



**The influence of Alkali and Alkaline Earth Metals on
Ru/YSZ Catalyst for Catalytic and Electrochemical
Promotion of Carbon Dioxide Methanation**

by

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LIST OF ABBREVIATIONS

A	Electron acceptor
Au	Gold
Ca	Calcium
CaO	Calcium oxide
CCR	Carbon capture and recycling
CCS	Carbon capture and storage
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
CE	Counter electrode
CV	Cyclic voltammetry
D	Electron donor
EPOC	Electrochemical promotion of catalysis
GHG	Greenhouse gases
K	Potassium
KOH	Potassium hydroxide
MACOR	Machinable ceramic
MFC	Mass flow controller
MIEC	Mixed ionic electronic conductor
Mg	Magnesium
MgO	Magnesium oxide
Na	Sodium
NaOH	Sodium hydroxide
NEMCA	Non-faradaic electrochemical modification of catalytic activity
NGTP	National green technology policy
Pt	Platinum
RE	Reference electrode
Ru	Ruthenium
RWGS	Reverse water gas shift
SEM	Scanning electron microscopy
SMSI	Strong metal support interactions
SOFC	Solid oxide fuel cells
tpb	Three phase boundaries

WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	Yttria-stabilised-zirconia

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LIST OF SYMBOLS

A	Frequency or pre-exponential factor
β	Full width at half maximum
θ	Peak position
d	Lattice spacing (\AA)
d_{Ru}	Crystallite size of Ru
e	Electron charge (C)
ε	Microstrain
F	Faraday's constant
i	Current density (A cm^{-2})
I	Applied current (A)
I_p	Peak height
K	Scherrer constant
k	Rate constant
λ	Wavelength of the X-Ray sources
n	Charge of ion
N_G	Moles of reactive oxygen moles uptake by the catalyst
PI_p	Promotional index
R	Ideal gas constant
r	Electropromoted catalytic rate under EPOC effect
r_{Na}	Catalytic rate promoted by Na
r_o	Unpromoted catalytic rate
O_0^X	Normal oxygen ion
ρ	Reaction rate enhancement ratio
P_{CO_2}	Carbon dioxide partial pressure
P_{H_2}	Hydrogen partial pressure
%X	Percentage of promoter
S	Selectivity
δ	Dislocation density
δ^-	Partial anionic charge
t	Time (s)
T	Temperature ($^{\circ}\text{C}$)
τ	EPOC time constant
U°_{WR}	Open-circuit ($I = 0$) value of U_{WR}
U_{WR}	Potential difference between the catalyst, or working electrode (W) and the reference electrode (R)

U_{WR}	Overpotential
V	Potential or voltage (V)
v	Scan rate, mvs^{-1}
$V_{\ddot{o}}$	Oxygen vacancy site in the solid electrolyte (YSZ)
$v^{1/2}$	Square root of the scan rate $(\text{mvs}^{-1})^{1/2}$
V_{WR}	Potential between working and reference electrodes (V)
$V_{WR,p}$	Peak potential
Δr	Difference in the catalytic rate
ΔU_{WR}	Change in overpotential between the working electrode and the reference electrode
$\Delta\theta_p$	Coverage of the promoting or poisoning species
$\Delta\Phi$	Variation of catalyst work function
Λ	Faradaic efficiency

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Pengaruh Logam Alkali dan Alkali Bumi Pada Pemangkin Ru/YSZ Terhadap Aktiviti Pemangkinan dan Penggalakan Elektrokimia Bagi Pemetanaan Karbon Dioksida

ABSTRAK

Karbon dioksida (CO_2) adalah penyumbang utama pelepasan gas rumah hijau global (GHG), yang menyebabkan peningkatan suhu global. Penggunaan CO_2 adalah pendekatan yang wajar untuk mengurangkan pelepasan CO_2 sambil memulihara sumber karbon. Salah satu cara untuk menggunakan CO_2 adalah melalui proses penghidrogenan yang membenarkan penukaran CO_2 yang cekap kepada bahan bakar bernilai tambah seperti metana (CH_4). Dalam kajian ini, penghidrogenan bermangkin CO_2 kepada CH_4 dan karbon monoksida (CO) oleh lapisan pemangkin rutenium yang disokong pada 8% mol yttria-distabilkan pada pelet zirkonia (Ru/YSZ) dan diubah suai secara luaran dengan beberapa spesies logam alkali dan logam alkali bumi, iaitu natrium (Na), kalium (K), kalsium (Ca) dan magnesium (Mg) pada liputan rendah (0.16%) telah disiasat di antara 250-400°C dalam reaktor kebuk tunggal. Satu kesan penggalakan yang lebih ketara terhadap aktiviti pemangkinan dan pemilihan produk dalam tindak balas pemetanaan telah diperhatikan bagi sistem Ru/YSZ yang diubah suai dengan logam alkali iaitu Na dan K. Daripada ini, satu aktiviti pemangkinan yang lebih ketara telah diperhatikan bagi Ru/YSZ yang diubah suai dengan K pada liputan rendah (0.16%), disebabkan oleh saiz hablur Ru yang lebih kecil dapat menghasilkan peningkatan dalam penyebaran pemangkin Ru. Sistem Ru-K/YSZ pada pelbagai liputan K (0.16-16%) diselidiki lebih lanjut dari segi kinetik tindak balas. Hukum tindak balas pemetanaan yang dihitung bersandarkan kepada kepekatan H_2 dan CO_2 menunjukkan mekanisma Eley-Rideal bagi sampel Ru, di mana salah satu daripada bahan tindak balas (CO_2) perlu menjerap, sementara bahan yang lain (H_2) boleh bertindak balas secara langsung dari fasa gas, namun, ini berubah pada liputan kalium yang lebih tinggi (16%), kepada mekanisma Langmuir-Hinshelwood di mana tindak balas bergantung kepada penjerapan kedua-dua bahan tindak balas kerana kedua-duanya mempunyai penjerapan kimia yang lemah. Peningkatan tenaga pengaktifan dengan liputan kalium yang lebih tinggi mungkin disebabkan oleh peningkatan dalam sawar aktiviti hakiki pada pemangkin kerana kehadiran spesis logam yang melindungi tapak permukaan aktif. Dalam pada itu, liputan kalium yang lebih tinggi menyokong penghasilan CO berkemungkinan disebabkan oleh penjerapan CO_2 yang lebih lemah. Penggalakan elektrokimia pemetanaan CO_2 menunjukkan ciri-ciri penggalakan terutamanya jenis 'gunung berapi terbalik' dengan kadar tindak balas yang ketara tidak bersifat faradaik kecuali bagi penghasilan CO pada 16% K (jenis 'gunung berapi'). Satu kesan sinergi, yang mana kadar tindak balas adalah lebih tinggi daripada yang disebabkan oleh penambahan K dan pengutuban dapat diperhatikan pada 16% K, menunjukkan bahawa kedua-dua spesis K dan limpahan oksigen ke atas pemangkin bertindak balas seperti yang dikehendaki sehingga suatu tahap tertentu untuk menggalakkan pemetanaan CO_2 .

The influence of Alkali and Alkaline Earth Metals on Ru/YSZ Catalyst for Catalytic and Electrochemical Promotion of Carbon Dioxide Methanation

ABSTRACT

Carbon dioxide (CO₂) is the major contributor of global greenhouse gas (GHG) emissions, leading to an increase in the global temperature. CO₂ utilisation is a sensible approach to mitigate the CO₂ emission while conserving the carbon resources. One of the ways to utilise CO₂ is through hydrogenation process which allows efficient conversion of CO₂ into value added fuels like methane (CH₄). In this study, catalytic hydrogenation of CO₂ into CH₄ and carbon monoxide (CO) was investigated over a ruthenium catalyst film supported on 8 mol% yttria-stabilised zirconia pellet (Ru/YSZ), externally modified with several alkali and alkaline earth metal species i.e. sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) at low coverage (0.16%) between 250-400°C in a single chamber reactor. A stronger promotion of the catalytic activity and product selectivity of the methanation reaction was observed in the Ru/YSZ system modified with alkali metals i.e. Na and K. Of these, a higher catalytic activity was observed for Ru/YSZ modified with K at low coverage (0.16%), attributed to the smaller Ru crystallite size which results in higher Ru catalyst dispersion. The Ru-K/YSZ system at varied K coverage (0.16-16%) was further investigated in terms of the reaction kinetics. The calculated order of methanation reaction with respect to H₂ and CO₂ concentrations indicated an Eley-Rideal mechanism for the Ru sample, in which one of the reactants (CO₂) needs to adsorb, while the other reacts directly from the gas phase, but this changed at higher potassium coverage (16%), to a Langmuir-Hinshelwood mechanism where reaction depends on both reactants' adsorption as both have weak chemisorption. The increase in the activation energy with higher potassium coverage may be due to the increase in the intrinsic activity barrier on the catalyst because of the presence of metal species which blocked the active surface sites. On the other hand, a higher potassium coverage was in favour of CO production possibly due to weaker adsorption of CO₂. Electrochemical promotion of CO₂ methanation mainly shows an inverted-volcano type promotional behaviour with strong non-faradaic rates except for CO production at 16% K (volcano type). A synergistic effect, in which reaction rate is higher than that caused by addition of K and polarisation can be observed at 16% K, indicating that both K and oxygen species spillover onto the catalyst react favourably to some extent to promote CO₂ methanation.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

The global annual average concentration of carbon dioxide (CO₂) in the atmosphere is now well over a record level of 400 ppm, at its highest level in over 800,000 years (Hannah Ritchie and Max Roser, 2017). CO₂ is the major contributor of global greenhouse gas (GHG) emissions, which constitutes 76% of the total global GHGs emissions equivalent to 52 gigatonnes CO₂ eq/yr. Of these, more than 40% is sourced by fossil fuel combustion for power and heat generation, and by the industrial sector. Consequently, this contributes to an increase in the global temperature and induces global climate change.

Malaysia has long participated actively in international treaties related to climate change such as the Montreal Protocol 1987 for the protection of the Earth's ozone layer, Kyoto Protocol in 1997 and United Nations (UN) Climate Change Copenhagen, 2009, in order to mitigate GHG emissions. In 2009, Malaysian government launched the National Green Technology Policy (NGTP) in which 5 strategic thrusts were developed involving public awareness and the initiatives to implement green technology for the growth of the nation while conserving the natural environment and resources, and minimising the negative impact of human activities including GHG emissions (Nizam et al., 2013). The NGTP is to ensure a continuous energy supply for growth of development as well as reduction in greenhouse gas emissions are planned and conducted in an effective and proper way (Oh et al., 2010). The key policies related to CO₂ emission has been reviewed in 2010 (Chua & Oh, 2010) and Malaysia has gave commitment towards further decrease

in the carbon intensity at the Climate Summit New York, 2014. In the 2016 Paris Agreement, Malaysia has agreed to commit to a reduction of up to 40% in terms of CO₂ emissions intensity per unit of GDP by the year 2020 and 45% by the year 2030 compared to emission levels in 2005. Malaysia have to make provision by developing a National Adaptation Plan to achieve the goals of the agreement (Lian, 2018). Therefore, adopting a strategy which aims for utilising the CO₂ emissions especially from industrial sectors is a sensible approach.

Numerous studies have been carried out to improve understanding of the technologies for CO₂ capture and utilisation. Carbon dioxide in exhaust gas streams can be reduced or put into good use by converting it into carbon containing fuels or other useful chemicals such as fertilisers, polymers etc. Utilisation of CO₂ for the synthesis of fuels may result in a convenient alternative for excessive usage of conventional fuels. There are various means to convert CO₂ into fuel in the form of methane, such as through photosynthesis and photocatalysis, electrochemical CO₂ reduction, biological CO₂ conversion, and thermal catalytic CO₂ methanation. Thermal catalytic CO₂ methanation is one of the core routes to utilise CO₂ by hydrogenating CO₂ into methane. The methane produced could be stored or transported through existing natural gas infrastructure (Götz et al., 2016), which is more preferable rather than having to deal with direct handling and storage of H₂ which are proved to be more challenging. Moreover, since the CO₂ is recycled, the approach does not only mitigate global warming to some extent, but also supports the government policy on renewable energy.

To produce a clean fuel in terms of energy usage, the combination of water electrolysis (for hydrogen source) (Ghaib & Ben-Fares, 2018; Su et al., 2016; Zheng et

al., 2016), powered by solar energy and the Sabatier reaction (producing CH_4 from CO_2) must come about together to enable methane synthesis by thermal catalytic or electrocatalytic process. Electrochemically assisted catalytic hydrogenation of CO_2 is also one of the means to enhance the catalytic activity and selectivity of a reaction, with the benefit of being tunable based on the external current supply. This method, known as electrochemical promotion of catalysis (EPOC) or non-faradaic electrochemical modification of catalytic activity (NEMCA) refers to a phenomenon whereby small current or overpotential application on a catalytic system results in significant changes of the catalytic activity of the reactions in a way that exceeds Faraday's Law expectation. The phenomenon is due to the migration (backspillover) of ionic promoting species generated at the gas-catalyst-solid electrolyte three phase boundaries (tpb), from the solid electrolyte to the catalyst surface that changes the magnitude and behaviour of the catalytic reaction. An introduction of externally applied promoter species e.g. sodium to the catalyst surface may result in further enhancement of the electrochemical promotion of carbon dioxide hydrogenation in terms of higher catalytic activity and better selectivity to methane possibly due to synergistic effect between the two promoter species.

1.2 Problem Statement

Carbon dioxide, one of the main components of greenhouse gases will become a threat if CO_2 from all sources are directly released to the atmosphere. One of the ways to overcome this problem is by undergoing CO_2 hydrogenation into useful chemicals like methane. To produce methane, CO_2 methanation process may proceed via several techniques including catalytic and electrochemically assisted catalytic reduction of CO_2 to CH_4 . At low pressures and temperatures between 200-350°C, CO_2 hydrogenation

proceeds via two competing reactions namely the reverse water gas shift (RWGS) and the methanation reactions. It is desirable to suppress the RWGS reaction and increase the selectivity towards the methanation reaction. CO₂ methanation is a strongly exothermic reaction and thermodynamically favoured at low temperature (Li et al., 2019; Stangeland et al., 2017). However, CO₂ is a very stable molecule (H. Yang et al., 2017; G. Zhao et al., 2017) and has high kinetic barriers, making CO₂ activation and conversion at low temperature is a critical challenge (Lu, 2016). Besides that, the reduction of fully oxidised carbon to methane which is an eight-electron process will require catalyst to enhance the CO₂ methanation process (W. Wang et al., 2011)

Studies on CO₂ methanation have shown that Ru-based catalyst shows good activity and selectivity towards methane production (Qiao et al., 2014). The higher activity of this catalyst in electrochemical promoted systems is attributed to the phenomenon of strong metal support interactions (SMSI) in which promoting species from the support interact with the catalyst enhancing its performance (both in terms of activity and selectivity) (Hernández Mejía et al., 2018; Pan et al., 2017). The effect of SMSI and the spillover of promoting species from the support to the catalyst have been widely acknowledged in heterogeneous catalysis; however, little work has been done to investigate the effect of multiple promoters on the catalytic activity and selectivity of reaction. The presence of multiple promoters may have a synergistic effect which further enhances the methanation reaction rate and selectivity to methane.

As such, the goal of this research is to study the effect of adding promoter species on catalytic CO₂ hydrogenation to methane by externally introducing surface species like alkali metal ions or alkaline earth metal ions to the surface of catalyst film supported on

yttria-stabilised-zirconia (YSZ), an O^{2-} conductor for further application in an electrochemically assisted catalytic systems.

1.3 Research Objectives

The main aim of this research is to improve the fundamental understanding of the role that metal promoters have on the promotion of CO_2 hydrogenation to enhance the production of methane. To accomplish this, the following objectives are planned in several phases along the course of research. The research included

- i. the screening of surface alkali and alkaline earth metal promoters addition for CO_2 methanation over Ru/YSZ
- ii. the selection of alkali metal promoters on the catalytic activity of CO_2 methanation at varying surface coverage, reaction temperature and hydrogen partial pressures
- iii. the characterisations and kinetics of CO_2 methanation of Ru/YSZ modified with selected alkali metal promoter at varied surface coverage
- iv. investigation of the electrochemical promotion of CO_2 methanation over Ru/YSZ with selected alkali metal promoter at varied coverage

1.4 Scope of Research

The main focus of this study is to evaluate the influence of promoter addition on Ru/YSZ catalyst system for CO_2 methanation process. In this study, as the catalyst system is aimed for future application in an electrochemical system, a testing rig similar to that

used for an electrocatalytic study was employed. A three-electrode system was used, consisting of ruthenium (Ru) metal film serving as both catalyst and working electrode (WE), and gold film (Au) as the counter (CE) and reference (RE) electrodes. The Ru/YSZ system was used due to the fact that Ru is one of the most active hydrogenation catalysts with high selectivity towards methane production. Ytria stabilised zirconia (YSZ) pellet was used as the solid electrolyte and support for the catalyst films deposited on its surface. As an oxygen ion conductor, an application of positive or negative potential on the catalyst supported on YSZ, will either supply or remove oxygen (electronic promoter) from the catalyst surface, while the addition of a structural promoter, alkali metal ion or alkaline earth metal ions such as sodium (Na), potassium (K), magnesium (Mg) or calcium (Ca), was conducted by external deposition of metal solutions on the surface of the catalyst. The performance of the Ru/YSZ catalyst system modified with alkali (Na and K) and alkaline earth metals (Mg and Ca) were investigated to screen for the most active metal promoter for CO₂ methanation.

The operating parameters varied and optimised for CO₂ methanation over Ru/YSZ modified with selected promoters include the reaction temperature and partial pressures of H₂, while the CO₂ partial pressure was kept constant at 1 kPa and the total flow rate was maintained at 200 mL/min. The catalytic activity and selectivity to methane were evaluated based on the concentrations of CO and CH₄ products measured continuously using an infrared CO-CO₂-CH₄ gas analyser which was pre-calibrated with calibration gas containing 2.8% CO₂, 0.8% CH₄ and 0.8% CO before the experiments were conducted.

Various surface analysis techniques were conducted on the Ru/YSZ modified with selected promoter at variable coverage to characterise the physical and chemical properties of samples such as surface morphology using a scanning electron microscopy (SEM), phase identification and determination of degree of crystallinity and crystallite size using an X-Ray diffraction (XRD) analyser and surface chemical identification using an X-ray photoelectron spectroscopy (XPS). For electrochemical characterisation, solid state cyclic voltammetry techniques were used. A preliminary electrochemical study was first conducted using Pt/YSZ as a model system to study in-situ of surface activities for the CO₂ reduction peak and then the target system of Ru/YSZ modified with selected promoters was investigated on the formation of electroactive species through the measurement of current as a function of the applied potential. In addition, the order of reaction and the activation energy were calculated to evaluate the kinetics of CO₂ methanation over Ru/YSZ modified with selected promoter at varied coverage.

Finally, an electrocatalytic study of CO₂ hydrogenation reactions was conducted on a nominally 'clean' Ru catalyst and Ru modified with selected promoter under the applied overpotentials (± 2 V) with regards to the open-circuit potential in a three-electrode system similar to that used for the catalytic system. The role of selected promoters in the Ru/YSZ system and the possible CO₂ hydrogenation pathways were also suggested.