

METHANATION OF SIMULATED NATURAL GAS USING ALUMINA  
SUPPORTED MANGANESE DOPED RUTHENIUM AND PALLADIUM OXIDE  
CATALYST

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*To my beloved father, mother and sisters.*

*You are the sunshine of my life.*

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## ABSTRACT

Malaysian crude natural gas categorized as a sour gas due to the contamination of CO<sub>2</sub> other gases. Therefore in this research, manganese oxide doped noble metal oxides supported on alumina were prepared for methanation reaction to convert CO<sub>2</sub> to CH<sub>4</sub>. All prepared Ru/Mn-Al<sub>2</sub>O<sub>3</sub>(10:90, 20:80, 25:75, 30:70, 35:75 and 40:60) catalysts were calcined at 400°C, and 1000°C and Pd/Mn-Al<sub>2</sub>O<sub>3</sub>(10:90 and 30:70) catalysts were only calcined at 400°C for 5 hours separately in screening process. Ru/Mn(25:75)-Al<sub>2</sub>O<sub>3</sub> catalyst then being calcined at 700°C, 800°C, 900°C and 1100°C for optimization parameter. In-house-built micro reactor with Fourier Transform Infra Red, (FTIR) detector and Gas Chromatography, (GC) were used to study the catalytic activity. It was found that the catalyst with Ru/Mn(25:75)-Al<sub>2</sub>O<sub>3</sub> calcined at 1000°C showed 60.21% conversion of CO<sub>2</sub> and 57.84% formation of CH<sub>4</sub> at reaction temperature 200°C. When using two series furnace reactors, Ru/Mn(25:75)-Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 1000°C achieved 95.12% CO<sub>2</sub> conversion and 53.10% CH<sub>4</sub> formation at reaction temperature 100°C. The same catalyst with coating more than one coat reducing the catalytic reaction compared with single coat. The catalyst finally reached 100% CO<sub>2</sub> conversion with 100% CH<sub>4</sub> formation after through the 3<sup>rd</sup> testing using 100°C of reaction temperature. In pretreatment testing, the catalyst managed to get 100% CO<sub>2</sub> conversion with 100% CH<sub>4</sub> formation at first test at reaction temperature 100°C. For adding compressed gas (O<sub>2</sub>) testing, the catalyst shows 100% of CO<sub>2</sub> conversion with 100% CH<sub>4</sub> formation with only 6% of compressed gas loading at reaction temperature 100°C. Using 1% of H<sub>2</sub>S, reduce the potential of the catalyst compared with using 0.5% of H<sub>2</sub>S feed. FESEM illustrated the catalyst surface is covered with small and dispersed particles with undefined shape. The X-Ray Diffraction (XRD) analysis revealed that the catalyst is crystalline. Nitrogen Gas Adsorption (NA) analysis showed that both fresh and spent catalysts are of mesoporous material with Type IV isotherm and type H<sub>3</sub> hysteresis loop.

## ABSTRAK

Gas asli Malaysia tergolong sebagai gas masam disebabkan kewujudan gas karbon dioksida ( $\text{CO}_2$ ) dan gas beracun yang lain. Dalam penyelidikan ini, mangan oksida campuran logam noble oksida berpenyokong alumina dihasilkan untuk proses methanasi bagi menukarkan  $\text{CO}_2$  kepada  $\text{CH}_4$ . Kesemua pemangkin Ru/Mn- $\text{Al}_2\text{O}_3$ (10:90, 20:80, 25:75, 30:70, 35:75 dan 40:60) dikalsinkan pada suhu  $400^\circ\text{C}$  dan  $1000^\circ\text{C}$  manakala pemangkin Pd/Mn- $\text{Al}_2\text{O}_3$ (10:90 dan 30:70) dikalsinkan hanya pada suhu  $400^\circ\text{C}$  selama 5 jam setiap satu pada proses pemilihan. Pemangkin Ru/Mn(25:75)- $\text{Al}_2\text{O}_3$  pula kemudian dikalsinkan pada suhu  $700^\circ\text{C}$ ,  $800^\circ\text{C}$ ,  $900^\circ\text{C}$  dan  $1100^\circ\text{C}$  untuk proses pengoptimuman. FTIR dan GC digunakan untuk mengkaji aktiviti pemangkin. Ru/Mn(25:75)- $\text{Al}_2\text{O}_3$  kalsin pada  $1000^\circ\text{C}$  menunjukkan peratus penukaran  $\text{CO}_2$  sebanyak 60.21% dan pembentukan  $\text{CH}_4$  sebanyak 57.84% pada suhu penyelidikan  $200^\circ\text{C}$ . Bila menggunakan dua siri reactor pada relau, pemangkin yang sama menghasilkan 95.12% penukaran  $\text{CO}_2$  dan 53.10% pembentukan  $\text{CH}_4$  pada suhu penyelidikan  $100^\circ\text{C}$ . Pemangkin yang sama menunjukkan penurunan dalam reaksi apabila dilaputi lebih pada satu lapisan. Pemangkin tersebut juga mencapai 100% penukaran  $\text{CO}_2$  dan 100% pembentukan  $\text{CH}_4$  apabila melalui tiga kali ujian. Dalam proses rawatan, pemangkin memperolehi 100% penukaran  $\text{CO}_2$  dan 100% pembentukan  $\text{CH}_4$  pada ujian yang pertama pada suhu reaksi  $100^\circ\text{C}$ . Untuk kemasukan gas mampat, ( $\text{O}_2$ ) pemangkin menunjukkan 100% penukaran  $\text{CO}_2$  dan 100% pembentukan  $\text{CH}_4$  dengan hanya 6% kemasukan gas mampat pada suhu reaksi  $100^\circ\text{C}$ . Dengan menggunakan 1% jumlah  $\text{H}_2\text{S}$  pada system, ia mengurangkan potensi pemangkin berbanding apabila menggunakan 0.5% jumlah  $\text{H}_2\text{S}$ . FESEM menunjukkan permukaan pemangkin diselaputi dengan zarah-zarah halus dengan bentuk yang pelbagai. XRD analisis pula menunjukkan pemangkin adalah dalam bentuk kristal. NA pula menunjukkan pemangkin yang baru dan yang telah digunakan masing-masing adalah mempunyai ciri bahan mesoporous dan *Type IV Isotherm* juga  $\text{H}_3$  lengkokkan histerisis.

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**LIST OF ABBREVIATIONS**

C <sub>2</sub> H <sub>6</sub>	-	Ethane
C <sub>3</sub> H <sub>8</sub>	-	Propane
C <sub>4</sub> H <sub>10</sub>	-	Butane
N <sub>2</sub>	-	Nitrogen
LNG	-	Liquefied Natural Gas
GC-MS	-	Gas Chromatography-Mass Spectroscopy
UNIPEM	-	Unit Petroleum Malaysia
AW	-	Atomic Weight
BET	-	Brunnauer, Emmet and Teller
CH <sub>4</sub>	-	Methane
CO	-	Carbon monoxide
CO <sub>2</sub>	-	Carbon dioxide
EDX	-	Energy Dispersive X-Ray Analysis
FESEM	-	Field Emission Scanning Electron Microscopy
XRD	-	X-Ray Diffractogram
FTIR	-	Fourier Transform Infrared
GC	-	Gas Chromatography
H <sub>2</sub> S	-	Hydrogen sulfide
S	-	Sulphur
Mn	-	Manganese
Ru	-	Ruthenium
Pd	-	Paladium
Al <sub>2</sub> O <sub>3</sub>	-	Alumina
LH	-	Langmuir-Hinshelwood
MW	-	Molecular Weight
NA	-	Nitrogen Adsorption
KBr	-	Potassium Bromide
FID	-	Flame Ionization Detector

PDF	-	Powder Diffraction File
$\lambda$	-	Wavelength
$d^*_{obs}$	-	d spacing values obtained from XRD analysis
$d^*_{ref}$	-	d spacing values obtained from the reference
$2\theta$	-	Diffraction angles in degrees



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## CHAPTER 1

### INTRODUCTION

#### 1.1 Natural Gas

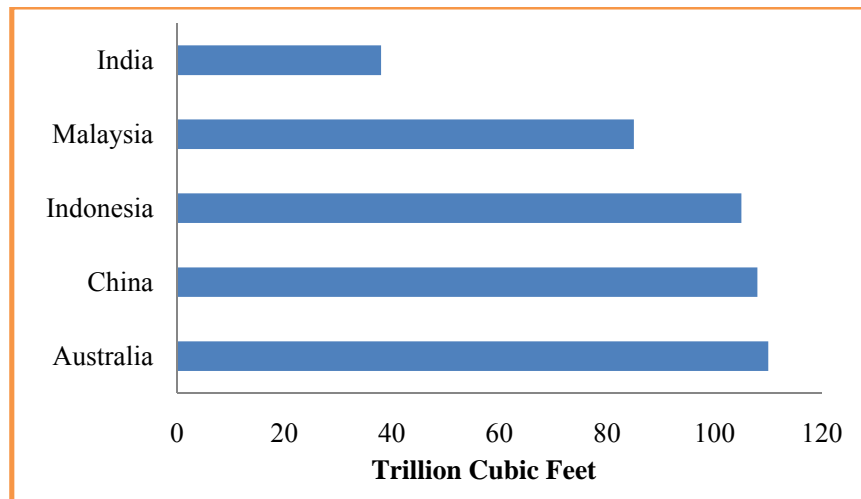
Natural gas can be normally described as the deep-seated or “fossil” gasses which are usually produced by the anaerobic decay of non-fossil organic material. This highly flammable and combustible gas is a homogenous liquid with low density and viscosity (Cury, 1981). The primary component of natural gas is methane ( $\text{CH}_4$ ) which depends on the heat, more likely formed in high temperature. It also contains heavier gaseous hydrocarbons such as ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ) and butane ( $\text{C}_4\text{H}_{10}$ ). Besides that it also contains other toxic and acidic gaseous impurities like  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{S}$ . Natural Gas considered as an environmental friendly clean fuel that offer important environmental benefits when compared to other fossil fuels. Natural gas requires minimal processing before use therefore natural gas is establishing world wide as the safest, cleanest and most application of all energy resource (Kidnay and Parish, 2006).

Natural gas that been found in oil fields contain both phases either dissolved or isolated crude. When this methane-rich gas is produced by the anaerobic decay of natural process, it is called biogas. The source of this biogas is at swamps, marshes and landfills. The process of organic mater is compressed under the earth at very high pressure for a long time is the natural converting organic matter to fossil

fuels. The higher temperature is exposed to the organic matter, more gas will be created. Deeper ground level usually contains natural gas having high pure methane.

Malaysia's oil productions normally located at offshore and near Peninsular Malaysia. There is also major production site in Sabah and Sarawak where all of this ranked Malaysia at the 14<sup>th</sup> largest gas reserves and 27<sup>th</sup> largest crude oil reserves in the world. Current oil reserves are estimated at approximately 3 billion barrels with a declining tendency, due to the lack of major new oil discoveries in the last years. Petronas is the state oil and gas company and followed by other company such as Sabah shell Petroleum Company and Sweden's Ludin Oil (T.G. Chuah *et al.*, 2006).

In Malaysia, the total natural gas reserves are three times larger than its oil reserves. It shows that Malaysia has a potential to develop more profit based on its total proven natural gas reserves of 2400 billion cubic metres. In year 2010, Malaysia recorded approximately 15% of total natural gas exports and was estimated to hold 83 trillion cubic metres of proven natural gas reserved as mentioned by EUMCCI (2011). About 60% of its marketed gas production is consumed domestically, three quarters (45%) of which is used for generating electricity. Malaysia is also the region's second largest LNG exporter, accounting for 14% of total world trade in LNG in 2002. Malaysia's reserves are mainly in eastern Malaysia, which is Sarawak and Sabah (59%) and the rest are at the offshore east coast of peninsular Malaysia. The largest gas field is in Miri, Sarawak, followed by Kota Kinabalu, Sabah.



**Figure 1.1:** Selected Southeast Asia proven natural gas reserves taken from EUMCCI, 2011

The country is seeking ways to increase its production of natural gas. Approximately 38% of Malaysia's reserves are under PetronasCarigaliSdn. Bhd. Malaysia also has offshore fields in the South China Sea, which are being developed by ExxonMobil (William, 2006). It is expected that total investment requirements in the gas sector will reach \$3.1 trillion, of which exploration and development will account for 55%, or \$1.7 trillion. Even though Malaysia succeeds in production of natural gas, it seems that the natural gas still consists more of the impurities such as sour gas, flue gas than any other country. This problem will absolutely lower the price of natural gas that Malaysia has produce but it also cause trouble distributing them.

Natural gas as one of the three main energy sources has many advantages such as combustible, abundant resource, lower price, high energy efficiency and gives a great deal of power upon consumption (Tiratsoo, 1979). In the chemical industry natural gas is becoming an alternative feedstock to crude oil whose supplies might run out in the present century (Borko and Guzzi, 2006). Table 1.1 shows the chemical composition of Malaysian crude natural gas, analyzed by using Gas Chromatography-Mass Spectroscopy (GC-MS). The primary component of natural gas is methane ( $\text{CH}_4$ ), the shortest and lightest hydrocarbon molecule. However, the gas often contains the other light alkanes and a variety of inorganic compounds that

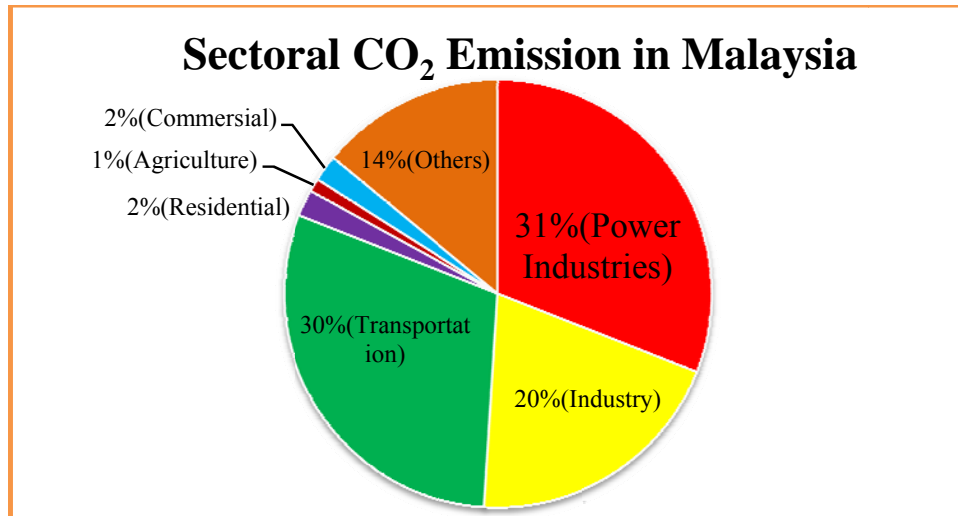
been called wet natural gas. It contains at most 20 to 30% of carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), helium (He) and hydrogen (H<sub>2</sub>).

**Table 1.1:** Chemical composition of Malaysian natural gas, source from Wan Azelee *et al.*, (2008)

<b>Gases</b>	<b>Composition (%)</b>
CH <sub>4</sub>	47.9
C <sub>2</sub> H <sub>6</sub>	5.9
C <sub>3</sub> H <sub>8</sub>	3.2
CO <sub>2</sub>	23.5
H <sub>2</sub> S	5.4
Others (CO, O <sub>2</sub> , N <sub>2</sub> )	24.1

Malaysian crude natural gas is categorized as a sour gas due to the contamination of H<sub>2</sub>S. The hydrogen sulfide in natural gas has several possible sources. One is the decomposition of amino acids which contain the thiol functional group, -SH. The anaerobic decay of sulfur-containing proteins or their thermal decomposition at mild conditions could liberate the sulfur as H<sub>2</sub>S. Similar to the H<sub>2</sub>S gas, CO<sub>2</sub> in the presence of water may enhance the production of carbonic acid which leads to the acid rain phenomena.

The development of technology that can increase the production and quality of Malaysian natural gas is not only the main thing, but it also came along with developing a green technology that meets the needs of society in ways that it can continue indefinitely into the future without damaging or depleting natural resources. With its rapid industrialization, Malaysia is becoming more and more dependent on conventional energy supplies such as fossil fuels. The escalating consumption of energy over the years that heavily relied on fossil fuels had resultant significant increment of greenhouse gas emissions (mainly carbon dioxide) from the sector (Rawshan and Joy, 2010). As the level of carbon dioxide increases the warming of the earth's surface will also increase (Schneider, 1989).



**Figure 1.2:** CO<sub>2</sub> emission in Malaysia according to sector taken Rawshan and Joy, 2010

## 1.2. Current Technologies Used in Purification of Natural Gas

Due to the various compositions of natural gas which contains not only hydrocarbons, but also non-hydrocarbons such as hydrogen sulfide and carbon dioxide which are considered as impurities, the natural gas must undergo several purification processes to produce high quality of natural gas. Gas purification involves the removal of vapour-phase impurities from gas stream. A variety of conventional separation methods are presently being used to remove the “acid gasses” CO<sub>2</sub> and H<sub>2</sub>S from crude natural gas. However, commercial application of the various gas-purification processes are frequently plagued by unpredictable problems of corrosion (Lieberman, 1987), side reactions, foaming (Cury, 1981), and catalyst deactivation (Trimm, 1980). A wide variety of acid gas removal technologies are available. They include absorption processes, such as the Benfield™ process (hot potassium carbonate solutions) and Amine Guard-FS™ process (formulated solvents); cryogenic processes; adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA) and iron sponge; and membranes (Du *et al.*, 2007)

Iron-sponge process is the oldest and also the most limited known for removal of sulfur compounds. It is a dry process consisting of iron oxide ( $\text{Fe}_2\text{O}_3$ ) impregnated on wood chips or shavings. It is usually used on small gas volumes with low  $\text{H}_2\text{S}$  contents. A vessel can operate 30 to 60 days either without any regeneration or with the partial generation that can be affected with air passage through the vessel. The vessel must be recharged with new iron-sponge material when gas sweetening is no longer possible. This process is selective toward  $\text{H}_2\text{S}$  only. Although this process seems to be less expensive, the operation and disposal of the spent sponge are difficult to handle. Hydrogen sulfide can also be removed by stripping. However, a toxic waste stream is created.

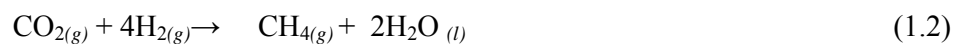
Alkanolamine process is commonly being used in the industry because it is a continuous operation liquid process using absorption for the acid gas removal with subsequent heat addition to strip the acid gas components from the absorbent solution (Herzog, H *et al.*, 2009). The primary disadvantages of this process are this process is not selective and absorbs total acid gas components. The absorbing alkanolamine solution (weak base) chemically reacts with the  $\text{H}_2\text{S}$  or  $\text{CO}_2$  (weak acid) to give a water soluble salt. Similarly, a significant amount of waste was formed with the absorption.

Among those techniques, membrane technique are selected to be the most practical technique for  $\text{H}_2\text{S}$  and  $\text{CO}_2$  removal because of this process has advantage in term of compactness, not having moving parts and being noise free. Currently, the only commercially viable membranes used for  $\text{H}_2\text{S}$  and  $\text{CO}_2$  removal are polymer based, for example, cellulose acetate, polyimides, polyamides, polysulphone, polycarbonates, and polyetherimide. However, this technique incurs high cost and low selectivity towards toxic gas separation (Houet *al.*, 2003). At present, the treatment of removing  $\text{CO}_2$  from the crude natural gas at Gas Refinery Plant was achieved using membrane technique. Meanwhile, the  $\text{H}_2\text{S}$  gas was removed using the catalyst known as Puraspec. Puraspec processes are based on fixed beds of catalysts and chemical absorbents which remove traces of contaminants from hydrocarbon gases and liquids. In particular the processes remove. Both of the above methods of treatment are very expensive and need stringent maintenance. As such,

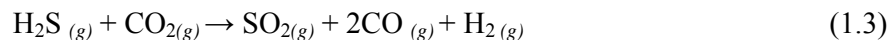
an alternative, viable and reliable cost effective method is crucial in running the production at cost effective mode.

In addition, hydrogen sulfide in the crud natural gas can be reduced to elemental sulfur by the Claus process (Smith, W. J *et al.*, 2007). H<sub>2</sub>S is partially burned to create a mixture of H<sub>2</sub>S and sulfur dioxide (SO<sub>2</sub>). The H<sub>2</sub>S and SO<sub>2</sub> then react in the presence of a catalyst to form sulfur and water. Sulfates formation is an undesired side reaction of Claus catalyst. However, when the proper metal is used, the spinel compound reacts to form sulfates that are unstable enough to react with H<sub>2</sub>S and other compounds to form elemental sulfur. Thus, sulfates do not inhibit catalyst performance. Then the sulfur produced can be sold commercially. There are problem arises when significant amounts of hydrocarbons reduce the catalyst efficiency. Hydrocarbons reduce to form graphite, which contaminates the sulfur.

Equation 1.1 shows the desulfurization reaction which is an endothermic process while Equation 1.2 shows the stoichiometric conditions for CO<sub>2</sub>/ H<sub>2</sub> conversion to methane.



Besides that, co-generation of heat is also possible because the methanation of CO<sub>2</sub> is an exothermic reaction, with  $\Delta H = -165$  kJ/mol. Removal of H<sub>2</sub>S is an oxidation reaction, while removal of CO<sub>2</sub> is a reduction reaction. Enthalpies of the reduction and oxidation reactions play an important role. CO<sub>2</sub> in this case can act as an oxidizing agent to oxidize the oxidation reaction.



The CO produced in the previous step can be converted to CH<sub>4</sub> in the presence of H<sub>2</sub>.





Moreover, the removal of sour gases via chemical conversion techniques using catalyst becomes the most promising technique. Methanation has received attention from a viewpoint of environmental protection because the emission of CO<sub>2</sub> in the atmosphere brings about global warming by the greenhouse effect and these harmful gases can simultaneously be converted to useful methane gas (Hayakawa *et al.*, 1999). This process can increase the purity of the natural gas without wasting the undesired components but fully used them to produce high concentration of methane. However, this reaction is an eight electron process involving thermodynamics. It is difficult to achieve this reaction under mild conditions due to kinetic barriers. These conditions are inconvenient in a laboratory because they required specialized equipment, and the rate of the reaction is difficult to control. Therefore, the development of catalysts to lower the activation energy of this reaction is needed.

Catalytic activity is defined as the rate at which a chemical reaction reaches the equilibrium. From the industrial point of view, activity is also defined as the amount of reactant transformed into product per unit of time and unit of reactor volume. Meanwhile, the selectivity of a catalyst is defined as the rate of reactant conversion into the desired products. Selectivity usually depends on reaction parameters such as temperature, pressure, reactants composition and also on the catalyst nature. Therefore, the main effect of a catalyst is to provide an alternative reaction path that permits to decrease the activation energies of the different reaction steps, reaching therefore the equilibrium in an easier and faster way. On the other hand, the catalyst should be high selectivity towards yielding of CH<sub>4</sub> and minimizes the possibility of side reactions. Equation 1.6 shows an undesired side reaction in this study.



Finally, present catalyst systems do not give high percentage of conversion due to instability of the catalysts at high temperature and the highly exothermic reaction of methanation reaction. Therefore, a new catalysts system must be studied in order to see what material can give the highest percentage conversion of CO<sub>2</sub> to methane from the methanation reaction. Since the catalytic process for methanation

reaction offer the best way to remove  $\text{CO}_2$  in the natural gas, therefore the researcher decided to carry an extensive study to develop a new effective catalyst was conducted using transition metal oxide based on manganese with modifying the dopants using noble metal such as paladium and ruhtenium which can give high conversion percentage of carbon dioxide to methane at low temperature.

### 1.3 Problem Statement

$\text{CO}_2$  removal is required because  $\text{CO}_2$  will form a complex,  $\text{CO}_2 \cdot \text{CO}_2$ , which is quite corrosive in the presence of water. For gas being sent to cryogenic plants, removal of  $\text{CO}_2$  may be necessary to prevent solidification of the  $\text{CO}_2$  (Sanjay, 1987). Moreover, according to United Nations Development Report (2007), Malaysia ranked as the 26<sup>th</sup> largest greenhouse gases emitters with the population over 27 million people. This showed that removing  $\text{CO}_2$  gases from natural gas is very important for maintaining a green environment.

In the presence of water,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  gases will react and lead to severe internal corrosion attack on the metallic piping and processing vessels. Moreover, carbon dioxide will reduce the heating value of a natural gas stream and wastes pipeline capacity. Carbon dioxide also may enhance the formation of carbonic acid when it reacts with the vapour. In addition,  $\text{H}_2\text{S}$  gases should be removed from the natural gas since it has an unpleasant smell, cause catalyst poisoning in refinery vessels and necessitates that many other expensive precautionary measures be taken. Thus it will add cost to the industry.

In addition, low temperature in natural gas process is very important because high temperature will require expensive construction materials for reactors therefore, methanation technology provide low reaction temperature. Even though others technologies have existing, there are still problems and limitation regarding to the technologies itself as discussed in Section 1.2. Thus,  $\text{CO}_2/\text{H}_2$  methanation technology is seen as the potential answer to all problems.

Many researchers chose to use Ni-based alumina supported system which is the traditional catalyst for methanation. One of the reason is because Ni are cheap and was proven to be able in producing high CO<sub>2</sub> conversion however, there are some point Ni are poor that is producing high CO<sub>2</sub> conversion at possible low reaction temperature and reproducibility properties. This is agreed by Wan Azelee (2011) in her researched using Pd/Ru/Ni (2:8:90)/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 400°C. After undergo 4<sup>th</sup> test of reproducibility testing, Pd/Ru/Ni (2:8:90)/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 400°C have 26.17% CO<sub>2</sub> conversion compared to fresh catalyst which was 43.60% at reaction temperature 200°C. Therefore, a new catalysts that have potential to convert CO<sub>2</sub> to CH<sub>4</sub> need to be found and it leed us to chose manganese as a n alternative based catalyst.

Several metals, including ruthenium are known to be active in CO<sub>2</sub>/H<sub>2</sub>methanation reaction however there are gap in findings in using ruthenium as dopant coupled with manganese as based catalyst. Ruthenium is believed to be known even more active in CO<sub>2</sub>/H<sub>2</sub>methanation reaction than other noble metals but is also considerable more expensive. By pairing with manganese and used as dopant material, small amount is only needed thus, create a good catalyst.

#### **1.4 Significant of Study**

In this research, the potential catalyst that can be used to remove which present in wet natural gas consisting of approximately 23% CO<sub>2</sub> was developed based on manganese oxide doped with noble metal. This catalyst offers very promising techniques for natural gas purification since unwanted CO<sub>2</sub> gas is being converted to the product, CH<sub>4</sub> thus will enhance the methane production.

The removal of acid gases (CO<sub>2</sub>, H<sub>2</sub>S and other sulfur components) from natural gas is often referred to as gas sweetening process. There are many acid gas treating processes available for removal of CO<sub>2</sub> natural gas. Besides, it may be necessary to avoid the corrosion and clogging to the delivery pipeline. This

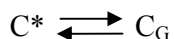
purification method will certainly improve the quality and quantity of Malaysian natural gas and increase the market price of our natural gas that will benefit to our country. The utmost important, the potential catalyst will contribute to the growth of the national economy and create green and sustainable environment.

The catalyst is easily prepared, environmental friendly and reusable. All the ingredients in the fabrication of the catalyst are easily available, cheap and stable. The beauty of the catalyst is safer to handle because it can be used at low reaction temperature. It requires minimum modification to the already existing system and offers cost effective operating system.

#### 1.4.1 Mechanism of Reaction Process

The researcher believe that in many cases of reaction process, it involves a Langmuir-Hinshelwood (LH) mechanism. This is because the most common surface reaction mechanism is one in which both reactants are adsorbed on the surface where they collide and form products. Adsorption, desorption and surface diffusion plays essential role in LH mechanism. It might be expected that the reaction rate should depend on surface coverage of both species.

Equation (1.7) shows the Langmuir-Hinshelwood equation which can be applied in any cases of surface reaction.



\* Adsorbed molecules

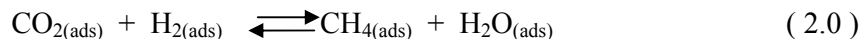
According to the equation (1.7) both compound are adsorbed without dissociation at different free sites on the catalyst surface. This is then followed by actual surface reaction between both activated species to produce the product,

adsorbed on the surface. Then the product is desorbed from the surface. In such a way, LH process assume that molecule from a fluid phase is in contact with a solid catalyst surface. The fluid phase will combine chemically with the solid surface. It will combine chemically with surface and reaction subsequently proceeds between chemisorbed molecule followed by desorption of the products.

#### 1.4.2 Mechanism of Methanation

Mechanism of methanation reaction has been studied a long time ago. A lot of researcher agreed that in methanation process involve LH mechanism to support the reaction process between active species and surface catalyst.

For the simplest possible reaction, methanation process can be describe as follows



\*S = Catalyst

According to Equation 1.8, carbon dioxide is reacting with the catalyst surface, (S) by chemisorptions and creates an active species that adsorbed onto catalyst surface. This is followed by hydrogen compound that also react with catalyst surface by chemisorptions and adsorbed onto catalyst surface as an active species. Both active species than react each other to produce products that is methane and water. Finally, (Equation 2.2) both products the researchers dissociated from the catalyst surface.

## 1.5 Research Objectives

The ultimate goal of this research is to synthesize a potential novel catalyst that is able to catalyze the reactions of CO<sub>2</sub> methanation at low temperature possible with as many conversions possible.

The objectives of the research are:

1. To synthesize potential manganese based catalyst doped with palladium and ruthenium for the methanation reaction.
2. To test the catalytic performance of the prepared catalysts towards methanation reaction.
3. To characterize the physical properties of the potential catalyst using various techniques for further understanding of the properties of the prepared catalyst.
4. To create a catalyst that can be regenerated.

## 1.6 Scope of Research

In this research, the series catalyst based on manganeseoxide doped noble metal from selected noble metals such as palladium and ruthenium that was prepared using impregnation method and also modification sol-gel method will be used for the synthesizing of manganese oxide based catalyst. Micro-reactor was used to prepare the catalysts activity by simulation natural gas and was monitored by FTIR and GC. The simulation is done by mixing the hydrogen gas and carbon dioxide for methanation process while desulphurization process is done by using hydrogen sulphide.

Then the potential catalyst was characterized using instruments such as X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope – Energy Dispersive X-ray Analysis (FESEM - EDX), Nitrogen Adsorption Analysis (NA), Fourier Transform Infrared Spectroscopy (FTIR)

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