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Methane Decomposition to Carbon Nanotubes and CO_x -Free H₂ over Transition Metal Catalysts

I-Wen Wang

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**Methane Decomposition to Carbon Nanotubes
and CO_x -Free H₂ over Transition Metal Catalysts**

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**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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2018

Keywords: Methane; Carbon Nanotube; Hydrogen; Transition Metal Catalysts

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Abstract

Methane Decomposition to Carbon Nanotubes and CO_x-Free H₂ over Transition Metal Catalysts

I-Wen Wang

Recently, shale gas has become a very important energy source in the United States. The abundance of shale gas resources presents opportunities to develop novel chemical processes that convert its major component, methane, into more valuable fuels and chemicals. Among various methods of hydrogen production, steam reforming of natural gas is the most popular and economical technology, but this process is highly endothermic. Therefore, catalytic methane decomposition (CMD) is an attractive alternative process since supported metal catalysts can be used to catalytically decompose hydrocarbons to produce CO_x-free H₂ at more moderate temperatures. This process generates carbon nanotubes (CNTs) or nanofibers along with hydrogen. In this work, the research is focused on the production of CNTs.

Herein, we investigate the mono- and bimetallic Ni, Fe, and Co with various mole ratios over SiO₂ support by incipient wetness and sol-gel technique. The catalysts were tested under the same reaction conditions and the properties of CNT were characterized by a number of analytical instrumentations such as TEM, XRD, and Raman spectroscopy to correlate with CMD performance. The synthesized bimetallic catalysts were found to have higher activity and stability than monometallic catalysts. Also, we prepared the Fe-based catalysts with different supports (Al₂O₃, ZSM-5, and SiO₂) and experimental results revealed that metal-support interaction played a key role in the base grown mechanism. Moreover, Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts were synthesized using a sol-gel method to enhance CMD performance. It was discovered that the metal-support interaction and tortuosity of the aerogel catalysts determine the activity and capacity. Moreover, the recovery of CNT and catalyst regeneration protocol was developed to explore industrial application potential.

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Chapter 1 Introduction

1.1 Motivation

Currently, hydrogen appears to be an environmentally benign source of energy since it can be converted into electricity and other energy forms with less pollution and high efficiency. Among various methods of hydrogen production, steam reforming of natural gas is the most popular and economical technology, which contributes to 50% of the world's hydrogen consumption [1]. However, these processes are highly endothermic (68.7 kJ/mol H₂) and produce large amounts of CO_x. As a result, steam reforming is accompanied by the water-gas shift reaction and pressure swing adsorption (PSA) other purification steps, thereby significantly increasing the cost of the process. Recently, shale gas has become a very important source of natural gas in the United States. It contributes only 3% of the United States natural gas production in 2005, rising to 35% by 2012 and is predicted to grow to almost 50% by 2035 [2]. Increase in demand for CO_x-free hydrogen and the abundance of shale gas resources present opportunities to develop novel chemical processes that convert its major component, methane, into more valuable fuels and chemicals. Direct decomposition of methane is an attractive alternative process since it is a less endothermic process (37.4 kJ/mol H₂) [3, 4] compared to steam reforming and also has a high H/C ratio compared to other hydrocarbons. This process generates CO_x-free hydrogen, which has a great application in low-temperature fuel cells and also generates valuable carbon nanotubes (CNTs) or nanofibers. In this work, we have concentrated more on the production of CNTs from methane. Methane thermally decomposes to atomic carbon, which eventually forms straight and hollow in chemical equation 1.1.

Carbon nanotubes (CNTs) or nanofibers are extensively studied due to their unique physical, chemical, mechanical, electrical and optical properties [5–8]. The applications of CNTs depend

on the number of walls, diameter, length, etc. which provides them with specific properties. They are long graphitic filaments with diameters ranging from 0.4 to 500 nm and lengths from micrometers to millimeters [8]. They can be single walled or multiwalled. Multiwalled carbon nanotubes (MWCNTs) are predominantly known to have a high surface area and mesoporous structure. These properties increase the application of CNTs as an adsorbent, catalyst support, and electrode material. It has been reported that depending on the process conditions, the carbons formed are different. The difference can be categorized into amorphous (disordered), turbostratic or pyrolytic (less ordered), and carbon filaments (highly ordered, crystalline and graphitic). It is very challenging to produce graphitic carbons (CNTs) by methane decomposition in the absence of a catalyst [9]. Several methods are known for producing high quality carbon nanotubes, such as laser ablation, arc discharge etc. These processes have drawbacks such as operating in high temperature (1200–3000 °C) and vacuum or low pressure. Non-catalytic decomposition of methane was studied at temperatures of 1000–1100°C which produced various forms of amorphous carbon [9]. For CNT synthesis, catalysts with nanometer-sized metal particles are essential, which will also help to reduce the temperature for methane decomposition.

1.2 Literature Review

1.2.1 Metals for catalysts

Transition metals are the typical catalyst metal material for methane decomposition since their partially filled 3d orbitals facilitate the decomposition due to the partial acceptance of the C-H bond of methane [10]. Among the metal catalysts used, most researchers have focused on Ni-based catalyst due to their high catalytic activity and capability of producing CNT [12, 13]. Although Ni catalysts showed superior performance, they deactivated immediately at temperatures above 600 °C [14, 15]. To improve the durability and reduce the deactivation of

the catalyst at the reaction temperatures, different metals, and metal oxides have been introduced to the Ni-based catalysts [16–21]. Iron-based catalysts have also been studied but showed a shorter lifetime and lower activity than Ni catalysts [21]. When Fe-based catalysts were used, a higher temperature range was required to achieve reasonable productivity. Cobalt catalysts have received less attention than Ni- and Fe-containing catalysts, but there are few studies which show their activity for methane decomposition [23–25]. Based on previous studies it can be summarized that the catalytic activity of iron group metals is in the order of $\text{Ni} > \text{Co} > \text{Fe}$ [23]. Unfortunately, the activity of the catalyst is gradually declined during the course of the reaction due to the coverage of active sites by the carbon. Recently, it was discovered from molecular simulation and experimental results that bimetallic catalysts have a significant influence on the growth properties of CNTs [26–28].

Bimetallic or alloy catalysts of Ni, Fe or Co have better stability than monometallic ones due to structural and electronic rearrangements that occur during alloy formation. This property can help reduce the activation energy, thereby lowering the CNT growth temperature. Also, these types of catalysts can form stable complexes or solid solutions of small nanoparticles that can prevent metal agglomeration, which causes the loss in catalytic activity. The growth of CNTs and metal particle size are very much related because metal particle size controls the CNT diameter. Hence it is very important to prepare a catalyst with controlled particle size in order to grow CNTs with a controlled diameter. A combination of monometallic catalysts with other active metals can lead to some promising catalysts [21, 23, 29, 30].

1.2.2 Supports for catalysts

It is accepted that metal nanoparticles dispersed over oxide supports can enhance the catalytic performance as the strong metal-support interaction (SMSI) changes the particle size or the electronic state of metal species [31, 32]. Takenaka et al. compared the performance of

Ni on various supports, i.e. SiO₂, TiO₂, graphite, Al₂O₃, MgO, and SiO₂·MgO, which had different activity and stability on methane decomposition [32]. Ermakova conducted a study of Fe-based catalyst on SiO₂, Al₂O₃, ZrO₂, TiO₂ and bare iron. Among these supports, SiO₂ had the maxima yield of carbon on the decomposition of methane [33]. Fe-Mo particles on alumina (Al₂O₃) produced a much higher amount of SWNTs than those grown on silica (SiO₂) [34]. This was ascribed to the stronger metal support interaction for Al₂O₃ support as compared with SiO₂. MgO is an attractive support material from the view of large-scale synthesis of SWNTs and DWNTs because the supported catalysts give high-quality nanotubes and MgO can be removed by relatively mild acidic treatment [35]. The metal-support interaction has been studied by using flat substrates such as Si, SiO₂, and crystals of sapphire (Al₂O₃) and MgO as a model system [36–38]. These studies have also shown that the support material significantly influences the catalytic activity of metal catalysts, suggesting the importance of the metal-support, in this case, metal-substrate, interaction. Recently a thorough study was published on the role of the metal–support interaction in the formation of CNT. Three metals, Cu, Fe, and Ni, of low, moderate, and high catalytic activity was chosen for this comparison on substrates including CaO, Al₂O₃, SiO₂, and TiO₂. Nickel provided the highest nanofiber yield among the 12 catalyst systems tested when supported on TiO₂. Ni supported on SiO₂ and Al₂O₃ was far less active and was virtually unreactive when supported on CaO. Cu was most active on CaO and SiO₂ and less so when supported on TiO₂ or Al₂O₃ [39].

1.2.3 Growth mechanisms for carbon nanotube

There are several models that can be utilized to explain the tip growth mechanism. It was assumed that carbon formed on the surface of the metal nanoparticle diffuses to the back side of the nanoparticle. Still, it is not known about the driving force which is responsible for the carbon diffusion. Some researchers suggested that carbon diffusion

was caused by the temperature gradient created in the particle due to the exothermic decomposition of methane on the surface and also the endothermic deposition of carbon on the rear surface [5, 69]. It was also explained that due to lower surface energy of basal planes of graphite compared to prismatic planes carbon filaments precipitate with the basal planes into a tubular structure [41]. Metal support interactions also have played an important role in the growth mechanisms in the carbon nanotubes. If the metal support interaction is weak (acute contact angle with the support), methane decomposes on the top surface of the metal and carbon diffuses towards the downside of the metal. The metal particle is squeezed out because of pressure build-up due to the formation of layers of graphite at the interior of the graphitic cap. When the metal is exposed to methane, growth continues until the surface of the metal is covered with excess carbon.

1.2.4 Base grown carbon nanotube

A majority of above-mentioned literature have shown that catalytic methane decomposition forms CNTs via “tip growth” mechanism. One of the main disadvantages of tip grown CNTs is that during the process of harvesting CNT from the catalyst using acid or base treatment the metal nanoparticles are dissolved and the catalyst is sacrificed. Also, for tip grown CNT, catalyst nanoparticle which is attached to its tip is considered as an impurity. Hence extraction of CNT with a complete recovery of the catalyst is most recommended. To overcome this problem, catalysts and reaction processes were designed in such a way to produce “base grown” CNT. Base grown CNT can be easily harvested, and the catalyst can be regenerated without getting consumed during the extraction process. In addition, the literature search has shown that very few research was done in the area of base growth CNTs, especially their advantages over tip growth CNTs. Hence a portion of our research is focused on the synthesis of base-growth CNT's. There are only few reports which show the base growth study of CNTs.

The base-growth mechanism was reported for MWCNTs [35, 36] and also for SWCNTs [37, 38]. One of them employed chemical vapor deposition (CVD) method using ethylene as the carbon source and iron oxide on porous Si as catalyst [46]. Iron oxide nanoparticles remain attached to the support during CNT growth. However, it remains unclear how to scale up these processes because of the lack of strategies in scaling up nanotube growth. Another report disclosed a growth process of carbon nanotubes from iron carbide (Fe_3C) nanoparticles in chemical vapor deposition using ethylene as the feedstock [44]. Based on the previous literature we have to incorporate the metal support interaction concept for the production of base growth CNT over Fe-based catalysts.

1.2.5 Purification of carbon nanotube

In the CDM process, the as-synthesized carbon nanotubes contained both metal particles and support. Further purification was required to remove metal and support impurities which could otherwise obstacle CNT utilization in several areas [40, 41]. Chemical oxidation was one commonly used method for CNT purification to open up the tip, end or the defect on sidewalls where functional groups can be added for other catalytic or chemical synthesis applications. Currently, mineral acids, such as sulfuric acid, nitric acid, or hydrochloric acid, were widely used for purification or functionalization [42–44]. Although some experimental works have been reported on either methane decomposition or purification of CNT separately, there are few papers investigating the integration of these two steps. Therefore, our research investigates the formation mechanism of CNT, purification of CNT, and characterization of CNT to correlate the surface property with the catalytic performance.

1.2.6 Synthesis by sol-gel method

Aerogels are highly porous materials, which are typically synthesized by the sol-gel method [45–49] and used in catalysts, thermal insulation, and energy storage [50–52]. Ni^{2+} -

doped Al_2O_3 aerogel has been widely used as a catalyst for many chemical reactions [53–56]. In this study, $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Co}/\text{Al}_2\text{O}_3$ aerogel catalysts were synthesized using a sol-gel method to demonstrate enhanced performance over those made from conventional incipient wetness approaches.

1.3 Objectives

The objectives of this work are:

- (1) To compare the activity of mono- and bimetallic metal (Ni, Fe, and Co) on SiO_2 with various mole ratio in methane decomposition reaction and their effects on carbon nanotubes formation.
- (2) To study the effect of the Fe-based catalyst with different supports (Al_2O_3 , ZSM-5, and SiO_2) on bases growth CNT. In addition, the separation and purification of the carbon nanotube are investigated.
- (3) To prepare Ni and Co aerogel catalysts supported on Al_2O_3 by sol-gel method and compare its activity with those prepared by incipient wetness technique.

Chapter 2 Experimental Methods and Analysis

2.1 Catalyst Preparation

Mono- and bimetallic Ni, Fe, and Co catalysts were synthesized by a dry impregnation or incipient wetness impregnation methods. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa-Aesar) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics) were used as precursors. Fumed SiO_2 (CAB-O-SIL-EH-5 untreated SiO_2 , CABOT) was used as support material. An aqueous solution of metal precursor (corresponding to 60 wt% metal loading) was impregnated onto the support. The sample was dried in an oven at 130 °C for overnight (16h). This as-synthesized catalyst was subjected to calcination in a muffle furnace and then reduced in 10% H_2 in Ar flow (70 ml/min). Monometallic Ni/ SiO_2 was calcined at 500 °C, at ramping rate of 5 °C/min for 10h and reduced at 450 °C, 10 °C/min for 4h; Fe/ SiO_2 was calcined at 500 °C, 5 °C/min for 10h and reduced at 700 °C, 10 °C/min for 4h; Co/ SiO_2 was calcined at 450 °C, 5 °C/min for 3h and reduced at 580 °C, 10 °C/min for 4h. Bimetallic Ni-Fe/ SiO_2 was calcined at 500 °C, 5 °C/min for 10h and reduced at 700 °C, 10 °C/min for 4h; Ni-Co/ SiO_2 was calcined at 750 °C, 5 °C/min for 5h and reduced at 700 °C, 10 °C/min for 2h; Fe-Co/ SiO_2 was calcined at 450 °C, 5 °C/min for 3h, and reduced at 580 °C, 10 °C/min for 4h. The present work concerns monometallic Ni, Fe, Co and bimetallic Ni-Fe, Ni-Co and Fe-Co catalysts. Bimetallic catalysts were prepared by a co-impregnation method with different mole ratios such as 1:1, 1:2, 2:1, 9:1, 4:1, 1:9. These catalysts are designated as xM-yN where M, N, and x, y stands for metal and mole number respectively.

2.2 Reactor Apparatus

A quartz-tube fixed-bed reactor with the length of 44.5 cm and diameter of 10 mm was used for catalytic performance tests. The schematic flow diagram of the reactor system is shown in Figure 2-1. In a typical test, 0.1 g catalyst was placed in the reactor and the reaction temperature was measured with a K- type thermocouple fixed at the catalyst bed. Prior to activity tests, the catalyst was subjected to a reduction at their respective temperatures and was later purged with N₂ for 30 min. Then the temperature was increased to 650 °C (10 °C/min) or 700°C in N₂ (70ml/min) and feed was switched to reactant gas (30% CH₄/N₂, 70ml/min) and a space velocity of 42000h⁻¹ was achieved. The composition of the outlet gas was measured by online gas chromatography (Perkin Elmer ARNEL, Clarus 500) equipped with a thermal conductivity detector. GC was calibrated with standard gases before analysis.

Figure 2-1. Schematic flow diagram of catalyst test unit

2.3 Catalyst Characterizations

2.3.1 Temperature programmed reduction (TPR)

Temperature-programmed-reduction (TPR) was performed for the catalysts using Micromeritics AutoChem HP chemisorption analyser equipped with a TCD detector. The catalysts were degassed in 200 °C for 1h. After cooling to RT, the temperature was ramped to 850 °C in 10 vol% H₂/Ar (50 ml/min) with a linear heating rate of 10 °C/min. and the TCD signal was recorded.

2.3.2 X-Ray Diffraction (XRD)

The catalysts with carbon deposition obtained after reaction at 650 and 700 °C were characterized by XRD. The XRD measurements were performed on PANalytical X'pert Pro using Cu K α radiation. The step scans were taken over the range of 10-90° and the scan rate was 5° /min.

2.3.3 Transmission Electron Microscopy (TEM)

The morphologies and microstructures of the carbon materials were characterized by Jeol TEM-2100 and the operating voltage was 200kV. The samples were prepared by sonication of the spent catalyst in isopropanol and the suspension was dropped onto a Cu grid for analysis.

2.3.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images were obtained through the measurement on a JEOL JSM-7600F SEM equipped with an Oxford INCA EDS. Raman experiments were carried out in Renishaw Invia Raman spectrometer at ambient atmosphere and room temperature. The Raman spectra were recorded using a green excitation line 532 nm. Thermogravimetric analysis was performed using the TA_SDT-650_Discovery model instrument in 5% O₂/He atmosphere, from 150-900 °C, at a constant heating rate of 2 and 5 °C/min.

Chapter 3 Mono- and Bimetallic Ni, Co, and Fe Catalysts for Methane Decomposition

3.1 Properties of Fresh and Spent Catalysts Supported on SiO₂

3.1.1 XRD analysis of fresh and spent catalysts

The characteristic peaks for all the metals (Ni, Fe, and Co) were identified using the XRD analysis. The amorphous peak of SiO₂ support was not visible in the diffraction pattern due to the high intensity of peaks for the metal loaded (60% metal on 40% SiO₂ support). The sharp peaks for metals confirmed the crystalline phase of the active element (Ni/Fe/Co) and the corresponding 2θ values represented their metallic state. The Ni characteristic peaks were observed at $2\theta = 44.6^\circ, 52.0^\circ, 76.6^\circ$ (JCPDS No. 04-850); Fe characteristic peaks were at $2\theta = 45.1^\circ, 65.5^\circ, 82.8^\circ$ (JCPDS No. 65-4899) and for Co the peaks were at $2\theta = 44.4^\circ, 51.6^\circ, 76^\circ$ (JCPDS No. 15-0806). For bimetallic Ni-Fe catalysts with different ratios, we observed a peak shifting which signified alloy formation (Figure 3-1 (b)). The transformation from the fcc to the bcc phase as a function of Fe content was observed in Ni-Fe bulk alloys [57, 58]. For the monometallic Ni catalyst, the (111) plane represents the fcc phase and for the monometallic Fe catalyst, the (110) plane represents the bcc phase. In the bimetallic catalyst, when Fe is introduced to a Ni-rich system (9Ni-1Fe) a single set of diffraction patterns corresponding to the fcc phase of Ni-Fe alloy was observed. This peak was also found to be shifted towards a lower 2θ value, converging to the diffraction pattern of the Ni fcc phase. Similarly, for the Ni-Co bimetallic catalyst, alloy formation was confirmed using XRD analysis (Figure 3-2). The fcc phase (111) of monometallic Co was observed at $2\theta = 44.4^\circ$, which was slightly shifted towards a higher 2θ value (Ni phase), representing the Ni-Co alloy formation. Also, for the Fe-Co bimetallic system, alloy formation was observed where the bcc phase for Fe was shifted towards the lower 2θ values, representing the fcc phase of Co and the Fe-Co alloy formation (Figure 3-3). Hence from XRD analysis, we could confirm the formation of alloy in the

bimetallic Ni/Fe/Co catalysts prepared, which thereby would help to increase the stability of the catalyst under the reaction conditions. After the reaction, the used catalysts were once again characterized by XRD analysis (Figure 3-4,5, and 6). The majority of the catalysts were stable in their metallic form but the monometallic Fe catalyst (Figure 3-4) transferred into iron carbide. But for the bimetallic catalysts, it was observed that the alloy formation has helped to prevent the oxidation of the metals and thereby increasing its lifetime or stability. From the XRD data, the mean crystallite size of metal nanoparticles before and after the reaction was calculated, using the Scherrer equation (Tables 3-1,2, and 3). The mean crystallite size of fresh Ni catalyst was found to be 25nm, while for fresh Fe catalyst it was 29nm. When Ni-Fe bimetallic catalysts were prepared, we could observe a significant decrease in the crystallite size, which even reduced up to 9nm for 2Ni-1Fe catalyst. In the case of fresh Co catalyst, the crystallite size was found to be 21nm. For fresh Ni-Co bimetallic catalysts, the crystallite size was found to be in between that of Ni and Co catalysts, 22-25nm. Also, for Fe-Co catalyst, we can observe the crystallite size of 17-28nm, which is in the range of Fe and Co monometallic ones. Even after the methane decomposition, there was a very little increase in the crystallite size of spent Ni-Fe/Ni-Co and Fe-Co catalysts. Hence there is not much agglomeration of the nanoparticles, which signifies the stable nature of the catalyst.

Figure 3-1 (a), (b). XRD of fresh mono and bimetallic Ni-Fe catalysts

Figure 3-2 (a), (b). XRD of fresh mono and bimetallic Ni-Co catalysts

Figure 3-3 (a), (b). XRD of fresh mono and bimetallic Fe-Co catalysts.

Figure 3-4. XRD pattern over spent mono and bimetallic Ni-Fe catalysts

Figure 3-5. XRD pattern of over spent mono and bimetallic Ni-Co catalysts

Figure 3-6. XRD pattern over spent mono and bimetallic Fe-Co catalysts

Table 3-1. Crystallite size of fresh and spent Ni-Fe bimetallic catalysts calculated from XRD

Catalyst	Crystallite size (nm)	
	Fresh	Spent
Fe/SiO ₂	29	13
1Ni-2Fe/SiO ₂	19	22
1Ni-1Fe/SiO ₂	17	20
2Ni-1Fe/SiO ₂	9	9
4Ni-1Fe/SiO ₂	10	12
9Ni-1Fe/SiO ₂	20	20
Ni/SiO ₂	25	25

Table 3-2. Crystallite size of fresh and spent Ni-Co bimetallic catalysts calculated from XRD

Catalyst	Crystallite size (nm)	
	Fresh	Spent
Co/SiO ₂	21	24
1Ni-9Co/SiO ₂	22	26
1Ni-1Co/SiO ₂	23	24
2Ni-1Co/SiO ₂	25	25
4Ni-1Co/SiO ₂	24	26
9Ni-1Co/SiO ₂	25	25
Ni/SiO ₂	25	25

Table 3-3. Crystallite size of fresh and spent Fe-Co bimetallic catalysts calculated from XRD

Catalyst	Crystallite size (nm)	
	Fresh	Spent
Fe/SiO ₂	29	13
9Fe-1Co/SiO ₂	28	31
4Fe-1Co/SiO ₂	26	28
2Fe-1Co/SiO ₂	23	25
1Fe-1Co/SiO ₂	17	18
1Fe-9Co/SiO ₂	17	18
Co/SiO ₂	21	24

3.1.2 TPR of fresh catalysts

H₂-TPR is a sensitive technique for the reducibility of the synthesized catalysts. The TPR results also supported XRD data for the alloy formation in the bimetallic catalysts. In the monometallic Ni catalyst, two reduction peaks were observed, one at around 367 °C and the other at 470 °C (Figure 3-7). First peak corresponds to the reduction of bulk NiO, which was weakly interacted with the SiO₂ support and the second weak reduction peak was associated with the reduction of NiO species, which had a very strong interaction with the SiO₂ support [66]. For monometallic Fe catalyst, a typical TPR profile has three peaks at around 470, 576 and 727 °C, respectively (Figure 3-7). These correspond to the three consecutive reduction steps, $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ [60, 61]. In the monometallic Co catalyst, the low temperature reduction peak centered at 306 °C and the second peak at 360 °C was assigned to the two-step reduction of spinel, i.e., $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ (Figure 3-8). An additional shoulder peak was also observed at around 433 °C [69]. However, the absence of high reduction temperature peaks shows that the interaction of cobalt with the SiO₂ support was not strong. TPR studies of bimetallic Ni–Fe catalysts showed that with the increase in Ni content the high

temperature reduction peaks of Fe were shifted towards the reduction temperature of Ni species (Figure 3-7). For Fe–Co catalysts, the increase in Co content lowered the reduction temperature of the catalyst or Co facilitated the reduction of Fe (Figure 3-9). When Fe was present in high concentrations, the catalyst exhibited the properties of Fe. Hence an increase in the Co reduction temperature was observed [62, 63]. The TPR profiles of Ni–Co catalysts (Figure 3-8) indicated that Co_3O_4 was easier to reduce than NiO , whereas an increase in Ni content retards the reduction of Co_3O_4 . Hence the incorporation of Co should improve the reducibility of NiO .

Figure 3-7. TPR analysis of fresh Ni-Fe catalysts

Figure 3-8. TPR analysis of fresh Ni-Co catalyst

Figure 3-9. TPR analysis of fresh Fe-Co catalysts

3.2 Effect of Catalyst Composition on CH₄ Decomposition and CNT Growth

3.2.1 Ni-Fe bimetallic catalysts

Initial studies were performed using monometallic Ni/SiO₂ catalyst. It was observed that even though Ni/SiO₂ showed a high CH₄ conversion of 50%, it started deactivating and reached a conversion of 40% in 60 min of reaction (Figure 3-10). Similarly, monometallic Fe/SiO₂ was tested, which showed a very low initial activity of 11% and gradually deactivated to 4% CH₄ conversion. Mono-metallic Ni/SiO₂ was a very active catalyst; unfortunately, it deactivated very fast. Hence the effect of Fe promoter addition on the activity of the Ni/SiO₂ catalyst for methane decomposition reaction has been shown. Several Ni-Fe mole ratios (9 : 1, 4 : 1, 2 : 1, 1 : 1, 1 : 2) were studied. 4Ni-1Fe/SiO₂ and 2Ni-1Fe/SiO₂ exhibited a similar activity to monometallic Ni/SiO₂ catalyst at TOS = 30 min., but afterwards it was observed that 4Ni-1Fe/SiO₂ catalyst retained its activity even after TOS = 60 min, whereas 2Ni-1Fe/SiO₂ deactivated like the Ni/SiO₂ catalyst. Reactions were also performed with 1Ni-1Fe/SiO₂ and 1Ni-2Fe/SiO₂, which showed a very low CH₄ conversion (16–20%) compared to the above catalysts, but they had maintained the activity throughout the reaction time. Thus, it was concluded that high Ni content in the Ni-Fe bimetallic catalyst exhibits higher conversion, which helps to increase the stability or the lifetime of the catalyst. Hence 9Ni-1Fe/SiO₂ was prepared, which showed an excellent conversion rate of 60%, the highest among all the Ni and Fe catalysts studied here, and its activity was very stable even at 60 min of reaction.

The H₂ yield was found to be in the range of 30–40% for catalysts with higher Ni content such as 9Ni-1Fe/SiO₂, 4Ni-1Fe/SiO₂, and 2Ni-1Fe/SiO₂, while the rest of the catalysts showed only 5–12% H₂ yield (Figure 3-11). The amount of carbon formed per gram of catalyst was calculated, which was found to be approximately 2.3–2.5 g over 9Ni-1Fe/SiO₂, 4Ni-1Fe/SiO₂, and 2Ni-1Fe/SiO₂ and was less than 0.4 g for the rest of the catalysts (Figure 3-12).

Figure 3-10. Methane decomposition over Ni-Fe/SiO₂ catalysts with various mole ratios

Figure 3-11. H₂ yield over Ni-Fe/SiO₂ catalysts with various mole ratios

Figure 3-12. Amount of carbon formed over Ni-Fe/SiO₂ catalysts with various mole ratios

3.2.2 Ni-Co bimetallic catalysts

Methane conversion over mono- and bimetallic Ni and Co catalysts are studied in this section. Under the reaction conditions, Co/SiO₂ showed a CH₄ conversion of 37% but deactivated to 9% within 5 min of reaction (Figure 3-13). Ni/SiO₂ already showed good initial activity but had a gradual deactivation during the course of the reaction. Hence, to improve the activity of Co/SiO₂ and to increase the stability of Ni/SiO₂ catalysts, we have prepared a bimetallic combination of Ni–Co catalysts with various Ni: Co mole ratios, such as 9Ni–1Co, 4Ni–1Co, 2Ni–1Co, 1Ni–1Co, 2Ni–1Co, and 1Ni–9Co, on a SiO₂ support. Similar to Ni–Fe catalysts, the Ni–Co combination also showed a maximum conversion of 55%. Ni–Co catalysts such as 9Ni–1Co, 4Ni– 1Co, 2Ni–1Co, and 1Ni–1Co showed a similar initial conversion of 50–55% and retained their activity throughout the reaction. A catalyst with higher Co content was also tested, 1Ni–9Co, which showed an initial conversion of 53%, but within 15 minutes of reaction. It was observed that the high Ni content in the Ni–Co bimetallic catalyst exhibited higher conversion and the presence of Co as a promoter contributed to increasing the catalyst lifetime.

H₂ yield was found to be in the range of 38–40% for catalysts with higher Ni content such as 9Ni–1Co/SiO₂, 4Ni–1Co/SiO₂, and 2Ni–1Co/SiO₂, whereas Co/SiO₂ and 1Ni–9Co/SiO₂ showed only an initial H₂ yield of 28–33% which reduced to 6% within 5 min of reaction (Figure 3-14). The amount of carbon formed per gram of catalyst was calculated, which was found to be approximately 2.3–2.5 g over 9Ni–1Co/SiO₂, 4Ni–1Co/SiO₂, and 2Ni–1Fe/SiO₂ and was 0.15–0.27 g for Co/SiO₂ and 1Ni–9Co/SiO₂ catalysts (Figure 3-15).

Figure 3-13. Methane decomposition over Ni-Co/SiO₂ catalysts with various mole ratios

Figure 3-14. H₂ yield over Ni-Co/SiO₂ catalysts with various mole ratios

Figure 3-15. Amount of carbon formed over Ni-Co/SiO₂ catalysts with various mole ratios

3.2.3 Fe–Co bimetallic catalysts

Methane decomposition reactions over mono- and bimetallic Fe–Co catalysts are explained in this section (Figure 3-16). Bimetallic Fe–Co/SiO₂ catalysts were prepared with various Fe : Co mole ratios, such as 9Fe–1Co, 2Fe–1Co, 1Fe–1Co, 1Fe–2Co, and 1Fe–9Co, over a SiO₂ support. It was observed that 1Fe–2Co/SiO₂ showed the highest CH₄ conversion of 51% but has undergone drastic deactivation and showed a conversion of only 15% at 60 min

Figure 3-16. Methane decomposition over Fe-Co/SiO₂ catalysts with various mole ratios

of reaction. Among the catalysts studied here, even though the activity is not excellent, the stability was better over 9Fe-1Co/ SiO₂ and 4Fe-1Co/SiO₂. The maximum H₂ yield of 29% (Figure 3-17) and carbon yield of 0.8 g was observed with 1Fe-2Co/ SiO₂ (Figure 3-18).

Figure 3-17. H₂ yield over Fe-Co/SiO₂ catalysts with various mole ratios

Figure 3-18. Amount of carbon formed over Fe-Co/SiO₂ catalysts with various mole ratios

3.3 Comparison of Activities of Reduced and Oxidized Catalysts

Generally, transition metal catalysts (Ni/Fe/Co) were used in their reduced forms ($\text{Ni}^0/\text{Fe}^0/\text{Co}^0$) for the CNT synthesis by methane decomposition. However, some literature reports have shown that it may not be necessary to pre-reduce the catalysts for the reaction [71]. For our experiments we have used oxidized and reduced forms of 9Ni–1Fe/SiO₂ catalyst since it has shown a very good activity for methane decomposition reactions (Figure 3-19). Both the catalysts showed a similar activity at the initial point of the reaction (ca. 60%). The activity shown by the oxidized catalyst can be due to the in-situ reduction of the lattice oxygen which supplied energy for methane decomposition, which is an endothermic process. In addition, there can be an in-situ consumption of H₂ formed, which assisted the shifting of the equilibrium towards the methane decomposition step or carbon formation [71]. As we have shown before (Figure 3-10), the reduced 9Ni–1Fe/SiO₂ catalyst showed a constant activity till the end of the reaction but the oxidized form of the catalyst was gradually deactivated from 60% to 41% conversion rate in 60 min of reaction time. The amount of carbon formed per gram of catalyst was also in the range of 2.2–2.5 g for both catalysts. In summary, in our case even though the oxidized form of the catalyst catalyzed the methane decomposition to carbon and H₂, the stability of the catalysts was lesser compared to that of their reduced forms. This may be because reduced forms are stabilized due to their alloy phases, which helps to increase their lifetime and stability.

Figure 3-19. Methane decomposition over reduced and oxidized forms of 9Ni-1Fe/SiO₂

3.4 The Properties of Carbon Nanotube

3.4.1 XRD analysis

All the XRD patterns of the used catalysts showed the presence of graphitic carbon by a very intense peak (002) at $2\theta = 26.2^\circ$ (Figures 3-4,5, and 6). All characteristic metal and alloy peaks were also identified and the d-spacing of CNTs were calculated using Bragg's equation ($d = \lambda/2\sin\theta$) for the graphitic peak, which was found to be 0.34 nm and it correlates well with distance of two graphite layers (0.3354 nm) implying the high crystallinity of the carbon grown over all the catalysts. The intensity of the (002) diffraction peak is related to the degree of graphitization (Figure 3-20). So lower intensity represents the less graphitized material [72]. In the case of Ni-Fe bimetallic catalysts, we can observe that 9Ni-1Fe/SiO₂ or the bimetallic catalyst with highest Ni content produced CNT with the highest degree of graphitization and its degree decreases with increase in the amount of Fe in the catalyst. The degree of graphitization for Ni-Fe catalyst was in the order 9Ni-1Fe>Ni>4Ni-1Fe>2Ni-1Fe>1Ni-2Fe>Fe. For Ni-Co bimetallic catalyst, 4Ni-1Co/SiO₂ produced CNT with highest graphitization degree and was in the order 4Ni-1Co>2Ni-1Co>Ni>1Ni-1Co=9Ni-1Co>1Ni-9Co>Co. For Fe-Co

catalysts the overall intensity of the CNT peak was very less compared to Ni-based catalysts and the whole set of Fe-Co catalysts produced less graphitized CNT. Hence in general Ni content in the bimetallic catalyst is influencing the degrees of graphitization of the carbon formed during the methane decomposition reaction.

Figure 3-20. XRD pattern of CNT over mono and bimetallic (a) Ni-Fe (b) Ni-Co and (c) Fe-Co catalysts

3.4.2 Thermogravimetric analysis (TGA)

Thermal stability of CNT was studied using thermogravimetric analysis. Spent catalysts such as 9Ni-1Fe/SiO₂, 9Ni-1Co/SiO₂, and 1Fe-2Co/SiO₂ were studied since these catalysts showed better activity than the rest of the catalysts (Figure 3-21). These catalysts were analyzed in 2%O₂/He atmosphere. The carbon deposited on the catalyst, amorphous or CNT decomposes into CO or CO₂ in O₂ atmosphere. In certain cases, there is a possibility that the catalyst species also get oxidized under these conditions. It was observed that there was no thermal degradation in the temperature range of 200-350 °C, which corresponds to the amorphous carbon. Hence, we could confirm that the carbon deposited on these catalysts is not amorphous in nature. The weight loss observed in all catalysts corresponds to the CNT deposited on the catalyst. From TGA analysis of CNTs it is understood that higher the degradation temperature of carbon, the higher its stability. For 9Ni-1Fe/SiO₂, the thermal degradation started at around 500 °C and there was a weight loss of 75%. For 9Ni-1Co/SiO₂ degradation started from 450 °C with a weight loss of 70%. For 1Fe-2Co/SiO₂ catalyst, there was a slight increase in weight, 2% at a temperature of around 350 °C, which can be due to the oxidation of Fe present in the catalyst. At around 410 °C, a weight loss of 45-50% was observed, which was lower than 9Ni-1Fe/SiO₂ and 9Ni-Co/SiO₂ catalysts. The onset temperatures for 9Ni-1Fe/SiO₂, 9Ni-Co/SiO₂, and 1Fe-2Co/SiO₂ are 500-660 °C, 450-650 °C and 410-640 °C respectively., which indicates that the CNT formed over 9Ni-1Fe/SiO₂ catalyst has a higher degree of graphitization, as well as lesser defects on the CNT's [73]. Hence it can be concluded that a smaller difference in the onset and end temperature indicates the formation of highly graphitized CNT's. It is also understood that there is no amorphous carbon formation during methane decomposition over these catalysts and the amount of carbon formed over 1Fe-2Co/SiO₂ is the minimum in comparison to 9Ni-1Fe/SiO₂ and 9Ni-Co/SiO₂ catalysts.

Figure 3-21. Thermal stability of carbon deposited over 9Ni-1Fe/SiO₂, 9Ni-1Co/SiO₂ and 1Fe-2Co/SiO₂ catalysts

3.4.3 Raman analysis

Raman spectroscopic study was performed to measure the quality and crystallinity of carbon (Figures 3-22,23,24). Two distinct bands were observed for all the catalysts, the D-band at 1336 cm⁻¹ and G-band at 1570 cm⁻¹. D-band represents either disordered or amorphous carbon and G-band represents the crystalline carbon [4]. From TGA analysis it was confirmed that there is no amorphous carbon deposited on the catalyst (Figure 3-21). Hence the intensity ratio, I_D/I_G explains the graphitization degree and the crystallinity of the CNTs [74]. The catalyst having lowest I_D/I_G carbon with the highest crystallinity. For Ni-Fe catalysts (Figure 3-22) we could observe that I_D/I_G value was lowest for 9Ni-Fe, 4Ni-1Fe, Ni, 1Ni-2Fe showed similar I_D/I_G value (0.829-0.874), better crystallinity than 2Ni-Fe, 1Ni-1Fe and Fe catalysts with higher I_D/I_G value (0.944-1.26). Raman spectra for Ni-Co catalysts (Figure 3-23) shows that 9Ni-1Co gave most crystalline CNT with lowest I_D/I_G (0.765), while Ni, 4Ni-Co, 1Ni-1Co showed similar I_D/I_G (0.868-0.883). We didn't observe any distant bands for Co and

1Ni-9Co catalysts since the amount of CNT formed for these catalysts were lesser than the detection limits. For 4Fe-1Co crystallinity calculated was the highest, ($I_D/I_G=0.896$), while Fe, 9Fe-1Co, 2Fe-1Co showed similar I_D/I_G (0.983-0.99). Remaining catalyst ratios such as 1Fe-1Co, Fe-2Co Fe-Co catalysts 4Fe-1Co formed CNT with highest I_D/I_G (1.019-1.042) due to the low crystallinity of the CNT formed (Figure 3-24).

Figure 3-22. Raman spectra of CNT over mono and bimetallic Ni-Fe catalysts

Figure 3-23. Raman spectra of CNT over mono and bimetallic Ni-Co catalysts

Figure 3-24. Raman spectra of CNT over mono and bimetallic Fe-Co catalysts

3.4.4 TEM analysis

Structural morphology, particle size, diameter and growth of CNT was studied using TEM technique. This analysis was limited to the certain catalysts from each set of bimetallic catalysts (Ni-Fe/Ni-Co and Fe-Co) which showed the best performance and stable nature in the methane decomposition reactions (Figure 3-25). Hence TEM analysis was performed over the used 9Ni-1Fe/SiO₂, 9Ni-1Co/SiO₂, and 1Fe-2Co/SiO₂ catalysts. It was observed that the CNT formed in our experiments are found to be MWCNT due to large crystallite size of active site metal nanoparticles, confirmed by XRD techniques. The CNTs formed over all these catalysts showed a very crowded dense population with entangled fibers. CNT's were growing in random directions due to space competition of growth [73]. The length of the CNT depends on the duration of the process, hence to obtain longer filaments, the duration of the reaction has to be extended.

For 9Ni-1Fe/SiO₂ catalyst it was observed that most of the CNT formed where of 100-120 nm. The wall of the tube was very thick with graphite layer stacked very closely. Another interesting feature was that when Ni-Fe catalyst was used we could observe a “tip growth” of CNT whereas the CNT grows it takes the metal nanoparticle along with it and is situated at the tip of the CNT. The shape of the metal nanoparticle was “cone or pear-shaped” tapered towards the end and forms an angle with the tubular axis. From HR-TEM it was observed that the wall of CNT formed were of “fishbone or herringbone” structure in which the graphene layers are stacked obliquely with respect to the fiber axis. In these type of CNT, the graphite planes are formed at an angle to the axis of the nanotube and hence there is a higher possibility for the edge plane sites/defects in these CNTs [75]. For 9Ni-1Co catalyst, MWCNT's with 50-60 nm diameters were formed, also with a metal nanoparticle at the tip. But from HR-TEM it was observed that the wall of these CNT's had a parallel morphology (graphite planes arranged parallel to the tubular axis). But certain fibers formed in these catalysts didn't have metal

nanoparticles at the tip and gave a mixture of tip and base grown CNT's. HR-TEM has confirmed the parallel morphology of the CNT wall for these catalysts.

Figure 3-25. Growth of carbon filaments over (a,b) 9Ni-1Fe/SiO₂, (c,d) 9Ni-1Co/SiO₂, (e,f) 1Fe-2Co/SiO₂ catalysts after methane decomposition

3.5 Conclusion

The catalytic activity, selectivity and stability of mono and bimetallic Ni/Fe/Co based catalysts was demonstrated for the methane decomposition study. The novelty in our work is that we investigated the performance of transition metal catalysts (Ni/Fe/Co) for the synthesis of both tip and base grown CNT's by methane decomposition. We have synthesized mono and bimetallic Ni/Fe/Co catalysts by dry impregnation over SiO₂ support. The XRD and H₂-TPR analysis confirmed the formation of the alloy in the

bimetallic catalysts. The effect of catalyst composition on methane decomposition and CNT growth was studied over various mole ratios of Ni, Fe and Co-based catalysts. High Ni content in the Ni-Fe bimetallic catalyst exhibited higher methane conversion and also contributed to an increase in the stability of the catalyst. In the case of Ni-Co bimetallic catalyst also higher Ni content exhibited higher conversion and Co present in the catalyst contributed to increase the catalyst lifetime. Among Fe-Co catalysts, the activity towards methane conversion was comparatively lower than Ni-Fe and Ni-Co catalysts. The quality of the CNT's formed over these catalysts was analysed using XRD, TGA, Raman and TEM techniques. From XRD analysis it was understood that Ni content in the bimetallic catalyst controls the degrees of graphitization of the carbon formed. From TGA analysis it was concluded that there was no amorphous carbon formation during methane decomposition over these catalysts. The quality of the carbon, that is the degree of crystallinity was calculated using Raman analysis. TEM analysis helped to understand the different morphologies of the CNT, diameter, wall type (parallel or fish bone type) and also the growth mechanism such as tip and base growth on different catalysts. It was understood that Ni-Fe catalyst selectively produced tip grown CNT's with fishbone wall pattern, while Ni-Co and Fe-Co catalysts formed a mixture of tip and base grown CNT's with parallel wall pattern.

Chapter 4 Fe-Based Catalysts with Different Supports

There are only very few studies that have correlated the catalyst properties (Fe loaded on SiO_2 , Al_2O_3 , or H-ZSM-5) which would help us to produce CO_x -free H_2 and synthesize base grown CNT's by methane decomposition. Base grown CNT's can be easily harvested and help in better regeneration of the catalyst. Hence in the present work, we prepared Fe-based catalysts on various supports and also investigated the strong metal interaction responsible for base grown CNT's. In addition to this, we have attempted to separate and purify the CNT's from the catalyst surface and also analyzed its purity.

4.1 Mechanism of Base Grown of CNT

Stronger interaction of metal nanoparticles with support (obtuse angle of metal with the support) facilitates “base growth” of carbon nanotubes [5]. Decomposition of methane and carbon diffusion in the initial stage is similar to that of the tip growth model but the carbon precipitated is unable to push away the metal upwards. Hence the precipitated carbon is compelled to emerge out from the upper side of the metal (away from the support surface). It is also known from the literature that the high surface energy of the metal nanoparticles is reduced by the deposition of the graphene planes, which are strongly chemisorbed on to the metal surface. A graphitic cap is formed on the metal nanoparticle which is lifted upwards, during the further deposition of carbon fragments. Hence, we observe a hollow carbon nanotube growing away from the metal nanoparticle, which is still attached to the support or a base growth of carbon nanotubes [76].

4.1.1 Synthesis of base grown CNT's

Based on previous literature we found out that Fe based catalysts generated base grown CNT's. Also, from our catalyst screening studies using mono and bimetallic Ni/Fe/Co catalysts we have discovered that 60% Fe/SiO₂ was selectively forming base grown CNT's during methane decomposition. Hence, we chose Fe/SiO₂ catalysts for our preliminary work. From our experimental results we found that Fe/SiO₂ had a very low methane conversion, 11 % and eventually got reduced to 4 % at T = 650 °C, TOS = 60 minutes, GHSV = 42000 h⁻¹. As a result, the reaction conditions have to be optimized to obtain better conversion and yields of H₂ and CNT.

4.2 Catalyst Preparation

Fe-based catalysts were prepared by incipient wetness technique. Fe(NO₃)₂·9H₂O (Alfa Aesar) was selected as a metal precursor and Al₂O₃ (Alfa Aesar), fumed SiO₂ (CAB-O-SIL-EH-5 untreated SiO₂, CABOT), and ZSM-5 (CBV-5524G, SiO₂/Al₂O₃ mole ratio = 50, Zeolyst International company) were utilized as catalyst supports. The 40 wt% supports were impregnated with an aqueous solution of iron nitrate corresponding to 60wt%. The samples were dried in air at 130°C overnight, and then calcined at 500°C for 10 h. The obtained catalysts were designed as Fe/Al₂O₃, Fe/SiO₂, and Fe/H-ZSM-5. Besides the 60 wt%Fe/Al₂O₃, we also prepared the 10 and 30 wt% Fe/Al₂O₃ for loading comparison. These catalysts were designated as X Fe/support (X means weight % loading of Fe).

4.3 Effect of Catalysts on Methane Decomposition

4.3.1 Methane conversion

The catalytic activity of Fe-catalysts on various supports (Fe/Al₂O₃, Fe/H-ZSM-5, and Fe/SiO₂) for methane decomposition at 700°C were studied. The main products from methane

decomposition are hydrogen gas and carbon or CNT. Quantification of H_2 was performed using GC analysis while carbon deposited on the catalyst was calculated based on the weight gain of the catalyst after the reaction and was characterized using different techniques. Growth rates of CNT on two supports suggest that the catalyst morphology can greatly affect the activity of the catalysts because in CCVD the rate determining step is the adsorption and decomposition of hydrocarbons by catalyst particles. From our experiments, we observed that the conversion of CH_4 depends on the types of support, such as Al_2O_3 , SiO_2 , and H-ZSM-5. For Fe/H-ZSM-5 and Fe/ SiO_2 catalysts, the initial conversions were 50% and 36% respectively (Figure 4-1 (a)). Even though Fe/ Al_2O_3 had a higher initial conversion (58%) the activity reduced (20%) within 1h of reaction. On Fe/H-ZSM-5 catalyst the initial conversion was also high (50%) but there was a drastic decrease in its activity to 15% in 15min. but it maintained this conversion rate throughout the reaction time. Similarly, Fe/ SiO_2 with an initial conversion of 36% got reduced to 9%. Above results indicated that supports had a significant impact on the catalysts. The support enhanced the performance of the catalyst activity, as the effect on electronic properties or structure was related to the interaction between metals and supports [77–79].

The support of H-ZSM-5 consisted of Al_2O_3 and SiO_2 , and it showed the lower conversion than pure Al_2O_3 support. Acidic Al_2O_3 support had higher activity than with SiO_2 . Also, the structure of the zeolite was a three-dimensional cage and channel, which was more complex and constrained. The cage structure of ZSM-5 might inhibit the distribution of Fe oxide particles. Hence, carbon may deposit on both the external surfaces of the catalyst and the internal channel, which induce the CNT deposition in the internal channel, and evenly block pores structure and the catalytic deactivation.

Catalytic activity for methane conversions of Fe/ Al_2O_3 was with time on stream over various Fe loading. The Fe loading were 10 wt%, 30 wt%, and 60 wt% which initial conversion were 18%, 40%, and 58%, respectively. The conversion increased as the loading of Fe

increased but after 15 min, all catalysts began to deactivate gradually. The conversion of 30% Fe/Al₂O₃ catalyst dropped from 40% to 18% and 10%Fe/Al₂O₃ decreased to 10%. In addition, 60%Fe/SiO₂ and 30%Fe/Al₂O₃ had similar methane conversion and hence supports clearly affect the activity of catalysts (Figure 4-1 (b)).

Figure 4-1. Methane decomposition over Fe-based catalysts at 700°C (a) different supports and (b) different loading of Fe/Al₂O₃

4.3.2 Yield of hydrogen and carbon

During decomposition of methane, hydrogen and carbon were produced. The hydrogen yield for each catalyst was similar to the methane conversion which followed the similar trend. 60% Fe/Al₂O₃ indicate the highest initial yield of hydrogen at ca. 26%. 60% Fe/ZSM-5 and 60% Fe/SiO₂ were 24% and 20%, respectively, as presented in Figure 4-2(a). Moreover, different loading of Fe, 30% Fe/Al₂O₃ and 10% Fe/Al₂O₃ were 16% and 2%, respectively, as shown in Figure 4-2 (b). All yield of carbon was an approximate measurement with per gram of catalyst after the reaction. Figure 4-2 (c) showed carbon formation of 60% Fe/Al₂O₃ was 0.785 g/g of catalyst the highest carbon amount and 60% Fe/ZSM-5 and 60% Fe/SiO₂ were both at around 0.1g/g of catalyst. In addition, the yield of 30% Fe/Al₂O₃ and 10% Fe/Al₂O₃ were ca. 0.38 and 0.07 g/g of cat., respectively, as shown in Figure 4-2(d).

Figure 4-2. The yield of hydrogen and carbon deposited over Fe-based catalysts at 700°C
(a) and (c) different support; (b) and (d) different loading of Fe/Al₂O₃

4.4 Properties of Catalysts and CNTs

4.4.1 XRD analysis

Characteristic peaks observed in the XRD pattern confirmed the metallic state of Fe catalyst after reduction (Figure 4-3 (a)). The characteristic peaks of Fe were at $2\theta = 44.9^\circ$ as well as additional peaks were at 65.2° and 82.5° . On the other hand, the characteristic peaks of Al₂O₃ and H-ZSM-5 supports were not visible in the XRD chromatogram due to the high loading of Fe (60wt% over the supports (40wt%). In addition, SiO₂ support was an amorphous phase and showed the much broader peak adding up to the background. While Al₂O₃ support can be observed in the lower loading amount of Fe (10wt% Fe loaded over 90wt% Al₂O₃) with characteristic peaks at $2\theta = 37.5^\circ$, 45.8° , and 67.05° corresponding to γ -Al₂O₃. After the methane decomposition, the used catalysts were investigated by XRD analysis. It was observed

that for the spent catalysts XRD diffractogram showed peaks at $2\theta = 37.8^\circ, 42.9^\circ, 43.8^\circ, 44.6^\circ, 44.9^\circ, 45.9^\circ, 48.6^\circ,$ and 49.1° which are the characteristic peaks for Fe_3C species (JCPDS Card no. 65-2413), as shown in Figure 4-3 (b). But in our previous studies on methane decomposition over nickel-based catalyst, we did not observe any evidence from XRD for the formation of Ni_xC as intermediate species. Carbide cycle mechanism can be used to explain the observation [81, 82]. During methane decomposition Fe_3C is formed on the free surface fragment of the catalytic particle. Since Fe_3C is metastable, it is decomposed to graphitized carbon and α species of Fe. The α -Fe along with Fe_3C facilitates methane decomposition and carbon growth. These active Fe species are deactivated by the encapsulation of these species by the growing carbon filament resulting in the fragmentary dispersion of Fe particles. The carbon deposited on the spent catalyst as proven by the XRD peak at $2\theta = 26.3^\circ$ which was assigned to characteristic peak of graphitic carbon (002) and indicating the CNTs have a good degree of graphitization. The carbon peak of 10% Fe/ Al_2O_3 was weak due to its low conversion.

Figure 4-3. XRD patterns of (a) fresh Fe-based catalysts after H_2 reduction and (b) spent catalysts Fe-based catalyst after methane decomposition at 700°C

4.4.2 TEM analysis

The morphology of metal particles and CNT formation mechanism over the catalyst were analyzed by TEM. The Fe-based catalysts were presented on a higher portion of base grown carbon nanotube compared with Ni/SiO₂ and Co/SiO₂ catalyst. As depicted in Figure 4-4, due to SMSI, metal particles could be inhibited by support and CNT grew from the bottom. The morphology of spent catalysts Fe/Al₂O₃ can form much longer CNT than Fe/SiO₂ and Fe/H-ZSM-5 during 1 h reaction time and its length can be up to 100 nm. In addition, the outer diameter of CNT over Fe/Al₂O₃ was smaller than other two catalysts due to nano-dispersion of Fe particles, which demonstrated that the Al₂O₃ support can effectively prevent the metal agglomeration. Moreover, TEM images clearly observed that the carbons grew as multi-walled CNT with several graphene layers. The black spots corresponded to the size and location of Fe metal particles and were located at either tip or base of the carbon nanotube.

Figure 4-4. Growth of carbon filaments over (a) Fe/Al₂O₃, (b) Fe/SiO₂, (c,d) Fe/H-ZSM-5 catalysts after methane decomposition

4.4.3 Raman analysis

The crystallinity of carbon nanotube was evaluated by Raman spectra. Figure 4-5 depicted the Raman spectra of carbon deposited over Fe catalysts on various supports. Two individual bands were observed the D-band at 1335 cm^{-1} due to the presence of disorder structure and G-band at 1580 cm^{-1} due to the in-plane oscillation of sp^2 carbon atoms and it indicated the well-ordered structure [80, 81]. The relative intensity of I_D/I_G ratio can be used to characterize the graphitic degree of CNT as well. Lower value for I_D/I_G indicates higher crystallinity for the carbon formed. Among the catalysts compared the I_D/I_G value is in the order Fe/H-ZSM-5($I_D/I_G=0.784$)>Fe/ Al_2O_3 (0.755)>Fe/ SiO_2 (0.699) shown in Figure 4-5. Raman spectra for Fe/ Al_2O_3 catalysts with different loading (10wt%, 30wt%, and 60wt%) also showed affected the quality of carbon formed. It was observed that 60wt% Fe/ Al_2O_3 formed the most crystalline carbon compared to its lower Fe loadings.

Figure 4-5. Raman spectra of carbon deposited over spent catalysts with different supports and Fe loading

4.5 Harvest of Carbon Nanotube

Here, we selected the 60% 9Ni-1Fe/SiO₂ and Fe/Al₂O₃ catalysts for purification because they have exhibited the best performance. About 0.3 g spent catalysts were suspended in a 3.0 M HNO₃ solution with a volume of 45 ml under reflux condition with magnetic stirring at 120°C for 24 h and 48 h. The purified CNT were filtered and washed with deionized water followed by drying overnight at 120°C. Most metal particles and supports on the spent catalysts used for the synthesis of the CNT were removed by acid-treatment and the results were presented below.

4.5.1 XRD and Raman analysis for purified CNT

To perform XRD analysis, the spent catalysts were purified with 3.0 M HNO₃ acid treatment for 24 and 48 h. Figure 4-6 (a) shows most metal particles and supports were removed from the spent catalysts which corresponded to the main peak position at the region $2\theta = 40\text{--}50^\circ$, while the weak peak of graphitic carbon (100) plane at $2\theta = 43^\circ$ appearing became stronger peak than before (JCPDS card no. 65–6212). In addition, Figure 4-6 (b) showed the Raman spectra of purified catalysts. The I_D/I_G ratio of spent Fe/Al₂O₃ was 0.755 and purified Fe/Al₂O₃ were 0.758 (24 h) and 0.73 (48 h). The I_D/I_G ratio of spent 9NiFe/SiO₂ was 0.822 and purified 9NiFe/SiO₂ were 0.834 (24 h) and 0.804 (48 h). Thus, the ratio of I_D/I_G did not change, which indicate the HNO₃ did not affect the crystalline structure of the formed CNT. CNT formed on different catalysts had different graphitization degree and Fe/Al₂O₃ can produce higher crystalline carbon. Both results revealed that the acid treatment for 48 h effectively metal and support residue of the spent catalyst but keep the crystalline structure of produced CNT's.

Figure 4-6. (a) XRD patterns of spent catalysts and purified CNT (24 h and 48 h);
 (b) Raman spectra of spent catalysts and purified CNT (24 h and 48 h)

4.5.2 TEM and SEM-EDS analysis for purified CNT

TEM images indicated the corn-shaped metal particle at the tip of CNT from 9Ni-1Fe/SiO₂ after acidic purification (Figure 4-7). There are trace metal nanoparticles without open tip encapsulated in the interior of carbon nanotubes. (All measurements were performed on the same conditions and the Au pattern was from the sample sputter coating. On the other hand, SEM-EDX demonstrated that, after treated with an acid solution for 48 h, there were almost no trace of metal and support detected on 60% Fe/Al₂O₃ and only with little oxygen signal, while 60% 9Ni-1Fe/SiO₂ still showed the signal of SiO₂ support, as presented in Fig. 4-8. Overall, acidic purification is good to remove alumina which is amphoteric substance, while not as effective as to purified CNTs from Fe/SiO₂ catalyst.

Figure 4-7. TEM images of purified CNT from 9Ni-1Fe/SiO₂ catalyst with HNO₃ for 48 h

Figure 4-8. SEM-EDX analysis (a) spent Fe/Al₂O₃, (b) purified CNT from Fe/Al₂O₃, (c) spent 9Ni-1Fe/SiO₂, and (d) purified CNT from 9Ni-1Fe/SiO₂

4.5.3 TGA analysis

TGA measurement was carried out to determine the content of metal impurity in CNT and reveal the stability of CNT at a given temperature. Less crystalline CNT will react preferentially with the oxidant and lose weight at a lower temperature compared with more highly crystalline CNT. The slight weight gained between 350°C and 500°C might be attributed to metal oxidation in spent 60% Fe/Al₂O₃ (Figure 4-9 (a) and (c)). The maximum weight loss was at 582°C and the endpoint was at 700°C and the residual was ca. 57 wt%. The maximal weight loss temperature shifted to 630°C and the end temperature at ca. 726°C for both 24 and 48 h. The residual catalyst was ca. 4.7 wt% and 3.8 wt% for 24 h and 48 h, respectively. Regarding 60% 9NiFe/SiO₂, the slight weight gain between 350°C and 500°C might be also attributed to metal oxidation (Figure 4-9 (b) and (d)). The maximum weight loss was at 612°C and the endpoint was at 730°C. The residual catalyst was ca. 57.4 wt%, which is slightly more than that of 60% Fe/Al₂O₃. After the purification, the maximal weight loss temperature shifted to 670°C (24 h) and 654°C (48 h) and the end temperature at 745°C (24 h and 48 h). The residual weight remains 17.2 wt% and 11.8 wt% for 24 h and 48 h, respectively. Therefore, TGA data confirmed that acidic purification was more effective for Al₂O₃ supported catalysts than that of SiO₂, which is consistent with the above-mentioned SEM-EDS results. Therefore, the weight loss before 500°C may be assigned to the decomposition of functional groups, carboxyl and hydroxyl groups which were consumed about 1.5-2% weight loss on both purified catalysts [82–84]. The thermal stability of CNT was improved slightly, due to the remove of catalytic particles and amorphous carbon impurities [87].

Figure 4-9. TGA profiles of spent catalysts and purified CNT: Weight loss (%)

(a) Fe/Al₂O₃, and (b) 9Ni-1Fe/SiO₂; Deriv. Weight (%/min) (c) Fe/Al₂O₃ and 9Ni-1Fe/SiO₂

4.5.4 The dispersion of purified catalysts

Due to their nanometer size and the weak attraction of van der Waals force between the CNT surface, they have a high tendency to become bundle together and agglomerated, which influenced its dispersion or miscibility in a solvent or polymer matrices [88]. Therefore, one way to prevent the agglomeration of CNT was to modify the CNT surface by chemical oxidation. After acid treatment, we speculate that the functional groups such as hydroxyl (C-OH), carbonyl (C=O), and carboxyl (COOH) were introduced on the sidewalls or ends of CNT [78,83, 84]. A comparison of dispersibility between before and after purification was performed as below. All samples were sonicated for 15 mins and suspended in a polar media, isopropanol. The good dispersion indicated the solution maintained a uniform black color without precipitation. Figure 4-10 presents the dispersion states of CNT after long-term deposition. The spent catalysts without acid treatment completely sediment after settled in a few hours, while samples with acid treatment still dispersed well in the solvent even after 60

days. Also, we expected that the metal particles and support might affect the dispersion state of CNT. Thus, the results confirmed as the acid treatment applied improved the dispersion stability of CNT.

Figure 4-10. Photographs of the spent catalysts and purified CNT dispersed in isopropanol
(a) just after sonication for 15 mins (b) after dispersion for 60 days

4.6 Conclusion

We have discovered that the Fe/SiO₂ catalyst formed base grown CNT. We continued to study Fe-based catalysts and to improve its activity and stability. The support and the loading of Fe on Al₂O₃. 60wt% Fe/Al₂O₃ catalyst demonstrated the best activity and stability. Catalysts were characterized using XRD, XPS, TEM, and Raman. After acid treatment, we also compared the properties of CNT by XRD, Raman, SEM-EDX, TEM, and TGA. XRD analysis showed almost all metal particles were removed from CNT. The results of Raman spectra did not change which means no detrimental damage. SEM-EDS measurement revealed the little support elements of SiO₂ can be detected. The amount of residual catalysts was presented by TGA and purified Fe/Al₂O₃ only remained 3.8 wt% of catalysts. Above results showed that the acid treatment was very effective in purifying Fe/Al₂O₃ catalyst. As a consequent, the acid treatment can influence the dispersion of CNT in the isopropanol.

Chapter 5 Synthesis Aerogel Catalyst for Methane Decomposition

5.1 Catalyst Preparation of Ni/Al₂O₃ and Co/Al₂O₃ Aerogel Catalysts

Analytical grade chemicals including AlCl₃·6H₂O, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, ethanol (anhydrous) and propylene oxide (PO) were purchased from Acros Organics and used as received without further purification. Deionized water was used in making the metal solutions. This section describes the preparation of 2 g 50 wt% Ni/Al₂O₃ aerogel catalyst as an example. In the preparation, 4.74 g of AlCl₃·6H₂O was mixed with 4.95 g of Ni(NO₃)₂·6H₂O, followed by adding 10 mL of deionized water and 15.5 mL anhydrous ethanol under rigorous agitation for 30 min. The beaker containing the solution was sealed and then heated in an oil bath at 80°C for 1 h. The solution was cooled to room temperature when 16 ml of propylene oxide (PO) was added. Keep the solution in an ice bath for 35 min and allow aerogel to form. After formation, the wet gel was washed with deionized water and soaked in anhydrous ethanol overnight to allow ethanol filling into the pores. The wet gel was vacuum dried for 9 h followed by calcination at 600°C for 8 h. Before the test, the Ni/Al₂O₃ aerogel catalyst was reduced at 450°C for 2.5 h. Co/Al₂O₃ aerogel catalysts were calcined at 500°C for 3 h and reduced at 600°C for 2.5 h. The details on the composition for the preparation of Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts are summarized in Table 5-1. Figure 5-1 (1) and (2) illustrate the major steps involved in the synthesis of aerogel catalysts. AlCl₃·6H₂O was chosen as a precursor for alumina oxide whereas ethanol and deionized water were used as solvents. PO was used as a gelation chemical that consumed protons from the hydrated metal species to facilitate sol-gel polymerization reaction [85, 86, 87].

Table 5-1. Details on Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts compositions

	Ni/Al ₂ O ₃ aerogel catalyst (2 g)			Co/Al ₂ O ₃ aerogel catalyst (2 g)		
	50 wt%	60 wt%	70 wt%	50 wt%	60 wt%	70 wt%
AlCl ₃ ·6H ₂ O /g	4.74	3.8	2.85	4.74	3.8	2.85
Ni(NO ₃) ₂ ·6H ₂ O/g	4.95	5.95	6.94	----	----	----
Co(NO ₃) ₂ ·6H ₂ O/g	----	----	----	4.93	5.92	6.91
EtOH /mL	15.5	15.5	15.5	15.5	15.5	15.5
PO /mL	16	16	16	16	16	16
H ₂ O /mL	10	10	10	10	10	10

Figure 5-1. The formation mechanism of (1) Ni/Al₂O₃ and (2) Co/Al₂O₃ aerogel catalysts

5.2 Methane Conversion over Aerogel Catalysts

As shown in Figure 5-2(a), in the initial 20 min, the 60 wt% Ni/Al₂O₃ aerogel catalyst exhibits the highest CH₄ conversion of 79.2%, but as the reaction proceeds, its conversion declines faster than 50 wt% and 70 wt% Ni/Al₂O₃ aerogel catalysts. It appeared that three Ni/Al₂O₃ aerogel catalysts had induction periods during the early stage of the reaction. After the induction period, the 50% Ni/Al₂O₃ catalyst exhibited the highest methane conversion. In Table 2, the amount of carbon formed per gram of aerogel catalyst was calculated, which was found to be approximately 0.63-0.83 g over 50 wt% Ni/Al₂O₃ aerogel catalyst, 3.31-3.39 g for 60 wt% Ni/Al₂O₃ aerogel catalyst and 0.53-0.65g for 70 wt% Ni/Al₂O₃ aerogel catalyst, respectively. Figure 5-2(b) shows hydrogen yields for Ni/Al₂O₃ catalysts.

Methane decomposition over three different metal loading Co/Al₂O₃ aerogel catalysts was carried out. As shown in Figure 5-2 (c), different from Ni/Al₂O₃ aerogel catalysts, the induction period is not observed over Co/Al₂O₃ aerogel catalysts. The methane conversion of Co/Al₂O₃ catalysts drops significantly to ca. 10% after 20 min which is explained by the enhanced pore size distribution and tortuosity of Ni/Al₂O₃ aerogel in the following sections. As shown in Figure 5-2 (d), for Co/Al₂O₃ catalyst, the H₂ yield is higher when the metal loading was 60 wt%.

Table 5-2. Carbon Productivity (gram carbon/gram catalyst per hour)

Catalyst	Metal Loading		
	50 wt%	60 wt%	70 wt%
Ni/Al ₂ O ₃	0.63-0.83	3.31-3.39	0.53-0.65
Co/Al ₂ O ₃	0.45-0.68	2.05-2.51	0.58-0.86

Figure 5-2. Methane decomposition over aerogel catalysts (a) Methane conversion over Ni/Al₂O₃ (b) H₂ yield over Ni/Al₂O₃ (c) Methane conversion over Co/Al₂O₃ (d) H₂ yield over Co/Al₂O₃

5.3 Characterization of Ni/Al₂O₃ and Co/Al₂O₃ Aerogel Catalysts

The properties of fresh and spent Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts were characterized using a number of analytical instrumentations including XRD, TGA, Raman, BET, SEM, and TEM measurements. The XRD patterns of fresh and spent Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts are presented in Figure 5-3 (a) and (b). The characteristic peaks associated with Ni, Co and Al₂O₃ support are shown in XRD spectra. Some peaks related to Al₂O₃ support are not visible in the XRD spectra because of the presence of high intensity metal peaks. The sharp peaks for metals indicate the formation of the crystalline phase of the active element (Ni and Co). The Ni oxide characteristic peaks are identified at $2\theta = 37.3^\circ$, 46.7° , 52.8° , 66.6° , and 76.6° (JCPDS No. 04-850) whereas Co characteristic peaks are observed at $2\theta = 44.8^\circ$, 48.2° , and 77.6° (JCPDS No. 15-0806). After the reaction, spent catalysts were once again characterized by XRD analysis. As shown in Figure 5-3 (a) and (b), compared to the fresh catalysts, XRD patterns of the spent Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts show the presence of graphitic carbon by a very intense peak (002) at $2\theta = 26.2^\circ$. Due to the limitation of XRD analysis, the microstructural features between CNT and similar graphitic structures are difficult to differentiate because their characteristic peaks are overlapping. The intensity of the (002) diffraction peak is related to the degree of graphitization. Lower intensity indicates the presence of the less graphitized material. The overall intensity of the CNT peaks over Co/Al₂O₃ catalysts appears to be much less compared to Ni/Al₂O₃ aerogel catalysts.

Figure 5-3. XRD analysis of fresh and spent catalysts (a) Ni/Al₂O₃ and (b) Co/Al₂O₃

Raman spectroscopic measurement was carried out to further investigate the quality and crystallinity of the carbon products. As presented in Figure 5-4 (a) and (b), two distinct bands are observed, the D-band at 1342 cm⁻¹ represents either defect or amorphous carbon whereas G-band at 1575 cm⁻¹ represents the crystalline carbon. The graphitization degree and the crystallinity of the CNTs can be simply measured through the intensity ratio of I_D/I_G . The aerogel catalyst with the lowest I_D/I_G carbon represents the highest crystallinity. The I_D/I_G ratio for 60 wt% Ni/Al₂O₃ aerogel catalyst is slightly higher than 50 wt% and 70 wt% Ni/Al₂O₃ aerogel catalysts. The I_D/I_G values for 70 wt% Co/Al₂O₃ and 60 wt% Co/Al₂O₃ aerogel catalysts are similar. Raman spectra showed that both 70 wt% Ni/Al₂O₃ and 70 wt% Co/Al₂O₃ aerogel catalysts form most crystalline CNTs with the lowest I_D/I_G (0.835 and 0.725). Although the 60% Ni/Al₂O₃ aerogel showed higher productivity than any of Co/Al₂O₃, the I_D/I_G was not lower implying the formation of defect CNTs (D band in Raman). We speculate that the length of CNTs on Ni/Al₂O₃ aerogel is much longer than those on Co/Al₂O₃ aerogel. Therefore, poor electron transfer that might affect crystallization causing the defect of CNTs. This result is

consistent with the TEM analysis which will be discussed in later section [95].

The spent Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts were characterized by TGA to study the thermal stability of CNTs. The TGA measurements were carried out in an atmosphere of 2% O₂/He. As shown in Figure 5-4 (c), there is no thermal degradation taking place in the temperature range of 150-350°C for Co/Al₂O₃ and Ni/Al₂O₃ aerogel catalysts. These ranges are corresponding to amorphous carbon decomposition. As shown in Figure 5-4 (c), for the 50 wt% Ni/Al₂O₃ aerogel catalyst, the thermal degradation starts at around 500°C with a weight loss of 84%. For the 60 wt% Ni/Al₂O₃ aerogel catalyst, the degradation starts at 500°C with a weight loss of 87%. Similar to the 60 wt% Ni/Al₂O₃ aerogel catalyst, the 70 wt% Ni/Al₂O₃ aerogel catalyst shows a weight loss of 78%. Thermal degradation temperature for Co/Al₂O₃ is much lower than over Ni/Al₂O₃. In addition, the amount of carbon formed over Co/Al₂O₃ aerogel catalysts was found much less than that on Ni/Al₂O₃ aerogel catalysts, which was consistent with the results of catalytic activity tests.

Figure 5-4. (a) Raman spectra of spent Ni/Al₂O₃ catalyst and (b) Raman spectra of spent Co/Al₂O₃ catalyst; (c) TGA analysis of spent Ni/Al₂O₃ and Co/Al₂O₃ catalyst

SEM and BET measurements were carried out to investigate the microstructure, pore size distribution and adsorption-desorption properties of the spent Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts. The measurements were limited to the 60 wt% Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts which showed the best performance in the reactions. As shown in Figure 5-5 (a), the isotherms of the 60 wt% Ni/Al₂O₃ and 60 wt% Co/Al₂O₃ aerogel catalysts are quite similar, and the BET surface area of these aerogel catalysts are measured to be 324, 271 m²/g, respectively. As shown in Figure 5-5 (b), the Barrett-Joyner-Halenda (BJH) pore sizes for 60 wt% Ni/Al₂O₃ aerogel catalyst is in the region of 10-25 nm whereas for the 60 wt% Co/Al₂O₃ aerogel catalyst, the pore size is mainly distributed at ca. 5-15 nm. The annealing can reduce the surface area, but the aerogel catalysts still exhibited a high surface area after heat treatment at 650°C and a broad pore size distribution at the mesoporous range. Nanocomposite Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts have high surface area and good adsorption properties, which helps to improve the catalytic activity and oxidative regeneration. High specific surface area facilitates the reactants adsorption step and provides more active species which are responsible for enhancing the catalytic performance. SEM images show that channels with the gap distance from a few tens to a few hundred nanometers are formed among colloidal particles. Cross-linking CNT's are formed among CNT's and catalyst particles. As presented in Figure 5-5 (c) and (d), SEM images show that the CNT's are interlaced and combined with support particles to form a reticular structure. CNT's are growing in random direction due to space competition and the length of CNT's depends on the reaction time. As shown in Figure 5-6, for 60 wt% and 70 wt% Ni/Al₂O₃ aerogel catalysts, the CNT's formed are found to be multiwall carbon nanotubes and the CNT's formed over Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts have a large portion of base-growth and crowded dense population with entangled fibers. Figure 5-6 (a-f) shows that the length of most of the CNT's formed is in the range of 50-250 nm. From the TEM analysis shown in Figure 5-6, it is observed that the walls of CNT's formed are of a linear

or curved structure in which the graphene layers are stacked obliquely. In this type of CNT's, the graphite planes are not aligned with the axis of CNT. When graphene layers stack up, the defects may form between the edge planes. This has explained the observation of D band in Raman spectra, but no amorphous phase was identified in TGA analysis. For 60 wt% and 70 wt% Co/Al₂O₃ aerogel catalysts, as displayed in Figure 5-7 (a-f), MWCNT's with 50-150 nm diameters are formed together with transition metal nanoparticles located at the bottom. Compared to CNT's formed over Ni/Al₂O₃ aerogel catalysts, the CNT's formed on Co/Al₂O₃ aerogel catalysts are relatively thin and smaller in diameter.

Figure 5-5. Characterization of the spent 60 wt% Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts
BET analysis of (a) N₂ adsorption-desorption isotherms (b) pore sizes distribution (c and d)
SEM images of 60 wt% Ni/Al₂O₃ aerogel catalyst

Figure 5-6. TEM images of the spent Ni/Al₂O₃ catalysts (a-c) 60 wt% and (d-f) 70 wt%

Figure 5-7. TEM images of he spent (a-c) 60 wt% and (d-f) 70 wt% Co/Al₂O₃ catalysts

5.4 Growth CNT over Ni/Al₂O₃ and Co/Al₂O₃ Aerogel Catalysts

The aim of this study was to elucidate the growth mechanisms in order to control the catalytic property that favors the formation of base-growth CNTs. TEM images have shown that CNTs formed over Ni/Al₂O₃ or Co/Al₂O₃ aerogel catalysts are base growth. This is attributed to the strong interaction between metal nanoparticles and aerogel support. During the decomposition reaction, in the initial stage, carbon diffusion occurred on Ni or Co that were

strongly anchored in the aerogel structure, therefore it is difficult for carbon to penetrate between the support and metal. It is also known from the literature that the graphene planes formed are strongly chemisorbed on a metal surface, reducing the surface energy of the metal nanoparticles and enhancing metal-support interaction. Furthermore, TEM measurement showed that graphitic caps were formed on the metal nanoparticles which were lifted upwards during the subsequent deposition of carbon fragments. TEM images reveal that CNTs grow away from the metal nanoparticles, forming a base-growth of carbon nanotubes [76].

5.5 Conclusions

The activity, selectivity, stability of the Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts were demonstrated in methane decomposition reaction. Characterization results indicated that metal oxide aerogel was a porous material with abundant pores and high specific surface area. In addition, during the synthesis of the aerogel catalysts, Ni and Co were incorporated into the structure of Al₂O₃ aerogel. As a result, the Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts developed in this study contained an increased number of active sites exhibiting strong metal-support interaction which led to the formation of base-growth CNTs. The Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts showed enhanced performance in terms of methane conversion. SEM images confirmed the formation of the small nanoparticles in the Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts. Among Co/Al₂O₃ aerogel catalysts the catalytic activity towards methane conversion was comparatively lower than the Ni/Al₂O₃ aerogel catalysts. The XRD analysis indicated that metal contents in the Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts control the degrees of graphitization of the carbon formed. TGA analysis elucidated unlikely formation of amorphous carbon over Ni or Co aerogel catalysts. It was discovered that both Ni/Al₂O₃ and Co/Al₂O₃ aerogel catalysts selectively produced base growth CNTs which are considered to be easy for harvesting without sacrificing the catalyst sites.

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