

SYNTHESIS AND CATALYTIC ACTIVITY OF COPPER AND IRON OXIDE
BASED CATALYSTS IN CARBON DIOXIDE METHANATION

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*To my beloved wife, childrens, father, mother, sisters and friends who
were always there when I needed them...*

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ABSTRACT

The high content of carbon dioxide (CO₂) in sour crude natural gas can cause damage to the pipeline system and reduce natural gas quality. Green technology via catalytic methanation reaction was found to be the best method for sour gas sweetening, whereby methane (CH₄) is produced thus increasing the gas quality. In this study, the manganese-ruthenium (Mn/Ru) oxide catalysts were modified through the addition of copper (Cu), chromium (Cr), iron (Fe), vanadium (V) and zinc (Zn) to produce excellent methanation catalysts. The catalysts were prepared via the wet impregnation method, followed by ageing process for one day and calcination at various temperatures for 5 hours, and tested on simulated natural gas (CO₂/H₂) using a Pyrex glass reactor with an internal diameter of 10 mm at atmospheric pressure. The catalysts have undergone several optimizations such as calcination temperatures, various loading amount of catalysts, weight hourly space velocity (WHSV) as well as reproducibility, regenerability and stability testing. The results showed that Ru/Mn/Cu(10:30:60)-Al₂O₃ catalyst calcined at 1000°C was the most active, with 98.5% CO₂ conversion and 19.7% CH₄ yield achieved at 220°C. The second most active catalyst was Ru/Mn/Fe(5:35:60)-Al₂O₃ with 93.2% CO₂ conversion and 19.2% CH₄ yield achieved at 270°C. The Cu based catalyst was verified by response surface methodology-central composite design (RSM-CCD) and the optimum conditions were with the loadings of 60% of Cu, 29.5% of Mn and 10.5% of Ru at calcination temperature of 1010°C with 1200 mL/g⁻¹h⁻¹ WHSV to achieve the 96.6% of CO₂ conversion, while the experimental result gave 98.5% CO₂ conversion, which was 1.9% higher than the suggested value. For Fe based catalyst, the optimum conditions were with the loadings of 60% of Fe, 34.5% of Mn and 5.5% of Ru at calcination temperature of 1010°C with 1200 mL/g⁻¹h⁻¹ WHSV to achieve the 96.6% of CO₂ conversion, while the experimental result gave 95.5% which was 1.1% less than the suggested value. Analysis of the results of the characterization by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) for Cu based catalyst showed the active species were RuO₂, Mn₃O₄ and CuO, while field emission scanning electron microscopy (FESEM) assigned the presence of small particles that were homogeneously distributed. For Fe based catalyst, the active species were RuO₂, Mn₃O₄ and Fe₃O₄ with small particles that distributed homogeneously on the catalyst surface as shown in the FESEM micrograph. Energy dispersion X-ray (EDX) analysis for both catalysts also confirmed the presence of all elements in the prepared catalysts. From the nitrogen adsorption (NA) analysis, a higher surface area and macroporous property of the materials may have contributed to the higher catalytic activity. Temperature programmed desorption (TPD) results also confirmed that both catalysts showed superior performance for sorption of CO₂, while the temperature programmed reduction (TPR) gave reduction sites at lower temperatures. The Ru/Mn/Cu(10:30:60)-Al₂O₃ catalyst was more efficient towards CO₂ conversion, exhibited good reliability and reproducibility as well as regenerability compared to the Ru/Mn/Fe(5:35:60)-Al₂O₃ catalyst. Furthermore, the mechanistic study by Fourier transform infrared (FTIR) spectroscopy suggested that Cu based catalyst has more tendency to form bridged bidentate carbonate and bidentate carbonate species, whereas the Fe based catalyst has more tendency to form monodentate species in the initial state, then forming the formate when it was hydrogenated, and to finally release methane.

ABSTRAK

Kandungan karbon dioksida (CO_2) yang tinggi dalam gas asli mentah masam boleh menyebabkan kerosakan pada sistem saluran paip dan menurunkan kualiti gas asli. Teknologi hijau melalui tindak balas metanasi bermangkin didapati adalah kaedah yang terbaik untuk merawat gas masam kepada gas asli manis, di mana gas metana (CH_4) yang dihasilkan akan dapat meningkatkan kualiti gas. Dalam kajian ini mangkin mangan-rutenium (Mn/Ru) oksida telah diubahsuai dengan penambahan kuprum (Cu), kromium (Cr), besi (Fe), vanadium (V) dan zink (Zn) untuk menghasilkan mangkin metanasi yang terbaik. Mangkin telah disediakan melalui kaedah pengisitepuan basah, diikuti dengan proses penuaan selama satu hari dan pengkalsinan pada pelbagai suhu selama 5 jam, dan diuji ke atas gas asli simulasi (CO_2/H_2) menggunakan reaktor kaca Pyrex berdiameter internal 10 mm pada tekanan atmosfera. Mangkin yang disediakan telah menjalani pelbagai pengoptimuman seperti suhu pengkalsinan, pelbagai jumlah muatan mangkin, halaju ruang berat setiap jam (WHSV) serta kebolehlulangan, penjanaaan semula dan ujian kestabilan. Keputusan menunjukkan bahawa mangkin Ru/Mn/Cu(10:30:60)- Al_2O_3 yang dikalsin pada suhu 1000°C adalah yang paling aktif, dengan 98.5% penukaran gas CO_2 dan 19.7% hasil gas CH_4 dicapai pada 220°C . Mangkin yang kedua aktif adalah Ru/Mn/Fe(5:35:60)- Al_2O_3 dengan 93.2% penukaran gas CO_2 dan 19.2% hasil gas CH_4 dicapai pada suhu 270°C . Mangkin berasaskan Cu telah tentusahkan dengan kaedah gerak balas permukaan-rekabentuk komposit berpusat (RSM-CCD) dan keadaan optimum ialah pada muatan 60% Cu, 29.5% Mn dan 10.5% Ru pada suhu pengkalsinan 1010°C dengan $1200 \text{ mL/g}^{-1}\text{h}^{-1}$ WHSV untuk mencapai 96.6% penukaran CO_2 , manakala keputusan eksperimen memberikan 98.5% penukaran CO_2 , di mana ianya 1.9% lebih tinggi daripada nilai cadangan. Untuk mangkin berasaskan Fe, keadaan optimum ialah pada muatan 60% Fe, 34.5% Mn dan 5.5% Ru pada suhu pengkalsinan 1010°C dengan $1200 \text{ mL/g}^{-1}\text{h}^{-1}$ WHSV untuk menghasilkan 96.6% penukaran CO_2 , manakala keputusan eksperimen memberikan 95.5% iaitu 1.1% lebih rendah daripada nilai cadangan. Analisis keputusan pencirian pembelauan oleh sinar-X (XRD) dan fotoelektron sinar-X (XPS) untuk mangkin berasaskan Cu menunjukkan spesies aktif adalah RuO_2 , Mn_3O_4 dan CuO , manakala mikroskopi imbasan elektron pancaran medan (FESEM) menyatakan kehadiran zarah kecil yang bertaburan dengan sekata. Untuk mangkin berasaskan Fe, spesies aktif adalah RuO_2 , Mn_3O_4 dan Fe_3O_4 dengan zarah kecil bertaburan secara sekata di permukaan mangkin seperti yang ditunjukkan dalam mikrograf FESEM. Analisis tenaga serakan sinar-X (EDX) untuk kedua-dua mangkin juga mengesahkan kehadiran semua unsur dalam mangkin yang disediakan. Daripada analisis penjerapan nitrogen (NA), luas permukaan yang lebih tinggi dan ciri makroliang bahan tersebut berkemungkinan menyumbangkan kepada aktiviti pemangkinan yang lebih tinggi. Keputusan penyahjerapan suhu berprogram (TPD) juga mengesahkan bahawa kedua-dua mangkin menunjukkan prestasi yang lebih tinggi terhadap penjerapan gas CO_2 , manakala penurunan suhu berprogram (TPR) memberikan kawasan penurunan pada suhu lebih rendah. Mangkin Ru/Mn/Cu(10:30:60)- Al_2O_3 adalah lebih cekap terhadap penukaran gas CO_2 , mempamerkan kebolehpercayaan yang baik, dan kebolehlulangan serta penjanaaan semula yang baik berbanding dengan mangkin Ru/Mn/Fe(5:35:60)- Al_2O_3 . Tambahan lagi, kajian mekanisme menggunakan spektroskopi inframerah transformasi Fourier (FTIR) mencadangkan mangkin berasaskan Cu lebih cenderung membentuk spesies karbonat bidentat berjejambat dan karbonat bidentat, manakala mangkin berasaskan Fe lebih cenderung membentuk spesies monodentat pada keadaan permulaan, kemudiannya membentuk format apabila ianya dihidrogenkan, dan akhirnya membebaskan gas metana.

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LIST OF ABBREVIATIONS

3D	-	Three Dimensional
ABS	-	Absorbance
Ads	-	Adsorbed
BET	-	Brunnauer, Emmet and Teller
BJH	-	Barret-Joyner-Halenda
c	-	Cubic
CCD	-	Central Composite Design
cf	-	Cubic feet
Cu K α	-	X-ray diffraction from Copper K energy levels rate of conversion (percentage)
d	-	Pore diameter
DRIFTS	-	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EDX	-	Energy Dispersive X-ray Analysis
ESR	-	Electron Spin Resonance
fcc	-	Face-centered cubic
FESEM	-	Field Emission Scanning Electron Microscope
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared
GC	-	Gas Chromatography
h	-	Hexagonal
hr	-	Hour
HRTEM	-	High Resolution Transmission Electron Microcopy
IWI	-	Incipient Wetness Impregnation techniques.
JCPDS	-	Joint Committee on Powder Diffraction Standard
MCM	-	Mobile Composition Matter
MS	-	Mass Spectroscopy
NA	-	Nitrogen Adsorption
o	-	Orthorhombic

PDF	-	Powder Diffraction File
PLC	-	Programmable Logic Controller
ppm	-	Part per million
P/P_0	-	Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure P_0 of the adsorbate at the temperature where the isotherm is measured
r	-	Rhombohedral
RSM	-	Response Surface Methodology
RWSG	-	Reverse Water Gas Shift
SMSI	-	Strong Metal Support Interaction
SNG	-	Substitute natural gas
STP	-	Standard temperature and pressure
t	-	Tetragonal
TEM	-	Transmission Electron Microcopy
TGA	-	Thermogravimetry Analysis
TM	-	Transition Metal
TPRD	-	Temperature Programmed Reduction-Desorption
wt%	-	Weight percentage
XPS	-	X-Ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction
α	-	Alpha
γ	-	Gamma
ΔH	-	Enthalpy change
θ	-	Half angle of diffraction beam
λ	-	Wavelength

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CHAPTER I

INTRODUCTION

1.1 Background of Study

Malaysia is one of the largest oil producers in South East Asia after Indonesia and second largest exporter of liquefied natural gas (LNG) in Qatar in 2013 (U.S EIA-Annual Energy Outlook, 2014). Therefore Malaysia is keen to ensure the quality of our primary energy source is up to the standards (EUMCCI, 2011).

Natural gas (NG) containing hydrogen sulfide and carbon dioxide is referred to as *sour*, and natural gas free from these two gases is referred to as *sweet* (Kidnay and Parrish, 2006) (Mokhatab *et al.*, 2015). According to the International Energy Agency, about 43% of the world's natural gas reserves (2,580 TCF) are sour and the Middle East, which has the world's most sour gas reserves, contains 60% sour gas (U.S IEA-Annual Energy Outlook, 2014). Sour gas is problematic due to its toxicity, flammability, able to damage drilling equipment and corrodes piping during gas transportation (Mokhatab and Poe, 2012). Removal of CO₂ is compulsory, as high content CO₂ will decrease the amount of energy yielded when burning gas. The process for liquefying natural gas in order to be transported requires extremely low concentrations of CO₂ with less than 50 parts per million (ppm) (William *et al.*, 2006). This is because when the gas is cooled for liquefaction (down to -160°C), CO₂ will freeze, causing blockage of flow lines and other operational problems. Furthermore the CO₂ can solidify, causing blockage of flow lines, thus increasing the maintenance process and further decreasing the value of NG (Lieberman, 1987).

Vast amount of methods were developed dedicated to the removal of CO₂ in NG, including membrane adsorption and cracking method. The methanation of CO₂ has the potential to address both of these problems if a catalyst can be developed that meets the activity, economic and environmental requirements to industrialize the process (Wang and Gong, 2011).

1.2 Statement of Problem

As one of the leading exporters of NG, Malaysia is keen on increasing the quality of its product and simultaneously solving one of the major problem faced; the CO₂ impurities in NG. Throughout time, researchers have developed methods to pertain the problem. Soda ash adsorption is one of the current method used as it acts as adsorbent to reduce the CO₂ from NG. However, the high amount of waste is generated using this procedure. Membrane separation was also developed with the same aim of filtering CO₂. Although it can achieve high waste reduction, it is hardly impossible to regenerate and reuse. The development of catalyst for CO₂ conversion was a greener alternative as it is converts CO₂ to other sellable products; methanol or methane (CH₄). Furthermore, it is waste-free and is recyclable. Although catalytic conversion might seem as the best solution, the major drawbacks are the cost of pertaining the catalyst suitable for CO₂ conversion is very expensive. Previous researchers (Wang and Gong, 2011), used noble metals such as Ru and Ni to obtain a high efficient catalytic conversion of CO₂ to CH₄, however these catalyst are very sensitive towards chemical attack whilst reaction due to presence of hydrogen sulphide or mercaptan and reactivated these catalyst only using harsh chemicals. In order to reduce the cost, researchers need to seek out alternatives such as using other cheaper metal oxides or a combination of metal oxides that still produces similar and comparable results to the noble metal catalyst. To the best of our knowledge, no research clearly focused on combination of metal oxides (trimetallic catalyst) as catalyst based on transition metals with the aim for CO₂ conversion to CH₄ at low temperatures as possible. The optimization of the combination metal oxides (trimetallic catalyst) was hoped to be a more greener and affordable alternative to

reduce CO₂ impurities from NG and could be a greener alternative for energy source production in a whole.

1.3 Objectives of the Study

The main goal of this research is to develop a combination of metal oxide catalyst (trimetallic catalyst) using affordable metal oxides from transition metals (TM) with the aim of catalyze CO₂ methanation reaction effectively at low possible temperature and room pressure atmosphere.

The objectives of this research are: -

1. To synthesize the best-supported chromium, copper, iron, vanadium and zinc oxides based catalysts for CO₂ methanation reaction.
2. To test the catalytic activity of prepared catalysts in CO₂ methanation using simulated natural gas.
3. To optimize the catalysts preparation, catalytic testing parameters and validation by response surface methodology (RSM)
4. To characterize the potential catalysts in order to understand the chemical and physical properties of the catalysts.
5. To study the mechanistic reaction involve over potential catalysts.

1.4 Scope of the Research

The study started with screening of first row transition metal oxides (chromium, copper, iron, vanadium and zinc) oxide supported on alumina to be selected as the best TM as base catalyst for CO₂ conversion. The dopant: Mn and co-dopant: Ru that were believed to enhance the catalytic activity of methanation reaction.

The two best performed TM-based catalyst was then selected based on its catalytic activity using a lab-scale reactor with simulated NG production connected to an Fourier transformed infra red spectrometer (FTIR). The preparation of the catalyst via incipient wetness impregnation method, the ratio of the combination of the metal oxides, the different of weight hourly space velocity (WHSV) and the calcination temperature were then optimized. Validation of catalyst optimization was performed by statistic method response surface methodology (RSM).

The optimum preparation method were then applied to the TM based catalyst to be tested and evaluated for its catalytic capability in the lab-scale reactor; (1) % CO₂ conversion, (2) % CH₄ yield, (3) maximum conversion temperature, (4) robustness and reusability of the catalyst, and (5) % CH₄ selectivity.

The optimized catalyst was also further characterized using x-ray diffraction analysis (XRD), field emission scanning electron microscopy-energy dispersion x-ray analysis (FESEM-EDX), Fourier transformed infra red spectrometer (FTIR), x-ray photoelectron (XPS), temperature programmed reduction analysis (TPR), CO₂-temperature programmed desorption analysis (CO₂-TPD) and nitrogen absorption analysis (NA).

A study on the mechanism of the catalyst and basic chemical reaction were also investigated using FTIR instrument tested on the simulated natural gas. A mechanistic study was divided into two parts, a) study on the catalyst surface and b) gases phase.

1.5 Significance of Study

The green technology by the catalytic CO₂ methanation is one of the most promising methods for the converting CO₂ to valuable product (CH₄). Using this

green technology, natural gas can be considered as an environmental friendly clean fuel, which offers important environmental benefits compared to other fossil fuels, and will help to reduce problems of acid rain, ozone layer depletion or greenhouse effect. If the proposed technology is successful, it may increase the price, quality and quantity of natural gas. The catalyst developed in this study will not only contributes to the national income but also to help country to achieved award as carbon credit. Furthermore, the catalyst is easy to prepare, environmental friendly technique, reusable, low price, robustness and can be highly activated at low temperature reaction.

The ultimate goal of this study is to produce the most potential catalyst in the natural gas treatment that can create sustainable environment and fulfilled the specifications above. Thus, this catalyst can be applied to real natural gas. The novelties of this research study are as follows:

- 1) The development of new trimetallic catalysts chromium, copper, iron, vanadium and zinc oxides as based catalysts. The addition of second and third metals towards based catalyst was carried out in order to increase the performances of CO₂ activity.
- 2) The use of alumina in the beads form as a support catalyst is not being used by researchers in their studies.
- 3) The optimize of the catalysts preparation, catalytic testing parameters and validation for potential catalyst by response surface methodology (RSM)-central composite design (CCD).
- 4) The study the mechanistic reaction involved over potential catalysts.

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