INTRODUCTION OF FOREIGN METALS ONTO UNSUPPORTED AND SUPPORTED NICKEL PRASEODYMIUM OXIDE CATALYST FOR CONVERSION OF CARBON DIOXIDE TO METHANE

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To my beloved father and mother
And all the special people in my life
that made me live my life to the fullest

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ABSTRACT

Nickel oxide based catalysts have long been known as one of the most used based materials applied for various catalyst developments. Researchers nowadays are trying to emerge with a suitable method to enhance the NiO catalyst capability for the benefit of the industries. It was observed that by introducing foreign metals with an optimized condition will increase the catalyst capability. In this study, a catalyst has been succesfully developed that can potentially be used for natural gas purification where CO_2 is catalytically converted to methane. A screening test was performed in the hope to find a suitable dopant for NiO catalyst. Seven chosen metals, M*; Mg, Zr, Mo, Mn, Fe, Co, and Cu, with a required addition of Pr from the lanthanide series was incorporated into NiO based catalyst in the weight ratio of (60% Ni: 30% M*: 10% Pr) and (60% Ni: 10% M*: 30% Pr). All prepared catalysts were aged for one day and calcined for 17 hours before tested for its ability to remove CO_2 using a home-built reactor. In assistance of X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) analysis, Scanning Electron Microscopy (SEM), nitrogen adsorption, single point BET and Fourier Transformed Infra Red analysis (FTIR) were also carried out to reinforce the results. It was found that the incorporation of Co and Pr enhances the catalytic performance by full removal of CO_2 as well as producing methane at a low temperature of 330°C. Optimization on the ratio was carried out and was catalytically tested. From the characterization of the best catalyst, the XRD results showed that the catalyst formed individual phases of NiO, Co_3O_4 and PrO_2, while SEM assigned the presence of small particles that homogeneously distributed. The study was continued using support for the Ni/Co/Pr catalyst, whereby three supports were chosen; alumina beads (Al_2O_3), molecular sieve ($Na_{12}[(AlO_2)_{12}]5SiO.\ x\ H_2O$), and cordierite ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$). Adsorption and impregnation method was used in coating the catalyst onto the support. Verifications have been made to optimize the preparation conditions; catalyst loading, time of dipping, ratio of catalyst, calcination temperature, and addition of binder. Results showed the most favorable support for Ni/Co/Pr catalyst was cordierite. From the catalytic activity, the optimum catalyst ratio for the supported catalyst was 60:35:5, and the best possible catalyst loading onto the cordierite is approximately 25 %. The optimum calcination temperature was at 400°C for 17 hours as concluded from the XRD analysis. However as the conversion of CO_2 to methane was extended for another 10 hours on stream test, it appeared that the catalytic performance declined. The decrease from a maximum of a 100 % of CO_2 conversion to 60 % conversion gave a lot of impact. From the XPS study it was found that throughout the stages of catalytic testing, the oxidation state of the individual phases changed from Ni^{2+} to Ni^{3+}, and from mixture of Co^{2+} and Co^{3+} to completely Co^{2+}. This finding was backed up by XRD analysis that also confirmed the changing of oxidation state. The changing of oxidation state in metal in supported catalyst resulted in rapid deactivation of catalytic performance that shortened the life span of the catalyst. The performance of the catalyst also declined as it was exposed to H_2S.

ABSTRAK

Mangkin yang berasaskan nikel oksida telah lama digunakan sebagai bahan asas di dalam pelbagai kaedah pemangkinan. Para penyelidik masa kini sedang mencuba untuk mencari kaedah yang sesuai untuk meningkatkan keupayaan mangkin NiO utuk digunakan di sektor industri. Di dalam kajian ini, satu mangkin telah dihasilkan di mana ia berpotensi untuk digunakan dalam penyulingan gas asli;CO_2 akan bertukar kepada metana dengan bantuan mangkin. Kaedah cubajaya digunakan untuk mencari bahan pendop yang sesuai untuk mangkin NiO. Tujuh logam terpilih, M*; Mg, Zr, Mo, Mn, Fe, Co, dan Cu, dan bahan pendopan yang wajib, Pr dari unsur lantanida telah dimasukkan bersama mangkin NiO di dalam nisbah berat (Ni 60%: M* 30%: Pr 10%) dan (Ni 60%: M* 10%: Pr 30%). Semua mangkin yang telah disediakan telah dikeringkan selama sehari dan dikalsin selama 17 jam sebelum keupayaan menyingkirkan CO_2 diuji menggunakan reaktor buatan sendiri. Selain daripada analisis pembelauan sinar X (XRD), dan spektroskopi elektron sinar X (XPS), analisis mikroskopi elektron (SEM), penyerapan gas nitrogen (NA), BET dan analisis infra merah (FTIR) juga telah dilakukan untuk memperkukuhkan lagi keputusan ujian. Ujian mendapati dengan penambahan Co dan Pr dapat meningkatkan keupayaan mangkin untuk menyingkirkan CO_2 sepenuhnya dan menghasilkan metana pada suhu terendah 330°C. Pengoptimaan nisbah logam telah dibuat dan diuji secara mangkin. Daripada pencirian mangkin terbaik, keputusan analisa XRD menunjukkan mangkin membentuk fasa individu NiO, Co_3O_4 dan PrO_2, manakala SEM mengesahkan pembentukan saiz zarah kecil yang sekata. Penyelidikan diteruskan dengan menggunakan bahan penyokong yang terpilih alumina (Al_2O_3), penapis molekul (molecular sieve, $Na_{12}[(AlO_2)_{12}]5SiO.xH_2O$) , dan kordierit ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$). Kaedah penyerapan dan pengisitepuan digunakan untuk menyalut mangkin pada bahan penyokong. Pengenalpastian dilakukan untuk mencari keadaan optima bagi penyediaan mangkin; peratusan kandungan mangkin, masa celupan, nisbah logam dalam mangkin, suhu pengkalsinan, dan penambahan bahan ikatan. Keputusan menunjukkan bahan penyokong yang paling sesuai bagi mangkin Ni/Co/Pr adalah kordierit. daripada ujian pemangkinan, nisbah mangkin yang optima bagi mangkin berpenyokong adalah 60:35:5, dan peratusan kandungan mangkin yang paling baik adalah sebanyak 25 %. Suhu kalsin optima adalah suhu 400°C selama 17 jam, dan ia disokong oleh keputusan daripada XRD. Namun begitu apabila ujian penukaran CO_2 kepada metana dilanjutkan kepada 10 jam tanpa henti, keupayaan mangkin semakin menurun. Penurunan daripada 100 % penukaran CO_2 kepada 60 % telah memberi impak yang besar. Daripada analisa XPS, ia mendapati bahawa semasa peringkat ujian pemangkinan, nombor pengoksidaan bagi fasa individu telah berubah daripada Ni^{2+} kepada Ni^{3+}, dan daripada campuran Co^{2+} dan Co^{3+}, kepada Co^{2+} sepenuhnya. Perubahan ini juga dibuktikan daripada XRD yang mengesahkan perubahan nombor pengoksidaan. Perubahan nombor pengoksidaan logam pada mangkin berpenyokong telah menyebabkan penurunan mendadak kepada keupayaan mangkin dan memendekkan jangka hayatnya. Keupayaan mangkin menyingkirkan CO_2 juga menurun apabila ia didedahkan kepada H_2S.

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BET	-	Brunnauer, Emmett and Teller
Conv.	-	Conversion
Cu K_α	-	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
EDF	-	Equilibrium deposition filtration
EIA	-	Energy Information Administration
FTIR	-	Fourier Transformed Infra Red
HC	-	Hydrocarbon
IR	-	Infra red
IUPAC	-	International Union of Pure and Applied Chemistry
IWI	-	Incipient Wetness Impregnation
NA	-	Nitrogen gas adsorption
NG	-	Natural gas
NO_x	-	Nitrogen oxides
OSC	-	Oxygen Storage Capacity
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
REO	-	Rare Earth Oxides
RT	-	Room Temperature
SEM	-	Scanning Electron Microscopy

SMSI	-	Strong Metal-Support Interaction
TG	-	Thermogravimetry
T_{LO}	-	Light-off Temperature
T_{max}	-	Maximum Conversion Temperature
TOF	-	Turnover frequency (repeated tests)
TWC	-	Three-way Catalyst
w/w %	-	Weight per weight percentage ratio.
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction
θ	-	Half Angle of Diffracted Beam
λ	-	wavelength
ΔE_{so}	-	Spinning orbital energy

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CHAPTER 1

INTRODUCTION

1.1 Natural Gas

Natural gas is a fossil fuel that was found far below the earth's crust, much further than oil deposits, formed when organic matter (remains of plants and animals) was compressed at high pressure for a long time. It is also known as thermogenic methane. Akin to the formation of oil, the particulates were piled up with mud and other sediment on top of the other occasionally until the weight of the debris puts a great deal of pressure on the organic matter. Combining with the heat from underneath, the organic matter will breakdown and form lower carbon-carbon bonds. It may also have been formed by slow out gassing of methane from vast deep deposits dating back to the origin of our planet. The formation of methane depends on the heat, whereby the lower temperature will form oil deposits and the higher temperatures primarily form methane (Kiricsi and Guczi, 1999).

Natural gas is a colorless and odorless in its pure form. It is combustible and has been proven to be a renewable energy source as it gives a great deal of power upon consumption (Olah and Molnar, 2003). Natural gas is the fastest growing primary energy source in the *International Energy Outlook 2004* (EIA, 2004) forecast (EIA, 2004). Consumption of natural gas worldwide is projected to increase by an average of 2.2 percent annually from 2001 to 2025, which is increase by nearly 70 percent higher than energy consumed in 2001. The projected demand is definitely

higher compared with annual growth rates of 1.9 percent for oil consumption and 1.6 percent for coal. Furthermore, the most robust growth in natural gas demand is expected among the developing nations, including Malaysia, where overall demand is projected to increase by an average of 2.9 percent per year from 2001 to 2025. Most of that increase is expected to be for daily usage of electricity generation through pipeline or in the form of liquefied natural gas (LNG).

The world natural gas reserves have generally trended upward since the mid-1970s (Figure 1.1) until now and it was proven that the developing countries accounted for virtually all in the increase in proved reserves (EIA, 2004; Radler, 2003). In 2002, Indonesia and Malaysia were the largest natural gas producers in developing Asia, exporting 1108 and 741 billion cubic feet of natural gas, respectively, and accounted for about 70 % of Asia's gas trade, both by way of pipeline (small amounts to Singapore) and as LNG (to Japan, South Korea, Taiwan and United States) (EIA, 2003).

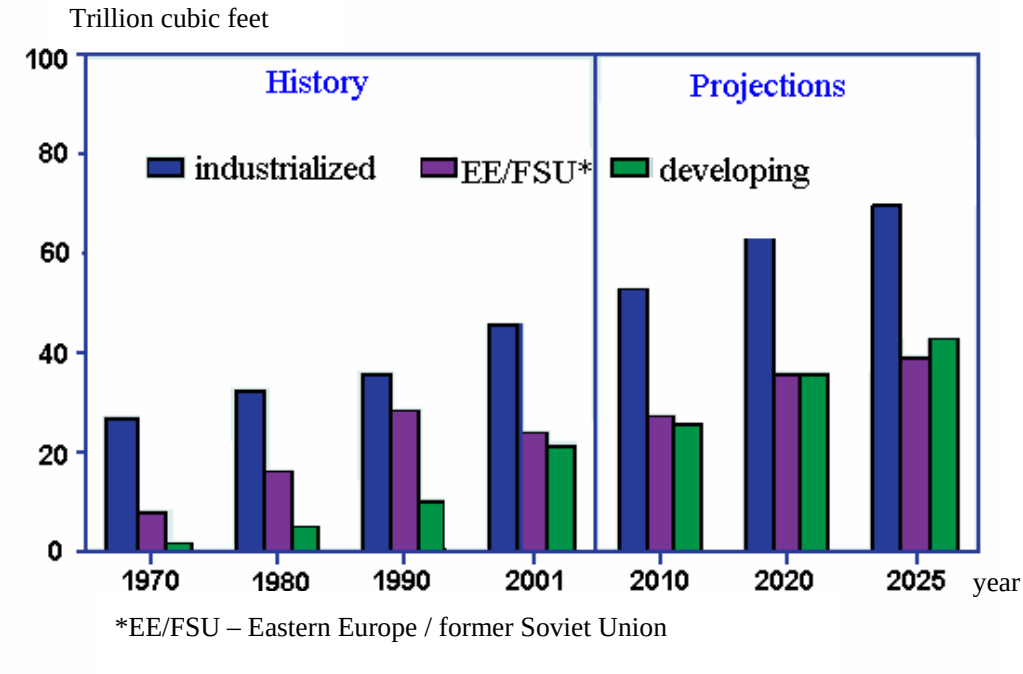

Figure 1.1 Natural Gas Consumption by Region, 1970-2025 (EIA, 2004)

Malaysia's proved gas reserves were estimated 75 million cubic feet (Radler, 2001). About 60 % of its marketed gas production is consumed domestically, three-quarters 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. It was followed by Kota Kinabalu, Sabah.

The country is seeking ways to increase its production of natural gas. Approximately 38 % of Malaysia's reserves are under Petronas Carigali Sdn. Bhd. (Muhamad, 2001). Malaysia also has offshore fields in the South China Sea, which have been developed by Exxon Mobil (EIA, 2004). The country is currently exporting 9.2 billion cubic feet of natural gas per year to Singapore via pipeline. The Malaysia-Thailand Joint Development Authority is a join-venture program by the two countries and now is being explored by Petronas and the Petroleum Authority of Thailand (PTT) as well as Amerada Hess and BP. Its purpose is to build a pipeline linked to a gas-fired electricity generation plant in Thailand near the Thailand's and Malaysia's boundaries, with plans for a future gas pipeline to Malaysia. Malaysia has also begun imports of Indonesian gas from Natuna offshore field through a connection to Malaysia's Duyong field pipeline (EIA, 2004) in order to position itself as Southeast Asia's gas hub.

In view of the expected growth in the demand for natural gas increasing attention is being devoted by the gas industry to upgrade of low quality of natural gas. Table 1.1 (Kiricsi and Guczi, 1999) showed the chemical composition of Malaysian raw untreated natural gas. It is primarily consists of low density hydrocarbons (methane, ethane, propane), and impurities (CO_2, H_2S, O_2, N_2 etc.)

From the comparison of the location, it is clearly stated that Malaysian raw natural gas consists of more of the impurities; sour gas and flue gas than any other countries stated above. These impurities will lower the price of natural gas in the worldwide market and will also cause trouble for distributing them.

Table 1.1: Chemical composition in crude natural gas in weight percent (w/w %) (Olah and Molnar, 2003; Minerals and Geoscience Department of Malaysia, 2001)

Location	CH_4	C_2H_6	C_3H_8	C_4H_{10}	Others (CO_2, H_2S, O_2, N_2)
United States	89.5	5.1	0.7	0.5	4.2
Algeria	86.9	9.0	2.6	1.2	0.3
Iran	74.9	13.0	7.2	3.1	1.8
North Sea	90.8	6.1	0.7	0.1	2.3
Malaysia	**70.0**	**13.0**	**6.0**	**1.0**	**10.0**

1.2 Current natural gas purification system

The major problem of having impurities in natural gas is not only it will lower the quality of natural gas, it will also affect worldwide price. High cost is needed in all the stages of providing customers with natural gas that met with US pipeline specification, which is that the natural gas must contain not more than 2 w/w% CO_2 and 4 ppm H_2S before being delivered to customers (Echterhoff and McKee, 1991). With steel pipelines as medium of transportation that easily can rust and corrode by carbonic acid from sour gas (Ertesva *et al.*, 2005; Zou *et al*., 2005), and very long distance is involved, whereby pipelines in South East Asia are over 4000 km in length, creating complications in the computation of costs to frequently replace with new pipelines (Wybrew-Bond and Stern, 2002). That is why in view of expected growth in the demand for natural gas, increasing attention is being devoted by the gas industry to the upgrading of low-quality natural gas.

A variety of conventional separation methods are presently being used to remove the "acid gasses", CO_2 and H_2S from crude natural gas (Abdellah *et al.*, 2003; Pei *et al.*, 2004; Vu *et al.*, 2003; Taulbee *et al*., 1996; Hao *et al*., 2002). These methods include gas adsorption on solid sorbents, absorption in liquid solvents, and chemical conversion.

1.2.1 Wet Scrubber system (WGS)

One of the suggestions was the use of limestone-based sorbents which is a flue gas desulphurization unit, for the removal of CO_2 from multi-component gas streams (Taulbee *et al.*, 1996). Wet scrubbers capture sulfur in flue gas to form both hydrated and slurry mixture of Ca, $Ca(OH)_2$ and $CaSO_4$. It was also been used as biotrickling filters for H_2S control in the environment (Gabriel *et al.,* 2004). An overview of the Wet Gas Scrubber system (WGS) used by one of the Malaysian NG company is in Figure 1.2 (Morris, 2002);

- The small, on-site WGS washes the flue gas removing both particulate and sulfur oxides.
- The cleaned flue gas is then exhausted to the atmosphere with residual particulate and sulphur oxides.
- Other streams entering the Wet Gas Scrubber are water and an alkali.
- A separate liquid purge stream leaves the WGS for further treatment.
- The purge stream, which contains the particulate and sulfur oxides removed from the flue gas, may either be treated in the refinery's existing wastewater treatment system or may be treated in a dedicated PTU (Purge Treatment Unit).
- The discharge from the PTU consists of earth moist solids suitable for sanitary landfill disposal and a benign liquid.

The advantages of using this method are it provides efficient chemical usage and it is also stable in low pH conditions. It does not promote scale and corrosion in the system and operates at low temperatures. However, the waste product exhibits a strong affinity for CO_2, whereby it was reacted with unsulfated Ca to form $CaCO_3$. Although it is able to absorb CO_2, a significant amount of waste is formed with the absorption. Furthermore, a separate disposal treatment has to be developed in order to treat the waste.

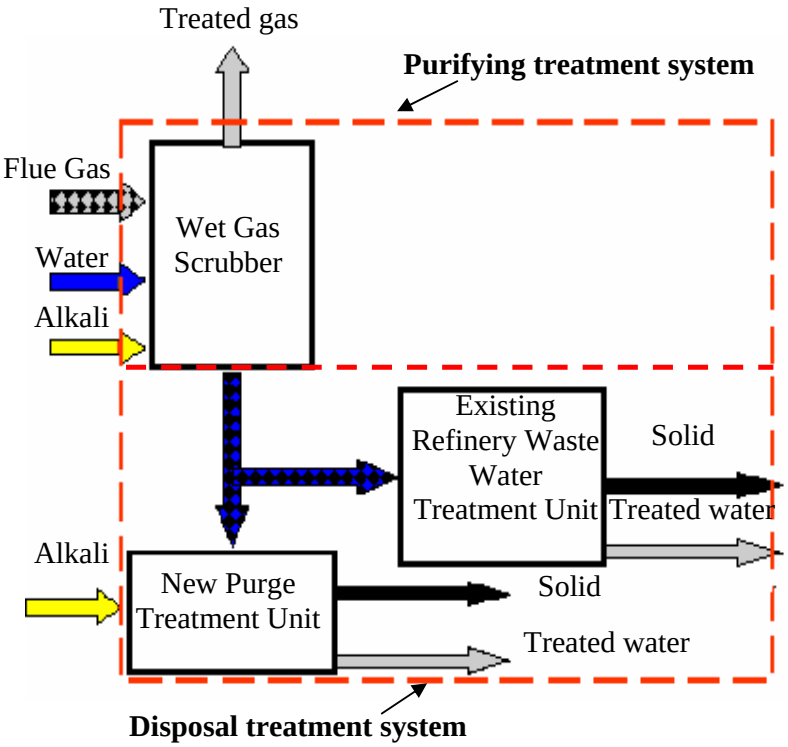

Figure 1.2 Diagram of complete scrubber process (Morris, 2002)

1.2.2 Membrane separation system

Membrane separation processes have also emerged as an alternative and offered a number of important advantages for the upgrading of crude natural gas (Abdellah *et al*., 2003). Membrane separation involves partially separating a feed containing a mixture of two or more components by use of a semi permeable barrier (the membrane) through which one or more of the species moves faster than another or other species. As shown in Figure 1.3, the basic process of the membrane separation involves a feed mixture separated into a *retentate* (part of the feed that does not pass through the membrane, i.e., is retained) and a *permeate* (part of the feed that passes through the membrane). It was found to economically reduce the concentrations of CO_2 and H_2S whereby it require polymer membranes that exhibit high CO_2/CH_4 or H_2S/CH_4 selectivity, or both types of membranes.

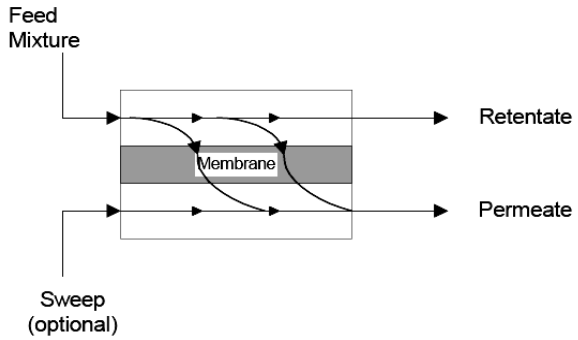

Figure 1.3 Diagram of basic membrane separation (Ali *et al*., 2000)

Hence the issue not considered in this study is the environmental impact of the permeate product streams. These streams will contain substantial amounts of H_2S and cannot be discharged to the atmosphere. For this reason and also because of economic considerations the permeate streams will have to be treated by a suitable sulphur recovery process. The nature of this process will depend on the composition and flow rates of the permeate streams (Hao *et al*., 2002).

1.2.3 Solvent system

Traditionally the preferred acid component removal routes were based on various amine-based or mixed solvent processes for relevant sulphur component removal, followed with drying of the gas by molecular sieves. Alternately, amine processes have been selected which did not remove the mercaptants, the latter being achieved by the molecular sieves or a physical solvent processes. These techniques have been adapted by oil and gas companies that are treating their feed gas which contains CO_2, H_2S and other organic sulphur components (Van der Graaf and Klinkenbijl, 2003).

The patented research by Triplett and Brauer (1970) has included the purification of petroleum along with natural gas. The process provides methods for dissolution of the petroleum products followed by displacement through the subterranean formation from one or more injection wells to one or more production wells. The process provides for downhole heating of the liquid solvent in each

injection well at the time the liquid solvent flows into the formation from the injection well. The liquid solvent is heated through the use of heat generated by radioactive waste material in general.

Processes such as this are mainly to be used when the petroleum is of low gravity and/or the formation is of low porosity, so that the petroleum has poor flow characteristics through the formation. Since the solvent dissolves the petroleum, and both the solvent and the solvent-petroleum solution have relatively low gravities and viscosities, flow through the formation is improved. But the problem is that another treatment has to be conducted in order to separate the solvent from the petroleum.

1.2.4 Catalytic conversion system

Then the researchers turn to the most promising alternative catalytic conversion. The research interest in the catalytic reforming of CO_2 to methane has been increasing. The hydrogenation of CO_2 to methane is potentially an important reaction. The reaction of CO hydrogenation into methane is a particularly favorable example for applying these techniques since it combines fast steps such as H_2 and CO activation (Agnelli *et al*., 1998), affordable system as only the catalyst has to be maintained and it possibly can be recycled, and environmental friendly as it does not permeate any toxic gasses during reaction into the air.

The basic reaction of methanation can be considered either as a target reaction for producing methane for further chemical use or for burning as an auxiliary heat source or as a detrimental route when higher hydrocarbons and/or oxygenates are targeted such as those for the Fischer-Tropsch process or for methanol or higher alcohols syntheses (Agnelli and Mirodatos, 2000).

Methanation can be accomplished by applying heterogeneous metal oxide catalysts. Due to the high activity of rhodium and ruthenium catalysts most of the recent investigation for methanation of CO_2 have been carried out using supported Rh and Ru catalyst (Kudo and Komatsu, 1999a; 1999b). Besides commonly used

supported metal catalysts, amorphous alloys have attracted great interest as catalyst and catalyst precursors (Yamasaki *et al.*, 1997; Habazaki *et al.*, 1998). Ni is also well-known catalyst that is suitable for hydrogenation and popular reported for its low price (Aksoylu and Onsan, 1997; Yamasaki *et al.*, 1997). It possesses high activity and selectivity for CO_2 elimination, while coke deposition, which deactivates Ni catalyst and blocks the reactor, is the main problem. A lot of promoters have been reported for Ni catalyst to depress coke deposition, increase catalytic activity, and also to lower the elimination temperature so that all the CO_2 will be removed at lowest temperature possible.

1.3 Problem statement

Natural gas, typically methane, is frequently contaminated with moisture, nitrogen gas, carbon dioxide and other hydrocarbons. At some point in the extraction, transportation or treatment stages, it is important that these impurities and extraneous hydrocarbon molecules be removed or separated. Nickel based catalysts are generally considered as reference methanation catalysts, able to work efficiently in the temperature and pressure ranges of 400 to 500°C and 1000–7000 kPa (Agnelli and Mirodatos, 2000). Deactivation processes remain, however, as the main drawback encountered for this reaction. The present work was devoted to study a suitable promoter needed towards finding an affordable novel catalyst for CO_2 elimination that is high in activity, stability and selectivity. The nickel based catalyst was doped with foreign metal oxide and added with Pr. The best promoted nickel catalyst was then supported on various supports to obtain the most fitting supported catalyst towards CO_2 methanation.

1.4. Research objectives

The objectives of this research are as follows;

1. To convert CO_2 to methane using catalytic conversion of CO_2 to fuel gas.
2. To observe the effect of different mixtures of metal oxides in different ratios towards CO_2 removal.
3. To modify the catalyst to enhance the capability in catalytic activity, selectivity and durability using affordable metals to lower the cost.
4. To study the suitability and potential of mixed oxide catalyst onto different forms of support for commercialization.

1.5 Scope of research

In this research, Ni/Pr catalyst was added with selected foreign metals, M* (M* = Mg, Mo, Zr, Mn, Fe, Co, Cu), in different ratios to compose a mixed metal oxide catalyst, Ni/M/Pr. The catalyst was tested in the hope to remove CO_2 with the presence of H_2 resulting in CO_2 hydrogenation. The best unsupported catalyst was then supported on various supports to determine its compatibility between the catalyst and support and to find out its physical changes as it was put through catalytic testing. The reducibility and characteristics of the Ni based catalysts were tested by means of FTIR for catalytic activity. XRD analysis was carried out to determined phase or structural changes and it was complimented by XPS analysis that determined the oxidation state. Meanwhile, SEM, nitrogen adsorption and single point BET analysis were carried out to verify the changes in surface area and pore size of the catalyst.