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Hydrogen Production via Thermo-catalytic Methane Decomposition

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CERTIFICATION OF APPROVAL

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By

Irene Lock Sow Mei

A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(IRENE LOCK SOW MEI)

ABSTRACT

Hydrogen production from the direct thermo-catalytic decomposition of methane is a promising alternative for clean fuel production because it produces pure hydrogen without any CO_x emissions. However, thermal decomposition of methane can hardly be of any practical and empirical interest in the industry unless highly efficient and effective catalyst, in terms of both catalytic activity and operational lifetime have been developed. In this work, the effect of introducing palladium as promoter onto nickel supported on alumina catalysts have been investigated by both co-precipitation and incipient wetness impregnation method. The calcined catalysts were characterized to determine their morphologies and physico-chemical properties by the application of Scanning Electron Microscopy (SEM) imaging, Energy Dispersive X-ray Spectroscopy (EDX) analysis, Brunauer-Emmett-Teller method, Temperature Programmed Reduction (TPR) and Thermogravimetric Analysis (TGA). In addition, experimental work is conducted at 873 K, 973 K and 1073 K to evaluate the performance of the catalysts for methane cracking process. The morphology studies suggested that the catalysts which were prepared by co-precipitation method exhibit homogenous morphology, higher surface area, have uniform nickel and palladium dispersion while the catalysts which were wet impregnated has higher thermal stability. This characteristics are significant to avoid deactivation of catalyst due to sintering and carbon deposition during methane cracking process. The experimental studies suggested that introducing palladium as promoter onto Ni/Al_2O_3 catalyst has a significant effect on the catalytic activity, operational lifetime and thermal stability of the catalysts. The $Ni\text{-}Pd/Al_2O_3$ catalyst which was synthesized by wet impregnation method gave the highest initial methane conversion which can be explained in term of the morphology of the catalyst in which accumulation of Ni and Pd particles on the active site of the catalyst promotes higher initial catalytic activity. However, this catalyst deactivated at a faster rate due to carbon deposition on the active sites of catalysts. On the other hand, the homogeneous morphology and higher surface area of the $Ni\text{-}Pd/Al_2O_3$ catalyst which was prepared by co-precipitation method enables longer operational lifetime and higher thermal stability to be achieved.

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LIST OF ABBREVATIONS

GHG	Greenhouse gas
SMR	Steam methane reforming
TCD	Thermal-catalytic decomposition
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared Spectroscopy
EDX	Energy Dispersive X-ray Spectroscopy
TPR	Temperature Programmed Reduction
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
CNT	Carbon nanotubes
FYP	Final Year Project

CHAPTER 1 INTRODUCTION

This chapter discusses about the background of study for the final year project. Besides that, this chapter also defines the problem statement, the objective and the scope of the research work.

1.1 Background of Study

The continuous growth of the global population has called upon the need to have sustainable energy supply while limiting the emissions of greenhouse-gas (GHG). This is because the rapid increase in the concentrations of greenhouse-gas, particularly carbon dioxide and methane has led to gradual increase in the atmospheric temperature and contribute towards global warming. The main contributors towards GHG emissions are due to the combustion of fuels to produce energy and electricity. Therefore, current research has been diverted to develop a green process to produce hydrogen from methane with minimum byproduct.

Nowadays, hydrogen appears to be one of the most promising and feasible alternative energy sources and clean fuel. This is because the combustion of hydrogen only produces water and does not contribute to any GHGs to the atmosphere. Moreover, the amount of energy which is produced during the combustion of hydrogen is higher as compared to the other type of fuels on a mass basis with a lower heating value. Hence, pure hydrogen production from fossil fuels, particularly natural gas (methane) has come into significant importance, given the massive resource of fossil fuels and the well-established industry base.

The current technologies of hydrogen production from fossil fuels are based on the steam methane reforming (SMR), biomass gasification, water electrolysis, coal gasification and thermo-chemical processes. Out of all these hydrogen producing methods, SMR has been the most commonly applied method in the industry due to the high efficiency of this process to produce hydrogen and its low cost. However, the drawback of the SMR method is that it causes high emission of carbon dioxide gas and the hydrogen produced has low purity due to the presence of large quantities of CO.

Hence, a catalytic method has been considered to improve the production of hydrogen from Methane. One of the most promising technologies is the thermal catalytic decomposition of methane (TCD) or methane cracking, in which methane will be thermally decomposed to solid carbon and hydrogen in this method. The TCD method is promising because it produces pure hydrogen without any CO_x emissions and it eliminates the need of water gas shift reaction and CO_2 sequestration step required by the conventional production process, which lead to additional economic saving.

Although methane decomposition reaction is an attractive alternative for producing clean energy fuel, it is a moderately endothermic reaction. In other words, non-catalytic decomposition of methane can only happen at extremely high temperature (~ 1300℃) to obtain reasonable yield of hydrogen due to the strong C-H bonding within methane. However, the use of catalyst in thermo catalytic decomposition (TCD) of methane can significantly decrease the operation temperatures of the methane cracking process and can increase the rate of methane decomposition to hydrogen. This justifies the need for the development of a novel catalyst which can enhance methane conversion to hydrogen and have long-term catalyst stability.

1.2 Problem Statement

Transition metals of group VIII (Fe, Co, Ni) based catalysts have been proven to be the most active metal for methane decomposition reaction to produce hydrogen. Ni based catalysts exhibit higher catalytic activity and durability at moderate temperatures for methane decomposition. The nickel-based catalyst enables the thermal-catalytic methane decomposition process to take place with promising yield of hydrogen at the temperature of 1073 K. However, at temperature below 1073 K, the methane conversion remains low below 40%. In addition, another challenge in developing nickel based catalyst for methane cracking process is that the catalyst tends to de-active within 2 hours on-stream due to sintering and carbon deposition during operation. Therefore, the objective of novel catalyst development for methane cracking process is to achieve high metal dispersion through high surface area and have long term thermal stability to attain high catalytic activity and long-term operational lifetime.

1.3 Objective

The main objective of the final year project is to develop and to synthesize Palladium promoted Nickel supported on alumina catalyst to increase the yield of hydrogen at temperature below 1073K to > 40 % and to improve the deactivation rate of the catalyst for methane decomposition process. To achieve this main objective, the following sub-objectives have to be achieved.

The sub-objective of the final year project is stated as follows:

1) To synthesize monometallic (Ni and Pd) and bimetallic(Ni-Pd) on alumina support (Al_2O_3) catalysts for thermo catalytic decomposition of methane for hydrogen production by using co-precipitation and wet impregnation method
2) To characterize the synthesized catalysts by using Brunauer-Emmett-Teller (BET) method, Energy Dispersive X-ray Spectroscopy (EDX), Temperature Programmed Reduction (TPR), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA)
3) To investigate the performance of the synthesized catalysts at 1073 K, 973 K and 873 K for hydrogen production through experimental studies

1.4 Scope of Study

The final year project focuses on the study regarding the relative catalytic activities of metals with alumina support in thermal cracking of methane. In this research work, it is aimed to develop three types of catalyst, which are the monometallic (Nickel and Palladium) and bimetallic (Nickel-Palladium) on alumina (Al_2O_3) support catalysts that will be used for the TCD of methane to produce hydrogen. These catalysts will be synthesized by using two methods, which are the co-precipitation method and wet impregnation method to compare the methodology that will produce the catalysts with higher Ni and Pd dispersion. In addition, the physico-chemical characteristics and morphologies of the catalysts will be investigated by using Brunauer-Emmett-Teller (BET) method, Energy Dispersive X-ray Spectroscopy (EDX), Temperature Programmed Reduction (TPR), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA)

The performance of the synthesized catalysts will be investigated by conducting a laboratory scale experiment in a fixed bed gas flow reactor for hydrogen production. The main aspects which will be study through the experimental work are the methane conversion, the purity and yield of the hydrogen gas produced, the temperature in which the reaction can be further reduced and the deactivation time of the catalysts. The catalytic activity of the catalysts will be evaluated to select the catalyst which will be the most effective and efficient for the production of hydrogen and the catalyst's mechanism can be further studied to develop a novel catalyst which can enhance methane conversion and have long term catalyst stability.

1.5 Relevancy of Project

Hydrogen appears to be one of the most promising and feasible energy sources for energy generation in the future because the combustion of hydrogen does not contribute towards any greenhouse gases emission to the atmosphere. Thermal-catalytic methane decomposition of methane to hydrogen is a promising and attractive method for hydrogen production because it does not contribute towards any greenhouse gases emission to the atmosphere. However, the methane cracking process can be hardly of any practical application in the real industry without the presence of catalyst because it can only produce reasonable hydrogen yield at temperature above 1573K.

Nickel-based catalyst has been proven to be an effective catalyst to reduce the temperature of the methane decomposition process to 1073K with reasonable hydrogen yield. However, the reaction temperature should be further reduced to ensure that the thermal-catalytic methane decomposition to hydrogen process can be widely applied in the industry for mass production of hydrogen. In addition, the catalyst de-active within 2 hours on-stream due to sintering and carbon deposition during the operation.

Therefore, this research project is significant for the development of a bimetallic catalyst which is capable of reducing the activation energy of the methane cracking process and to reduce the temperature in which the reaction can take place. In addition, this project also focus on the study of the preparation method which can produce a well-dispersed alumina supported Ni-Pd catalyst to improve the deactivation rate of the catalyst. Other than that, this research project is relevant for the development of a catalyst which can provide high methane conversion, high hydrogen yield, and high purity of hydrogen and long deactivation time of catalyst. Besides that, this research project is important because it focuses on the study of the morphologies and catalytic activity of the catalysts. The information is important to enable the development of a novel catalyst which can enhance the methane cracking process.

1.6 Feasibility of Project

The final year project requires in-depth understanding in Chemical Engineering to perform detailed and comprehensive analysis on the final results. The project is feasible to be conducted by the author because the project revolves around three chemical engineering study fields, namely reaction kinetics and mechanisms, thermodynamics and quantum mechanics study. Although the project is a new scope of study in UTP, it is possible for the author to master the project because extensive researches have been conducted by the other researchers, thereby providing credible sources for validation of theories and experimental results. There are extensive documents, thesis paper, journals and books which can help the author in understanding and learning about the thermal-catalytic methane decomposition to hydrogen process.

Since the project is a new scope of research work in UTP, the first two months has to be spent in collecting and purchasing the required chemical materials, designing and setting up of the reactors for the experimental work and the setting up for the gas analysis system to analyze the hydrogen gas yield. After that, the experimental work can be conducted to synthesize the catalysts, to characterize the catalysts and to evaluate the performance of the synthesize catalysts. At the same time, the study of the catalysis mechanism of the methane decomposition process can be performed by investigating the reaction mechanism, reaction barriers, transition state and activation energy for the process. The project is feasible to be completed within the 8 months period and is appropriate to be selected as the topic for the final year project.

CHAPTER 2 LITERATURE REVIEW

This chapter reviews and compares the different methods for hydrogen production and clarifies the role of catalysts in methane decomposition to hydrogen. Besides that, this chapter also summarizes the type of heating sources, reactors, types of catalysts and analysis techniques that have been applied in the previous research work for the study of TCD of methane.

2.1 Global demand for hydrogen

Hydrogen is one of the most promising and sustainable clean energy sources because the combustion of hydrogen for energy production only produces water and does not contribute towards any greenhouse gases emission to the atmosphere. The combustion reaction for hydrogen to generate energy can be represented by Equation 1.

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)} \tag{1}$$

Besides that, hydrogen has the highest energy density as compared to other types of conventional fossil fuels such as methane, gasoline and coal. This is because the amount of energy produced during hydrogen combustion is higher than the other fuel on a mass basis with a lower heating value (Abbas and Wan Daud, 2010).

According to Navigant Research (2013), the global demand for hydrogen is at 250 million kg in 2013 and they forecasted that the global hydrogen demand will continue to increase in the future as indicated in Figure 1.

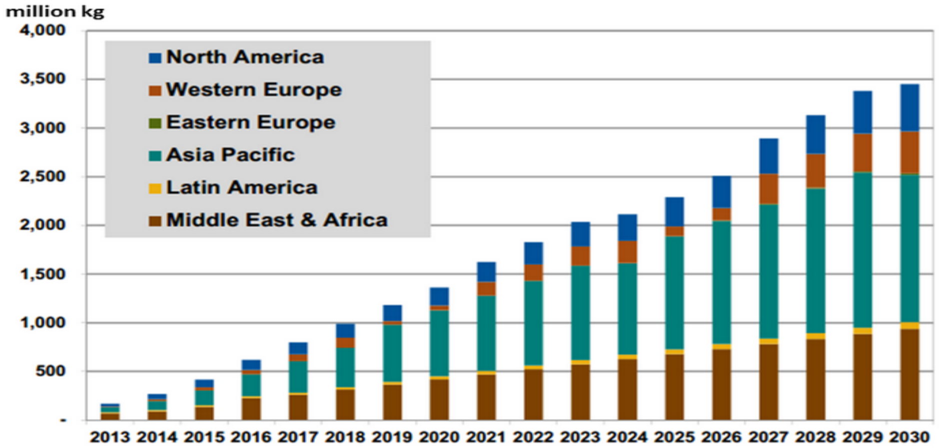


Figure 1 Forecast of hydrogen demand

(Data from Navigant Research, 2013)

Hydrogen is mainly used as a potential source for the development of photon exchange membrane (PEM) fuel cells, fuel source in oil refineries, and raw materials for ammonia and methanol production. The most promising application of hydrogen is for the development of fuel cell, which is a device transforming chemical energy into electricity and heat energy to power automobiles (Valdes-Solis & Marban, 2007).

2.2 Hydrogen production technologies

Extensive research has been conducted for the development of safe, cost effective and efficient hydrogen production method to meet the large global demand for hydrogen. The production of hydrogen from fossil fuels, particularly from natural gas such as methane has become increasingly important, given the large available resource and the established industrial base. The current methods of producing hydrogen are based on steam reforming (SMR), biomass gasification, water electrolysis and coal gasification and thermo-chemical processes. The comparison between the hydrogen production technologies is summarized and listed in Table 1.

Table 1 Comparison between hydrogen production technologies

(Data from Abbas and Wan Daud, 2010)

Production Technology	Energy efficiency (%)	Hydrogen selling price ($/kg)	Limitations
Steam methane reforming (SMR)	83	0.75	Production of CO_2 and CO
Partial oxidation of methane	70-80	0.98	Production of CO_2 and CO
Auto-thermal reforming	71-74	1.93	Production of CO_2 and CO
Coal gasification	63	0.92	Production of CO_2 and CO
Direct biomass gasification	40-50	1.21-2.42	Production of CO_2 and CO
Water electrolysis	45-55	1.95	Energy consuming process
Photo-catalytic water splitting	10-14	4.98	Low efficiency and expensive method

Among the hydrogen production technologies, steam methane reforming (SMR) is the most frequently route used to produce hydrogen because the process has high efficiency, low heating value and low operating cost. In this process, methane stream or other natural gases will be reacted with steam under the catalyst to produce hydrogen and carbon dioxide as indicated in Equation 2 and 3.

$$CH_{4(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3H_{2(g)} \tag{2}$$

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)} \tag{3}$$

However, the drawback of using the SMR technology is that it is not environmental-friendly due to the generation of high quantities of greenhouse gases (GHG), which is estimated to be 13.7 kg CO_2/ kg of hydrogen produced (Wu *et al.*, 2013). Moreover, separation of CO from the hydrogen product is important because the Pt-based electro catalyst used in a PEM fuel cell is highly sensitive to CO. More specifically, the CO concentration in hydrogen streams which is used as fuel source for PEM fuel cells has to be lower than 20ppm to prevent deactivation of the electro catalyst, hence requiring a complicated CO separation process to obtain the required purity (Muradov, 2001).

The recent discovery that methane can be directly decomposed into carbon and hydrogen according to the following reaction has drawn the attention for hydrogen production through methane thermo-catalytic decomposition (TCD) process, alternatively known as the catalytic cracking of methane. According to Wang and Lua (2013), this process is feasible because it does not produce CO or CO_2 as by-products and do not require water-gas shift and additional separation stages to remove CO_2 as compared to the traditional hydrogen production method. In addition, the production cost for hydrogen by methane TCD can be significantly reduced by marketing the solid carbon for construction material. The hydrogen gas produced through TCD of methane can also be channeled directly to the PEM fuel cell without fear of poisoning the platinum electro-catalyst inside the cell due to the presence of CO gas.

Conversely, the other methods to produce hydrogen such as SMR and partial oxidation of methane produce an outlet stream consisting of H_2, CO_2 and CO gases, which requires additional water-gas shift reaction step following by methanation to separate CO_2 and CO from the pure H_2. The additional separation and purification steps will add to the complexity of the process and lead to higher operational costs.

2.3 Thermal decomposition of methane to hydrogen

In this process, methane will be thermally decomposed into carbon and hydrogen as represented by Equation 4 without contributing towards any CO_2 emission to the atmosphere. The thermal decomposition of methane to hydrogen is a moderately endothermic process and it is reported that 75.6 kJ of heat is required for the decomposition of 1 mole of methane ($\Delta H^o = 75.6\ kJ/mol$).

$$CH_{4(g)} \rightarrow C_{(s)} + 2H_{2(g)} \tag{4}$$

Lane and Spath (2011) estimated that hydrogen can be produced by the thermo-catalytic decomposition (TCD) of methane at a selling price of (7-21) \$/GJ (Note: 1

GJ= 1.05461 MMBtu), depending on the cost of natural gas and the manufacturing price of carbon. Besides that, Steinberg (2000) made a comparison between the SMR and methane TCD processes for the de-carbonization of natural gases and showed that the TCD of methane appears to have several advantages as compared to the well-developed and established SMR process, with the major advantage that it is easier to sequester carbon in the stable solid form produced by methane TCD rather than as the CO_2 or CO produced as reactive gas during the SMR process.

Moreover, Dufou *et al.* (2010) made a comparison between different technologies for hydrogen production (SMR, SMR with CO_2 capture and storage, methane autocatalytic decomposition and methane thermal decomposition) by applying life-cycle assessment tools to evaluate their relative environmental feasibilities and CO_2 emissions. They commented that thermo-catalytic decomposition of methane is the most environmentally-friendly method for production of hydrogen because it has the lowest total environmental impact and CO_2 emission. They also stated that although the CO_2 emission can be significantly reduced in the SMR process by adding in CO_2 capture and storage unit, it still possesses a high total environmental impact.

2.4 Role of catalysts in methane decomposition

Due to the strong C-H bonds, methane decomposition is a moderately endothermic reaction and under the absence of catalysts, thermal decomposition of methane can only happen at temperature higher than 1200℃ to yield high conversion of methane and reasonable hydrogen production. The presence of catalysts provides an alternative reaction mechanism with a different transition state and lower activation energy. Hence, higher number of molecular collisions can achieved the energy required to reach the transition state and enable the reaction to take place at lower temperature as indicated in Figure 2.

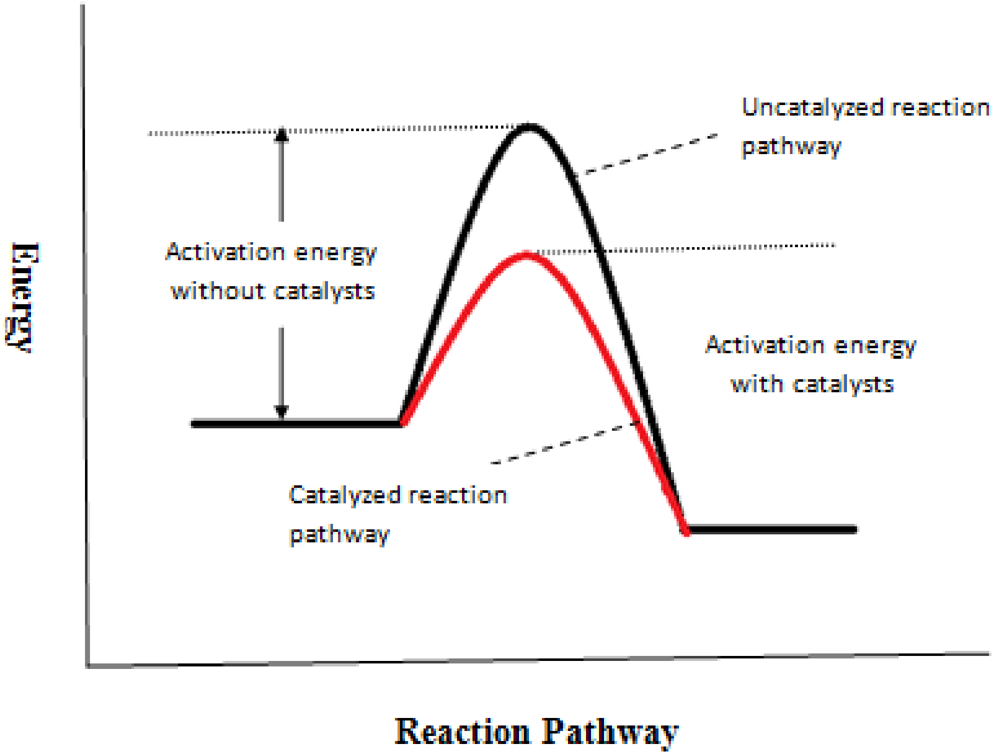


Figure 2 Potential energy diagram showing the effect of a catalyst in chemical reaction by lowering the activation energy

Extensive researches have been performed continuously to determine the optimum condition in which the TCD process can take place to increase the conversion of methane into hydrogen, to improve the yield of hydrogen product and to decrease the temperature in which the decomposition of methane can take place. In addition, researchers has conducted continuous research work to determine the type of heating sources and the type of reactors which can improve the methane cracking process.

In general, many research works are using electrical furnace as a heating source for the TCD reactor but recent researchers have shifted their attention to the application of concentrated solar energy as a potential energy source for the production of hydrogen in mass volumes. Maag *et al.* (2010) commented in their research work that concentrated solar energy is a clean source of high temperature process heat and direct solar irradiation of the reactants provides efficient heat transfer.

As for the reactor types, researchers have studied different types of reactors such as packed bed reactor (PBR), fluidized bed reactor (FBR), free-volume reactor, aerosol bed reactor and tubular reactors and majority of them concluded that the FBR was the most effective reactor for large-scale operation of TCD of methane because it provides constant flow of solids through the reaction zone, making it appropriate for continuous addition and removal of catalyst from the reactor (Ammendola *et al.*, 2010) . The type of heating sources, reactors, and analysis technique which has been applied for methane TCD studies is summarized in Figure 3.

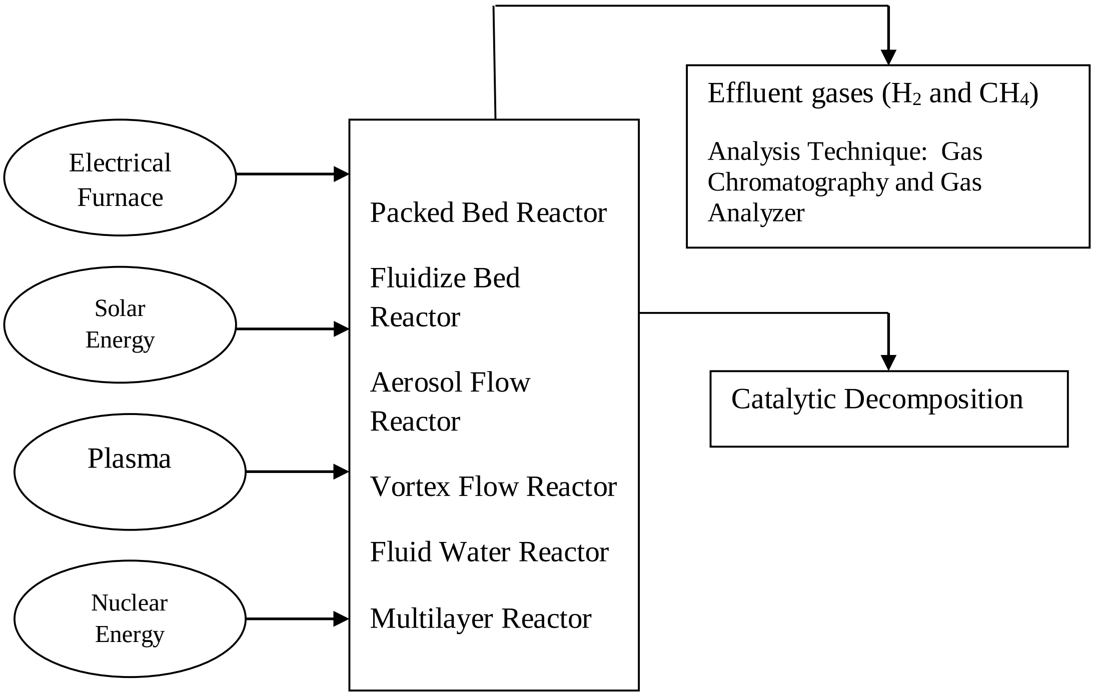
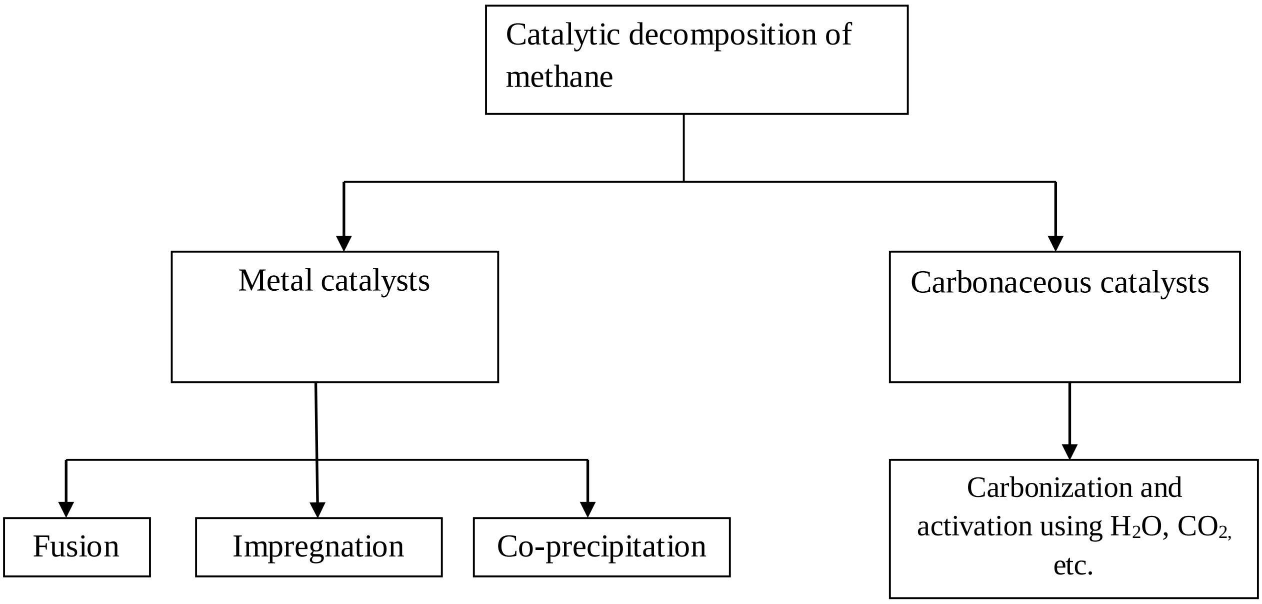


Figure 3 Type of heating sources, reactor type and analysis technique for methane TCD,

(Data from Ammendola et al. (2010), Longmeir et al. (2012) and Maag *et al*. (2010)

2.5 Catalyst development for TCD of methane

Methane TCD can hardly be of practical interest in the real industry for hydrogen production unless highly efficient and effective catalysts have been developed. The catalyst plays an important role in triggering methane thermal decomposition and determining its performance. Catalysts efficiency does not only include the specific activity, but also the useful operational life-span of the catalysts due to accumulation of carbon on the surface of the catalysts. As a whole, two different types of catalyst have been developed, which can be categorized into metal and carbonaceous catalysts. Based on literature, the catalytic decomposition of methane can be summarized in Figure 4



Fresh and deactivated catalysts characterization techniques

Surface Area Analyzer

Particles Size Analyzer

Scanning Electron Microscopy (SEM)

Transmission Electron Microscopy (TEM)

X-Ray Diffraction (XRD)

Raman Spectroscopy

Figure 4 Catalyst and catalysts characterization techniques in methane TCD studies

(Data from Ahmed (2013), Jin *et al.* (2013), Konno *et al.* (2013), Lee *et al.* (2013) and Zhou *et al.* (2014)

2.6 Metal catalysts for thermo-catalytic decomposition of methane

Table 2 lists the recent studies using different types of metal catalysts, their preparation methods and physical properties and the major findings from the previous research work which is important to enable the selection of the metal catalysts which will be synthesized in this final year project for thermo-catalytic methane decomposition to hydrogen.

Table 2 Recent studies on metal catalysts for methane TCD, preparation methods and major findings

Types of catalyst and Catalyst composition	Catalyst preparation technique	Major findings	References
Unsupported nickel catalyst	Fusion method	1. Methane pre-reduction would produce coke to act like a support for the Ni catalyst. The TCD of methane has the highest methane conversion at 1073K. 2. Higher concentration of methane resulted in better methane conversion, but at a higher deactivation rate.	Zhou *et al*. (2014)
Ni/ Ce-MCM-41 (noted as cerium promoted mesoporous materials) catalysts	Wet incipient impregnation	The methane conversion reached 60-75% with 100% selectivity towards hydrogen at temperature 540℃. In addition, no catalyst deactivation is observed for the 1400 min of reaction.	Guevara *et al.* (2010)
Comparison of the performance for AC, Fe/AC and γ-Al_2O_3 catalysts	Fe/AC catalyst was prepared by wet impregnation method	AC catalyst gives the highest yield of hydrogen and highest methane conversion (41.7%) as compared to Fe/AC and γ-Al_2O_3 catalyst at 900℃.	Ahmed (2013)
Activated carbon supported Fe-Al_2O_3 catalyst	Wet impregnation method	When the ratio of Fe/ Al_2O_3 is 16/24 to 24/16 at the total solid loading of 40%, the prepared catalyst has narrow mesopore distributions and relative high methane conversion (~ 40%).	Jin *et al*. (2013)
Ni/SiO_2, Cu-Ni/SiO_2, Rh-Ni/SiO_2, Pd-Ni/SiO_2, Ir-Ni/SiO_2, Pt-Ni/SiO_2	Wet impregnation method	Addition of Pd into supported Ni catalysts improved significantly the catalytic life and hydrogen yield. The highest yield of hydrogen and carbon, 390 g H_2/ g (Pd+Ni) and 1170 gC/g (Pd+Ni) with 50 mole% of Pd and total metal loading of 37% on carbon nanofiber support.	Takenaka *et al.* (2003)

Table 2 (*Continued.*)

Types of catalyst and Catalyst composition	Catalyst preparation technique	Major findings	References
Ni catalysts supported on silica (Solid loading 30 to 70%)	Wet impregnation method and co-precipitation method	1. The catalytic activity and the yields of hydrogen and carbon nanofiber strongly depend on the loading amount of Ni. 2. 50% Ni/SiO_2 catalyst prepared by wet impregnation method shows higher methane conversion and hydrogen yield as compared to the other catalysts.	Saraswat and Pant (2012)
Ni-Cu/AC catalysts	Dry impregnation method	1. The addition of copper on Ni/AC catalysts did not have significant effect on methane conversion, but it improved the stability of the Ni/AC catalysts at high temperature. 2. The Ni/AC catalysts without copper loading rapidly deactivated due to the formation of condensed encapsulating carbon on the catalysts.	Adrian *et al*. (2012)
Tri-metallic Ni-Fe-Al catalyst	Co-precipitation technique	1. The catalyst with Ni/Fe/Al mole ratio of 2:1:1 shows extremely high stability and is still active after 210 h of reaction. 2. N-Fe alloy is formed in the Ni-Fe-Al catalyst and becomes an active phase for carbon nanofiber (CNFs) growth. 3. The addition of appropriate amount of Fe can enhance carbon diffusion rate and decrease carbon formation rate, leading to higher stability of catalyst.	Wang *et al*. (2013)
Bimetallic Ni-Fe, Ni-Co and Fe-Co supported on MgO catalysts	Wet impregnation method	1. A higher yield of hydrogen and carbon nanotubes (CNTs) was achieved over bimetallic Fe-Co catalyst as compared to the Ni-Fe and Ni-Co containing catalysts. 2. Bimetallic 25% Fe-25% Co/MgO catalyst exhibited remarkable higher activity and stability up to 10 h time-on-stream with respect to H_2 production.	Awadallah *et al*. (2014)

Table 2 (*Continued.*)

Bimetallic Ni-Cu catalysts supported on Al_2O_3 catalysts	Co-precipitation method	1. Copper additives can improve the carbon capacity of Ni/Al_2O_3 catalysts, which will lead to increase lifetime and efficiency of $Ni+Cu/Al_2O_3$ catalysts. 2. Ni-Cu alloy systems are promising catalysts for methane decomposition and methane decomposition can achieve 40% at 675℃.	Tatyana *et al.* (2003)
Pd-based alloy catalyst	Wet impregnation method	1. Highly concentration hydrogen and carbon nanofibers were produced through methane decomposition in a temperature range of 973-1123 K. 2. Pd-based alloys containing Ni, Co, Rh or Fe showed high catalytic activity and long life for methane decomposition at 973 K.	Hitoshi *et al.* (2006)
Ni doped carbons catalysts	In-situ carbonization method	1. Ni doped carbon catalyst has higher and more stable activity than metal (Ni/SiO_2 and Ni/Al_2O_3) catalysts and carbon catalysts at temperature of 850℃. 2. Carbon composition in Ni doped carbon will supress the initial activity of Ni particles, but Ni particles can be formed with the time on stream, resulting in increased methane conversion.	Zhang *et al.* (2013)
Ni/ Al_2O_3 catalyst	Wet impregnation method	1. The catalytic activity of Ni/Al_2O_3 catalysts was high at the initial times of reaction but decreased with time on stream due to the deactivation of the catalyst. 2. The 10% Ni/Al_2O_3 catalyst leads to a higher yield of hydrogen due to the higher amount of active phases which can catalyse further the number of methane molecules as compared to the 5% Ni/Al_2O_3 and 7.5% Ni/Al_2O_3 catalysts at the same operating condition.	Makvandi and Alavi (2011)
Bimetallic M-Fe (M= Pd, Mo or Ni) catalysts	Wet impregnation method	1. Bimetallic M-Fe catalysts produced hydrogen at higher rates than monometallic catalysts. 2. The Pd-Fe catalyst was found to be the most active methane activation catalyst at temperature of 973 K.	Huffman *et al.* (2004)

2.7 Selection of transition metal for methane decomposition to hydrogen

Based on the literature review performed, Nickel (Ni) and Palladium (Pd) has been selected as the transition metal which will be utilized in the research work for the development of catalysts for methane decomposition to hydrogen. This is because most of the research work has reported that supported Ni catalysts are effective for methane decomposition above the temperature of 1073 K. However, the limitation of the Ni catalyst is that the hydrogen yield at temperature below 1073 K is not promising (<40%) and it can be deactivated easily due to the decomposition of carbon on the surface of the catalysts.

Besides that, Palladium is selected because researchers such as Huffman *et al.* (2004) and Hitoshi *et al.* (2006) has proven that the presence of Pd can significantly improve the methane decomposition into hydrogen by improving the stability and catalytic activity of the catalysts. However, limited research work has yet to be performed by using Pd because it is a rare type of transition metal. Therefore, the present study is aimed to investigate the improved activity of alumina supported Ni catalysts by the addition of Pd metal. In addition, the effect of temperature and the preparation method of catalyst on the methane decomposition rate and hydrogen yield is hoped to be investigated through this study.

CHAPTER 3 METHODOLOGY

This chapter discusses about the research methodology and project activities that are planned for the project. Besides that, this chapter also includes the discussion about the raw materials and chemicals that are required, the technique which is employed to characterize the catalysts, the experimental setup to evaluate the performance of the catalysts and the method to study the mechanism and kinetics of catalysts. The key milestone and Gantt chart is also attached along in this chapter.

3.1 Research Methodology and Project Activities

The planned project activities for this research are based on extensive literature researches and experimental studies. After extensive and comprehensive literature review is completed, experimental work can be conducted to develop the monometallic (Ni and Pd) and bimetallic (Ni and Pd) catalysts on alumina support which will be tested to evaluate their efficiency in TCD of methane. Figure 5 demonstrates the flow of the research work in this study.

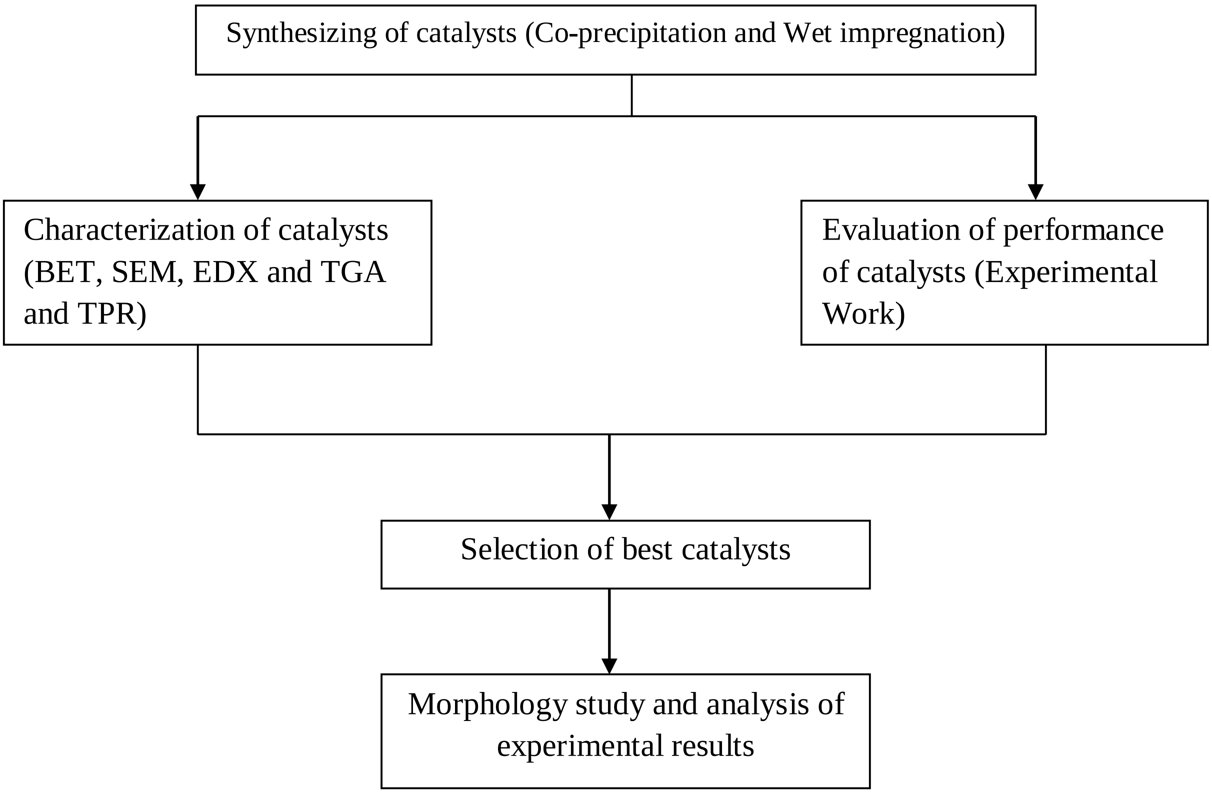


Figure 5 Schematic diagram depicting the flow for the FYP project

3.2 Raw Materials and Chemicals Needed

In this research work, several raw materials and chemicals are required to ensure the success of the project. They are listed as follows:

i) Laboratory-scale pure gases:
   Methane (CH_4) Hydrogen (H_2) and Argon(Ar)

ii) Chemicals
   a) Aluminum Nitrate ($Al(NO_3)_3 \cdot 9H_2O$)
   b) Gamma-Aluminium Oxide (γ-Al_2O_3)
   c) Nickel Nitrate ($Ni(NO_3)_2.6H_2O$)
   d) Tetraamminepalladium (II) chloride monohydrate ($Pd(NH_3)_4Cl_2.H_2O$)
   e) Ammonia (NH_3)
   f) Deionized water

3.3 Equipment Required

There are two kinds of instruments that will be widely employed in this research work, which are analytical instrument and experimental instrument. Analytical instruments will be used for the characterization of the catalysts which are listed below together with its functionality:

i) Brunauer-Emmet-Teller (BET) Surface Area Analysis

   The BET Surface Area Analysis is aimed to provide precise specific surface area evaluation of the catalysts by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. This technique encompasses external area and pore area evaluations to determine the total specific surface area to study the effects of surface porosity and particle size in TCD of methane.

ii) Temperature-programmed Reduction (TPR) Analysis

   TPR is a technique for the characterization of solid materials and is often used in the field of heterogeneous catalysts to determine the most efficient reduction condition. In this method, the oxidized catalyst precursor will be submitted to the programmed temperature rise while a reducing gas mixture is flowed over it.

iii) Scanning Electron Microscopy (SEM) Analysis

SEM provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field.

iv) Energy Dispersive X-ray Spectroscopy (EDX) Analysis

EDX mapping is an analytical technique used to investigate the dispersion of metal particles on the surface of the catalysts. In addition, EDX mapping provides useful and reliable information for the elemental analysis and chemical characterization of the synthesized catalysts.

v) Thermo Gravimetric Analysis (TGA)

TGA is a method of thermal analysis in which changes in physical and chemical properties of the catalysts are measured as a function of increasing temperature and time

The equipment which is required for the catalyst preparation is listed as follows:

a) Weighing Balance

Weighing balance plays an essential role in measuring the weight of samples and or chemicals required to synthesize the catalysts.

b) Hotplate Magnetic Stirrer

Hotplate magnetic stirrer is important to heat up the slurry solution to the desired temperature. In addition, the magnetic stirrer ensures that perfect mixing can be achieved within the solution to ensure well-dispersed phase within the catalysts.

c) Furnace chamber

The furnace chamber is important for the calcination of the catalysts. Calcination is the process of heating up the catalysts to a high temperature, but below their melting point to ensure thermal decomposition to take place.

3.4 Preparation of Catalysts

In this research work, the monometallic (Pd and Ni) and the bimetallic (Ni-Pd) catalysts on alumina (Al_2O_3) support will be prepared by using two methods, which are the co-precipitation method and wet impregnation method. The main reason is to evaluate and to select the methodology that will produce higher metal precursor dispersion on the support of the catalysts. Achieving high Nickel and Palladium dispersion is important to avoid deactivation of the catalysts due to sintering and carbon decomposition on the surface of the catalysts during the methane cracking process.

3.4.1 Co-precipitation Method

The first step to synthesize the catalysts by using co-precipitation method is to prepare the standard stock solution. In this research work, 0.1 g/mL of Ni solution, 0.25 g/mL of alumina solution and 0.003 g/mL of Pd solution is prepared by dissolving the correct amount of the chemicals in crystal/powder form into the volumetric flask. After that, the solution is stirred for 30 minutes by using magnetic stirrer at 200 rpm. The steps for preparing the Ni standard solution is indicated in Figure 6 while the methods which is employed for the preparation of the alumina and Pd solution is similar to that of the Ni standard solution.

Nickel Nitrate Crystals ($Ni(NO_3)_2.6H_2O$)

Nickel Nitrate solution with non-soluble crystals

Stirring of nickel nitrate solution for 30 minutes to homogenous solution

Figure 6 Steps for the preparation of 0.1 g/mL of Ni standard solution

The calculation for the amount of chemicals which is required to prepare the standard stock solution is indicated clearly in Appendix and the results is tabulated in Table 3 while the prepared standard solution is indicated in Figure 7.

Table 3 Amount of chemical salts required for the preparation of standard stock solution

Standard Stock Solution	Chemicals Required	Amount Required (g)	Volume of volumetric flask (mL)
0.1 g of Ni solution	Nickel Nitrate, $Ni(NO_3)_2.6H_2O$	49.55	100
0.25 g of Al_2O_3 solution	Aluminium Nitrate, $Al(NO_3)_3\ 9H_2O$	229.94	250
0.003 g/mL of Pd solution	Tetraamminepalladium (II) chloride monohydrate, $Pd(NH_3)_4Cl_2.H_2O$	0.74	100

a) 0.1 g/mL of Ni solution

b) 0.25 g/mL of alumina solution

c) 0.003 g/mL of Pd solution

Figure 7 Standard stock solution for synthesizing of catalysts by co-precipitation method

The co-precipitation method involved mixing Nickel or Palladium with aluminum precursor solutions, and then adjusting the pH to precipitate a solid. For instance, to synthesize 20g of 1%Ni 99% Al_2O_3 catalysts, 2 mL of nickel nitrate ($Ni(NO_3)_2.6H_2O$,*Aldrich*) solution is titrated drops by drops into 79.2 mL of aluminum nitrate ($Al(NO_3)_3.9H_2O$, *Aldrich*) solution to enable perfect mixing to take place. After that, the mixture of solution was stirred at 60°C while a 5% ammonia solution ($NH_3.H_2O$) was added drop wise to increase the pH of the solution to a value of 9. The temperature was then increased to 90°C and the solution was stirred for 1 h before being filtered and washed five times with deionized water. Then, the Ni sample will be dried at 120°C overnight and calcined at 500°C for 6 hours in flowing oxygen (20mL/min). The proper method to synthesize 1% of Nickel doped on alumina catalyst by using the co-precipitation method is indicated as follows:

Titration of Ni standard solution into aluminum nitrate solution to ensure perfect mixing.

Heating up of solution to 60°C with constant stirring at 250rpm.

Addition of ammonia solution by drop wise until pH of solution reaches 9.

Precipitation of Ni doped on alumina support catalysts as the pH of the solution increases.

Stirring of slurry solution at 90°C with constant stirring at 350rpm for 1 hour.

Washing and filtration of catalysts to eliminiate excess ammonia.

Drying of catalysts overnight at temperature of 120 °C.

Grinding and crushing of catalysts into finer particles.

Calcination of catalysts at 500℃ for 6 hours with ramping rate of 5℃/min.

Ni doped alumina catalysts after calcination by co-precipitation method.

The catalysts which are developed by using the co-precipitation method in this Final Year Project are as follow:

1) 1%Ni 99% Al_2O_3
2) 1%Pd 99% Al_2O_3
3) 0.5%Ni 0.5% Pd 99% Al_2O_3

The method to synthesize the other two catalysts (1%Pd 99% Al_2O_3 and 0.5%Ni 0.5% Pd 99% Al_2O_3) is similar to that of the 1%Ni 99% Al_2O_3 catalysts. However, the correct amount of the active metal precursor solution has to be titrated into the aluminum nitrate standard solution and the calculation to determine the amount that has to be added is shown clearly in Appendix. The amount of standard solution which is required to prepare these catalysts by using co-precipitation method is indicated in Table 4.

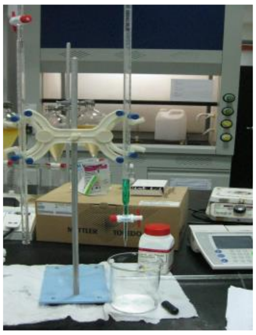
Table 4 Amount of standard solution required for synthesizing catalysts by co-precipitation method

Catalysts (wt%)			Basis (g)	Standard alumina solution (mL)	Standard Ni solution (mL)	Standard Pd solution (mL)
Ni	Pd	Al_2O_3				
1	0	99	20	79.2	2	0
0	1	99	20	79.2	0	66.67
0.5	0.5	99	20	79.2	1	33.33
			Total	237.6	3	100

3.4.2 Wet Impregnation Method

0.1 g/mL of Ni standard stock solution and 0.0018g/mL of Pd standard solution is prepared by dissolving the correct amount of Nickel Nitrate, $Ni(NO_3)_2.6H_2O$ and Tetraamminepalladium (II) chloride monohydrate, $Pd(NH_3)_4Cl_2.H_2O$ with deionized water. In addition, the support of the catalysts which is aluminum oxide (γ-alumina) is pre-calcined in air by using the furnace chamber at 900°C for 12 hours with a ramping rate of 5°C/min.

Unlike the co-precipitation method, the standard stock solution containing the active metal precursor is titrated drops by drops into the pre-calcined alumina catalysts. For example, to synthesize 20g of 1% Ni 99% Al_2O_3 catalysts, 2 mL of standard Ni solution is titrated by drop wise into 19.8g of pre-calcined gamma-alumina oxide (γ-Al_2O_3) which is in powder form. After that, 30 mL of deionized water is added into the solution and the mixture is stirred for 1 hour with constant stirring at 500 rpm. After that, the solution is dried overnight at 100°C and the catalyst is calcined at 500°C for 6 hours with ramping rate of 5°C/min. The proper method to synthesize 1% of Nickel doped on alumina catalyst by using the wet impregnation method is indicated as follows:



Titration of Ni standard solution by drop wise into γ-Al_2O_3 in powder form.

Addition of 30 mL of deionized water into solution. The solution is stirred for 1 hour at 500 rpm at room temperature to ensure homogenenous mixing.

Drying of catalysts overnight at temperature of 100℃. The catalyst is calcined at temperature of 500℃ for 6 hours with ramping rate of 5℃/min.

Ni doped alumina catalyst prepared by using wet impregnation method.

The catalysts which are developed by using the wet impregnation method in this Final Year Project is the same as the catalysts which is developed by the co-precipitation method. This is important for the evaluation and determination of the better method which can provide higher Ni and Pd dispersion on the surface of the catalysts. The method to synthesize the other two catalysts (1%Pd 99% Al_2O_3 and 0.5%Ni 0.5% Pd 99% Al_2O_3) is similar to that of the 1%Ni 99% Al_2O_3 catalysts. However, the correct amount of the active metal precursor solution has to be titrated into the pre-calcined gamma-alumina which is in powder form and the calculation to determine the amount that has to be added is shown clearly in Appendix. The amount of standard solution which is required to prepare these catalysts by using co-precipitation method is indicated in Table 5.

Table 5 Amount of pre-calcined γ-Al_2O_3 and standard stock solution required for synthesizing of catalysts by wet impregnation method

Catalysts (wt%)			Basis (g)	Amount of pre-calcined γ-Al_2O_3 (g)	Standard Ni solution (mL)	Standard Pd solution (mL)
Ni	Pd	Al_2O_3				
1	0	99	20	19.8	2	0
0	1	99	10	9.9	0	55.56
0.5	0.5	99	10	9.9	0.5	27.78
			Total	39.6	2.5	83.34

3.5 Reaction Performance

The catalytic activity and thermal stability of the synthesized catalysts were evaluated at atmospheric pressure on a conventional fixed bed gas-flow system (Figure A 1) with 500 mg of catalysts. Pure argon gas at 20 mL/min was allowed to flow though the reactor to create an inert atmosphere in the reactor. The synthesized catalysts were reduced in a flow of hydrogen gas at 30 mL/min at 600℃ for 1 hour. After reduction, the experimental set-up was flushed with pure argon gas until the gas chromatography system showed a complete disappearance of hydrogen gas.

The methane decomposition test rig system consists of 3 main components, which are the gas mixing system, the reactor for methane cracking process to take place and an on-line gas chromatography system. The methane decomposition test rig system is indicated in Figure 12. In the gas mixing system, 15 ml/min of highly pure methane gas (99.99% purity, *Sigma Aldrich*) was diluted with 5 mL/min of argon gas (99.88% purity, *Sigma Aldrich*) before the gas mixture is introduced into the reactor. The flow of methane, hydrogen and argon can be regulated by a mass flow controller which is located at the inlet stream to the reactor. A thermocouple and temperature controller was used to measure and to monitor the temperature of the catalyst bed in the reactor. The reactor effluent is analyzed by using an online gas chromatography system (Hewlett Packard Series 6890) at the outlet of the reactor. The evaluation of the performance of the synthesized catalyst can be conducted by analyzing the hydrogen yield, the conversion of methane, the operating temperature in which the methane cracking process can be further reduced and the deactivation rate of the catalysts.

The catalysts were tested at three temperatures, which are 800℃, 700℃ and 600℃ respectively while the flow rate of methane and argon is maintained at a constant value for 4 hours. The conversion of methane and the yield of hydrogen were provided by the gas chromatography system by Equation 5 and Equation 6, respectively.

$$Conversion\ of\ methane\ (\%) = \frac{Mole\ of\ methane\ reacted}{Mole\ of\ methane\ input} \times 100\% \tag{5}$$

$$Yield\ of\ hydrogen\ (\%) = \frac{Mole\ of\ hydrogen\ produced}{Mole\ of\ methane\ input \times 2} \times 100\% \tag{6}$$

3.6 Gantt Chart and Planned Milestones for FYP I and FYP II

NO	Week DETAIL	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	🟨	🟨													
2	Preliminary Research Work and Literature Review		🟨	🟨	🟨	🟨										
3	Submission of First Draft of Extended Proposal Defence					●										
4	Submission of Extended Proposal Defence						●									
5	Preparation for Oral Proposal Defence							🟨								
6	Oral Proposal Defence Presentation									🟨 ●						
7	Preliminary Research Activity (Purchasing of chemicals, setting up of reactor and gas analysis system)									🟨	🟨	🟨	🟨	🟨	🟨	🟨
8	Preparation of Interim Report			🟨	🟨	🟨	🟨	🟨		🟨	🟨	🟨	🟨	🟨		
9	Submission of Interim Report- First Draft														●	
10	Submission of Interim Final Report															●

● Planned milestone

🟨 Process of activity

DETAIL	Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Collection of chemicals and testing of reactor	🟨	🟨													
2	Synthesizing of monometallic and bimetallic supported on alumina catalysts		🟨	🟨	🟨	🟨										
3	Characterization of catalysts				🟨	🟨	🟨									
4	Performing experimental work					🟨	🟨	🟨		🟨	🟨					
5	Preparation for Progress Report Submission							🟨		🟨 ●						
5	Selection of highest performance catalyst									🟨						
6	Study of catalyst mechanism for TCD of methane									🟨	🟨	🟨	🟨	🟨		
7	Pre-SEDEX Presentation												●			
8	Submission of Draft Report												●			
9	Submission of Dissertation (Soft bound)													●		
10	Submission of Technical Paper													●		
11	Oral presentation														●	
12	Submission of Project Dissertation (Hard Bound)															●

● Planned milestone
🟨 Process of activity

CHAPTER 4 RESULTS & DISCUSSION

This chapter discusses about the results that is obtained from this research work. In addition, thorough discussion and analysis is performed to provide clear and significant understanding on the thermo-catalytic methane decomposition to hydrogen process.

4.1 Characterization of synthesized catalysts

Characterization of catalysts is significant because it enables the researchers to have a better insight on the physical properties and chemical properties of the catalysts. The physical properties of the catalysts may include pore size, surface area, morphology of the carrier and the geometry and strength of the support while the chemical properties may include the composition, structure, nature of the carrier and the active catalytic components. The catalysts which is developed and is studied in this research work is labeled as listed in Table 6.

Table 6 Labeling of synthesized catalysts

Label of Catalysts	Type of Catalysts
CAT-1	1% Ni 99% Al_2O_3 catalysts prepared by co-precipitation method
CAT-2	1% Pd 99% Al_2O_3 catalysts prepared by co-precipitation method
CAT-3	0.5 % Ni 0.5 % Pd 99% Al_2O_3 catalysts prepared by co-precipitation method
CAT-4	1% Ni 99% Al_2O_3 catalysts prepared by wet impregnation method
CAT-5	1% Pd 99% Al_2O_3 catalysts prepared by wet impregnation method
CAT-6	0.5 % Ni 0.5 % Pd 99% Al_2O_3 catalysts prepared by wet impregnation method

4.1.1 Brunauer Emmet Teller (BET) Surface Area Analysis

The N_2 adsorption-desorption isotherms for the synthesized catalysts were measured on a *Micromeritics ASAP 2020*. All the samples were evacuated at 300 ℃ in vacuum to remove water and other contaminants prior to the measurement. From N_2 absorption at 77 K, the specific surface area was calculated by using the BET method. The BET surface area of the catalysts were determined by using Equation 6 in which S_T is the total surface area of the catalysts, X_m is the monolayer capacity, L_{av} is the Avogadro's number, A_m is the cross sectional area of the adsorbate and equals to 0.162 nm^2 for an absorbed nitrogen molecule, and M_V is the molar volume (22414mL).

$$S_T = \frac{X_m L_{av} A_m}{M_v} \tag{6}$$

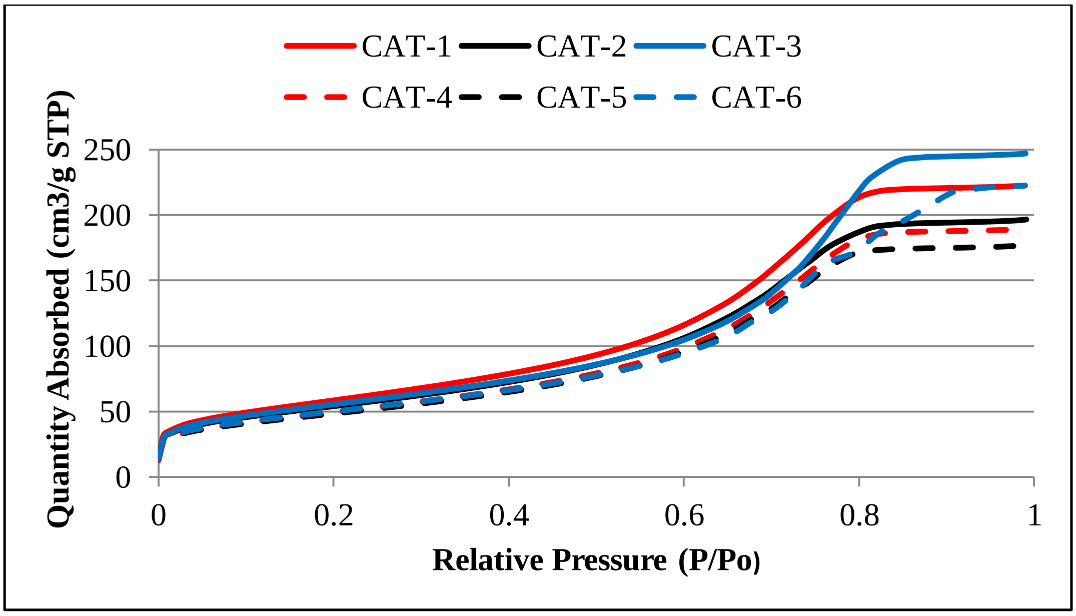
The total pore volume was determined at a relative pressure$\frac{P}{P_o}$. On the other hand, the pore size distribution were calculated from the de-sorption isotherms by using the Barrett-Joyner-Halenda (BJH) model. The BJH model is based on the assumption that pores have a cylindrical shape and that pore radius is equal to the sum of the Kelvin radius and the thickness of the film absorbed on the pore wall. The specific surface area and pore volumes determined by N_2 physisorption for the synthesized catalysts were given in Table 9. In addition, the adsorption/desorption isotherms are shown in Figure 8 while the pore size distribution is indicated in Figure 9.

Table 9: Specified surface area and pore volumes for pre-calcined Al_2O_3, CAT-1, CAT-2, and CAT-3 by N_2 physisorption

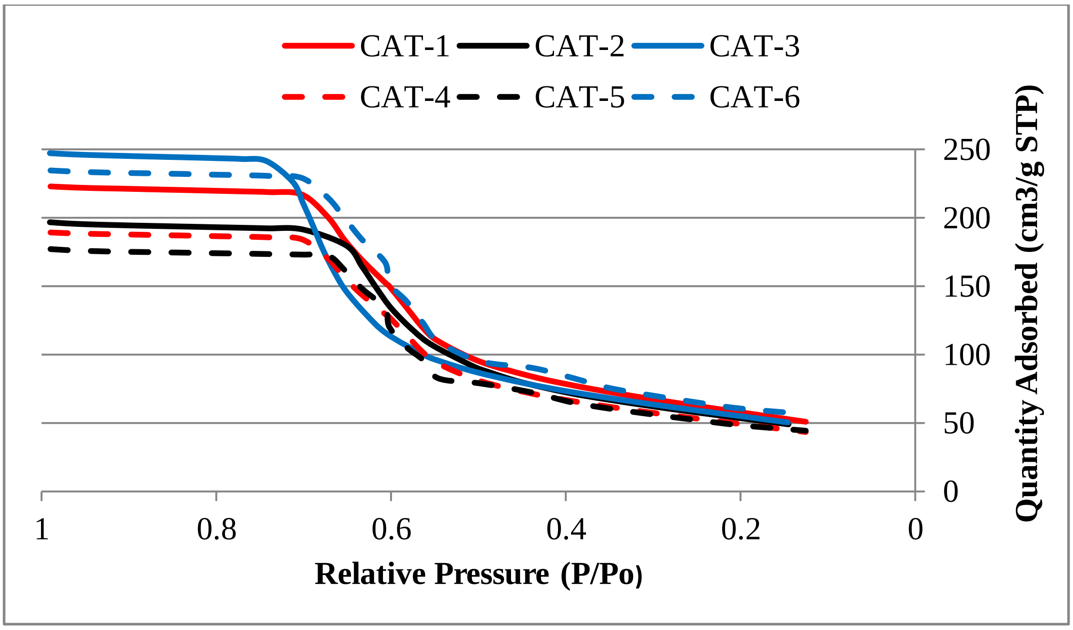
Type of catalysts	Surface Area (m^2/g)	Pore Volume (cm^3/g)
γ-Al_2O_3	208.00	0.38
CAT-1	201.03	0.34
CAT-2	195.31	0.30
CAT-3	212.80	0.38
CAT-4	186.34	0.34
CAT-5	182.89	0.32
CAT-6	196.73	0.31

A value of 208 m^2/g for the commercial γ-Al_2O_3 support compares well with the nominal value of 180 m^2/g which was reported by Li *et al*. (2006). For the catalysts which were prepared by wet impregnation method (CAT-4, CAT-5 and CAT-6), it can be observed that the addition of Ni and Pd onto the pre-calcined alumina support reduced the surface areas and pore volumes, suggesting that the impregnated Ni and Pd metal has blocked some pores of the support.

The surface areas for the synthesized catalysts varied between 182.89 and 212.80 m^2/g while the pore volume varied between 0.30 and 0.38 cm^3/g. The in-house prepared co-precipitation catalysts demonstrated higher surface area and wider pore volume as compared to the catalysts which were synthesized by wet impregnation method. The development of high surface area catalysts are important in order to achieve high metal dispersion on the surface of the alumina support. In addition, larger pore volumes might be feasible for rapid molecular transportation, namely higher diffusion efficiency of reactants and products and to avoid the blockage of the active sites of the catalyst due to carbon deposition during the reaction.



(a)



(b)

Figure 8 Adsorption (a) and desorption (b) isotherms for CAT-1, CAT-2, CAT-3, CAT-4, CAT-5 and CAT-6 by N_2 physisorption

The adsorption and desorption isotherm for the synthesized catalysts (Figure 8) shows good agreement with specific surface area and pore volume measurement results. The adsorption and desorption isotherm indicates that larger amount of N_2 gas can be adsorbed and desorbed by CAT-3 due to its larger surface area and larger pore volume.

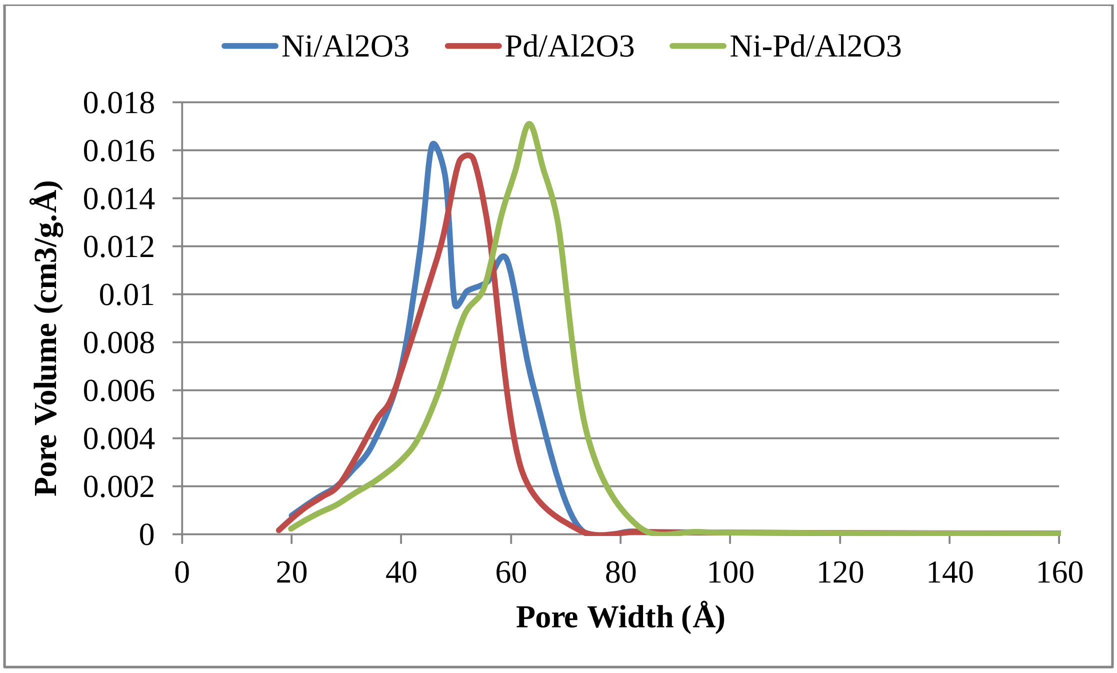


Figure 9 Pore Size Distribution monometallic and bimetallic on alumina support catalyst by N_2 physisorption

From Figure 9, it can be observed that Ni/Al_2O_3 catalyst had a bimodal pore size distribution with one peak around 45 Å and another peak around 60 Å. In comparison, the peak maximums occurred at approximately 50 Å and 70 Å for Pd/Al_2O_3 and $Ni\text{-}Pd/Al_2O_3$, respectively. The pore distribution and metal dispersion on the surface of the alumina support has to be further investigated by Scanning Electron Microscopy (SEM) analysis to provide better insight on the morphology of the catalysts.

4.1.2 Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) images were recorded on a Philips XL30/FEI ESEM operating at an accelerating voltage from 5 to 30kv. The samples were coated with graphite before the SEM images were taken at 500x, 1000x, 3000x, 5000x, 10000x and 30000x magnification. SEM images representative of the morphology of the catalysts in their as produced state are indicated in Figure 10, 11, 12, 13, 14 and 15 with different magnification as follows.

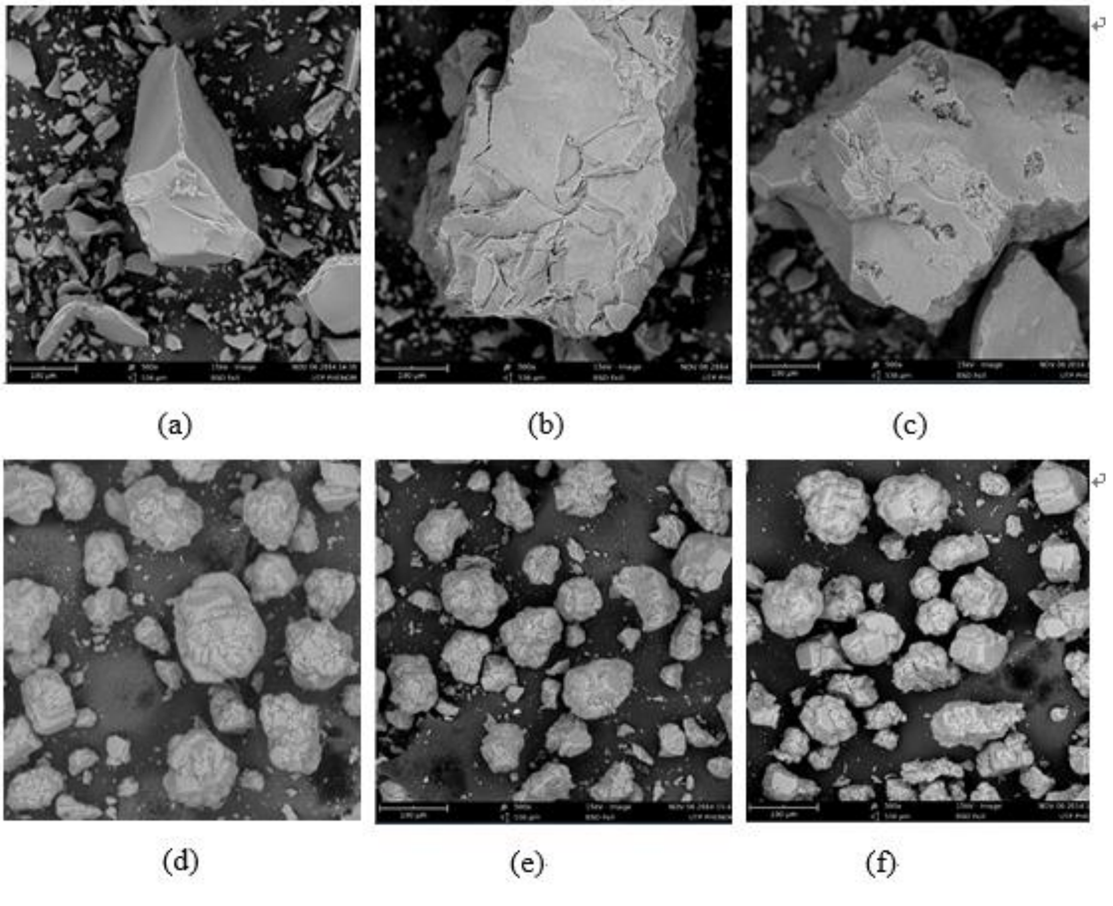


Figure 10 SEM images of catalysts at 500x magnification (100 µm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4, (e) CAT-5 and (f) CAT-6

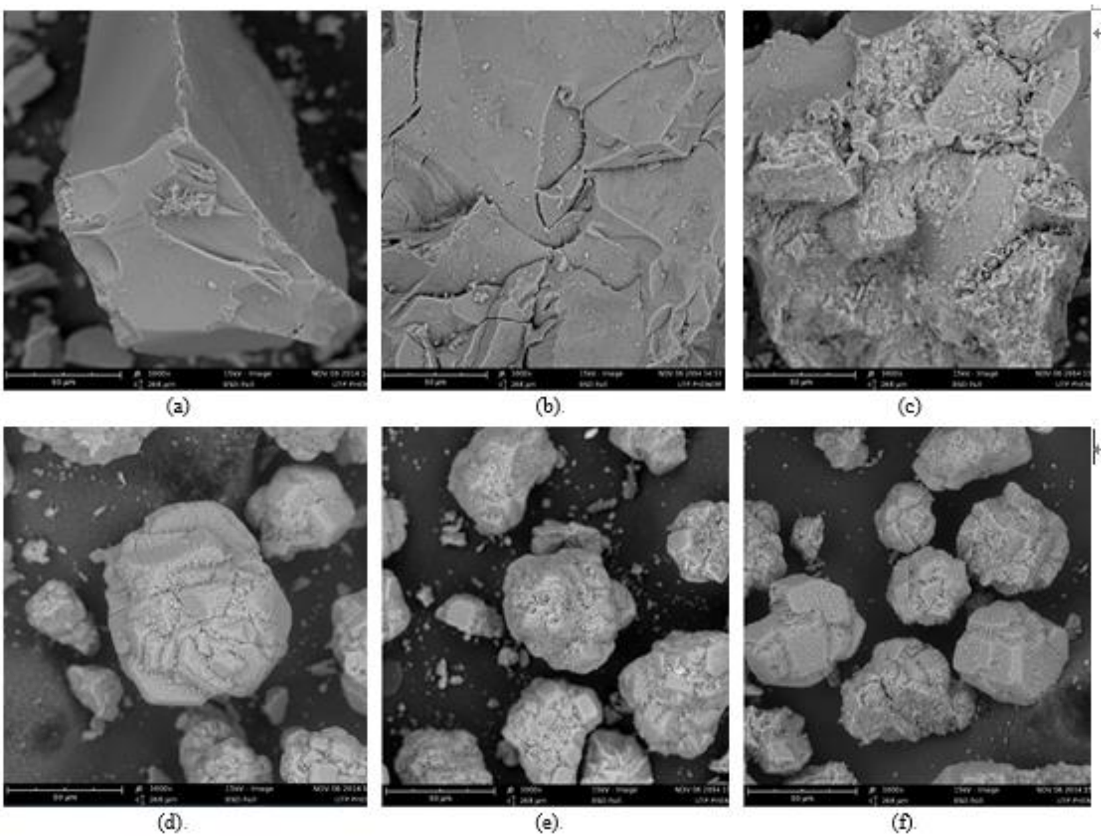


Figure 11 SEM images of catalysts at 1000x magnification (80 µm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4, (e) CAT-5 and (f) CAT-6

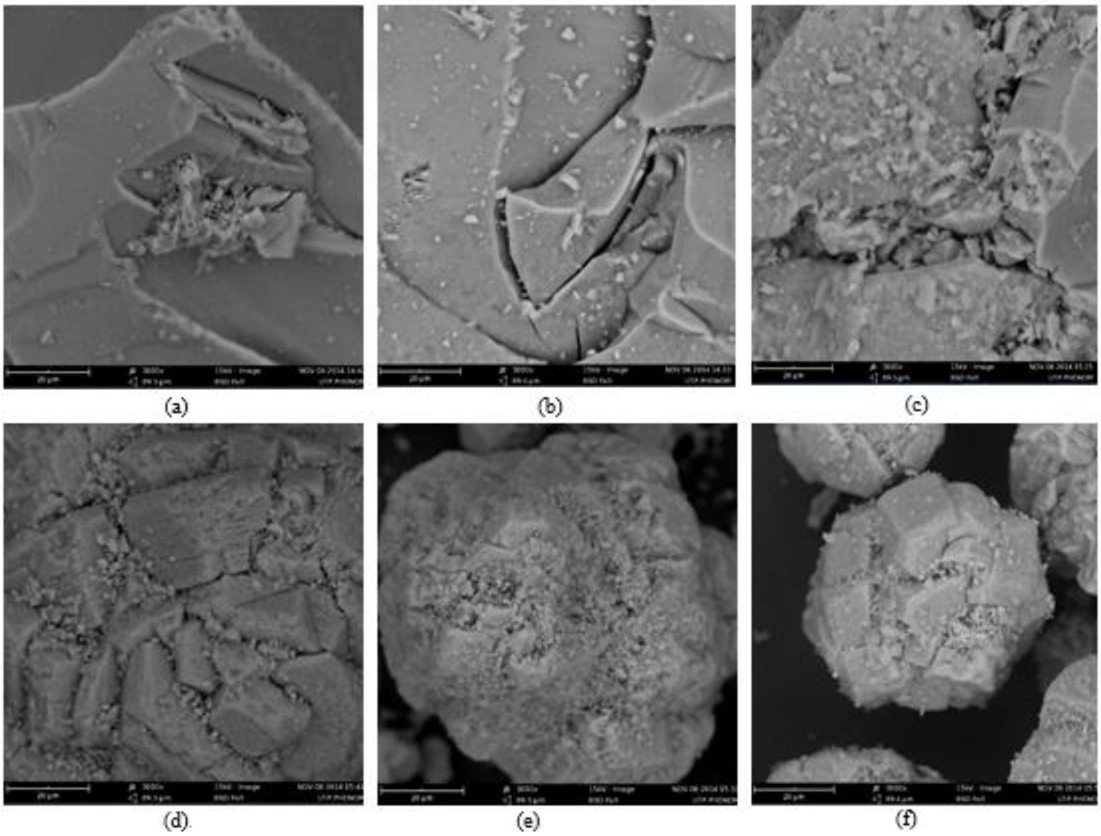


Figure 12 SEM images of catalysts at 3000x magnification (20 µm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4, (e) CAT-5 and (f) CAT-6

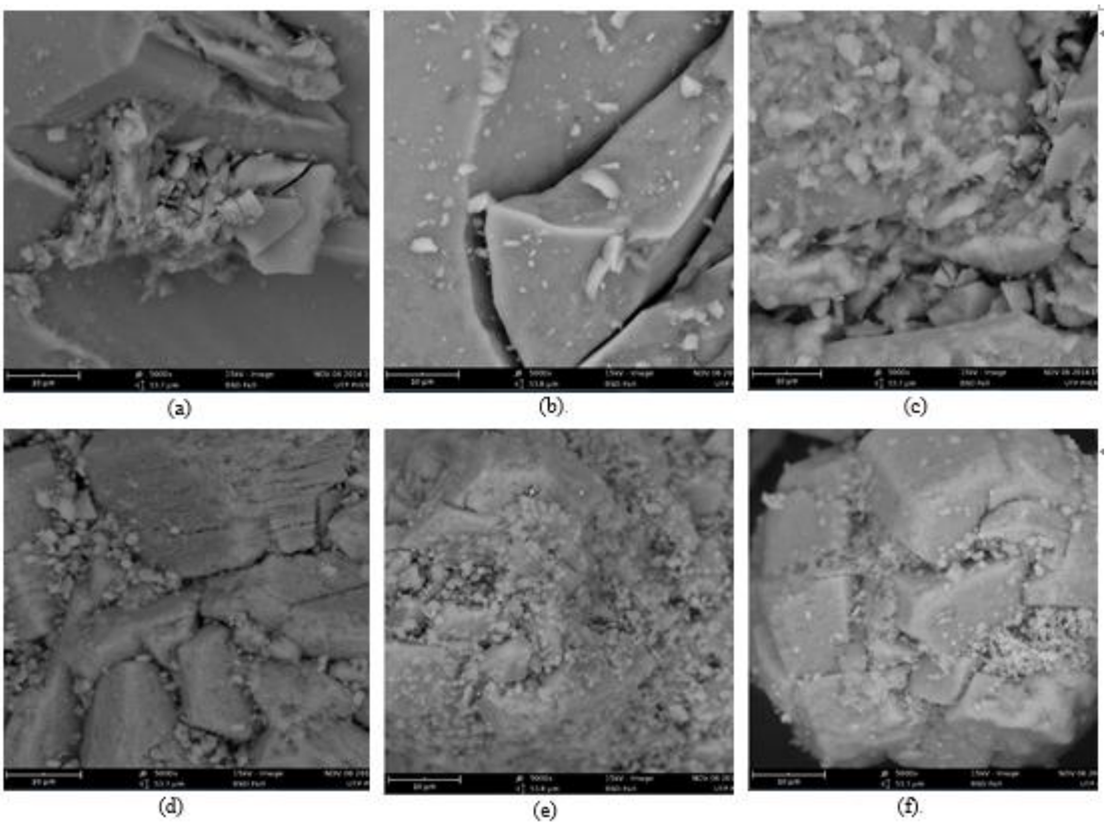


Figure 13 SEM images of catalysts at 5000x magnification (10 µm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4, (e) CAT-5 and (f) CAT-6

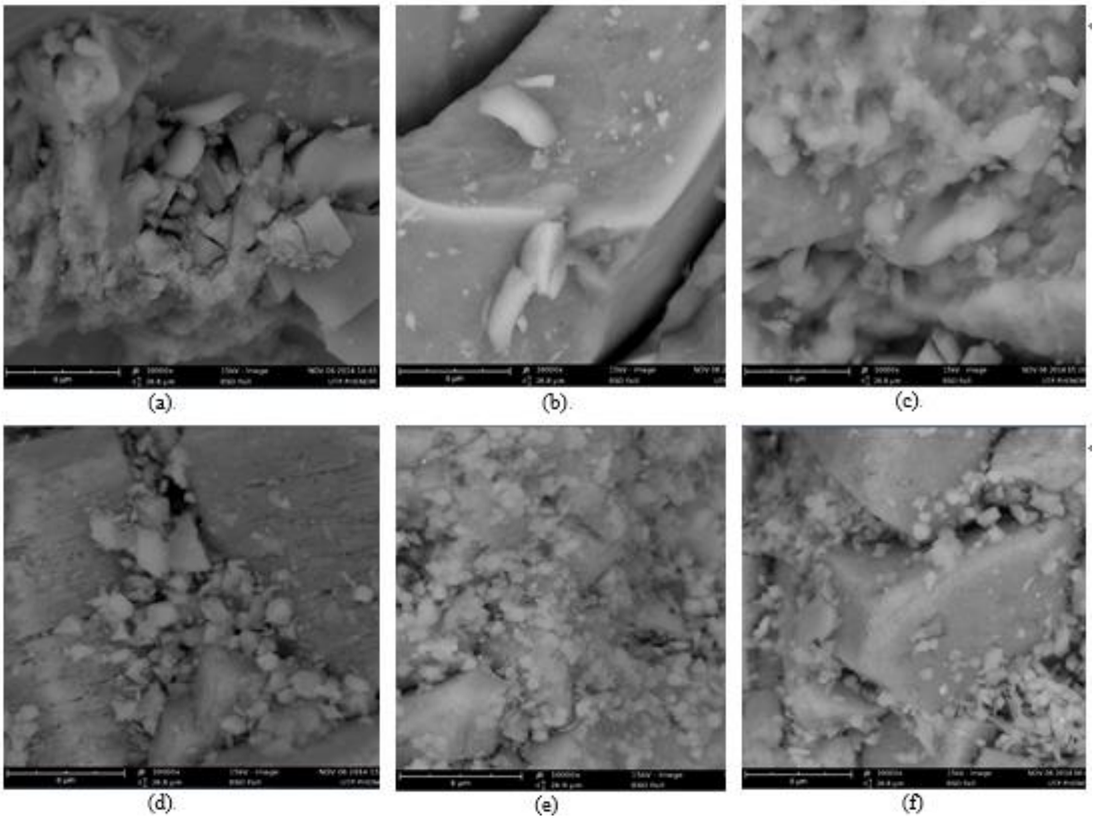
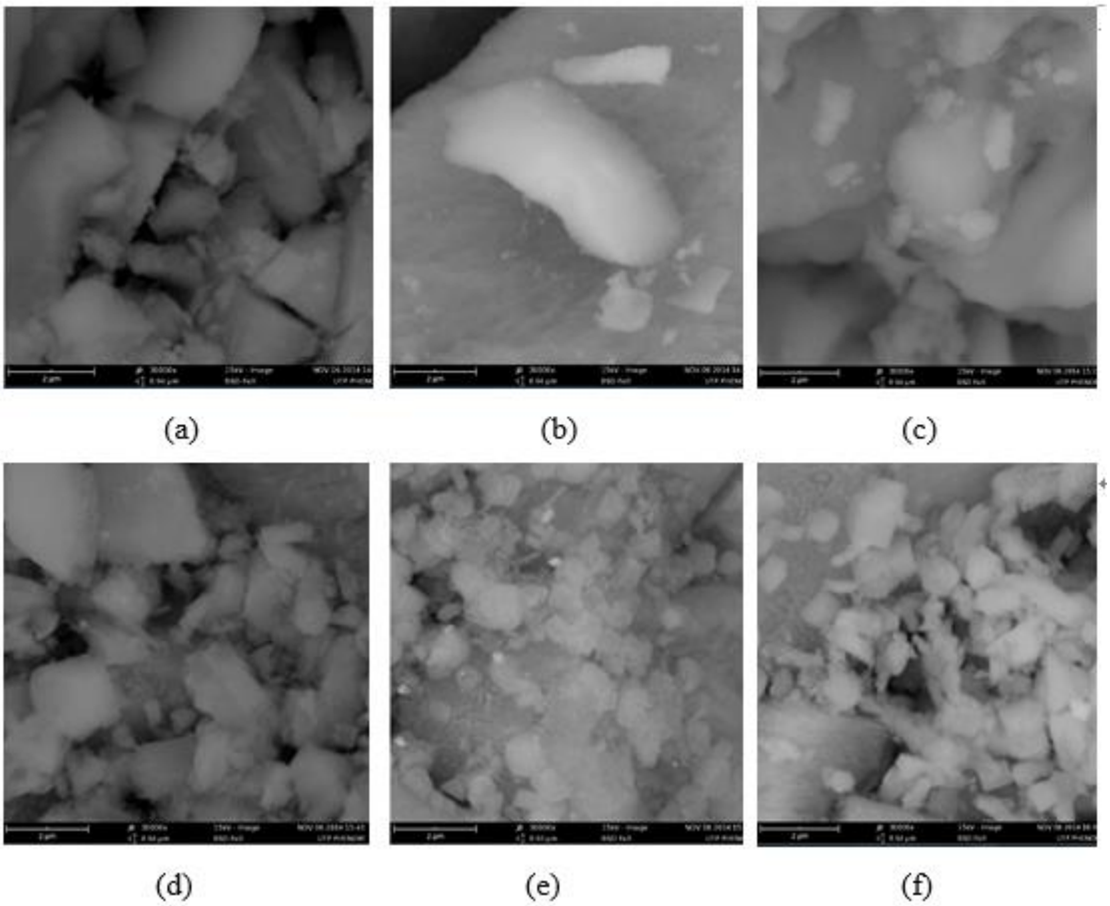


Figure 14 SEM images of catalysts at 10000x magnification (8 µm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4, (e) CAT-5 and (f) CAT-6



(a) (b) (c)

(d) (e) (f)

Figure 15 SEM images of catalysts at 30000x magnification (2 µm scale): (a) CAT-1, (b) CAT-2, (c) CAT-3, (d) CAT-4, (e) CAT-5 and (f) CAT-6

SEM images indicate that the catalysts which were prepared by co-precipitation method exhibited tetrahedron shape while the catalysts which were prepared by wet impregnation method demonstrated spherical geometry. In addition, it can be observed that smaller nickel and palladium particles were dispersed on the surface of γ-Al_2O_3 support for the catalysts which were synthesized by the co-precipitation method. Smaller particles size has been considered as one of the main factors for the development of effective catalysts for methane thermo-catalytic decomposition process because large particles dispersion may promote the formation of carbon on the surface of the catalysts, thereby causing deactivation and sintering of the catalysts.

Besides that, SEM images of the catalysts prepared by co-precipitation method (CAT-1, CAT-2 and CAT-3) revealed a surface with higher homogeneous morphology. In contrast, the catalyst prepared by wet impregnation method (CAT-4, CAT-5 and CAT-6) demonstrated an uneven and wrinkled surface, which may affect the dispersion of nickel and palladium particles on the catalyst. The homogeneous morphology of CAT-

1, CAT-2 and CAT-3 suggested that higher diffusion of Ni^{2+} and Pd^{2+} into the bulk structure of γ-Al_2O_3 may be achieved by using co-precipitation method. However, Energy Dispersive X-ray Spectroscopy (EDX) mapping has to be employed to evaluate the dispersion of nickel and palladium particles on the surface of γ-Al_2O_3 support.

4.1.3 Energy Dispersive X-ray Spectroscopy (EDX) Mapping Analysis

EDX analysis was performed on a Philips XL30/FEI ESEM to determine the actual and uniform nickel and palladium dispersion. The EDX mapping results are indicated in Appendix for CAT-1, CAT-2, CAT-3, CAT-4, CAT-5 and CAT-6, respectively for reference purpose. The nickel particles were indicated as light green spots, palladium particles were indicated as purple spots, oxygen elements were indicated as dark blue spots and aluminum particles were indicated as orange spots. In addition, the atomic percentage of the individual elements were determined from the EDX mapping to evaluate whether correct amount of metal precursors have been incorporated into the synthesized catalysts. The results for the EDX analysis were indicated as follows.

Table 7 Determination of weight percentage of Al, O and Ni element for CAT-1 (1% Ni 99% Al_2O_3)

Atomic Number	Element	Atomic Percentage (%)	Error Percentage (%)
13	Aluminium	41.80	0.6
8	Oxygen	56.30	0.8
28	Nickel	1.90	5.7
	Total	100	

Table 8 Determination of atomic percentage of Al, O and Pd element for CAT-2 (1% Pd 99% Al_2O_3)

Atomic Number	Element	Weight Percentage (%)	Error Percentage (%)
13	Aluminium	42.10	0.5
8	Oxygen	57.10	0.8
46	Palladium	0.80	11.1
	Total	100	

Table 9 Determination of weight percentage of Al, O, Ni and Pd element for CAT-3 (0.5% Ni 0.5% Pd 99% Al_2O_3)

Atomic Number	Element	Weight Percentage (%)	Error Percentage (%)
13	Aluminium	43.20	0.7
8	Oxygen	55.4	1.0
28	Nickel	1.00	5.4
46	Palladium	0.40	30.8
	Total	100	

Table 10 Determination of weight percentage of Al, O, and Ni element for CAT-4 (1% Ni 99% Al_2O_3)

Atomic Number	Element	Weight Percentage (%)	Error Percentage (%)
13	Aluminium	39.50	0.3
8	Oxygen	59.60	0.4
28	Nickel	0.90	8.4
	Total	100	

Table 11 Determination of weight percentage of Al, O, and Pd element for CAT-5 (1% Pd 99% Al_2O_3)

Atomic Number	Element	Weight Percentage (%)	Error Percentage (%)
13	Aluminium	41.50	0.3
8	Oxygen	57.60	0.5
46	Palladium	0.90	4.6
	Total	100	

Table 12 Determination of weight percentage of Al, O, Ni and Pd element for CAT-3 (0.5% Ni 0.5% Pd 99% Al_2O_3)

Atomic Number	Element	Weight Percentage (%)	Error Percentage (%)
13	Aluminium	41.60	0.3
8	Oxygen	57.50	0.5
28	Nickel	0.50	10.2
46	Palladium	0.40	8.6
	Total	100	

The EDX mapping results indicated that nickel and palladium were sufficiently and uniformly dispersed on the γ-Al_2O_3 support surface for the catalysts which are synthesized by co-precipitation technique. The uniform dispersion may have strengthened the catalyst and thereby enabled effective methane cracking process to take place. In addition, the active metals distribution and placement in the channels in an even manner is expected to contribute towards a successful methane thermo-catalytic cracking reaction. On the other hand, the Ni and Pd metal particles tend to accumulate on the active sites of the catalysts which are prepared by wet impregnated method, leading to higher concentration of Ni^{2+} and Pd^{2+} around the active region of the catalyst.

The weight percentage of each element identified from the analysis shows good agreement with the actual weight percentage of nickel and palladium which is expected to be introduced into the γ-Al_2O_2 support. This has proven that the catalysts had been successfully synthesized by using both co-precipitation and wet impregnation method. The EDX analysis also indicated that the amount of oxygen element is higher than the amount which is expected to be incorporated onto the catalysts (46.5% O) due to the oxidation reaction.

4.1.4 Thermal analysis of synthesized catalysts

Thermogravimetric Analysis (TGA) was carried out to evaluate and to investigate the weight loss, thermal behavior and structural decomposition of the samples at a heating rate of 10°C/min up the temperature of 800°C. The weights of the samples were initially at 0.1 g and TGA analysis was performed under sweeping air atmosphere at 10 mL/min.

Figure 16 indicates the relationship between weight percentages with the decomposition temperature for the calcined catalysts. As it can be observed from Figure 16, all the calcined catalysts demonstrated good resistance towards decomposition at temperature as high as 800 °C. The catalysts should be able to exhibit long term and high thermal stability to prevent decomposition of the catalysts when the methane cracking process take place. However, as it can be observed from Figure 16, the catalysts which were synthesized by co-precipitation has higher weight loss (~14%) as compared to the catalysts which were wet impregnated. This might be due to the different interaction between the Ni^{2+} and Pd^{2+} species with the support during the preparation process.

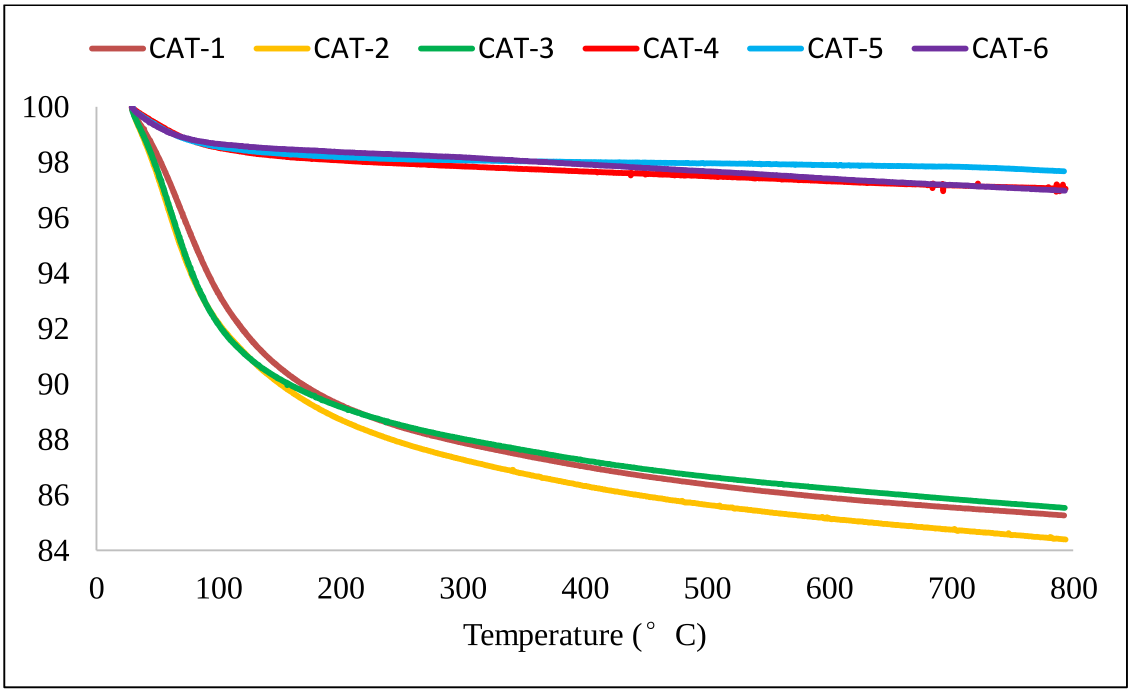


Figure 16 Weight percentage (%) versus decomposition temperature (°C) for calcined catalysts

4.1.5 H2- TPR Analysis

The reducibility behavior of the monometallic (Ni and Pd) and bimetallic (Ni-Pd) catalysts will be investigated by H_2-TPR technique on a Thermo Finnigan (TPRRO 1100) equipment. Prior to H_2 reduction, the samples were pretreated under nitrogen at 300 °C with a flow rate of 20 mL/min and ramping rate of 10 °C/min and finally holding at 300 °C for 30 minutes to eliminate any impurities before cooling down to room temperature. TPR analysis was then carried out in 5 % H_2/ N_2 with a flow rate of 20 mL/min. The samples were heated with a ramping rate of 20 °C/min from room temperature to 800 °C and the reduction profile was shown in a plot of hydrogen consumption as a function of linearity temperature.

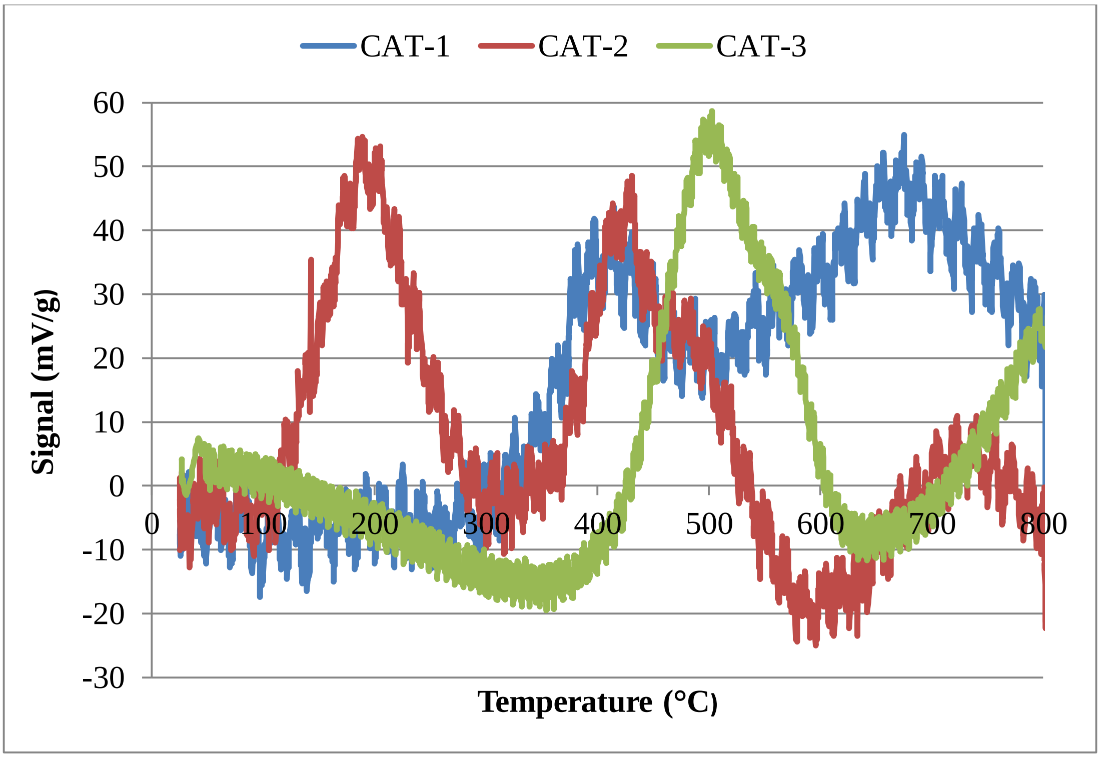


Figure 17 Temperature-programmed reduction profiles of catalysts prepared by co-precipitation method; heating rate of 20 °C/min in 5% H_2/N_2

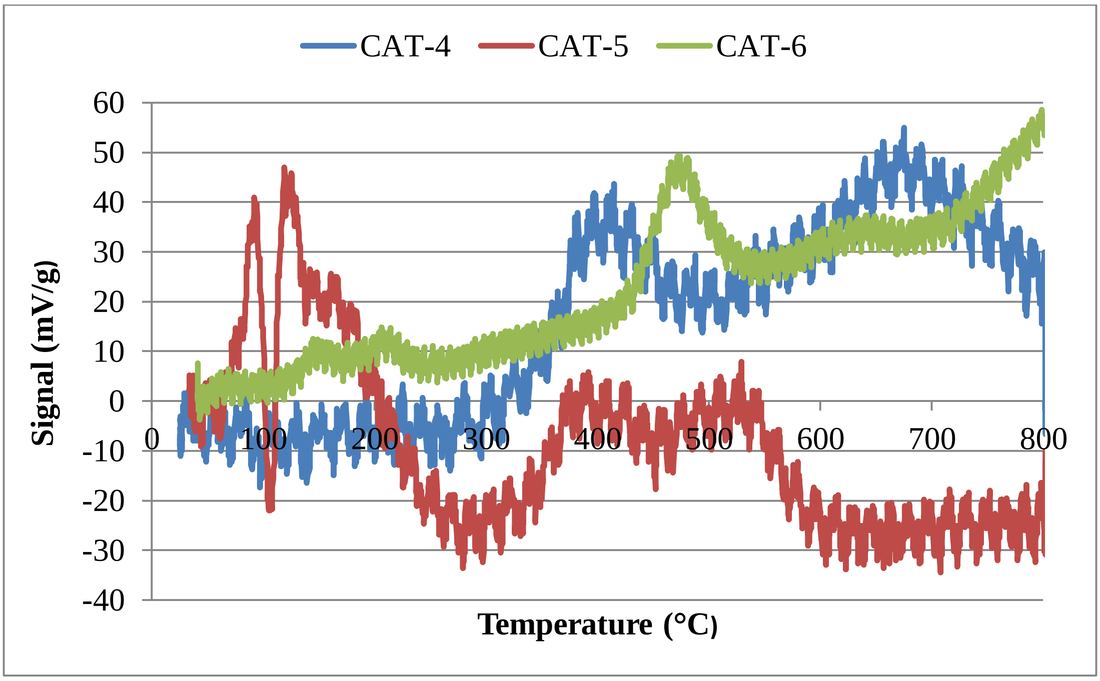


Figure 18 Temperature-programmed reduction profiles of catalysts prepared by wet impregnation method; heating rate of 20℃/min in 5% H_2/N_2

Table 13 Peak temperature of synthesized catalysts

Type of catalyst	Peak Temperature (℃)
CAT-1	400, 700
CAT-2	200, 450
CAT-3	200, 500, 800
CAT-4	400, 700
CAT-5	100
CAT-6	200, 500, 800

Figure 17 indicates the TPR profiles of the catalysts which are prepared by using co-precipitation method while Figure 18 shows the TPR profiles for the catalysts which are prepared by wet impregnation method. The $Ni/\gamma\text{-}Al_2O_3$ catalysts which were prepared by both method exhibit similar TPR profiles. In the case of Ni/Al_2O_3 catalysts, two reduction regions were identified. The first peak at 400 ℃ was assigned to the nitrate decomposition. The second peak is observed at higher temperature (700℃) and corresponded to the reduction of Ni^{2+} species highly dispersed and nickel aluminate which has stronger interaction with the support.

The TPR traces of the Pd monometallic catalyst which is prepared by the co-precipitation method exhibited a main hydrogen consumption peak at 200℃, which may be attributed to the reduction of PdO species and to the formation of palladium hydrides. This catalyst also demonstrated a peak at 450 ℃ which could be related to the decomposition of the β-PdH phase. When these species interact weakly with the Al_2O_3 support, the palladium hydrides may be eliminated during reduction. On the other hand, the Pd/Al_2O_3 catalyst which was prepared by the wet impregnation method was reduced at 100 ℃ and no reduction peak was observed at higher temperature. Therefore, these results suggested that the Pd^{2+} is easier to be reduced in the catalyst which is prepared by wet impregnation method as compared to co-precipitation method.

The TPR profile of $Ni\text{-}Pd/Al_2O_3$ catalysts present a complex reduction behavior which is quite distinct from that which should be observed from a simple combination of the profiles recorded for Ni/Al_2O_3 and Pd/Al_2O_3. These results suggested the existence of an interaction between the Ni and Pd particles. The TPR profile showed three peaks at 200, 500 and 800℃. The first peak at 200 ℃ corresponded to palladium oxide or nickel oxide reduction. Furthermore, it can be observed from the TPR profiles that the presence of palladium shifted the peaks of nickel aluminate and superficial Ni^{2+} reduction from 700 ℃ to lower temperature of 500 ℃. Therefore, the palladium addition to Ni/Al_2O_3 catalyst promoted the reduction of nickel oxides. These results suggested the presence of a strong interaction between nickel oxide and palladium within the structure of the catalyst. The third peak at 800 ℃ may be due to the complicated $NiAl_2O_4$ and $PdAl_2O_4$ phase formed by the diffusion of Ni^{2+} and Pd^{2+} into the support.

4.1.9 Reaction Performance

Figure 19, 20 and 21 shows the methane conversion profile for the synthesized catalysts as a function of time for the decomposition of methane to hydrogen and carbon within 4 hours on stream at 873 K, 8973 K and 1073 K, respectively. The effect of introducing Palladium as a promoter to Nickel supported on alumina catalysts and the effect of the preparation method were investigated by comparing and evaluating the performance of the synthesized catalysts which will provide high methane conversion with long-term operational lifetime.

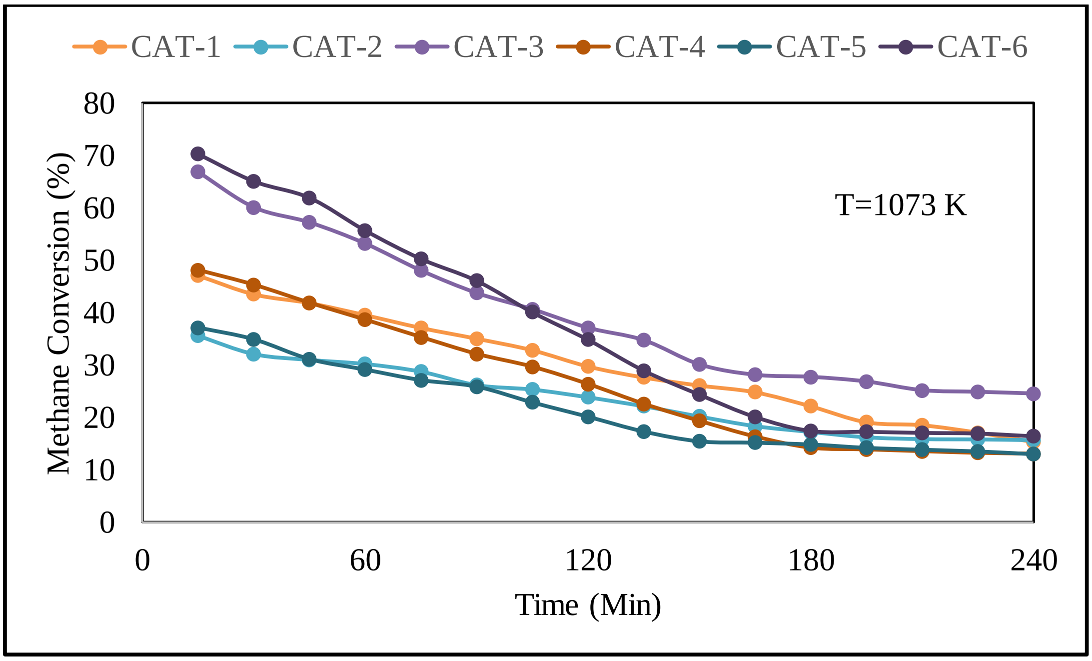


Figure 19 Methane conversion against time at reaction temperature of 1073 K

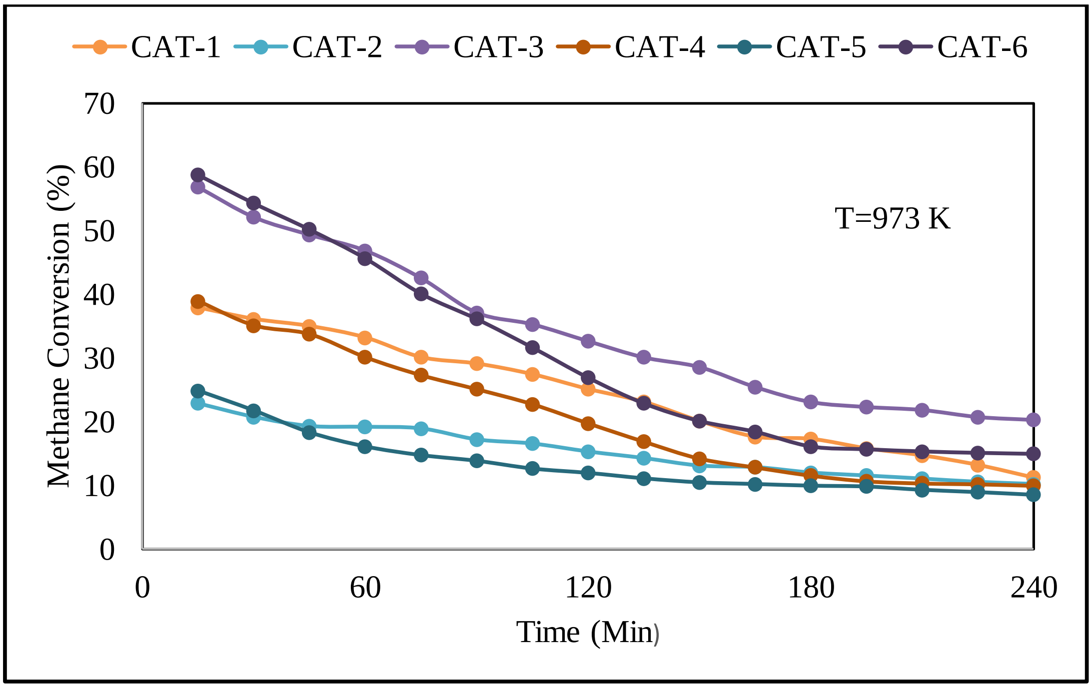


Figure 20 Methane conversion against time for reaction temperature at 973 K

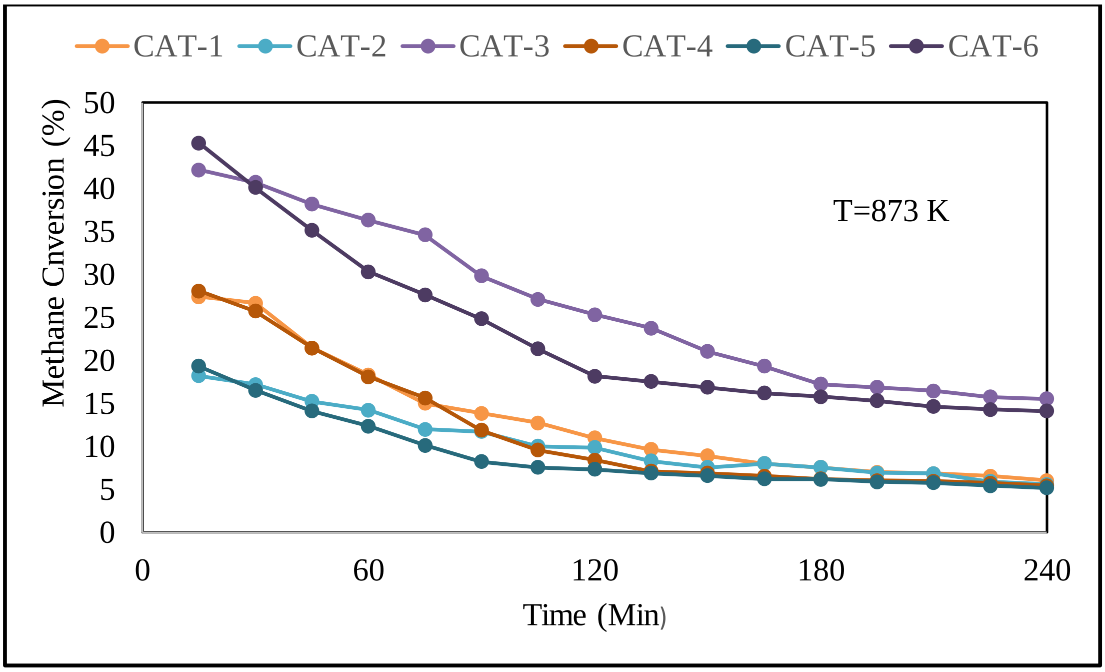


Figure 21 Methane conversion against time for reaction temperature of 873 K

The experimental results indicate that as reaction temperature is higher, the catalytic activity also increased significantly. The experimental studies indicate that methane conversion values were the lowest at T= 873 K for all the synthesized catalysts due to the reduced amount of energy available to break the C-H bonding within methane into hydrogen. The experimental results also indicates that the methane conversion decreases over time due to carbon deposition on the active sites of the catalysts, resulting in sintering and deactivation of the catalysts during the operation. This results is consistent with the observation and findings which were obtained from other studies (Uddin et al., 2014; Al-Hassani et al.,2014; Adrian *et al.*, 2012)in which the catalytic activity of the catalysts decrease rapidly within 2 hours on stream even though the initial hydrogen production rate was promising.

The methane conversion obtained for all the synthesized catalyst within 15 mins on stream are summarized in Table 14 .

Table 14: Methane conversion and hydrogen yield within 15 mins on stream

Catalyst	Temperature (K)					
	873		973		1073	
	CH_4 conv. (%)	H_2 yield (%)	CH_4 conv. (%)	H_2 yield (%)	CH_4 conv. (%)	H_2 yield (%)
CAT-1	27	27	38	38	47	47
CAT-2	18	18	23	23	36	36
CAT-3	42	42	57	57	67	67
CAT-4	28	28	39	39	48	48
CAT-5	19	19	25	25	37	37
CAT-6	45	45	59	59	70	70

The percentage of methane conversion has similar value with the percentage of hydrogen yield which suggested the production CO_x- free hydrogen gas because all of the reacted methane has been converted into hydrogen without the production of any by-products. This results is consistent with the experimental results which is reported by Mohd Zabadi *et al.* (2003) in which the all the methane is converted into pure hydrogen. The experimental results indicate that when Ni/Al_2O_3 catalyst is used for the methane cracking process without introducing Palladium as a promoter, the methane conversion below 1073 K is below 40%. At 973 K, the methane conversion is approximately 37% while the methane conversion is only 27% at 873 K. The methane conversion is the lowest for Pd/Al_2O_3 catalysts in which the methane conversion is only at 18-19% at 873 K and ~23% at 973 K. However, when palladium is introduced as promoter onto the nickel-based catalysts, the methane conversion has improved significantly from 48 % to 70 % at 1073K, from 38% to 58% at 973 K and from 28 % to 45 % at 673 K. The experimental results suggested that the formation of a strong Ni-Pd alloy bonding within the alumina-supported catalysts is beneficial for methane cracking process. This is because the formation of the Ni-Pd bonding increases the catalytic activity of the catalysts, which can catalyse a greater number of methane molecules to hydrogen and carbon.

The experimental results also suggested that the catalysts which are prepared by wet impregnation method gave higher intital methane conversion as compared to the copreicpitation technique. The difference in the catalytic performance can be explained in terms of the morphology and physico-chemical characteristics of the catalysts which were synthesized by using different methods. The SEM analysis and EDX mapping suggested that unlike the catalysts which were prepared by co-precipitation method which gives high and unform metal dispersion, the Palladium and Nickel particles tend to accumulate at the active sites of the catalysts. Therefore, methane gases is more actively absorbed onto the active sites of these catalysts to enable methane decomposition process to take place.

The methane conversion for the synthesized catalysts after they have been used for 240 mins on stream are summarized in Table 15.

Table 15 Methane conversion and hydrogen yield within 240 mins on stream

Catalyst	Temperature (K)					
	873		973		1073	
	CH_4 conv. (%)	H_2 yield (%)	CH_4 conv. (%)	H_2 yield (%)	CH_4 conv. (%)	H_2 yield (%)
CAT-1	6	6	11	11	15	15
CAT-2	5	5	10	10	16	16
CAT-3	16	16	20	20	25	25
CAT-4	5	5	9	9	13	13
CAT-5	5	5	8	8	13	13
CAT-6	14	14	15	15	16	16

From Table 15, it can be observed that the methane conversion after 4 hours on-stream for CAT-3 and CAT-6 are higher than the methane conversion which is obtained for the monometallic supported on alumina catalyst. This is atrributed to the presence of Palladium within the structure of the catalysts, which has enhanced the thermal stability of the catalyst at higher temperature by reducing the tendency of the catalyst to deactive due to coking and sintering. However, in constrast to the results which is obtained when the catalysts were allowed to be on-stream for 15 minutes, the Ni-Pd/Al_2O_3 catalyst which is prepared by wet impregnation method gave lower methane conversion after it has been used for 240 mins. This is because accumulation of Ni and Pd on the active sites results in more rapid carbon deposition, which blocks the pores and active sites of the catalyst. In addition, the the wrinkled and uneven surface of these catalyst promote higher chance for carbon to deposit on the active sites of the catalysts, leading to drastic decaying in the catalytic activity of the catalysts.

On the other hand, the Ni-Pd/Al_2O_3 catalyst which was prepared by co-precipitation method is more active after it has been used on-stream for 4 hours as compared to the wet impregnated catalyst. This is because the higher surface area and homogeneous morphology of the catalyst resulted in an improved capability of the catalyst to accumulate carbon, thus contributing towards higher operational lifetime of the catalysts by making it less susceptible to deactivation and coking. In addition, the uniform dispersion of Ni and Pd particles enables higher interaction between the catalyst and methane to take place, even when some of the active sites of the catalyst has been blocked by carbon particles.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

This chapter discusses about the conclusion of the progress for the research work. In addition, further recommendations for the future work have also been discussed in this section to ensure that this research work can be extended for more promising and significant results.

5.1 Conclusion

The morphology study on the synthesized cataysts by SEM and EDX mapping suggested that a homogeneous morphology is obtained by co-precipitation method while an uneven and wrinkled surface is achieved by wet impregnation method. In addition, the EDX analysis indicates that uniform Ni and Pd dispersion can be achieved by using co-precipitation technique while the Ni and Pd particles tend to accumulate at the active sites of the catalysts. Other than that, BET surface area analysis revealed that the catalysts which are prepared by co-precipitation method demonstrated higher surface area which is feasible for higher diffusion of methane molecule onto the pores of the catalysts during reaction, leading to higher reaction rate. TGA analysis on the catalysts suggested that all the synthesized catalysts demonstrated goof resistance towards decomposition at temperature as high as 800℃ while TPR profiles of the synthesized catalysts suggested the presence of a strong interaction between Ni and Pd particles in $Ni\text{-}Pd/Al_2O_3$ catayst because a complex reduction behavior which is quite distinct from that which should be observed from a simple combination of the profiles recorded for Ni/Al_2O_s catalysts and Pd/Al_2O_3 catalysts is obtained.

The testing of the cataytic activity through experimental work suggested that the introduction of Palladium on Ni/Al_2O_3 catalysts for thermo-catalytic decomposition of methane has increased the methane conversion below 1073 K to above 40%. The formation of Ni-Pd alloy on the alumina supported catalysts is beneficial to enhance the catalytic activity of the catalysts for all the operating temperature tested. In addition, it was observed that the presence of palladium enhanced the thermal stability of the Ni/Al_2O_3 at elevated temperature. The Ni/Al_2O_3 catalysts without Palladium loading which were prepared by both wet impregnation and co-precipitation method deactivated within 4 hours on-stream due to the formation of condensed encapsulating carbon particles on the active sites of the catalysts during operation.

On the other hand, the Ni-Pd/Al_2O_3 was observed to exhibit higher stability throughout the methane cracking reaction with slower deactivation rate. The improvement in thermal stability is attributed to the introduction of Pd loading onto the catalyst. The interaction between Pd with the Ni particles resulted in the formation of Ni-Pd alloys, which can improved its ability to accumulate carbon.This help to prolong the catalytic lifetime of the catalysts by making it less susceptible to sintering and coking. The experimental study also suggested an interesting trend in which the Ni-Pd/Al_2O_3 catalyst which was prepared by wet impregnation method gave the highest intial methane conversion which is due to the accumulation of Ni and Pd on the active sites of the catalyst, leading to higher catalytic activity. However, when the catalyst is allowed to be on-stream for 4 hours, the Ni-Pd/Al_2O_3 catalyst which is prepared by co-precipitation technique exhibits longer catalytic lifetime as compared to the wet impregnation method.

Further reseach work on the thermo-catalytic decomposition of methane over Ni-Pd/Al_2O_3 catalysts may pay higher attention and focus on the effect of different Pd and Ni loading onto the alumina supported catalysts. In addition, the effect of methane flowrate on the catalytic activity of the catalysts should be further investigated to enable high yield of hydrogen to be obtained at higher flowrate of methane. This is significant in order to make this process more promising and feasible for the application in the real industry.

5.2 Recommendations

As the research of thermal-catalytic decomposition is indefinitely wide, various future works can be performed to extend the research work to ensure more promising outcome. For the development of a novel catalyst which can reduce the activation energy and reaction temperature in which methane decomposition can take place, continuous research work has to be performed in the laboratory scale to explore the possible way to optimize the methane cracking process. The recommendations that are suggested for the future work are as follows:

i) Explore the possibility of using other types of metallic catalysts (i.e. Copper, Molybdenum and Ferum) in the thermal-catalytic decomposition of methane to hydrogen

ii) Explore the possibility of introducing different transition metals with the Nickel-based catalysts for the development of novel bimetallic and tri-metallic catalysts which can enhance methane cracking process

iii) Explore the effect of parameters such as concentration of solution and submerging time on the solid loading of catalysts

iv) Explore the utilization of other types of natural gases(ethane, propane, etc.) for decomposition to hydrogen

v) Detail study of the catalytic mechanism of methane decomposition of hydrogen at the molecular level by using Density Functional Theory (DFT)

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APPENDIX

A1 Preparation of standard stock solution

The molecular weights of the chemicals which are utilized for synthesizing of catalysts are indicated in the table below:

Component	Molecular Weight (g/mol)
$Ni(NO_3)_2.6H_2O$	290.81
$Al(NO_3)_3\ 9H_2O$	375.13
$Pd(NH_3)_4Cl_2.H_2O$	263.46

A2 Preparation of standard stock solution

A2.1 Preparation of standard Ni solution

Concentration of Ni solution= 0.1 g/mL

Metal salt used= $Ni(NO_3)_2.6H_2O$

Standard flask used=100mL

Weight of $Ni(NO_3)_2.6H_2O$ salt required

$$= 100mL \times \frac{0.1\ g\ Ni}{mL} \times \frac{290.81}{58.69} = 49.55\ g$$

A2.2 Preparation of standard alumina solution

Concentration of alumina solution= 0.25 g /mL

Standard flask used= 250 mL

Weight of $Al(NO_3)_3\ 9H_2O$ salt required

$$= 250\ mL \times \frac{0.25\ g}{mL} \times \frac{375.13}{101.96} = 229.94\ \text{g}$$

A2.3 Preparation of standard Pd solution

Concentration of Pd solution= 0.003 g /mL

Standard flask used= 100 mL

Weight of $Pd(NH_3)_4Cl_2.H_2O$ salt required

$= 100\ mL \times \frac{0.003\ g}{mL} \times \frac{263.46}{106.42}$= 0.74 g

A2 Preparation of catalyst using co-precipitation technique

Catalyst type 0.5 Ni-0.5Pd/99 Al_2O_3

Basis= 10 g of catalyst

Amount of alumina required

$= \frac{99}{100} \times 10\ g = 9.9\ g\ alumina$

Amount of $Al(NO_3)_3\ 9H_2O$ solution required

$= 9.9\ g\ alumina \times \frac{1\ mL\ solution}{0.25\ \ g\ alumina} = 39.6\ mL$ of alumina solution

Amount of Ni required

$= \frac{0.5}{100} \times 10\ g = 0.05\ g\ Ni$

Amount of Ni solution required

$= 0.05\ g\ Ni\ \times \frac{1\ mL\ solution}{0.1\ \ g\ Ni} = 0.5\ mL$ of Ni solution

Amount of Pd required

$=\frac{0.5}{100} \times 10\ g = 0.05\ g\ Pd$

Amount of Pd solution required

$= 0.05\ g\ Pd\ \times \frac{1\ mL\ solution}{0.003\ g\ Ni} = 16.67\ mL$ of Pd solution

A3 Preparation of catalyst using wet impregnation technique

Catalyst type 0.5 Ni-0.5Pd/99 Al_2O_3

Basis= 10 g of catalyst

Amount of alumina required

$= \frac{99}{100} \times 10\ g = 9.9\ g\ alumina$

Amount of Ni required

$= \frac{0.5}{100} \times 10\ g = 0.05\ g\ Ni$

Amount of Ni solution required

$= 0.05\ g\ Ni\ \times \frac{1\ mL\ solution}{0.1\ \ g\ Ni} = 0.5\ mL$ of Ni solution

Amount of Pd required

$=\frac{0.5}{100} \times 10\ g = 0.05\ g\ Pd$

Amount of Pd solution required

$= 0.05\ g\ Pd\ \times \frac{1\ mL\ solution}{0.003\ g\ Ni} = 16.67\ mL$ of Pd solution

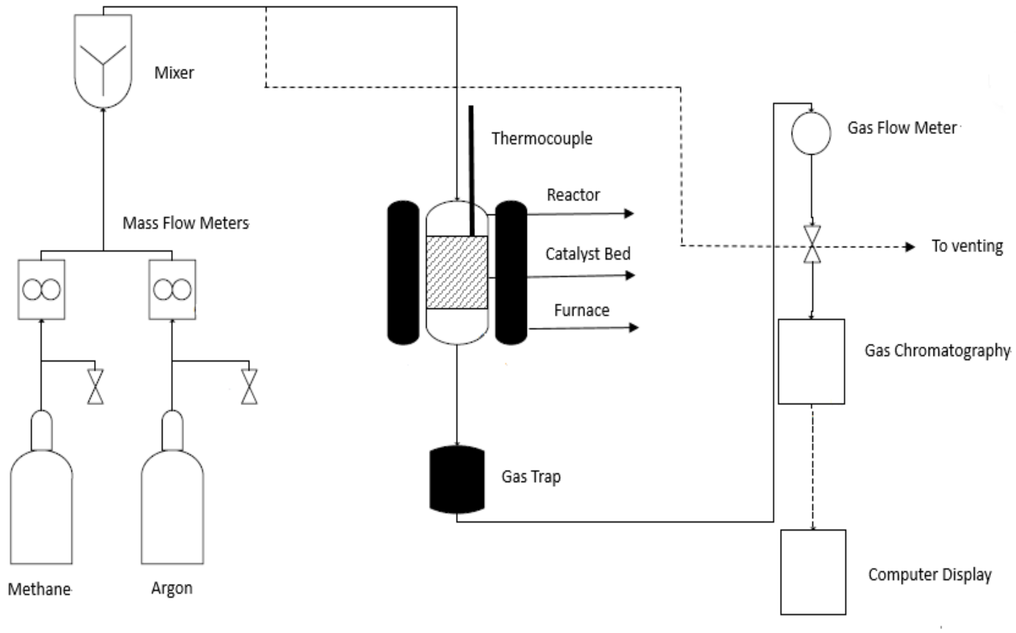
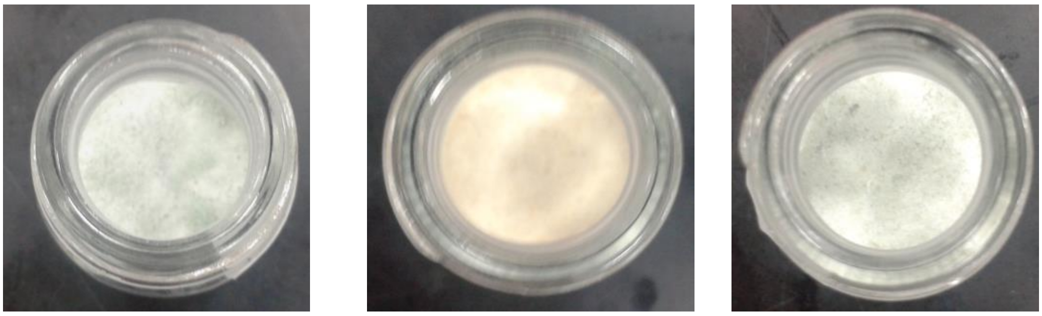
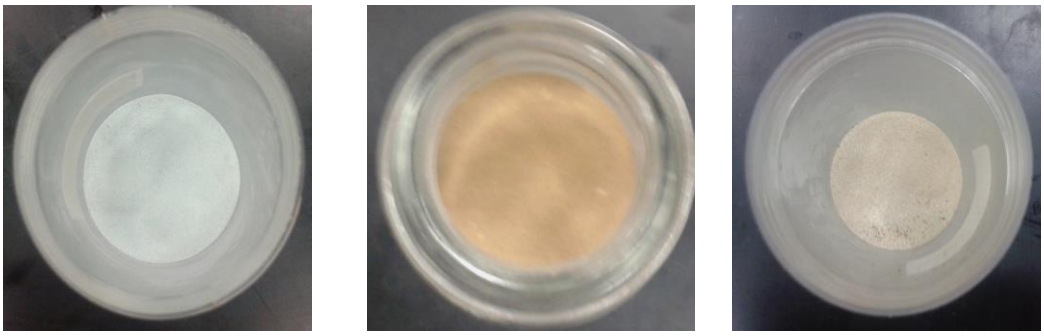


Figure A 1 Methane decomposition test rig for evaluation of catalysts performance

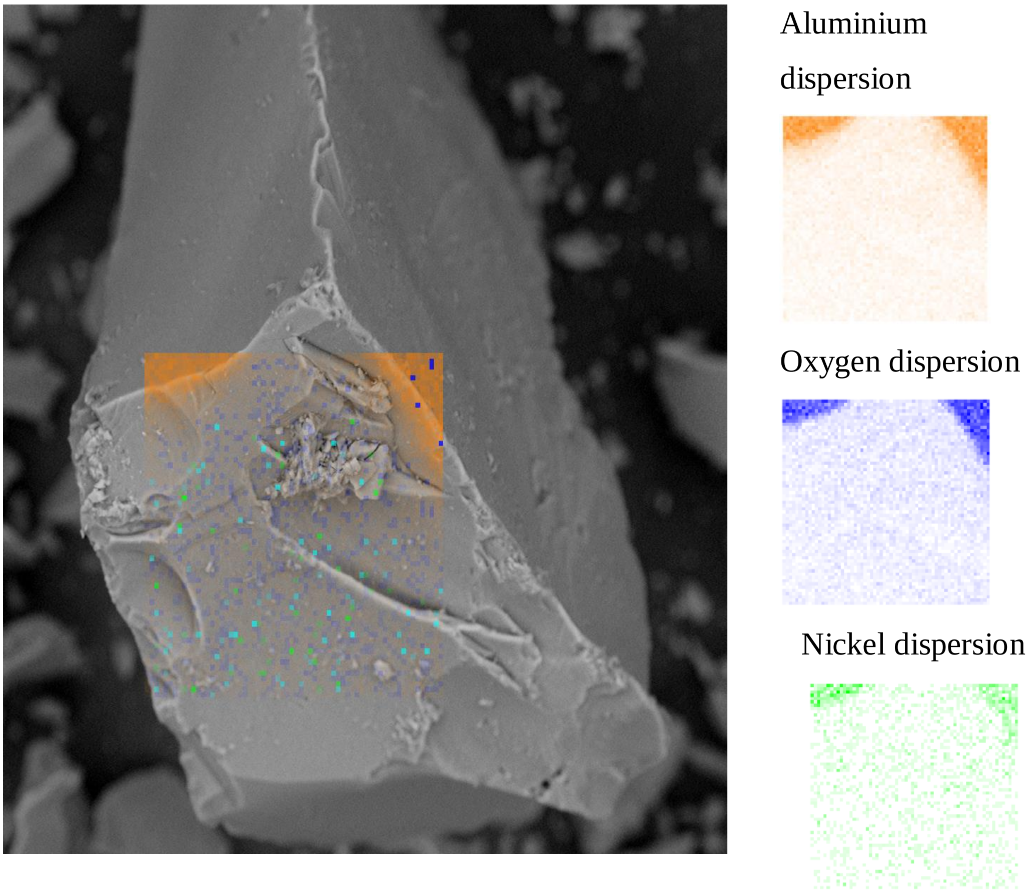


a) CAT-1 b) CAT-2 c) CAT-3



d) CAT-4 e) CAT-5 f) CAT-6

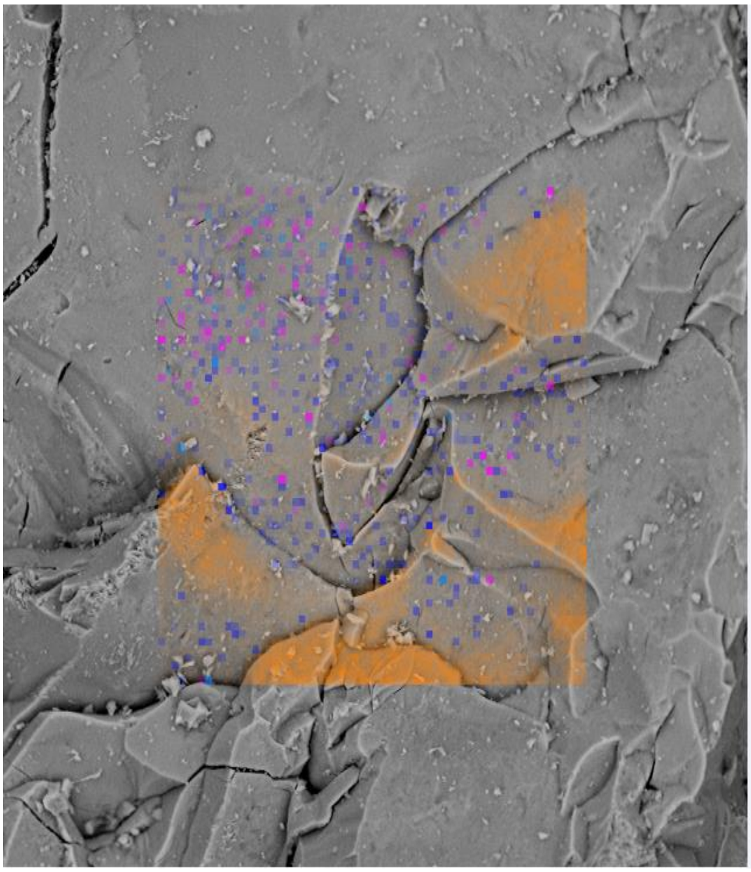
Figure A 2 Physical appearance of synthesized catalysts by co-precipitation and wet impregnation method


Aluminium dispersion

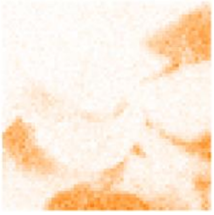
Oxygen dispersion

Nickel dispersion

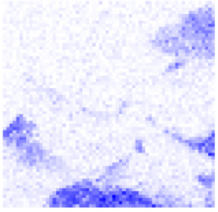
Figure A 3 EDX mapping for CAT-1 (1% Ni/99% Al_2O_3)



Aluminium dispersion



Oxygen dispersion



Palladium dispersion

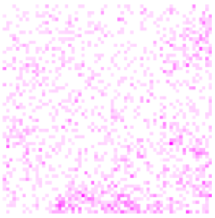


Figure A 4 EDX mapping for CAT-2 (1% Pd/99% Al_2O_3)

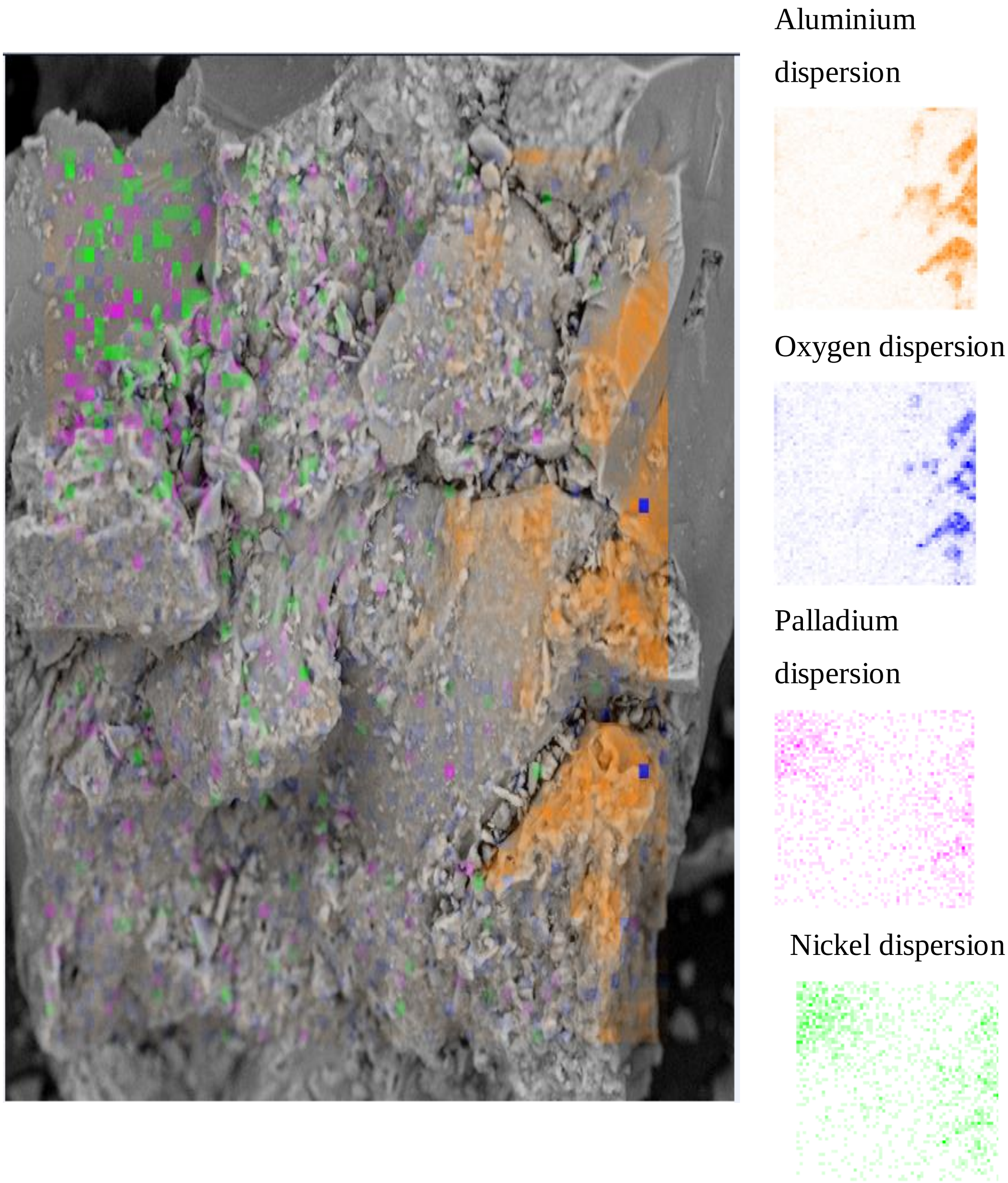
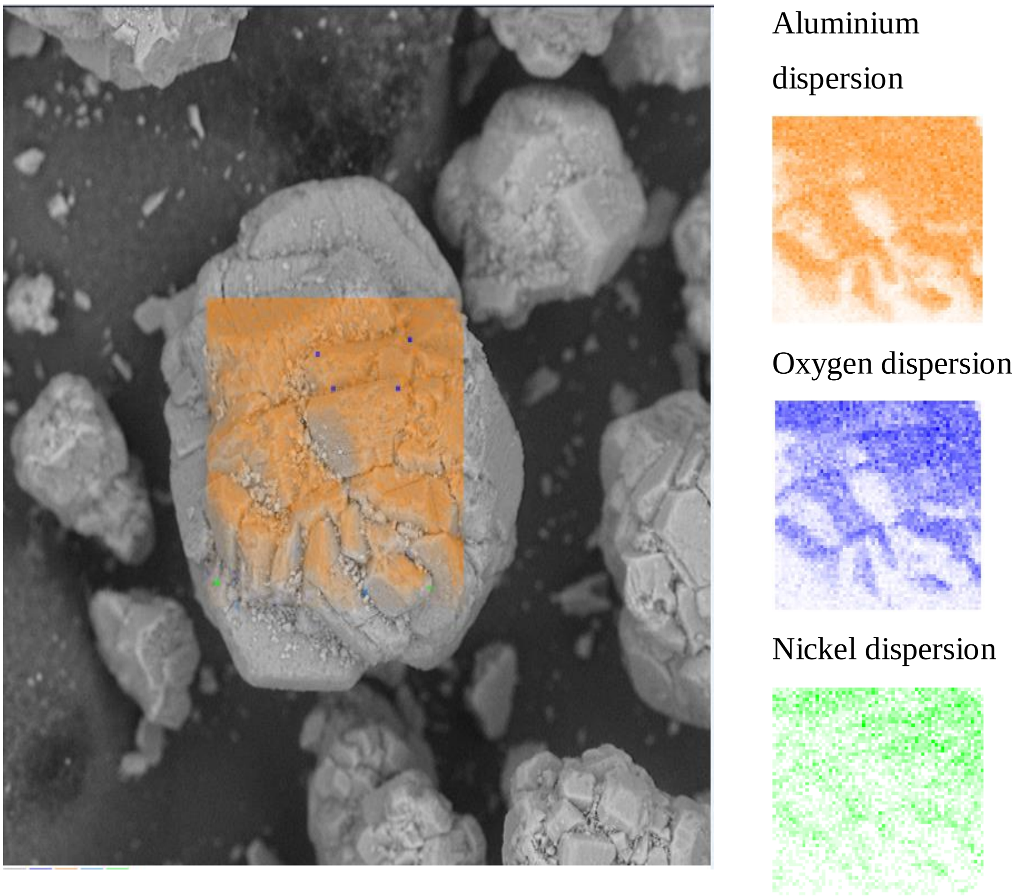


Figure A 5 EDX mapping for CAT-3 (0.5% Ni 0.5% Pd/99% Al_2O_s)



Aluminium dispersion

Oxygen dispersion

Nickel dispersion

Figure A 6 EDX mapping for CAT-4 (1%Ni/99% Al_2O_3)

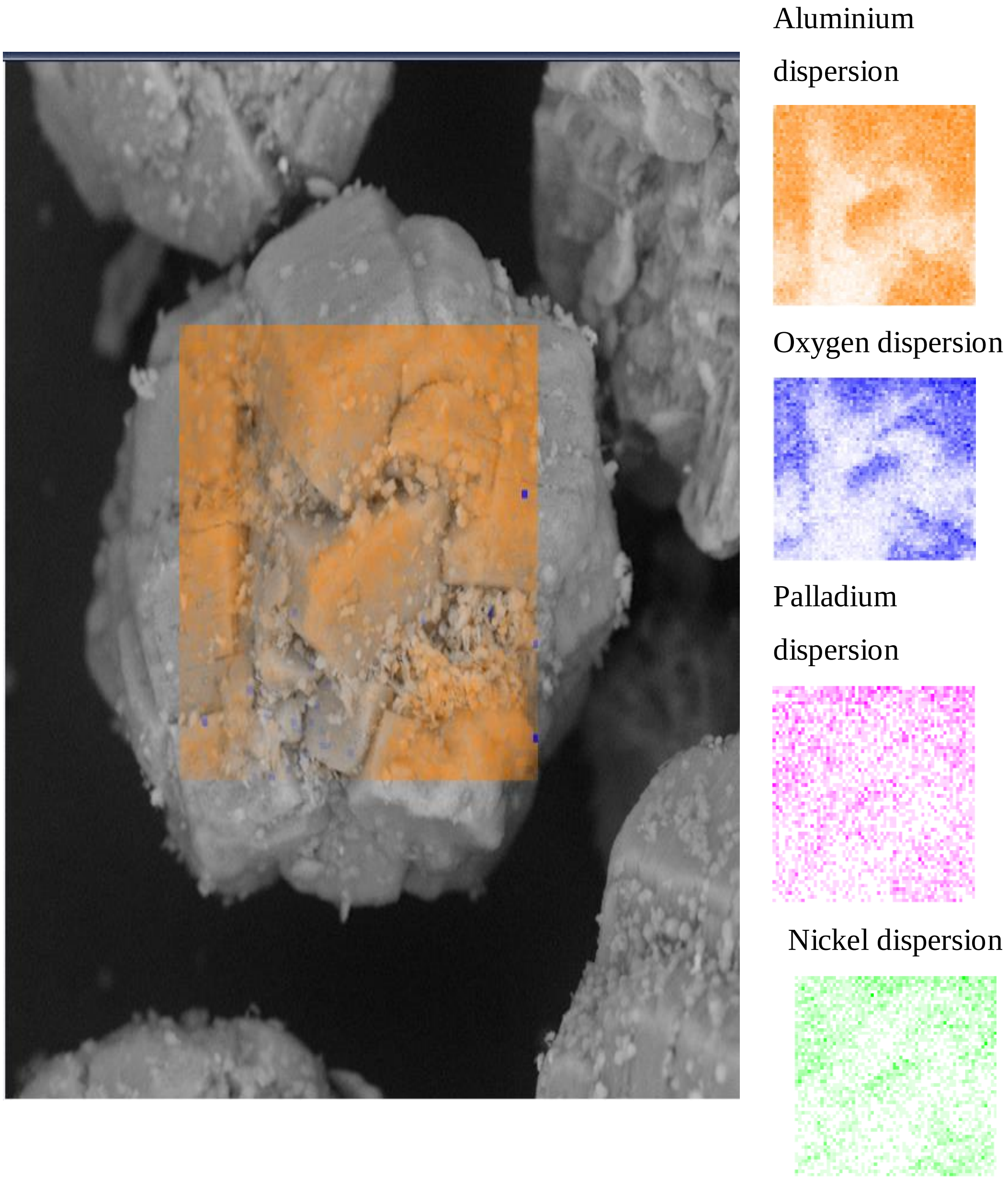
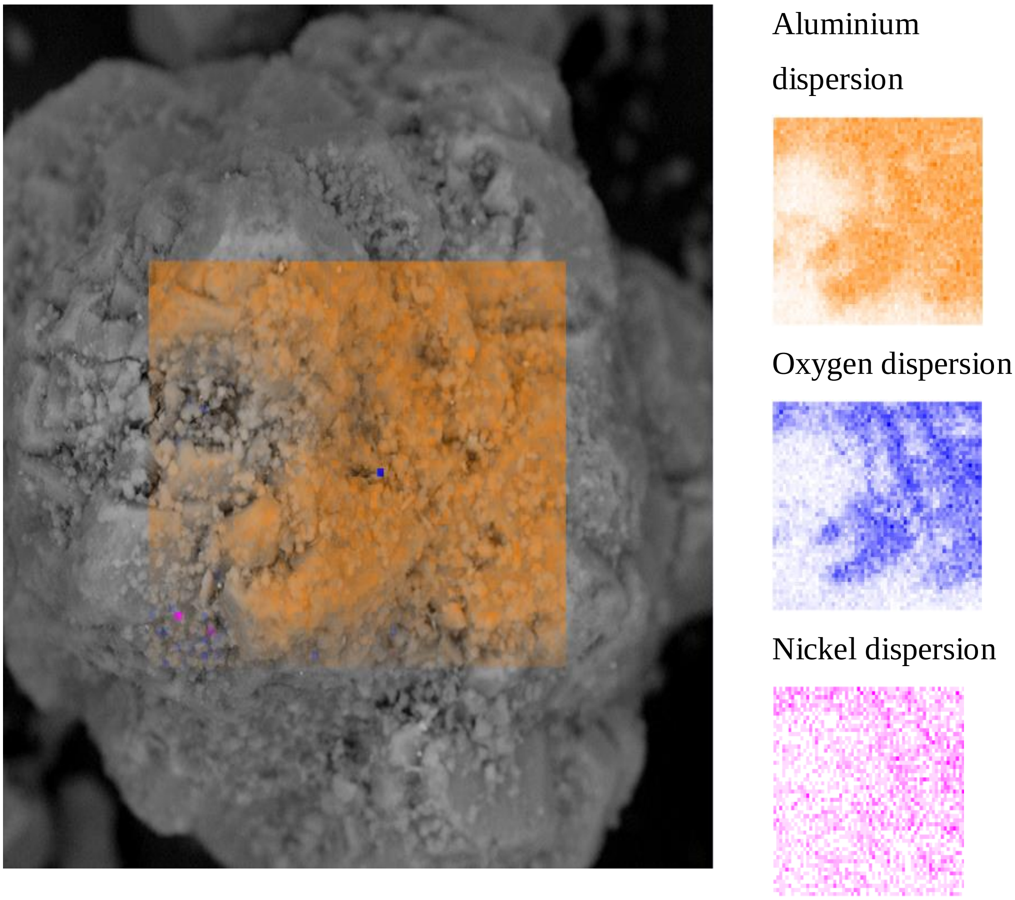


Figure A 7 EDX mapping for CAT-6 (0.5% Ni 0.5% Pd/99% Al_2O_3)



Aluminium dispersion

Oxygen dispersion

Nickel dispersion

Figure A 8 EDX mapping for CAT-5 (1%Pd/99% Al_2O_3)

Figure A 9 Deactivation of catalyst due to carbon formation