DESIGN AND OPTIMIZATION OF LANTHANIDE OXIDES BASED CATALYSTS FOR CARBON DIOXIDE METHANATION

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ABSTRACT

The Malaysian crude natural gas contains toxic and acidic gases such as carbon dioxide, CO_2 (20-30%), and hydrogen sulfide, H_2S (0-1%), therefore it should be treated. The current gases treatment process including chemical solvents, adsorption process using hybrid solvents and membrane failed to meet the processing requirement. Instead, catalysts used for the CO_2 methanation have been extensively studied and high potential towards converting CO_2 gas to methane. In this research, a series of lanthanide oxide based catalysts supported on alumina and doped with manganese and ruthenium were prepared by wetness impregnation method. The lower performance of monometallic and bimetallic oxide catalysts have steered the exploration of trimetallic oxide catalyst. The potential trimetallic oxide catalysts were calcined at 400^oC, 700^oC, and 1000^oC for 5 hours separately. In-home-built micro reactor, Fourier transform infrared (FTIR) spectroscopy and gas chromatography analysis (GC) were used to study the catalytic performance by determining the percentage of CO_2 conversion and also the percentage of CH_4 formation. From the catalytic screening, it was found that the catalysts with Ru/Mn/Ce (5:35:60)/Al_2O_3 calcined at 700^oC, and Ru/Mn/Sm (5:35:60)/Al_2O_3 calcined at 1000^oC achieved 100% CO_2 conversion, Ru/Mn/Pr (5:30:65)/Al_2O_3 calcined at 800^oC achieved 96% CO_2 conversion were potential catalysts. The active species in the methanation reaction for each catalyst were MnO_2, and RuO_2 and CeO_2 or Sm_2O_3 or Pr_2O_3 respectively. Using two series furnace reactors, all three potential catalysts showed the increasing of CH_4 formation. For optimization, the parameters studied were calcination temperatures, based loadings, and catalyst dosage. The optimization was done by using response surface methodology (RSM) with Box-Behnken design which showed the significant parameters and optimum result of cerium with calcination temperature of 697.47^oC, based metal ratio of 60.38% and catalyst dosage 6.94 g as suggested by RSM. This result was tested and verified experimentally with difference of only 1%. X-rays diffraction analysis showed that the catalysts imposed an amorphous phase, while field emission scanning electron microscopy illustrated the catalyst surface was covered with small and dispersed particles with undefined shape. From electron dispersive X-rays analysis revealed that there were a reduction of Ru in the used catalyst compared to the fresh catalyst for each potential catalysts. Nitrogen gas adsorption showed that the catalysts were mesoporous structure with type H3 hysteresis loop and Type IV isotherm. Electron spin resonance spectrum showed a free electron interaction due to the presence of the peak for each potential catalyst. Temperature programmed reduction analysis of Ru/Mn/Ce (5:35:60)/Al_2O_3 catalyst showed more reducible species compared to catalysts containing Sm and Pr due to the presences of more reduce species at lower reduction temperature. The postulated methanation reaction follows the Langmuir Hinselwood mechanism which initially involves adsorption of CO_2 and H_2 gases on the catalyst surface. For Ru/Mn/Ce (5:35:60)/Al_2O_3 and Ru/Mn/Sm (5:35:60)/$A_{l2}O_3$ catalysts the product obtained were CH_4, CH_3OH and H_2O. Meanwhile, for Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst only CH_4 and H_2O were observed as a products of the reaction. Lastly, the spent catalysts were successfully regenerated by running under O_2 flow at 100^oC for 1 hour.

ABSTRAK

Gas asli mentah Malaysia mengandungi gas toksik dan berasid seperti karbon dioksida, CO_2 (20-30%), dan hidrogen sulfida, H_2S (0-1%). Oleh itu, ia perlu dirawat. Pada masa kini, proses rawatan gas termasuk pelarut kimia, proses penjerapan menggunakan pelarut hibrid dan membran gagal memenuhi keperluan pemprosesan. Sebaliknya, mangkin yang digunakan untuk metanasi CO_2 telah dikaji secara meluas dan mempunyai potensi yang tinggi untuk menukarkan gas CO_2 kepada metana. Dalam kajian ini, satu siri mangkin berasaskan lantanida oksida disokong pada alumina dan didopkan dengan mangan dan rutenium telah disediakan dengan kaedah pengisitepuan basah. Prestasi mangkin mono logam dan dwilogam oksida yang lebih rendah telah mendorong kepada penerokaan mangkin trilogam oksida. Mangkin trilogam oksida yang berpotensi telah dikalsin pada suhu 400^{o}C, 700^{o}C, dan 1000^{o}C selama 5 jam secara berasingan. Reaktor mikro buatan tempatan dengan spektroskopi infra-merah transformasi Fourier (FTIR) dan gas kromatografi (GC) telah digunakan untuk mengkaji prestasi mangkin dengan menentukan peratusan penukaran CO_2 dan juga peratusan pembentukan CH_4. Daripada penyaringan mangkin didapati bahawa mangkin Ru/Mn/Ce (5:35:60)/Al_2O_3 pada suhu 700^{o}C, dan Ru/Mn/Sm (5:35:60)/Al_2O_3 pada suhu 1000^{o}C mencapai 100% penukaran CO_2, Ru/Mn/Pr (5:30:65)/Al_2O_3 pada suhu 800^{o}C mencapai 96% penukaran CO_2 adalah mangkin-mangkin berpotensi. Dalam tindak balas metanasi, spesies aktif untuk setiap mangkin adalah MnO_2 dan RuO_2 dan CeO_2 atau Sm_2O_3 atau Pr_2O_3. Dengan menggunakan reaktor relau dua siri, ketiga-tiga mangkin berpotensi menunjukkan peningkatan pembentukan CH_4. Untuk pengoptimuman, parameter yang dikaji ialah suhu pengkalsinan, nisbah asas, dan dos pemangkin. Proses pengoptimum ini telah dilakukan dengan menggunakan kaedah respon permukaan (RSM) dengan reka bentuk Box-Behnken yang menunjukkan parameter penting dan keputusan yang optimum untuk cerium dengan suhu pengkalsinan 697.47^{o}C, nisbah asas 60.38% dan dos pemangkin 6.94 g seperti yang dicadangkan oleh RSM. Keputusan ini telah diuji dan disahkan secara eksperimen dengan perbezaan hanya 1%. Analisis belauan sinar X menunjukkan bahawa mangkin membentuk fasa amorfus, manakala pelepasan medan mikroskopi pengimbasan elektron menggambarkan permukaan mangkin itu dipenuhi dengan zarah kecil dan tersebar dengan bentuk yang tidak sekata. Dari tenaga serakan sinar-X analisis pula menunjukkan terdapat pengurangan Ru pada mangkin yang telah digunakan berbanding dengan mangkin yang belum digunakan bagi setiap mangkin berpotensi. Penjerapan gas nitrogen menunjukkan mangkin berstruktur liang meso dengan keluk jenis histerisis H3 dan isoterma Jenis IV. Spektrum resonan putaran elektron menunjukkan interaksi elektron bebas yang disebabkan oleh kehadiran puncak bagi setiap mangkin berpotensi. Analisis penyahjerapan pengaturcaraan suhu dari mangkin Ru/Mn/Ce (5:35:60)/Al_2O_3 menunjukkan banyak spesies terturun berbanding mangkin yang mengandungi Sm dan Pr kerana kehadiran banyak spesies terturun pada suhu yang lebih rendah. Tindak balas metanasi diramal mengikut mekanisme Langmuir Hinselwood yang pada mulanya melibatkan penjerapan gas CO_2 dan H_2 pada permukaan mangkin. Untuk mangkin Ru/Mn/Ce (5:35:60)/Al_2O_3 dan Ru/Mn/Sm (5:35:60)/Al_2O_3, produk yang dapat adalah CH_4, CH_3OH, dan H_2O. Manakala, untuk mangkin Ru/Mn/Pr (5:30:65)/Al_2O_3 hanya CH_4 dan H_2O dihasilkan sebagai produk tindak balas. Akhir sekali, pemangkin yang telah digunakan dan tidak aktif dijana semula di bawah keadaan aliran O_2 pada 100^{o}C selama 1 jam.

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LIST OF ABBREVIATIONS

ABS	Absorbance
BET	Brunnauer, Emmet and Teller
BJH	Barret-Joyner-Halenda
Btu	British thermal unit
CHA	Concentric hemispherical analyzer
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
ESR	Electron Spin Resonance
eV	Electronvolt
FESEM	Field Emission Scanning Electron Microscope
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
ΔH	Enthalpy change
hr	Hour
hν	Photon's energy
IUPAC	International Union of Pure and Applied Chemistry
LNG	Liquefied Natural Gas
MgKα	X-ray diffraction from Magnesium K energy levels rate of conversion (percentage)
MS	Mass Spectroscopy
MW	Molecular Weight

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
SMSI	Strong metal support interaction
tcf	Trillion cubic feet
TGA	Thermogravimetry Analysis
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
α_0	Cell constant
θ	Half angle of diffraction beam
λ	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most useful of all energy sources. Natural gas affords clean burning and emits lower levels of potentially harmful by-products into the air (Curry, 1981). Natural gas is considered 'dry' when it is almost pure methane, having most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is 'wet'.

Naturally, natural gas is produced by the anaerobic decay of non-fossil organic materials. The primary component of natural gas is methane (CH_4). It also contains heavier hydrocarbon gaseous such as ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}). Besides that, it also contains other toxic and acidic gaseous like CO_2, N_2, mercury (Hg) and H_2S as investigated by Curry, (1981).

Malaysia is currently a net exporter of natural gas and is the world's third largest exporter after Algeria and Indonesia. In 2001, the country exported 49.7% of its natural gas production in the form of liquefied natural gas (LNG) to Japan which is the world biggest user, as well as to the Republic of Korea and Taiwan under long-term contracts. The other 50.3% of Malaysia's natural gas was delivered to the gas processing plants (Radler, (2003)).

However, Malaysia's natural gas consists of several gaseous and impurities such as non-hydrocarbon gases which includes carbon dioxide. The presence of these impurities could make the natural gas fall under "sour natural gas" as they can cause the formation of corrosive compounds such as carbonic acid in the presence of water according to Speight, (2007). Sour gas also contains hydrogen sulfide, whereas sweet gas contains very little, if any, hydrogen sulfide. This will result in lowering the price of natural gas in worldwide market as well as causing difficulties for its distribution to the market.

The chemical composition of Malaysia's natural gas before it is refined is shown in Table 1.1 (*Van Rossum, 1986*).

Table 1.1 Chemical composition of Malaysia's natural gas

Chemical Name	**Percentage (%)**
Methane (CH_4)	40–50
Ethane (C_2H_6)	5–10
Propane (C_3H_8)	1–5
Hydrogen Sulphide (H_2S)	1–5
Carbon Dioxide (CO_2)	20–30

Consequently, due to the impurities of the natural gas, especially CO_2, the percentage of CO_2 gases in the Malaysia and world have increased year by year. Figure 1.1 shows the percentage of CO_2 emission based on various activities in Malaysia (Yusof *et al*., 2010). Fossil fuels supply more than 98% of the world's energy needs, though unfortunately, the resulting combustions from the utilization of fossil fuels are one of the major sources of the green house gas CO_2.

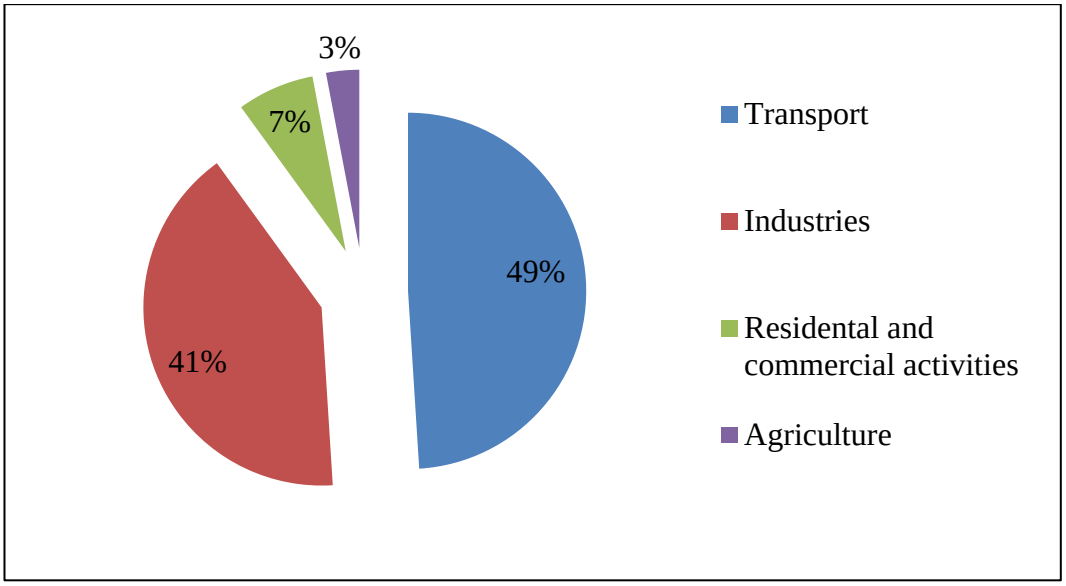

Figure 1.1 Percentage of CO_2 emission from various activities in Malaysia (Yusof *et al*., 2010).

The main objective of the United Nations Framework Convention on Climate Change (UNFCCC) is the stabilization of greenhouse gas concentrations in the atmosphere at a certain level to avoid the interference of dangerous anthropogenic with the climate system (Strakey *et al*., (1975)). The Protocol was adopted by Parties to the UNFCCC in 1997, and entered into force in 2005 as also been reported by Md Yassin (1987). As part of the Kyoto Protocol, which is an international treaty that sets binding obligations on industrialized countries to reduce emissions of greenhouse gases, many developed countries have agreed to a legal binding that required them to reduce their emissions of greenhouse gases in two commitment periods. The first commitment period applies to emissions in between 2008-2012, while the second commitment period applies to emissions flanked by the year 2013-2020. The protocol was amended in 2012 to accommodate the second commitment period (Raupach et al., (2007)) but this amendment has not (as of January 2013) entered into legal force (James and Mark (2009)).

For the developed countries to trade their commitments under Kyoto Protocol, they are allowed to trade their emission quotes among themselves and could receive credit for financing emission reduction as been reported by Zou et al., (2005). A carbon credit is a term for any tradable certificate or permit representing

the right to emit one tonne of carbon dioxide or the mass of another greenhouse gas with a carbon dioxide equivalent to one tonne of carbon dioxide (Mc Naught and Wilkinson (1997)). The aim for carbon credit is to allow market mechanisms to drive industrial and commercial processes in the direction of low emissions or less carbon intensive approaches than those used when there is no cost to emit carbon dioxide and other GHGs into the atmosphere.

Therefore, it is necessary to develop technologies that will allow the utilization of fossil fuels while reducing the emissions of green house gases. Green technology is an alternative that reduces fossil fuels and demonstrates less damage to human, animal and plant.Green technologies include such area as renewable energy sources, waste management, and remediation of environmental pollutants, sewage treatment and recycling together with water purification, as discussed by Ismail and Ishak (2011). Commercial CO_2 capture technology that exists today is very expensive and energy intensive. Improved technologies for CO_2 capture are necessary in order to achieve low energy penalties. Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of CO_2 from high pressure gas streams such as those encountered in Integrated Gasification Combined Cycle (IGCC) systems (Haldor (2005)).

At present, Malaysia has already committed under UNFCCC to implement and regularly update to mitigate climate change by reducing the emission of all greenhouse gases. Oil and gas have been the main sources of energy in Malaysia which projected to upward trend from 1244 Petajoule (PJ) in 2000 to an estimated 2218 PJ in 2010. Currently, the energy mix supply is made of gas (70%), coal (22%), oil (2%) and hydropower (6%). A new project to combust methane at Seelong Sanitary Landfill is expected to reduce CO_2 emission more than 100,000 tonnes a year and the Jendarata Steam and power plant and Jenderata Palm Oil mill have the expected combined CO_2emission reduction of more than 30,000 tonnes annually as reported by Lau *et al*., (2009) and Razak and Ramli (2008).

1.2 Gas Purification Process

Gas processing is necessary to ensure that the natural gas intended for use is clean-burning and environmentally acceptable. One of the most important procedures 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.

Amine treating is one of the processes used to remove CO_2 and H_2S from natural gas. Amine has a natural affinity for both CO_2 and H_2S which allows it to be very efficient and effective in the removal process. When CO_2 reacts with water, it creates carbonic acid which is corrosive. CO_2 also reduces the BTU value of gas and the gas is unmarketable as it reaches concentrations of more than 2% or 3 %. H_2S is an extremely toxic gas that is also tremendously corrosive to equipment. Amine plant design is based on proven amine regeneration technology and incorporates several patent-pending processes to improve the reliability and ease of operation. This process has many advantages, especially in regards to its lower installation and removal costs. Amine sweetening processes remove these contaminants so that the gas is marketable and suitable for transportation (William and David (2005)). However, this method has a few limitation which are complex and have high capital, operating, and installation costs; a relatively high fuel cost and potential environmental issues.

Another method is PRISM membrane from Air Product Company that can be used as a gas scrubber for natural gas. The CO_2 gas needs to be removed to improve the heating value of the gas and to meet the pipeline specification. The benefits of this process include minimal maintenance cost, no involvement of hazardous chemical, as well as being easy to be installed and operated. Prism membranes will effectively separate carbon dioxide from hydrocarbon vapours (Michael, 2010). However, the performance is highly dependent on CO_2 content in the raw feed gas, CO_2 specification in product, supply pressure; permeate pressure, and operating temperature as investigated by Stookey, (1986).

Membrane separation process performs on the principle of selective gas permeation. When gas mixture is introduced to membrane, component of gas permeated along into membrane material and diffuses through the membrane material. Gas treating membrane provides a safe and efficient option for water vapour and carbon dioxide from natural gas. Components with higher permeation rates (such as CO_2, H_2, and H_2S) will permeate faster through the membrane module than components with lower permeation rates (such as N_2, Cl, C_2H_6 and heavier hydrocarbons). The primary driving force of the separation is the differential partial pressure of the permeating component. Therefore, the pressure difference between the feed gas and permeate gas and the concentration of the permeating component determine the product purity and the amount of carbon dioxide membrane surface required.

For years, the iron sponge type process has widely been used by the industry to treat sour gas. An iron sponge is a cylinder shaped vessel containing iron oxide treated wood chips. The iron oxide reacts with hydrogen sulfide to from relatively inert iron sulfide and water. However, the iron oxide does not last forever and the effectiveness of the wood chips will eventually fall below acceptable standards. When this occurs, the iron sponge must be taken off-line and the old wood chips are replaced by a new fully charged material. There are increase concerns of the environmental impact associated with the disposal of spent material and labor costs for replacement. These would increase the number of scavengers with better disposal properties.

Clauss process is the most significant method known in the removal of sulphur from hydrogen sulphide gaseous. The multi-step Claus process recovers sulfur from the hydrogen sulfide gaseous found in raw natural gas and for over 25% H_2S contents. The Clauss process contains two steps which is thermal and catalytic. In the thermal step, hydrogen sulfide-laden gas reacts in a substoichiometric combustion at temperatures above 850°C such that elemental sulfur precipitates in the downstream process gas cooler. Usually, 60 to 70% of the total amounts of elemental sulfur produced in the process are obtained in the thermal process step. Then the process continues with catalytic processing which involves the use of

activated aluminiums (III) or titaniums (IV) oxide and serves to boost the sulfur yield. More hydrogen sulfide (H_2S) reacts with the SO_2 during combustion in the reaction furnace in the Claus reaction, and the product is in gaseous, and elemental sulfur.

Even though several methods as mentioned above have been developed for the removal of acid gases from the natural gas composition, these methods have several general drawbacks such as its high cost and production of high heat of reaction. Therefore, a new method was focused in this study which is a more promising method that involves the utilization of the catalytic conversion system by using supported mixed metal oxides catalyst.

1.3 Catalytic Methanation

Methanation is a physical-chemical process to generate methane from a mixture of various gases out of biomass fermentation or thermal-chemical gasification as defined by Ponee (1978). Meanwhile, catalytic methanation reaction refers to a process for removing carbon monoxide and carbon dioxide from gas stream for producing methane by using catalyst (Mills and Fred, 1974).

The essential requirement for the correct selection of the metal oxide catalyst system is its ability to accept and to activate CO_2 and H_2S. The acidic nature of CO_2 and H_2S requires the employment of a catalytic system with Lewis basic properties such as Group VIII metals. The major reason for the much slower development of the catalyst science of mixed metal oxide is its significant complexity compared with single metal based catalysts such as the possible presence of multiple oxidation states, variable local coordination, coexisting bulk and surface phases as well as different surface termination functionalities such as M-OH, M=O or M-O as mentioned by Ertesva, *et al*., (2005).

The relative activity of various transition metals for methanation and desulphurization can be determined at atmospheric pressure under the conditions in which most other hydrocarbon molecules are likely to form. In a previous research by Vannice (1987), the order of decreasing activity of transition metals was Fe > Ni > Co and the activation energy for methanation of CO_2 and H_2 was in the range of 23-25 kcal/mole.

In natural gas purification, the conversion of carbon dioxide to methane is an important process. To form methane (CH_4), hydrogen gas is used along with carbon dioxide and carbon monoxide gas (from incomplete methanation reaction) through methanation process as shown in Equation 1.1 and 1.2 below:

$$CO_2\,(g) + 4H_2\,(g) \xrightarrow{\text{Catalyst}} CH_4\,(g) + 2H_2O\,(l) \qquad (1.1)$$

$$CO\,(g) + 3H_2\,(g) \xrightarrow{\text{Catalyst}} CH_4\,(g) + H_2O\,(l) \qquad (1.2)$$

The catalytic reactions depend on the interactions between the active sites and the reactants, in a series of adsorption-desorption and surface reaction steps, as well as heat and mass transfer (Saluko, 2005).

Since the catalytic process through methanation reaction provides the most effective way to remove CO_2 and H_2S in the natural gas, therefore, the present study was conducted in order to develop a catalyst based on lanthanide oxide by modifying the dopants using noble metal in order to fully remove these sour gases at high conversion percentage and, possibly, at low temperature. Lanthanide oxide was used because the chemistry of the lanthanides differs from the main group elements and the transition metals. The nature of the 4f orbitals and its ions has slightly different radii, leading to a small difference in solubility as reported by Holden and Coplen (2004).

1.4 Response Surface Methodology

Response surface methodology (RSM) is a set of techniques used in the empirical study of relationship between one or more responses and a group of variables (Cornell, 1990). RSM is useful for developing, modelling, improving, and optimizing the important response variable in an experiment run through the analyzing of programs. RSM comprises of three techniques or methods (Montgomery, 1999): (1) statistical experimental design, particularly the two level factorial or factorial design, (2) regression modeling techniques, and (3) optimization for optimum operating conditions through experimental methods. The most common application of RSM is in industrial, biological and clinical science, social science, food science, and physical and engineering sciences. According to research conducted by Myers *et al.,* (1992), the first-order model was motivated by Box and Hunter, (1954) by using *orthogonal design*. The second-order model, which is most frequently used, consists of the 3^k *factorial, central composite designs (CCD),* and *Box-Behnken design*. An approximate of the relationship between y and the independent variables for second-order model is shown in Equation 1.3 and 1.4 where xi and xj are the design variables and β are the tuning parameters.

$$y = \beta_0 + \beta_1 x_1 + \cdots + \beta_k x_k + \varepsilon \tag{1.3}$$

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \tag{1.4}$$

The CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points (Joglekar and May, (1987)). Alternatively, Box-Behnken presents some advantages such as requiring few experimental points for its application (three levels per factor) and high efficiency as discussed by Khuri and Mukhopadhyay, (2010). The use of Box-Behnken design is popular in industrial research because it is an economical design and requires only three levels for each factor where the settings are -1, 0, and 1. Recently, more emphasis for an improvement in response instead of finding the optimum response has been placed by chemical and processing fields (Myers *et al*, 1992).

1.5 Mechanism of Methanation Reaction Process

The CO_2/H_2 methanation reaction follows the Langmuir Hinshelwood (LH) mechanism which involves initially the adsorption of CO_2 and H_2 gases on the catalyst surface. Adsorption, desorption and surface diffusion play an essential role in LH mechanism. Four assumptions of Langmuir-Hinshelwood are: (1) the surface of the adsorbent is uniform, (2) adsorbed molecules do not interact, (3) all adsorption occurs through the same mechanism, and (4) at the maximum adsorption, only a monolayer is formed.

Therefore, it might be expected that the reaction rate should depend on the surface coverage of both species. Moreover, the dissociation of adsorbed H_2 molecule results in the formation of active H atom species, followed by dissociation of CO_2 molecule. This theory was supported by Solymosi *et al.*, (1981), who stated that CO_2 dissociation on supported precious metal catalysts using a conventional pulse reaction was promoted by the presence of H and CH_X fragments on a catalyst surface. They also proposed that CO_2 adsorption and subsequent dissociation on transition metals proceed through electron transfer from a metal to a CO_2 molecule to form anion radical species. Therefore, the adsorbed species attains a lower energy state once it has been adsorbed to the metal, thus lowering the activation barrier between the gas phase species and the support-adsorbed species. Afterward, the active H atom species attaches to the O atom to form water molecule and this process continuous until the carbon atom is fully attached with H atom to form methane.

According to Equation 1.5, 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 molecule that also reacts 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.

For the simplest possible reaction, methanation process can be described as shown in Equation 1.5 to 1.9.

$$CO_2 + S \rightleftharpoons CO_{2(ads)} \quad (1.5)$$

$$H_2 + S \rightleftharpoons H_{2(ads)} \quad (1.6)$$

$$CO_{2(ads)} + H_{2(ads)} \rightleftharpoons CH_{4(ads)} + H_2O_{(ads)} \quad (1.7)$$

$$CH_{4(ads)} \rightleftharpoons CH_{4(desorp)} + S \quad (1.8)$$

$$H_2O_{(ads)} \rightleftharpoons H_2O_{(desorp)} + S \quad (1.9)$$

*S = Catalyst Surface

(ads) = adsorption of molecule on the catalyst surface

(desorp) = desorption of molecule on the catalyst surface

1.6 Statement of Problem

In Malaysia, population in urbanized area has been increasing rapidly and at the same time, demands for certain types of product by have increased in order to meet the current demands of the society. Modern society is highly dependent on vehicles such as cars, trucks and railways. Emissions from the vehicles rely mostly on burning fossil fuel, thus contributing to the many predominant green house gases (CO_2, SO_2, NO_2) emitted into the air either locally or globally. Carbon dioxide is the most significant green house gas produced from the transportation activities and the effects brought by it is attributed to the global warming phenomenon if adequate controls or mitigation measures are not taken as investigated by Yusof *et al*., (2010).

The natural gas contains the most significant impurities, which are carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Due to the impurities of CO_2 and H_2S, the natural gas will have lower quality and worldwide price. The reaction of CO_2 and H_2S with water could result into a highly corrosive acid which could rapidly destroy the pipelines and equipment as well as reducing the lifetime of equipment (Dortmundt *et al*., 1999). H_2S itself is a colorless and flammable gas. It smells like rotten eggs that is toxic at extremely low concentration and can cause the loss of a

human's sense of smell. Therefore, these gaseous need to be removed in order to prevent or minimize the release of hazardous gases into the environment. This will help to reduce problems such as acid rain, ozone layer depletion or greenhouse effect. Hence, suitable methods are needed to overcome this problem.

Many methods on conversion of CO_2 such as amine treating, membrane separation, and others have been developed and investigated by researchers. However, these methods have several drawbacks such as low selectivity, high cost, and most importantly, the methods only work in the presence of $CO_2 \leq 10\%$. As Malaysia's natural gas contains $\geq 23\%$ of CO_2 most of these methods are inapplicable in the efforts to convert the country's natural gases. Therefore, an alternative method is needed that is more economical and environmental-friendly.

Recently, an alternative method has been developed which is the catalytic conversion of CO_2 *via* methanation reaction. This method removes the toxic CO_2 gas and produces valuable methane simultaneously. It is also an economical method since the catalysts can be recycled, and it is also environmentally friendly as it does not emit any toxic gas into the air while the reaction takes place.

From previous study, most catalysts used were nickel, cobalt, ruthenium, and iron deposited on an alumina support for CO_2/H_2 methanation technique. However, these catalysts are very sensitive towards chemical attack, thus the performance of catalysts was not promising due to lower conversion of CO_2 in methanation process. Therefore, lanthanide oxide doped with noble metal was used in this study in order to overcome these problems by increasing the percentage conversion of CO_2 at lower reaction temperature. The potential of lanthanide oxide has been widely used as a based catalyst in ethanol reforming, adsorbent for desulfurization in realistic fuel processor, polymerization, ammonia synthesis, oxygen assisted water gas-shift, and HCOOH hydrogenation.

1.7 Objectives

Based on the problem statement which was focused on methanation reaction and the efforts to find the best catalysts for the conversion of CO_2 gas and production of higher methane, several objectives for this study were developed. The objectives of this research are as follow:-

1. To synthesize, characterize, and test the catalytic activity of supported lanthanide oxide doped manganese and cobalt with ruthenium as co-dopant catalysts for carbon dioxide methanation using fixed bed home-built micro reactor coupled with FTIR.
2. To optimize the catalysts preparation by various calcination temperatures, ratio based loadings and catalyst dosage ratio in the catalytic testing by response surface methodology.
3. To regenerate the spent catalysts from the reaction by running under O_2 flow at 100^{o}C for 1 hours.
4. To propose the reaction mechanism through the analysis on the metal oxide surface and flue gas mixture.

1.8 Significance of Study

The increasing carbon dioxide and other green house gases content in Malaysia which contributes to global warming must be treated. The most significant reason that contributes to CO_2 emission is from transportations and chemical industries. Natural gas contains 23% of CO_2 gas that contributes to acid rain phenomena when it reacts with water. Therefore, CO_2 gas must be remove via methanation process which offers a green and clean technology to convert it into valuable methane gas. The methane produced can be used as fuel and in the case of natural gas, will improve the gas quality. This process is low cost and the catalyst used can be recycled. Lanthanide metals were used as the alternative catalysts and

are expected to be in low price, highly effective in reaction and can be highly activated at low temperature.

1.9 Scope of Study

In this research, lanthanide (samarium, cerium, praseodymium, lanthanum, neodymium, and gadolinium) oxides were used as catalyst's based while the dopants used were manganese and cobalt nitrate salt as precursor. The preparation of catalyst was conducted by incipient wetness impregnation method. Then the catalytic activity testing was conducted by using simulated natural gas and was carried out by the mixing of hydrogen and carbon dioxide gases (4:1) in a house-built micro reactor. The optimization parameters was done by Box-Behnken design with three critical parameters which are calcination temperature, ratio based loadings and catalyst dosage. The mechanistic study was conducted using Ru/Mn/Ce (5:35:60)/Al_2O_3, Ru/Mn/Sm (5:35:60)/Al_2O_3 and Ru/Mn/Pr (5:35:60)/Al_2O_3 catalysts using FTIR, GC and HPLC. The characterizations of catalyst were conducted by using various analytical techniques such as TGA-DTA, FESEM-EDX, XPS, ESR, TPR, XRD, FTIR, and NA techniques. The detailed research study is summarized in Figure 3.1.

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