Theoretical analysis and experimental investigation of hydrogen production by thermo-catalytic decomposition of methane

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**THEORETICAL ANALYSIS AND EXPERIMENTAL
INVESTIGATION OF HYDROGEN PRODUCTION BY
THERMO-CATALYTIC DECOMPOSITION OF
METHANE**

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School of Mechanical and Aerospace Engineering

2020

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INVESTIGATION OF HYDROGEN PRODUCTION BY
THERMO-CATALYTIC DECOMPOSITION OF METHANE**

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University

in partial fulfilment of the requirement for the degree of

Master of Engineering

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

18 May 2020

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

18 May 2020

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Professor Lua Aik Chong

Authorship Attribution Statement

This thesis contains material from one paper published in the following peer-reviewed journal in which I am listed as an author.

Chapter 5 is published as Q. Chen and A.C. Lua. Kinetic reaction and deactivation studies on thermocatalytic decomposition of methane by electroless nickel plating catalyst. Chemical Engineering Journal, Vol. 389, 124366, (2020).

The contributions from the co-author are as follows:

- Professor Lua Aik Chong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. Professor Lua revised the final manuscript which was accepted for publication.
- I did the modelling work and the formulation of the equations which were revised and corrected by Professor Lua.
- I prepared all the modelling results and compared with the experimental results in the graphical plots, and the discussion of results which were revised by Professor Lua.

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Abstract

One of the most promising alternative energy carriers and clean fuels would be hydrogen, which is widely considered. Therefore, significant effort has been focused on developing efficient, economic and environmental friendly approaches for the production of hydrogen. Among the many hydrogen generation techniques, the catalytic decomposition of methane (CDM) over supported nickel catalysts has gained much interest. This hydrogen generation method will eliminate the requirement for CO_x separation and subsequent processes altogether. The main objectives of this research project are to synthesis high efficient and long active-life catalysts and to optimize the experimental process in order to generate hydrogen by thermal decomposition of methane with high conversion ratio. In this thesis, a comprehensive study on a series of supported nickel nanoparticle catalysts was presented. These supported catalysts prepared in a novel and creative method showed comparable catalytic activity as the other supported catalysts prepared by traditional method such as coprecipitation and impregnation. These catalysts offered two major advantages by (1) providing high-loading supported nickel catalyst with tunable nanoparticle size and (2) preventing nickel nanoparticles from severe aggregation and loosing catalytic activity very rapidly, resulting from moderate interaction with support. To the best knowledge of the author, this study was the second time that investigated the catalytic activities and deactivation mechanisms of electroless nickel plating technique towards CDM systematically. The thesis consisted mainly of the two following parts:

(1) Supported nickel nanoparticles were prepared by a creative method and these nanoparticles showed promising catalytic activity towards catalytic decomposition of

methane. The addition of silver nanoparticles as seeds led to the formation of nickel particles with smaller crystalline size and high dispersion on the support than those of Ni particles prepared by another similar technique. Unlike the conventional supported catalysts, it was only required to introduce a small amount of hydrogen to the reactor to reduce the surface oxidation of nickel particle and to avoid catalyst particles sintering into bigger ones during the reaction. The objective of this part of the project was to investigate the preparation of the active phase composition and the other physicochemical properties of catalyst synthesized by electroless nickel plating method. The textural and microstructural properties of the deposited carbon were also characterized in detail. A series of decomposition atmospheres ($\text{CH}_4\text{-N}_2$ in different volumetric flow rate) were used to investigate their effects on the equilibrium between carbon diffusion among nickel bulk and the formation of carbon nanotubes. The effects of reaction temperatures on the catalytic activity were also studied. The resulting Ni particles with 32 wt.% loading on SBA-15 showed promising catalytic activities for methane decomposition at temperatures of 575°C . The stability of the catalysts was discussed and this work provided helpful guidance on the deactivation mechanism proposed in Chapter 4.

(2) In Chapter 5, a detailed catalytic deactivation study was carried out. A series of kinetic experiments had been conducted using two types of catalysts (26 wt.% Ni/SBA-15 and 32 wt.% Ni/SBA-15). The effects of W/F ratio (the ratio of the weight of catalyst to the molar flow rate of methane) and reaction temperatures on the methane decomposition rate were studied. The reaction order and activation energy of 32 wt.% Ni/SBA-15 catalyst were calculated based on Genetic Algorithm, with correlation coefficient >0.99 . Different deactivation mechanisms of 32 wt.% Ni/SBA-15 catalyst were proposed and discussed.

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List of Symbols

A	Decay amplitude	dimensionless
a	Normalized catalyst activity factor : $r(t)/r_{\max}$	dimensionless
C_{CH_4}	Molar concentration of methane	mmol L ⁻¹
Dp	Average pore width	nm
d	Deactivation order	dimensionless
d_{002}	interplanar distance of (002) planes	nm
E_a	Activation energy	kJ/mol
F	Molar flow rate of methane	mmol s ⁻¹
k	Rate constant	mol/(g _{cat} min atm ⁿ)
L_c	Domain crystalline size along the c-axis direction	nm
n	Reaction order	dimensionless
p_i	Partial pressure of component i	atm
R	Gas constant: 8.31	J/(molK)
$r(t)$	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
S_{BET}	Surface area derived by BET method	m ² /g
T	Reaction temperature	K
t	Reaction time	min
t^*	Decay constant	min
v	Pre-exponential factor	mol/(g _{cat} min atm ⁿ)
V_p	Total pore volume from N ₂ adsorption at p/p ₀ =0.99	cm ³ /g
W	Weight of catalyst	g
θ_s	Fractions of active sites that are vacant	dimensionless
χ_{CH_4}	Methane conversion ratio	dimensionless
ΔH	Heat of adsorption	J/mol

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
PSA	Pressure swing adsorption
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

Chapter 1 Introduction

1.1 Introduction

Fossil based fuel has powered the industrialization since the last century. The abundance of energy harvested from it has brought the living standard of mankind to a new height. Nevertheless, it is widely understood that the source of fossil fuels is depleting at an accelerated rate, due to the rising demand of energy from an enlarging population. In the meantime, the extraction of fossil energy comes with severe impact on the environment, such as global warming, acid rains, air pollution, etc. [1-4]. The deterioration of the environment, in turn, affects everyone's living conditions.

Much effort has focused on the study of various renewable energies, such as wind, solar and biomass, with the objective of achieving a sustainable growth. However, in the short term, these alternative forms of energy have limited contributions to the overall energy supply as they are associated with high processing costs and immature technologies [5]. Nuclear energy is another promising alternative given its mature technology and extensive global applications [6]. Nonetheless, it remains controversial given that the uranium reserves are limited and there are many serious safety concerns [5-8]. Therefore, fossil fuels will continue to play the leading role in global energy supply given its reliability and cost effectiveness. As such, there is an urgent need to address its environmental impact [4, 9-11].

For fossil based fuels, the historical trend reveals that an evolution in the type of fossil,

from solids (woods and coal) in the pre-19th century, to liquids (oil) in mid-19th and then to gases since late-19th century (methane and hydrogen), as shown in Fig. 1.1 [12-14]. From an atomic perspective, the hydrogen (H) to carbon(C) ratio per molecule for each type of fossil fuel has increased, which is an indication of high energy intensity, as shown in Table 1.1 [13]. In other words, the evolution is a “decarbonization” process. Continuing from this trend, hydrogen will inevitably become the dominant future energy carrier. It will help to realize a carbon-free energy system [15]. Meanwhile, the use of hydrogen is also environmentally friendly given that its combustion generates neither greenhouse gases nor toxic or hazardous gases [14]. Other than that, hydrogen also plays key roles in a number of industrial applications, such as ammonia production, oil refineries and methanol production.

Fig. 1.1 Global energy systems transition [12-14].

Table 1.1 Heat of combustion of various fuels [16].

Fuel	Energy(kcal/g)
Hydrogen	34
Petroleum	10.3-8.4
Paraffin	10.3-9.8
Graphite(Coal)	7.8
Castor oil	9.4
Wood	4.2

Statistics show that nearly 48% of hydrogen is produced from natural gas (NG), due to the availability of commercially feasible technology [16]. The other 30% comes from petroleum, 18% from coal, and 4% from water electrolysis [17]. In the near future, hydrogen production will still rely heavily on fossil fuels, primarily natural gas [18]. The economic feasibility technology would be the main reason for the high contribution of natural gas [19-21]. However, the current method of hydrogen production will generate large quantities of CO₂ and CO, which will contribute to global warming. In order to overcome these problems, there is an increasing interest for the production of clean hydrogen [8, 22]. In addition, its application is limited in growing technologies such as fuel cell, which is susceptible to electro-catalyst poisoning by these contaminants. Therefore, much research is being conducted, exploring ways to increase the efficiency of this conversion and aiming to bring down the rates of CO₂ and CO generation.

1.2 Objectives and scope

Generally speaking, the supported catalyst preparation technique is categorized on the basis of the metal-support interaction intensity. Impregnation and deposition-precipitation result

in a weak metal-support interaction (MSI) while sol-gel and coprecipitation are favorable for forming a strong MSI. Each method can exhibit good catalytic behavior under optimum conditions. For methods to prepare catalysts with strong bonding with supports, it is essential to form small metal particles on the support to achieve high reduction and high operation temperatures. However, pure metallic nickel without promoter could easily deactivate when the temperature is above 600 °C. This could be attributed to the fact that the methane diffusion rate was slower than the methane dissociation rate, resulting in encapsulation of nickel particles by carbon layer. Therefore, for the preparation of pure nickel catalyst with support, impregnation and deposition-precipitation could be regarded as preferred choices. Li *et al.* [23] studied Ni/CeO₂ catalysts with different preparation techniques and found that deposition-precipitation method showed much higher performance for hydrogen formation rate than that synthesized by a coprecipitation method. However, it is very challenging for catalysts prepared by impregnation and deposition-precipitation methods to achieve high metal loadings (e.g. >20 wt. %). In order to overcome these restrictions, there is an increasing demand for other new preparation method such as electroless nickel plating technique. To the best of the author's knowledge, the work by El Nagggar *et al.* [24] was the only one that had tested a catalyst prepared by electroless nickel plating for catalytic decomposition of methane (CDM). The best result was 35 vol.% of hydrogen produced at 700 °C using Ni-B catalyst supported on glass fiber.

The main objectives of this research project are to develop electroless nickel plating technique with excellent catalytic activity towards CDM, to study the mechanism of catalyst deactivation process and to develop theoretical models for CDM. The organization

of the thesis consists of the following:

Chapter 1. To briefly introduce the main innovation of eletroless nickel plating technique and contribution towards methane decomposition reaction.

Chapter 2. To illustrate the current research development on methane decomposition reaction.

Chapter 3. To prepare catalysts by electroless nickel plating technique having a wide range of nickel loadings from 19 to 37 wt. %.

Supported Ni/SBA-15 catalysts are to be prepared by a novel and creative method and evaluated for their catalytic activities towards methane decomposition. The effects of the loadings of the nickel on the morphology and crystalline size of the nickel nanopartciels will be discussed. A series of decomposition atmospheres ($\text{CH}_4\text{-N}_2$ in different volumetric flow rate) will be used to investigate their effects on the morphology of the carbon nanotube and coke formation. The reaction conditions (e.g. reaction temperature) will be discussed and optimized.

Chapter 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 reaction rate expression in the form of power law type followed by parameter evaluations for the methane decomposition reaction will be analyzed by theoretical models. The activation energy value for hydrogen and carbon nanofiber production over a catalyst

will be estimated in the temperature range of 525-600 °C. The kinetic models of Langmuir-Hinshelwood mechanism would be analyzed in order to define the rate-determining step during the catalytic decomposition of methane by catalyst. Deactivation kinetics of the catalyst will be studied using different reaction temperatures and different reactant contacting times by varying the methane flow rate for a constant weight of the catalyst. 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 method of global hydrogen production mainly relies on steam reforming of natural gas (which is mainly methane) as shown in Fig. 2.1 [25]. When compared with other fossil fuels, methane shows great potential for hydrogen production. It is a great underutilized resource because it has great reserves when compared with other liquid petroleum. Moreover, the proven world methane reserve grows more increasingly than other fossil fuels [26]. From the chemical point of view, it has the highest hydrogen to carbon ratio. Generally, steam reforming methane and partial oxidation of methane are two main methods for hydrogen production.

Fig. 2.1 Feedstock used in the current global production of hydrogen [25]

2.1.1 Steam reforming of methane (SRM)

Hydrogen produced by SRM occupies about half of the world's hydrogen production due to its least expensive production cost [27, 28]. This process basically involves three main

steps. Firstly, methane is reformed at high temperatures from 500°C to 950°C and high pressures of up to 30 bar using a Ni catalyst in a metal alloy tube. The reforming reaction (Eq. 2.1) is highly endothermic. In order to prevent the deactivation of Ni catalyst, methane has to be desulphurized before being fed into the reformer by adding zinc oxide or activated carbon [14, 28, 29].

Secondly, after synthesizing a syngas mixture of H₂ and CO, catalytic water-gas shift reaction occurs to combine CO and H₂O to produce H₂ product.

This reaction (Eq. 2.2) is conventionally conducted at a lower temperature (350-500°C) as compared to reforming reaction. Iron-based catalysts are commonly used for higher temperature shift (400°C) while copper-based catalyst are used for lower temperature shift (250°C) [22].

Thirdly, chemical adsorption unit or pressure swing adsorption is applied to separate water, methane, CO₂ and CO from H₂ product. This process is known as purification in order to produce 99.99% pure hydrogen product. In order to satisfy the need of commercial applications, palladium membrane, selective methanation may also be required to further purify [28, 30].

2.1.2 Partial oxidation of methane (POM)

Partial oxidation of methane (Eq. 2.3) is the exothermic reaction with input of oxygen and steam when the oxygen-to-methane ratio is less than the required amount for combustion reaction. Partial oxidation can occur with catalyst or without catalyst. The input of oxygen

and steam vapor could advance the reaction with no requirement for external energy when compared with SRM [31]

Autothermal reforming of methane is a combination of both steam reforming and partial oxidation of methane. Although it takes advantage of no external heat needed unlike SRM, the efficiency of hydrogen production is limited at 65-75% [32]. Similarly, the partial oxidation of methane is mildly exothermic and therefore it does not require heat input. However, as oxygen is added into the reaction, partial oxidation suffers from somewhat higher reforming cost which limits its industrial application.

2.1.3 Thermal decomposition of methane (TDM)

The fundamental of thermal decomposition of methane is to decompose the methane into hydrogen and carbon in the environment where there is free of water and air. This reaction is a moderate endothermic process (Eq. 2.4)

Fig. 2.2 [33] shows that hydrocarbon is unstable at an elevated high temperature and methane is one of the most stable hydrocarbons at low temperature because the free energy of formation for methane is negative during that temperature range. Consequently, non-catalytic thermal decomposition of methane is carried out at high temperatures. Since the discovery of carbon black produced through TDM was published in the 1950s, extensive efforts have been made to study the mechanism of TDM [34]. Holmen [33] has reported that the overall process of TDM at high temperature could be described as a stepwise dehydrogenation as follows:

The free radical mechanism could explain the primary product of methane as described by the following equations.

The homogenous dissociation of methane (Eq. 2.6) is the rate-determining step and the only main source producing free radicals. Subsequently, this reaction is followed by a series of consecutive and parallel reactions and finally elemental carbon is produced.

Fig. 2.2 Standard free energy of formation (ΔG_f°) of some hydrocarbons as a function of temperature [33].

2.1.4 Catalytic decomposition of methane (CDM)

Fig. 2.3 illustrates that the equilibrium conversion of methane is influenced by pressure and temperature. It highlights that combining high temperature and low pressure (1atm) could favour high conversion rate. As TDM could only be conducted at high temperature (over 1400°C), development of efficient catalysts to decrease the required high temperature is the main solution to this problem. This process is termed as catalytic decomposition of methane (CDM).

Fig. 2.3 Equilibrium conversion of methane under different pressures and temperatures [35].

Since the late 19th century, CDM has been applied in the production of carbon filaments with hydrogen as a by-product and supplemental fuel. With the invention of transmission electron microscope (TEM), there are extensive studies focusing on the mechanism of growth of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) [29, 36]. Meanwhile, a

great cumulative effort is underway to improve the methane conversion rate at a moderate temperature by preparing suitable catalysts [37]. Unlike SRM, the CDM process has the advantage of producing 100% pure hydrogen which could be utilized on some hydrogen applications such as hydrogen fuel-cell. In fact, even for proton exchange membrane fuel cells (PEMFC), 20ppm CO could be poisonous [34, 38]. For alkaline fuel cells, ppm levels of CO₂ are a strong poison. Separation of CO and CO₂ from H₂ in ppm level is an expensive and complicated process.

2.2 CDM reaction process

CDM reaction is often classified to include three key steps, namely, methane activation, carbon nucleation and CNT or CNT growth as shown in Fig. 2.4 [29]. Firstly, a hydrocarbon precursor adsorbs and dissociates on the surface of the active phase to form carbon atoms. Subsequently, the elementary carbon atoms dissolve in the active phase to become a metastable carbide in the form of liquid and thus diffuse within the particle. It is also possible that the elemental carbon atoms diffuse through the surface\subsurface of metal particle. Conclusively, solid carbon precipitates at the opposite surface of the metal particles where the surface of the metal particle is directly exposed to the hydrocarbon precursor and then forms a carbon nanofilament. However, this mechanism over simplifies the process because the formation of CNFs or CNTs involves many physical and chemical steps.

Fig. 2.4 The three steps involved in the VLS mechanism: a) decomposition of the carbon-containing precursor on the surface of the catalyst particle; b) diffusion of carbon atoms through the particle as a solid solution; and c) precipitation of carbon at the metal-support interface and formation of a nanofiber or a nanotube. [29]

2.2.1 Methane activation on metal surface

The dissociation of methane on the surface of metal begins when the metal has non-filled electron configuration like transition metals. The metal nanoparticles catalyze the dissociation of the hydrocarbon by transferring an amount of its electron density from the adsorbing methane [39].

Audier and coworkers [40] noticed that for bcc pure metal, the metal/gas interface was always on the (100) surface while (111) plane for fcc metal. There exists a crystallographic preference for methane dissociation which induces the activation energy on some specific crystallographic planes to be low enough to catalyze the methane. For example, for nickel, Yang *et al.* [41] inferred from simulations and selected area electron diffraction that Ni

(110) and Ni (100) surfaces are the gas/metal interface. Beebe *et al.* [42] reported that Ni (110) was the most reactive for methane activation while Ni (111) was the least reactive surface. Some activation energy deduced from first-principle calculations [43] show that CH₄ chemisorption on Ni (100) has activation energy of 65±5 kJ/mol while activation energy of 80 kJ/mol on Ni (111). Obviously, for transition metal of nickel, the plane (100) is more active for methane dissociation.

2.2.2 Affinity for carbon: carbon solubility and formation of carbides

Overall, the ability of transition metals to bond with carbon atoms decreases with the number of filled d-orbitals. Metals such as Cu or Zn, without d-vacancies in their electronic structure, have no affinity for carbon while metals such as Ni, Co and Fe, with few d-vacancies, display a finite carbon solubility. The Fe-group metals such as Ti and Mo, with many d-vacancies, can form strong chemical bond with carbon and thereby highly stable carbide compounds. Fig. 2.5 [44] shows elements from Ni to Fe forming carbides of increasing stability and increasing carbon share. Fe is a special case. Fe forms a metastable carbide (Fe₃C), the solubility of carbon is relatively low in α -Fe (0.1 at.% at 700°C) but high in γ -Fe (4 at.% at 800°C) [45]. Moreover, in addition to the nature of transition metals, the particle size can influence the solubility of carbon and stability of carbides. Overall, thermodynamic model predict an increase of the solubility of carbon inside metal particles of decreasing size. The critical concentration for the formation of solid carbon is the solubility limit of carbon in the metal. Moreover, based on various experimental observations, catalysts with moderate carbon solubility (between 0.5 and 1.5 wt.%) and not forming stable carbides are amenable to growth of CNTs or CNFs[46].

Fig. 2.5 Ellingham diagram for carbides of 3d transition metals [44].

2.2.3 Carbon diffusion: bulk, surface and subsurface

There are three different mechanisms relating to the carbon atom diffusion paths: bulk diffusion, surface diffusion and sub-surface diffusion as demonstrated in Fig. 2.6 [47].

Fig. 2.6 Schematic of three carbon diffusion mechanisms in CDM [44]

Bulk diffusion proposed by Baker *et al.* [48] received substantial support because of a very good consistency between the measured activation energy for the growth of carbon nanofibers and values determined for diffusion of carbon atom through the whole particle. Another strong evidence was proposed by Snoeck and coworkers [49] that at lower temperatures, the dissociation rate of the hydrocarbon on the surface of the catalyst was lower than diffusion rate of the hydrocarbon on the surface of the catalyst. Therefore, carbon atoms have enough time to diffuse in the bulk homogeneously and nucleate on the entire back surface of the catalyst particle, which results in formation of carbon filaments without hollow cores. On the contrary, at the higher temperature, in order to compensate for the higher nucleation rates, the short diffusion path is favoured while the long path is extruded. It is attributed to the formation of CNTs as shown in Fig. 2.7.

Fig. 2.7 Schematic picture of the formation of a CNF (left) and CNT (right) [49].

For bulk diffusion, there are some general trends as given below:

- (i) The bulk diffusion of carbon atoms is much faster than that of host metal atoms because the carbon atoms diffuse interstitially while the metal atoms diffuse substitutionally.
- (ii) Interstitial diffusion relies on the geometry of the host metal lattice and is faster in more open structures. For example, the activation energy for carbon diffusion in close-packed fcc Fe is 1.53-1.57 eV while that in bcc Fe is only 0.83 eV [50].
- (iii) The lower the melting-point of the host metal, the larger the diffusion constant of the carbon atoms. For example, in the case of α -Fe, V and Mo (all bcc metals), the diffusion constants conversely follow the order of the melting points, that is Fe ($T_m=1535^\circ\text{C}$) > V ($T_m=1887^\circ\text{C}$) > Mo ($T_m=2617^\circ\text{C}$).
- (iv) The diffusion constant relies conversely upon the solid solubility.

From various literature papers, it has long revealed that the bulk diffusion of carbon strongly depends on the carbon concentration on the bulk. When the dissolved amount of carbon increases up to 6%, the energy barrier for bulk diffusion of carbon in fcc-Fe reduces from 1.55eV to 1.24eV [51]. In the case of Ni, when carbon concentrations is above 50% in the first subsurface layer, the activation energy for carbon diffusion would decrease from

1.6eV to 1.0eV [52]. It is frequently explained by the lattice expansion related to the addition of carbon and repulsion between carbon atoms at close distance. However, for very high carbon contents such as concentration to form carbides, it is commonly discovered that the energy barrier for carbon diffusion are much higher than that in pure metal as seen in Fig. 2.8[44]. This may be ascribed to the fact that carbon diffusion in carbides is not interstitial but mediated by thermal vacancies in the metal. Moreover, studies on the diffusion rate of carbon have revealed an influence of addition of other elements. The diffusion rate of carbon atoms in fcc-Fe increases in the presence of Ni and Cu, but decreases with the concentration of carbide-forming elements such as Cr, W, Mo [53].

Fig. 2.8 Bulk diffusion constants of carbon in various metals and metal carbides as a function of temperature [44].

Based on the in-situ high-resolution transmission electron microscopy (HRTEM) and in-situ X-ray photoelectron spectroscopy (XPS), Hofmann *et al.* [54, 55] found that there is

no evidence for the formation of bulk carbide during the growth of nanofiber which could not support the bulk diffusion mechanism. The same group recently investigated the kinetics of the reaction and then illustrated that a much higher activation energy for bulk diffusion is usually obtained when compared with that of surface diffusion [47, 55]. Based on the theoretical and simulation work including ab initio plane wave density and first principle calculation, some research groups voted for surface diffusion mechanism because the activation energy for surface diffusion is significantly lower than for bulk diffusion [56, 57]. On the account of computer simulations, Zhu and co-workers [58] deduced that bulk activation energy could be substantially decreased with increasing carbon concentration in bulk, which means that when the dissociation rate is higher than the surface diffusion rate, the bulk diffusion mechanism is preferentially in place of surface diffusion.

Fig. 2.9 Energy as function of the distance of carbon to the Ni (100) and Ni (111) surfaces. a1 and b1 show the adsorbed systems, a2 and b2 the transition states, and a3 and b3 the systems with subsurface carbon [60].

Recently, it has been calculated by Hofmann's group [59] that sub-surface (one layer below surface) energy barrier is lower than surface or bulk diffusion. Fig. 2.9 illustrates that

carbon migration to the sub-surface is energetically favoured for both Ni (111) and Ni (100). The activation energy for Ni (111) and Ni (100) migration to subsurface is relatively high: 1.92 eV and 1.45 eV respectively [60]. However, after diffusion to subsurface, each carbon atom could obtain 0.3 eV which means the carbon p states are more stabilized. Based on in-situ X-ray diffraction (XRD) and density function theory (DFT) simulation, the subsurface diffusion mechanism has been proposed that after catalyzing by active phase, the carbon atoms penetrated into the Ni (111) and Ni (100) and then form a surface carbide layer and finally migrate to octahedral subsurface sites [61]. Although hypothesis receives support from preliminary DFT calculations, it still requires other calculations to verify such as molecular dynamics (MD).

2.2.4 The driving force for the bulk diffusion

For the bulk diffusion mechanism, the driving force for the carbon diffusion was ascribed either to temperature gradient or to a concentration gradient. Baker and his co-workers [48] assumed that the driving force for pushing carbon atoms to diffuse is the temperature gradient inside the nanoparticles because the dissociation of carbon containing gas precursor on the surface of the nanoparticles is exothermic while the precipitation of solid carbon is endothermic. However, this assumption could not receive support when Tibbetts and co-workers [62] calculated the temperature gradient which is smaller than 10^{-5} K. Therefore, the other alternative assumption for the driving force has been proposed by Rostrup-Nielsen and Trimm [63]: carbon solubility at the gas/metal interface is different with metal/carbon interface which attributes to the driving force for carbon atom diffusion through the whole nanoparticle.

2.2.5 Catalyst state in reaction

Fig. 2.10 FIM images (left) and corresponding ball model (right) of the a) the starting clean Ni crystal ($T=61\text{K}$), b) after exposure to H_2 (600°C), and c) after exposure to C_2H_2 [61]

Several research groups found that metal nanoparticles go through agglomeration and reconstruction process during the initial period of reaction. Li and co-workers [64] observed that the metal particles not only enlarge but also change in crystal shape from spherical to polyhedral after reaction at 500°C . Moors and coworkers [65] observed the chemical state of active phase when carbon nanotube begins to nucleate when using combined field ion/electron microscopy with in-situ local chemical probing applied on a single nanosized nickel crystal as seen in Fig. 2.10. Heat treatment of H_2 could motivate a major transformation of the Ni nanoparticle as shown in Fig. 2.8. After exposure to H_2 at

600°C, catalyst changes from a well-characterized hemispherically shape to polyhedral morphology where the major surfaces are large areas of (001) top and (111)/(011) side planes. Between these two planes, stepped plane (113) facets were observed which played an important role as nucleation site to form graphene sheet. Subsequently, after C₂H₂ introduction, the reconstruction of crystalline shape occurred again which was represented by shrinking areas of the central (001) and the surrounding (111) side planes. However, the nanoparticle changed its shape again after cooling to low temperature in inert gas, which failed to characterize the successive transformations of post reaction.

2.2.6 Carbon structure interactions with metal surfaces

The interaction of atomic carbon with various metal surfaces has been widely studied. With reference to the stability of the ideal C sp² structure such as graphene, the adsorption energy of a carbon atom can directly show whether a carbon atom is preferentially binding to the tube or to the metal. For Ni and Co, the carbon atom favours the hollow (100) semi-octahedral sites than compact facets [66]. When suitable surface coverage is satisfied, it will result in the (2×2) P4g surface reconstruction occurring on Ni (100). For Fe, due to carbon adsorption on the different facets, the surface energies of various surfaces are modified greatly, potentially explaining changes of the nanoparticle shape observed during growth [67].

Starting from individual carbon atom, the next stage is the study of the interaction of tubes with flat surfaces or metal particles. In this situation, carbon atoms have already bonded with other nearby carbons and thereby the interaction with metal phase is weaker. Ding and

co-workers [68] have highlighted the importance of a strong carbon-metal interaction during the growth period in order to prevent the detachment of the tube. They observed that Pd and Au bind weaker to the tube and hence perform poorer than Fe, Co and Ni. Larsson *et al.* [69] simulated the adhesion energy between metal and SWCNT and Fe and Co performed better bonding than Ni. Much weaker interaction energies can be obtained when carbon structure such as graphene overlies flat on the metal surface. However, calculations using DFT face difficult challenges since the method applied on DFT overestimates the adhesion energy.

2.2.7 Coking as the main deactivation process in methane decomposition

Metal catalyst deactivation in hydrocarbon reaction is attributed by carbon deposition or coking for a prolonged time. Coking generally refers to the deposition of different types of carbon species including carbonaceous species with high carbon-to-hydrogen ratio, amorphous carbon and graphite. Coking may affect catalyst reactivity in various ways as shown below:

- (i) The carbon deposition can adsorb intensively on the metal surrounding and hinder access to the metal surface.
- (ii) The carbon can encapsulate the metal nanoparticle.
- (iii) The micro and mesopores can be plugged, which block access to the active phase inside the pores.
- (iv) Due to the accumulation of strong carbon filaments, the catalyst can be disintegrated.
- (v) In the extreme case, carbon deposition can physically block the reactor.

So, from a practical point of view, it is of great importance to determine the deactivation

mechanism and process in order to design the catalyst properly and optimize the reaction.

In methane decomposition process, the elemental carbons are supposed to remove and transfer to nucleation site for CNTs or CNFs growth as well as to keep the active surface clean. Therefore, in the steady state, the rate of methane dissociation, elemental carbon atom diffusion and CNTs/CNFs growth should be almost the same. Once the diffusion rate is lower than decomposition rate, the carbon atom will accumulate at active surface which leads to termination of methane dissociation. The most common deactivation phenomenon is that catalyst nanoparticles found at the tips of CNFs/CNTs are covered by carbon layers as seen in Fig. 2.9. It also could be attributed by the fact that due to solubility limitation of carbon in transition metal and when the dissolved carbon reaches its saturation content, the encapsulating carbon will be formed.

Therefore, based on coking-based deactivation, carbon deposited on metal/gas interface formed a layer called encapsulating carbon which hinders the reactant access. Studies on encapsulating carbon have revealed an inverse dependence of the methane partial pressure and hydrogen partial pressure [70, 71]. Moreover, increasing temperature has a positive effect on the encapsulating carbon formation rate.

Except for the coking deactivation mechanism, another mechanism that could explain the decrease of reactivity of catalysts is that metal particles are fractured within the hollows of fibers due to the quasi-liquid state of metal particles at high temperature [64, 72]. Avdeeva *et al.* [73] also proposed that the limited space also led to catalyst deactivation since the

space at the tip filament would stop the Ni particle moving when the CNFs reached near close-packed structure which would result in nickel encapsulation by carbon. Similarly, limited space for the formed filaments could impede each other which further inhibit the CNFs growth.

For the bimetallic catalysts such as Ni-Cu catalyst, atomic erosion of the catalyst was assumed to be the deactivation phenomenon [73]. Salmones and coworkers [74] had postulated that different Ni contents in Ni-Mg-Al catalyst, i.e. 15 wt.% , 25 wt.%, and 50 wt.%, would have influence on the catalytic activity and life time of the catalyst. It have been reported that the catalyst with lower Ni content deactivated much slower than that of high Ni content and postulated that it was related to the pore geometry of the catalyst. The high Ni content leads to ink-bottle shape pores in catalyst which are embedded by CNTs/CNFs in a short period with little problem. On the contrary, the Ni nanoparticles in the catalysts with low Ni content are commonly found at the pore openings and situated on the tip of the CNTs/CNFs, maintaining the high accessibility of the catalyst for successive reaction. Italiano [75, 76] had observed Ni and Co supported catalysts and postulated that sintering of the catalyst particles and formation of filamentous carbon with metal particle at tip were two reasons for the destruction and deactivation of the catalyst. One efficient solution for preventing Ni sintering is the addition of Mg and La species rather than K and Cl. For Co catalysts, the strong interaction between Co and Al_2O_3 could impede Co sintering.

2.2.8 Factors affecting catalyst deactivation

Fig. 2.11 Methane conversion vs. time, at 600°C (squares), 550°C (circles), and 500°C (triangles) [77].

The catalyst deactivation rate is substantially influenced by operating conditions such as methane flow rate (the gas hourly space velocity, GHSV), reaction temperature, methane partial pressure and hydrogen partial pressure. Suelves and co-workers [77] found that temperature and methane flow rate had direct positive effects on the catalyst deactivation rate as shown in Fig. 2.11. Villacampa *et al.* [70] investigated the effect of hydrogen partial pressure on the deactivation rate and reported that the total amount of carbon deposited increased with a small amount of hydrogen although the conversion rate was lower as shown in Fig. 2.12. It could be explained by the fact that hydrogen might adsorb on the active site, stop the methane from adsorbing and decrease both the conversion rate and the deactivation rate. However, for the effect of methane partial pressure, increasing P_{CH_4} raised both conversion rate and deactivation rate and slightly decreased the total deposited carbons. Therefore, it could be concluded that the effects of the various factors on the reaction rate and deactivation rate are as follows: any parameters increasing the reaction

rate have positive effect on deactivation rate.

Fig. 2.12 Influence of hydrogen partial pressure on (a) carbon formation rate and (b) carbon content deposited on the catalyst [70].

2.3 Synthesis-structure relationship in carbon nanotubes

The conformation of the formed carbon involves information of its growth mechanism. Various nanocarbon structures such as CNTs, CNFs and nanotubes are observed in the CDM reaction as seen in Fig. 2.13 [7]. On this part, for each carbon structural characterization, the experimental parameters are summarized to emphasize the most influential dependence and the dominant trends.

Fig. 2.13 Various nanocarbon formed in CMD reaction. (A) SWCNTs; (B) MWCNTs; (C,D,E) regular CNFs with different α values; (F) octopus CNFs; (G) bamboo-shaped CNFs; (H) carbon nanooions [7].

2.3.1 SWCNTs and MWCNTs

As the simplest CNT, the growth mechanism of SWCNTs has been widely studied by many research groups and there is already a well-supported growth mechanism for SWCNTs as shown in Fig. 2.14 [78]. At the beginning of the CMD reaction, the instable carbides quickly expel the carbon atoms that dissolved in the bulk to the surface and subsurface and then a cap forms. After the formation of carbon cap, carbon atoms preferentially minimize their energy. Whether the catalyst particle grows a SWCNT or gets encapsulated (form fullerene) relies on the interplay between curvature energy and the adhesion energy of carbon to the metal particle. In the case of small catalyst particles, the curvature energy plays a decisive role, which means the energy per carbon atom is lower when forming a SWCNT than a spherical fullerene due to the exceeding curvature. Therefore, in order to minimize their total energy, the catalyst particle prefers to grow SWCNT instead of

formation of a fullerene around the catalyst particle. However, in the case of larger particles, the curvature energy becomes similar for a spherical fullerene and a SWCNT. The catalyst particle either grows a SWCNT or gets encapsulated (form fullerene) which relies on the comparison between curvature energy and the adhesion energy of carbon to the metal particle. The formation of SWCNT is favorable if the work of adhesion is low or if the temperature of the reaction is high.

Fig. 2.14 The mechanism of the growth of SWCNTs [78].

For the growth mechanism of MWCNTs, one crucial problem is to explain how carbon atoms diffuse and grow the inner wall of a MWCNT. One explanation is bulk diffusion mechanism which is straight-forward. However, the more reasonable explanation is that carbon atoms diffuse not only on the surface of the metal particle but also on the subsurface. The possible mechanism for growth of MWCNTs is shown in Fig. 2.15 [78].

Fig. 2.15 Possible paths for carbon diffusion during the growth of MWCNTs. Green and red arrows show possible and prohibited paths, respectively. The growth of the outmost wall occurs by surface diffusion of carbon atoms. However, as the outmost tube is attached to the catalyst particle, the growth of the inner walls is unlikely to occur via surface diffusion too. Although bulk diffusion is excluded, calculation showed that sub-surface diffusion (in the first 2 atomic layers) of carbon atoms is likely [78].

2.3.2 Nanotube outer diameter and inner diameter

A relationship between the size of the catalyst particle and the diameter of the nanotubes is frequently investigated. For example, Cheung *et al.* [79] observed that iron nanoparticles of diameter of 3, 9 and 13 nm led to the formation of MWCNTs with average diameters of 3, 7 and 12 nm respectively. Similarly, Chen *et al.* [80] reported the correlation between the size of metal particle and the diameter distribution of SWCNTs.

Based on in-situ TEM studies, a dynamic reshaping of the particle could be the answer to explain the relationship between a nanotube and its catalyst particle. In the case of Fe, Co and Ni, the catalyst particle exhibits a pear-like shape and the top of pear fits the inner diameter of the carbon nanotube while the bottom of pear fits the outer diameter as shown

in Fig. 2.16. Moreover, increasing the growth temperature is reported to have a positive effect on the MWCNT diameter distribution since thermal coarsening can increase the diameter of nanoparticle. On the contrary, for SWCNTs, Yao *et al.* [81] observed that the diameter of individual SWCNT decreases with increasing temperature. A similar result was obtained by Mahjouri-Samani [82].

Obviously, the inner diameter of CNTs is related to the outer diameter. Moreover, the carbon-bearing precursor also affects the inner diameter. Sharma *et al.* [83] investigated that the lower precursor supply decreased the number of walls.

Fig. 2.16 In situ ETEM observation of the growth of a four-wall CNT from a fluctuating catalyst nanoparticle of $(\text{Fe}, \text{Mo})_{23}\text{C}_6$ -type structure [84].

2.3.3 Proportion of catalyst particles active for nanotube growth

It is commonly found that many catalyst particles do not produce nanotubes. For example, applying individual Ni particles with 4.7 ± 1.5 nm, Paillet *et al.* [85] measured that the

proportion of active particles producing nanotubes ranged from 0.5% to 20%. Ishida and co-workers [86] used Fe particles of 1.7 ± 0.6 nm to test the proportion and they obtained a low proportion of produced nanotube which was approximately 10%. Since the growth of carbon nanotubes strongly depends on the size of particles, the various distribution of particle size is the likely reason for explaining the low proportion of produced carbon nanotubes. The encapsulation of active particle by a graphitic layer is intensively observed among low proportion of active phase as shown in Fig. 2.17 [87]. Rummeli *et al.* [88] had proposed that the formation of encapsulating carbon was due to supersaturated catalyst particle since the biggest particles exhibited a larger volume to surface area ratio which would promote encapsulating by precipitating carbon. Therefore, preventing the particle from encapsulation and reducing the catalyst coarsening are the two main solutions applied to grow high-yield CNT samples.

Fig. 2.17 Nickel particles encapsulated by a thick (a) or single-layer (b) graphitic observed after nanotube growth together with active catalyst particles [87].

2.3.4 Fishbone type of CNTs

Fishbone type CNTs were observed on Ni-based catalyst at a comparatively low temperature [89]. Two structural models have been widely applied to explain the fishbone-

type CNTs, i.e. cup-stack and helical texture models as seen in Fig. 2.18 [90]. The cup-stack model describes the formation of carbon which is bowl-shaped like and they are parallel to each other. The helical model explains that one sheet forms continuous graphite layers. Although these two models cannot be characterized by TEM, Monthieux and co-workers [90] supported the cup-stack model due to easy formation of fragmented CNT samples when subjected to a low shearing stress. The non-continuous structure is also deduced by the non-uniform growth rate and the jump of the metal particles.

Fig. 2.18 Sketches for the two possible models account for the herringbone texture of nanotubes. (A) Cup-stack model, each cup is made of an independent carbon sheet. (B) Helical model, the fiber forms with one continues carbon sheet [90].

2.3.5 Bamboo-shaped CNTs

Given the specific morphology of the bamboo-shaped CNTs, Chen *et al.* [91] proposed a growth mechanism where two different kinds of movement of active phase were included. The smooth movement is the first one where the driving force is the formation of new carbon layers at the carbon/metal interface, which results in the growth of continuous and uniform wall. The jump of metal particle is the second one and is a highly likelihood only

when the metal particle is in a quasi-liquid state and has low wetting with graphene surface. The driving force for the jump of metal particle is attributed to the fact that due to insertion of new carbon layer, there exists the accumulation of stress which is larger than the combination force of carbon and metal as shown in Fig. 2.19 [91].

Fig. 2.19 Schematic diagram of the growth of bamboo-shape CNT [91].

2.4 Catalyst for the reaction

Methane is the most stable organic molecule because it has very strong C-H bond (440 kJ/mol) and high symmetry of the molecular structure. Its decomposition can only be carried out efficiently at a temperature higher than 1200°C without the presence of a catalyst. Therefore, in order to reduce the high reaction temperature, catalytic methane decomposition is widely developed and various metal catalysts for this reaction have been studied extensively. The general reaction mechanism has been assumed to be almost the same even with different metal catalysts. However, the chemical composition and preparation method, the support and the promoter will not only affect the activity and stability of catalyst but will also affect the structure of the CNTs.

2.4.1 Active phase

Fig. 2.20 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 [92]

Iron group (Ni, Co, Fe) metals are the most extensively used catalysts in the methane decomposition reaction. Ni-based and Co-based catalysts have sufficient catalytic activity for methane decomposition at 500-800°C while Fe-based catalysts over 700°C. Fig. 2.20 [92] illustrates, based on recent literature data, the favored temperature range of reaction and carbon product when compared with Co-based and Fe-based catalysts, Ni-based catalysts have higher catalytic activity and stability. This reason is that it is related to carbon solubility and the formation of carbides. The affinity for carbon increases from the right side to the left side of the periodic table. Moreover, only the decomposition of unstable metal carbide-like phase could form filamentous carbon. Obviously, Ni_3C is most unstable when compared with Co_2C and Fe_3C . Meanwhile, it was reported that the activity order for

Ni/Al₂O₃, Co/Al₂O₃ and Fe/Al₂O₃ catalysts was the same as that for their initial temperatures for the deactivation [93].

2.4.2 The physical state of the catalyst

It is of much importance to realize the physical state of the catalyst during CNT growth because it affects several properties including the solubility of the carbon and so on. Firstly, in the case of elements exhibiting eutectic point with carbon in phase diagram, the melting point can be reduced significantly, even up to a few hundred degrees as shown in Eq. 2.9.

$$T_m(r) = T_m^{bulk} \left(1 - \frac{4\sigma_{sl}}{H_f \rho r}\right) \quad (2.9)$$

where $T_m(r)$ and T_m^{bulk} are the particle and bulk melting points, respectively; σ_{sl} is the surface tension at the solid/liquid interface, H_f is the bulk latent heat and ρ is the density of the particle.

Secondly, when the particle is in the range of 1-10 nm, the equilibrium vapour pressure increases greatly based on the Gibbs-Thomson equation (Eq. 2.10)

$$\text{Gibbs-Thomson equation: } p = p_0 \exp\left(\frac{2V\sigma_{sg}}{kTr}\right) \quad (2.10)$$

where p and p_0 are the equilibrium vapour pressures on curved and flat surfaces, respectively; σ_{sg} is the surface tension at the metal/gas interface, V is the volume of an atom in the nanoparticle, k is the Boltzmann constant and T is the temperature. This equation shows the fact that a high surface/volume ration particle is unstable. Hence, the particles have tendency to evolve into larger sizes

All these influences stem from the large occupation of surface atoms to the total energy of

the system. Moreover, when nanoparticles are deposited on supports, their melting points are modified due to the interaction between the nanoparticles and the supports. Shibuta *et al.* [94] calculated that in the presence of supports, the melting point of nickel particle is increased up to 200°C.

2.4.3 Effect of the catalyst crystallite size

It has long been recognized that the catalytic activity can be influenced by the size and the surface structure of the catalyst since catalytic reaction is termed as structure-sensitive reaction. In general, the reactivity of a metal surface is correlated to both its geometric features and its electronic structure. Modification of the number of reactive sites, such as terrace, steps, kinks, surface defects, with decreasing particle size could influence the structural sensitivity of a catalytic reaction. Nanometric size effects could be explained by the decrease of the density of states at the Fermi level [95]. For a small particle consisting of a few hundreds of atoms, the electronic properties can be changed dramatically when compared with the bulk material since quantum confinement effect will be present.

For methane decomposition reaction, it was reported that there existed an optimum size range for CNTs/CNFs growth. Catalyst particles will display a negligible activity towards CNF growth if the size of particle is too large or too small. Chen *et al.* [96] applied a variety of nickel catalysts with different sizes to test nanometric size effects as seen in Fig. 2.21. Their studies clearly depicted that the optimum crystallite size of Ni catalyst for the highest carbon yield and initial CNF growth rate was about 34nm. Similarly, Ermakova *et al.* [97] observed that the favourable average particle size for producing CNTs was within the range

of 30 to 40nm. Moreover, after 1h, all catalysts with different initial particle sizes reached the same thermodynamic size by the way of dispersion or merger. Based on numerous literature databases, it could be summarized that with increasing temperature (e.g. $500^{\circ}\text{C} \rightarrow 550^{\circ}\text{C} \rightarrow 580^{\circ}\text{C} \rightarrow 700^{\circ}\text{C}$), the optimal particle size reduces (e.g. $60\text{-}100\text{nm} \rightarrow 30\text{-}40\text{nm} \rightarrow 34\text{nm} \rightarrow 10\text{-}20\text{ nm}$). These phenomena could be explained by the influence of the particle size on the solid solubility of carbon and the stability of mixed compounds like carbides. Based on thermodynamic models, the solubility of carbon inside the nanoparticle increases with decreasing nanoparticle size. Recently, Diarra *et al.* [98] found that at a constant carbon chemical potential and temperature, a larger fraction of carbon was dissolved in the smaller nickel nanoparticles due to the larger carbon solubility in sub-surface than in the bulk. Moreover, small catalyst particles are also more exposed to their environment and are therefore more sensitive.

Fig. 2.21 Effects of NiO crystal size on the growth rate (left) and the final carbon yield (right) of CNF. Reaction conditions: $T=580^{\circ}\text{C}$, $P_{\text{tot}}=100\text{kPa}$, $P_{\text{CH}_4}=80\text{kPa}$, $P_{\text{H}_2}=5.5\text{kPa}$. Total flow: 50ml/min [93].

2.4.4 Effect of support

The dissociation behavior of metal catalyst not only relies on its size and surface structure but also on its interaction with the support. Strong metal-support interaction (SMSI) is defined as the decrease of catalytic activity of metal particles on certain supports. SMSI are commonly influenced by two aspects: (i) the modification of the electronic structure of the nanoparticle through charge transfer and (ii) the physical encapsulation of the particle.

Interaction between metal particle and oxide surface leads to charge redistribution at the interface where there are only the first few atomic layers. The driving force for this charge redistribution is the difference of electronegativities between metal and support. However, this charge modification has only significant effect on particles smaller than 2nm [95]. For insulating oxide such as Al_2O_3 , MgO and SiO_2 , local electronic interaction is the main phenomenon while in the case of conducting oxides such as TiO_2 , ZrO_2 and ZnO , charge modification is long ranged and thus promote the chemical interaction [99].

Physical encapsulation of the particles by a layer of support refers to chemical interaction corresponding to atom diffusion at the metal-oxide interface [95]. In general, encapsulation is a way to minimize the surface energy since it includes mass transfer from the oxide support to the surface of the metal phase. It affects the metals especially with high surface energy anchored on the oxide surfaces with low surface energy like Pt and Pd particles supported on TiO_2 . Besides, coarsening (or sintering) is another way to minimize the energy of the system. Coarsening of supported catalyst could be classified in two ways: the diffusion of single metal atom from small particle to larger one (Ostwald ripening) and

migration and coalescence of whole catalytic particle (Smoluchowski ripening). The driving force for Ostwald ripening is that metal atoms remove more quickly from small particle than larger one due to small vapor pressure corresponding to larger particle size, which leads to a net flow of mass from the smaller one to larger one. In tremendous cases, it was reported that the introduction of oxygen greatly promotes particle sintering due to the formation of more mobile metal oxide [100]. The possibility of Smoluchowski ripening increases with the surface density of particle and their migration coefficients, but also relies on the diameter, shape and nature of the particle. The study of Ni particles supported on SiO_2 [101] and Al_2O_3 supported Ni particle [102] indicated that migration coalescence dominates when temperature is less than 700°C and the time is typically less than 1h while Ostwald ripening at higher temperature and longer times.

Fig. 2.22 Standard enthalpies of formation of some 3d transition metal silicide [7].

Several research groups reported that transition metal tends to diffuse into silicon and then form metal silicide which has much lower catalytic activity such as formed nickel silicide at 225°C [103], cobalt at 450°C and iron at $800\text{--}850^\circ\text{C}$ [104]. The tendency of a given metal to form silicide is apparent in the silicide formation enthalpies as seen in Fig. 2.22

[7]. Pauling electronegativity is also a good reason to explain the chemical affinity of transition metals to oxide surface. Metals whose electronegativity is lower than 1.5 have propensity to form strong chemical bonds with silica [99]. Mattevi and coworkers [105] found that due to lower electronegativity of Al compared to Si, the interaction of Fe with Al_2O_3 is much stronger than with SiO_2 .

For methane decomposition reaction, Takenaka *et al.* [106] compared a series of nickel catalysts with different supports such as SiO_2 , graphite, TiO_2 , ZrO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, MgO/SiO_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the way of impregnations. The catalyst supported on TiO_2 , SiO_2 and graphite showed higher reactivity than the ones supported on Al_2O_3 or MgO shown in Fig. 2.21. It was explained that the mixture of nickel oxide and support ($-\text{O}-\text{Ni}-\text{O}-\text{M}$; $\text{M}=\text{Mg}$, Al and Si) was inactive catalysts demonstrating that Ni was not completely reduced due to the SMSI.

Fig. 2.23 Methane conversion over Ni catalysts supported on different supports at 500°C [106].

However, Suelves and co-worker also prepared a series of nickel supported by fusing to test methane conversion under 450°C. On the contrary, Ni catalysts supported on Al₂O₃ and MgO gave good performance than catalysts supported on SiO₂ and TiO₂. Due to SMSI, Ni catalysts supported on Al₂O₃ and MgO only formed 10-30nm crystallites while on SiO₂ and TiO₂ formed a larger domain size of 50nm. Based on the preceding discussions, it seems that catalysts prepared through SMSI could facilitate the formation of smaller metal catalyst crystallites. Undoubtedly, the size of particle plays a dominant role in CMD reaction. However, SMSI will sometimes result in the formation of spinal phases such as NiAl₂O₄ using co-precipitation at high calcination temperature which could not participate in the methane decomposition process. Finally, under heat treatment, metal support on silica/alumina can also form surface silicates/aluminates. Although in silicate forms, the reactivity of catalyst could be partially recovered using a reduction treatment. For example, cobalt silicates and aluminates can be partially recovered into cobalt using hydrogen when reduction temperature is in the range of 700-900°C while CoO and Co₃O₄ could be reduced to Co at 300-400°C under H₂ [107].

2.4.5 Effect of promoters

As the methane decomposition reaction is endothermic, higher methane conversion is favorable by a high reaction temperature. However, supported nickel catalyst shows the optimal performance at temperature of less than 600°C [108]. In order to improve catalytic activity and stability at high temperature, adding other elements termed as promoters is being investigated.

Fig. 2.24 Hydrogen (black dot) and carbon (white dot) 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°C [109].

Copper without d-vacancies in its electron configuration displays a negligible affinity for carbon indicating that it is inert in the methane decomposition reaction. However, it is an efficient promoter to form bimetallic catalyst with transition metals and thus increases the stability of the catalysts. Baker *et al.* [48] conducted a comprehensive investigation of various ratios of Ni-Cu-MgO catalysts. They found that Ni-MgO exhibited limited activity at temperatures over 650°C while Ni-Cu-MgO catalysts had high catalytic activity and stability at 665 to 725°C as shown in Fig. 2.22 [109]. In Ni-Cu-MgO system, copper has a propensity of segregation on the surface of the Ni-Cu bimetallic alloy which reduces the number of surface Ni^0 sites, indicating lower deactivation rate. It could be concluded that the promotion effect is actually achieved by lowering the intrinsic activity of nickel, therefore moderating the deactivation of catalyst and adjusting to a higher working temperature. Moreover, Avdeeva *et al.* [110] studied that copper could greatly increase the catalytic lifetime and efficiency of methane decomposition reaction in Ni-Cu- Al_2O_3 system at 625 - 675°C . Suelves *et al.* [111-113] comprehensively investigated Ni-Cu catalysts with

various supports (Al_2O_3 , SiO_2 , MgO , or TiO_2) prepared by co-precipitation, fusion and impregnation methods. After adding copper, catalyst composition is the only significant parameter to influence the catalytic activity, irrespective of the preparation methods. Cunha *et al.* [114, 115] investigated the formation of encapsulating carbon which could be prevented by adding copper since copper could dilute the active phase and thereby decrease the encapsulation rate of carbon. Some conclusions related to the effects of copper could be drawn from the various literatures as follows:

- (i) Pure Ni is more active than metallic Ni diluted with Cu for methane dissociation. The reason could be that Cu may have electronic effects on Ni and therefore lower the catalytic efficiency of Ni.
- (ii) Ni, Co and Fe are much more difficult to reduce than Cu. In the reduction process, Cu is frequently reduced at low temperature and then it becomes the centre for H_2 activation and promotes the reduction of NiO which means that some mixture oxides such as the spinel-like phases (NiAl_2O_4) could be reduced relatively easily and thereby increasing the operable amount of Ni sites.
- (iii) Doping of copper could increase the temperature to form quasi-liquid state, which will disintegrate the catalyst into fractured particles and thus could end the reaction. This tendency decreases with decreasing content of Cu.
- (iv) The segregation of Cu in the Ni-Cu bimetallic system is commonly discovered. This “ensembled effect” advances the formation of “octopus-like” carbon filaments and prolongs the catalyst performance.

ZnO is also deemed as the promoter to increase the reactivity and stability of $\text{Ni}/\text{Al}_2\text{O}_3$

[116]. It was reported that the appearance of the quasi-liquid state of the Ni particles at 750°C would be retarded in the presence of the ZnO. Moreover, the addition of ZnO will underline the wetting effect of the metal particles on the growing carbon layers and hence the encapsulation and deactivation of the catalyst will also be delayed. All these were contributed by the formation of ZnAl_2O_4 spinel-like structure.

The bimetallic catalysts are deemed as more active than monometallic catalysts. It could be explained by the fact that the doping effect of different active metal elements with different optimal working temperatures seem to constrain the deactivation and improve the overall reactivity. Shah *et al.* [117] studied the catalytic decomposition of carbon-bearing precursors (methane, ethane, propane) over binary Fe-M/ Al_2O_3 (M= Pd, Mo, Ni) catalysts and Fe-M/ Al_2O_3 showed better performance than Fe/ Al_2O_3 and Pd/ Al_2O_3 . The doping effects of different metals (Cu, Rh, Pd, Ir, and Pt) supported on Ni catalysts were investigated by Takenaka *et al* [118]. It was discovered that only the addition of Pd led to delay on the deactivation of catalyst and prolong the catalytic life while others led to a decrease of the total H_2 yields when compared with Ni/ SiO_2 as shown in Fig. 2.26 [118]. Chesnokov and Chichkan [119] compared the differences amongst prepared Ni/ Al_2O_3 , Ni-Cu/ Al_2O_3 and Ni-Cu-Fe/ Al_2O_3 . The addition of Ni, Cu and Fe simultaneously produced much higher carbon yields and stability at 700°C than Ni or Ni-Cu catalyst and the explanation was due to the formation of small dispersed Ni-Cu-Fe alloy phase. The doping effect of Fe can decrease methane decomposition rate and increase the carbon diffusion rate because diffusion constant of carbon atoms through Fe is three orders of magnitude higher than that through nickel.

Fig. 2.25 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 [118].

2.5 Catalyst preparation

Catalysts prepared by different techniques can result in different particle sizes, compositions and SMSI and thereby also display also different catalytic reactivities. Diversed preparation methods involving deposition-precipitation, impregnation, reversed impregnation, sol-gel, co-precipitation and fusion have been tested for synthesis of active and stable catalysts for CMD reaction.

Generally, the catalytic reactivity is not a linear function of the amount of transition metal present in the catalyst/support matrix. For example, Venugopal *et al.*[120] had carried out experiments for different nickel loadings in the 5-90% range to examine the catalyst performance. The results showed that increasing metal loading could positively improve the methane conversion and catalyst stability up to 30% metal loading. Increasing the active phase percentage beyond 30% led to poorer performance for the CMD reaction as

shown in Fig. 2.27 [7]. Therefore, catalytic preparation techniques are classified into two groups: low metal loading methods and high metal loading methods to further compare these two groups with their characterizations.

Fig. 2.26 Methane conversion over various Ni/SiO₂ catalysts at 600°C[120].

2.5.1 Preparation methods for low metal loading catalysts

Catalysts prepared by impregnation and deposition-precipitation are characterized by weak interaction between metal and support and they are deemed as techniques to synthesize low metal loading catalysts (e.g. <20 wt.%). Li and co-workers [121] had tested Ni/CeO₂ catalyst with a loading of 10 wt.% using different preparation methods and their results showed that the co-precipitation method displayed much lower hydrogen formation rate than those prepared by impregnation and deposition-precipitation due to the formation of Ni-O-Ce solid in promoting SMSI.

Sol-gel preparation method had also been applied to synthesize low metal loading catalyst,

particularly for the work targeted to produce thin diameter MWCNTs and SWCNTs [122]. This method like co-precipitation also promotes SMSI. For instance, Ni-Al and Co-Al catalysts synthesized by sol-gel method are difficult to reduce due to the presence of spinel-like phases. Piao *et al.* [123] synthesized nickel catalysts supported on an alumina with properties of large surface area and high porosity. After reduction, small particles less than 10nm were obtained and hence the diameters of the carbon nanotubes were in the range of 10-20nm.

2.5.2 Preparation methods for high metal loading catalysts

High metal loading catalysts could be prepared by co-precipitation, reversed impregnation and fusion techniques. The co-precipitation method had been applied since 1910s and Feitknecht compound (FC) could be obtained from this process. FC is a compound with one stack of two kinds of layered structure as shown in Fig. 2.28 [7]. One is termed as brucite layer composed of packed double layers where oxygen and hydroxide ions combined with metal cations located at the octahedral sites formed between the dense double layers. The other is deemed as anionic interlayer composed of anions and water molecules. This FC structure is well-crystallized but the interlayer is highly disordered and the amount of water inside the interlayer is affected by temperature, water vapor pressure and the nature of the anions.

Fig. 2.27 Schematic diagram of the three-dimensional structure of hydrotalcite-like compounds. The gray blocks represent the brucite layer, which composes densely packed double layer of hydroxyl anions and metal cations locating in the octahedral sites of the double layers. The black balls illustrate the compensation anions and water molecules. This structure allows a uniform distribution of the metal cations [7].

It has been long realized that if a metal catalyst is derived from the reduction of metal oxide, it is of importance to ensure the uniformity of the oxide precursor before reduction. The co-precipitation method allows the formation of FC structure and thereby maximizes the uniformity of oxide precursor. Moreover, the calcination of the FC structure using different temperatures could result in different phases. In the case of $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, if the calcination temperature is low (approximately 330°C), a nickel oxide phase containing dissolved aluminum ions and an alumina phase containing dissolved nickel ions will be obtained while if the calcination temperature is high (approximately 730°C), a pure nickel oxide phase and NiAl_2O_4 phase will be obtained. All these phases have strong interactions and exhibit spinal-like phase which is characterized for good dispersion and thermal stability of the nickel oxide. In $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts derived from FC precursor, a strong interaction between Ni and hard-to-reduce Al_2O_3 leads to a paracrystalline structure of Ni phase with small equivalent particle size which is favorable for CMD reaction as shown in

Fig. 2.29 [7]. Ni/Al₂O₃ and Ni-Cu/ Al₂O₃ using co-precipitation method showed great activity for the reaction [124].

Fig. 2.28 The illustration of the Ni paracrystallinity. Distortion of Ni lattice cells by the inclusion of irreducible aluminate groups. This distorted structure can be prepared by the reduction of mixed oxide precursors [7].

Ermakova *et al.* [72] applied a reversed impregnation technique to prepare a high Ni loading catalyst. This method involved two steps: NiO was first synthesized by precipitation followed by drying and calcination. Then, Ni ions were impregnated onto the precursor with ions forming a promoter such as SiO₂, Al₂O₃ and TiO₂. This method takes advantage of obtaining particles with a desired size and loading easily. In this structure model shown in Fig. 2.30, the alumina acts as a stabilizer on the NiO particle. With this type of catalyst, they reported that the yield of carbon increased with increasing Ni content and reached the maximum when nickel loading was 90-96 wt.%.

Fig. 2.29 Hard-to reduce oxide arrangement in the structure of NiO matrix. This model accounts for the stabilization of high metal content catalyst stabilized by a support like alumina [7].

Direct fusion of nitrate salts and followed by calcination have been used for synthesizing high metal loading catalysts and this technique does not need filtration and washing. Suelves *et al.* [113] compared the Ni-Al and Ni-Cu-Al catalysts synthesized by coprecipitation and fusion techniques and concluded that the fusion method was as good as the co-precipitation method.

2.6 Reaction mechanism and kinetic studies

The CNT or CNF growth process from methane decomposition could be described by different kinetic models in the literature. In general, the deduced rate equations can be roughly classified into two categories: Langmuir-Hinshelwood-Hougen-Watson (LHHW) model and power law model.

2.6.1 Langmuir-Hinshelwood-Hougen-Watson model

In the LHHW model, it is assumed that there is one slowest reaction step while the others steps are in quasi-equilibrium. For catalytic methane decomposition, the reaction starts

with methane adsorption on the metal surface. Generally, two different mechanisms, non-dissociative methane adsorption (N-DMA) [125, 126] and dissociative methane adsorption (DMA) [127-131] on the metal surface, have been proposed. For the N-DMA, the methane molecule is first adsorbed (molecular adsorption) and then moves forward to dissociation. These pathways are shown in Table 2.4. In molecular adsorption, N-(1) shows the adsorption of methane molecule on the active surface and N-(2) to N-(5) steps depict the formation of methyl species and hydrogen atoms adsorbed on the active surface. N-(6) shows the formation of coke and N-(7) represents desorption of hydrogen from the active surface. Borghei *et al.* [132] proposed that the first step in non-dissociative methane adsorption is the rate-determining step and the rest are in quasi-equilibrium.

Table 2.1 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 dissociative methane adsorption, 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 2.2 Summary of mechanistic rate equations on supported metal catalysts

Reference	Reaction condition	Reaction rate equation	Rate-limiting step
Bernardo <i>et al.</i> [133]	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) 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> [134]	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 cat)⁻¹ h⁻¹kPa⁻¹) K_H: hydrogen adsorption constant (kPa^{-0.5}) </p>	N-(1)

		K_e : equilibrium constant (kPa) k_d : deactivation rate constant (h^{-1}) n : number of active sites involved in controlling step	
Snoeck <i>et al.</i> [135]	ICI 46-9P steam Reforming catalyst micro balance 500-550°C CH_4-H_2 Activation energy: 59 kJ/mol	$r = \frac{k_M^+ K_{CH_4} \cdot (P_{CH_4} - \frac{1}{K_M^*} P_{H_2}^2)}{(1 + \frac{1}{K_T'} P_{H_2}^2 + K_{CH_4} \cdot P_{CH_4})^2} \quad (2.13)$ 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 constant for methane cracking (kPa) K_T' : incorporated coefficient (kPa ^{-1.5})	N-(2)
Alstrup and Taveres [136]	Ni/SiO ₂ Microbalance 450-550°C CH_4-H_2 Activation energy: 90 kJ/mol	$r_1 = k_1 (P_{CH_4} S^2 - \frac{S_{CH_3} S_H}{K_1}) \quad (2.14)$ $r_2 = k_2 (S_{CH_3} S - \frac{S_{CH_2} S_H}{K_2}) \quad (2.15)$ 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) $S = 1 - S_H - S_{CH} - S_{CH_2} - S_{CH_3} - S_C$	D-(1) D-(2)
Zavarukhin and Kuvshinov [137]	Ni/Al ₂ O ₃ Fluidized bed 490-590°C CH_4-H_2	$r_{max} = k \frac{P_{CH_4} - \frac{P_{H_2}^2}{K_p}}{(1 + K_H P_{H_2}^{0.5})^2} \quad (2.16)$ 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}) ³ h/g ³ a : activity coefficient	D-(1)

Borghei <i>et al</i> [138]	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)
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Fig. 2.30 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 [139]

Fig. 2.31 Methane cracking: parity diagram based on the results for the sequential experiments on used catalysts samples[135].

2.6.2 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 [134,137-138,140]. 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 reaction temperature, methane and hydrogen partial pressure.

Demicheli *et al.* [134] 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.* [138] 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. 2.32 Plot of activity expression in relation to time (d=2) at 650°C [138]

Phenomenological approaches [137,141] 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% [137].

Fig. 2.33 Experimental (points) and calculated (lines) time dependencies of specific carbon content on the catalyst in a perfect-mixing reactor at 550°C [137].

Hazra *et al.*[142] 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 [143], 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. 2.34 Predicted and experimental change in carbon specific weight with time. Reaction conditions: $T=500^{\circ}\text{C}$; Total reaction gas flow rate =120 ml/min with 10 mg of catalyst: (a) $P_{\text{total}}=10$ bar, 10 vol% H_2 and balance CH_4 ; (b) $P_{\text{total}}=1$ bar, 5 % H_2 and balance CH_4 [142].

2.7 Summary

Hydrogen production from fossil fuels such as natural gas, which can be free CO/CO_2 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 not 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 SiO₂ and Al₂O₃. 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 Catalyst Preparation and Characterization

This chapter described the catalyst preparation methods, characterization methods and catalytic activity evaluation process. Ni/SBA-15 supported catalyst using electroless nickel plating technique with a wide range of nickel loadings from 19 to 37 wt. % 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 acetate Tetrahydrate	$\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$	Purity $\geq 98.5\%$ Sigma-Aldrich, Singapore
Silver nitrate	AgNO_3	Purity $\geq 99\%$ Sigma-Aldrich, Singapore
Ammonium hydroxide solution	NH_4OH	Purity $\geq 98\%$ Sigma-Aldrich, Singapore
Sodium hydroxide	NaOH	Purity $\geq 99\%$ Sigma-Aldrich, Singapore
Formaldehyde solution	HCHO	Purity $\geq 99\%$ Sigma-Aldrich Singapore

Deionized water	H ₂ O	In-house
Hydrazine monohydrate	NH ₂ NH ₂ ·H ₂ O	Purity ≥99% Sigma-Aldrich
Mesoporous silica	SBA-15	In-house
Methane	CH ₄	99.999% Air Liquide Singapore
Nitrogen	N ₂	99.999% Air Liquide Singapore
Hydrogen	H ₂	99.999% Air Liquide Singapore

3.2 Catalytic activity evaluation setup

The experiment setup for the catalytic decomposition of methane is shown in Fig.3.1. Three different gas sources were used in the reaction, i.e., CH₄, N₂ and H₂. The gases flowed from their respective storage cylinders to the mixing point. CH₄ was the source for the hydrogen production reaction. It was usually diluted in the experiments to reduce the rate of catalyst deactivation by coke formation. N₂ was used as the common dilution stream, which was also present in the original H₂ storage cylinder for safety precautions. H₂ was used for reducing the metal-oxide to the metal state for use as the active catalyst. This H₂ stream was also diluted to avoid aggressive temperature increase in the exothermal reaction. As the decomposition of CH₄ generated H₂ by itself, the process was self-sustaining and the introduction of external H₂ source was required only at the starting phase of the experiment. The various gas streams were regulated by mass flow controllers (MFC, Alicat Scientific, MC-100SCCM-D/5M). These mass flow controllers would be used to determine the gas flow velocity during the reaction and the composition of the gas feed.

To ensure thorough gas mixing, small ceramic rings were attached to the gas mixer to promote mixing. In the reaction chamber, the conventional metallic reactor wall was known

to introduce uncertainty to the experiment due to its catalytic effect. Hence, a quartz tube with 10 mm inner diameter and 800 mm length was used as the reactor. The quartz tube reactor was inserted into the tube furnace, where external heat was introduced. The tube furnace temperature (Lenton, LTF/12/28/500) was controlled by a temperature programmer. Its temperature readings were taken from a K-type thermocouple attached to the quartz reactor wall. Typically, a certain amount of catalyst was placed inside the reactor at approximately its mid-length. The catalyst was placed on a quartz wool tray for the convenience of insertion or removal. Another K-type thermocouple was placed near the catalyst bed to monitor the catalyst temperature. To minimize safety exposure to process gas leak, Teflon ferrules and stainless steel fittings were used in the gas lines to ensure airtightness.

To analyze the gases after the reaction, a HP-molesieve column and a Gas Chromatograph Thermal Conductivity Detector (GC-TCD, Agilent Technologies 6890N) was connected to the quartz reactor outlet. Helium was used as the gas carrier for the GC-TCD. A six-way valve with automation control collected the sample gas at 5 min interval. Prior to usage, the GC-TCD was calibrated against fixed gas composition gas mixtures of CH₄, H₂ and N₂ with expanded uncertainty of 0.1%-1%. During the actual test, the concentrations of CH₄ and H₂ were determined by comparing the ratio of CH₄ to H₂ against the calibrated data and then finally the methane conversion (defined as the number of moles of consumed methane divided by the initial number of moles of methane) was determined.

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

3.3 Catalyst preparation procedures

3.3.1. Preparation of Ni/SBA-15 catalysts

Monometallic nickel particles supported on SBA-15 (denoted as Ni/SBA-15) were synthesized via an electroless nickel plating process [144]. Firstly, 0.5 wt. % Ag/SBA-15 was prepared as seeds for the subsequent nickel deposition. 10 g SBA-15 was added to 425 mL of mixture solution at 40 °C and stirred for 4h. The mixture solution consisted of

$4.71 \times 10^{-2} \text{ g L}^{-1} \text{ AgNO}_3$, $8.82 \times 10^{-2} \text{ g L}^{-1}$ ammonia, $1.18 \times 10^{-2} \text{ g L}^{-1} \text{ NaOH}$ and $4.71 \times 10^{-3} \text{ g L}^{-1} \text{ HCHO}$. The resulting Ag/SBA-15 was collected and washed with distilled water and then dried at 90°C for 8h. Secondly, to prepare the plating solution, different amounts (2, 3, 4 and 5g) of nickel acetate tetrahydrate ($\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$) were dissolved in distilled water and mixed with hydrazine monohydrate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$) ($[\text{N}_2\text{H}_4]/[\text{Ni}^{2+}]=5$) whilst being stirred. The total volume of this nickel plating solution was 80 mL. 20 mL NaOH ($[\text{OH}^-]/[\text{Ni}^{2+}]=1.25$) solution was then added into this solution which was being stirred. Lastly, the Ni/SBA-15 catalyst was prepared as follows. 2 g Ag/SBA-15 was added into 100 mL of the nickel plating solution. The suspension was maintained at 85°C for 15 min, cooled to room temperature and then filtered. The black residue was washed with distilled water until $\text{pH}=7-8$ and finally washed with ethanol to remove water. The resulting Ni/SBA-15 catalyst was dried at 90°C overnight. Henceforth, the final nickel catalyst supported on SBA-15 (used in the methane decomposition reaction) is abbreviated as $x\text{Ni/SBA-15}$ where x is the weight percentage of Ni on support. Four samples with varying nickel loadings were prepared, i.e., 19Ni/SBA-15, 26Ni/SBA-15, 32Ni/SBA-15 and 37Ni/SBA-15.

3.3.2 Procedures for catalyst reduction and catalytic activity evaluation

The catalytic activities of the samples were carried out using an experimental set-up shown in Fig. 3.1. In a typical process, 140 mg of the Ni/SBA-15 catalyst was loaded into a quartz tube with an internal diameter of 23mm and a length of 800 mm. The quartz tube was placed in the mid-section of a stainless steel reactor which was heated in a vertical electric furnace (Carbolite). Any NiO/SBA-15 remnants were reduced to Ni/SBA-15 catalyst under

15 mL min⁻¹ 10% H₂/N₂ flow for 4 min at 450 °C. (The small amounts of NiO/SBA-15 present were due to the oxidation of the Ni/SBA-15 surface to NiO/SBA-15 when the catalyst was exposed to the atmosphere after preparation. Ni is reactive and will be readily oxidized to NiO in the atmosphere). The subsequent methane decomposition reaction was carried out at a total flow rate of 15 mL min⁻¹ of CH₄/N₂ gas mixture corresponding to a flow ratio of CH₄/N₂=1/1. The gas hourly space velocity (GHSV) at this condition was 6428 mL g_{cat}⁻¹ h⁻¹. The outgoing product gases after the reactor were analyzed using a calibrated gas chromatograph (Agilent 6890-5973 GC-MS network systems) equipped with a TCD. With preliminary methane conversion studies on the samples, the catalyst with a specified Ni loading which had the best performance in terms of methane conversion was further studied. Before conducting stability tests, the best catalyst (i.e., 32Ni/SBA-15) was subjected to different gas hourly space velocities in order to choose the most suitable GHSV. The methane conversion (χ_{CH_4}) was calculated using the following equation:

$$\chi_{CH_4} = \frac{C_{H_2}}{C_{H_2} + 2C_{CH_4}} \quad (3.1)$$

where C_{H_2} and C_{CH_4} are the concentrations of hydrogen and methane at the outlet of the reactor, respectively. Based on methane conversion, the carbon yield rate and hydrogen formation rate were calculated using the following reaction equation:

$$r_{carbon\ formation} = \frac{1}{2} r_{hydrogen\ formation} = F \times \chi_{CH_4} \quad (3.2)$$

3.3.3 Parameter study of methane decomposition process

After the formation of metallic nickel catalyst, the methane decomposition reaction was carried out at stepwise heating temperatures. Increasing the furnace temperature to the desired reaction temperature (525, 550, 575 and 600 °C) with a ramp-up rate of 5°C/min and held for a long time (>8 hours) for the reaction was carried out on the catalyst with various nickel loadings. Besides, different volumetric flow rate (10, 15, 20, 25 and 30 ml/min) were also used in another experiment to optimize the reaction condition. Methane gas diluted with N₂ (the mixture consisting of 50% methane and 50% of N₂) was used as the reacting gas with a total flow rate of 15 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 thermal conductivity detector (TCD) using helium as the carrier gas.

3.3.4 Experiments for kinetic studies

The general process of CDM using the two types of electroless nickel plating catalysts was carried out which were similar to the procedures described previously. In order to evaluate the catalyst full performance including the whole deactivation process, fixed amount of catalyst was used. Typically, 0.14g of the catalyst (Ni/SBA-15) was loaded in the middle of the reactor and reduced into metallic catalyst in 15 mL min⁻¹ 10%H₂/N₂ flow for 4 min 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 15 ml/min N₂ flow. After reaching the desired reaction temperature, a fixed CH₄ partial pressures (50%) with different total volumetric flow rate

(10, 15, 20, 25 and 30 ml/min) 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. To ensure that the transport resistances are negligible, stability tests were conducted for a typical catalyst such as 26Ni/SBA-15 catalyst. 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
26Ni/ SBA-15 (0.112, 0.14, 0.178g)	Room temperature to 450° C Heating rate: 5°C/min	Flow rate: 15 ml/min Feed: H ₂ -N ₂ (H ₂ :10%)	Heating rate: 5°C/min Flow rate: 15 ml/min Feed: N ₂	575°C	Flow rate: 10, 15, 20, 25 and 30 ml/min Feed: CH ₄ -N ₂ , CH ₄ concentration: 50% in volume
32Ni/ SBA-15 (0.14g)				525°C, 550°C, 575°C, 600°C	Flow rate: 15 ml/min Feed: CH ₄ -N ₂ , CH ₄ concentration: 50% in volume

3.4 Characterization of the catalysts and carbon deposits

An ion chromatography (Thermo Scientific Dionex, ICS-110) equipped with UV/Vis detector ($\lambda = 530\text{nm}$) was used to identify and quantitate the sample ion concentration in the solution. The range of nickel ion concentration for the calibration procedures was from 50 to 1500 ppm. Hence, the original concentration of nickel precursor at the initial stage of the synthetic reaction was diluted eighty times to do the ion analysis. After the synthetic reaction, the remaining solution was kept to do another ion analysis without dilution.

To analyze the crystalline structures of the catalysts, X-ray diffraction (XRD) patterns were measured with a diffractometer (Philips, PW1830) using $\text{CuK}\alpha$ ($\lambda = 1.5406\text{\AA}$). The X-ray generator was set at 40 kV and 40 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 $1^\circ/\text{min}$.

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.

A transmission electron microscope (JEOL JEM 2010) was used to observe the morphology and the physical characteristics of the catalysts and the resulting carbon nanofibers. 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.

Hydrogen temperature-programmed reduction (H_2 -TPR) was conducted using a chemisorption analyzer (Micromeritics, AutoChem II) which was equipped with a thermal conductivity detector. The Ni/SBA-15 catalyst was loaded into a quartz tube which was subjected to a gas mixture comprising 10% H_2 /Argon at a flow rate of 50 mL min⁻¹. The temperature was increased from 50 to 800 °C at a ramping rate of 10 °C min⁻¹ to obtain the TPR profiles of the samples.

Chapter 4 Preparation and Characterization of Ni/SBA-15 catalyst and Evaluation of Their Catalytic Activities

4.1 Introduction

Catalysts exhibit different catalytic performances which are dependent on the catalyst particle size, phase distribution and metal-support interaction. Impregnation is used for the preparation of low metal loading catalyst and this method requires the metal oxide to be reduced to pure metal by hydrogen gas. However, this method would lead to particle agglomeration under the hydrogen gas environment because of the weak interaction between metal and support. On the other hand, coprecipitation produces a metal oxide which has strong interaction with the support that could lead to incomplete metallic phase under the normal decomposition temperature as this reduction takes place simultaneously during the decomposition process. The temperature for the reduction of oxide compound (e.g. $-O-Ni-O-M-$; $M=Mg, Al$ and Si) is higher than that for catalytic methane decomposition. In this work, an electroless nickel plating on SBA-15 technique was presented. This technique shows medium interaction of the catalyst with the support and exposes a higher nickel loading on the support surface. The activity of the catalysts was investigated under two temperature-programmed processes involving a constant temperature mode and a stepwise heating temperature mode. The Ni/SBA-15 catalyst was

characterized using ion chromatography, transmission electron microscopy, X-ray diffraction and hydrogen temperature-programmed reduction.

4.2 Results and discussion

4.2.1 Characterization of the precursors and catalysts

In electroless nickel plating, hydrazine solution is used as the reductant to produce pure nickel nanoparticles in basic solution.

During the reaction between nickel acetate and hydrazine, the light blue colour of the reagent solution would eventually turn transparent at the end of the reaction which would then indicate that all nickel acetate was reduced to nickel by the reducing agent and deposited on the support. The actual nickel content on the support was calculated on the basis of the amount of reagent involved in the synthetic reaction. Fig. 4.1 shows the nickel ion concentrations at the initial stage of the chemical reaction and at the end of the synthetic reaction for the four catalysts. The nickel ion concentrations of the four remaining solutions after chemical reaction were about 105 ppm without dilution, indicating that the total amount of nickel precursor involved in the synthetic reaction was almost completely transferred as nickel metal on the support. Hence, the actual nickel loading on the SBA-15 could be determined.

Fig. 4.1 Typical ion chromatography results of nickel ion concentration before reaction (diluted 80 times) and after reaction (1) 19Ni/SBA-15, (2) 26Ni/SBA-15, (3) 32Ni/SBA-15, and (4) 37Ni/SBA-15 catalysts.

Fig. 4.2 shows the morphologies of Ni/SBA-15 as observed by transmission electron microscopy (TEM). The samples consisted of spherical nickel particles dispersed over the external surface of SBA-15. In the nickel electroless plating technique, a large amount of nickel nanoparticles were deposited on the silver seeds that accelerated drastically the autocatalysis of nickel plating process. More than 180 minutes was required in the plating process if there were no Ag seeds in the plating solution [145]. This high plating rate is beneficial in generating a mass of nickel nuclei during the inducing period, leading to small and uniform nickel nanoparticles. The TEM micrographs clearly show the successful

outcome in synthesizing homogeneous Ni particles with high Ni loading in the present synthetic work. In addition, no significant large particle agglomerations were seen in the catalysts except for 37Ni/SBA-15 (Fig. 4.2 (4)-1 and (4)-2), indicating that the SBA-15 support could distribute and disperse the active nickel metal particles effectively when the nickel loading was less than 37 wt.%. The interaction between the nickel particles and SBA-15 was further revealed by the H₂-TPR results. The peak particle diameters varied from 50 nm to 65 nm and 150 nm with increasing nickel loading on support. With reference to the synthesis process, electroless nickel plating basically consisted of coating the SBA-15 with Ag nanoparticles in the initial step and then coating nickel nanoparticles over Ag nanoparticles. Therefore, the number of Ag seeds would largely determine the number of nickel nanoparticles formed in this technique. For the four samples in Fig. 4.2, increasing nickel loading from 19 to 37 wt.% increased the overall particle size progressively as the number of Ag seeds were fixed (0.5wt.% Ag/SBA-15) and the probability of overlapping individual Ni particles on the support increased, thereby apparently increasing the particle size.

Chapter 4 Preparation and Characterization of Ni/SBA-15 catalyst and Evaluation of Their Catalytic Activities

Fig. 4.2 Typical TEM micrographs (left) and particle size distributions (right) of (1) 19Ni/SBA-15, (2) 26Ni/SBA-15, (3) 32Ni/SBA-15, and (4) 37Ni/SBA-15 catalysts.

Fig. 4.3 XRD patterns of (1) 19Ni/SBA-15, (2) 26Ni/SBA-15, (3) 32Ni/SBA-15, and (4) 37Ni/SBA-15 catalyst.

Figure 4.3 shows the XRD patterns of the pristine Ni/SBA-15 catalysts. The broad peak located at around 22.5° was attributed to the mesoporous silica. The three distinct diffraction peaks at $2\theta = 44.4^\circ$, 51.9° and 76.1° could be indexed to metallic Ni planes (1 1 1), (2 0 0) and (2 2 0), respectively. The minor spikes located at 37.0° and 62.8° were attributed to the (1 1 1) and (2 2 0) crystalline planes of NiO which was formed as Ni was oxidized to NiO when the catalyst was exposed to atmosphere as explained earlier. With increasing nickel content, the peaks corresponding to metallic nickel increased in magnitude and intensity, which were due to the increasing crystalline size. For the XRD patterns for NiO in Fig. 4.3, the NiO spikes increased in slight intensity for decreasing Ni

loading. As decreasing Ni loading was associated with decreasing Ni particle size (Fig. 4.2), the smaller particle has a larger specific surface area which resulted in more surface area of the catalyst being oxidized to NiO.

Fig. 4.4 N₂ adsorption-desorption isotherms of SBA-15 for no and various Ni loadings

The N₂ adsorption-desorption isotherms of SBA-15 for no and various Ni loadings are shown in Fig. 4.4. It is observed that the physisorption isotherms of the SBA-15 are not reversible at high P/P_0 and this phenomenon is termed adsorption hysteresis. Under the IUPAC classifications of physisorption isotherms, these isotherms are classified as Type IV isotherm with capillary condensation taking place in mesopores and a limiting uptake over a range of high P/P_0 . The Type IV isotherms as exhibited by the SBA-15 support in Fig. 4.4 are generally applicable to mesoporous adsorbents with pore sizes of 2 - 50 nm. The Type IV isotherms observed for the pristine and Ni-loaded SBA-15 samples verified

that Ni loading on SBA-15 supports would not destroy the mesoporous structures of SBA-15 which were also similarly reported for other Ni/SBA-15 related catalysts [11-13]. Even with Ni loading of 37 wt. %, the Type IV isotherm prevailed with the mesoporous structure still in place. However, starting from the pristine SBA-15 and with increasing Ni loading on the SBA-15 support, the volume adsorbed progressively decreased for all P/P_0 values. It is surmised that the nickel particles deposited on the SBA-15 external surface partially block the pore entrances and prevent the adsorption of N_2 molecules in the internal pore surfaces. Table 4.1 shows the textural characteristics of the pristine SBA-15 and Ni/SBA-15 catalysts with different Ni loadings. As expected, the unloaded SBA-15 had the largest BET surface area due to its unrestricted passage into the internal pores to the N_2 molecules. Increasing Ni loading on the Ni/SBA-15 surface increased the pore entrance blockage to N_2 molecules and therefore decreased the BET surface area continuously. There were no significant changes in the average pore widths despite wide variations in the nickel loading for the Ni/SBA-15 catalysts including the unloaded SBA-15.

Table 4.1. Textural characteristics of pristine SBA-15 and Ni/SBA-15 catalysts with different Ni loadings.

Catalyst	S_{BET}^a ($m^2 g^{-1}$)	$\sigma_{S_{BET}}^b$ ($m^2 g^{-1}$)	Dp^c (nm)
0Ni/SBA-15	444	11	10.1
19Ni/SBA-15	352	26	9.5
26Ni/SBA-15	326	19	7.6
32Ni/SBA-15	303	16	8.9
37Ni/SBA-15	291	18	9.4

^a BET surface area. ^b Standard deviation of BET surface area ^c Average pore width calculated by the Barrett-Joyner-Halenda (BJH) method.

Fig. 4.5 TPR profiles of the pristine Ni/SBA-15 catalysts with varying Ni loadings. (1) 19Ni/SBA-15, (2) 26Ni/SBA-15, (3) 32Ni/SBA-15, and (4) 37Ni/SBA-15

Fig. 4.5 shows the TPR profiles of the pristine Ni/SBA-15 catalysts. The peaks at the low temperature zone (100 to 400 °C) are associated with the reduction of pure NiO species that has no interaction with the support while the peaks in the intermediate temperature zone (400 to 500 °C) are linked to the reduction of NiO species with weak interaction with the support. The reduction of NiO species with medium strength interaction with the support is displayed as peaks ranging from 500 to 600 °C [146]. Based on these broad categories, the TPR results for the pristine Ni/SBA-15 catalysts are classified in order to examine the metal-support interaction intensity and these data are presented in Table 4.2.

The Ni/SBA-15 catalysts were prepared and handled under atmospheric environment and hence it was not possible to prevent the surface partial oxidation of Ni to NiO. Hence, the presence of NiO planes (1 1 1) and (2 2 0) is shown in Fig. 4.3. The three catalysts, viz., 32Ni/SBA-15, 26Ni/SBA-15 and 19Ni/SBA-15, showed that a significant amount of hydrogen consumption occurred between 400 and 600 °C while a lesser amount of hydrogen consumption took place between 150 to 300 °C. These phenomena verified that these three catalysts had weak to medium interactions with the supports which could reduce the possibility of nickel sintering during the reduction and methane decomposition reaction processes. A further increase in the nickel amount in 37Ni/SBA-15 catalyst led to a dramatic increase in the TPR spike between 100 to 250 °C (Fig. 4.5) coinciding with the NiO species without bonding on the support. No peaks representing bound NiO species to the support were present. The non-bound free NiO species in 37Ni/SBA-15 catalyst could easily migrate and aggregate during the reduction process, thereby giving rise to larger Ni particles for the decomposition reaction than the other three catalysts. In summary, the 19Ni/SBA-15 required the most hydrogen consumption, indicating a greater amount of nickel oxide formation which was consistent with the result shown in the XRD patterns (Fig. 4.3). In order to obtain a higher content of pure nickel for the catalytic decomposition of methane and the desire to include those NiO species with weak interactions with the support, the reduction temperature for NiO was set at 450 °C which could assure the highest amount of small nickel particles available for the methane decomposition reaction process.

Table 4.2 Deconvoluted TPR region showing the nature of metal-support interaction

Catalyst	Hydrogen consumption	Hydrogen consumption
	(cm ³ /g _{cat} at STP) (<300 °C: Pure NiO with no MSI ^a)	(cm ³ /g _{cat} at STP) (300 - 600 °C: NiO with weak and medium MSI ^a)
19Ni/SBA-15	1.836666	54.6098
26Ni/SBA-15	1.507153	22.32687
32Ni/SBA-15	4.874707	17.39348
37Ni/SBA-15	32.70438	0

^a MSI: metal-support interaction

4.2.2 Catalytic activity

To investigate the activities of the catalysts, the conversions of methane for the electroless nickel plating catalysts under stepwise heating temperatures are shown in Fig. 4.6. The 32Ni/SBA-15 catalyst produced the best catalytic activity with stable methane conversion values of 0.32 and 0.45 at 550 and 575 °C respectively, when compared with the other loadings. Methane conversion increased to 0.53 at 600 °C but it decreased gradually with prolonged reaction time. Increasing Ni loading from 19 to 32 wt. % enhanced the concentration of active phase, leading to increasing methane conversion. However, further increased loading of Ni to 37 wt. % decreased the catalytic activity due to the reduction in the catalyst surface area arising from the sintering of the active particles. In addition, the catalyst particle size will affect the catalyst performance in CDM. The catalysts with Ni loadings of 19 and 26 wt. % showed smaller crystalline and particle sizes while the 37 wt. %

catalyst had larger particle size as shown in Fig. 4.2. The above sintering effect and the excessive large particle size would reduce the reaction activity. It is possible that there is a critical domain size range for the active Ni particles to impact on the growth of the carbon nanotubes – either too small or too large a particle size would have adverse effects on such growth. Smaller particles would result in lower carbon concentration gradient in nickel particles, thereby reducing the driving force for carbon diffusion. Larger particles would lead to a decrease in the active surface area of the catalyst. Chen *et al.* [96] obtained the best performing sample with an average particle size of 34 nm amongst a variety of Ni particle sizes. Takenaka *et al.* [147] found that Ni/SiO₂ catalyst with a crystallite size ranging from 60 to 100 nm achieved good performance in CDM reaction. In this present work, nickel particle diameters ranging from 50 to 150 nm as evidenced in the 32 wt. % nickel loaded on SBA-15 support (Fig. 4.2), is thermodynamically preferable.

Fig. 4.6 Methane conversion for the catalysts using stepwise heating temperatures. The numbers present in the curves refer to the corresponding step temperature. (Experimental conditions: $\text{CH}_4:\text{N}_2=1:1$, total flow rate = 15 ml min^{-1} ; catalysts mass: 140 mg).

With the exception for the 37 wt.% nickel loading on SBA-15 in Fig. 4.6, the optimum methane decomposition reaction temperature for the Ni/SBA-15 catalysts for stable methane conversion was estimated to be 575 °C which was similar to that of Ni-CNT catalyst as reported by Shen and Lua [148]. At this decomposition reaction temperature, the SBA-15 support was still stable thermally and structurally to hold the active Ni particles in place as individual particles and to facilitate the growth of the carbon fibers by providing anchoring support. The maximum conversion achieved at 575 °C could also be attributed to the formation of the equilibrium between the adsorbed isolated carbon atoms and the surface migration and diffusion of carbon atoms through the nickel nanoparticles [72].

Fig. 4.7 Effect of temperature and gas hourly space velocity (GHSV) on methane conversion using 32Ni/SBA-15 catalyst.

Tests were carried out with the 32Ni/SBA-15 catalyst to determine the optimal GHSV for the long term life-span tests for the catalysts. Figure 4.7 shows that the maximum methane conversion was achieved at a gas hourly space velocity of $6.428 \text{ L h}^{-1} \text{ g}_{\text{cat}}^{-1}$ for all the velocities tested. At a GHSV value of $6.428 \text{ L h}^{-1} \text{ g}_{\text{cat}}^{-1}$, the residence time of the methane gas in the reactor would be the longest among all the GHSV values tested. The long residence time increased methane conversion for this lowest GHSV value. Evidently, if lower GHSV value (than those in Fig. 4.7) were to be used, the methane conversion should increase for increasing residence time for reaction. The methane conversion increased greatly from 32.9 to 57.5% with increasing reaction temperature from 525 to 625 °C, respectively, at constant GHSV of $6.428 \text{ L h}^{-1} \text{ g}_{\text{cat}}^{-1}$ and similar trends were observed for other GHSVs. Since methane catalytic decomposition reaction is moderately endothermic, increasing temperature increases methane conversion. From the series of GHSV results in Fig. 4.7, the GHSV for long term life-span tests was set at $6428 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$.

To study the life spans of catalysts prepared by electroless nickel plating technique, some preliminary experiments were required to ensure that transport resistances were negligible. In the kinetically controlled reaction regime, the conversion of the reactant should be independent of the total gas flow rate for a fixed value of the W/F ratio, where W is the weight of the catalyst in the reactor (g) and F is the molar flow rate of the reactant (mmol/s).

This hypothesis was experimentally tested with the 26Ni/SBA-15 catalyst at a reaction temperature of 575 °C as shown in Fig. 4.8. It was found that there was practically little change in the methane conversion (about 40%) whilst varying the molar flow rate of methane from 0.0041 to 0.0065 mmol/s. The weight of catalyst varied from 0.112 g to 0.178 g for a fixed W/F ratio of 27.388 s.g_{cat}/mmol. Therefore, it was concluded that the effect of external diffusion was absent over the entire temperature range studied. For the molar flow rate of 0.0026 mmol/s methane and a catalyst weight of 0.07 g with the same W/F ratio, the methane conversion was also about 40% for 4.5 min at the initial stage but commenced to decline thereafter due to the onset of deactivation of the catalyst which had a comparatively smaller amount in weight.

Fig. 4.8 Effect of transport resistance on methane conversion at a fixed value of W/F ratio using 26Ni/SBA-15 catalyst.

Fig. 4.9 Life span kinetic curves of methane conversion for different catalysts at decomposition reaction of 575 °C. (Experimental conditions: $\text{CH}_4:\text{N}_2=1:1$, total flow rate = 15 ml min^{-1} , catalyst mass: 140 mg).

The long term life-span tests on the catalysts at 575 °C are shown in Fig. 4.9. Except for the highest loading of nickel for 37Ni/SBA-15, the developmental curve of the Ni/SBA-15 composes of three steps: induction stage, plateau stage and deactivation stage which are in agreement with the results reported by Avdeeva *et al.* [73]. The optimal catalytic stability was achieved using the catalyst with a Ni loading of 32 wt.%. Methane conversion after 450 minutes of reaction at 575 °C was still 40% with 32Ni/SBA-15 catalyst. From the results in Figs. 4.6 and 4.8, it can be concluded that there exists an appropriate nickel

loading that can improve methane conversion and increase the life span of the catalyst but excessive loading of the active phase would lead to a considerable decrease in methane conversion and catalytic stability. Similar conclusions were reported by Venugopal *et al.* [120] who prepared Ni/SiO₂ catalysts with nickel loading from 5 to 90% using wet-impregnation technique. The best catalytic activity and stability were obtained for a 30 wt. % Ni/SiO₂ catalyst. However, with a nickel loading greater than 30 wt. %, methane conversion decreased sharply. They reported that even for the 30 wt. % Ni/SiO₂ catalyst, the maximum methane conversion was only 18%.

Fig. 4.10 Life span kinetic curves of methane conversion at different decomposition temperatures using 32Ni/SBA-15. (Experimental conditions: total volumetric flow rate = 15 cm³/min and catalyst mass = 0.14g).

Figure 4.10 shows the life-span kinetic curves of methane decomposition over 32Ni/SBA-15 catalyst at different reaction temperatures. At a reaction temperature of 550 °C, the

catalyst maintained stable operation for about 1000 min with an average 32% methane conversion, which was approximately two times longer than the other reaction temperatures. As methane dissociation is an endothermic reaction, therefore at higher reaction temperatures, the dissociation rate becomes greater than the diffusion rate, leading to the presence of excess carbon on the metal/gas interface. These excess carbon deposits on and encapsulates the nickel surface, resulting in catalyst deactivation. Hence, increasing reaction temperature increased methane conversion but reduced the life span of the catalyst as deactivation occurred earlier [77].

Nickel-based catalyst performance in CDM is highly dependent on the synthesis method. From the literature, it was found that electroless nickel plating as a type of deposition-precipitation technique was only used once to synthesize catalysts for methane decomposition reaction. This work was reported by El Naggar *et al.* [24] who prepared highly loaded Ni-B alloy electroless catalyst plated on carbon felt. However, the maximum hydrogen yield volume percentage was only 10% within the first 200 minute. This low yield might be attributed to the thick layers of Ni plated on the macro-sized carbon felt resulting in the reduction of exposed surfaces of nickel nanoparticles. Further, particle agglomeration would occur which could result in particle sintering during high temperature reaction, thereby also contributing to the low yield. For the deposition precipitation method, the advantage is that the nickel nanoparticles will be fully exposed to the gas environment. Therefore, the aim of the electroless nickel plating method in this study was to deposit the small active Ni particles with high loadings onto the SBA-15 supports. El Naggar *et al.* [24] achieved the high Ni-B loading but could not control the particle sizes within the nano-

sized scales due to the formation of a thick layer of nickel on the support. In this work, a pre-seeding process was introduced in the preparation procedures whereby Ag nanoparticles were deposited on the SBA-15 support first. This step was critical because the formation of small sized nickel particles was dependent on the generation of highly dispersed nuclei on supports to provide seeds for nickel particle deposition. The selective deposition of nickel metal on the seeds resulted to the growth of nickel particles [149]. Fig. 4.2 shows the successful synthesis of highly distributed small Ni particles with high metal loading in the present synthetic work. Furthermore, the TPR results in Fig. 4.5 revealed a moderate metal-support interaction that could lead to sinter-resistance at high reaction temperatures. The 32 wt. % Ni/SBA-15 catalyst exhibited a stable methane conversion at 575 °C within 50 minutes, with the best methane conversion of 0.44, thus showing the feasibility of this preparation technique.

In general, the normal methods found in the literature for preparing catalysts with weak interaction on supports for CMD reaction are impregnation and deposition-precipitation. However, these methods are only suitable for the preparation of catalysts with low metal loading (< 25 wt. %). The synthesized method in this study is a completely different approach to achieve a higher Ni loading (32 wt. %). Urdiana *et al.* [150] prepared Ni/SBA-15 catalysts using an impregnation method and the catalytic activity results showed the 12.8 wt.% Ni/SBA-15 catalyst maintained stable methane conversion of 18% for 13 h at 500 °C. Berndt and Perez-Lopez [151] carried out tests on 10 wt.% Ni catalyst prepared by impregnation which yielded the best performance of 30% for the production of hydrogen from methane decomposition. Naresh *et al.* [152] prepared mono Ni (20 wt.%) catalyst on

zeolite supports by the impregnation method which achieved the highest methane conversion of 0.32. Hence, a higher nickel loading exerts positive influence on methane conversion into hydrogen. However, some studies using the impregnation method produced a higher content of nickel with limited stability. Rastegarpanah *et al.* [153] investigated the performance of catalysts with various nickel loadings (10, 25, 40 and 55 wt.%) and supported on mesoporous $\text{MgO} \cdot \text{Al}_2\text{O}_3$ using the impregnation method. The sample with the highest amount of Ni (55 wt.% Ni/2 $\text{MgO} \cdot \text{Al}_2\text{O}_3$) exhibited an acceptable catalytic performance but its yield deteriorated after 100 minutes with only 15% methane conversion achieved. The electroless nickel plating method used in this study improved the Ni loading on the support and maintained the stability of catalyst even with high Ni loading.

4.2.3 Characterization of the deposited carbon

The performance of the Ni/SBA-15 catalysts could also be elucidated from the morphology and structure of the resulting carbon material which would provide important information on the CDM process. Figure. 4.11 shows the carbon nanofibers (CNFs) resulting from the decomposition process with the 32Ni/SBA-15 catalyst at 575 °C. Figure 4.11 (4) shows a typical conical pure nickel nanoparticle located at the tip of a CNF and no support material was present, indicating that the electroless nickel plating catalyst followed the tip-based growth mechanism [154]. This mechanism generally exists when the interaction between the support and active phase is not strong, which is in agreement with the TPR profiles shown in Fig. 4.5 and discussed therein. Takenaka *et al.* [106] used different supports with equivalent surface area to determine the methane conversion and found out that the higher

the interaction between the nickel and support, the lower would be the methane conversion. This might be attributed to the formation of nickel oxide species ($-\text{O}-\text{Ni}-\text{O}-\text{M}-$; $\text{M} = \text{Mg}$, Si and Al) which could be bound strongly onto the support and rendering the decomposition reaction to be inactive. Moreover, the catalyst deactivation rate was found to become faster when the interaction of metal and support increased as shown and discussed for 19Ni/SBA-15 in Figs. 4.5 and 4.8. This type of deactivation is similar to catalysts prepared by co-precipitation method in which they exhibit a strong nickel/support binding force. The encapsulating carbon formation is dominant and thus it results in a rapid deactivation of the catalyst [155]. The nickel nanoparticles are trapped in the interiors of the carbon nanofiber filaments as shown in Fig. 4.11 (1) and (3), thereby resulting in catalyst deactivation. Fig. 4.11 (2) also showed the distortion of the nickel nanoparticle whereby the pear-like nickel particle was the result of the uplifting of the particle during the reaction process [49]. In this case, for the interaction between nickel and support to be broken, a deformation of the particle occurred resulting in a pear-shaped particle. Except for this phenomenon, the appearance of the carbon filament was mostly in the form of CNF instead of carbon nanotube which was due to the low reaction temperature. At low reaction temperatures, the carbon filament nucleation/precipitation rate is faster than the carbon atom diffusion through the metal particle and hence nucleation occurs more uniformly when the nickel particle detaches from the support [156].

Fig. 4.11 TEM micrographs of the carbon nanofibres using ^{32}Ni /SBA-15 catalyst at 575°C.

Fig. 4.12 TEM micrographs of the carbon nanofibres using ^{32}Ni /SBA-15 catalyst at 575°C .

In order to elucidate the deactivation of the Ni/SBA-15 catalysts prepared by electroless nickel plating method, TEM micrographs were obtained for the used $^{32}\text{Ni}/\text{SBA-15}$ catalysts after complete deactivation. Figure 4.12 showed two types of deposited carbon after the reaction. One type consisted of filamentous carbon with nickel particles on the tips as shown in Figs. 4.12 (2) and 4.12 (3) and the other consisted of large lumps of carbon surrounding the nickel particles (Figs. 4.12 (1) and 4.12 (4)). These two types of deposited carbon would pose negative effects on catalyst stability. The filamentous carbon had tendency to be entangled together which would leave limited space for the existing carbon nanofibers to grow whilst the large lumps of carbon could impede the active phase from exposure to the reagent gas, eventually stopping the reaction altogether. In the case of the impregnation method, this situation would become even worse because of the severe narrow space of the pore structure. Takenaka *et al.* [106] reported that the tip of a carbon filament coming into contact with the inside walls of the silica supports during the methane decomposition reaction would stop the growth of the carbon irreversibly. Moreover, the results from Ermakova *et al.* [97] indicated that nickel supported on silica with the widest pore performed the highest methane conversion and longest life span.

4.3 Summary

Various loadings of metallic nickel supported on SBA-15 were synthesized by the electroless nickel plating method. It was found that SBA-15 was an effective support for stabilizing the nickel nanoparticles. The effects of nickel loading on the SBA-15 catalysts were studied. The physicochemical properties of the catalysts were characterized using

TEM, XRD and TPR techniques. The reaction activity and stability of the catalysts were found to be strongly dependent on the loading of the Ni metal. It was found that the 32 wt.% Ni/SBA-15 catalyst exhibited superior activity and catalytic life span when compared with the other Ni loadings. The 32 wt. % Ni/SBA-15 catalyst had a stable methane conversion of 0.45 at 575 °C and maintained a life span of 700 min at the same temperature. Finally, it can be concluded that the 32 wt. % Ni loading on SBA-15 is a suitable catalyst for the catalytic decomposition of methane.

Chapter 5 Kinetic Studies and Modelling Work

5.1 Introduction

In this chapter, a series of experiments were carried out to study the intrinsic kinetic reaction rate, reaction mechanism and catalyst deactivation in methane decomposition using electroless nickel plating on SBA-15 as the catalyst in a fixed bed reactor. The experiments were conducted under atmospheric pressure at a temperature range of 525-600 °C and different methane contact times based on varying methane flow rates over a catalyst bed of fixed weight and depth. Transmission electron microscopy (TEM) was carried out to characterize the deactivated catalysts. For detailed description of experimental procedures, please refer to Section 3.3.1

5.2 Results and discussion

5.2.1 Operational conditions and kinetics reaction data

To study the global kinetics of methane decomposition over the 32Ni/SBA-15 catalyst, experiments were conducted to ensure that transport resistances were negligible. In the kinetically controlled reaction regime, the conversion of the reactant should be independent of the total gas flow rate for a fixed value of the W/F ratio where W is the weight of catalyst in g and F is the molar flow rate of methane in mmol s⁻¹. This proposition was experimentally tested with the 26Ni/SBA-15 catalyst at a reaction temperature of 575 °C as shown in Fig. 4.8. It was found that there was practically little change in the methane

conversion (about 40%), whilst varying the molar flow rate of methane from 0.0041 to 0.0065 mmol/s. The total weight of catalysts varied from 0.112g to 0.178g for a fixed W/F ratio (average $W/F = 27.3842 \text{ s.g}_{\text{cat}}/\text{mmol}$). It was therefore inferred that the effect of external diffusion was negligible.

Table 5.1 shows the experimental results for methane conversion (χ_{CH_4}), the reaction rate (r) of methane decomposition for different temperatures (T) at different ratio of W/F for the 32Ni/SBA-15 catalyst. To determine the intrinsic reaction rate, the data on the fraction of methane conversion were collected within the first hour of reaction when the reaction was under steady-state conditions. The reaction rate, r , of methane decomposition is defined as:

$$r = \frac{F}{W} \cdot \chi_{CH_4} \quad (5.1)$$

The overall profiles of methane conversion for varying W/F values and different reaction temperatures were computed by curve fitting of experimental data for methane conversion versus W/F using a third-order polynomial equation based on correlation coefficients higher than 0.99. Fig. 5.1 shows the best fit curves based on the experimental data for the 32Ni/SBA-15 catalyst. For a fixed W/F value, methane conversion increased with increasing reaction temperature from 525 to 600 °C as expected.

Table 5.1 Summary of kinetics reaction data for 32Ni/SBA-15.

T °C	W/F (s.g _{cat} /mmol)	χ_{CH_4}	r (mmol/g _{cat} .s)	P_{CH_4}/P_0	P_{H_2}/P_0
525	73.33913	0.329	0.004486	0.253052	0.249901
	55.00435	0.323	0.005872	0.257333	0.243415
	44.00348	0.316	0.007181	0.259883	0.240708
	36.66956	0.314	0.008563	0.260225	0.234616
	31.43106	0.306	0.009736	0.264052	0.231761
550	75.63672	0.359	0.004746	0.241648	0.272426
	56.72754	0.352	0.006205	0.245021	0.26743
	45.38203	0.344	0.007580	0.248188	0.260772
	37.81836	0.341	0.009017	0.249161	0.258338
	32.41574	0.332	0.010242	0.252663	0.253537
575	77.93431	0.44	0.005646	0.221125	0.34741
	58.45074	0.43	0.007357	0.225974	0.340985
	46.76059	0.414	0.008854	0.231372	0.329108
	38.96716	0.395	0.010137	0.238797	0.314184
	33.40042	0.38	0.011377	0.246314	0.303982
600	80.23191	0.54	0.006730	0.178793	0.420685
	60.17393	0.518	0.008608	0.189074	0.406152
	48.13914	0.489	0.010158	0.200731	0.386638
	40.11595	0.473	0.011791	0.206126	0.372524
	34.38510	0.45	0.013087	0.216292	0.355747

Fig. 5.1 Methane conversion as a function of W/F for 32Ni/SBA-15 catalyst at various temperatures (reaction conditions: 0.14g catalyst, various methane/nitrogen feeds with molar ratio of $\text{CH}_4/\text{N}_2=1:1$ at 525, 550, 575 and 600 °C)

5.2.2 Determination of kinetics of catalytic decomposition of methane

In order to determine the reaction rate r of methane decomposition, a power law model is applied to determine the reaction parameters using the following equation:

$$r = k_0 e^{-E_a/RT} C_{\text{CH}_4}^n \quad (5.2)$$

where k_0 is the pre-exponential factor for the chemical reaction, E_a is the activation energy for reaction, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the reaction temperature, C_{CH_4} is the concentration of methane and n is the reaction order. Eq. (5.2) can be written in logarithmic form as follows:

$$\ln(r) = \ln(k_0) + \left(-\frac{E_a}{R}\right)\frac{1}{T} + n\ln(C_{CH_4}) \quad (5.3)$$

As methane decomposition is a gas phase expansion reaction, the methane concentration C_{CH_4} at any section of the catalysis bed for an isothermal and constant pressure reaction can be expressed as follows:

$$C_{CH_4} = C_{CH_4 0} \frac{(1-\chi_{CH_4})}{(1+\alpha\chi_{CH_4})} \quad (5.4)$$

where $C_{CH_4 0}$ is the molar concentration (mmol L⁻¹) of methane before reaction and α is the expansion factor which is equal to 1 for the thermocatalytic decomposition of methane reaction of $CH_4 \rightarrow C + 2H_2$. Expansion factor is the fractional change in volume of the system between no conversion and complete conversion of methane, which is calculated to be 1.

Combining Eq. (5.3) and Eq. (5.4) will result in the following:

$$\ln(r) = \ln(k_0) + \left(-\frac{E_a}{R}\right)\frac{1}{T} + n\ln\left(C_{CH_4 0} \frac{1-\chi_{CH_4}}{1+\chi_{CH_4}}\right) \quad (5.5)$$

where n is the reaction order of catalytic decomposition of methane and k_0 is the pre-exponential factor for the methane reaction.

Fig. 5.2 Relationship between methane concentration and reaction rate at different temperatures using 32Ni/SBA-15 catalyst. (reaction conditions: 0.14g catalyst, various methane/nitrogen feed with molar ration of $\text{CH}_4/\text{N}_2=1:1$)

The kinetic parameters were estimated using the Genetic Algorithm (GA) method [157, 158] to fit the experimental data for 32Ni/SBA-15 catalyst in order to minimize the errors between the reaction rate equation and the experimental data. Minimization of the objective function was started by the initial random setting created using the GA method for each parameter. After the initial random guess, this algorithm proceeded the natural selection where the fittest values for objective function were selected for reproduction in order to produce offspring of the next iteration. Once the minimum value of the objective function

was obtained, the estimation of parameters by the Genetic Algorithm would stop running. The GA results are compared with the experimental data in Fig. 5.2. The traditional method of the Arrhenius plot of $\ln k$ against $1/T$, where k is the rate constant, was applied to validate the feasibility of GA method. The experimental data in Table 5.1 were used to estimate the parameters in Eq. (5.5). The best fit was attained with $n=2$ (correlation coefficient >0.99 using experiments conducted at 600 °C). The values of k_0 and activation energy E_a were calculated to be 2980.96 and 113.99 kJ mol⁻¹, respectively. Hence, the reaction rate equation for the catalytic decomposition of methane reaction using electroless nickel plating catalyst can be written as:

$$r = 2980e^{-113993/RT} C_{CH_4}^2 \quad (5.6)$$

where T is the temperature in K. The reaction order of 2 for methane decomposition in this study was comparatively high when compared with 0.63 for unsupported nickel catalyst [159] and 1 for supported nickel catalyst [160]. Furthermore, methane decomposition using activated carbon was reported as having half-order reaction [161]. The differences could be due to the following reasons. Firstly, it is possible that the weight of catalyst and volumetric flow rate used may affect the results. The weights of catalyst used in this study ranged from 0.112 to 0.178 g which was high in contrast with the weights used by other researchers whereby 10-50 mg of catalysts were generally used for their kinetic studies. However, the volumetric flow rates varying from 7.5 ml/min to 17.5 ml/min in this study were conversely low when compared with a range of 20 ml/min to 50 ml/min which was commonly used by other researchers. Increasing catalyst weight while decreasing methane volumetric flow rate may result in gradually decreasing methane partial pressure with increasing depth of the catalyst bed since the produced hydrogen could dilute the gas phase

concentration. Secondly, the nickel nanoparticles synthesized by electroless nickel plating had proper bonding with the SBA-15 support as shown in TPR profile. This adequate bonding has relatively higher reaction order when compared with supported nickel catalyst with strong interaction on support. A strong metal-support interaction affects the reduction of the metal oxide and the mobility of the active particles on the support surface. This would attribute to the faster catalyst deactivation rate [23]. Besides the two above mechanisms, a different approach used to estimate the kinetic parameters could explain for the different reaction order (n) result obtained in this study. The usual method to determine the methane decomposition reaction order is to carry out experiments using various methane partial pressures at different temperature ranges at a constant total flow rate. The reaction order and activation energy were estimated separately. For the activation energy, it was generally determined from the Arrhenius plot of $\ln k$ against $1/T$ when the value of reaction order is fixed. However, the Genetic Algorithm used in this approach could estimate all parameters at the same time and avoid the local minimization, and hence GA increases the reliability of the final result. Hence, this method could provide an alternative option to analyse the kinetic behaviours of catalysts. The results from the Arrhenius equation and Genetic Algorithm are all compared with the experimental data in Fig. 5.2.

The activation energy of $113.99 \text{ kJ mol}^{-1}$ obtained in the methane decomposition study here is within the range of the activation energy ($60\text{-}236 \text{ kJ mol}^{-1}$) [163, 164] reported by other researchers. In this context, methane decomposition reactions exhibited wide ranges of activation energy for different catalysts. Holmen *et al.* [165] conducted kinetic modelling of methane decomposition at $1773\text{-}2273 \text{ K}$ at 0.1 atm pressure of methane and an activation

energy of 370 kJ mol^{-1} was obtained. Steinberg [166] carried out methane decomposition experiments for the temperature range of 973-1173K at 28-56 atm and obtained an activation energy of 131 kJ mol^{-1} . Kim *et al.* [167] reported values of activation energy ranging from 186 to 198 kJ mol^{-1} for using different carbon black resources. Muradov *et al.* [161] obtained activation energy values ranging from 160 to 201 kJ mol^{-1} using various types of carbons as catalysts. The activation energy of $113.99 \text{ kJ mol}^{-1}$ obtained in this study is much lower than the energy of 416 kJ mol^{-1} which is required for the breakage of single C-H bond in methane. The wide range of activation energies reported by other authors could result from catalytic characteristics such as carbon black having less activity compared to transition metal leading to higher activation energy. Experimental parameters such as pressure and temperature would also attribute to the variance on activation energy. Because for methane decomposition, the number of moles of product gas (H_2) is two times of the number of moles of reactant gas (CH_4). Supported by the Le Chatelier's principle, with the whole system pressure increasing, the side of the equilibrium with fewer moles is more favorable, which indicates that the methane decomposition to hydrogen by catalyst is more difficult in high-pressure environment and thus it requires the higher energy to break C-H bond in methane.

5.2.3 Reaction Mechanism

In the thermocatalytic methane decomposition reaction of $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$, the reaction mechanism and the identification of the rate-controlling steps were investigated in the

present study using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. In this model, it is assumed that the rate-controlling step is the slowest while the others are in equilibrium. In dissociative adsorption mechanism which was postulated by Alstrup and Tavares [168], methane undergoes dissociation and adsorption on the active sites simultaneously while in molecular adsorption mechanism, methane is adsorbed firstly and then followed by dissociation. In dissociative adsorption, the pathways are shown in the following parts:

where S is the active surface site of the catalyst, CH_xS with $x = 1, 2, 3$ being the chemisorbed species on the catalyst surface and CS and HS are respectively the carbon atom and hydrogen atom adsorbed on the catalyst surface. It is assumed that step (5.7) of the dissociative adsorption pathway as the rate-limiting step, the rate law is formulated as below:

$$r_1 = k_1 P_{CH_4} \theta_S^2 - k_{1b} \theta_{CH_3S} \theta_{HS} \quad (5.12)$$

where k_1 and k_{1b} are the rate constants of the forward and backward reactions of step (5.7) respectively. θ_S , θ_{CH_3S} and θ_{HS} are the fractions of active sites that are vacant or occupied by the species CH_3 and H , respectively. P_{CH_4} is the partial pressure of methane.

Except for step (5.7), the other steps are elementary and in equilibrium. Therefore, the

following expressions could be deduced from the rate law.

$$\theta_{CH_3S} = \theta_{CH_2S} \theta_{HS} / \theta_S K_2 \quad (5.13)$$

$$\theta_{CH_2S} = \theta_{CHS} \theta_{HS} / \theta_S K_3 \quad (5.14)$$

$$\theta_{CHS} = \theta_{CS} \theta_{HS} / \theta_S K_4 \quad (5.15)$$

Assume a_H represents the activity of H, then $\theta_{HS} = a_H \theta_S$ could be deduced and

$$a_H = (P_{H_2} / K_5)^{1/2} \quad (5.16)$$

in which K_2 , K_3 , K_4 and K_5 are constants, and P_{H_2} is the partial pressure of hydrogen. The partial pressures of methane P_{CH_4} and hydrogen P_{H_2} can be determined from the methane conversion χ_{CH_4} . From the stoichiometry of the methane decomposition reaction, P_{CH_4} and P_{H_2} can be expressed as follows:

$$P_{CH_4} = \frac{P_0(1-\chi_{CH_4})}{1+\alpha\chi_{CH_4}} \quad (5.17)$$

$$P_{H_2} = \frac{2P_0(\chi_{CH_4})}{1+\alpha\chi_{CH_4}} \quad (5.18)$$

where P_0 is the initial partial pressure of methane before reaction, χ_{CH_4} is the methane conversion and α is the expansion factor which is 1 for the methane decomposition reaction.

The calculated values of P_{CH_4}/P_0 and P_{H_2}/P_0 are given in Table 1 where P_0 is also the methane feed pressure in this study.

Substitution of θ_{CH_3S} , θ_{CH_2S} , θ_{CHS} and θ_{HS} on the right-hand sides of Eq. (5.13), Eq. (5.14), Eq. (5.15) and Eq. (5.16) into Eq. (5.12), the new expression of rate law could be formulated as follows:

$$\begin{aligned}
 r_1 &= k_1 P_{CH_4} \theta_S^2 - k_{-1} \theta_{CH_3S} \theta_{HS} = k_1 (P_{CH_4} \theta_S^2 - P_{H_2}^{3/2} \theta_{CS} (P_{H_2}/K_5)^{1/2} \theta_S / K_1 K_2 K_3 K_4 K_5^{3/2}) \\
 &= k_1 (P_{CH_4} \theta_S^2 - P_{H_2}^2 \theta_{CS} \theta_S / K_1 K_2 K_3 K_4 K_5^2)
 \end{aligned} \quad (5.19)$$

where θ_{CS} is the fraction of active site occupied by C species. Dividing Eq. (5.19) by $P_{H_2}^2$, the reaction rate can be written as:

$$r_1/P_{H_2}^2 = k_1 \theta_S^2 P_{CH_4}/P_{H_2}^2 - \theta_{CS} \theta_S k_1 / K_1 K_2 K_3 K_4 K_5^2 \quad (5.20)$$

Fig. 5.3 Modeling of linear kinetic equation of catalytic decomposition of methane by 32Ni/SBA-15 catalyst at different temperatures

In Eq. (5.20), θ_{CS} and θ_S are independent of partial pressures of methane and hydrogen and these fractions of active sites could be considered constant. The values of K_1 , K_2 , K_3 , K_4 and K_5 are constant. If there were a linear relationship between $r_1/P_{H_2}^2$ and $P_{CH_4}/P_{H_2}^2$ on

the basis of the experimental data and using r_1 as r in Table 5.1, this would verify that the assumed mechanism and the rate-controlling step are correct. Using the experimental data in Table 5.1 and plotting $P_{CH_4}/P_{H_2}^2$ versus $r_1/P_{H_2}^2$ in Fig. 5.3, the linear relationships with high correlation coefficients for different decomposition temperatures agreed well with the model as given in Eq. (5.20). Hence, the assumed mechanism with the dissociative adsorption of methane in step (5.7) as the rate limiting step is consistent with the experimental data. This observation is in good agreement with the results reported by Kuvshinov *et al.* [164], Narkiewicz *et al.* [169] and Borghei *et al.* [132]. This could be more reliably measured by molecular study using isotopic methane (CH_4 , CD_4 , and $^{13}CH_4$) and hydrogen (H_2 and D_2) as investigated by Otsuka *et al.* [170]. They demonstrated that once the breaking of the C-H bond of CH_4 occurs, the following pathways of C-H bond breakings in CH_3 , CH_2 and CH would be very fast [30]. This could be well explained by first-principles density functional theory calculations of reaction barriers for each step in the overall decomposition of CH_4 . Although reaction step (5.10), $CHS + S \rightleftharpoons CS + HS$, exhibits the highest activation energy, $CH_4 + 2S \rightleftharpoons CH_3S + HS$ is considered to be the slowest reaction step in the methane decomposition reaction. This could be attributed by the low coverage of methane on active sites resulting from the highly entropically favored desorption of methane on catalyst surface [171]. The reaction step (5.8) has obviously lower energy barrier than the reaction step (5.7) on catalyst surfaces [172]. Moreover, the reaction step (5.9) has the lowest reaction barrier and is the fastest among all the reaction steps. Many research publications using first-principles density functional theory focused on the methane dissociative adsorption as more important for the overall reaction. Experimental and theoretical studies conducted by Yang and Chen [41] showed that the

gas/metal interfaces were found to be the Ni(1 0 0) and Ni(1 1 0) surfaces while the graphite/metal interfaces were the Ni(1 1 1) and Ni(3 1 1) surfaces. Measurements of the apparent activation energy for CH₄ dissociative adsorption on Ni(1 1 1) surface were conducted by Egeberg *et al.* [173] and they reported a value of 74 ± 10 kJ/mol which was much higher than 59 ± 1.5 kJ/mol on Ni(1 0 0) surface as reported by Nielsen *et al.* [174].

5.2.4 Deactivation kinetics of the electroless nickel plating catalyst

The activity of the electroless nickel plating catalyst, $a(t)$, is defined as:

$$a(t) = \frac{r_c(t)}{r_{c0}} \quad (5.21)$$

where $r_c(t)$ and r_{c0} are the methane conversion rate at time t and the initial methane conversion for a pristine catalyst, respectively. For a constant pressure reaction, the activity of the catalyst will be dependent on the reaction temperature and the residence time of the methane over the catalyst. Hence, the deactivation rate of a catalyst can be expressed as a function of the deactivation rate constant (k_d), the residence time (t_R) and activity (a), and subsequently in terms of the Arrhenius equation as follows:

$$-\frac{da}{dt} = k_d t_R^m a^d = k_{d0} e^{-E_d/RT} t_R^m a^d \quad (5.22)$$

where m is the exponent related to t_R , d is the deactivation order, k_{d0} is the pre-exponential factor, E_d is the activation energy for the deactivation reaction, R is the gas constant and T is the temperature. For constant values of k_d and residence time t_R , the

integral of Eq. (5.22) can be evaluated as follows:

$$\ln a = -k_d t_R^m t \quad (d = 1) \quad (5.23)$$

$$a^{1-d} = 1^{1-d} - (1-d)k_d t_R^m t \quad (d \neq 1) \quad (5.24)$$

where $a=1$ for the initial condition when $t = 0$.

Various values of d ($d=0, 0.5, 1, 1.5$ and 2) were attempted to fit Eq. (5.24). The highest correlation coefficient (>0.99) was obtained for $d = 0.5$. Hence, the activity in the deactivation equation can be expressed as:

$$a^{0.5} = 1 - 0.5k_d t_R^m t \quad (5.25)$$

Using Eq. (5.25) and plotting $a^{0.5}$ versus t , the results should produce a linear line of slope (s) of $-0.5k_d t_R^m$ and intercept of 1. This linear relationship is proven in Fig. 5.4(a) for 3 sets of experimental data at a methane decomposition temperature of 575°C for three methane flow rates in this study. The slopes of the lines in Fig. 5.4(a) are dependent on the residence time t_R . The residence time t_R can be calculated from the volume flow rate of methane and the depth of the catalyst bed in the reactor. Hence, plotting $\ln(-s)$ against $\ln(t_R)$ will yield the values of k_d and m from the following relationship:

$$\ln(-s) = \ln(0.5k_d) + m \ln(t_R) \quad (5.26)$$

This relationship is shown in Fig. 5.4(b) whereby the slope of the line will yield m and the k_d value can be obtained from the intercept with $\ln(-s)$ axis. Another different approach was used to calculate the values of k_d for a fixed methane flow rate of 7.5ml/min but at different reaction temperatures of $550, 575$ and 600°C .

Fig. 5.4 Activity versus time for fifth order deactivation kinetics at 575 °C. (a) Different methane flow rates and contact times for a fixed 32Ni/SBA-15 catalyst weight of 140mg.

Fig. 5.4 Activity versus time for fifth order deactivation kinetics at 575 °C. (b) Relationship between slope $\ln(-s)$ versus methane contact time $\ln(t_R)$ for reaction under 32Ni/SBA-15 catalyst.

Fig. 5.5 Activity versus time for fifth order deactivation kinetics at 550, 575 and 600 °C. (a) Different reaction temperatures at a constant methane flow rate and a fixed 32Ni/SBA-15 catalyst weight of 140mg.

Fig. 5.5 Activity versus time for fifth order deactivation kinetics at 550, 575 and 600 °C. (b) Arrhenius plot of $\ln k_d$ versus $(1/T)$ where k_d is the deactivation rate and T is the reaction temperature.

In Fig. 5.4(a), values of $a^{0.5}$ were plotted against time for the three temperatures, hence k_d values could be deduced from the slopes of the lines with m value obtained from Fig. 5.4(b) and t_R was determined from the volume flow rate and the bed depth. The activation energy of the deactivation was estimated using the Arrhenius plot of $\ln k_d$ versus $1/T$ which is shown in Fig. 5.5(b). The slope of the linear line is $(-E_d/R)$ where E_d is the activation energy for the deactivation reaction and R is the gas constant. The activation energy for the deactivation of methane decomposition using electroless nickel plating catalyst was calculated as $147.864 \text{ kJ mol}^{-1}$ and the value of the pre-exponential factor (k_{d0}) was 1082128. The value of d for the deactivation kinetics is the same as the result reported by other researcher where a half-order ($d=0.5$) deactivation kinetics was also obtained [162]. The usual reported method in the literature to determine the deactivation kinetic order is based on the analyses of the methane partial pressures whereas in this work, the residence time is used. This is a new approach. Hence, the proposed model for the deactivation rate in methane decomposition is given as:

$$-\frac{da}{dt} = 1082128e^{-17785/RT} t_R^{-1.4123} a^{0.5} \quad (5.27)$$

Hence, the activity a is given as:

$$a^{0.5} = 1 - 0.5(1082128e^{-17785/T}) t_R^{-1.4123} t \quad (5.28)$$

The expression for the activity in Eq. (5.28) was validated by comparing with the experimental data for the activity based on Eq. (5.21) for different reaction temperatures at a constant flow rate in Fig. 5.6(a-c) and for various flow rates (residence times) at a constant temperature of 575°C in Fig. 5.6(d-f).

Fig. 5.6 Activity versus time for fifth order deactivation kinetics for 32Ni/SBA-15 catalyst at different reaction temperatures for a fixed methane flow rate of 7.5 ml/min (a-c) and various contact times at 575 °C (d-f).

The percentage mean deviation (MD) between the experimental catalyst activities based on Eq. (5.21) and the calculated activities using Eq. (5.28) was obtained using the following formula:

$$MD = \frac{\sum_{i=1}^N \frac{(a_{model} - a_{experiment})}{a_{model}}}{N} \times 100 \quad (5.29)$$

where N is the number of data points in the experiments. Results of MD calculations were 11.54%, 0.14% and 9.17% for methane decomposition temperatures of 550, 575 and 600 °C, respectively, and 0.14%, 1.48% and 2.34% for residence times of 33.2214s, 24.9162s and 19.9326s, respectively. The model predictions of the catalyst activity were in good agreement with the activity derived from the experimental data. MD values were lower than 10% in most of the experimental/modelling results obtained in this study.

5.2.4 Deactivation mechanism of electroless nickel plating catalyst

In order to elucidate the deactivation mechanism for the electroless nickel plating method, transmission electron microscope micrographs were obtained for the used 32Ni/SBA-15 catalysts after complete deactivation as shown in Fig. 5.7(1- 4). Two different kinds of deposited carbon were observed after the reaction - a filamentous carbon with nickel particles on the tips (Fig. 5.7(2, 3)) and large lumps of carbon surrounding the nickel particles (Fig. 5.7(1, 4)). These two types of deposited carbon pose negative effects on catalyst stability. The filamentous carbons have a tendency to be entangled together, leaving limited space for further carbon nanofiber growths while large lumps of carbon could impede the active catalytic phase from exposure to the reagent methane gas which

Fig. 5.7 TEM micrographs of the CNFs obtained from $^{32}\text{Ni}/\text{SBA15}$ catalyst at 575°C .

would eventually stop the reaction. In the case of the impregnation method for producing nanoparticles implanted into support, the overcrowding due to carbon growths is severe if the spaces in the pore structures are narrow. Takenaka *et al.* [106] reported that the tip of a

carbon filament coming in contact with the inside walls of silica supports during the methane decomposition would stop the growth of the carbon irreversibly. Furthermore, the results from Ermakova *et al.* [97] indicated that nickel supported on silica with the widest pores performed the highest methane conversion and the longest lifetime.

5.3 Summary

Experimental results on the catalytic decomposition of methane using electroless nickel plating catalyst in a fixed bed reactor at temperatures of 525-600 °C and different methane contact times were used to determine the kinetics reaction rate, reaction mechanism and catalyst deactivation activity.

The kinetics model used resulted in a reaction order of 2 and an activation energy of 113.99 kJ mol⁻¹. A reaction mechanism in the dissociative adsorption of methane based on the rate controlling step was assumed and was in good agreement with the experimental data. A proposed model that establishes the relationship between the time dependent deactivation activity in methane decomposition and the methane residence time over the catalyst is proposed. A deactivation order of 0.5 and a deactivation energy of 147.864 kJ mol⁻¹ were obtained using this model. The percent mean deviation between this deactivation model and the experimental data was lower than 10% in most of the results obtained in this study.

Chapter 6 Summary

The main conclusions of this project are as follows:

(1) Various loadings of metallic nickel supported on SBA-15 with promising catalytic activity for methane decomposition were prepared by an electroless nickel plating method. The addition of silver nanoparticles as seeds led to the formation of nickel particles with smaller crystalline size and high dispersion on support than those of Ni particles prepared by the similar technique. Unlike the conventional supported catalysts, it was vital to introduce a little amount of hydrogen to the reactor at lower temperature to avoid the catalysts from sintering into bigger particles. It was found that SBA-15 was an effective support for stabilizing the nickel nanoparticles. The effects of nickel loading on the SBA-15 catalysts were studied. The physicochemical properties of the catalysts were characterized using TEM, XRD and TPR techniques. The reaction activity and stability of the catalysts were found to be strongly dependent on the loading of the Ni metal. It was found that the 32 wt. % Ni/SBA-15 catalyst exhibited superior activity and catalytic life span when compared with the other Ni loadings. The 32 wt. % Ni/SBA-15 catalyst had a stable methane conversion of 0.48 at 575 °C and maintained a life span of 725 min at the same temperature. Finally, it can be concluded that the 32 wt. % Ni loading on SBA-15 is a suitable catalyst for the catalytic decomposition of methane.

(2) Experimental results on the catalytic decomposition of methane using electroless nickel plating catalyst in a fixed bed reactor at temperatures of 525-600 °C and different methane contact times were used to determine the kinetics reaction rate, reaction mechanism and catalyst deactivation activity. The kinetics model used resulted in a reaction order of 2 and an activation energy of 113.99 kJ mol⁻¹. A reaction mechanism in the dissociative adsorption of methane based on the rate controlling step was assumed and was found to be in good agreement with the experimental data. A proposed model that establishes the relationship between the time dependent deactivation activity in methane decomposition and the methane residence time over the catalyst is proposed. A deactivation order of 0.5 and a deactivation energy of 147.864 kJ mol⁻¹ were obtained using this model. The percent mean deviation between this deactivation model and the experimental data was lower than 10% in most of the results obtained in this study.

Chapter 7 Recommendations for Future studies

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 could be synthesized and further optimized to increase the methane conversion.
 - (ii) The reactor can be scaled up and larger 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) can be combined with the hydrogen generation set-up.
 - (ii) The power generated can be tested using electrochemical measurements and can be used to run motors, which may be used on-board the ship in the future.
 - (iii) The total thermal efficiency of the fossil fuel utilized in the power generation systems can be studied and compared to the efficiency of a hydrogen powered system such as fuel cells.

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Publications

Publications arising from this research are as follows:

1. Q. Chen and A.C. Lua, Kinetic reaction and deactivation studies on thermocatalytic decomposition of methane by electroless nickel plating catalyst, Chemical Engineering Journal, 389 (2020) 124366.
2. Q. Chen and A.C. Lua, Synthesis of electroless Ni catalyst supported on SBA-15 for hydrogen and carbon production by catalytic decomposition of methane, To be submitted to journal.