

NICKEL AND COBALT OXIDES BASED CATALYSTS FOR THE  
METHANATION REACTION

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*Specially dedicated to my beloved family and buddies for the continuous supports  
and prayers*

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## ABSTRACT

The presence of acidic and toxic gases of carbon dioxide (CO<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S) will lead to the corrosion in natural gas pipeline system and material in processing plant. Alternatively, CO<sub>2</sub> and H<sub>2</sub>S can be removed using green technology via catalytic methanation reaction by converting CO<sub>2</sub> to methane (CH<sub>4</sub>) gas. Nickel (Ni) and cobalt (Co) oxides are well known catalysts to exhibit higher activity however they are easily deactivated. It is essential to activate these catalysts by incorporating dopants to enhance the catalytic performance. So far, the alteration of these oxides catalysts by adding zirconium, cerium and samarium dopants did not boost up the activity. In this research, a series of alumina (Al<sub>2</sub>O<sub>3</sub>) supported Ni/Co oxides based catalysts doped with manganese (Mn) and noble metal oxides such as ruthenium (Ru) and palladium (Pd) were prepared by wetness impregnation method followed by calcination. Various parameters were studied in this research include compositions of catalyst, calcination temperatures, effect of H<sub>2</sub>S gas, different Mn precursors, effect of sonication, two series furnace testing, reproducibility and stability testing towards CO<sub>2</sub>/H<sub>2</sub> methanation reaction. The catalysts were subjected to characterization process using various techniques such as XRD, FESEM-EDX, Nitrogen Adsorption, TGA-DTG and FTIR in order to study their physical properties. XRD diffractogram illustrated that the supported catalysts were in amorphous state at 1000°C calcination temperature and became crystalline at 1100°C. FESEM micrographs showed that both fresh and used catalysts have spherical shape with small particle sizes in agglomerated and aggregated mixtures. Elemental analysis performed by EDX confirmed the presence of Al, O, Ni, Co, Mn and Ru on the catalysts. Nitrogen Adsorption analysis revealed that both catalysts were in mesoporous structures with BET surface area in the range of 46-60 m<sup>2</sup>/g. The prepared catalysts were subjected to catalytic screening using micro reactor coupled with FTIR to study the performance of the catalysts by determining the percentage of CO<sub>2</sub> conversion, meanwhile the percentage of CH<sub>4</sub> formation was analyzed using GC. For nickel based catalyst, Ru/Mn/Ni(5:35:60)/Al<sub>2</sub>O<sub>3</sub> calcined at 1000°C was found to be the potential catalyst which gave 99.74% of CO<sub>2</sub> conversion and 72.4% of CH<sub>4</sub> formation at the maximum reaction temperature of 400°C. This catalyst can be reused for seven recycles without treatment. Meanwhile, for cobalt oxide based catalyst, Ru/Mn/Co(5:40:55)/Al<sub>2</sub>O<sub>3</sub> calcined at 1000°C was found to be the most potential catalyst which gave 96% of CO<sub>2</sub> conversion at low reaction temperature of 250°C with 76% of CH<sub>4</sub> formation. This catalyst can be reused for three recycles without treatment. In the presence of H<sub>2</sub>S, the CO<sub>2</sub> conversion exhibited very low conversion to CH<sub>4</sub> for both Ru/Mn/Ni(5:35:60)/Al<sub>2</sub>O<sub>3</sub> and Ru/Mn/Co(5:40:55)/Al<sub>2</sub>O<sub>3</sub> catalysts.

## ABSTRAK

Kehadiran gas berasid dan toksik seperti karbon dioksida ( $\text{CO}_2$ ) dan hidrogen sulfida ( $\text{H}_2\text{S}$ ) akan menyebabkan hakisan dalam sistem penyaluran gas asli dan bahan-bahan dalam loji pemprosesan. Secara alternatif,  $\text{CO}_2$  dan  $\text{H}_2\text{S}$  boleh dirawat dengan menggunakan teknologi hijau melalui tindak balas metanasi bermangkin yang menukarkan  $\text{CO}_2$  kepada metana ( $\text{CH}_4$ ). Nikel (Ni) dan kobalt (Co) oksida diketahui umum dapat memberi aktiviti yang tinggi namun mereka mudah dinyahaktifkan. Justeru itu, adalah amat penting untuk mengaktifkan mangkin ini dengan penambahan dopan untuk meningkatkan prestasi mangkin. Setakat ini, penambahbaikan terhadap kedua-dua mangkin dengan dopan zirkonia, cerium dan samarium tidak dapat meningkatkan aktiviti pemangkinan. Dalam kajian ini, satu siri mangkin yang berasaskan Ni/Co berpenyokong alumina ( $\text{Al}_2\text{O}_3$ ) yang didopan dengan oksida mangan (Mn) dan logam nadir seperti rutenium (Ru) dan paladium (Pd) telah disediakan menggunakan kaedah pengisitepuan basah dan diikuti dengan pengkalsinan. Pelbagai parameter telah digunakan dalam kajian ini, antaranya ialah komposisi mangkin, suhu pengkalsinan, kesan gas  $\text{H}_2\text{S}$ , perbezaan Mn pemula, kesan sonikasi, ujian dua siri reaktor, ujian kebolehulangan dan kestabilan terhadap tindak balas metanasi  $\text{CO}_2/\text{H}_2$ . Mangkin yang disediakan dicirikan menggunakan pelbagai teknik seperti XRD, FESEM-EDX, penyerapan nitrogen, TGA-DTG dan FTIR untuk mengkaji sifat-sifat fizikal mangkin tersebut. Belauan XRD menunjukkan mangkin berkeadaan amorfus pada suhu pengkalsinan  $1000^\circ\text{C}$  dan menjadi hablur pada suhu  $1100^\circ\text{C}$ . Mikrograf FESEM menggambarkan kedua-dua mangkin sebelum dan selepas digunakan berbentuk sfera dengan saiz yang kecil dalam campuran aglomerat dan agregat. Analisis unsur daripada EDX mengesahkan kehadiran Al, O, Ni, Co, Mn dan Ru pada permukaan mangkin. Analisis jerapan nitrogen menunjukkan kedua-dua mangkin dalam keadaan liang bersaiz meso dengan luas permukaan BET di dalam julat  $46\text{-}60\text{ m}^2/\text{g}$ . Mangkin tersebut telah menjalani ujian saringan dengan menggunakan reaktor mikro bersambung dengan FTIR untuk mengkaji prestasi setiap mangkin dengan menentukan peratusan penukaran  $\text{CO}_2$ , manakala peratusan penghasilan  $\text{CH}_4$  dianalisis oleh GC. Untuk mangkin berasaskan nikel, Ru/Mn/Ni(5:35:60)/ $\text{Al}_2\text{O}_3$  yang dikalsin pada suhu  $1000^\circ\text{C}$  merupakan mangkin berpotensi yang telah menghasilkan 99.74% penukaran  $\text{CO}_2$  dan pembentukan 72.4%  $\text{CH}_4$  pada suhu tindak balas maksimum,  $400^\circ\text{C}$ . Mangkin ini menunjukkan kebolehulangan sebanyak tujuh kali tanpa rawatan. Sementara itu, mangkin Ru/Mn/Co(5:40:55)/ $\text{Al}_2\text{O}_3$  yang dikalsin pada suhu  $1000^\circ\text{C}$  merupakan mangkin berpotensi yang telah menghasilkan 96% penukaran  $\text{CO}_2$  dan 76% pembentukan  $\text{CH}_4$  pada suhu tindak balas yang rendah iaitu  $250^\circ\text{C}$  bagi mangkin berasaskan kobalt. Mangkin ini menunjukkan kebolehulangan tiga kitaran tanpa perlu rawatan. Dengan kehadiran  $\text{H}_2\text{S}$ , peratusan penukaran  $\text{CO}_2$  kepada  $\text{CH}_4$  bagi mangkin Ru/Mn/Ni(5:35:60)/ $\text{Al}_2\text{O}_3$  dan Ru/Mn/Co(5:40:55)/ $\text{Al}_2\text{O}_3$  adalah rendah.

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**LIST OF ABBREVIATIONS**

ASTM	American Society for Testing Material
BET	Brunnauer, Emmet and Teller
Cu K	X-ray diffraction from Copper K energy levels rate of conversion (percentage)
DEA	Diethanolamine
DIPA	di-isopropanolamine
DGA	Diglycolamine
EPA	Environmental Protection Agency
FESEM-EDX	Field Emission Scanning Electron Microscope- Energy Dispersive X-Ray
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
FTS	Fisher-Tropsch synthesis
GC	Gas Chromatography
K	Kelvin
kPa	Kilo pascal
LNG	Liquefied Natural Gas
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MPa	Mega pascal
NA	Nitrogen Gas Adsorption
PDF	Powder Diffraction File
TEA	Triethanolamine
Tcf	Trillion cubic feet
TGA-DTA	Thermogravimetry Analysis-Differential Thermal Analysis
TPR	Temperature Programmed Reduction
TOF	turnover frequency

WGS	Water gas shift
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

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## **CHAPTER I**

### **INTRODUCTION**

#### **1.1 Background of Study**

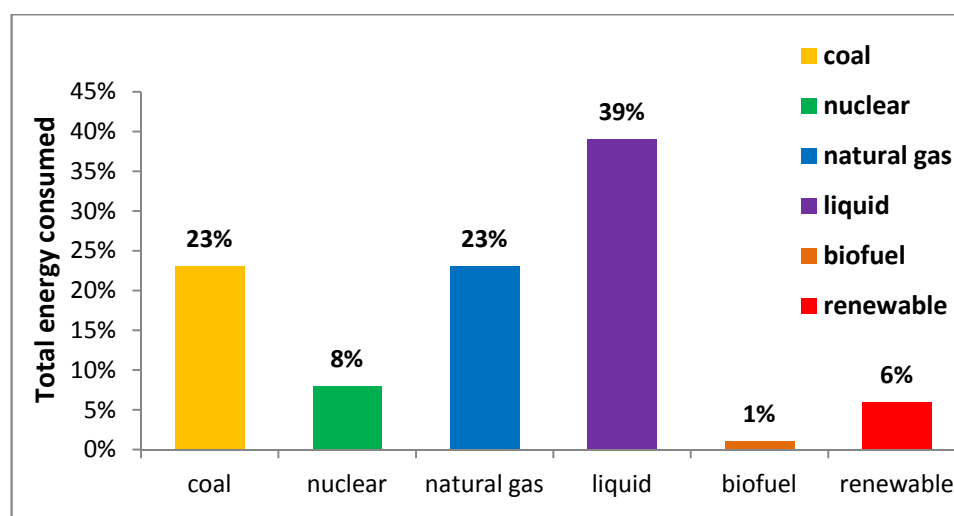
Environmental pollution received a great global concern since it could affect the living things and earth. Chemicals, particulate matter and biological materials which released into the air are known as a pollutant which can lead to the air pollution. Numbers of anthropogenic (human) activities which mostly related to the different kind of fuel burning have been responsible to these severe pollutions. Amongst the most significant are the power plants, manufacturing factories, petrochemical refineries, waste incinerations and much more. Vehicles, chemicals, and waste deposition in landfills as well as natural sources also may contribute to the releasing hazardous substance into the air. Air pollution may cause the deterioration of air quality and give negative impact to the human health and damage to the living organisms such as food crop and natural environment. Thus, it is very necessary to control the pollutants released into the air by giving much effort to obtain clean environmental.

Since emission from burning fuel and vehicles become a major contribution to the air pollution, it is very important to overcome this problem. According to Environmental Protection Agency (EPA), coal and oil release higher level of harmful gas emissions which contain carbon, sulfur dioxide, nitrogen oxides as well as particulate matters. Alternatively, natural gas can be used in many ways to reduce the emissions of pollutants into the atmosphere to maintain a clean and healthy environment. Burning of natural gas is considered as environmental friendly clean

fuel and emits few harmful pollutants. Moreover, natural gas is economical and efficient energy since directly delivered to the customer's facility through safe and efficient pipeline system.

Natural gas can be ascribed as the deep-seated or 'fossil' gases which usually composed of hydrocarbons and non-hydrocarbons compounds in various proportions. This highly flammable and combustible gas normally found associated with crude petroleum as gaseous phase of crude oil (Tiratsoo, 1979). It is also can be found in oil, natural gas and coal fields. Natural gas is well established in the world which supplies 23.5% of energy sources (Kidnay and Parish, 2006). Moreover, natural gas known as the most cleanest, safest and has been applied in various sectors.

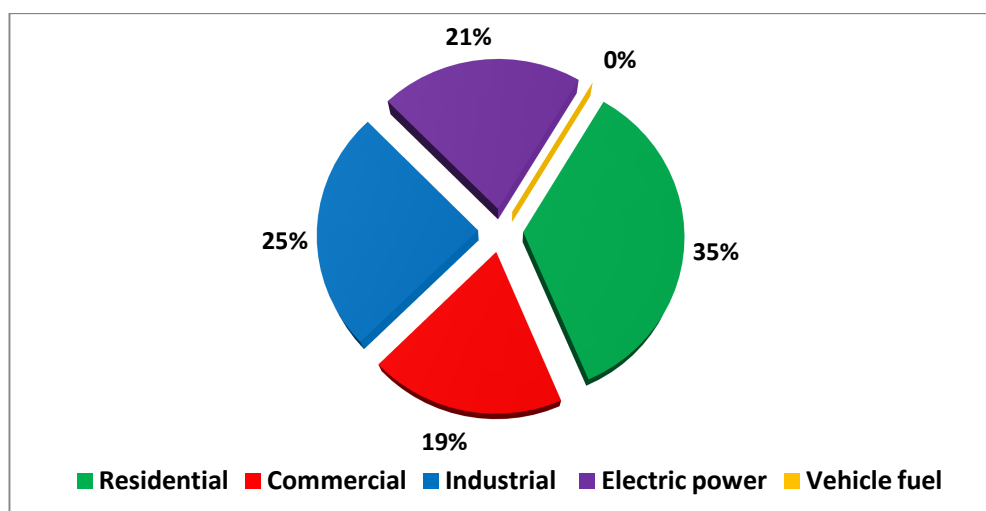
According to the Energy Information Administration (EIA), about 23% of the energy consumption comes from natural gas making it a vital component of the nation's energy supply. Total energy consumed in the US as depicted in Figure 1.1.



**Figure 1.1** Total Energy Consumed in the U.S.-2007 (Source: EIA-Annual Energy Outlook 2009)

Since natural gas offers a number of environmental benefits over other sources of energy, it has been utilized across all sectors. Figure below gives an idea of the proportion of natural gas used per sector. About 35% of natural gas is mainly consumed by the residential sector than others. Home owners use natural gas for heating, cooking, clothes drying and gas fireplaces and logs. While, the commercial

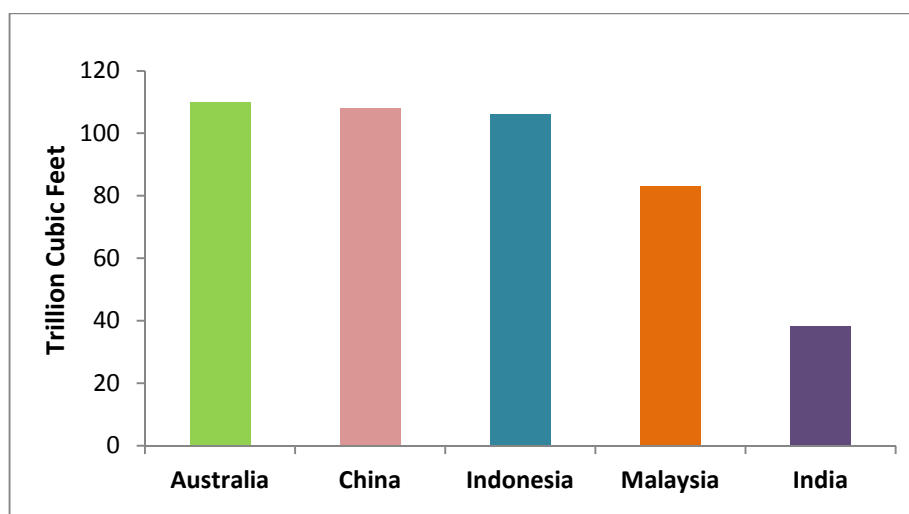
sector such as office buildings, schools and hotels, use natural gas for space heating, water heating and cooling. Thousands of factories also consume natural gas as a fuel burning as industrial customers. The fraction of natural gas consumptions by sectors are shown in Figure 1.2.



**Figure 1.2** Natural Gas Consumption by Sector (Source: EIA – Annual Energy Outlook 2009)

### 1.1.1 Natural Gas in Malaysia

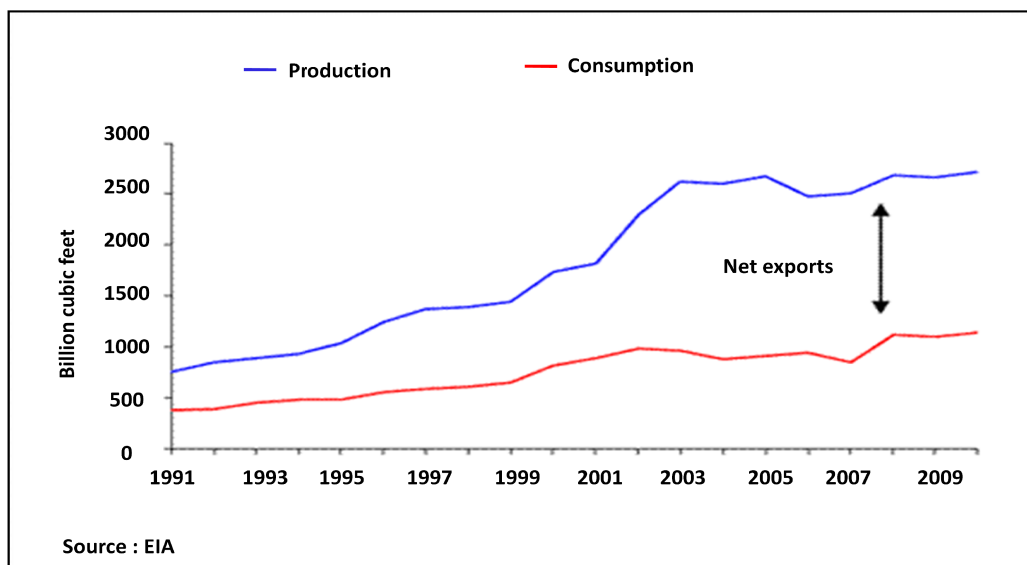
Malaysia which strategically located in the middle of important routes for the seaborne energy trade of the Straits of Malacca and South China Sea is a major oil and natural gas producer. Malaysia has 83 trillion cubic feet (Tcf) of proven natural gas reserved dated January 2011 as stated in Oil and Gas Journal. In Asia-Pacific, Malaysia was recognized as the fourth largest natural gas reserves holder as shown in Figure 1.3. Most of the Malaysian gas reserves are located in the eastern area, predominantly offshore Sarawak which contributes 48% of the gas, meanwhile 38% and 14% of gas reserves at peninsular Malaysia and offshore Sabah, respectively (Gas Malaysia Sdn. Bhd.).



**Figure 1.3** Natural gas reserves in Asia-Pacific (Source: Oil and Gas Journal)

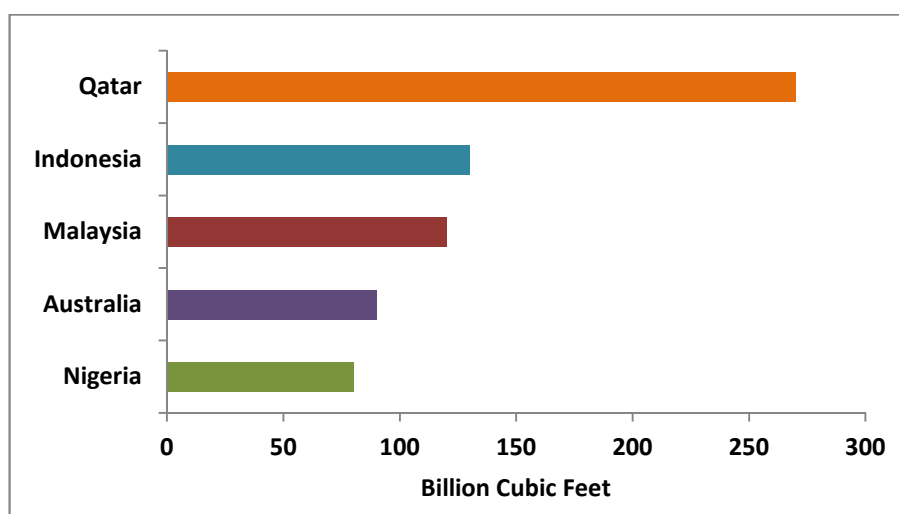
Oil and natural gas sectors in Malaysia are dominated by Petronas, in which has monopoly on all upstream and downstream natural gas developments and liquefied natural gas (LNG) trade. Petronas has collaborated with foreign companies such as Shell and Murphy Oil in operating natural gas production. The production of raw natural gas has been increased progressively until it reached 2.7 Tcf in 2010. Meanwhile, domestic natural gas consumption in various sectors such as residential, commercial and industrial has increased to 1.1 Tcf in 2010 in which 42% of gas production. There are several important projects ongoing on the offshore Sarawak and Sabah such as Malaysia-Thailand Joint Development Area (JDA) and New Sarawak Natural Gas Projects are expected to enlarge natural gas production. Figure 1.4 displays the production and consumption of Malaysia natural gas from the year 1991-2010.





**Figure 1.4** Malaysian natural gas production and consumption 1991-2010

The main hub and the largest Malaysian natural gas are located in Bintulu, Sarawak. In 2010, Malaysia was the third largest exporter of liquefied natural gas (LNG) in the world after Qatar and Indonesia, which 1 Tcf of LNG is estimated at 10% of total world LNG export. Malaysian natural gas has been supplied to Japan, South Korea, Taiwan and China since they are the largest purchasers. Mostly, LNG is transported by Malaysia International Shipping Corporation (MISC), which owns and manages 27 LNG tankers. MISC is 62% owned by Petronas which holds majority interests in three LNG processing plants at Bintulu, Sarawak (offshore fields). Figure 1.5 shows the world LNG exporters in the year 2010.



**Figure 1.5** Top world LNG exporters in year 2010

However, crude Malaysian natural gas consists of CO<sub>2</sub> and H<sub>2</sub>S at higher percentages which considered as sour natural gas. Sour gas is unfavorable because it contains sulfur compounds and carbon dioxide that can be extremely harmful which will lead to severe environmental pollution and corrode the pipeline system. The chemical composition of Malaysian natural gas and United State before it is being refined is shown in Table 1.1. Since Malaysian natural gas consists of 23% of CO<sub>2</sub> and 5% of H<sub>2</sub>S, it is necessary to purify in order to remove all the impurities and to enhance the production of methane.

**Table 1.1** Composition of natural gas between United State and Malaysia

Chemical Name	United State (%)	Malaysia (%)
Methane (CH <sub>4</sub> )	89	48
Carbon dioxide (CO <sub>2</sub> )	2	23
Hydrogen sulfide (H <sub>2</sub> S)	1	5
Others	8	24

Prior to transporting to end-use markets, natural gas is processed to meet pipeline quality standards or conventional practice. According to American Society for Testing Material (ASTM), the minimum and maximum qualities that are needed for natural gas pipeline quality are as shown in Table 1.2.

**Table 1.2** Quality needed for natural gas pipeline

	Maximum Value (% mol)	ASTM Method
Methane	65 < x < 100	D 1945*
Ethane	14	D 1945*
Propane	5	D 1945*
Nitrogen	18	D 1945*
Carbon dioxide	3	D 1945*
Hydrogen	5	D 2650
Carbon Monoxide	0.1	D 1946
Hydrogen Sulfide	5.7 mg/m <sup>3</sup>	D 2725
Water Vapour	110 mg/m <sup>3</sup>	D 1142

\* D 1945 – Standard test method for analysis of natural gas by GC

### 1.1.2 Purification of Natural Gas

Gas processing of crude natural gas is crucial to guarantee a clean-burning and environmentally acceptable produced by natural gas. In gas processing, the most important part is the removal of undesired compound; CO<sub>2</sub> and H<sub>2</sub>S. This process always referred as sweetening processes. There are many methods available for the treatment of acidic natural gas such as physical solvents, adsorption process, chemical solvents, hybrid solvents and also physical separation as stated by Kohl and Nielsen (1997).

Earlier study by Hao *et al.* (2002), to upgrade the low quality of natural gas using selective polymer membranes. This membrane processes are designed to reduce the concentration of CO<sub>2</sub> and H<sub>2</sub>S. However, this method acquires high cost and low selectivity towards toxic gas separation. Moreover, Rangwala (1996) suggested this method need further development on membrane since the performance depends on the specific characteristics of flue gas composition, and the specific features of the separation such as low pressure source, large volumetric flow rate, high temperature and low commodity value of H<sub>2</sub>S and CO<sub>2</sub>. Furthermore, this process also requires a clean gas feed in order to remove impurities.

Meanwhile, chemical absorption processes using aqueous alkanolamine solutions to treat gas streams containing H<sub>2</sub>S and CO<sub>2</sub>. They can exhibit good reactivity at low cost and very flexible in design and operation. However, different amines need to be selected depends on the composition and operating conditions of the feed gas as to meet the product gas specification as told by Mokhatab *et al.*(2006). Alkanolamine that regularly have been used for absorption desulfurization process such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), di-isopropanolamine (DIPA), diglycolamine (DGA), and methyldiethanolamine (MDEA). For instance, MDEA is effectively remove CO<sub>2</sub> from natural gas but did not effectively remove H<sub>2</sub>S gas (Salako and Gudmundsson, 2005). Amine treating method is costly and impractical as amine solution are expensive as well as corrosion may be favoured if high heat reaction applied.

Another method can be used to remove H<sub>2</sub>S only which is known as Iron Sponge process. This method has been applied as batch-type function thus is not easily adapted in continuous operating cycle. This process allows sour gas to pass through a bed of wood chips that have been impregnated with a special hydrated form of iron oxide which can attract H<sub>2</sub>S. Regeneration of the bed earns higher operating cost and excessive maintenance. Even H<sub>2</sub>S gas can be totally removed using this method; however CO<sub>2</sub> still remains in the gas, thus it is not suitable for reducing large content of CO<sub>2</sub> (Curry, 1981).

Besides, molecular sieves processes are highly selective for the removal H<sub>2</sub>S gas (as well as other sulfur compounds) and water from gas streams and own high absorption efficiency. Thus, it is known as dehydration and desulfurization process. However, gas that has excessively high water content may require upstream dehydration. Similar to the Iron sponge process, regeneration of the bed is achieved by passing heated clean gas over the bed. When temperature increases, it will release the adsorbed H<sub>2</sub>S into the regeneration gas stream. Moreover, some of natural gas may lost by the adsorption of hydrocarbon components by molecular sieves (Speight, 2007).

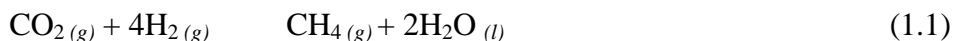
All the above methods are currently applicable in industry, even though they are not economical. Therefore, an alternative method should be used in order to improve the quality of natural gas. CO<sub>2</sub> and H<sub>2</sub>S gas can be removed from natural gas simultaneously via catalytic methanation reaction. Catalysts for CO<sub>2</sub> methanation have been widely studied because of their potential and application in the conversion of CO<sub>2</sub> gas to produce methane using green technology, (Wan Abu Bakar *et al.*, 2008). Usually, the catalyst was prepared various precursor salts to produce metal oxide because of the expensiveness of pure metal. This process gives several advantages such as can increase the purity, quantity and quality of the natural gas without wasting the undesired components (CO<sub>2</sub> and H<sub>2</sub>S) but fully used them in order to produce methane.

## 1.2 Reactions involved in proposed technology

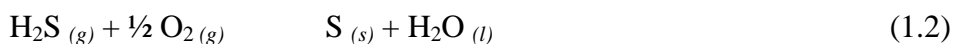
There are two reactions involved in this technology which are methanation and desulfurization reactions. Referring to previous literature, the proposed mechanism is postulated to study the reaction in details.

### 1.2.1 Methanation and desulfurization reactions

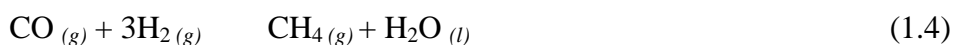
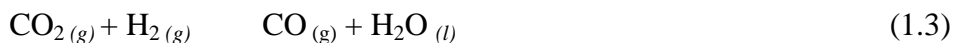
In this proposed natural gas purification, the conversion of carbon dioxide to methane is an important process. To form methane (CH<sub>4</sub>), hydrogen gas is used along with carbon dioxide gas through methanation process as shown in Equation 1.1 below. This reaction is moderately exothermic,  $\Delta H^\circ = -165 \text{ kJ/mol}$  in the presence of catalyst to speed up the reaction.



Meanwhile, H<sub>2</sub>S desulfurization can also be reduced to elemental sulfur simultaneously by oxidation reaction as in Equation 1.2 below:



In order to enhance the catalytic methanation, a suitable catalyst must be chosen to promote selective CO<sub>2</sub> methanation because side products (carbon monoxide, CO and water) are also possible to form (Equation 1.3), which obviously should be avoided. Thus, high selectivity of the catalyst in promoting CO<sub>2</sub> methanation is very necessary. Based on Equation 1.3, CO produced by this reaction also can be used to form methane in the presence of hydrogen as in Equation 1.4.

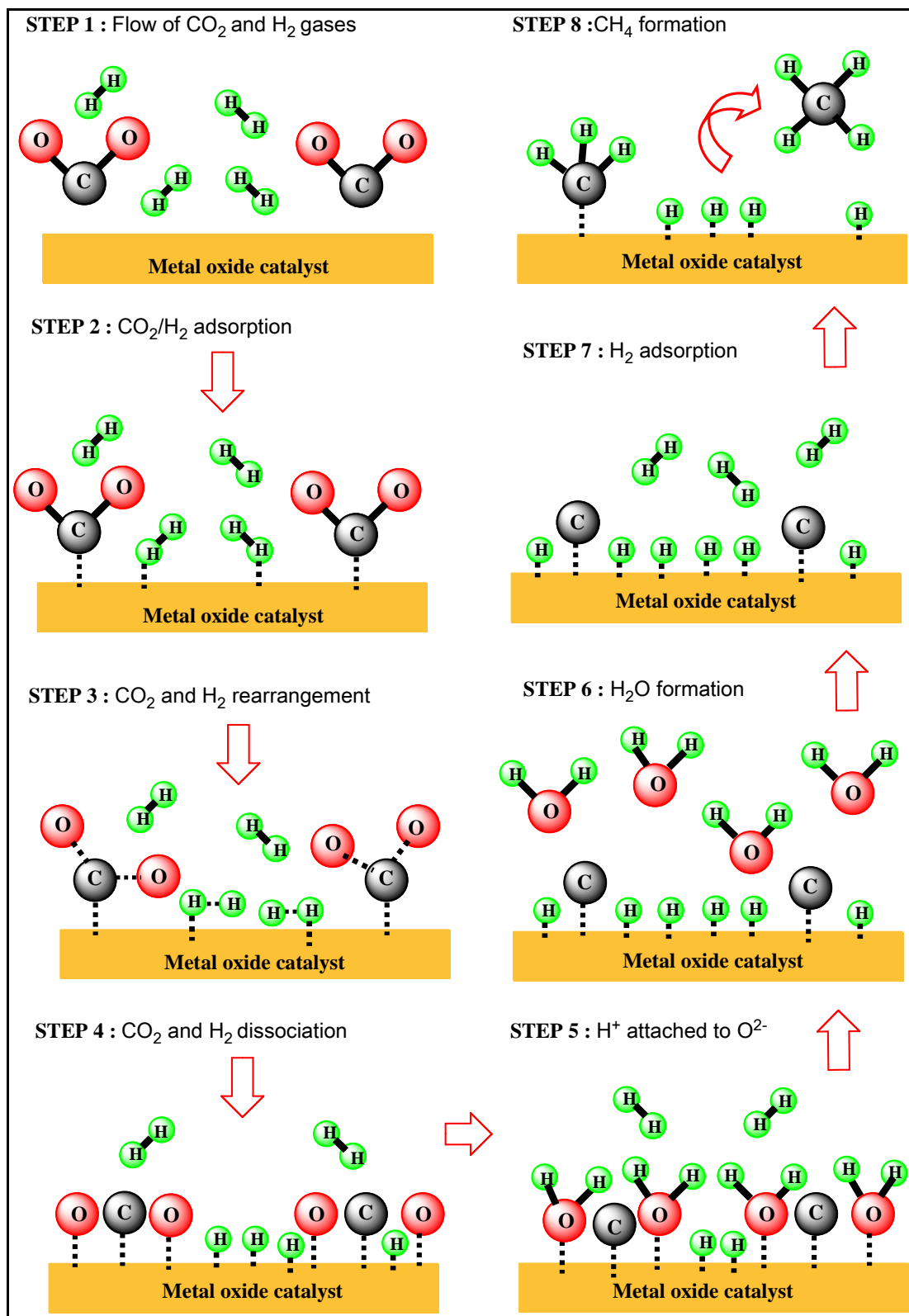


Since this technology offers a number of benefits, thus the present study is aimed to develop a modifying nickel and cobalt oxide based with the incorporation of manganese and noble metals. Perhaps, high conversion can be achieved possibly at low reaction temperature (below than 200°C).

### 1.2.2 Mechanism of Methanation Reaction

Mechanism of methanation reaction has been studied a long time ago. Many researchers agreed that the methanation process involves Langmuir-Hinshelwood mechanism to support the reaction process between active species and catalyst surface.

A study by Jacquemin and co-workers (2010), suggested the mechanism of methanation reaction over Rh/Al<sub>2</sub>O<sub>3</sub> catalyst involves three steps. First step could be the chemisorptions of CO<sub>2</sub> on the surface catalyst. Secondly, the adsorbed CO<sub>2</sub> would disassociate to form CO<sub>(ads)</sub> and O<sub>(ads)</sub> species on the surface catalyst. Third step is the reaction of dissociated species with hydrogen. The dissociative adsorption of CO<sub>2</sub> into carbon monoxide and oxygen has been proven by in situ DRIFT experiments by the presence of bands signify to Rh-CO, Rh<sup>3+</sup>-CO and Rh-(CO<sub>2</sub>)<sub>2</sub>. The methanation is proposed below:



**Figure 1.6** The proposed mechanism of methanation reaction over Ru/Mn/Ni(5:35:60)/Al<sub>2</sub>O<sub>3</sub> catalyst (adapted from Jacquemin *et al.* 2010)

According to Figure 1.6, carbon dioxide and hydrogen molecule is reacting with the catalyst surface by chemisorptions and created an active species that

adsorbed onto the surface catalyst. The adsorbed  $\text{CO}_2$  will dissociate to form  $\text{CO}_{(\text{ads})}$  and  $\text{O}_{(\text{ads})}$ . Meanwhile, hydrogen molecule dissociate become an active H atom species (Step 3 and 4). Water has been formed when  $\text{H}^+$  is attracted to oxygen species (Step 5 and 6). Next, four hydrogen atoms filled the gap left from oxygen in carbon molecule to produce methane (Step 7 and 8). This catalytic cycle continuously occurs as new molecules are attracted to the surface catalyst.

### 1.3 Statement of problem

Carbon dioxide and hydrogen sulfide is a major impurity in Malaysian natural gas with the composition of 20-30% of  $\text{CO}_2$  and 5% of  $\text{H}_2\text{S}$ . The presence of both toxic gases will lead to severe environmental pollution as well as the delivery system of natural gas.  $\text{CO}_2$  emission into the atmosphere is very high particularly from fossil fuels burning thus contribute to the global warming. In the presence of water,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  tend to form carbonic and sulfuric acid respectively, which will corrode the delivery pipeline in the meantime, may induce the acid rain phenomena. Moreover, at low temperature,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are potentially to freeze during the cryogenic process since their melting points are higher than the boiling point of methane. The delivery pipelines and storage vessels tend to clog when freezing, thus have produced various maintenance issues and less effective production. Thus, for the reasons given, it is completely necessary to treat these hazardous and toxic gases in order to purify the natural gas.

Various technologies have been implemented in sweetening process of natural gas such as membrane separation, iron sponge and amine treating. However, these methods are still inefficient, low selectivity and not cost effective as well as only capable to remove 10% of  $\text{CO}_2$  in crude natural gas. Alternatively,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  can be removed using green technology via catalytic methanation reaction by converting  $\text{CO}_2$  to methane gas to increase methane production besides creating an environmental friendly approach for purification of natural gas.



In this proposed technology, variety of catalysts has been developed for CO<sub>2</sub>/H<sub>2</sub> methanation reaction. Monometallic oxide (Ni and Co) catalyst has been proved to exhibit high conversion however easily deactivated. By incorporating dopants into the system, it will enhance the stability of the catalyst as well as to increase the catalytic conversion. Early studies proved that Ru/Mn catalyst had achieved higher CO<sub>2</sub> conversion at low reaction temperature. However, higher composition of noble metal (bimetallic oxide) leads to increase the cost of producing catalyst. Thus, taking the benefit of this catalyst, nickel and cobalt were incorporated in Ru/Mn system to reduce the cost besides both nickel and cobalt is known to be active in methanation reaction, high activity and selectivity towards methane. These types of catalyst have not been discovered yet in any published material in methanation reaction.

#### **1.4 Objectives of the research**

The objectives of this research are:-

1. To prepare the alumina supported nickel and cobalt oxide based catalysts using wet impregnation method.
2. To characterize the potential catalysts.
3. To test the prepared catalysts in methanation process using simulated natural gas.
4. To optimize the catalyst preparation and catalytic testing parameters.

#### **1.5 Scope of the research**

This research involves the preparation of nickel and cobalt oxide based catalysts by incipient wetness impregnation method in CO<sub>2</sub>/H<sub>2</sub> methanation reaction. The incorporation of manganese and noble metals such as ruthenium and palladium as dopants were believed to enhance the catalytic methanation. The prepared

catalysts were calcined at the respective calcination temperature of 400°C, 700°C and 1000°C. The catalytic activity was performed using in house built micro-reactor connected to FTIR. Simulated natural gas comprises of carbon dioxide and hydrogen gases were used in the ratio of 1:4 (CO<sub>2</sub>:H<sub>2</sub>) according to the real natural gas composition. Methane yield was analyzed by GC-FID to confirm the formation of methane from CO<sub>2</sub> conversion.

Potential catalysts will be further studied by several optimization parameters to investigate the optimum condition to contribute the highest conversion. Last but not least, these potential catalysts were characterized to study the properties of the catalyst that responsible to the catalytic activity. Various techniques were also implemented to the catalysts such as Field Emission Scanning Electron Microscope-Energy Dispersive Analysis of X-Ray (FESEM-EDX), Nitrogen Gas Adsorption (NA), X-ray Diffraction (XRD), Thermogravimetry Analysis-Differential Thermal Analysis (TGA-DTA) and Fourier Transform Infrared Spectroscopy (FTIR).

## **1.6 Significance of the research**

Present commercialized methanation catalyst comprises of supported noble metal such as Ru, Rh and Pd. Even though they found to exhibit high activity and stability, considering their high cost and restricted availability thus make them unsuitable to be used in industry. Taking the advantages of noble metal, nickel and cobalt will be used in order to reduce the cost of producing catalyst. Apart from it, nickel and cobalt commonly applied in few reactions such as hydrogenation and methanation due to its high activity and surface area. In this research, manganese and noble metal were incorporated with nickel/cobalt oxide in the hope to avoid the catalyst deactivation. This catalyst comes with low price since the use of noble metal was fixed 5 wt% and working at low temperature since achieving high conversion at 250°C reaction temperature.

This catalyst offers very promising technique since unwanted  $\text{CO}_2$  can be used to produce methane without wasting undesired component ( $\text{CO}_2$ ). Catalytic methanation can remove acid gases ( $\text{CO}_2$  and  $\text{H}_2\text{S}$  simultaneously) which are hazardous to environment. Using this green technology, natural gas can be considered as an environmentally friendly clean fuel when offering important environmental benefits compared to other fossil fuels, thus it will help to reduce problems of acid rain, ozone layer or greenhouse effect.

If the proposed technology is successful, it may increase the price, quality and quantity of natural gas as well as national income. The ultimate goal of this research is to produce the most potential catalyst that can create sustainable environment and fulfilled the specifications above. Thus, this catalyst can be applied using real natural gas.

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