oxalate dihydrate samples as determined by the FESEM and TEM (insets). With increasing concentration of reactant, the nickel oxalate particles varied from nano-sheets (Figs. 5.2 (a), (b)) to nano-rods with square ends (Figs. 5.2 (c), (d)) and finally to nano-needles with sharp ends (Figs. 5.2 (e)). Some studies had produced metal oxalate rods and cubes from a reverse micelles process in which special solvent, surfactant, co-surfactant were indispensable and played a vital role in controlling the size and morphology of the oxalate particles [191, 192]. However, in this study, the morphology of the oxalate particles could be easily controlled by adjusting the concentration of the reactants (nickel nitrate and oxalic acid). As the

concentration of the reactants increased, the aspect ratio of the nickel oxalate particles increased.

Fig. 5.2 FESEM and TEM (insets) micrographs of nickel oxalate dihydrates (a) Nioxa-C1, (b) Nioxa-C2, (c) Nioxa-C3, (d) Nioxa-C4, and (e) Nioxa-C5

A closer inspection of the TEM micrograph (Fig. 5.2 (a) inset) revealed that one particle was actually composed of bundles of nano-wires which were stacked in a parallel

fashion. If the morphology of the nickel oxalate particles was correlated with their microstructures, it could be better understood. In the experimental conditions used in this study, the nickel oxalate crystallized in the orthorhombic phase as shown in the XRD patterns; the structures were composed of pile-up leaves, each leaf constituting of parallel oxalate ribbons. The cohesion of the structures resulted from the hydrogen bonds between the ribbons due to the H_2O molecules as shown in Fig. 5.3 [193, 194]. Every nickel ion was bonded by two C_2O_4 ions to form a planar molecule in the complexes. There were two coordinated H_2O molecules at each side of the molecular plane and two molecular planes were connected by the H_2O molecule [195]. Therefore, a higher concentration of reactants would lead to a longer chain of nickel oxalate ribbons.

Fig. 5.3 Schematic molecular structure of nickel oxalate dihydrate ribbons

After the nickel oxalates were reduced in diluted methane gas stream under temperatures up to 450 °C, the resulting products were characterized by FESEM. Fig. 5.4 shows the FESEM micrographs of the metallic nickel catalysts. It could be seen that the rod-like

nickel oxalates had become aggregates of spherical shaped particles. With increasing concentration of the reactants, the particle size increased. For the higher concentrations (Figs. 5.4 (d), (e)), the spherical particles in close proximity would link up and form larger particles.

Fig. 5.4 FESEM micrographs of metallic nickel particles (a): Ni-C1-M0.2, (b): Ni-C2-M0.2, (c): Ni-C3-M0.2, (d): Ni-C4-M0.2, and (e): Ni-C5-M0.2

The crystalline structures of the as-prepared metallic nickel catalysts were characterized by XRD. The XRD patterns of the metallic nickel particles as shown in Fig. 5.5 indicated that the nickel oxalate was completely decomposed into metallic nickel (JCPDS 4-0850). The crystalline sizes were calculated according to the half-width of the diffraction peak of the Ni (111) plane. It could be seen that the crystalline size of the nickel particles increased from 21.8 to 25.1 nm with increasing crystalline size of the nickel oxalate precursor.

Fig. 5.5 XRD patterns of metallic nickel particles obtained by reduction in methane gas stream

After the nickel oxalate was decomposed into metallic nickel, it was used as a catalyst in the production of hydrogen by methane decomposition. Fig. 5.6 shows the methane conversion at 550 °C for more than 8 hours. It should be noted that a CH₄-N₂ stream was introduced into the reactor system from the beginning of the reaction process, thus

enabling the catalysts to *in situ* activate methane decomposition when the temperature was high enough. In the tests reported here, when the reactor temperature reached 450 °C, the gas mixture from the outlet of the reactor was then analyzed. Therefore, in Fig. 5.6, each methane conversion curve had an ascending slope at the very beginning which was due to the rising temperature. The subsequent steady stage (horizontal line) represented the catalytic activity at a constant temperature of 550 °C. If the nickel crystalline size or particle size were to be correlated to the catalytic behaviour of methane decomposition, it could be readily seen that the metallic nickel with the smallest crystalline size and particle size prepared in the lowest reactant concentration solution had the highest methane conversion

Fig. 5.6 Methane conversion and hydrogen formation rate over nickel catalysts prepared from different nickel oxalate concentrations (Reaction conditions: 0.15g nickel oxalate dihydrate, 20% methane balanced by nitrogen, methane-nitrogen combined flow rate = 25ml/min, reaction temperature = 550 °C)

However, it seemed that the crystalline size did not have a significant effect on the methane conversion despite the very wide range of reactant concentrations. Hence, these catalysts with varying crystalline sizes showed only slight differences in terms of their catalytic activities.

Fig. 5.7 TEM micrographs of catalysts and deposited carbons after > 8 hours of decomposition reaction (a) Ni-C1-M0.2, (b) Ni-C2-M0.2, (c) Ni-C3-M0.2, (d) Ni-C4-M0.2, (e) Ni-C5-M0.2, and (f) Ni-C1-M0.2 (high magnification)

TEM tests were then conducted after the decomposition reaction. In all the cases (Fig. 5.7), the deposited carbons exhibited filamentous structures with very small hollow cores. Different from the other catalysts, the used catalyst of sample Ni-C1-M0.2 in Figs. 5.7 (a)

and (f) consisted of some small particles (10-30 nm in diameter) encapsulated by carbon layers. As seen from Fig. 5.4 (a), the fresh nickel catalyst Ni-C1-M0.2 consisted of relatively smaller primary particles as compared with the other four catalysts. It is surmised that there is a lower limit for the size of the catalyst particle to nucleate CNFs [8]; for catalyst particles less than this size, there is not enough driving force for the carbon to diffuse in the metal particles due to lower concentration gradient. Otherwise, the carbon would form a covering layer on the active surface of the nickel particles

5.2.2 Effect of atmosphere

Nickel oxalate has been used as the precursor to produce metallic nickel in inert gas or vacuum condition for many years [196]. However, nickel oxalate has never been used as a precursor for producing catalysts in methane condition. The effect of atmosphere on the nickel oxalate to produce nickel catalyst and its subsequent catalytic activity would be studied.

A series of flowing gas streams including pure N_2 or CH_4 - N_2 in different ratios were used as the gas atmosphere for the preparation of the metallic nickel catalysts. Fig. 5.8 shows the catalytic activities of the catalysts prepared under different atmospheres. In the labeling of the catalysts, for instance, the last symbol M0.75 denotes 75% methane and 25% N_2 ; M0 denotes pure N_2 atmosphere whereas M1 denotes pure methane atmosphere.

Fig. 5.8 Methane conversion for nickel catalysts originating from nickel oxalate reduced in different atmospheres (Reaction conditions: 0.15g nickel oxalate dihydrate, methane 20% balanced by nitrogen, flow rate = 25ml/min, reaction temperature = 550 °C).

It could be seen that the catalytic performance was highly dependent on the reduction atmosphere. The catalyst prepared in methane atmosphere showed the most steady and highest catalytic activity for the test duration. The effect of methane concentration in the gas stream was not significant although its composition varied from 5% to 100%. The catalyst reduced in pure N₂ atmosphere showed the lowest methane conversion and lost its catalytic activity completely within the test duration.

Fig. 5.9 TGA graph of nickel oxalate dihydrate in N₂ atmosphere

In order to explain the phenomena, the evolution of nickel particles under different atmospheres was studied using TGA, TEM, FESEM and XRD.

In reducing or inert atmosphere, the oxalate decomposes according to reactions (5.1) and (5.2) above [197]. As seen from the TGA graph of nickel oxalate in N₂ in Fig.5.9, the nickel oxalate dihydrate had an endothermic peak at around 230 °C which was accompanied by a weight loss of 18.6%, primarily due to dehydration (According to reaction 5.1, the theoretical weight loss is 19.7%). The second endothermic peak at around 390 °C with a corresponding weight loss of 46.9% could be attributed to the decomposition of the oxalate groups. (According to reaction 5.2, the theoretical weight loss is 48.1%). However, a slow mass increase was observed after the completion of the

decomposition which could be attributed to the oxidation by O₂ impurity in the flowing atmosphere [198].

To determine the various stages of the formation of the metallic nickel catalyst, the nickel oxalate precursor was heated from room temperature to 450 °C under pure N₂ or 20% CH₄ atmosphere. The resulting products at different stages (350 °C, 400 °C, 450 °C) were examined by TEM, FESEM and XRD.

Figs. 5.10 (a) to (f) show the TEM micrographs while Figs. 5.10 (g) and (h) show the FESEM micrographs of the products of the nickel oxalate decomposition process in pure N₂ or 20% CH₄ atmospheres. At 350 °C, the reduction of the nickel oxalate had just started and the formation tracks of the metallic nickel nucleus could be clearly observed in Figs. 5.10 (a) and (d) as pointed by the white arrows. The appearance of the metallic nickel was accompanied by the partial fragmentation of the nickel oxalate fibres under the action of the gaseous product of CO₂ which was produced. As the heating continued, the simultaneous appearance and growth of a large number of these metallic nickel nuclei became agglomerates of particles as shown in Figs. 5.10 (b), (c), (e), and (f). As shown in Fig. 5.10 (b) and (e), at 400 °C, agglomerates of small nickel particles were formed in both atmospheres as confirmed by the XRD patterns (Fig. 5.11). Upon further increase in temperature to 450 °C under N₂ atmosphere, the nickel nuclei formed very large particles (100 to 200 nm) as shown in Figs. 5.10 (c) and (g) but for those nickel oxalate subjected to 20% methane, the metallic nickel particles were small, spherically shaped aggregates with primary sizes of 30-40 nm as seen in Figs. 5.10 (f) and (h).

Fig. 5.10 TEM micrographs (a), (b), (c), (d), (e), (f) and FESEM micrographs (g), (h) of the products resulting from nickel oxalate decomposition at different temperatures and atmospheres

Molecular nitrogen is normally not adsorbed in detectable amounts on clean nickel surfaces above room temperature [199]. Therefore, under the N_2 atmosphere and without support materials, the N_2 molecules are non-reactive with the nickel crystallites. The heating process would cause the primary small nickel crystallites (Fig. 5.10 (b) at 400 °C)

to coalesce and agglomerate together, resulting in large nickel particle aggregates (Fig. 5.10 (g) at 450 °C). For heating under the methane atmosphere, the interaction of CH₄ with the transition metal surfaces has been explored extensively by many experimental surface techniques [200]. It was shown that the adsorption of methane on nickel was dissociative in character with the formation of surface CH₂ and CH₃ groups, followed by further dissociation into atomic carbon and H₂[201]. It has been reported that carbon began to grow around 387 °C, then the growth rate increased with temperature[143] . In the experiments here, trace H₂ was detected below 450 °C but the carbon in the catalyst below 450 °C cannot be detected by EDS or XRD due to its low concentration. The initially formed atomic carbon species would prevent the sintering of nickel crystallites and therefore lead to the formation of individual nano-sized primary particles. Li *et al* found that the temperature of the induction period strongly affects the morphology of the Ni-Cu/Al₂O₃ catalyst particles due to the reconstruction of the particle surface during the induction period [136]. Similarly, for these tests here, for the unsupported nickel, the introduction of methane at the lower temperature is very important to prevent the immediately formed metallic nickel particles from agglomeration. Hence, increasing the concentration of methane would strengthen this effect and generate more dispersible and smaller primary particles, resulting in relatively higher catalytic activity as shown by the experimental tests in Fig. 5.8.

Fig. 5.11 XRD patterns of the resulting products of nickel oxalate decomposition in N₂ and CH₄ atmospheres

Fig. 5.11 shows the XRD patterns of the resulting products of nickel oxalate decomposition in N₂ and CH₄ atmospheres during heating from room temperature up to 450 °C. At 320 °C under N₂ atmosphere, the XRD pattern showed no peak for the metallic nickel; the XRD patterns for the dehydrated nickel oxalate were observed [202]. When the temperature was increased to 350 °C, the peaks of the metallic nickel became more pronounced while the peaks for the nickel oxalate weakened. This would suggest a single step reaction with no intermediates. At 400 °C, the complete decomposition of the nickel oxalate was achieved and thus only peaks of metallic nickel were observed. The crystalline sizes of metallic nickel under the methane and N₂ decomposition atmospheres stabilized at 22.9 and 22.5 nm respectively. There was no pronounced increase in the crystalline size throughout the whole decomposition under the methane or N₂ atmosphere

as shown in Fig. 5.11. Further, increasing the temperature to 450 °C, the crystalline size only rose slightly and the difference in the crystalline sizes under methane and N₂ atmosphere was very small. However, their catalytic activities differed greatly as shown in Fig. 5.8. It is surmised that the crystalline size of the catalyst particle is not the only determining factor.

It is well known that the catalytic performance is highly dependent on the catalyst particle domain size. In the literature, most of the studies were based on supported metal catalysts [8, 25, 121, 203] and there was no unanimous conclusion due to the different support materials. Different from the supported nickel particles, the active unsupported nickel catalysts like Raney-nickel [29], fibrous metallic nickel [28], underwent disintegration to produce in-situ small single crystallites which would be active for methane decomposition. Li *et al.* [28] prepared pure fibrous nickel and found that the catalytic activity for methane decomposition was strongly related to the crystalline size of the reduced Ni. Increasing the nickel crystalline size from 10.8 nm to 26 nm led to extremely low catalytic activity. The unique morphology was also considered as a reason for the good catalytic activity. Cunha *et al.* [29] reported that the active activity was due to the fragmented microstructures of the catalysts with the original particle size ranging from 20 to 200 µm without mentioning the crystalline size effect. Therefore, in this study, it would be of interest to determine the influence of the crystalline size and particle size at different stages of evolution of the catalyst particles.

In general, the formation of the carbon nano-fibres involved three stages. Firstly, the

methane molecules adsorb dissociatively on the active surface Ni (100) of the catalysts which may exist as aggregation of small nickel crystals. Subsequently, the carbon released from the methane will undergo diffusion into the bulk of a nickel crystal and filaments would rapidly grow on the Ni (111) face of the crystal. Finally, this nickel crystal will be taken away and stay on the tip of the growing carbon filament. This will also prevent small crystals contacting with neighboring particles or sintering into bigger ones. The balance among the methane decomposition rate, the carbon diffusion and the precipitation rate required a small crystal size (R) and consequently a large diffusion time constant (D/R^2), where D is the diffusivity of carbon in metal [188]. A small time constant, as in a large crystal, results in an increased diffusion resistance relative to the surface decomposition rate which will cause surface encapsulation by carbon build-up. The crystalline sizes of supported nickel are usually measured by XRD and the nickel usually exists as dispersed particles separated by supports. For the unsupported ones, the nickel particles are more like large aggregation of nickel crystals, for instance, Raney-nickel with particle sizes up to 200 μm . So, the crystalline size measured by XRD is not sufficient to predict the catalytic activity. Other factors influencing the feasibility of carbon filament formation include the particle size and the surface area. A smaller particle size and a larger surface area (more porous structure) will increase the likelihood for the methane molecules to approach the active surface and to draw the nickel crystals away and be supported on the tip of CNFs so as to prevent them from sintering into bigger crystals. Hence, in this study, the metallic nickel catalyst, prepared under N_2 atmosphere had similar crystalline size as that prepared under methane atmosphere (Fig. 5.11) but much larger particle size (Figs. 5.10 (b) and (c)) and consequently smaller surface area

($S_{\text{BET}} = 6.708 \text{ m}^2/\text{g}$), showed much worse catalytic activity than that prepared under methane atmosphere (Fig. 5.8). The addition of CH_4 in the atmosphere during nickel oxalate reduction effectively prevented sintering and led to aggregates of smaller particles with larger surface ($S_{\text{BET}} = 14.146 \text{ m}^2/\text{g}$) and therefore a much higher and sustained catalytic activity.

Fig. 5.12 TEM micrographs of catalysts and deposited carbon after > 8 hours of catalytic decomposition reaction (a) Ni-C4-M0.2, (b) Ni-C4-M0, and (c) Ni-C4-M0

Fig. 5.12 shows the TEM micrographs of the deposited carbons on the Ni catalysts after the test runs. Fig. 5.12 (a) shows the morphology of the used catalyst Ni-C4-M0.2. The nickel particles (20-50 nm) were all located at the tips of the CNFs. In contrast, Fig. 5.12 (b) and (c) show the sample Ni-C4-M0 after the reaction which exhibited two typical kind of deposited carbons: - filamentous carbon with small spherical particles (20-50nm) on the tips and large lumps of carbon with large nickel particles (>100nm) embedded in Fig. 5.12 (b). Although the filamentous carbons did exist, they were prone to be entangled together to form big masses which would also impede carbon growth (Fig. 5.12 (c)). It had been proposed that the deactivation of the Ni catalysts could also occur when the

carbon filament stopped moving due to the space limit [26].

5.2.3 Effect of ramp-up rate

Fig. 5.13 Methane conversion for nickel catalysts at different temperature ramp-up rate (Reaction conditions: 0.15g nickel oxalate, methane 20% balanced by nitrogen, flow rate = 25ml/min, reaction temperature=550 °C)

Fig. 5.13 shows the effect of the ramp-up rate temperature on the methane conversion performance. Five different ramp-up rates were tested and it was found the highest conversion rate was obtained when a slower ramp-up rate was used, such as 2 °C and 5 °C. Different from supported catalyst which has metal-support interaction, unsupported nickel catalyst will be sintered or aggregated under high temperatures. Therefore, it is necessary to introduce methane atmosphere at low temperature. The initially formed atomic carbon species would prevent the sintering of nickel crystallites. Slower ramp-up

rate would take a longer time to reach the final reaction temperature which would lead to the formation of more carbon fibres. Hence, decreasing the ramp-up rate would strengthen this effect and result in relatively better catalytic activity as shown by the experimental tests in Fig.5.13. Therefore, a ramp-up rate of 5 °C was chosen in other experiments of this chapter and the following chapters.

5.2.4 Effect of reaction temperature

Fig.5.14 Methane conversion for nickel catalysts at different reaction temperatures (Reaction conditions: 0.15g nickel oxalate, methane 20% balanced by nitrogen, flow rate = 25ml/min)

Fig. 5.14 shows the effect of the reaction temperature on the methane conversion performance. The initial rate of methane conversion at 575 °C was the highest. However, the rate declined and dropped to the lowest at the end of the test durations for all the temperatures. With decreasing reaction temperature from 575 °C, the conversion

continually decreased. At steady state, the rate of methane dissociation and carbon diffusion should be equal. This was actually the case for the lowest reaction temperature of 525 °C in which there was sustained methane conversion throughout the whole test duration, after its initial rate.

Fig. 5.15 Morphology of carbon formed at different temperatures (a) 525 °C, (b) 550 °C, and (c) 575 °C

Generally, increasing reaction temperature increases the methane dissociation due to the endothermic nature of the reaction, while the diffusion rate also increases accordingly. The balance is broken when the dissociation rate is much faster the carbon diffusion rate and subsequently carbon layer will be formed on the active surface of the catalysts which is so called deactivation. Therefore, small diffusion time constant as in small crystals favours high temperature reaction. TEM micrographs of samples in Fig. 5.15 confirmed this view. At 525 °C (Fig. 5.15 (a)), the filaments exhibited a wide range of diameters (30-110 nm) with similar sizes of nickel particles on the tips. Increasing the temperature to 550 °C led to relatively thinner CNFs with diameters ranging from 30 nm to 70 nm. At 575 °C, long filaments with apparently uniform diameters of about 30-40 nm were

observed and the nickel particles on the tips of the CNFs were also kept at similar small sizes. It was proposed that the nickel catalyst could be viewed as a self-organizing system[25]. Nickel particles undergo active transformation and gradually stabilize at thermodynamically favourable sizes [28]. CNFs can only be produced when the balance between methane dissociation rate and carbon diffusion rate is maintained. At lower reaction temperature as for the 525 °C reaction temperature in Fig. 5.15, the size of the active nickel particle was not so stringent. However, at a higher temperature as for the 575 °C in Fig. 5.15, only small particles which could maintain high diffusion rate (small time constant) were able to balance the high dissociation rate. Therefore, the distribution of the catalyst particle size or the diameter of the CNFs is more uniform than that at lower temperature.

5.3 Lifetime tests of the catalysts

Fig. 5.16 shows the conversion of methane under different temperatures for 0.015g nickel oxalate dihydrate precursor (about 4.77 mg metallic nickel) with a feed of pure methane at a flow rate of 20 ml/min. The conversions of methane could be stable for up to about 20 h, dependent strongly on the reaction temperature. It could be seen that the conversion of methane remained stable for a longer time for a lower reaction temperature. However, they all became deactivated eventually. The final amounts of carbon formed under 550, 525 and 500 °C were 217gC/gNi, 282 gC/gNi and 302gC/gNi respectively; the weights were obtained after the removal of the solid matters from the reactor. However, these amounts of carbon yields were much lower than that produced from Ni-Cu catalyst at 600 °C (650-750 gC/gNi) [153, 204] but comparable to that from nickel catalysts at

500 °C (350-490gC/gNi) [28, 120]. Further optimization of the reaction process including feed flow rate and catalyst mass could improve the carbon yields.

Fig. 5.16 Kinetic curves of methane conversions during methane decomposition over Ni catalysts at different temperatures. (Reaction conditions: 0.015 g nickel oxalate dihydrate, methane 100%, flow rate = 20 ml/min)

Fig. 5.17 Morphology of carbon formed after complete deactivation at different temperatures (a) 500 °C, (b) 525 °C, and (c) 550 °C

From previous studies, several mechanisms have been proposed for catalyst deactivation including carbon encapsulation[82, 101, 102], the structural changes of catalysts [103, 104]and space limitation[26, 105]. In order to elucidate the deactivation mechanism, TEM micrographs were obtained for the used catalysts after complete deactivation as shown in Fig. 5.17.

It was interesting to find that each deactivated catalyst particle was supported on the tips of two CNFs which was different from the active Ni particles during the reaction as they were usually on the tip of one CNF only. However, upon closer inspection of the deactivated catalyst, it was found that two Ni particles had in fact collided and coalesced together with two CNFs connecting them. All the micrographs of the totally deactivated Ni catalysts (not shown here) suggested that the collisions between two Ni catalyst particles or between Ni particles and CNFs might also be a reason contributing to catalyst deactivation. From the appearance of the completely deactivated catalysts from the reactor, it was observed that the nanocarbons were woven into rather dense and hard granules indicating that space limitation probably caused the collisions of the catalyst particles. Li *et al* [77] also suggested that catalyst deactivation was caused by the diffusion barrier for the reactant and the spatial limitation of the growth.

5.4 Summary

Unsupported metallic nickel particles with promising catalytic activity were prepared by the decomposition of nickel oxalate in methane atmosphere. The concentrations of the reactants (nickel nitrate and oxalic acid) were found to influence the crystalline size and

morphology of the nickel oxalate and subsequently had an impact on the final metallic nickel particles. The effect of the reducing atmosphere was also investigated and it was found that the addition of methane gas in the nitrogen stream could lead to the formation of small dispersed nickel particles but of similar crystalline size as those of pure nitrogen stream.

The catalytic performance of nickel particle aggregations for methane decomposition was influenced by both the crystalline size and particle size. Increasing the crystalline size from 21.5 to 25 nm had insignificant influence on the catalytic activities of the nickel particles. The nickel particle aggregates with smaller primary particle size (30-40 nm) prepared in methane atmosphere enabled the methane molecules to approach the active surfaces easier and to draw the nickel crystals away and be supported on the tips of the CNFs so as to prevent them from sintering into bigger crystals. But, nickel particle aggregations with larger primary particle size prepared in nitrogen stream would lead to a rapid deactivation due to the carbon encapsulation on the active surfaces of the nickel particles or the limited space for carbon growth. Slower ramp -up rate led to better catalytic activity. By examining the catalyst and deposited carbon after the reaction using TEM, it was revealed that the self-regulating system allowed the formation of active nickel particles and CNFs with different sizes for different temperatures. It was found that collisions between two Ni catalyst particles or between Ni particles and CNFs might be a reason contributing to catalyst deactivation as a result of a limit on growth space. Higher reaction temperature would tend to form uniformly smaller active nickel particles and CNFs. In Chapter 5, a simpler method to produced Ni catalyst was developed. In

Chapter 4, Ni catalyst was prepared using the conventional process: calcination in air and reduction in hydrogen which led to larger nickel particles. The Ni particles prepared by directly decomposition of nickel oxalate in methane (Chapter 5) possessed smaller particle size and showed better catalytic activity and stability at higher temperatures

Chapter 6 Systematic Preparation of Ni-Cu Alloy Particles and Evaluation of Their Catalytic Activity

6.1 Introduction

In this chapter, a series of Ni-Cu alloy particles with different atomic ratios of Ni/Cu were prepared in methane atmosphere. The influence of copper on the morphology and structure of the oxalate and alloy was investigated as well as the evolution of unsupported Ni-Cu particles during the CDM reaction. The conditions for the formation of quasi-liquid state metal were studied systematically, including the effects of the Ni/Cu ratio, the effects of temperature and the particle size on the catalytic activities of the Ni-Cu alloy catalysts. The deactivation mechanism of Ni-Cu catalysts with varied composition was also examined and analyzed. Without a textual promoter or support, this method enables a better study and understanding of the mechanism involved in the CDM. For detailed description of experimental procedures, please refer to section 3.3.3.

6.2. Results and discussion

6.2.1 Characterization of the catalysts

In order to prepare Ni-Cu alloys, mixed Ni-Cu oxalates were prepared. Nickel oxalate dihydrate (NiC_2O_4) belongs to the magnesium series (Mg, Mn, Fe, Co, Ni and Zn) which

can crystallize in α form (monoclinic) or β form (orthorhombic) depending on different preparation conditions [177]. Usually, the oxalates contain two structural water molecules, e.g., $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Copper oxalate does not belong to the magnesium series, and different water contents are proposed in the literature ($\text{CuC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, $0 < x < 1$, e.g. $x = 1/3$, $1/2$) [178-180].

Fig. 6.1 XRD patterns of (a) copper oxalate and nickel oxalate hydrates reference and (b) Ni-Cu oxalates with different Ni/(Ni+Cu) ratios (Ni content: Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5% ; Ni-Cu-3: 75% ; Ni-Cu-4: 62.5% ; Ni-Cu-5: 50% ; Ni-Cu-6 43.75% ; Ni-Cu-7: 37.5%)

Fig. 6.2 TEM micrographs of Ni-Cu oxalates and pure copper oxalate: (a) Ni-Cu-1, (b) Ni-Cu-2, (c) Ni-Cu-3, (d) Ni-Cu-4, (e) Ni-Cu-5, (f) Ni-Cu-6, (g) Ni-Cu-7, (h) and (i) copper oxalate

The crystalline structure of the as-synthesized Ni-Cu oxalate powders was characterized by XRD analysis as shown in Fig. 6.1. Fig. 6.1 (a) shows the reference patterns for copper oxalate hydrate and nickel oxalate hydrate. As compared with the reference patterns, in the samples with higher nickel content, all the diffraction peaks showed the

characteristics of the nickel oxalate hydrate phase which could be indexed to the orthorhombic phase of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS 25-0582). With increasing copper content, the peak at 22.9° became more pronounced which could be ascribed to the diffraction of plane (110) of copper oxalate $\cdot x\text{H}_2\text{O}$ (JCPDS 21-0297).

Fig. 6.2 shows the morphologies of the Ni-Cu oxalate hydrate samples as determined by the TEM. With increasing amount of copper, the fibre-like oxalate particles tended to be more disordered and spherical particles of Cu oxalate hydrate were observed as shown Fig. 6.2(d)-(g). The structure of the nickel oxalate dihydrate consists of pile-up leaves, each leaf comprising of parallel oxalate ribbons. The cohesion of the structures results from the hydrogen bonds between the ribbons due to the H_2O molecules [193, 194]. However, copper oxalate has a different structure; its oxalate ribbons are approximately perpendicular to one another to form a three dimensional packing structure [179]. Pure copper oxalate hydrate was prepared in this study and characterized for comparison with nickel oxalate hydrate. Fig. 6.2 (h) and (i) show the copper oxalate samples having spherical particles with sizes ranging from 5 to 10 nm in diameter. The tests indicated that there was a limit for the copper oxalate to insert or mix with the nickel oxalate to form smooth fibres of oxalate. Once the amount of copper oxalate exceeds the limit, the redundant copper oxalate will form spherical particles separately as shown in Fig. 6.2 (i).

Fig. 6.3 XRD patterns of reference (a) and Ni-Cu alloy (b) with different Ni/(Ni+Cu) ratios obtained by reduction in methane gas stream. (Ni content: Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3: 75%; Ni-Cu-4: 62.5%; Ni-Cu-5: 50%; Ni-Cu-6 43.75%; Ni-Cu-7: 37.5%, reduction temperature: 450 °C)

The crystalline structures of the as-prepared Ni-Cu alloy were characterized by XRD as shown in Fig.6.3. By comparing with the reference patterns of Ni and Cu in Fig.6.3 (a), it could be seen that the decomposition of the mixed oxalate had reduced it into Ni-Cu alloy. The crystalline sizes were calculated in accordance to the half-width of the diffraction peak of the Ni-Cu (111) and (200) planes. It could be seen that with increasing amount of

Cu, the crystalline sizes of the alloy particles first decreased and then increased, with the smallest crystalline sizes obtained for Ni-Cu-4, with Ni concentration of 62.5%.

Table 6.1 Compositions of different Ni-Cu alloy samples

Sample	Ni/(Ni+Cu) (atomic ratio, %)		
	Nominal	Based on XRD	Analyzed by EDX
Ni-Cu-1	93.75	96.37	94.17
Ni-Cu-2	87.5	85.14	87.29
Ni-Cu-3	75	71.46	76.49
Ni-Cu-4	62.5	37.99	65.71
Ni-Cu-5	50	34.94	51.25
Ni-Cu-6	43.75	14.08	45.79
Ni-Cu-7	37.5	13.99	39.62

The nominal and actual compositions of the Ni-Cu alloy particle catalyst are summarized in Table 6.1. According to the lattice parameter of each Ni-Cu alloy sample, the composition of the alloys was calculated based on Vegard's law[181]. EDX was also used to analyze the compositions which were closer to the nominal ratios. The slightly enrichment in Cu as determined from lattice parameter was in agreement with other studies[205] [206] which indicated that compared to copper, nickel reduction needed a higher temperature which probably led to the formation of a core slightly enriched in Cu and a surface enriched in nickel.

Fig. 6.4 FESEM micrographs of Ni-Cu alloy with different Ni/(Ni+Cu) ratios: (a) Ni-Cu-1, (b) Ni-Cu-2, (c) Ni-Cu-3, (d) Ni-Cu-4, (e) Ni-Cu-5, (f) Ni-Cu-6 and (g) Ni-Cu-7 obtained by reduction in methane gas stream

The morphological appearances of the fresh Ni-Cu alloy are shown as FESEM

micrographs in Fig. 6.4. All the samples appeared as large agglomerates of particles. The primary particles in close proximity had linked up and formed irregular shaped particles. However, it could be clearly observed that alloy particles with moderate Cu content as shown in Fig. 6.4(d) and Fig. 6.4(e) showed relatively smaller sizes as well as smaller crystalline size (Fig. 6.3 (b)).

6.2.2 Catalytic activity

Fig. 6.5 (a) Methane conversions during step-wise rising temperature reaction and (b) average methane conversion values, over Ni-Cu alloy catalysts of different Ni/Cu ratios (Reaction conditions: 0.15g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, test duration: 30min at each reaction temperature, Ni content: Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3: 75%; Ni-Cu-4: 62.5%; Ni-Cu-5: 50%; Ni-Cu-6 43.75%; Ni-Cu-7: 37.5%)

Fig. 6.5 (a) shows the methane conversion at different reaction temperatures for Ni-Cu alloy catalysts with different Ni/Cu ratios using a stepwise heating mode while Fig. 6.5 (b) shows the average conversion rate for each temperature. The results showed that at the lower temperature range (500-600 °C), the conversion was the highest for the sample with

the lowest copper content. However, the best conversions were obtained by samples with higher copper contents at temperatures of 700 °C and above. Fig. 6.5 (a) shows that for all the samples, increasing temperature greatly increases the conversion rate since it is an endothermic reaction. However, above a critical temperature, the catalyst deactivated rapidly.

Fig. 6.6 Methane conversions using different catalysts with varying Ni/(Cu+Ni) ratios at (a) 700 °C and (b) 750 °C reaction temperatures (Reaction conditions: 0.15g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)

Fig. 6.6 shows the performance of catalysts at constant reaction temperatures of 700 and 750 °C. At 700 °C, the methane conversion rates for samples Ni-Cu-1 and Ni-Cu-2 which had lower copper contents decreased rapidly at the early stage of the reaction especially for sample Ni-Cu-1. With increasing copper content, the stability of the catalyst improved. On further increases in the copper content, the stability decreased gradually for samples Ni-Cu-5, Ni-Cu-6 and Ni-Cu-7 as shown in Fig. 6.6 (a). Sample Ni-Cu-3 with 25% copper content showed the highest methane conversion of 80% and good stability.

However, at 750 °C (Fig. 6.6 (b)), it exhibited poor stability and its catalytic activity decreased very abruptly at 750 °C. At 750 °C, samples Ni-Cu-4 and Ni-Cu-5 which had higher copper contents showed steady catalytic activity and achieved about 82% methane conversion as shown in (Fig. 6.6 (b)).

Fig. 6.7 Methane conversions using different catalysts for various different samples (a) pure Ni, (b) Ni-Cu-1, (c) Ni-Cu-2, (d) Ni-Cu-3 and (e) Ni-Cu-5 (Reaction conditions: 0.15g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, Ni content: Pure Ni:100%, Ni-Cu-1: 93.75% ; Ni-Cu-2: 87.5%; Ni-Cu-3:75%; Ni-Cu-5: 50%)

In order to confirm the stabilization effect of copper in the Ni-Cu catalysts, lower reaction temperatures were also studied as shown in Fig. 6.7. The trend was similar to the step-wise heating mode reaction in Fig. 6.5 (a). Starting from pure Ni catalyst, increasing copper content in catalyst would shift from an initial base reaction temperature of 550 °C for pure Ni catalyst to higher reaction temperature for stable catalytic activity. From pure Ni to Ni-Cu-5, the increase in reaction temperature for prolonged stable catalytic activity was about 50 °C for each increment of Cu content in Fig. 6.7. In the case for sample Ni-Cu-5, it exhibited the highest initial catalytic activity at 800 °C reaction temperature in Fig. 6.5. However, at this reaction temperature of 800 °C and even at 775 °C, the catalyst was unable to achieve stable catalytic activity until the reaction temperature was reduced to 750 °C as shown in Fig. 6.7 (e).

Fig. 6.8 XRD patterns of spent catalysts under different reaction temperatures: (a) 700 °C and (b) 750 °C

Fig. 6.8 shows the XRD profiles of the spent catalysts after the catalytic reaction at

700 °C and 750 °C while Fig. 6.9 and Fig. 6.10 show the TEM micrographs of the used Ni-Cu catalysts at the reaction temperatures of 700 °C and 750 °C respectively. From the XRD patterns in Fig. 6.8, the nickel and copper remained in the alloy state in all the catalysts after the reaction. The crystalline sizes of the used catalysts were calculated in accordance to the peak of the (200) plane. From the observations of the TEM micrographs of the used catalysts in Figs. 6.9 and 6.10, it could be deduced that the catalyst particles were of the polycrystalline state and each particle might consist of several small Ni-Cu crystallites. The graphene distances, $d_{(002)}$, of the deposited carbon increased from 0.3406 nm in the sample Ni-Cu-1 with the highest Ni content to 0.3379 nm in the sample Ni-Cu-7 at 700 °C. The same trend was found in the reaction at 750 °C. Perfect graphite has an interplanar distance of basal planes of 0.3354 nm while interplanar distances of 0.344 nm have been measured in highly disordered turbostratic carbons[207]. The same tendency of decreasing interplanar distance of basal planes with introduction of more copper was observed in other studies [125, 155] .

On the basis of the catalytic performance results in Fig6.6 (a) and the TEM micrographs in Fig.6.9 (a), it could be deduced that at 700 °C, the catalysts with low copper content (Ni-Cu-1 and Ni-Cu-2) deactivated due to carbon encapsulation of the catalyst particles. This commonly occurs in pure nickel catalyst under high reaction temperature usually >650 °C. .

Fig. 6.9 TEM micrographs of carbon deposits on different Ni-Cu catalysts: (a) Ni-Cu-1, (b) Ni-Cu-2, (c)(d) Ni-Cu-3, (e) Ni-Cu-4, (f) Ni-Cu-5, (g) Ni-Cu-6 and (h), (i) Ni-Cu-7, at a reaction temperature of 700 °C

From the results in Fig. 6.6 (a), with increasing copper content, the stability of the catalyst was enhanced. From the findings in previous studies, the doping effect of copper has been well investigated and can be summarized into two aspects: diluting the active

sites of nickel (100 and 110) for the dissociation of methane and promoting more precipitation sites (111) for carbon filament formation [8, 26, 139]. Copper itself is inactive for methane decomposition and therefore the addition of copper into nickel will have the effect decreasing the methane decomposition rate. Copper segregation on the alloy surface which results in island-like sectors is characteristic of the Ni-Cu system [131, 189]. The copper segregation on the Ni (111) planes facilitates the formation of several carbon filaments growing from one particle which promotes carbon transportation. In the sample Ni-Cu-3, two types of catalyst particles were observed: (i) droplet-like particles with part of them being engulfed within the bodies of the CNFs (Fig. 6.9(c)), and (ii) active spherical particles with growing octopus-like carbon filaments which are most prevalent for Ni-Cu-3 catalyst (Fig. 6.9 (d)). With further increase in the copper content, large active spherical catalyst particles (150-300 nm) were mostly observed (Fig. 6.9 (e),(f),(g)). However, if the concentration of copper were too high, the catalyst would be deformed into hard-edged particles with curved facets as seen in Fig. 6.9 (h) and (i). In this case, the particles might be embedded into the CNFs easily and the exposed surfaces becoming less and less, which the catalyst particles would be deactivated finally.

Fig. 6.10 TEM micrographs of carbon deposits on different Ni-Cu catalysts: (a),(b)Ni-Cu-3, (c) Ni-Cu-4, (d) Ni-Cu-5, (e) Ni-Cu-6, and (f) Ni-Cu-7, at a reaction temperature of 750 °C

Five samples with high copper content ($\geq 25\%$) were evaluated at a reaction temperature of 750 °C. For the catalyst Ni-Cu-3, there was a predominance of small particles (around 30-40 nm) during the reaction at 750 °C. However, these small particles could turn into a quasi-liquid state at 750 °C and were then easily split into even smaller ones and engulfed into the bulk of CNFs, thereby losing its catalytic activity. This occurrence was confirmed by the formation of bamboo-like and hollow CNFs as shown in Fig. 6.10 (a) and (b). On the other hand, some large particles (>100 nm) were also observed and were usually covered by deposited carbon as shown in Fig. 6.10 (a). With increasing copper content, large Ni-Cu alloy particles (100-400 nm) were formed and stayed active for the reaction.

Samples Ni-Cu-4 and Ni-Cu-5 still retained their spherical particles, forming thick CNFs. However, for samples Ni-Cu-6 and Ni-Cu-7 with a high copper content, the spherical catalyst particles were deformed into pear-shaped or large droplet like-particles which would gradually be covered by the growing CNFs.

It is generally accepted that metal particles are in a crystalline state at low temperature and in a quasi-liquid state at high temperature[8]. It was reported that at high temperature, above 700 °C, hollow CNFs were grown by the catalysis of droplet-like catalyst particles whereby the CNFs were easily cut into small particles and this tendency became pronounced increasing copper content [135]. However, in this study, except for the sample Ni-Cu-3, other catalysts with higher copper content such as Ni-Cu-5 or Ni-Cu-6, showed round and faceted particles with particle sizes ranging from 100 to 400 nm after the decomposition reaction. Besides temperature and composition, the quasi-liquid phenomena is also related to the particle size. In these alloy catalysts, copper has a melting point of 1083 °C, while that for nickel is even lower at 1493 °C. Hence, in this case, the reaction temperature of 750 °C was considerable lower than the melting points of copper and nickel. Therefore, the existence of the catalyst in a quasi-liquid state at 750 °C could only be attributed to the size effect of nano-metal particles and the interfacial effect between the nano-carbon and the nano-metal [106]. However, if the particle size is large enough (300-400 nm), the initial temperature for the formation of liquid form metal is increased. CDM reaction over unsupported Ni-Cu alloy catalyst is a self-regulating system. With increasing copper content, the particle size of the catalyst during the reaction also increased which effectively prevented catalyst deactivation due to the

occurrence of liquid from the catalyst. Therefore, it can be concluded that with higher reaction temperature ($>700\text{ }^{\circ}\text{C}$), lower copper concentration ($<25\%$) and smaller particle size ($<50\text{ nm}$), the likelihood of quasi-liquid phenomena occurring increases.

6.2.3 Stability and deactivation mechanism of the catalysts

Fig. 6.11 Methane conversions using different catalysts at $700\text{ }^{\circ}\text{C}$ for complete catalyst deactivation. (Reaction conditions: 0.015 g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate= 20 ml/min)

In order to compare the activity life of different catalysts, five catalysts were tested until fully deactivated. In order to avoid blockage in the reactor, a very small amount of catalyst (15 mg oxalate) was used and the feed gas was $\text{CH}_4\text{-N}_2$ ($\text{CH}_4/\text{N}_2 = 0.25\%$) with a flow rate of 20 ml/min . The carbon yield was obtained by weighing the catalyst bed before and after the reaction. The final weights of the carbon deposits after the reaction were 154.2 gC/gNi , 279.3 gC/gNi , 211.7 gC/gNi , 121.8 gC/gNi and 81.2 gC/gNi for

sample Ni-Cu-3, Ni-Cu-4, Ni-Cu-5, Ni-Cu-6, Ni-Cu-7 respectively. Fig. 6.11 showed that samples Ni-Cu-3, Ni-Cu-4 and Ni-Cu-5 yielded longer periods of activity. For samples with higher copper contents (Ni-Cu-6 and Ni-Cu-7), the catalytic activities decreased right from the beginning and continued to decrease until complete deactivation. Ni-Cu-4 showed the longest catalytic life. TEM micrographs of the used catalysts after complete deactivation were obtained to study the catalyst deactivation mechanism.

Fig. 6.12 TEM micrographs of carbon deposits on the different Ni-Cu catalysts after total deactivation: (a),(b) Ni-Cu-3, (c),(d) Ni-Cu-4, and (e),(f) Ni-Cu-7 (Reaction conditions: 0.015g Ni-Cu oxalate, methane 20% balanced by nitrogen, flow rate=20 ml/min, reaction temperature :700 °C)

From the TEM micrographs in Fig. 6.12, the spherical catalyst particles and octopus-like carbon fibres were not observed. Instead, straight carbon fibres with dispersed metal

fragments (black dots) were observed. Based on extended x-ray absorption fine structure (EXAFS) data, Avdeeva *et al* [26] speculated that half of the nickel was atomically dispersed in or over the carbon filaments in deactivated Ni-Cu/Al₂O₃ samples. This dispersion was suggested as some kind of erosion process whose mechanism was not explained. From the observation here, the CDM reaction over the Ni-Cu catalysts seemed to stop when the catalyst particles were fragmented into small pieces as shown in Fig. 6.12 (a)-(d). When compared with the active and large catalyst particles in Fig. 6.9, much smaller cone-shaped particles were found at the ends of the CNFs with sizes of 10-20 nm as shown in the inset of Fig. 6.12 (a). Most of the catalyst fragments were dispersed in the bodies of the CNFs (Fig. 6.12 (c)).

Obviously, this fragmentation process was caused by the growth of CNFs. In the process of their growth, the released carbon from the methane molecules needs to dissolve first and diffuse through the catalyst bulk (or subsurface). Carbon dissolution and diffusion in copper are negligible when compared with nickel. For instance, the carbon solubilities in copper and nickel are 0.0004% and 10.7% respectively [74]. The large differences in the carbon solubility and diffusivity for both nickel and copper would probably lead to selective diffusion paths during carbon diffusion. Baker *et al* [131] studied the surface composition of Ni-Cu alloy under ethylene or hydrogen atmospheres. The authors suggested that the metals in an alloy tend to collect up in the form of clusters rather than being uniformly dispersed and postulated the arrangement of two alloys with bulk compositions of Ni-Cu (7:3) and (3:7) as shown in Fig. 6.13 (a) and (b). Together with the observations in this study, the clusters of nickel atom and copper atom might lead to

the selective carbon diffusion paths as shown in Fig.13 (c) and (d). The black dots represent the carbon atoms which selectively dissolve and diffuse in nickel clusters. Therefore, it was suggested that this unique kind of carbon migration in Ni-Cu alloy particles would cause distortion in the bulk of the catalyst which probably led to fragmentation, eg. splitting or tearing of the metal particles into smaller inactive units and deactivation gradually.

Fig. 6.13 Postulated model of the arrangements of nickel and copper atoms and the selective carbon diffusion path in the surface of (a), (c) Ni/Cu (7:3) and (b), (d) Ni/Cu (3:7) alloys [131]

However, for samples with the higher copper content (Ni-Cu-6 and Ni-Cu-7), the morphology of the catalyst dominated the catalytic activity. With a high content of copper, the catalyst particles tended to be conical, elongated particles with thicker CNFs forming on curved facets (Fig. 6.10 (d),(e). This is probably because the copper content is too high to inhibit the tendency for the catalyst particles to become quasi-liquid. This catalyst deformation and encapsulation would lead to even faster deactivation rate than that of

fragmentation.

6.3 Summary

A series of unsupported Ni-Cu alloy particles with promising catalytic activity were prepared by decomposition of Ni-Cu oxalates in methane atmosphere. The highest methane conversion of about 82% was achieved for a Ni-Cu alloy catalyst with 62.5% nickel content at a reaction temperature of 750 °C. The ratios of Ni/Cu were found to influence the morphology of the Ni-Cu oxalate. The concentration of 62.5% Ni in the alloy led to alloy particles with the smallest crystalline size and particle size among the many Ni/Cu ratios studied. With increasing copper content, the catalyst stability had improved but further continual increase in the copper content from 56.25% to 62.5% led to an abrupt decrease in the stability again. This was related to the morphology of the catalyst particle. When the copper content was less than 25%, the performance of the alloy catalyst was similar to that of the pure nickel and particle size dominated the catalytic activity. At a high reaction temperature (700 °C), small particles (30-40 nm) produced the highest conversion rate and stability. However, at a higher temperature (750 °C), the small particles were affected and produced poorer stability and decreased catalytic activity due to the appearance of quasi-liquid state catalyst. In contrast, when the copper content was more than 25%, the morphology of the catalyst particle dominated its performance. The addition of an appropriate amount of copper (25%-50%) led to the formation of isometric, round and large catalyst particles (150-400) nm with many small facets which resulted in the formation of octopus-shaped nano-carbons. But, if the content of copper was too high (>50%), the catalyst particles became conical and

elongated with thicker CNFs forming on the curved facets. This type of catalyst particles were found to be deactivated more easily and were gradually encapsulated by the growing CNFs.

The long term activity evaluation of the catalyst showed that stable catalysts, under certain conditions, could suffer deactivation gradually due to a fragmentation process. This was probably due to the selective diffusion of carbon in the bulk of the Ni-Cu alloy catalysts. The catalyst with too high or too low copper content could be deactivated due to carbon encapsulation.

Chapter 7 Systematic Preparation of Ni-Cu-Co Alloy Particles and Evaluation of Their Catalytic Activity

7.1 Introduction

Besides the performance studies on Ni-Cu alloy catalysts in Chapter 6, cobalt is another element which shows considerable catalytic activity towards the CDM process. In this work, cobalt was doped into Ni-Cu-3 (Ni/Cu=3/1) to increase the catalyst stability at high temperature. The objective of this part of the project was to investigate the genesis of the phase composition and properties of Ni-Cu-Co alloy catalysts. Six samples with varied Ni/Cu/Co compositions were studied. The content of the copper in all the catalysts was kept 25% which was the same as the Ni-Cu-3 sample. For detailed description of experimental procedures, please refer to section 3.3.4.

7.2 Experiment results

7.2.1 Characterization of the catalysts

Fig. 7.1 shows the morphologies of the Ni-Cu-Co oxalate hydrate samples as determined by TEM. When comparing with the single or binary metal oxalate, the structures of the ternary oxalates would tend to be more disordered and irregular. The ternary oxalates were made up of mixtures of wide and fine fibres. Similar to nickel oxalate, pure cobalt

oxalate also showed fibre-like structures with smooth surfaces as shown in Fig. 7.1 (g).

Fig. 7.1 TEM micrographs of Ni-Cu-Co oxalates, Co-Cu oxalate and pure cobalt oxalate: (a) Ni-Cu-Co-1, (b) Ni-Cu-Co-2, (c) Ni-Cu-Co-3, (d) Ni-Cu-Co-4, (e) Ni-Cu-Co-5, (f) Co-Cu and (g) Co (Ni/Co/Cu ratios: Ni-Cu-Co-1(0.7/0.05/0.25), Ni-Cu-Co-2(0.625/0.125/0.25), Ni-Cu-Co-3(0.5/0.25/0.25), Ni-Cu-Co-4(0.375/0.375/0.25), Ni-Cu-Co-5(0.25/0.5/0.25), Co-Cu(0/0.75/0.25))

Fig. 7.2 FESEM micrographs of Ni-Cu, Co-Cu and Ni-Cu-Co alloys: (a) Ni-Cu-3, (b) Ni-Cu-Co-1, (c) Ni-Cu-Co-2, (d) Ni-Cu-Co-3, (e) Ni-Cu-Co-4, (f) Ni-Cu-Co-5, (g) Co-Cu

The morphological characteristics of the pristine Ni-Cu-Co alloy are displayed in Fig. 7.2. All the samples appeared as large agglomerates of particles similar to the Ni-Cu series. The primary particles in close proximity had linked up and formed irregular shaped particles. When compared with the binary alloys Ni-Cu-3 (Fig. 7.2 (a)) and Co-Cu (Fig. 7.2 (g)), the ternary alloys showed smaller primary particle sizes.

Fig. 7.3 XRD patterns of (a) reference and (b) Ni-Cu-Co alloys by reduction in methane

The crystalline structures of the as-prepared Ni-Cu-Co alloy were characterized by XRD as shown in Fig. 7.3. By comparing with the reference patterns of Ni and Cu in Fig.7.3 (a), it could be seen that the decomposition of the mixed oxalates had given rise to Ni-Cu-Co alloys. The crystalline sizes were calculated and the domain sizes of Ni-Cu-Co ranged from 12.6 to 15.9 nm. The nominal and actual compositions of the Ni-Cu-Co catalyst are summarized in Table 7.1. The content of the copper in all the catalysts was kept 25% which was the same as the Ni-Cu-3 sample.

Table 7.1 Compositions of different Ni-Cu-Co alloy samples

Sample	Ni/Co/Cu atomic ratios	
	Nominal	Analyzed by EDX
Ni-Cu-3	0.75/0.25	0.777/0.223
Ni-Cu-Co-1	0.7/0.05/0.25	0.743/0.054/0.202
Ni-Cu-Co-2	0.625/0.125/0.25	0.670/0.127/0.202
Ni-Cu-Co-3	0.5/0.25/0.25	0.536/0.239/0.225
Ni-Cu-Co-4	0.375/0.375/0.25	0.405/0.373/0.220
Ni-Cu-Co-5	0.25/0.5/0.25	0.269/0.502/0.228
Cu-Co	0/0.75/0.25	0/0.787/0.212

7.2.2 Catalytic activity

Fig. 7.4 shows the methane conversions at different reaction temperatures for a series of Ni-Cu-Co alloy catalysts using a stepwise temperature heating mode. For all the samples, increasing temperature greatly increased the conversion rate as the process was an endothermic reaction. Without Ni, the sample Co-Cu yielded a much lower methane

conversion when compared with samples which had Ni contents. All the ternary alloy samples exhibited high initial catalytic activities up to 750 °C. At 700 °C and below, the best conversion at each reaction temperature was obtained by the sample with the highest nickel content and the lowest cobalt content. However, at 750 °C, the differences in conversion among the ternary samples were insignificant. A reaction temperature of 800 °C was a limit for these ternary alloy catalysts and beyond this temperature, a breakdown in the catalyst was observed.

Fig. 7.4 Methane conversions during step-wise rising temperature reaction for Ni-Cu-Co alloy catalysts (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, test duration: 30min at each reaction temperature, Ni/Co/Cu ratios: Ni-Cu-Co-1(0.7/0.05/0.25), Ni-Cu-Co-2(0.625/0.125/0.25), Ni-Cu-Co-3(0.5/0.25/0.25), Ni-Cu-Co-4(0.375/0.375/0.25), Ni-Cu-Co-5(0.25/0.5/0.25), Co-Cu(0/0.75/0.25))

Figs. 7.5 and 7.6 show the performance of catalysts with time at constant reaction

temperatures of 700 °C and 750 °C respectively. At 700 °C, all the Ni-Cu-Co alloy samples and the Ni-Cu alloy sample provided and supported good stability in methane conversions. Generally, a higher Ni content (Ni-Cu-Co-1 and Ni-Cu-3) produced higher methane conversion due to the good catalytic activity of nickel, with the best methane conversion of about 80% achieved by the catalyst sample Ni-Cu-Co-1. However, when the reaction temperature was increased to 750 °C, only the samples with cobalt contents of 25% and greater were able to provide stable catalytic activities over the time duration tested.

Fig. 7.5 Methane conversions using different catalysts at 700 °C (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)

Fig. 7.6 Methane conversions using different catalysts at 750 °C (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)

Fig. 7.7 Methane conversions using Ni-Cu-Co-1 at various reaction temperatures (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)

Fig. 7.8 Methane conversions using Ni-Cu-Co-3 at various reaction temperatures (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min)

In order to determine the optimum operating reaction temperature for samples Ni-Cu-Co-1 and Ni-Cu-Co-3 which had shown to have good catalytic activities at 700 and 750 °C in Fig. 7.5 and Fig. 7.6 respectively, these samples were tested at various temperatures ranging from 650 to 775 °C as shown in Fig. 7.7 and Fig. 7.8. For both samples, their activities were greatly affected by temperatures. An optimum temperature that yielded the best methane conversion existed for each sample. For sample Ni-Cu-Co-1, the best methane conversion of about 82% with stable catalytic activity was obtained for a reaction temperature of 700 °C (Fig. 7.7) whereas for sample Ni-Cu-Co-3, that reaction temperature was 750 °C with similar performance in methane conversion (Fig. 7.8). For an reaction temperature which was 25 °C greater than these optimum temperatures, a slow deactivation with time would occur. However, for 50 °C greater than the optimum values, rapid deactivation would follow.

Fig. 7.9. shows the XRD profiles of the spent catalysts after reactions at 700 °C and 750 °C. For most of the alloys, nickel, copper existed in the alloy state after the reaction. However, for the catalysts with high cobalt content, such as Ni-Cu-Co-5 and Co-Cu, copper existed as a single phase as confirmed by the peak at 43.4° although these catalysts could form alloys before the reaction as shown in Fig. 7.3. From Chapter 6, it was shown that nickel and copper could easily form an alloy at any ratio and the alloy remained stable at reaction temperatures up to 750 °C. However, after cobalt was added and was predominant in the composition of the alloy, such as Ni-Cu-Co-5 and Co-Cu, phase separation was likely to occur at high reaction temperatures of 700 °C and greater.

Fig. 7.9 XRD patterns of spent catalysts at different reaction temperatures: (a) 700 °C and (b) 750 °C

After the reaction, the catalyst particles had sintered into much bigger particles as shown in Fig. 7.10 as compared with their corresponding pristine catalyst particles in Fig. 7.2. In the TEM micrographs of carbon deposited over Ni-Cu-Co catalysts in Fig. 7.10, no typical straight fibres were observed. After careful examination at high magnification, the “carbon fibres” were actually stacks of carbon fragments (Fig. 7.10 (h)). They were joined so loosely that after the sample preparation process for TEM analysis, the fibre structure was destroyed already as shown in Fig. 7.10 (d), (e) and (f). With increasing cobalt content (Fig. 7.10 (a)) to Fig. 7.10 (e)), geometrical shape of the catalyst also showed slight changes, from isometric morphologies with facets to spherical ones. Upon

Fig. 7.10 TEM micrographs of spent catalysts: (a) Ni-Cu-3, (b) Ni-Cu-Co-1, (c) Ni-Cu-Co-2, (d) (h) Ni-Cu-Co-3, (e) Ni-Cu-Co-4, (f) Ni-Cu-Co-5, (g) Co-Cu at a reaction temperature of 700 °C.

further increasing cobalt content and decreasing nickel content, like sample Ni-Cu-Co-5 (Fig. 7.10(f)) or Co-Cu (Fig. 7.10(g)), phase separation occurred as shown in Fig. 7.9. As observed from Fig. 7.10 (g), the catalyst showed a rigid bulk followed by a conical tail which was probably a copper phase and separated from the Co-Cu alloy due to lower

melting points and interfacial impact between carbon and liquid-state metal.

Fig. 7.11 TEM micrographs of spent catalyst Ni-Cu-Co-1 at a reaction temperature of 750 °C

At a reaction temperature of 750 °C, samples with lower Co content became unstable. Two types of carbon were formed: hollow CNFs (Fig. 7.11. (a), (b)) and carbon shells with big catalyst particles embedded (Fig. 7.11.(c)). The catalyst particles underwent a dispersing process with increasing temperature in order to maintain the balance of a carbon migration cycle. Therefore, smaller Ni-Cu-Co alloy particles (50-70nm) were formed as shown in Fig. 7.11 (a). The liquid-like catalyst particle appeared with a tail which led to form hollow CNFs as shown in 7.11 (b). The shape of the hollow carbon fibres suggested that it was formed by jumping off from the catalyst metal tips at regular time intervals over similar distances. Larger particles (>100 nm) were covered by carbon which led to abrupt deactivation (Fig. 7.11(c)). With increasing cobalt content, the particle size was not so crucial as compared with the particle dispersing process in Fig. 7.11 (a). In this case, large spherical alloy particles (>200nm) were formed and no quasi-liquid catalyst particles were observed as shown in Fig. 7.12.

Fig. 7.12 TEM micrographs of spent catalysts: (a) Ni-Cu-Co-2, (b) Ni-Cu-Co-3, and (c) Ni-Cu-Co-4 at a reaction temperature of 750 °C

Fig. 7.13 TEM micrographs of spent catalysts: Ni-Cu-Co-2 at different reaction temperature of (a) 775 °C and (b), (c) 800 °C

To evaluate the effect of reaction temperature on the catalyst, the content of Co in the alloy is critical. Too low in the Co constituent in the alloy will result in a quasi-liquid state at or below the appropriate reaction temperature such as the sample Ni-Cu-Co-1 in Fig. 7.11 (a). Too high in the Co constituent will elude the occurrence of the quasi-liquid state and its effects on the catalysis reaction. Based on the results on the spent catalysts in Fig. 7.11 and Fig. 7.12, the sample Ni-Cu-Co-2 with the desired Co content was selected

to evaluate the temperature effect on the catalyst reaction. At 750 °C, spherical Ni-Cu-Co alloy particles were mostly observed as shown in Fig. 7.12. (a). When the reaction temperature was set at 775 °C, the catalyst transformed itself into a quasi-liquid state and formed hollow CNFs as shown in Fig. 7.13 (a). At 800 °C, elongated liquid-like catalyst particles or smaller split particles (Fig. 7.13 (b) and (c)) were widely observed which led to abrupt deactivation with the formation of bamboo-like carbon or carbon shells.

7.3 Discussion

Table 7.2 Physico-chemical properties of selected transition metals. NA = data not available[74]

Macroscopic property	Iron	Cobalt	Nickel	Copper	Molybdenum
Density, at 20 °C (liquid state) (kg m ⁻³)	7874(7035)	8900(7670)	8902(7780)	8960(7940)	10220(9330)
Melting temperature (T _{melt}) (°C)	1536	1495	1453	1083	2617
Surface tension at 20 °C (at 2000 °C) (N m ⁻¹)	1.95 (1.72)	2.1 (1.68)	1.86 (1.57)	1.75(0.95)	2.2 (NA)
Equilibrium vapour pressure (at t= 1216 °C)(Pa)	5.5×10 ⁻³	4.7×10 ⁻³	4.0×10 ⁻³	7.1×10 ⁻¹	7.6×10 ⁻¹¹
Carbon solubility (at.%) at T _{melt}	20.2	13.9	10.7	2×10 ⁻⁴	60-70
Carbon diffusion coefficient in metal (m ² s ⁻¹) (at t=1000 °C)	1.5×10 ⁻¹¹	1×10 ⁻¹¹	2×10 ⁻¹¹	NA	NA

Chesnokov and Chichkan *et al.*[149] studied the catalytic activity of 70Ni-10Cu-10Fe/Al₂O₃ catalyst for CDM in a rotating reactor. The catalyst was prepared by the mechanochemical activation of a mixture of transition metal oxides (Fe₂O₃, NiO, CuO). Their results showed that the addition of Fe to Ni-Cu resulted in an enhancement in the stability of the catalyst. They explained that the diffusion coefficient of carbon atoms

through the iron metal is three orders of magnitude higher than that through the nickel metal. This makes the diffusion of carbon atoms through the bulk of the Ni-Fe-Cu alloy particles faster than through the Ni-Cu alloy particles. The physico-chemical properties of selected transition metals including carbon solubility and diffusion coefficient in metals are summarized in Table 7.2. The carbon diffusion coefficients in the following metals in decreasing order are nickel, iron and cobalt. The carbon solubilities in metal at melting points decrease in the order of iron, cobalt and nickel. Therefore, the alloy effect on the catalyst stability of Ni-Fe-Cu or Ni-Cu-Co cannot be ascribed to the differences on carbon diffusion coefficient. It is more reasonable to relate the alloy synergism to the effect due to the melting point. Based on the performance of Ni-Cu-3 (Ni/Cu=3/1), Ni-Cu-Co-1 (Ni/Co/Cu=2.8/0.2/1), Ni-Cu-Co-2 (Ni/Co/Cu=2.5/0.5/1) and Ni-Cu-Co-3 (Ni/Co/Cu=2/1/1) at 750 °C (the results shown in Fig. 7.6) and their TEM micrographs (Fig. 7.11 and Fig. 7.12), it can be concluded that the addition of cobalt prevents the occurrence of quasi-liquid state in the catalyst. As shown in Table 7.2, copper has the lowest melting point at 1083 °C, which is still much higher than the highest reaction temperature in the tests conducted here. In addition, nickel, cobalt and iron have much higher melting point temperatures which are 1453, 1495 and 1536 °C respectively. Usually, the alloy will have a melting point which will fall somewhere in between their respective melting points. The existence of the quasi-liquid - like metal at about 700-750 °C for the Ni-Cu-Co alloy catalysts in the tests here, which is much lower than their respective melting temperatures, can only be attributed to the size effect of the metal at nanometre level and the interfacial effect between the carbon and the metal catalyst [106]. The lower the melting point will result in the quasi-liquid phenomena occurring easier.

Therefore, it is reasonable to expect the temperature of the initial occurrence of the quasi-liquid state catalyst to be higher for Ni-Cu-Co than that of Ni-Cu series with the same copper content.

The activities of Ni-Cu-Co and Ni-Cu catalysts whose compositions are shown in Fig. 7.14 were compared. By comparing sample A (Ni:Co:Cu =1.75:1.75:0.5) and sample A1(Ni:Cu =3.5:0.5), it could be seen that the replacement of half of Ni content with Co, led to a higher maximum reaction temperature by 50 °C for sample A. This behavior could be attributed to two reasons: firstly, the cobalt delayed the occurrence of the quasi-liquid state phenomena, secondly, the addition of cobalt decreased the decomposition rate of methane which could better balance the carbon migration cycle and therefore prevent the encapsulation process. The other pair of samples B and B1 showed a similar trend.

Fig. 7.14 Methane conversions during step-wise rising temperature reaction using Ni-Cu-Co and Ni-Cu alloy catalysts (Reaction conditions: 0.15g Ni-Cu-Co oxalate, methane 20% balanced by nitrogen, flow rate=25 ml/min, test duration: 30min at each reaction temperature)

7.4 Summary

A series of unsupported Ni-Cu-Co alloy particles with promising catalytic activity were prepared by thermal decomposition of Ni-Cu-Co oxalates in methane atmosphere. The addition of cobalt led to the formation of alloy particles with smaller crystalline size and particle size than those of Ni-Cu alloy or pure Ni particles. With increasing cobalt content, the catalyst stability at higher reaction temperature had improved but further continual increase of cobalt content led to a phase separation. In general, given the same copper content, the addition of cobalt would improve the stability of the catalyst at a higher reaction temperature such as at 750 °C. This was because cobalt has a higher melting point temperature than nickel and copper, which would therefore delay the occurrence of the quasi-liquid state. However, without nickel, cobalt and copper could not remain in the stable alloy state in the reaction. Thus, the cobalt particles would be deactivated easily due to carbon encapsulation.

So far, three types of unsupported catalyst Ni, Ni-Cu, Ni-Cu-Co had been prepared and evaluated for their catalytic activities. In Chapter 4, NiO and NiO-CuO had been prepared first, followed by a reduction process. In chapters 5,6 and 7, metallic catalysts were prepared from decomposition of metal oxalates in methane atmosphere. The latter methods lead to smaller catalyst particles (Ni or Ni-Cu) which showed better catalytic activity and stability (Fig 4.6 vs.Fig.5.14 and Fig.4.7 vs.Fig,6.6). Catalyst Ni-Co-Cu showed better stability than Ni-Cu under 750 °C with the same copper content. Further optimization of Ni-Cu-Co catalyst may be investigated in future studies.

Chapter 8 Kinetic Studies and Modelling Work

8.1 Introduction

Kinetic analysis is an important aspect in any catalysis process. Kinetic studies are chemical steps performed in order to find a model that describes the rate of reaction and defines the chemical process. In other words, kinetic analysis means fitting kinetic models to the experimental data. The kinetic models can be empirical or mechanistic. However, the conventional kinetic analysis involving mechanistic models is not always reliable because it does not provide predictions of the behavior of the catalyst over the reaction time. In order to determine the change in catalytic activity with time, the effects of operating conditions have to be considered. In this chapter, a detailed catalytic deactivation study was carried out. The typical experimental conditions used in this study were summarized in Table 3.2. For detailed description of experimental procedures, please refer to section 3.3.5.

8.2 Reaction rate kinetic studies

Before the kinetic studies, it was necessary to test whether diffusion effect existed during the reaction. As the catalyst particles were nearly non-porous materials, the internal diffusion problem was assumed to be negligible. The external diffusion effect could be detected by increasing the linear velocity with residence time being kept constant. The external mass transfer resistance is assumed to be negligible if the conversion did not change upon an increase in the linear velocity as shown in Fig.8.1. Therefore, these

results were related to the intrinsic kinetic study of the catalyst performance.

Fig 8.1 Influence of gas liner velocity on the conversion of methane (Reaction conditions: total flow rate/amount of nickel oxalate =10ml /0.0075g, 20ml/0.015g, 30ml/0.0225g, 40ml/0.03g, methane 20% balanced by nitrogen, reaction temperature =525 °C)

The effects of methane partial pressure and reaction temperature on the H_2 formation rate as a function of reaction time are shown in Fig. 8.2. Increasing methane concentration increased the hydrogen formation rate and generally increased the catalyst life-time. Further, increasing reaction temperature resulted in increasing hydrogen formation rate and decreasing deactivation time.

Fig. 8.2 H_2 formation rate versus reaction time for Ni catalyst under different methane partial pressures (P_{CH_4}) and different reaction temperatures: (a) 575 °C, (b) 550 °C, and (c) 525 °C (Reaction conditions: 0.015 g nickel oxalate dihydrate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min)

In order to determine the reaction order, a parameter estimation was carried out using an empirical model based on a power law [208]:

$$r = kP_{CH_4}^n \quad (8.1)$$

where r is the reaction rate, k is the rate constant, P is the reaction partial pressure, and n is the reaction order. The initial hydrogen formation rate was based on the results in Fig. 8.2. Plotting $\ln r_{\max}$ against the methane partial pressure P_{CH_4} in logarithmic scales produced a straight line and the slope of the line yielded the reaction order as shown in Fig. 8.3. The values of reaction order range from 0.60 to 0.64 with the correlation coefficient in the range of 0.99 to 1 for the three reaction temperatures used. The average

reaction order for methane decomposition over unsupported nickel was found to be 0.63 and the rate equation can be written as follows:

$$r_{\max} = kP_{\text{CH}_4}^{0.63}$$

Fig. 8.3 Dependence of the maximal hydrogen formation rate $r_{\max}$ versus partial pressure of methane P_{CH_4} at different temperatures for reaction under Ni catalyst (Reaction conditions: 0.015 g nickel oxalate dihydrate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min)

The rate constant k can be determined from Arrhenius law:

$$k(T) = \nu \cdot e^{-E_a/RT} \quad (8.2)$$

where ν is the pre-exponential factor, E_a is the activation energy (kJ mol^{-1}) and R is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$). Usually, it is expressed as follows:

$$\ln k(T) = \ln v - \frac{E_a}{R} \frac{1}{T} \quad (8.3)$$

The activation energy E_a can be determined from the experimental results by plotting the logarithm of the rate constant against the reciprocal temperature, in which the slope of the line is $-E_a/R$. From the Arrhenius plot in Fig. 8.4, E_a was found to be 65.4 kJ mol⁻¹ which is close to the activation energy values of 60 kJ/mol and 64.6 kJ/mol for the CDM over Ni based catalysts as reported by Zein *et al* [209] and Kvande *et al* [210], respectively.

The maximum rate can then be expressed as

$$r_{\max} = k(T)P_{CH_4}^{0.63} = 1047.3 \cdot e^{-7872/T} P_{CH_4}^{0.63} \quad (8.4)$$

Fig. 8.4 Arrhenius plot $\ln k$ vs. $(1/T)$ (Reaction conditions: 0.015 g nickel oxalate dihydrate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min)

The effects of methane partial pressure and reaction temperature on the H_2 formation rate over Ni-Cu-Co-3 (2Ni-1Cu-1Co) catalyst as a function of reaction time are shown in Fig. 8.5. In general, the performance of 2Ni-1Cu-1Co alloy catalyst was greatly different from that of pure nickel catalyst. Firstly, there was an initial induction period during which the H_2 formation rate kept increasing. After the H_2 formation rate reached a maximum point, the deactivation process commenced. As shown in Fig. 8.5, the induction period shortened with increasing methane concentration. Secondly, increasing methane partial pressure greatly enhanced the hydrogen formation rate but shortened the catalyst lifetime. Thirdly, similar to pure nickel catalyst, higher reaction temperature led to higher hydrogen formation rate and faster deactivation.

Fig. 8.5 H_2 formation rate versus reaction time for 2Ni-1Cu-1Co catalyst under different methane partial pressures (P_{CH_4}) and different reaction temperatures: (a) 750 °C, (b) 700 °C, and (c) 650 °C (Reaction conditions: 0.015 g 2Ni-1Cu-1Co oxalate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).

Plotting $\ln r_{\text{max}}$ against the methane partial pressure in logarithmic scales produced a

straight line and the slope of the line yielded the reaction order as shown in Fig. 8.6. The average value of the reaction order under different reaction temperatures was 0.76. The rate constant k can be determined using the Arrhenius plot of $\ln k$ against $1/T$ in which the slope of the line is $-E_a/R$ which is shown in Fig. 8.7. The expression of $r_{\max}$ for reaction over 2Ni-1Cu-1Co catalyst can be expressed as follows:

$$r_{\max} = k(T)P_{CH_4}^{0.76} = 164.9 \cdot e^{-7153.9/T} P_{CH_4}^{0.76} \quad (8.5)$$

The activation energy of the reaction over 2Ni-1Cu-1Co catalyst was found to be 59.4 kJ mol⁻¹ which is smaller than the activation energy of CDM over pure Ni based catalyst. It was reported that a lower activation energy meant that the reaction rate was less sensitive to temperature [211].

Fig. 8.6 Dependence of the maximal hydrogen formation rate $r_{\max}$ versus partial pressure of methane P_{CH_4} at different temperatures for reaction under 2Ni-1Cu-1Co catalyst (Reaction conditions: 0.015 g 2Ni-1Cu-1Co oxalate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).

Fig. 8.7 Arrhenius plot $\ln k$ vs. $(1/T)$ (Reaction conditions: 0.015 g 2Ni-1Cu-1Co oxalate, feed: methane balanced with nitrogen, methane pressures range from 0.2 to 0.8, total flow rate = 20 ml/min).

8.3 Deactivation analysis and modelling work of based on Ni catalyst

As stated in Chapter 2, one of the principal objectives of the catalyst deactivation study is to correlate the deactivation rate with the process variables such as reactant concentration and temperature, in the form of a deactivation rate expression which predicts the specific activity as a function of these process variables.

The normalized activity is defined by the following expression:

$$a = \frac{\text{reaction rate over time on stream}}{\text{reaction rate with fresh catalyst}} = \frac{r}{r_{\max}} \quad (2.18)$$

where r is the reaction rate at any time t and $r_{\max}$ is the maximal reaction rate when the

catalyst commences to deactivate. Therefore, the measurement of the rate in relation to time can be explained using the concept of activity factor which assumes the maximum number of active sites on the fresh catalyst but during the reaction it decreases due to catalyst deactivation.

The following equation is considered as a general form for the determination of activity factor which is also called the general power law equation (GPLe).

$$\frac{da}{dt} = r_d a^d \quad (2.19)$$

where d is called the order of deactivation and r_d is assumed to be a function of temperature and methane partial pressure. The deactivation order d depends on the mechanism involved in the deactivation process. In principle, d is assumed to be constant throughout the whole deactivation reaction.

The equation is usually used in the integrated form by integrating Eq.2.19 as follows

$$a = \exp(r_d t) + c \quad \text{if } d=1 \quad (8.6)$$

$$a = \frac{1}{[1 + (d-1)r_d t]^{1/(d-1)}} + c \quad \text{if } d \neq 1 \quad (8.7)$$

where c is a constant.

Abbas and Daud [212, 213] used this model to fit the deactivation process of carbon catalyst during the CDM process with d as an unknown constant. Under constant reactant partial pressure and temperature, various equation forms (with $d = 0, 0.5, 1, 1.5$ and 2) were tried for equation (8.7). The value of $d = 0.5$ was found to be the best fit with the highest correlation coefficient (>0.99).

In some studies [214, 215], the values of the kinetic order d were calculated with the consideration of the number of sites involved in the controlling step of the main reaction (m) and of the deactivation reaction (h) as follows: $d = (m+h-1)/m$. For the case of methane decomposition, the assumed values for m and h are 2 and 1, respectively.

In the studies here, different models were proposed to describe the experimental data and the mechanism of the deactivation process was discussed.

As discussed in Section 2.5.4, several mechanisms have been proposed for catalyst deactivation which includes carbon encapsulation, structural changes of catalyst, space limitation and carbon fibre collisions. In order to elucidate the deactivation mechanism, TEM micrographs were obtained for the used catalyst after complete deactivation. Fig. 8.8 shows the Ni catalyst structure in the first 10 mins of the reaction under different methane partial pressures whereas Fig. 8.9 shows the spent Ni catalyst after complete deactivation.

Fig. 8.8 TEM micrographs of Ni catalyst after 10 min of reaction under different methane partial pressures at 525 °C (a) $P_{\text{CH}_4} = 0.2$ (b) $P_{\text{CH}_4} = 0.4$, and (c) $P_{\text{CH}_4} = 0.8$

Fig. 8.9 Spent Ni catalyst after complete deactivation with $P_{\text{CH}_4} = 0.2$ for different reaction temperatures (a) 525 °C, (b) 550 °C, and (c) 575 °C

From the micrographs in Fig. 8.9, it was found that each deactivated catalyst particle was supported on top of two CNFs which was different from the active Ni particles during the reaction as each Ni particles was usually present on top of only one CNF as shown in Fig. 8.8. However, upon closer inspection of Fig. 8.9, it was found that two Ni particles actually collided and coalesced together with two CNFs connecting them. All the micrographs for the totally deactivated Ni catalysts (not shown here) confirmed the conclusion that the collisions among the Ni catalyst particles led to progressive catalyst deactivation which has been discussed in section 5.3.

Based on the evidence of a progressive deactivation of catalyst, the widely used empirical model GPLE (Eqs.8.6 and 8.7) and a phenomenal model (Eq.8.8) were used to fit the experimental results.

The phenomenal model was proposed based on the decreasing mode of activity factor

with time which consisted of a long period of slow decay followed by an abrupt reduction.

A general expression of exponential decay function is proposed as follows:

$$a = a_0 - A \exp\left(-\frac{t}{t^*}\right) \quad (8.8)$$

where a_0 is the offset, A is the decay amplitude, and t^* is the decay constant. Both A and t^* are assumed to be a function of temperature and methane partial pressure.

At the start of the deactivation process, $a = 1$ when $t = 0$. Then, a_0 was calculated to be $1+A$. Hence, Eq. (8.8) becomes

$$a = 1 + A(1 - \exp\left(-\frac{t}{t^*}\right)) \quad (8.9)$$

Three equations (Eqs. (8.6) (8.7) and (8.9)) were used to simulate the activity factor decay process as shown in Figs. 8.10, 8.11 and 8.12. The equations of GPLE model ($d \neq 1$) and exponential decay function were edited in the Origin software. The calculations of the kinetic parameters were carried out by non-linear regression fitting routine implemented in the Origin software. The fitting parameters in GPLE ($d \neq 1$) consist of d and r_d while A and t^* are the parameter to be determined in the exponential decay model.

Fig. 8.10 Activity versus time at 525 °C for different methane partial pressures (a) 0.8 atm, (b) 0.6 atm, (c) 0.4 atm, and (d) 0.2 atm.

Fig. 8.11 Activity versus time at 550 °C for different methane partial pressures (a) 0.8 atm, (b) 0.6 atm, (c) 0.4 atm, and (d) 0.2 atm.

Fig. 8.12 Activity versus time at 575 °C for different methane partial pressures (a) 0.8 atm, (b) 0.6 atm, (c) 0.4 atm, and (d) 0.2 atm.

From the results in Figs. 8.10, 8.11 and 8.12, it is obvious that the GPLE model ($d=1$) does not fit the experimental results. The fitting parameters are summarized in Tables 8.1 and 8.2. By comparing the values of R^2 in Figs. 8.10, 8.11 and 8.12, it is obvious that the

exponential decay model provides the best fits to the experimental data for most of the reaction temperatures and partial pressures studied. Furthermore, the d value which is usually a positive number, was found to be a negative value and the best fitted value varied for different reaction temperatures and methane partial pressures. The experimental study here concludes that the conventional GPLE model cannot explain the deactivation mechanism of unsupported nickel catalysts.

Table 8.1 Decay amplitude, decay constant and coefficient of determination R^2 for the Exponential Decay Model at different temperatures and methane partial pressures

Temperature(°C)	P_{CH_4}	A	t^*	R^2
525	0.8	0.00209	110.1	0.986
	0.6	0.00235	121.9	0.986
	0.4	0.0091	135.3	0.925
	0.2	0.02591	160.9	0.951
550	0.8	0.00379	65.98	0.961
	0.6	0.00646	70.7743	0.950
	0.4	0.0184	86.49	0.953
	0.2	0.0504	111.4	0.967
575	0.8	0.0052	30.8	0.982
	0.6	0.00255	37.7	0.972
	0.4	0.0232	43.4	0.974
	0.2	0.07257	62.0	0.974

Table 8.2 Deactivation order, deactivation function and coefficient of determination R^2 for the General Power law Equation ($d \neq 1$) at different temperatures and methane partial pressures

Temperature(°C)	P_{CH_4}	d	r_d	R^2
525	0.8	-7.65	0.000192	0.618
	0.6	-3.6	0.000306	0.867
	0.4	-3.4	0.000383	0.924
	0.2	-3.8	0.000404	0.942
550	0.8	-5.17	0.000478	0.929
	0.6	-5.21	0.000502	0.861
	0.4	-5.46	0.000529	0.679
	0.2	-3.2	0.000834	0.912
575	0.8	-9.59	0.00067	0.682
	0.6	-5.26	0.00113	0.764
	0.4	-4.6	0.0013	0.683
	0.2	-3.02	0.00181	0.995

In the exponential decay model, i.e, equation 8.10, A is the decay amplitude, and t^* is the decay constant. As shown in Table 8.1, with increasing partial pressure, the decay amplitude and decay constant decreased. In this equation, a large decay amplitude and a small decay constant will lead to a large activity decay factor. Under a high methane partial pressure, the decay amplitude value is small. This phenomenon is ascribed as the dispersing effect. As discussed in Chapters 4 and 5, for unsupported nickel catalyst,

methane acts as a stabilizing agent as it can disperse the nickel catalysts into nano particles rapidly by growing CNTs or CNFs. This was confirmed by the higher activity of the catalyst under higher methane partial pressure at the beginning of the test. However, the TEM micrographs of the total deactivated catalysts (Fig. 8.9) showed that the collisions between two catalyst particles or between the catalysts and the ends of the CNFs, caused the deactivation of the catalysts. This could be due to the decrease of free space for the growth of CNFs, thereby increasing the probability of collisions. An abrupt deactivation was usually observed under high methane partial pressure probably due to high carbon yield and the tremendous shrinkage of free space. Hence, the deactivation of unsupported catalyst was influenced by its initial dispersion and the limited growing space.

In order to quantify the relationship between the kinetic parameters (A and t^*) and the reaction conditions (methane partial pressure and reaction temperature), various equation forms had been attempted. A linear relationship between the logarithmic form of parameters (A , t^*) and the methane partial pressure was found to fit the experimental data well with a correlation coefficients of higher than 0.94 for $\ln A$ vs $\ln P_{\text{CH}_4}$ in Fig. 8.13 and 0.98 for $\ln t^*$ vs $\ln P_{\text{CH}_4}$ in Fig. 8.14.

Fig. 8.13 Logarithmic decay amplitude A versus logarithmic methane partial pressure at different reaction temperatures

Fig. 8.14 Logarithmic decay constant t^* versus logarithmic methane partial pressure at different reaction temperatures

Reaction temperatures were also correlated to the slope and intercept of the fitted lines in Figs. 8.13 and 8.14. The values of the slope and intercept were found to be linearly dependent on the reaction temperature and the best fitted equations are as follows:

$$\ln A = (-0.0028T + 4.2025) \ln P_{CH_4} + 0.0168T - 14.239 \quad (8.10)$$

$$\ln t^* = (-0.0044T + 3.2164) \ln P_{CH_4} + 0.0132T + 16.034 \quad (8.11)$$

Therefore, the activity a can be expressed as

$$a = 1 + e^{0.0253T - 26.849} P^{(0.00287T - 4.208)} \left(1 - \frac{t^*}{e^{-0.0262T + 25.621} P^{(-0.0044T + 3.2)}} \right) \quad (8.12)$$

Hence, the transient hydrogen formation rate can be derived as

$$r = r_{\max} a = 1047.3 \cdot e^{-7872/T} P_{CH_4}^{0.628} \left[1 + e^{0.0253T - 26.849} P^{(0.00287T - 4.208)} \left(1 - \frac{t^*}{e^{-0.0262T + 25.621} P^{(-0.0044T + 3.2)}} \right) \right] \quad (8.13)$$

The developed model was validated by comparing the transient hydrogen formation rate in Eq. 8.13 with the experimental data as shown in Fig. 8.15.

Fig. 8.15 Hydrogen formation rate versus reaction time for different methane partial pressures at reaction temperatures of (a) 525 °C, (b) 550 °C, and (c) 575 °C: solid line – experimental data; dash line – activity calculated from Eq. 8.13

The percent mean deviation (MD) between the catalyst H₂ formation rate as calculated from Eq. 8.13 and the experimental data was obtained using the following relation:

$$MD = \frac{\sum_{i=1}^N \left| \frac{\text{calculated from model} - \text{experimental data}}{\text{calculated from the model}} \right|}{N} * 100 \quad (8.14)$$

where N is the number of data points in each batch of experiment. The results of the MD calculations are shown in Table 8.3. The model predictions of the catalyst hydrogen formation rate were in good agreement with the experimental data. The MD was lower than 10% in most of the conditions used in this study.

Table 8.3. Mean deviation between the experimental and model results of catalyst hydrogen formation rate under different operating conditions

Operation conditions		Mean Deviation (MD %)
Reaction temperature (°C)	Methane partial pressure (atm)	
525	0.8	9.69
	0.6	3.92
	0.4	6.57
	0.2	4.48
550	0.8	9.08
	0.6	3.16
	0.4	3.36
	0.2	4.10
575	0.8	8.60
	0.6	9.00
	0.4	10.60
	0.2	8.65

8.4 Deactivation mechanism of Ni-Cu-Co alloy catalysts

The additions of copper and cobalt had totally changed the structure of the Ni catalyst. Due to the octopus-like structures of the deposited carbon, it is surmised that the branches of the CNFs will prevent the collisions of the catalyst particles. This was confirmed by

the TEM micrographs of the deactivated 2Ni-1Cu-1Co catalysts as shown in Fig. 8.16.

Fig. 8.16 Spent 2Ni-1Cu-1Co catalysts after complete deactivation for $P_{CH_4} = 0.2$ under different reaction temperatures of (a) 650 °C, (b) 700 °C, and (c) 750 °C (insets: high magnification)

Fig. 8.17 TEM micrographs of 2Ni-1Cu-1Co catalysts after reaction for 10 min for $P_{CH_4} = 0.2$ at different reaction temperatures of (a) 650 °C, (b) 700 °C, and (c) 750 °C

Fig. 8.17 shows the catalyst structures in the first 10 mins of the reaction under different reaction temperatures. With increasing reaction temperature, the catalyst particle size increased greatly due to the sintering effect under higher temperature. During the reaction, octopus-like carbons were obtained using Ni-Cu or Ni-Cu-Co catalysts with the catalyst particles located in the centre (inset of Fig. 8.17 (c)). However, the deposited carbons

after the complete deactivation of the catalyst (2Ni-1Cu-1Co) exhibited different morphologies as shown in Fig. 8.16. The spherical catalyst particles and the octopus-like carbon fibres were hardly observed. Instead, straight carbon fibers with dispersed metal fragments (black dots) were observed. This was explained as the catalyst atomic erosion existing in the Ni-Cu system [26]. From the observations in this study, the Ni-Cu or Ni-Cu-Co alloy catalysts underwent a fragmentation process due to the growth of CNFs. This is probably because carbon dissolution and diffusion in copper is very negligible [74] and the selective diffusion path of the carbon leads to a fragmentation of the catalyst particles which finally lead to catalyst deactivation. For this reason, catalyst particles were barely found in the deactivated Ni-Cu-Co catalysts as they were widely scattered in the CNFs.

8.5 Summary

A series of kinetic experiments had been conducted using two types of catalysts (Ni and 2Ni-1Cu-1Co). The effects of methane partial pressure and reaction temperatures on the maximal hydrogen formation rate were studied. The reaction order and activation energy were found to be 0.63 and 65.4 kJ mol⁻¹ for Ni catalyst, and 0.76 and 59.4 kJ mol⁻¹ for 2Ni-1Cu-1Co catalyst.

Based on the TEM micrographs and the evidence of a progressive deactivation of catalyst, the widely used empirical model (General Power Law Equation) and a phenomenal model (Exponential Decay Model) were used to fit the experimental results of Ni catalysts. By comparing the R^2 , it was found that the exponential decay model provided

the best fits to the experimental data for most of the reaction temperatures and partial pressures studied. It was proposed that the deactivation of unsupported catalyst was influenced by its initial dispersion and the limiting growing space. By quantifying the relationship between the kinetic parameters and the reaction conditions (methane partial pressure and reaction temperature), transient hydrogen formation rate over the reaction time was derived and validated by comparing with the experimental data. The percent mean deviation between the model and the experimental data was lower than 10% in most of the conditions used in this study.

The mechanism of deactivation of 2Ni-1Cu-1Co was different from that of pure Ni catalyst. Due to the octopus-like structures of the deposited carbon, it is surmised that the branches of the CNFs will prevent the collisions of the catalyst particles. Similar to the Ni-Cu system, 2Ni-1Cu-1Co underwent a fragmentation process during the growth of CNFs, probably due to the selective diffusion path of the carbon.

Chapter 9 Conclusions

Main conclusions based on this project can be drawn as follows:

(1) Unsupported NiO and NiO-CuO particles with promising catalytic activity for methane decomposition were prepared by a facile method. The decomposition of fibrous oxalate precursors resulted in the formation of porous oxide aggregates: NiO and NiO-CuO (surface area of 40 to 60 m²/g) with small primary particles (8-20 nm). When compared with conventional supported catalyst, these porous oxide aggregates required significant lower temperature in the reduction to become metallic state. Unlike the supported catalysts, it was vital to introduce methane to the reactor at lower temperature to avoid the catalysts from sintering into bigger particles. The initial CNFs acted as transporting agents and supports to take individual catalyst particles away and prevent them from sintering with adjacent particles. The unsupported Ni catalyst showed stable activity at a reaction temperature of 500 °C whereas the unsupported Ni-Cu catalyst exhibited stable activity for a wider temperature range of 500 to 750 °C.

(2) Unsupported metallic nickel particles with promising catalytic activity were prepared by the decomposition of nickel oxalate in methane atmosphere. The preparation condition was systematically studied and optimized. With increasing concentration of reactant, the nickel oxalate particles varied from nano-sheets to nano-rods and finally to nano-needles. The effect of the reducing atmosphere was also investigated and it was found that the addition of methane gas in the nitrogen stream could lead to the formation

of small dispersed nickel particles but of similar crystalline size as those of pure nitrogen stream. Slower ramp-up rate led to higher methane conversion rate. The self-regulating system allowed the formation of active nickel particles and CNFs with different sizes for different temperatures.

(3) A series of Ni-Cu alloy particles with different atomic ratios of Ni/Cu were prepared by the thermal decomposition of fibrous Ni-Cu oxalate precursors in methane atmosphere. The highest methane conversion of about 82% was achieved for a Ni-Cu alloy catalyst with 62.5% nickel content at a reaction temperature of 750 °C. The ratios of Ni/Cu were found to influence the morphology of the Ni-Cu oxalate, the crystalline size of alloys and accordingly the catalytic activity and stability. With increasing copper content, the catalyst stability had been improved but further continual increase in the copper content from 56.25% to 62.5% led to an abrupt decrease in the stability. This was firstly found related to the morphology of the catalyst particle. At a high reaction temperature (700 °C), small particles (30-40 nm) produced the highest conversion rate. However, at a higher temperature (750 °C), the small particles were affected and produced poorer stability and decreased catalytic activity due to the appearance of quasi-liquid state catalyst. In contrast, when the copper content was more than 25%, the morphology of the catalyst particle dominated its performance. The addition of an appropriate amount of copper (25%-50%) led to the formation of isometric, round and large catalyst particles (150-400) nm with many small facets which resulted in the formation of octopus-shaped nano-carbons. But, if the content of copper was too high (>50%), the catalyst particles became conical and elongated with thicker CNFs forming on the curved facets. This type

of catalyst particles were found to be deactivated more easily and were gradually encapsulated by the growing CNFs.

(4) A series of unsupported Ni-Cu-Co alloy particles with promising catalytic activity were firstly prepared by thermal decomposition of Ni-Cu-Co oxalates in methane atmosphere. With increasing cobalt content, the catalyst stability at higher had improved but further continual increase of cobalt content led to a phase separation. In general, given the same copper content, the addition of cobalt would improve the stability of the catalyst at a higher reaction temperature such as at 750 °C. This was probably because cobalt has a higher melting point temperature than nickel and copper, which would therefore delay the occurrence of the quasi-liquid state. It was found that, without nickel, cobalt and copper could not remain in the stable alloy state in the reaction and would be deactivated easily due to carbon encapsulation.

(5) Two deactivation mechanisms were proposed for these unsupported catalysts. Based on direct observations, it was proposed that collisions between two Ni catalyst particles or between Ni particles and CNFs might be a reason contributing to catalyst deactivation as a result of a limit on growth space. For Ni-Cu and Ni-Co-Cu, the long term activity evaluation of the catalyst showed that stable catalysts, under certain conditions, could suffer deactivation gradually due to a fragmentation process. Carbon dissolution and diffusion in copper are negligible when compared with nickel and cobalt which probably lead to the selective diffusion of carbon in the bulk of the Ni-Cu or Ni-Co-Cu alloy catalysts. This unique kind of carbon migration in Ni-Cu alloy particles

would cause distortion in the catalyst bulk which probably led to fragmentation, e.g. splitting or tearing of the metal particles into smaller inactive units and deactivation gradually.

(6) A series of kinetic experiments had been conducted using two types of catalysts (Ni and Ni-Cu-Co). The effects of methane partial pressure and reaction temperatures on the maximal hydrogen formation rate were studied. The reaction order and activation energy were found to be 0.63 and 65.4 kJ mol⁻¹ for Ni catalyst, and 0.76 and 59.4 kJ mol⁻¹ for 2Ni-1Cu-1Co catalyst. A phenomenal model (Exponential decay) provided the best fits to the experimental data of Ni catalyst for most of the reaction temperatures and partial pressures studied. It was proposed that the deactivation of unsupported catalyst was influenced by its initial dispersion and the limiting growing space. By quantifying the relationship between the kinetic parameters and the reaction conditions (methane partial pressure and reaction temperature), transient hydrogen formation rate over the reaction time was derived and validated by comparing with the experimental data.

Chapter 10 Future studies

The future works to be conducted consist of the following:

- (1) Optimizing the reaction process to achieve high methane conversion and hydrogen yield.

Technically, several approaches can be used:

- (i) The composition of catalyst of Ni-Cu-Co needs to be further optimized to increase the methane conversion
 - (ii) The reactor can be scaled up and more amounts of catalyst can be loaded.
 - (iii) A multi-layered reactor can be designed and fabricated which may increase the final methane conversion rate.
- (2) Fabricating the prototype of electric power generator using integrated fuel cells fuelled with hydrogen produced from methane decomposition.
 - (i) Proton exchange membrane fuel cells (PEMFCs) or solid oxide fuel cells (SOFCs) will be combined with the hydrogen generation set-up.
 - (ii) The power generated will be tested using electrochemical measurements and can be used to run motors, which may be used on-board ship in the future.
 - (iii) The total thermal efficiency of the fossil fuel utilized in the power generation systems will be investigated.

References

- [1]. Karl, T.R., and Trenberth, K.E., Modern Global Climate Change, *Science*, vol. 302, no. 5651, pp. 1719-1723, 2003.
- [2]. Veziroglu, T.N., Hydrogen technology for energy needs of human settlements, *International Journal of Hydrogen Energy*, vol. 12, no. 2, pp. 99-129, 1987.
- [3]. Crowley, T.J., Causes of Climate Change Over the Past 1000 Years, *Science*, vol. 289, no. 5477, pp. 270-277, 2000.
- [4]. Overpeck, J.T., and Cole, J.E., Abrupt Change in Earth's Climate System, *Annual Review of Environment and Resources*, vol. 31, no. 1, pp. 1-31, 2006.
- [5]. Bauen, A., Future energy sources and systems - Acting on climate change and energy security, *Journal of Power Sources*, vol. 157, no. 2, pp. 893-901, 2006.
- [6]. Muradov, N.Z., and Veziroglu, T.N., "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies, *International Journal of Hydrogen Energy*, vol. 33, no. 23, pp. 6804-6839, 2008.
- [7]. Hoffert, M.I., Caldeira, K., Benford, G., Criswell, D.R., Green, C., Herzog, H., Jain, A.K., Kheshgi, H.S., Lackner, K.S., Lewis, J.S., Lightfoot, H.D., Manheimer, W., Mankins, J.C., Mauel, M.E., Perkins, L.J., Schlesinger, M.E., Volk, T., and Wigley, T.M.L., Advanced technology paths to global climate stability: Energy for a greenhouse planet, *Science*, vol. 298, no. 5595, pp. 981-987, 2002.
- [8]. Li, Y.D., Li, D.X., and Wang, G.W., Methane decomposition to CO_x-free hydrogen and nano-carbon material on group 8-10 base metal catalysts: A review, *Catalysis Today*, vol. 162, no. 1, pp. 1-48, 2011.
- [9]. Abraham, S., The Bush Administration's Approach to Climate Change, *Science*, vol. 305, no. 5684, pp. 616-617, 2004.
- [10]. Rostrup-Nielsen, J.R., Fuels and energy for the future: The role of catalysis, *Catalysis Reviews - Science and Engineering*, vol. 46, no. 3-4, pp. 247-270, 2004.
- [11]. Song, C., Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century, *Catalysis*

Today, vol. 77, no. 1-2, pp. 17-49, 2002.

[12]. Ming, A. *The challenges and opportunities of the hydrogen storage*. in *2005 AIChE Spring National Meeting, Conference Proceedings*. 2005.

[13]. Dunn, S., Hydrogen futures: Toward a sustainable energy system, *International Journal of Hydrogen Energy*, vol. 27, no. 3, pp. 235-264, 2002.

[14]. Navarro, R.M., Pena, M.A., and Fierro, J.L.G., Hydrogen production reactions from carbon feedstocks: Fossil fuels and biomass, *Chemical Reviews*, vol. 107, no. 10, pp. 3952-3991, 2007.

[15]. Han, J., Kim, I.S., and Choi, K.S., Purifier-integrated methanol reformer for fuel cell vehicles, *Journal of Power Sources*, vol. 86, no. 1, pp. 223-227, 2000.

[16]. Jain, I.P., Hydrogen the fuel for 21st century, *International Journal of Hydrogen Energy*, vol. 34, no. 17, pp. 7368-7378, 2009.

[17]. Tanksale, A., Beltramini, J.N., and Lu, G.M., A review of catalytic hydrogen production processes from biomass, *Renewable and Sustainable Energy Reviews*, vol., no., 2009.

[18]. Konieczny, A., Mondal, K., Wiltowski, T., and Dydo, P., Catalyst development for thermocatalytic decomposition of methane to hydrogen, *International Journal of Hydrogen Energy*, vol. 33, no. 1, pp. 264-272, 2008.

[19]. Dufour, J., Serrano, D.P., Gálvez, J.L., Moreno, J., and García, C., Life cycle assessment of processes for hydrogen production. Environmental feasibility and reduction of greenhouse gases emissions, *International Journal of Hydrogen Energy*, vol. 34, no. 3, pp. 1370-1376, 2009.

[20]. Seo, J.G., Youn, M.H., and Song, I.K., Hydrogen production by steam reforming of liquefied natural gas (LNG) over nickel catalyst supported on mesoporous alumina prepared by a non-ionic surfactant-templating method, *International Journal of Hydrogen Energy*, vol. 34, no. 4, pp. 1809-1817, 2009.

[21]. Moon, D.J., Hydrogen Production by Catalytic Reforming of Gaseous Hydrocarbons (Methane & LPG), *Catalysis Surveys from Asia*, vol., no., pp. 1-15, 2008.

[22]. Amin, A.M., Croiset, E., and Epling, W., Review of methane catalytic cracking for hydrogen production, *International Journal of Hydrogen Energy*, vol. 36, no. 4, pp.

2904-2935, 2011.

[23]. Shah, N., Ma, S.K., Wang, Y.G., and Huffman, G.P., Semi-continuous hydrogen production from catalytic methane decomposition using a fluidized-bed reactor, *International Journal of Hydrogen Energy*, vol. 32, no. 15, pp. 3315-3319, 2007.

[24]. Latorre, N., Cazana, F., Martinez-Hansen, V., Royo, C., Romeo, E., and Monzon, A., Ni-Co-Mg-Al catalysts for hydrogen and carbonaceous nanomaterials production by CCVD of methane, *Catalysis Today*, vol. 172, no. 1, pp. 143-151, 2011.

[25]. Ermakova, M.A., Ermakov, D.Y., Kuvshinov, G.G., and Plyasova, L.M., New Nickel Catalysts for the Formation of Filamentous Carbon in the Reaction of Methane Decomposition, *Journal of Catalysis*, vol. 187, no. 1, pp. 77-84, 1999.

[26]. Avdeeva, L.B., Goncharova, O.V., Kochubey, D.I., Zaikovskii, V.I., Plyasova, L.M., Novgorodov, B.N., and Shaikhutdinov, S.K., Coprecipitated Ni-alumina and Ni-Cu-alumina catalysts of methane decomposition and carbon deposition. II. Evolution of the catalysts in reaction, *Applied Catalysis A: general*, vol. 141, no. 1-2, pp. 117-129, 1996.

[27]. Toebe, M.L., Bitter, J.H., van Dillen, A.J., and de Jong, K.P., Impact of the structure and reactivity of nickel particles on the catalytic growth of carbon nanofibers, *Catalysis Today*, vol. 76, no. 1, pp. 33-42, 2002.

[28]. Li, Y., Zhang, B., Xie, X., Liu, J., Xu, Y., and Shen, W., Novel Ni catalysts for methane decomposition to hydrogen and carbon nanofibers, *Journal of Catalysis*, vol. 238, no. 2, pp. 412-424, 2006.

[29]. Cunha, A.F., Orfao, J.J.M., and Figueiredo, J.L., Catalytic decomposition of methane on Raney-type catalysts, *Applied Catalysis A: general*, vol. 348, no. 1, pp. 103-112, 2008.

[30]. Li, Y., Zhang, B., Tang, X., Xu, Y., and Shen, W., Hydrogen production from methane decomposition over Ni/CeO₂ catalysts, *catalysis communications*, vol. 7, no. 6, pp. 380-386, 2006.

[31]. Ferreira-Aparicio, P., Rodríguez-Ramos, I., and Guerrero-Ruiz, A., Methane interaction with silica and alumina supported metal catalysts, *Applied Catalysis A: general*, vol. 148, no. 2, pp. 343-356, 1997.

- [32]. Choudhary, T.V., Sivadinarayana, C., Chusuei, C.C., Klinghoffer, A., and Goodman, D.W., Hydrogen production via catalytic decomposition of methane, *Journal of Catalysis*, vol. 199, no. 1, pp. 9-18, 2001.
- [33]. Igarashi, H., Murakami, H., Murakami, Y., Maruyama, S., and Nakashima, N., Purification and characterization of zeolite-supported single-walled carbon nanotubes catalytically synthesized from ethanol, *Chemical Physics Letters*, vol. 392, no. 4-6, pp. 529-532, 2004.
- [34]. Chungchamroenkit, P., Chavadej, S., Yanatatsaneejit, U., and Kitiyanan, B., Residue catalyst support removal and purification of carbon nanotubes by NaOH leaching and froth flotation, *Separation and Purification Technology*, vol. 60, no. 2, pp. 206-214, 2008.
- [35]. Hassmann, K., and Kuhne, H.M., Primary energy sources for hydrogen production, *International Journal of Hydrogen Energy*, vol. 18, no. 8, pp. 635-640, 1993.
- [36]. Kothari, R., Buddhi, D., and Sawhney, R.L., Comparison of environmental and economic aspects of various hydrogen production methods, *Renewable & Sustainable Energy Reviews*, vol. 12, no. 2, pp. 553-563, 2008.
- [37]. Balat, M., Possible Methods for Hydrogen Production, *Energy Sources Part a-Recovery Utilization and Environmental Effects*, vol. 31, no. 1, pp. 39-50, 2009.
- [38]. Lunsford, J.H., Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century, *Catalysis Today*, vol. 63, no. 2-4, pp. 165-174, 2000.
- [39]. Rostrupnielsen, J.R., Catalysis and large scale conversion of natural gas, *Catalysis Today*, vol. 21, no. 2-3, pp. 257-267, 1994.
- [40]. Steinberg, M., and Cheng, H.C., Modern and prospective technologies for hydrogen production from fossil fuels, *International Journal of Hydrogen Energy*, vol. 14, no. 11, pp. 797-820, 1989.
- [41]. Ogden, J.M., Prospects for building a hydrogen energy infrastructure, *Annual Review of Energy and the Environment*, vol. 24, no., pp. 227-279, 1999.
- [42]. Steinberg, M., Fossil fuel decarbonization technology for mitigating global warming, *International Journal of Hydrogen Energy*, vol. 24, no. 8, pp. 771-777, 1999.

- [43]. Seo, Y.S., Shirley, A., and Kolaczowski, S.T., Evaluation of thermodynamically favourable operating conditions for production of hydrogen in three different reforming technologies, *Journal of Power Sources*, vol. 108, no. 1-2, pp. 213-225, 2002.
- [44]. Choudhary, V.R., Rajput, A.M., and Prabhakar, B., Nonequilibrium Oxidative Conversion of Methane to CO and H₂ with High Selectivity and Productivity over Ni/Al₂O₃ at Low Temperatures, *Journal of Catalysis*, vol. 139, no. 1, pp. 326-328, 1993.
- [45]. Rostrup-Nielsen, J.R., New aspects of syngas production and use, *Catalysis Today*, vol. 63, no. 2-4, pp. 159-164, 2000.
- [46]. O'Connor, A.M., Schuurman, Y., Ross, J.R.H., and Mirodatos, C., Transient studies of carbon dioxide reforming of methane over Pt/ZrO₂ and Pt/Al₂O₃, *Catalysis Today*, vol. 115, no. 1-4, pp. 191-198, 2006.
- [47]. Laosiripojana, N., Sutthisripok, W., and Assabumrungrat, S., Synthesis gas production from dry reforming of methane over CeO₂ doped Ni/Al₂O₃: Influence of the doping ceria on the resistance toward carbon formation, *Chemical Engineering Journal*, vol. 112, no. 1-3, pp. 13-22, 2005.
- [48]. Laosiripojana, N., and Assabumrungrat, S., Catalytic dry reforming of methane over high surface area ceria, *Applied Catalysis B: Environmental*, vol. 60, no. 1-2, pp. 107-116, 2005.
- [49]. Tsyganok, A.I., Tsunoda, T., Hamakawa, S., Suzuki, K., Takehira, K., and Hayakawa, T., Dry reforming of methane over catalysts derived from nickel-containing Mg-Al layered double hydroxides, *Journal of Catalysis*, vol. 213, no. 2, pp. 191-203, 2003.
- [50]. Tsyganok, A.I., Inaba, M., Tsunoda, T., Hamakawa, S., Suzuki, K., and Hayakawa, T., Dry reforming of methane over supported noble metals: A novel approach to preparing catalysts, *catalysis communications*, vol. 4, no. 9, pp. 493-498, 2003.
- [51]. Ferreira-Aparicio, P., Rodríguez-Ramos, I., Anderson, J.A., and Guerrero-Ruiz, A., Mechanistic aspects of the dry reforming of methane over ruthenium catalysts, *Applied Catalysis A: general*, vol. 202, no. 2, pp. 183-196, 2000.
- [52]. Muradov, N., Hydrogen via methane decomposition: an application for decarbonization of fossil fuels, *International Journal of Hydrogen Energy*, vol. 26, no. 11,

pp. 1165-1175, 2001.

- [53]. Kirk-Othmer, Encyclopedia of chemical Technology, *wiley*, vol. 4, no. 631, 1992.
- [54]. Dean, A.M., Detailed kinetic modeling of autocatalysis in methane pyrolysis, *Journal of Physical Chemistry*, vol. 94, no. 4, pp. 1432-1439, 1990.
- [55]. Chen, C.J., Back, M.H., and Back, R.A., Mechanism of the thermal decomposition of methane, *ACS Symposium Series*, vol., no. 32, pp. 1-16, 1976.
- [56]. Holmen, A., Olsvik, O., and Rokstad, O.A., Pyrolysis of natural gas: chemistry and process concepts, *Fuel Processing Technology*, vol. 42, no. 2-3, pp. 249-267, 1995.
- [57]. Choudhary, T.V., and Goodman, D.W., CO-free production of hydrogen via stepwise steam reforming of methane, *Journal of Catalysis*, vol. 192, no. 2, pp. 316-321, 2000.
- [58]. Ahmed, S., Aitani, A., Rahman, F., Al-Dawood, A., and Al-Muhaish, F., Decomposition of hydrocarbons to hydrogen and carbon, *Applied Catalysis a-General*, vol. 359, no. 1-2, pp. 1-24, 2009.
- [59]. Abbas, H.F., and Daud, W., Hydrogen production by methane decomposition: A review, *International Journal of Hydrogen Energy*, vol. 35, no. 3, pp. 1160-1190, 2010.
- [60]. Fer, I., and Haugan, P.M., Dissolution from a liquid CO₂ lake disposed in the deep ocean, *Limnology and Oceanography*, vol. 48, no. 2, pp. 872-883, 2003.
- [61]. Bonura, G., Di Blasi, O., Spadaro, L., Arena, F., and Frusteri, F., A basic assessment of the reactivity of Ni catalysts in the decomposition of methane for the production of "CO_x-free" hydrogen for fuel cells application, *Catalysis Today*, vol. 116, no. 3, pp. 298-303, 2006.
- [62]. Metkemeijer, R., and Achard, P., Ammonia as a feedstock for a hydrogen fuel cell reformer and fuel cell behavior, *Journal of Power Sources*, vol. 49, no. 1-3, pp. 271-282, 1994.
- [63]. Choudhary, T.V., Sivadinarayana, C., and Goodman, D.W., Catalytic ammonia decomposition: CO_x-free hydrogen production for fuel cell applications, *Catalysis Letters*, vol. 72, no. 3-4, pp. 197-201, 2001.
- [64]. Liu, H.C., Wang, H., Shen, J.G., Sun, Y., and Liu, Z.M., Preparation, characterization and activities of the nano-sized Ni/SBA-15 catalyst for producing CO_x-

- free hydrogen from ammonia, *Applied Catalysis a-General*, vol. 337, no. 2, pp. 138-147, 2008.
- [65]. Garcia-Garcia, F.R., Ma, Y.H., Rodriguez-Ramos, I., and Guerrero-Ruiz, A., High purity hydrogen production by low temperature catalytic ammonia decomposition in a multifunctional membrane reactor, *catalysis communications*, vol. 9, no. 3, pp. 482-486, 2008.
- [66]. Halseid, R., Vie, P.J.S., and Tunold, R., Effect of ammonia on the performance of polymer electrolyte membrane fuel cells, *Journal of Power Sources*, vol. 154, no. 2, pp. 343-350, 2006.
- [67]. Uribe, F.A., Gottesfeld, S., and Zawodzinski, T.A., Effect of ammonia as potential fuel impurity on proton exchange membrane fuel cell performance, *Journal of the Electrochemical Society*, vol. 149, no. 3, pp. A293-A296, 2002.
- [68]. Choudhary, V.R., Banerjee, S., and Rajput, A.M., Hydrogen from step-wise steam reforming of methane over Ni/ZrO₂: factors affecting catalytic methane decomposition and gasification by steam of carbon formed on the catalyst, *Applied Catalysis a-General*, vol. 234, no. 1-2, pp. 259-270, 2002.
- [69]. Hughes., T.V., and Chambers, C.R., Manufacture of carbon filaments, *U.S. Patent*, vol. 405,480, no., 1889.
- [70]. Radushkevich, L., and Lukyanovich, V., obrazujucesja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte, *Zhurn. fisic. Chim*, vol. 26, no., pp. 88, 1952.
- [71]. Mi, W., Lin, Y.S., and Li, Y., Vertically aligned carbon nanotube membranes on macroporous alumina supports, *Journal of Membrane Science*, vol. 304, no. 1-2, pp. 1-7, 2007.
- [72]. De Jong, K.P., and Geus, J.W., Carbon nanofibers: Catalytic synthesis and applications, *Catalysis Reviews-science and Engineering*, vol. 42, no. 4, pp. 481-510, 2000.
- [73]. Tessonnier, J.P., and Su, D.S., Recent Progress on the Growth Mechanism of Carbon Nanotubes: A Review, *Chemsuschem*, vol. 4, no. 7, pp. 824-847, 2011.
- [74]. Moisala, A., Nasibulin, A.G., and Kauppinen, E.I., The role of metal nanoparticles

- in the catalytic production of single-walled carbon nanotubes - a review, *Journal of Physics-Condensed Matter*, vol. 15, no. 42, pp. S3011-S3035, 2003.
- [75]. Rodriguez, N.M., Chambers, A., and Baker, R.T.K., Catalytic engineering of carbon nanostructures, *Langmuir*, vol. 11, no. 10, pp. 3862-3866, 1995.
- [76]. MacKenzie, K.J., Dunens, O.M., and Harris, A.T., An Updated Review of Synthesis Parameters and Growth Mechanisms for Carbon Nanotubes in Fluidized Beds, *Industrial & Engineering Chemistry Research*, vol. 49, no. 11, pp. 5323-5338, 2010.
- [77]. Li, Y.D., Chen, J.L., Qin, Y.N., and Chang, L., Simultaneous production of hydrogen and nanocarbon from decomposition of methane on a nickel-based catalyst, *Energy & Fuels*, vol. 14, no. 6, pp. 1188-1194, 2000.
- [78]. Baker, R.T.K., and Waite, R.J., Formation of carbonaceous deposits from platinum-iron catalyzed decomposition of acetylene, *Journal of Catalysis*, vol. 37, no. 1, pp. 101-105, 1975.
- [79]. Baker, R.T.K., Harris, P.S., Thomas, R.B., and Waite, R.J., Formation of filamentous carbon from iron, cobalt and chromium catalyzed decomposition of acetylene, *Journal of Catalysis*, vol. 30, no. 1, pp. 86-95, 1973.
- [80]. Baker, R.T.K., Barber, M.A., Harris, P.S., Feates, F.S., and Waite, R.J., Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene, *Journal of Catalysis*, vol. 26, no. 1, pp. 51-62, 1972.
- [81]. Snoeck, J.W., Froment, G.F., and Fowles, M., Filamentous carbon formation and gasification: Thermodynamics, driving force, nucleation, and steady-state growth, *Journal of Catalysis*, vol. 169, no. 1, pp. 240-249, 1997.
- [82]. Helveg, S., López-Cartes, C., Sehested, J., Hansen, P.L., Clausen, B.S., Rostrup-Nielsen, J.R., Abild-Pedersen, F., and Nørskov, J.K., Atomic-scale imaging of carbon nanofibre growth, *Nature*, vol. 427, no. 6973, pp. 426-429, 2004.
- [83]. Helveg, S., and Hansen, P.L., Atomic-scale studies of metallic nanocluster catalysts by in situ high-resolution transmission electron microscopy, *Catalysis Today*, vol. 111, no. 1-2, pp. 68-73, 2006.
- [84]. Dupuis, A.C., The catalyst in the CCVD of carbon nanotubes - a review, *Progress in Materials Science*, vol. 50, no. 8, pp. 929-961, 2005.

- [85]. Yang, R.T., and Chen, J.P., Mechanis of carbon filament growth on metal catalysts, *Journal of Catalysis*, vol. 115, no. 1, pp. 52-64, 1989.
- [86]. Beebe, T.P., Goodman, D.W., Kay, B.D., and Yates, J.T., Kinetics of the activated dissociative adsorption of methane on the low index palens of nickel single crystal surfaces, *Journal of Chemical Physics*, vol. 87, no. 4, pp. 2305-2315, 1987.
- [87]. Swang, O., Faegri, K., Groppen, O., Wahlgren, U., and Siegbahn, P., A theoretical study of the chemisorption of methane on a Ni (100) surface, *Chemical Physics*, vol. 156, no. 3, pp. 379-386, 1991.
- [88]. Lai, W.Z., Xie, D.Q., and Zhang, D.H., First-principles study of adsorption of methyl, coadsorption of methyl and hydrogen, and methane dissociation on Ni(100), *Surface Science*, vol. 594, no. 1-3, pp. 83-92, 2005.
- [89]. Henkelman, G., Arnaldsson, A., and Jonsson, H., Theoretical calculations of CH₄ and H₂ associative desorption from Ni(111): Could subsurface hydrogen play an important role?, *Journal of Chemical Physics*, vol. 124, no. 4, 2006.
- [90]. Watwe, R.M., Bengaard, H.S., Rostrup-Nielsen, J.R., Dumesic, J.A., and Norskov, J.K., Theoretical studies of stability and reactivity of CH_x species on Ni(111), *Journal of Catalysis*, vol. 189, no. 1, pp. 16-30, 2000.
- [91]. Zhu, Y.A., Dai, Y.C., Chen, D., and Yuan, W.K., First-principles calculations of CH₄ dissociation on Ni(100) surface along different reaction pathways, *Journal of Molecular Catalysis A-chemical*, vol. 264, no. 1-2, pp. 299-308, 2007.
- [92]. Nielsen, B.O., Luntz, A.C., Holmblad, P.M., and Chorkendorff, I., Activated dissociative chemisorption of methane on Ni(100): A direct mechnism under thermal conditions., *Catalysis Letters*, vol. 32, no. 1-2, pp. 15-30, 1995.
- [93]. Egeberg, R.C., Ullmann, S., Alstrup, I., Mullins, C.B., and Chorkendoff, I., Dissociation of CH₄ on Ni(111) and Ru(0001), *Surface Science*, vol. 497, no. 1-3, pp. 183-193, 2002.
- [94]. Wirth, C.T., Hofmann, S., and Robertson, J., State of the catalyst during carbon nanotube growth, *Diamond and Related Materials*, vol. 18, no. 5-8, pp. 940-945, 2009.
- [95]. Hofmann, S., Csanyi, G., Ferrari, A.C., Payne, M.C., and Robertson, J., Surface diffusion: The low activation energy path for nanotube growth, *Physical Review Letters*,

vol. 95, no. 3, 2005.

[96]. Zhu, Y.A., Dai, Y.C., Chen, D., and Yuan, W.K., First-principles study of carbon diffusion in bulk nickel during the growth of fishbone-type carbon nanofibers, *Carbon*, vol. 45, no. 1, pp. 21-27, 2007.

[97]. Rinaldi, A., Tessonnier, J.P., Schuster, M.E., Blume, R., Girgsdies, F., Zhang, Q.A., Jacob, T., Hamid, S.B.A., Su, D.S., and Schlogl, R., Dissolved Carbon Controls the Initial Stages of Nanocarbon Growth, *Angewandte Chemie-International Edition*, vol. 50, no. 14, pp. 3313-3317, 2011.

[98]. Moors, M., Amara, H., de Bocarme, T.V., Bichara, C., Ducastelle, F., Kruse, N., and Charlier, J.C., Early Stages in the Nucleation Process of Carbon Nanotubes, *Acs Nano*, vol. 3, no. 3, pp. 511-516, 2009.

[99]. Rostrup-Nielsen, J., and Trimm, D.L., Mechanisms of carbon formation on nickel-containing catalysts, *Journal of Catalysis*, vol. 48, no. 1-3, pp. 155-165, 1977.

[100]. Holstein, W.L., The roles of ordinary and soret diffusion in the metal catalyzed formation of filamentous carbon, *Journal of Catalysis*, vol. 152, no. 1, pp. 42-51, 1995.

[101]. Takenaka, S., Serizawa, M., and Otsuka, K., Formation of filamentous carbons over supported Fe catalysts through methane decomposition, *Journal of Catalysis*, vol. 222, no. 2, pp. 520-531, 2004.

[102]. Kobayashi, K., Kitaura, R., Kumai, Y., Goto, Y., Imagaki, S., and Shinohara, H., Fabrication of single-wall carbon nanotubes within the channels of a mesoporous material by catalyst-supported chemical vapor deposition, *Carbon*, vol. 47, no. 3, pp. 722-730, 2009.

[103]. Takenaka, S., Ogihara, H., and Otsuka, K., Structural Change of Ni Species in Ni/SiO₂ Catalyst during Decomposition of Methane, *Journal of Catalysis*, vol. 208, no. 1, pp. 54-63, 2002.

[104]. Takenaka, S., Kato, E., Tomikubo, Y., and Otsuka, K., Structural change of Ni species during the methane decomposition and the subsequent gasification of deposited carbon with CO₂ over supported Ni catalysts, *Journal of Catalysis*, vol. 219, no. 1, pp. 176-185, 2003.

[105]. Zhang, T., and Amiridis, M.D., Hydrogen production via the direct cracking of

methane over silica-supported nickel catalysts, *Applied Catalysis A: general*, vol. 167, no. 2, pp. 161-172, 1998.

[106]. Li, Y.D., Chen, J.L., Ma, Y.M., Zhao, J.B., Qin, Y.N., and Chang, L., Formation of bamboo-like nanocarbon and evidence for the quasi-liquid state of nanosized metal particles at moderate temperatures, *Chemical Communications*, vol., no. 12, pp. 1141-1142, 1999.

[107]. Zavarukhin, S.G., and Kuvshinov, G.G., The kinetic model of formation of nanofibrous carbon from CH₄-H₂ mixture over a high-loaded nickel catalyst with consideration for the catalyst deactivation, *Applied Catalysis a-General*, vol. 272, no. 1-2, pp. 219-227, 2004.

[108]. Salmones, J., Wang, J.A., Valenzuela, M.A., Sanchez, E., and Garcia, A., Pore geometry influence on the deactivation behavior of Ni-based catalysts for simultaneous production of hydrogen and nanocarbon, *Catalysis Today*, vol., no.

[109]. Italiano, G., Espro, C., Arena, F., Parmaliana, A., and Frusteri, F., Doped Ni Thin Layer Catalysts for Catalytic Decomposition of Natural Gas to produce hydrogen, *Applied Catalysis a-General*, vol. 365, no. 1, pp. 122-129, 2009.

[110]. Italiano, G., Espro, C., Arena, F., Frusteri, F., and Parmaliana, A., Catalytic decomposition of natural gas for CO_x-free hydrogen production in a structured multilayer reactor, *Applied Catalysis A: general*, vol. 357, no. 1, pp. 58-65, 2009.

[111]. Italiano, G., Espro, C., Arena, F., Frusteri, F., and Parmaliana, A., *Ni thin layer catalysts for making H₂ "CO_x-free" by decomposition of natural gas in a structured multilayer reactor*, in *Studies in Surface Science and Catalysis*. 2006, Elsevier. p. 633-640.

[112]. Frusteri, F., Italiano, G., Espro, C., Cannilla, C., and Bonura, G., H₂ production by methane decomposition: Catalytic and technological aspects, *International Journal of Hydrogen Energy*, vol. 37, no. 21, pp. 16367-16374, 2012.

[113]. Muradov, N.Z., and Veziroglu, T.N., From hydrocarbon to hydrogen-carbon to hydrogen economy, *International Journal of Hydrogen Energy*, vol. 30, no. 3, pp. 225-237, 2005.

[114]. Avdeeva, L.B., Reshetenko, T.V., Ismagilov, Z.R., and Likholobov, V.A., Iron-

containing catalysts of methane decomposition: accumulation of filamentous carbon, *Applied Catalysis A: general*, vol. 228, no. 1–2, pp. 53-63, 2002.

[115]. Ermakova, M.A., and Ermakov, D.Y., Ni/SiO₂ and Fe/SiO₂ catalysts for production of hydrogen and filamentous carbon via methane decomposition, *Catalysis Today*, vol. 77, no. 3, pp. 225-235, 2002.

[116]. Chen, J.L., Zhou, X.Z., Cao, L., and Li, Y.D., CO_x-free hydrogen and carbon nanofibers production by decomposition of methane on Fe, Co and Ni metal catalysts, in *Natural Gas Conversion VII*, X. Bao and Y. Xu, Editors. 2004. p. 73-78.

[117]. Ermakova, M.A., Ermakov, D.Y., and Kuvshinov, G.G., Effective catalysts for direct cracking of methane to produce hydrogen and filamentous carbon Part I. Nickel catalysts, *Applied Catalysis a-General*, vol. 201, no. 1, pp. 61-70, 2000.

[118]. Chen, D., Christensen, K.O., Ochoa-Fernandez, E., Yu, Z.X., Totdal, B., Latorre, N., Monzon, A., and Holmen, A., Synthesis of carbon nanofibers: effects of Ni crystal size during methane decomposition, *Journal of Catalysis*, vol. 229, no. 1, pp. 82-96, 2005.

[119]. Ermakova, M.A., Ermakov, D.Y., Plyasova, L.M., and Kuvshinov, G.G., XRD studies of evolution of catalytic nickel nanoparticles during synthesis of filamentous carbon from methane, *Catalysis Letters*, vol. 62, no. 2-4, pp. 93-97, 1999.

[120]. Takenaka, S., Kobayashi, S., Ogihara, H., and Otsuka, K., Ni/SiO₂ catalyst effective for methane decomposition into hydrogen and carbon nanofiber, *Journal of Catalysis*, vol. 217, no. 1, pp. 79-87, 2003.

[121]. Pinilla, J.L., Suelves, I., Lázaro, M.J., Moliner, R., and Palacios, J.M., Influence of nickel crystal domain size on the behaviour of Ni and NiCu catalysts for the methane decomposition reaction, *Applied Catalysis A: general*, vol. 363, no. 1-2, pp. 199-207, 2009.

[122]. Takenaka, S., Ogihara, H., Yamanaka, I., and Otsuka, K., Decomposition of methane over supported-Ni catalysts: effects of the supports on the catalytic lifetime, *Applied Catalysis A: general*, vol. 217, no. 1-2, pp. 101-110, 2001.

[123]. Takenaka, S., Ishida, M., Serizawa, M., Tanabe, E., and Otsuka, K., Formation of carbon nanofibers and carbon nanotubes through methane decomposition over supported cobalt catalysts, *Journal of Physical Chemistry B*, vol. 108, no. 31, pp. 11464-11472,

2004.

[124]. Suelves, I., Lázaro, M.J., Moliner, R., Echegoyen, Y., and Palacios, J.M., Characterization of NiAl and NiCuAl catalysts prepared by different methods for hydrogen production by thermo catalytic decomposition of methane, *Catalysis Today*, vol. 116, no. 3, pp. 271-280, 2006.

[125]. Echegoyen, Y., Suelves, I., Lázaro, M.J., Sanjuán, M.L., and Moliner, R., Thermo catalytic decomposition of methane over Ni-Mg and Ni-Cu-Mg catalysts: Effect of catalyst preparation method, *Applied Catalysis A: general*, vol. 333, no. 2, pp. 229-237, 2007.

[126]. Chen, J.L., Ma, Q., Rufford, T.E., Li, Y.D., and Zhu, Z.H., Influence of calcination temperatures of Feitknecht compound precursor on the structure of Ni-Al₂O₃ catalyst and the corresponding catalytic activity in methane decomposition to hydrogen and carbon nanofibers, *Applied Catalysis a-General*, vol. 362, no. 1-2, pp. 1-7, 2009.

[127]. Moliner, R., Echegoyen, Y., Suelves, I., Lázaro, M.J., and Palacios, J.M., Ni-Mg and Ni-Cu-Mg catalysts for simultaneous production of hydrogen and carbon nanofibers: The effect of calcination temperature, *International Journal of Hydrogen Energy*, vol. 33, no. 6, pp. 1719-1728, 2008.

[128]. Li, Y., Chen, J., and Chang, L., Catalytic growth of carbon fibers from methane on a nickel-alumina composite catalyst prepared from Feitknecht compound precursor, *Applied Catalysis A: general*, vol. 163, no. 1-2, pp. 45-57, 1997.

[129]. Cunha, A.F., Órfão, J.J.M., and Figueiredo, J.L., Methane decomposition on Ni-Cu alloyed Raney-type catalysts, *International Journal of Hydrogen Energy*, vol. 34, no. 11, pp. 4763-4772, 2009.

[130]. Cunha, A.F., Órfão, J.J.M., and Figueiredo, J.L., Methane decomposition on Fe-Cu Raney-type catalysts, *Fuel Processing Technology*, vol. 90, no. 10, pp. 1234-1240, 2009.

[131]. Rodriguez, N.M., Kim, M.S., and Baker, R.T.K., Deactivation of copper nickel catalysts due to changes in surface composition, *Journal of Catalysis*, vol. 140, no. 1, pp. 16-29, 1993.

[132]. Kim, M.S., Rodriguez, N.M., and Baker, R.T.K., The interaction of hydrocarbons

with copper nickel and nickel in the foramtion of carbon filaments, *Journal of Catalysis*, vol. 131, no. 1, pp. 60-73, 1991.

[133]. Wang, H.Y., and Baker, R.T.K., Decomposition of methane over a Ni-Cu-MgO catalyst to produce hydrogen and carbon nanofibers, *Journal of Physical Chemistry B*, vol. 108, no. 52, pp. 20273-20277, 2004.

[134]. Li, Y., Chen, J., Chang, L., and Qin, Y., The doping effect of copper on the catalytic growth of carbon fibers from methane over a Ni/Al₂O₃ catalyst prepared from feitknecht compound precursor, *Journal of Catalysis*, vol. 178, no. 1, pp. 76-83, 1998.

[135]. Chen, J., Li, Y., Li, Z., and Zhang, X., Production of CO_x-free hydrogen and nanocarbon by direct decomposition of undiluted methane on Ni-Cu-alumina catalysts, *Applied Catalysis A: general*, vol. 269, no. 1-2, pp. 179-186, 2004.

[136]. Li, D., Chen, J., and Li, Y., Evidence of composition deviation of metal particles of a Ni-Cu/Al₂O₃ catalyst during methane decomposition to CO_x-free hydrogen, *International Journal of Hydrogen Energy*, vol. 34, no. 1, pp. 299-307, 2009.

[137]. Shaikhutdinov, S.K., Avdeeva, L.B., Goncharova, O.V., Kochubey, D.I., Novgorodov, B.N., and Plyasova, L.M., Coprecipitated NiAl and NiCuAl catalysts for methane decomposition and carbon deposition I. Genesis of Calcined and reduced catalysts, *Applied Catalysis A: general*, vol. 126, no. 1, pp. 125-139, 1995.

[138]. Shaikhutdinov, S.K., Zaikovskii, V.I., and Avdeeva, L.B., Coprecipitated Ni-alumina and Ni-Cu-alumina catalysts of methane decomposition and carbon deposition .3. Morphology and surface structure of the carbon filaments, *Applied Catalysis a-General*, vol. 148, no. 1, pp. 123-133, 1996.

[139]. Aapg BulletinReshetenko, T.V., Avdeeva, L.B., Ismagilov, Z.R., Chuvilin, A.L., and Ushakov, V.A., Carbon capacious Ni-Cu-Al₂O₃ catalysts for high-temperature methane decomposition, *Applied Catalysis A: general*, vol. 247, no. 1, pp. 51-63, 2003.

[140]. Dussault, L., Dupin, J.C., Guimon, C., Monthieux, M., Latorre, N., Ubieta, T., Romeo, E., Royo, C., and Monzon, A., Development of Ni-Cu-Mg-Al catalysts for the synthesis of carbon nanofibers by catalytic decomposition of methane, *Journal of Catalysis*, vol. 251, no. 1, pp. 223-232, 2007.

[141]. Monzon, A., Latorre, N., Ubieta, T., Royo, C., Romeo, E., Villacampa, J.I.,

Dussault, L., Dupin, J.C., Guimon, C., and Montieux, M., Improvement of activity and stability of Ni-Mg-Al catalysts by Cu addition during hydrogen production by catalytic decomposition of methane, *Catalysis Today*, vol. 116, no. 3, pp. 264-270, 2006.

[142]. Suelves, I., Pinilla, J.L., Lázaro, M.J., Moliner, R., and Palacios, J.M., Effects of reaction conditions on hydrogen production and carbon nanofiber properties generated by methane decomposition in a fixed bed reactor using a NiCuAl catalyst, *Journal of Power Sources*, vol. 192, no. 1, pp. 35-42, 2009.

[143]. Chen, J., Qiao, Y., and Li, Y., Promoting effects of doping ZnO into coprecipitated Ni-Al₂O₃ catalyst on methane decomposition to hydrogen and carbon nanofibers, *Applied Catalysis A: general*, vol. 337, no. 2, pp. 148-154, 2008.

[144]. Shah, N., Panjala, D., and Huffman, G.P., Hydrogen production by catalytic decomposition of methane, *Energy & Fuels*, vol. 15, no. 6, pp. 1528-1534, 2001.

[145]. Shah, N., Wang, Y.G., Panjala, D., and Huffman, G.P., Production of hydrogen and carbon nanostructures by non-oxidative catalytic dehydrogenation of ethane and propane, *Energy & Fuels*, vol. 18, no. 3, pp. 727-735, 2004.

[146]. Wang, Y.G., Shah, N., and Huffman, G.P., Simultaneous production of hydrogen and carbon nanostructures by decomposition of propane and cyclohexane over alumina supported binary catalysts, *Catalysis Today*, vol. 99, no. 3-4, pp. 359-364, 2005.

[147]. Takenaka, S., Shigeta, Y., Tanabe, E., and Otsuka, K., Methane decomposition into hydrogen and carbon nanofibers over supported Pd-Ni catalysts: Characterization of the catalysts during the reaction, *Journal of Physical Chemistry B*, vol. 108, no. 23, pp. 7656-7664, 2004.

[148]. Takenaka, S., Shigeta, Y., Tanabe, E., and Otsuka, K., Methane decomposition into hydrogen and carbon nanofibers over supported Pd-Ni catalysts, *Journal of Catalysis*, vol. 220, no. 2, pp. 468-477, 2003.

[149]. Chesnokov, V.V., and Chichkan, A.S., Production of hydrogen by methane catalytic decomposition over Ni-Cu-Fe/Al₂O₃ catalyst, *International Journal of Hydrogen Energy*, vol. 34, no. 7, pp. 2979-2985, 2009.

[150]. Ashok, J., Reddy, P.S., Raju, G., Subrahmanyam, M., and Venugopal, A., Catalytic Decomposition of Methane to Hydrogen and Carbon Nanofibers over Ni-Cu-

- SiO₂ Catalysts, *Energy & Fuels*, vol. 23, no. 1, pp. 5-13, 2009.
- [151]. Gallego, G.S., Barrault, J., Batiot-Dupeyrat, C., and Mondragon, F., Production of hydrogen and MWCNTs by methane decomposition over catalysts originated from LaNiO₃ perovskite, *Catalysis Today*, vol. 149, no. 3-4, pp. 365-371, 2010.
- [152]. Reshetenko, T.V., Avdeeva, L.B., Ismagilov, Z.R., Chuvilin, A.L., and Fenelonov, V.B., Catalytic filamentous carbons-supported Ni for low-temperature methane decomposition, *Catalysis Today*, vol. 102, no., pp. 115-120, 2005.
- [153]. Li, J., Lu, G., Li, K., and Wang, W., Active Nb₂O₅-supported nickel and nickel-copper catalysts for methane decomposition to hydrogen and filamentous carbon, *Journal of Molecular Catalysis A: Chemical*, vol. 221, no. 1-2, pp. 105-112, 2004.
- [154]. Echegoyen, Y., Suelves, I., Lázaro, M.J., Moliner, R., and Palacios, J.M., Hydrogen production by thermocatalytic decomposition of methane over Ni-Al and Ni-Cu-Al catalysts: Effect of calcination temperature, *Journal of Power Sources*, vol. 169, no. 1, pp. 150-157, 2007.
- [155]. Lázaro, M.J., Echegoyen, Y., Suelves, I., Palacios, J.M., and Moliner, R., Decomposition of methane over Ni-SiO₂ and Ni-Cu-SiO₂ catalysts: Effect of catalyst preparation method, *Applied Catalysis A: general*, vol. 329, no., pp. 22-29, 2007.
- [156]. Avdeeva, L.B., Kochubey, D.I., and Shaikhutdinov, S.K., Cobalt catalysts of methane decomposition: accumulation of the filamentous carbon, *Applied Catalysis a-General*, vol. 177, no. 1, pp. 43-51, 1999.
- [157]. Nuernberg, G.B., Fajardo, H.V., Mezalira, D.Z., Casarin, T.J., Probst, L.F.D., and Carreno, N.L.V., Preparation and evaluation of Co/Al₂O₃ catalysts in the production of hydrogen from thermo-catalytic decomposition of methane: Influence of operating conditions on catalyst performance, *Fuel*, vol. 87, no. 8-9, pp. 1698-1704, 2008.
- [158]. Ermakova, M.A., Ermakov, D.Y., Chuvilin, A.L., and Kuvshinov, G.G., Decomposition of Methane over Iron Catalysts at the Range of Moderate Temperatures: The Influence of Structure of the Catalytic Systems and the Reaction Conditions on the Yield of Carbon and Morphology of Carbon Filaments, *Journal of Catalysis*, vol. 201, no. 2, pp. 183-197, 2001.
- [159]. Avdeeva, L.B., Reshetenko, T.V., Ismagilov, Z.R., and Likholobov, V.A., Iron-

containing catalysts of methane decomposition: accumulation of filamentous carbon, *Applied Catalysis A: general*, vol. 228, no. 1-2, pp. 53-63, 2002.

[160]. Jiang, X., and Goodman, D.W., The effect of sulfur on the dissociative adsorption of methane on nickel, *Catalysis Letters*, vol. 4, no. 2, pp. 173-180, 1990.

[161]. Hanley, L., Xu, Z., and Yates, J.T., Methane activation on Ni(111) at high-pressures, *Surface Science*, vol. 248, no. 3, pp. L265-L273, 1991.

[162]. Lee, M.B., Yang, Q.Y., and Ceyer, S.T., Dynamics of the activated dissociative chemisorption of CH₄ and implication for the pressure gap in catalysis: a molecular beam-high resolution electron energy loss study, *Journal of Chemical Physics*, vol. 87, no. 5, pp. 2724-2741, 1987.

[163]. Chorkendorff, I., Alstrup, I., and Ullmann, S., XPS study of chemisorption of CH₄ on Ni(100), *Surface Science*, vol. 227, no. 3, pp. 291-296, 1990.

[164]. Campbell, R.A., Szanyi, J., Lenz, P., and Goodman, D.W., Methane activation on clean and oxidized Ni(100), *Catalysis Letters*, vol. 17, no. 1-2, pp. 39-46, 1993.

[165]. Bernardo, C.A., Alstrup, I., and Rostrupnielsen, J.R., Carbon deposition and methane steam reforming on silica-supported Ni-Cu catalysts, *Journal of Catalysis*, vol. 96, no. 2, pp. 517-534, 1985.

[166]. Demicheli, M.C., Ponzi, E.N., Ferretti, O.A., and Yeramian, A.A., Kinetics of carbon formation from CH₄-H₂ mixtures on nickel alumina catalyst, *Chemical Engineering Journal and the Biochemical Engineering Journal*, vol. 46, no. 3, pp. 129-136, 1991.

[167]. Snoeck, J.W., Froment, G.F., and Fowles, M., Kinetic study of the carbon filament formation by methane cracking on a nickel catalyst, *Journal of Catalysis*, vol. 169, no. 1, pp. 250-262, 1997.

[168]. Alstrup, I., and Teresa Tavares, M., The kinetics of carbon formation from CH₄ + H₂ on a silica-supported nickel catalyst, *Journal of Catalysis*, vol. 135, no. 1, pp. 147-155, 1992.

[169]. Borghei, M., Karimzadeh, R., Rashidi, A., and Izadi, N., Kinetics of methane decomposition to CO_x-free hydrogen and carbon nanofiber over Ni-Cu/MgO catalyst, *International Journal of Hydrogen Energy*, vol. 35, no. 17, pp. 9479-9488, 2010.

- [170]. Bernardo, C.A., Alstrup, I., and Rostrup-Nielsen, J.R., Carbon deposition and methane steam reforming on silica-supported NiCu catalysts, *Journal of Catalysis*, vol. 96, no. 2, pp. 517-534, 1985.
- [171]. Abbas, H.F., and Wan Daud, W.M.A., Deactivation of palm shell-based activated carbon catalyst used for hydrogen production by thermocatalytic decomposition of methane, *International Journal of Hydrogen Energy*, vol. 34, no. 15, pp. 6231-6241, 2009.
- [172]. Kuvshinov, G.G., Mogilnykh, Y.I., and Kuvshinov, D.G., Kinetics of carbon formation from CH₄-H₂ mixtures over a nickel containing catalyst, *Catalysis Today*, vol. 42, no. 3, pp. 357-360, 1998.
- [173]. Hazra, M., Croiset, E., Hudgins, R.R., Silveston, P.L., and Elkamel, A., Experimental investigation of the catalytic cracking of methane over a supported Ni catalyst, *Canadian Journal of Chemical Engineering*, vol. 87, no. 1, pp. 99-105, 2009.
- [174]. Pinder, K.L., Fogler, H. S. "elements of chemical reaction engineering", prentice-hall, englewood cliffs, New Jersey 07632, 1986, 769 pages. Price \$74.15 Canadian, *The Canadian Journal of Chemical Engineering*, vol. 65, no. 3, pp. 526-527, 1987.
- [175]. Jana, P., O'Shea, V.A.D., Coronado, J.M., and Serrano, D.P., Cobalt based catalysts prepared by Pechini method for CO₂-free hydrogen production by methane decomposition, *International Journal of Hydrogen Energy*, vol. 35, no. 19, pp. 10285-10294, 2010.
- [176]. Li, Y., Liu, Q.Y., and Shen, W.J., Morphology-dependent nanocatalysis: metal particles, *Dalton Transactions*, vol. 40, no. 22, pp. 5811-5826, 2011.
- [177]. Angermann, A., and Töpfer, J., Synthesis of magnetite nanoparticles by thermal decomposition of ferrous oxalate dihydrate, *Journal of Materials Science*, vol. 43, no. 15, pp. 5123-5130, 2008.
- [178]. Michalowicz, A., Girerd, J.J., and Goulon, J., EXAFS determination of the copper oxalate structure-relation between structure and magnetic properties, *Inorganic Chemistry*, vol. 18, no. 11, pp. 3004-3010, 1979.
- [179]. Fichtnerschmittler, H., Comments on the structure of copper (II) oxalate : disussion of X-ray powder diffraction and EXAFS results as a basis for the interpretation of magnetic properties, *Crystal Research and Technology*, vol. 19, no. 9, pp.

1225-1230, 1984.

[180]. Romann, J., Valmalette, J.-C., Chevallier, V., and Merlen, A., Surface Interactions between Molecules and Nanocrystals in Copper Oxalate Nanostructures, *Journal of Physical Chemistry C*, vol. 114, no. 24, pp. 10677-10682, 2010.

[181]. Durivault, L., Brylev, O., Reyter, D., Sarrazin, M., Belanger, D., and Roue, L., Cu-Ni materials prepared by mechanical milling: Their properties and electrocatalytic activity towards nitrate reduction in alkaline medium, *Journal of Alloys and Compounds*, vol. 432, no. 1-2, pp. 323-332, 2007.

[182]. Hornes, A., Bera, P., Fernandez-Garcia, M., Guerrero-Ruiz, A., and Martinez-Arias, A., Catalytic and redox properties of bimetallic Cu-Ni systems combined with CeO₂ or Gd-doped CeO₂ for methane oxidation and decomposition, *Applied Catalysis B-environmental*, vol. 111, no., pp. 96-105, 2012.

[183]. Li, P., Liu, J., Nag, N., and Crozier, P.A., In situ preparation of Ni-Cu/TiO₂ bimetallic catalysts, *Journal of Catalysis*, vol. 262, no. 1, pp. 73-82, 2009.

[184]. Chang, T.H., and Leu, F.C., Dynamics of bimetallic Ni-Cu catalysts, *Journal of the Chemical Society-Faraday Transactions*, vol. 92, no. 12, pp. 2291-2296, 1996.

[185]. Cangiano, M.D., Ojeda, M.W., Carreras, A.C., Gonzalez, J.A., and Ruiz, M.D., A study of the composition and microstructure of nanodispersed Cu-Ni alloys obtained by different routes from copper and nickel oxides, *Materials Characterization*, vol. 61, no. 11, pp. 1135-1146, 2010.

[186]. Ji, Y.G., Zhao, Z., Duan, A.J., Jiang, G.Y., and Liu, J., Comparative Study on the Formation and Reduction of Bulk and Al₂O₃ Supported Cobalt Oxides by H₂-TPR Technique, *Journal of Physical Chemistry C*, vol. 113, no. 17, pp. 7186-7199, 2009.

[187]. Roh, H.S., Potdar, H.S., Jun, K.W., Kim, J.W., and Oh, Y.S., Carbon dioxide reforming of methane over Ni incorporated into Ce-ZrO₂ catalysts, *Applied Catalysis a-General*, vol. 276, no. 1-2, pp. 231-239, 2004.

[188]. Yang, R.T., and Chen, J.P., Mechanism of carbon filament growth on metal catalysts, *Journal of Catalysis*, vol. 115, no. 1, pp. 52-64, 1989.

[189]. Cale, T.S., and Richardson, J.T., In-situ characterization of Ni-Cu/SiO₂ catalysts, *Journal of Catalysis*, vol. 79, no. 2, pp. 378-389, 1983.

- [190]. Fenelonov, V.B., Derevyankin, A.Y., Okkel, L.G., Avdeeva, L.B., Zaikovskii, V.I., Moroz, E.M., Salanov, A.N., Rudina, N.A., Likholobov, V.A., and Shaikhutdinov, S.K., Structure and texture of filamentous carbons produced by methane decomposition on Ni and Ni-Cu catalysts, *Carbon*, vol. 35, no. 8, pp. 1129-1140, 1997.
- [191]. Vaidya, S., Rastogi, P., Agarwal, S., Gupta, S.K., Ahmad, T., Antonelli, A.M., Ramanujachary, K.V., Lofland, S.E., and Ganguli, A.K., Nanospheres, nanocubes, and nanorods of nickel oxalate: Control of shape and size by surfactant and solvent, *Journal of Physical Chemistry C*, vol. 112, no. 33, pp. 12610-12615, 2008.
- [192]. Ahmad, T., Ganguly, A., Ahmed, J., Ganguli, A.K., and Alhartomy, O.A.A., Nanorods of transition metal oxalates: A versatile route to the oxide nanoparticles, *Arabian Journal of Chemistry*, vol. 4, no. 2, pp. 125-134, 2011.
- [193]. Drouet, C., and Alphonse, P., Synthesis of mixed manganites with high surface area by thermal decomposition of oxalates, *Journal of Materials Chemistry*, vol. 12, no. 10, pp. 3058-3063, 2002.
- [194]. Bowen, P., Pujol, O., Jongen, N., Lemaitre, J., Fink, A., Stadlerman, P., and Hofmann, H., Control of morphology and nanostructure of copper and cobalt oxalates: Effect of complexing ions, polymeric additives and molecular weight, *Nanoscale*, vol. 2, no. 11, pp. 2470-2477, 2010.
- [195]. Yang, L., Wang, G., Tang, C., Wang, H., and Zhang, L., Synthesis and photoluminescence of corn-like ZnO nanostructures under solvothermal-assisted heat treatment, *Chemical Physics Letters*, vol. 409, no. 4-6, pp. 337-341, 2005.
- [196]. Carney, C.S., Gump, C.J., and Weimer, A.W., Rapid nickel oxalate thermal decomposition for producing fine porous nickel metal powders Part 1: Synthesis, *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, vol. 431, no. 1-2, pp. 1-12, 2006.
- [197]. D, D., The thermal decomposition of oxalates. A review, *Thermochimica Acta*, vol. 117, no. 0, pp. 331-363, 1987.
- [198]. Mohamed, M.A., Galwey, A.K., and Halawy, S.A., A comparative study of the thermal reactivities of some transition metal oxalates in selected atmospheres, *Thermochimica Acta*, vol. 429, no. 1, pp. 57-72, 2005.

- [199]. King, D.A., Nitrogen adsorption on nickel and palladium films, *Surface Science*, vol. 9, no. 3, pp. 375-395, 1968.
- [200]. Haroun, M.F., Moussounda, P.S., and Legare, P., Theoretical study of methane adsorption on perfect and defective Ni(111) surfaces, *Catalysis Today*, vol. 138, no. 1-2, pp. 77-83, 2008.
- [201]. Plate, S.E., Bobrov, A.V., Kadushin, A.A., and Kimmelfeld, Y.M., Study of methane adsorption on nickel films by raman-effect method, *Kinetics and Catalysis*, vol. 27, no. 2 pt 2, pp. 429-431, 1986.
- [202]. Małecka, B., Małecki, A., Drożdż-Cieśla, E., Tortet, L., Llewellyn, P., and Rouquerol, F., Some aspects of thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, *Thermochimica Acta*, vol. 466, no. 1-2, pp. 57-62, 2007.
- [203]. Chen, D., Christensen, K.O., Ochoa-Fernández, E., Yu, Z., Tørdal, B., Latorre, N., Monzón, A., and Holmen, A., Synthesis of carbon nanofibers: Effects of Ni crystal size during methane decomposition, *Journal of Catalysis*, vol. 229, no. 1, pp. 82-96, 2005.
- [204]. Chen, J.L., Li, X.M., Li, Y.D., and Qin, Y.N., Production of hydrogen and nanocarbon from direct decomposition of undiluted methane on high-nickel Ni-Cu-alumina catalysts, *Chemistry Letters*, vol. 32, no. 5, pp. 424-425, 2003.
- [205]. Hornes, A., Munuera, G., Fuerte, A., Escudero, M.J., Daza, L., and Martinez-Arias, A., Structural, catalytic/redox and electrical characterization of systems combining Cu-Fe with CeO_2 or $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$ ($\text{M} = \text{Gd}$ or Tb) for direct methane oxidation, *Journal of Power Sources*, vol. 196, no. 9, pp. 4218-4225, 2011.
- [206]. Lua, A.C., and Wang, H.Y., Decomposition of methane over unsupported porous nickel and alloy catalyst, *Applied Catalysis B: Environmental*, vol. 132-133, no. 0, pp. 469-478, 2013.
- [207]. Fujimoto, H., Theoretical X-ray scattering intensity of carbons with turbostratic stacking and AB stacking structures, *Carbon*, vol. 41, no. 8, pp. 1585-1592, 2003.
- [208]. Pirard, S.L., Douven, S., Bossuot, C., Heyen, G., and Pirard, J.P., A kinetic study of multi-walled carbon nanotube synthesis by catalytic chemical vapor deposition using a Fe-Co/ Al_2O_3 catalyst, *Carbon*, vol. 45, no. 6, pp. 1167-1175, 2007.
- [209]. Zein, S.H.S., Mohamed, A.R., and Sai, P.S.T., Kinetic studies on catalytic

decomposition of methane to hydrogen and carbon over Ni/TiO₂ catalyst, *Industrial & Engineering Chemistry Research*, vol. 43, no. 16, pp. 4864-4870, 2004.

[210]. Kvande, I., Chen, D., Yu, Z., Ronning, M., and Holmen, A., Optimization and scale-up of CNF production based on intrinsic kinetic data obtained from TEOM, *Journal of Catalysis*, vol. 256, no. 2, pp. 204-214, 2008.

[211]. Bai, Z., Chen, H., Li, W., and Li, B., Hydrogen production by methane decomposition over coal char, *International Journal of Hydrogen Energy*, vol. 31, no. 7, pp. 899-905, 2006.

[212]. Abbas, H.F., and Daud, W., Hydrogen production by thermocatalytic decomposition of methane using a fixed bed activated carbon in a pilot scale unit: Apparent kinetic, deactivation and diffusional limitation studies, *International Journal of Hydrogen Energy*, vol. 35, no. 22, pp. 12268-12276, 2010.

[213]. Abbas, H.F., and Daud, W., Deactivation of palm shell-based activated carbon catalyst used for hydrogen production by thermocatalytic decomposition of methane, *International Journal of Hydrogen Energy*, vol. 34, no. 15, pp. 6231-6241, 2009.

[214]. Rodríguez, J.C., Peña, J.A., Monzón, A., Hughes, R., and Li, K., Kinetic modelling of the deactivation of a commercial silica-alumina catalyst during isopropylbenzene cracking, *The Chemical Engineering Journal and The Biochemical Engineering Journal*, vol. 58, no. 1, pp. 7-13, 1995.

[215]. Latorre, N., Romeo, E., Villacampa, J.I., Cazana, F., Royo, C., and Monzon, A., Kinetics of carbon nanotubes growth on a Ni-Mg-Al catalyst by CCVD of methane: Influence of catalyst deactivation, *Catalysis Today*, vol. 154, no. 3-4, pp. 217-223, 2010

Publications

Publications arising from this research are as follows:

- 1) H.Y.Wang and A. C. Lua*. Development of metallic nickel nano-particle catalyst for the decomposition of methane into hydrogen and carbon nanofibres. *Journal of physical chemistry C*, 2012, 116 (51), pp 26765–26775
- 2) A. C. Lua*. H.Y.Wang, Decomposition of methane over unsupported porous nickel and alloy catalyst. *Applied catalysis B: Environmental*, Volumes 132–133, 27 March 2013, Pages 469–478
- 3) H.Y.Wang and A. C. Lua*, Hydrogen production by thermo-catalytic methane decomposition, *Heat Transfer Engineering*, 34:11-12, 896-903
- 4) H.Y.Wang and A.C. Lua, Hydrogen production by thermo-catalytic methane decomposition, *Proceedings of Innovative Materials for Processes in Energy Systems 2010*, 29 Nov – 1 Dec 2010, Singapore, pp 107 – 113
- 5) Hydrogen production from decomposition of methane over Ni-Cu alloy nano-particle catalysts, H.Y.Wang and A.C. Lua, submitted.
- 6) Hydrogen production from catalytic decomposition of methane over Ni-Cu-Co alloy particles, H.Y.Wang and A.C. Lua, submitted.
- 7) Kinetic studies of unsupported Ni catalysts towards hydrogen production from methane decomposition, H.Y.Wang and A.C. Lua, in preparation.