NICKEL OXIDE DOPED NOBLE METALS SUPPORTED CATALYSTS FOR CARBON DIOXIDE METHANATION AND DESULFURIZATION REACTIONS

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BISMILLAHIRROHMANIRROHIM.....

A Special Dedication to my beloved family especially mum and dad for their everlasting support

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In the name of Allah, the Most Gracious, the Most Merciful,

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ABSTRACT

Malaysia has one of the most extensive natural gas pipeline networks in Asia. Using pipeline system, the gas will be channelled to the onshore station where the natural gas will undergo separation of acidic gases. Nowadays, the removal of toxic gases such as H_2S and CO_2 via chemical conversion attracted many researchers due to the effectiveness of the technique. In this research, new catalysts of high industrial impact that can catalyze the reactions of CO_2 methanation and H_2S desulfurization were developed. A series of catalysts based on nickel oxide doped with ruthenium, rhodium, palladium and platinum were prepared. Then, the best two catalysts were subjected to undergo several optimizations such as different calcination temperature of catalysts, calcinations temperature of alumina, different support materials, preparation method, reproducibility testing and regeneration testing. Pd/Ru/Ni $(2:8:90)/Al_2O_3$ and Rh/Ni $(30:70)/Al_2O_3$ catalysts exhibited the most potential catalysts resulted from the activity testing monitored by FTIR and GC. These catalysts were prepared using wetness impregnation technique, aging at 85^oC and followed by calcination at 400^oC. Both catalysts achieved 100% H_2S desulfurization below 200^oC. In the presence of H_2S gas, only 3.64% CH_4 was produced over Pd/Ru/Ni $(2:8:90)/Al_2O_3$ catalyst from 57.31% CO_2 conversion, while 0.5% CH_4 was obtained from 4.53% CO_2 conversion over Rh/Ni $(30:70)/Al_2O_3$ at temperature of 400^oC, respectively. However, the methane percentage increased to 39.73% for Pd/Ru/Ni $(2:8:90)/Al_2O_3$ catalyst from 52.95% CO_2 conversion and 70.75% for Rh/Ni $(30:70)/Al_2O_3$ catalyst from 90.1% CO_2 conversion during testing without flowing of H_2S gas. Moreover, the XRD diffractogram showed that both catalysts are highly amorphous in structure with BET surface area in the range of 220-270 m^2g^{-1}. FESEM analysis indicated a rough surface morphology and non-homogeneous spherical shape with the smallest particles size in the range 40-115 nm for fresh Pd/Ru/Ni $(2:8:90)/Al_2O_3$ catalyst and formation of aggregates with rough surface morphology for fresh Rh/Ni $(30:70)/Al_2O_3$ catalyst. The elemental analysis performed by EDX confirmed the presence of Ni, Ru, Pd, Al and O in the Pd/Ru/Ni $(2:8:90)/Al_2O_3$ catalyst while, Ni, Rh, Al and O in the Rh/Ni $(30:70)/Al_2O_3$ catalyst. Characterization by FTIR and TGA-DTG revealed the existence of nitrate and hydroxyl ions on the catalysts surface.

ABSTRAK

Malaysia mempunyai rangkaian pempaipan gas asli yang luas di Asia. Dengan menggunakan sistem pempaipan, gas asli akan dibawa ke daratan bagi menjalankan proses pemisahan gas berasid. Pada masa kini, penyingkiran gas toksik seperti H_2S dan CO_2 menggunakan penukaran kimia telah menarik perhatian banyak penyelidik kerana keberkesanannya. Dalam penyelidikan ini, mangkin baru berimpak industri yang tinggi telah dibangunkan bagi memangkinkan tindak balas methanasi CO_2 dan penyahsulfuran H_2S. Siri mangkin berasaskan nikel didopkan dengan rutenium, rodium, paladium dan platinum telah disediakan. Kemudian, dua mangkin terbaik akan menjalani beberapa pengoptimisinan seperti suhu pengkalsinan mangkin yang berbeza, suhu pengkalsinan bahan penyokong, pelbagai bahan penyokong, pelbagai kaedah penyediaan, ujian pemboleh ulangan dan ujian penjanaan semula. Pd/Ru/Ni (2:8:90)/Al_2O_3 dan Rh/Ni (30:70)/Al_2O_3 merupakan mangkin yang berpotensi yang dikenal pasti daripada ujian aktiviti yang dipantau oleh FTIR dan GC. Mangkin-mangkin ini disediakan menggunakan kaedah pengisitepuan, dikeringkan pada 85^oC diikuti pengkalsinan pada suhu 400^oC. Mangkin-mangkin ini mencapai 100% penyahsulfuran pada suhu bawah 200^oC. Dalam kehadiran gas H_2S ini, hanya 3.64% gas metana dihasilkan daripada 57.31% penukaran CO_2 bagi mangkin Pd/Ru/Ni (2:8:90)/Al_2O_3 manakala, 0.5% gas metana dihasilkan oleh Rh/Ni (30:70)/Al_2O_3 daripada 4.53% penukaran CO_2 pada suhu 400^oC, masing-masing. Walau bagaimanapun, peratusan gas metana ini meningkat ke 39.73% bagi mangkin Pd/Ru/Ni (2:8:90)/Al_2O_3 daripada 52.95% penukaran CO_2 dan 70.75% bagi mangkin Rh/Ni (30:70)/Al_2O_3 daripada 90.10% penukaran CO_2 semasa ujian tanpa aliran gas H_2S. Selain itu, difraktogram XRD menunjukkan kedua-dua mangkin ini mempunyai struktur sangat amorfos dengan luas permukaan BET di dalam anggaran 220-270 m^2g^{-1}. Analisis FESEM mempamerkan struktur permukaan yang kasar dan ketidaksekataan bentuk dengan saiz zarah yang kecil di dalam julat 40-115 nm bagi mangkin Pd/Ru/Ni (2:8:90)/ Al_2O_3 dan pembentukan agregat serta struktur permukaan yang kasar bagi mangkin Rh/Ni (30:70)/Al_2O_3. Analisis EDX telah mengenal pasti kewujudan element Ni, Ru, Pd, Al dan O dalam mangkin Pd/Ru/Ni (2:8:90)/Al_2O_3 manakala elemen Ni, Rh, Al dan O dalam mangkin Rh/Ni (30:70)/Al_2O_3. Pencirian oleh FTIR dan TGA menunjukkan kewujudan ion nitrat dan hidroksil di atas permukaan mangkin.

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LIST OF ABBREVIATIONS

ABS	-	Absorbance
BET	-	Brunnauer, Emmet and Teller
BJH	-	Barret-Joyner-Halenda
Btu	-	British thermal unit
c	-	Cubic
cf	-	Cubic feet
Cu Kα	-	X-ray diffraction from Copper K energy levels rate of conversion (percentage)
d	-	Pore diameter
DTA	-	Differential Thermal Analysis
EDX	-	Energy Dispersive X-ray Analysis
fcc	-	Face-centered cubic
FESEM	-	Field Emission Scanning Electron Microscope
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared
GC	-	Gas Chromatography
GHSV	-	Gas Hourly Space Velocity
ΔH	-	Enthalpy change
h	-	Hexagonal
hr	-	Hour
IWI	-	Incipient Wetness Impregnation techniques.
LNG	-	Liquefied Natural Gas
m	-	Monoclinic
MgKα	-	X-ray diffraction from Magnesium K energy levels rate of conversion (percentage)
MS	-	Mass Spectroscopy
NA	-	Nitrogen Adsorption

P/P_o	-	Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure P_o of the adsorbate at the temperature where the isotherm is measured
PDF	-	Powder Diffraction File
PKS	-	Palm Kernel Shell
ppm	-	Part per million
PROX	-	Prefential oxidation
RWSG	-	Reverse Water Gas Shift
SMSI	-	Strong metal support interaction
SDS	-	Sodium dodecyl sulphate
SNG	-	Substitute natural gas
tcf	-	Trillion cubic feet
TGA	-	Thermogravimetry Analysis
UGC	-	Urea gelation co-precipitation
VOC	-	Volatile Organic Compounds
wt%	-	Weight percentage
WGS	-	Water Gas Shift
XRD	-	X-ray Diffraction
θ	-	Half angle of diffraction beam
λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1   Natural Gas

Natural gas is a vital component of the world's supply of energy and one of the most useful of all energy sources. It is considered as an environmental friendly clean fuel, offering important environmental benefits when compared to other fossil fuels. Natural gas is colorless, odorless, tasteless, shapeless and lighter than air. Natural gas is the flammable gaseous mixture that occurs alone or with petroleum in underground reservoirs. It is predominantly methane (CH_4) and some higher molecular weight paraffins (C_nH_{2n+2}) generally containing up to four carbon atom.

Natural gas is the result of the decay of animal and plant remains (organic debris) that has occurred over millions of years. Over time, the mud and soil that covered the organic debris changed to rock and trapped the debris beneath the newly-formed rock sediment. Pressure and to some extent, heat changed some of the organic material into coal, some into oil (petroleum) and some into natural gas. Whether or not the debris formed coal, petroleum or gas depended upon the nature of the debris and the localized conditions under which the changes occurred (James, 2007).

Natural gas is produced in many countries around the world and most of those countries produce both oil and natural gas, a few produce only natural gas (James, 2007). Figure 1.1 shows natural gas reserves around the world. As illustrated in the figure, most of the world supply is in Eastern Europe and the Middle East. The

Eastern European reserves are dominated by Russian gas reserves (85% of the Eastern European gas reserves), which exceed 1,680 trillion cubic feet (tcf). Some of the undeveloped fields may contain more than 1,000 tcf of gas. In the Middle East, the major reserves are in Iran (940 tcf). Qatar, in a series of gas fields known as the "North Field", has more than 910 tcf of proven reserves (Seddon, 2006).
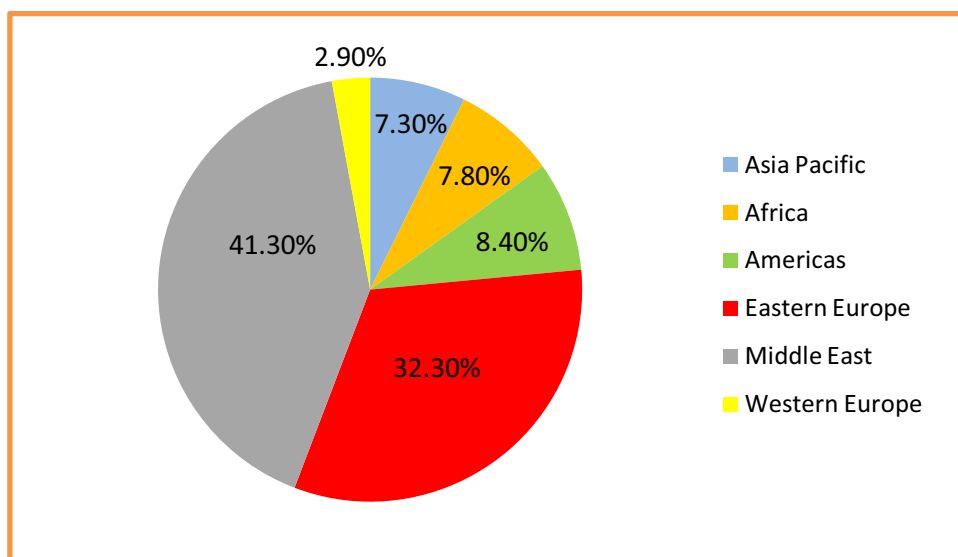
Figure 1.1   World gas reserves (6102 tcf) (Taken from Gas Usage and Value: The Technology and Economics of Natural Gas Use in the Process Industries, 2004)

Malaysia is the world's 13th largest natural gas reserves and 24th largest crude oil reserves. Malaysia is also the world's 3rd largest producer of Liquefied Natural Gas (LNG) with production capacity of 23 million metric ton per year. Our country is important to world energy markets because of its 75 tcf of natural gas reserves and its net oil exports of over 940,000 barrels per day. Natural gas consumption in 2002 was estimated at 1.0 tcf, with LNG exports of around 0.7 tcf mostly to Japan, South Korea and Taiwan (Ching, 2008).

When cooled to -160°C, natural gas enters the liquid phase, in which it occupies six hundred times less volume than in its gaseous state. The importance of liquefied natural gas (LNG) thus lies in transportation whereas natural gas requires long, expensive pipelines for global export and import while, LNG can be transferred in secure tanks by ship or truck. In order to produce liquefied natural gas (LNG), the

gas from offshore platform as the raw material needs to undergo various processes. Using pipeline system, the gas will be channel to the onshore station where the natural gas will undergo separation of acidic gas. This separation involved the removal of toxic gases such as H_2S and CO_2. Technology used for liquefying natural gas so that it can be transported in tankers is improving. As technology continues to expand the options for gas transportation, demand for natural gas is expected to grow.

Gas customers or end users, fall into three broad classes which are residential, commercial and industrial. In addition, utilities and power suppliers use gas to generate electricity and some fleets of vehicles use gas as a transportation fuel. Figure 1.2 shows the domestic, commercial and industrial utilization of natural gas. Homeowners and other residential customers use gas for heat, hot water, cooking and cloth drying as well as in gas fireplaces and logs. Commercial businesses which account for about 14% of gas consumption use gas mainly for heat and hot water. Some larger buildings are also air-conditioned by gas powered equipment and many restaurants use gas to cook. Industrial customers who represent about 44% of all gas consumed use the fuel in tens of thousands of factories and mills to manufacture a great variety of product, from paper to cars (Busby, 1999).
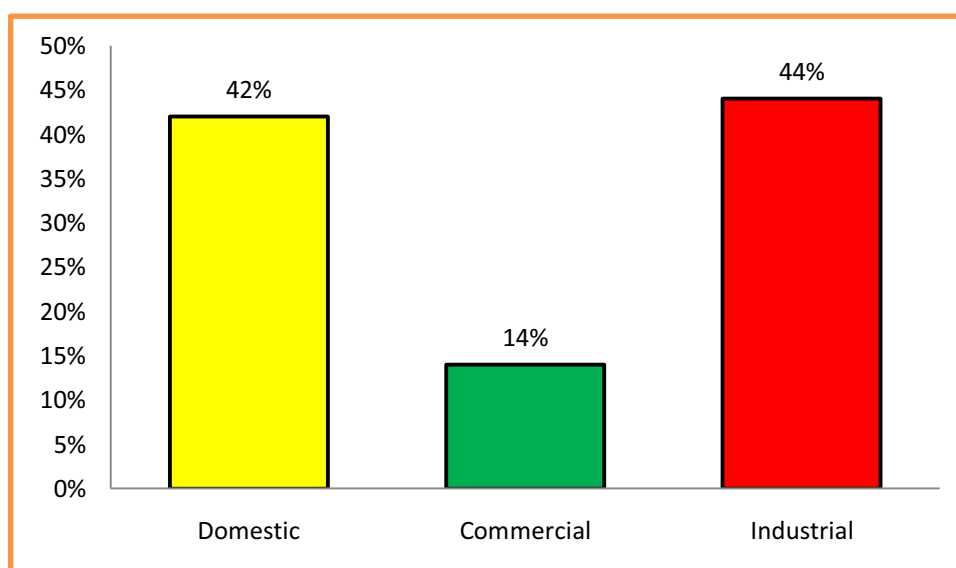
Figure 1.2   Domestic, commercial and industrial utilization of natural gas (Taken from Natural Gas in Non-Technical Language, 1999)

This means that people tends to use more energy rather than conserve it because demand is strongly affected by price. Future supplies of natural gas and other limited energy resources will depend on how much energy we consume, how much we attempt to preserve for future generations and how well we learn to develop and use our remaining resources efficiently.

1.2   Acid Gas Treating Processes

Growing demand for natural gas is leading to an increase in the production of standard and contaminated natural gas. Malaysia large reserves and the existence of huge gas reserves in the nearby countries have ensured that natural gas is the future energy resource for Malaysia (Md. Yasin, 1987). Malaysia also has one of the most extensive natural gas pipeline networks in Asia. Table 1.1 shows the chemical composition of Malaysian crude natural gas which was analyzed by using Gas Chromatography-Mass Spectroscopy (GC-MS). It is consists mainly of simplest hydrocarbon which is methane (CH_4), along with heavier hydrocarbons such as ethane (C_2H_6) and propane (C_3H_8). Often, natural gas also contains impurities such as carbon dioxide, hydrogen sulfide and water as well as nitrogen, helium and other trace gases. The composition of a natural gas as it comes from the well varies from one location to another. It must be purified before it can be sold, liquefied or fed to a gas to liquids process.

Table 1.1   Chemical composition of crude natural gas from Telaga Bergading, Petronas Carigali Sdn. Bhd. (Taken from Laboratory Services Unit (UNIPEM), 2003)

Gases	Composition (%)
CH_4	47.9
C_2H_6	5.9
C_3H_8	3.2
CO_2	23.5
H_2S	5.4
Others (CO, O_2, N_2, H_2O)	24.1

Gas processing is necessary to ensure that the natural gas intended for use is clean-burning and environmentally acceptable. Natural gas used by consumers is composed almost entirely of methane but natural gas that emerges from the reservoir at the wellhead contains many components that need to be extracted. Although, the processing of natural gas is less complicated rather than the processing and refining of crude oil, it is equal and necessary before it can be used by end user.

One of the most important parts of gas processing is the removal of carbon dioxide and hydrogen sulfide. The removal of acid gases (CO_2, H_2S 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_2 and H_2S from natural gas. These processes include Chemical solvents, Physical solvents, Adsorption Processes Hybrid solvents and Physical separation (Membrane) (Kohl and Nielsen, 1997).

According to previous research done by Hao *et al.* (2002), there are ways to upgrading the low quality natural gas with selective polymer membranes. The membrane processes were designed to reduce the concentrations of CO_2 and H_2S in the natural gas to US pipeline specifications. However, this technique incurs high cost and low selectivity towards toxic gas separation. This technique also needs further development because the performance of membrane depends upon the specific characteristics of flue gas composition, and the specific features of the separation (i.e. large volumetric flow rate, low pressure source, high temperature, and the relative low commodity value of H_2S and CO_2) (Rangwala, 1996).

Another method of H_2S removal and one that leaves the CO_2 in the natural gas is called the Iron Sponge process. The disadvantage of this is that it is called a batch-type function and is not easily adapted to continuous operating cycle. The Iron Sponge is simply the process of passing the sour gas through a bed of wood chips that have been impregnated with a special hydrated form of iron oxide that has a high affinity for H_2S. Regeneration of the bed incurs excessive maintenance and operating costs, making this method inconsistent with an efficient operating program. If there are any real advantages in using this process, it is a fact that CO_2 remains in the gas,

thereby reducing the shrinkage factor which could be significant for very large volumes with an otherwise high CO_2 content (Curry, 1981).

Chemical absorption processes with aqueous alkanolamine solutions are used for treating gas streams containing H_2S and CO_2. They offer good reactivity at low cost and good flexibility in design and operation. However, depending on the composition and operating conditions of the feed gas, different amines can be selected to meet the product gas specification (Mokhatab *et al.,* 2006). Some of the commonly used alkanol-amine for absorption desulfurization are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), di-isopropanolamine (DIPA) and methyldiethanolamine (MDEA). MDEA allows the selective absorption of H_2S in the presence of CO_2 but can be use effectively to remove CO_2 from natural gas in present of additives (Salako and Gudmundsson, 2005).

On the other hand, CO_2 and H_2S can be removed from natural gas via chemical conversion techniques. Catalysts for CO_2 methanation had been extensively studied because of their application in the conversion of CO_2 gas to produce methane, which is the major component in natural gas (Wan Abu Bakar *et al.*, 2008a). Usually, the catalysts were prepared from the metal oxide because of the expensiveness of pure metal. This process can increase the purity and quality of the natural gas without wasting the undesired components but fully used them to produce high concentration of methane (Ching, 2008). Methane (CH_4) gas was formed from the reaction of hydrogen gas and carbon dioxide gas through methanation process by reduction reaction as shown in Equation 1.1 below:-

$$CO_{2\,(g)} + 4H_{2\,(g)} \quad \rightarrow \quad CH_{4\,(g)} + 2H_2O_{\,(l)} \tag{1.1}$$
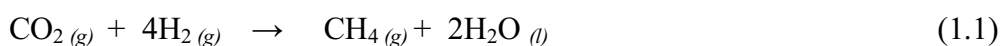
This reaction is moderately exothermic, H^o = -165 kJ/mol. Meanwhile, H_2S can also be reduced to elemental sulfur simultaneously by oxidation reaction as in Equation 1.2 below:-

$$H_2S_{\,(g)} + \tfrac{1}{2}O_{2\,(g)} \quad \rightarrow \quad S_{\,(s)} + H_2O_{\,(l)} \tag{1.2}$$
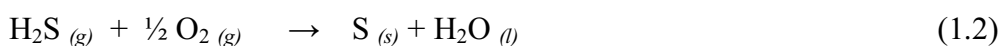
In order for this method to be effective, a suitable catalyst must be applied to promote selective CO_2 methanation because of the main side product under this reaction also will be form (Eq. 1.3), which obviously should be avoided. Thus, high selectivity of the catalyst in promoting CO_2 methanation is paramount importance. In Equation 1.3, carbon monoxide produced by this reaction can also be used to form methane by reaction in Equation 1.4 with hydrogen.

$$CO_{2\ (g)}\ +\ H_{2\ (g)}\ \rightarrow\ CO_{(g)} + H_2O_{\ (l)} \tag{1.3}$$

$$CO_{(g)}\ +\ 3H_{2\ (g)}\ \rightarrow\ CH_{4\ (g)} + H_2O_{\ (l)} \tag{1.4}$$
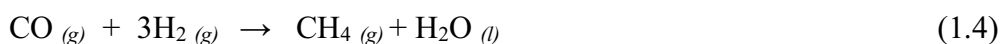
Since the catalytic process through methanation and desulphurization reactions offers the best way to remove CO_2 and H_2S in the natural gas, therefore, the present study is to develop a catalyst based on nickel oxide with modifying the dopants using noble metal in order to fully remove these sour gasses at high conversion percentage possibly at low temperature.

1.3   Problem Statement

Carbon dioxide and hydrogen sulfide are commonly referred to as acid gases because they form acids or acidic solution (corrosive compounds) in the presence of water. These gases are generally undesirable components of natural gas. Natural gas can contain up to 28% of H_2S gas, consequently, it maybe an air pollutant near petroleum refineries and in oil and gas extraction areas. H_2S itself is colorless and flammable gas. It smells like rotten eggs that is toxic at extremely low concentration and can cause loss of the sense of smell. Inhalation of excessive levels of H_2S gas in confined space can result in unconsciousness, respiratory failure and death. It also has potential to corrode pipelines, storage tanks and other ship component which may cause operability problems including engine breakdown (Fred and Hans,1998). Besides that, the removal of H_2S gas from natural gas often necessary before combustion. The combustion of natural gas in the presence of H_2S yielded sulfur dioxide which when dissolved in water turn to very corrosive sulfuric acid or sulfurous acid. This may cause the acid rain phenomena to the earth which leads to

the increase of acidity of the soil and affect the chemical balance of lakes and streams.

Carbon dioxide is also referred to as diluents because none of them burn and thus they have no heating value. This gas is not very harmful and may actually be used sometimes as "fillers" to reduce the heat content of the supply energy. Thus, its removal may be required in some instances merely to increase the energy content of the gas per unit volume. CO_2 removal may also be required because it forms a complex, $CO_2 \cdot CO_2$, which is quite corrosive in the presence of water. For gas being sent to cryogenic plants, removal of CO_2 may be necessary to prevent solidification of the CO_2 (Sanjay, 1987). Since the melting points of CO_2 and H_2S are higher than the boiling point of methane, it can potentially freeze during the cryogenic process. Freezing can lead to clogged LNG pipelines and storage vessels, producing various maintenance issues and hindering overall process efficiency. Similar to the H_2S gas, CO_2 in the presence of water may enhance the production of carbonic acid which leads to the acid rain phenomena. Furthermore, carbon dioxide is one of the greenhouse gases. As the level of carbon dioxide increases the warming of the earth's surface will also increase (Schneider, 1989). This phenomenon is called as greenhouse effect thus, can cause global warming. However, if none of these situations are encountered, there is no need to remove CO_2.

The existence of both carbon dioxide and hydrogen sulphide will reduce the quality of natural gas and at the same time increase the production cost of natural gas to fulfill the US Pipeline Specification, in which, the natural gas should only consist of 2 w/w % CO_2 and 4 ppm H_2S before it can be distributed to world market (Echterhoff and McKee, 1991). These gaseous are needed to be removed in order to prevent or minimize the release of hazardous gases into environment. This will helps to reduce problems of acid rain, ozone layer depletion or greenhouse effect. Many scientists believe that increasing levels of carbon dioxide in the earth's atmosphere will change the global climate.

1.4   Significant of Study

In this research, the potential catalyst that can be used to remove CO_2 and H_2S simultaneously which are present in wet natural gas consisting of 23% CO_2 and 5% H_2S was developed based on nickel oxide doped with noble metal. This catalyst offers very promising techniques for natural gas purification since H_2S gas is being converted to stable element of sulfur and unwanted CO_2 gas is being converted to the product, CH_4 thus will enhance the methane production.

The purification technique via this catalyst can remove acid gases in wet natural gas which is hazardous to the environment. This will help to prevent phenomena of acid rain, ozone layer depletion or greenhouse effect. 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.

1.5   Objectives of the Research

The main goal of this research is to develop the catalyst that can catalyze methanation and desulfurization reactions effectively and simultaneously at a very low temperature.

The objectives of this research are :-

1. To synthesize the best supported nickel oxide based for carbon dioxide methanation and H_2S desulphurization reactions.
2. To test the catalytic activity of the prepared catalysts by using in-house built micro reactor coupled with FTIR.
3. To conduct several optimization parameters of the best prepared catalyst.
4. To characterize the best prepared catalysts in order to understand the physical properties of the prepared catalyst.

1.6   Scope of the Research

A series of alumina supported catalyst based on nickel oxide doped with noble metal were prepared using wetness impregnation techniques. Ruthenium chloride, nitrate salts of rhodium, palladium and platinum had been used as precursor for the dopants in this research. Meanwhile, catalytic testing was carried out by using house-built micro reactor coupled with FTIR towards the prepared catalysts. The production of methane gas was determined by Gas Chromatography analysis. All the prepared catalysts were tested based on trial and error basis where different mixed metal oxides with 90 wt% nickel loading were tested until the best performance catalyst was obtained. Then, the best two prepared catalysts were optimized according to the amount of nickel loading, different calcination temperatures of catalysts, different calcination temperatures of alumina support, various support materials and various preparation method. Lastly, the potential catalysts were tested on its reproducibility and regeneration activity. The characterization of the potential catalysts were conducted by various techniques in order to understand the physical properties of the catalysts such as X-Ray Diffraction for bulk structure, Field Emission Scanning Electron Microscope for morphology study, Energy Dispersive X-Ray Analysis for elemental composition study, Nitrogen Adsorption for pore texture and surface area of the catalyst. Meanwhile, Thermal Gravimetric Analysis to study the mass loss of the catalyst during temperature change and Fourier Transform Infrared Spectroscopy for the functional group study present in the catalyst.