Carbon Dioxide Hydrogenation using Ru/YSZ Promoted with Low-Coverage Alkaline Earth Metals

Tan Sze Yen\textsuperscript{1}, Naimah Ibrahim\textsuperscript{1}, Umi Fazara Md Ali\textsuperscript{1} and Mohamed Kheireddine Aroua\textsuperscript{2}

\textsuperscript{1}School of Environmental Engineering, Universiti Malaysia Perlis, 02600, Arau, Perlis, Malaysia.
\textsuperscript{2}School of Science and Technology, Sunway University, 47500 Subang Jaya, Selangor, Malaysia.

E-mail: naimah@unimap.edu.my

Abstract. Utilization of CO\textsubscript{2}, which is the main contributor to the global climate change is one of the means to produce useful chemicals and fuels while at the same time reduce CO\textsubscript{2} concentration in the atmosphere. Ruthenium (Ru) was chosen as the probe catalyst in carbon dioxide hydrogenation based on its ability to selectively enhance methanation reaction. Ru supported on YSZ solid electrolyte (Ru/YSZ) was modified with alkaline earth metal promoters i.e. calcium (Ca) and magnesium (Mg) at low coverage (0.16\%). It was found that Ca-modified system is more favorable to enhance the catalytic activity and selectivity of reaction towards methane production compared to Mg-modified system, perhaps due to the higher basicity of Ca.

1. Introduction
Methanation of carbon dioxide is one of the routes for mitigation of carbon dioxide emission by recycling low-carbon waste to produce methane (CH\textsubscript{4}) \cite{1}. Carbon dioxide hydrogenation undergoes through two competing reactions i.e. the catalytic hydrogenation of CO\textsubscript{2} to methane (methanation reaction) shown in Equation (1) and reverse water gas shift (RWGS) reaction of CO\textsubscript{2} to CO, shown in Equation (2).

\begin{equation}
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \Delta H = -165 \text{kJ/mol}
\end{equation}

\begin{equation}
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}, \Delta H = 41.1 \text{kJ/mol}
\end{equation}

In heterogeneous catalysis, addition of additives plays an important role in promoting the catalytic activity and selectivity of a reaction. Koizumi et al. reported that Pd catalysts supported on the conventional amorphous silica without promoters exhibited only weak activities in CO\textsubscript{2} hydrogenation for methanol synthesis, while addition of K, Mg and Ca significantly enhanced their activities \cite{2}. In another study, Malik et al. showed that addition of Ca to PdZn/CeO\textsubscript{2} catalyst has slightly improved the selective conversion of CO\textsubscript{2} for methanol synthesis with methanol selectivity of \textasciitilde 100\% at low temperature of 220\textdegree C by raising the amount of oxygen-vacant sites \cite{3}. CaO modified Ni/Al\textsubscript{2}O\textsubscript{3} was found to improve the catalytic activity of CO\textsubscript{2} methanation at low-temperature compared to unpromoted Ni/Al\textsubscript{2}O\textsubscript{3} by restraining the growth of NiO nanoparticles, improving the dispersion of NiO, and weakening the interaction between NiO and Al\textsubscript{2}O\textsubscript{3} which eased the activation of adsorbed CO\textsubscript{2} and H\textsubscript{2} reactants on the Ni atoms \cite{4}.
Mg was also found to improve the performance of perovskite catalyst over La-Mg-Cu-Zn-O in methanol synthesis by favoring the formation of small particles, lowering reduction temperature, increasing Cu dispersion, and improving the formation of both weak and strong basic sites, thus increasing hydrogen desorption at low temperature that resulted in high selectivity for methanol [5]. Other than that, mixed oxides of aluminium and MgO [6] in support were also found to improve the performance of Fe-K catalyst for catalytic conversion of CO2 hydrogenation to hydrocarbons, in which CO2 chemisorption was observed to correlate with MgO content, attributed to increase in the basicity of the catalyst system.

In this preliminary work, an introduction of the two alkaline earth species e.g. Ca and Mg to a probe catalyst (Ru/YSZ) is investigated over CO2 hydrogenation, with the aim to enhance the catalytic activity and selectivity to CH4. This is expected to be a basis for further work in electrochemical promotion of CO2 hydrogenation which would utilize similar catalyst configuration.

2. Methodology

2.1. Sample preparation and characterisation
Catalyst/electrode system preparation was done following the procedures previously published [7-8]. The solid electrolyte was prepared using approximately 2 g of 8 mol% yttria-stabilised-zirconia (YSZ) powder (Pi-Kem Ltd.), pressed using uniaxial hydraulic pressing to form a pellet and sintered at 1500°C for 4 hours in air. The resulting pellets of approximately 15 mm in diameter and 1.5 mm in thickness were polished with SiC paper, cleaned with isopropyl alcohol for 3 min using an ultrasonic bath, rinsed with distilled water and left to be air-dried [9-10]. Ruthenium (III) chloride hydrate, RuCl3.xH2O (Merck Millipore) dissolved in isopropyl alcohol at 50°C was painted on YSZ pellet followed by one-hour sintering at 500°C in air to produce thin film catalyst. Alkaline earth metal solutions of magnesium oxide (MgO) or calcium oxide (CaO) by Sigma Aldrich was then deposited in dropwise manner (volume of 2 /g541L) onto the ruthenium catalyst surface using a micropipette of 0.1-2.5 /g541L range (Eppendorf). The pellet was then heated in the reactor at 400°C for 1 hour for further use. The surface morphology of ‘clean’ Ru/YSZ and Mg and Ca-modified Ru/Y SZ was characterized using scanning electron microscopy (JSM-6010LV).

2.2. Experimental
A testing rig for catalytic experiment was set up as shown in Figure 1. All gases used were provided by Linde Malaysia. The reactants in the experiments were 3% CO2 and 30% H2; both balanced in N2. The partial pressure of CO2 was set at 1 kPa while the partial pressure of H2 was varied from 1-20% respectively depending on the type of experiment.

A single chamber electrochemical reactor made of quartz, with 22 mm internal diameter, 165 mm length and 60 cm³ volume was placed in a temperature programmable tubular furnace (Vecstar). The quartz reactor was fitted with stainless steel Swagelok Ultra-Torr vacuum fittings having provisions for the inlet and outlet of gases. The actual operating temperature of the catalyst inside the reactor was measured using a K-type thermocouple inserted into the reactor, near to the catalyst surface and connected to KM34 digital thermometer. The feed and total gas flow rate were regulated using mass flow controller (MFC) with total gas flow rate of 200 mL/min in standard room temperature and pressure. The product gases were measured using an infrared gas analyzer (IR Technologies).
The catalytic experiments of CO₂ hydrogenation over Mg and Ca-modified Ru/YSZ were conducted at varying temperature from 250-400°C and partial pressure of H₂ from 1-20 kPa.

### 3. Results and Discussions

#### 3.1. SEM analysis

Figure 2(a) shows the SEM image of nominally ‘clean’ Ru, while Figure 2(b) and Figure 2(c) show the SEM images of Ru0.16%Mg and Ru0.16%Ca respectively. 

Fresh and modified Ru/YSZ pellets pre-treated with hydrogen were used for SEM analysis. Figure 2(a) shows that ruthenium film has continuous film network with some film discontinuity. The dark, background part in the image refers to YSZ, while the irregular shaped, agglomerated particles represent the Ru catalyst, with some film discontinuity [11]. The ruthenium particle size is around 0.5 μm, based on particle of circular shape observed in Fig. 2(a). Figure 2(b) shows that with magnesium addition, the Ru particles became even more irregularly packed and scattered, with some flaky attachment. Figure 2(b) and 2(c) shows irregular micro-structural shape, uneven surface and agglomerates of Ru particles with Ca addition. The images showed Ru particles dispersed on YSZ support.

**Figure 1.** Experimental setup schematic diagram for CO₂ hydrogenation
3.2. Mg and Ca on Ru/YSZ

Figure 3 compares the influence of Mg and Ca addition on CH₄ and CO production rate over Ru/YSZ at 350°C with a constant flow of 1 kPa CO₂ and 10 kPa H₂, in excess of 1:4 (CO₂: H₂) stoichiometric condition for methanation reaction.

![SEM images of fresh (a) Ru b) Ru0.16%Mg; and (c) Ru0.16%Ca](image)

Figure 2. SEM images of fresh (a) Ru b) Ru0.16%Mg; and (c) Ru0.16%Ca

![CH₄ and CO production rate over Mg and Ca-modified Ru/YSZ](image)

Figure 3. CH₄ and CO production rate over Mg and Ca-modified Ru/YSZ
In addition to the slight increase observed in CH4 production rate over Ru-0.16%Mg and Ru-0.16%Ca compared to the nominally ‘clean’ Ru; CO production rate also increases in both modified systems. In between Ca and Mg, addition of Ca appears to better promote Ru in production of CH4.

On the other hand, Figure 4 compares CH4 and CO production rate in Ru/YSZ catalyst system modified with Mg and Ca over temperatures of 250, 300, 350 and 400°C under flow of 1 kPa CO2 and 10 kPa H2. Based on the result, Mg can be seen to act better at low temperatures (250 and 300°C) while Ca works better at higher temperatures (350 and 400°C) to promote CH4 production. CO production is found to be suppressed at lower temperature of 250 and 300°C in both Mg and Ca-modified system but increases with the rise in temperature to 350 and 400°C.

**Figure 4.** Influence of temperature on CH4 and CO production rate over Mg and Ca-modified Ru/YSZ

Figure 5 shows the influence of Mg and Ca addition to CH4 production over Ru/YSZ at varying partial pressure of H2 ranging from 1 to 20 kPa. Since H2 is one of the limiting reactants in methanation reaction, an increase in the supply of H2 is expected to enhance CH4 production at least in the ‘clean’ system. As can be observed, both Ca- and Mg-modified systems promote CH4 production as the H2 partial pressure is increased from 5 to 20 kPa, with Ca being slightly better promoter. On the other hand, at 1 kPa H2, CH4 production is low as H2 is insufficient (less than the stoichiometric ratio), while CO production is suppressed in excess H2 (from 5 kPa onwards).

In a previous work, Bart et al. proposed that the acid/base properties of the support can lead the reaction towards desired product, while suppressing side reactions [12]. It possible that Ca shows better promoting effect in CO2 methanation due to Ca surface species being more basic and reactive than Mg, and thus has a higher affinity for CO2 chemisorption. Yamazaki et al. reported in CO2 reforming of methane that CaO promoted catalyst shows higher affinity for the acidic CO2 chemisorption due to the high basicity of CaO [13-14]. The higher basicity and reactivity of CaO compared to MgO can be explained to be due to the smaller CaO Madelung ionic crystal potential used to electrostatically stabilize surface anions [15].
4. Conclusions
In this study, the surface species of alkaline earth metal (Mg and Ca) was found to promote CO$_2$ hydrogenation over Ru/YSZ. CH$_4$ production over Ca-modified Ru/YSZ is higher with the increase in temperature and H$_2$ partial pressure compared to Mg, possibly due to Ca being more basic and has higher affinity for CO$_2$ chemisorption, one of critical steps in CO$_2$ methanation.

Acknowledgements
This work was financially supported by Newton Fund Institutional Links (Ref: 172697003) under British Council.

References
[1] Wang W and Gong J 2011 Front Chem Sci Eng. 5 p 2-10
[2] Koizumi N, Jiang X, Kugai J and Song C 2012 Catal. Today. 194 p 16-24
[3] Malik A S, Zaman S F, Al-Zahrani A A, Daous M A, Driss H and Petrov L A 2018 Appl. Catal. A-Gen. 560 p 42-53
[4] Yang W, Feng Y and Chu W 2016 Int. J. Chem. Eng.
[5] Zhan H, Li F, Gao P, Zhao N, Xiao F, Wei W, Zhong L and Sun Y 2014 J. Power Sources 251 p 113-121
[6] Kishan G, Lee M, Nam S, Choi M and Lee K 1998 Catal. Letters 56 p 215-219
[7] De Ridder M, Vervoort A G J, Van Welzenis R G and Brongersma H H 2003 156 p 255-262
[8] Ibrahim N, Poulidi D, Rivas M E, Baikie I D and Metcalfe I S 2012 Electrochim. Acta 76 p 112-119
[9] Yoon S P, Nam S W, Han J, Lim T H, Hong S A and Hyun S H 2004 Solid State Ion. 166 p 1-11
[10] Phark J, Duarte S, Kahn H, Blatz M B and Sadan A 2009 Dent. Mater. J. 5 p 1541-1550
[11] Makri M, Symillidis A, Grigoriou D, Katsaounis A and Vayenas C G 2018 Materials Today: Proceedings 5 p 27617-27625
[12] Hereijgers B P C and Weckhuysen B M 2009 Chem. Sus. Chem. 2, p 743-748
[13] Zhang Z, Verykios X E, Macdonald S M and Affrossman S 1996 J. Phys. Chem. 100 p 744-754
[14] Yamazaki O, Nozaki T, Omata K and Fujimoto K 1992 Chem. Lett. 21 p 1953-1954
[15] Pacchioni G, Ricart J J M and Illas F 1994 J. Am. Chem. Soc. 116 p 10152-10158