SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION OF CERIUM AND CALCIUM OXIDES BASED CATALYSTS TOWARDS CARBON DIOXIDE METHANATION REACTION

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DEDICATION

This thesis is dedicated to the most honourable personality of the whole universe to **Muhammad (SALLALLAHOU ALAYHE WASALLAM)**.

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Malik Muhammad Asif Iqbal

ABSTRACT

Novel trimetal-oxide (Ru/Fe/Ce) supported on γ-Al_2O_3 catalysts were synthesized by simple impregnation method. The conversion of CO_2 to CH_4 was optimized using response surface methodology (RSM) based on the amount of catalyst loading, calcination temperatures and catalyst dosages. In addition, stability, reliability, robustness, reproducibility, and regeneration testing were also investigated. Superior catalytic performance was obtained using catalyst with ruthenium content of 5 wt% loading, iron content of 10 wt% loading and cerium content of 85 wt% loading which was calcined at 1000°C for 5 h. The CO_2 conversion achieved 97.2% at 275°C with CH_4 formation of 93.5%. The Ru/Fe/Ce (5:10:85)/γ-Al_2O_3 catalyst exhibits excellent catalytic stability up to 65 h. CO_2-TPD results revealed this catalyst possesses medium-strength basic sites while TPR study revealed the catalyst exhibits best reduction pre-treatment at >250°C. Meanwhile, the BET analysis illustrated the catalyst possesses a mesoporous structure. XRD revealed the transformation of cubic Al_2O_3 calcined at 1000°C to rhombohedral at 1100°C. TEM micrographs revealed the d-spacing value is in accordance with XRD analyses. FESEM micrographs displayed the catalyst surface is covered with small, dispersed spherical particles. EDX mapping profile showed good distributions of Ce, Fe, and Ru on the catalyst surface. The physicochemical analyses have shown that the active sites of the potential catalyst Ru/Fe/Ce (5:10:85)/γ-Al_2O_3 are RuO_2 (t), Fe_2O_3 (r), Al_2O_3 (c), Al_2O_3 (r) and CeO_2 (c) with a particle size <10 nm. The mechanistic studies have shown that CO_2 methanation occurs via the adsorption of CO_2 on surface of ceria and iron oxide, and then stepwise hydrogenation leading to CH_4 formation through carboxylate intermediate by the hydrogen spilled over from Ru surface. As a result, dissociated hydrogen over ruthenium reacts with surface carbon, leading to formation of *CH intermediate, which subsequently hydrogenated to produce *CH_2, *CH_3 and finally to the desired product methane. The Ru/Fe/Ca (5:25:70)/γ-Al_2O_3 catalyst calcined at 1000°C gave a maximum conversion of 85.59% CO_2 with CH_4 formation of 79.58% at a reaction temperature of 300°C which was less as compared to the potential catalyst Ru/Fe/Ce (5:10:85)/γ-Al_2O_3.

ABSTRAK

Mangkin baharu trilogam-oksida (Ru/Fe/Ce) yang disokong pada γ-Al_2O_3 telah disintesis melalui kaedah pengisitepuan mudah. Penukaran CO_2 kepada CH_4 telah dioptimumkan menggunakan kaedah permukaan gerak balas (RSM) berdasarkan jumlah muatan mangkin, suhu pengkalsinan dan dos mangkin. Tambahan lagi, ujian kestabilan, kebolehpercayaan, keteguhan, kebolehulangan dan penjanaan semula telah juga dikaji. Prestasi pemangkinan unggul diperolehi menggunakan mangkin dengan kandungan rutenium 5 wt%, muatan kandungan ferum10 wt%, dan muatan kandungan serium 85 wt% yang dikalsinkan pada 1000°C selama 5 j. Penukaran CO_2 mencapai 97.2% pada 275°C dengan pembentukan CH_4 93.5%. Mangkin Ru/Fe/Ce (5:10:85)/γ-Al_2O_3 mempamerkan kestabilan pemangkinan yang sangat baik sehingga 65 j. Keputusan CO_2-TPD mendedahkan mangkin ini mempunyai tapak bes berkekuatan sederhana manakala kajian TPR mendedahkan mangkin ini mempamerkan pengurangan pra-rawatan terbaik pada >250°C. Sementara itu, analisis BET menunjukkan mangkin mempunyai struktur mesoporos. XRD mendedahkan transformasi Al_2O_3 kubik dikalsinkan pada 1000°C kepada rombohedral pada 1100°C. Mikrograf TEM mendedahkan nilai d-jarak adalah bersesuaian dengan analisis XRD. Mikrograf FESEM memaparkan permukaan mangkin ditutupi dengan zarah-zarah kecil berbentuk sfera yang tersebar. Profil pemetaan EDX menunjukkan penyebaran yang baik bagi Ce, Fe, dan Ru pada permukaan mangkin. Analisis fisikokimia menunjukkan bahawa tapak aktif bagi mangkin yang berpotensi Ru/Fe/Ce (5:10:85)/γ-Al_2O_3 adalah RuO_2 (t), Fe_2O_3 (r), Al_2O_3 (c), Al_2O_3 (r) CeO_2 (c) dengan saiz zarah <10 nm. Kajian mekanistik menunjukkan bahawa metanasi CO_2 terjadi melalui penjerapan CO_2 pada permukaan seria dan ferum, dan kemudian penghidrogenan langkah demi langkah membawa kepada pembentukan CH_4 melalui perantaraan karboksilat oleh hidrogen yang terbebas dari permukaan Ru. Akibatnya, hidrogen yang terpisah pada rutenium bertindak balas dengan permukaan karbon, yang membawa kepada pembentukan perantaraan *CH dan penghidrogenan selanjutnya menghasilkan *CH_2, *CH_3 dan akhirnya produk metana yang dikehendaki. Mangkin Ru/Fe/Ca (5:25:70)/γ-Al_2O_3 yang dikalsin pada 1000°C memberi penukaran maksimum, 85.59% CO_2 dengan pembentukan CH_4 ,79.58% pada suhu tindak balas 300°C yang mana ia lebih rendah berbanding dengan mangkin berpotensi Ru/Fe/Ce (5:10:85)/γ-Al_2O_3.

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LIST OF ABBREVIATIONS

3D	-	Three dimensional
ABS	-	Absorbance
Ads	-	Adsorbed
BBD	-	Box-Behnken design
BET	-	Brunnauer, Emmet and Teller
BJH	-	Barret-Joyner-Halenda
DRIFTS	-	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EDX	-	Energy Dispersive X-rays Analysis
fcc	-	Face-centred cubic
FESEM	-	Field Emission Scanning Electron Microscopy
FID	-	Flame Ionization Detector
FT	-	Fischer-Tropsch
FTIR	-	Fourier Transform Infrared
HC	-	Hydrocarbon
HRTEM	-	High Resolution Transmission Electron Microscopy
JCPDS	-	Joint Committee on Powder Diffraction Standard
MgKα	-	X-ray diffraction from magnesium K energy levels rate of conversion (percentage)
NA	-	Nitrogen Adsorption
MS	-	Mass spectrometer
o	-	Orthorhombic
ppm	-	Parts per million
P/P°	-	Relative pressure
r	-	Rhombohedral
Rf	-	Response factor
RSM	-	Response Surface Methodology
RWSG	-	Reverse water Gas Shift
SNG	-	Substitute natural gas
STP	-	Standard Temperature Pressure
t	-	Tetragonal

TEM	-	Transmission Electron Microscopy
TGA	-	Thermogravimetry Analysis
TPR	-	Temperature Programmed Reduction
wt%	-	Weight percentage
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction
ΔH	-	Enthalpy change
CuKα	-	X-rays diffraction from Copper K energy levels rate of conversion (percentage)

LIST OF SYMBOLS

cf	-	Cubic feet
d	-	Pore dimeter
α	-	Alpha
γ	-	Gamma
θ	-	Half angle of diffraction beam
λ	-	wavelength
hr	-	Hour

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CHAPTER 1

INTRODUCTION

1.1 Background

Anaerobic decomposition of non-fossil organic material produces natural gas. This highly flammable gas is a homogenous liquid with low density and viscosity. Moreover, acidic gases such as CO_2 and H_2S are also present in the natural gas (Curry, 1981). Malaysia has been extracting sour natural gas. Before the purification process begins, Malaysian natural gas consists of several gaseous impurities (Bakar and Ali, 2010). The chemical composition of crude Malaysian natural gas is shown in Table 1.1

Table 1.1 Chemical composition of crude natural gas, Terengganu, Malaysia (Bakar and Ali, 2010).

Chemical Name	Chemical formula	Percentage (%)
Methane	CH_4	40-50
Ethane	CH_3-CH_3	5-10
Propane	CH_3-CH_2-CH_3	1-5
Carbon dioxide	CO_2	3-20
Hydrogen sulphide	H_2S	0-1

To increase the calorific value of natural gas and prevent corrosion of pipelines and process equipment, it is essential to eliminate the presence of CO_2 in raw natural gas. Moreover, at a very low temperature, CO_2 tends to freeze to form solidified CO_2,

which leads to clogging of the pipeline. This impurity in natural gas can reduce its quality and thus reduces the market price of gas. Therefore, the elimination of carbon dioxide from the natural gas is very important to prevent or minimize the emission of hazardous gases into the environment. Among the multiple human activities that produce GHGs, the usage of energy is undoubtedly the largest source as shown in Figure 1.1.

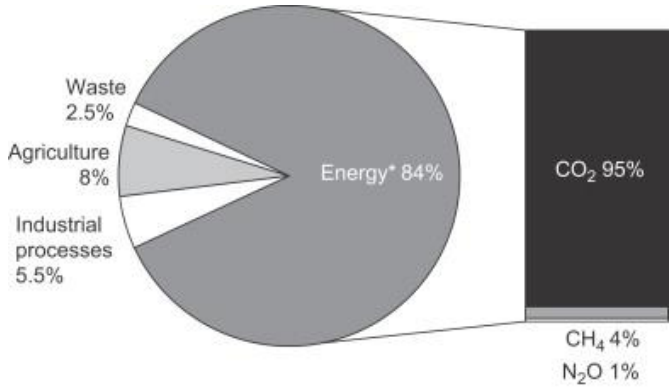

Figure 1.1 Shares of global anthropogenic GHGs emission (Quadrelli and Peterson, 2007).

1.2 Various technologies for the CO_2 removal from natural gas

At present, there are many ways to capture and separate CO_2. Three general categories of processes available for removal of CO_2 from refinery gas streams are chemical solvents, physical solvents, and solid adsorbents (Maples, 2000).

1.2.1 Chemical absorption method

Alkanolamine includes the family of organic compounds such as mono-ethanolamine (MEA), diglycol amine (DGA), diisopropanol amine (DIPA), methyl diethanolamine (MDEA), diethanolamine (DEA) and triethanolamine (TEA). Among these amines, MEA is the strongest because it can remove both CO_2 and H_2S from the gas streams. In the chemical absorption process, typically amine solution such as MEA

is employed and its recovery rate for CO_2 is 98%. The MEA solution absorption process has been used commercially in the gas industry for 60 years and is considered the most mature process (Mokhatab *et al.*, 2018). However, this method can only work if CO_2 is present not more than 10%.

1.2.2 Physical adsorption method

Adsorption process is generally considered as low energy intensive and very cost-effective method. Physical adsorbents such as zeolites, molecular sieves, polymers, templated silicas, and activated carbon typically adsorb water vapor better over CO_2 and their CO_2 adsorption capacity at low pressure is not sufficiently high (Bell *et al.*, 2010; Olajire, 2010). However, the main drawback of this process is the high amount of adsorbent required due to large amount of flue gases in stationary plants.

1.2.3 Membrane technology

The quality of natural gas can also be improved with special polymer membranes. These membranes can reduce the concentration of H_2S and CO_2, but they are not as effective for the separation of toxic gases and require high cost (Omidvar *et al.*, 2019). This method uses polymeric membranes (contains semi-permeable elements), which are responsible for the separation of gas constituents by selective permeation in contact with the membrane. A two-stage membrane system is considered better than a single-stage hydrocarbons recovery system. Moreover, the system is highly effective at low flow rates, but its performance is reduced when the flow rate exceeds the set limit. Thus, this method is economically ineffective as the flow rate increases (Kohl and Riesenfeld, 1997). UOP polymeric membranes are more effective for the removal of H_2S from natural gas, although natural gas has higher concentration of H_2S and higher operating pressures. These membranes cut off acidic gases to a reduction level from 70-90% (Cnop *et al.*, 2007). However, polymeric

membranes have drawbacks like low permeability and selectivity, plasticization at high temperatures, but also insufficient thermal and chemical stability.

1.3 Catalytic methanation

Methanation of CO_2 is an important process for the purification of natural gas. Hydrogen gas is used in addition to the carbon dioxide gas to form methane (CH_4). The methanation process is shown in the equation below.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1.1)$$

The advantage of catalytic methanation has led researchers to choose this process due to its higher thermal stability, good chemical resistance to solvents, high mechanical strength, recyclable and long lifetime.

Our previous studies (Bakar *et al.*, 2015; Rosid *et al.*, 2019; Toemen *et al.*, 2016; Toemen *et al.*, 2018; Zamani *et al.*, 2014) has drew attention on methanation reaction, which highlights that how adsorption strength of CO_2 is controlled by Lewis basicity of catalyst, and the charge transfer from metal surface to chemisorbed CO_2. Different transition metals and lanthanide elements such as Ni, Pd, Rh, Cu, Mn, Ru and Ce supported on alumina were investigated. Zamani *et al.* (2014) has reported the methanation of carbon dioxide over Ru/Mn/Cu(10:30:60)/Al_2O_3 catalyst calcined at 1035°C could give 98.5% CO_2 conversion and 70% methane (CH_4) formation at reaction temperature of 220 °C. The use of high loading makes it more economical, and it shows less formation of methane as well as showed stability for seven hours only that makes it unfit to use it in industrial application. In another study by Bakar *et al.* (2015), the Ru/Mn/Ni(5:35:60)/Al_2O_3 catalyst calcined at 1000°C showed excellent methanation catalytic activity. They reported the potential catalyst exhibited the highest catalytic activity at a reaction temperature of 400°C, which gave 99.74% of CO_2 conversion with a low yield of 72.36% of methane. The Ru/Mn/Ni (5:35:60)/Al_2O_3 catalyst calcined at 1000°C showed reproducibility for several times

and also shows good stability and no deactivation for up to 100 h. However, a high reaction temperature of 400°C and low yield of 72.36% are the main drawbacks of this catalyst.

The CO_2 conversion using neodymium doped with manganese and ruthenium was studied by Rosid *et al.* (2019). They evaluated that Ru/Mn/Nd (5:20:75)/Al_2O_3 calcined at 1000°C gave CO_2 conversion of 100% and CH_4 formation of 40.0% at a reaction temperature of 400°C under molar ratio of 4:1 (H_2:CO_2). This result suggested that a lot of formation of by products along with the methane and higher reaction temperature makes it unfit to use at industrial level. Ceria is a well-known oxygen storage material, able to store and release in a reversible manner large amounts of oxygen was used by Toemen *et al.* (2018) for the production of SNG from CO_2 hydrogenation. The ceria based catalyst impregnated with Ru/Mn/Al_2O_3 was developed. The experimental results have shown that Ru/Mn/Ce (5:30:65)/Al_2O_3 catalyst calcined at 1000°C achieved 97.73% of CO_2 conversion with 91.31% of CH_4 at a reaction temperature of 200°C. The catalyst started to deactivate (spent catalyst) at 6^{th} cycle with a CO_2 conversion of 41.17%. This catalyst also faces a problem in terms of low stability.

1.4 Role of metal oxides in methanation reaction

1.4.1 Role of ceria in methanation reaction

In many catalytic reactions, CeO_2 is an active component because it can absorb and release oxygen by transformation between Ce^{4+} and Ce^{3+} (Zhou *et al.*, 2016). The bulk vacancies created in CeO_2 catalyst after reduction at high temperature could enhance the carbon dioxide methanation (Trovarelli *et al.*, 1995). Due to its high basicity, CO_2 is easily adsorbed on CeO_2 catalyst that could contribute to high CO_2 conversion (Tada *et al.*, 2014).

1.4.2 Role of calcium oxide in methanation reaction

CaO is widely used as an excellent promoter for various catalysts owing to its high CO_2 chemisorption capacity (Sengupta and Deo, 2015). It has been identified that CaO is good adsorbing material for CO_2 because of its low cost, natural abundance and stoichiometric reactive sorption capacity of 0.785(g of CO_2/g of oxide) which is higher than other metal oxide such as BaO has 0.287 (g of CO_2/g of oxide), K_2O has 0.468 (g of CO_2/g of oxide), SrO has 0.425 (g of CO_2/g of oxide), ZnO has 0.540 (g of CO_2/g of oxide) (Feng *et al.*, 2007).

1.4.3 Role of iron oxide in methanation reaction

The lower iron content was characterized by the highest selectivity with respect to CH_4 while the catalyst with the highest Fe content had the lowest methane selectivity. The increase in iron content resulted in a decrease in both carbon dioxide conversion and methane production (Kang *et al.*, 2011). Iron oxide is responsible for the elongation and bending of linear structure molecule of CO_2 to facilitate the lower reaction temperature of methanation (Jo *et al.*, 2000).

1.4.4 Role of ruthenium oxide in methanation

Ruthenium is the most active metals for CO_2 methanation (Wang *et al.*, 2016). Ru cluster size also affects the product selectivity during CO_2 reduction with H_2. With increasing particle size, Ru increase selectivity with respect to methane formation and decreases the production of carbon monoxide (Kwak *et al.*, 2013). High activity, low load and long-time stability are vital factors leading to the use of Ru in the methanation reaction. Ru is an excellent noble metal for breaking H_2 gases into H atoms on the surface of the catalyst.

1.5 Response Surface Methodology (RSM)

Response surface methodology (RSM) is a set of statistical and mathematical methods beneficial for the development, improvement, and optimization of processes. In recent years, RSM is the common most used for optimization methods. The experimental design and statistical analysis are carried out using the Design-Expert software. The development of experiments is now of importance due to their significant advantages, such as the reduction of the number of experiments, the minimization of operating costs and time, as well as the improvement of the analysis of the results obtained. RSM is a powerful statistical and mathematical analysis method that is used to extend, develop, and modify the catalytic optimization process through numerous studies (Toemen *et al.*, 2014). To assess the impact of process variables and their interaction on the response to achieve optimal conditions, Box-Behnken design (BBD) was used in this research.

1.6 Problem Statement

Carbon dioxide is one of the major natural gas impurities by its composition of 20-30%. The CO_2 presence leads to the environmental pollution as well as the natural gas delivery system. The emitted CO_2 into the atmosphere contributes to global warming. At the same time, the presence of CO_2 can cause corrosion in main pipelines. The delivery pipeline is generally blocked by freezing, resulting in various maintenance problems and reduced production efficiency. Hence, it is necessary to completely remove hazardous CO_2 gas in natural gas. Several technologies like chemical absorption method, physical absorption method and membrane technology are used in the natural gas sweating process. But these methods are still not effective, have a low selectivity and are not economically efficient. They can remove only 10% of CO_2 in the crude natural gas. Green technology can be applied to remove CO_2 by a catalytic methanation reaction. CO_2 can be converted to methane gas so that methane production can be increased.

The previous studies have shown that methanation catalysts such as cobalt, nickel, manganese, copper and zinc deposited on alumina support face challenges in terms of stability, reproducibility, regeneration, and operating temperature catalysts. Therefore, the development of a highly active catalysts is an important goal aiming the production of methane at low temperatures and high conversions of CO_2. Problems have been revealed with rapid deactivation of methane catalysts in reaction conditions and low selectivity with respect to desirable products such as methane.

1.7 Research Objectives

The main purpose of this study is to develop potential catalysts that can operate effectively at very low possible temperature for CO_2 methanation reaction. The main objectives of this study are:

1. To synthesize, characterize and optimize the catalytic activity of alumina supported CeO_2 and CaO based bi- and tri-metallic catalysts using Fe_2O_3 and RuO_2 for the hydrogenation of CO_2 to methane.
2. To verify the optimal conditions attained in laboratory experiments by comparing its results with the predicted value of RSM.
3. To investigate the reproducibility, regeneration, and stability of the potential catalyst.
4. To propose the methanation reaction mechanism over potential catalyst.

1.8 Scope of study

The aim of this study is to prepare cerium and calcium-oxides based catalysts for CO_2 methanation reaction. The catalysts were prepared by incipient wetness impregnation method and supported on γ-Al_2O_3. The incorporation of iron and ruthenium as co-catalysts was added in order to enhance the catalytic methanation.

The prepared catalysts were calcined at 400°C, 700°C and 1000°C and was tested in home built microreactor connected to FTIR.

In order to determine the optimal conditions for catalysts that contribute to the highest CO_2 conversion, several optimization parameters such as calcination temperatures, co-catalyst loadings, catalyst dosages, reliability testing, reproducibility testing and stability testing were studied. Catalytic optimization validation was executed using the statistical method of response surface methodology (RSM). Various analytical methods such as Nitrogen Adsorption method (NA), Thermo-gravimetry Analysis-Differential Thermal Analysis (TGA-DTA), X-rays Diffraction (XRD), Field Emission Scanning Electron Microscope-Energy Dispersive Analysis of X-Ray (FESEM-EDX), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS) were used to study the physical properties of the catalysts. Adsorption properties of CO_2 depending on the reaction temperature were studied using IR analysis.

1.9 Significance of study

The present study is of interest from the perspective of the concept that CO_2 present in natural gas can be used to produce valuable methane without the loss of undesired component (CO_2). The methanation process can be used to process a large quantity of CO_2 in a short time. The catalysts developed were effective at low temperature, stable, moderately basic in nature and resistant to chemicals. This “green technology” approached for the production of methane gas was considered as an environmentally friendly method for waste to wealth concept. This green technology helps to reduce problems associated with acid rain, ozone depletion or greenhouse effect, and to improve the quality of natural gas. Catalysts developed in this study have contributed not only to economic growth, but also to the creation of a green environment. Furthermore, the catalysts were easy to prepare, environmentally friendly, stable, reusable and used at low reaction temperatures.

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