PRODUCTION OF SYNGAS VIA DRY REFORMING OF METHANE WITH CARBON DIOXIDE OVER DOLOMITE SUPPORTED COBALT-BASED CATALYST

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FS 2018 65
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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

September 2018
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Chairman : Prof. Taufiq Yap Yun Hin, PhD
Faculty : Science

Dry reforming of methane with carbon dioxide (DRM) has received great attention from researchers as this reaction is utilizing two main greenhouse gases which are CH₄ and CO₂ gases in producing valuable syngas. In addition, H₂/CO ratio produced in this reaction is equivalent to 1. Due to this, the syngas produced is compatible with various chemical and liquid fuel syntheses. However, the formation of carbon on the surface of the catalysts hinders the active sites to take part in the reaction is the main drawback in DRM reaction. The main objective of this study is to develop cobalt based catalysts with dolomite as support by impregnation method with different types of non-noble metals such as Ce, Ni and La.

A series of monometallic catalysts (Co-based) at different metal loadings, 5 wt% - 25 wt%, were prepared in order to determine the optimum loading of Co. Meanwhile, for bimetallic catalysts, Co with other metal with wt% ratio of 20:10 was impregnated on dolomite to form Co-La/Dol, Co-Ce/Dol and Co-Ni/Dol catalyst. The synthesized catalysts were characterized by various methods including X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR), CO₂-temperature programmed desorption (CO₂-TPD), Field emission scanning electron microscope with energy dispersive X-ray spectrometer (FESEM-EDX), thermal gravimetric analysis (TGA) and N₂ adsorption-desorption to determine their physico-chemical properties of the prepared catalysts as well as the carbon formation on the used catalysts.

The catalytic evaluation showed that both monometallic and bimetallic catalysts gave high (> 90%) conversion of CH₄ and CO₂ at 900 °C without in-situ reduction with 5% H₂ gas. However, as the temperature goes down to 850 – 750 °C, the unreduced Co/Dol catalyst gave poor catalytic performance with conversion around 59%-20%. The monometallic catalyst was reduced prior to reaction in order to obtain high conversion of CH₄, 35% - 94% at 750 – 850 °C. Meanwhile, for unreduced bimetallic catalysts,
only Co-Ni/Dol catalyst gave high activity, with conversion of 80% for both feed gases at 800 °C, whilst other bimetallic catalysts have to be reduced prior to the reaction to obtain high conversion of CH₄ and CO₂ gas. Among these catalysts, Co-Ni/Dol catalyst exhibited the highest catalytic performance either reduced or unreduced. In addition, it showed good thermal stability for 72 h at lower temperature, 750 °C with conversion of 91% and 92% for CH₄ and CO₂ gas, respectively with CO₂:CH₄ at 1:1 ratio.
Abstrak tesis dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGHASILAN SYNGAS MELALUI PEMBENTUKAN SEMULA KERING METANA DAN KARBON DIOKSIDA DENGAN Dolomit SEBAGAI PENYOKONG DALAM MANGKIN KOBALT

Oleh

ARFAEZA BINTI ANUAR

September 2018

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Proses pembentukan semula kering metana dengan karbon dioksida (DRM) mendapat perhatian dalam kalangan penyelidik kerana proses ini menggunakan dua gas rumah hijau yang utama, iaitu metana (CH$_4$) dan karbon dioksida (CO$_2$) bagi pengetulisan syngas yang bernilai. Tambahan pula, nisbah H$_2$/CO yang dihasilkan melalui tindak balas ini menghampiri kepada 1. Oleh yang demikian, syngas yang dihasilkan bersesuaian untuk sintesis pelbagai jenis bahan kimia dan bahan api cecair. Walau bagaimanapun, pembentukan karbon di atas permukaan mangkin menghalang tapak aktif untuk mengambil bahagian dalam tindak balas ini yang merupakan kelemahan utama bagi tindak balas DRM. Objektif utama kajian ini untuk membangunkan mangkin kobalt (Co) dengan dolomit sebagai penyokong melalui kaedah pengisitepuan dengan pelbagai jenis logam bukan nobel seperti Ce, Ni dan La.

Satu siri mangkin monologam (berasaskan Co) disediakan dengan jumlah muatan yang berbeza, 5 wt% - 25 wt% bagi menentukan muatan optimum Co. Manakala, untuk mangkin dwilogam, Co dan logam yang lain dengan nisbah muatan 20:10 disitepukan ke atas dolomit membentuk mangkin Co-La/Dol, Co-Ce/Dol dan Co-Ni/Dol. Mangkin yang disintesis telah dicirikan dengan pelbagai kaedah termasuklah pembelauan sinar-X (XRD), program suhu penurunan H$_2$ (H$_2$-TPR), program-suhu-nyahjerapan karbon dioksida (CO$_2$-TPD), mikroskop imbasan elektron pancaran medan - tenaga serakan sinar-X (FESEM-EDX), analisis termogravimetrik (TGA) dan penjerapan-penyahjerapan gas N$_2$ bagi menentukan sifat fizik-ko-kimia mangkin serta mengenalpasti pembentukan karbon pada mangkin yang telah digunakan.

Kajian penilaian pemangkinan menunjukkan kedua-dua mangkin monologam dan dwilogam mempunyai aktiviti yang tinggi (>90%) bagi penukaran gas CH$_4$ dan CO$_2$ pada suhu 900 °C tanpa penurunan in-situ menggunakan 5% gas H$_2$. Namun begitu, prestasi pemangkinan mangkin Co/Dol tanpa penurunan in-situ menurun kepada 59% -
20% apabila suhu tindak balas diturunkan kepada 850 – 750 °C. Mangkin monologam tersebut perlu diturunkan terlebih dahulu sebelum tindak balas dijalankan untuk mencapai penukaran gas CH₄ yang tinggi, 35% - 94% pada suhu 750 °C – 850 °C. Manakala, bagi mangkin dwilogam tanpa penurunan in-situ, hanya Co-Ni/Dol menunjukkan lebih daripada 80% pada suhu 800 °C, sementara mangkin dwilogam yang lain perlu diturunkan terlebih dahulu bagi memastikan penukaran CH₄ dan CO₂ yang tinggi. Antara mangkin-mangkin ini, Co-Ni/Dol menunjukkan sifat terbaik dengan prestasi pemangkinan yang tinggi sama ada tanpa penurunan in-situ ataupun diturunkan secara in-situ. Tambahan pula, mangkin ini menunjukkan sifat kestabilan terma untuk 72 jam pada suhu yang lebih rendah, 750 °C dengan penukaran CH₄ dan CO₂ masing-masing menunjukkan 91% dan 92% dengan nisbah CH₄:CO₂ adalah 1:1.
ACKNOWLEDGEMENT

Firstly and foremost, I would like to thank Allah SWT for HIS blessings, the strength and patience He bestowed on me to complete my study.

I wish to extend my sincere thanks to my supervisor, Professor Dr. Taufiq Yap Yun Hin, for his guidance, suggestion, support, unceasing encouragement and the knowledge that have been shared as well as invaluable supervision towards the completion of my study in Universiti Putra Malaysia.

To my co-supervisor, Dr. Izham Saiman and Dr. Salmiaton Ali, I would like to express my gratitude for the valuable guidance and knowledge that have been shared for all this while.

I am thankful to all individuals that have contributed and co-operated during my study especially to PutraCAT members for their willingness to share their knowledge, support and friendship.

Last but not least, I would like to express my appreciation to my beloved parents and family members, whom has given their support, prayers and valuable comments and suggestions throughout my study. May Allah bless all of us.
I certify that a Thesis Examination Committee has met on 13 September 2018 to conduct the final examination of Arfaezah binti Anuar on her thesis entitled "Production of Syngas via Dry Reforming of Methane with Carbon Dioxide Over Dolomite Supported Cobalt-Based Catalyst" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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<tbody>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative Thermogravimetric</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>i.d</td>
<td>Internal Diameter</td>
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<tr>
<td>T&lt;sub&gt;calcination&lt;/sub&gt;</td>
<td>Calcination Temperature</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<tr>
<td>T&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Temperature at maximum peak</td>
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<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
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<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
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<tr>
<td>T&lt;sub&gt;reaction&lt;/sub&gt;</td>
<td>Reaction Temperature</td>
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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The usage of fossil fuel as the main primary energy source globally is about 35% and approximately 81% of total energy in the United States is powered by fossil fuel such as coal, petroleum and natural gas. However, burning of fossil fuel release large amount of greenhouse gases (GHG) to the environment and causing a serious threat to the humankind. Excessive emissions of GHGs’ cause global warming and triggered drastic climate change. It was also reported that the temperature of Arctic and Antarctic has increased by 5 °C in the 20th century (Anisimov & Fitzharris, 2001). This is proven by the amount of GHGs’ released to the atmosphere has started since Industrial Revolution. Furthermore, rapid growth in world population in the developing countries increased the energy demand over the years that led to massive exploitation and usage of fossil fuels. As mentioned by Akbari et al. (2017), the energy demand is expected to increase by 57% from 2004 to 2030. Thus, numerous methods are being done to reduce the dependency on fossil fuel usage as primary energy sources as it has been exploited for long time where the amount of production could not compensate for the total annual demand (Aramouni et al., 2017). Besides, finding an alternative energy source may reduce the amount of GHG emissions and enable to mitigate the effects of global warming (Marcos et al., 2014).

There are two types of energy; non-renewable and renewable energy. Non-renewable energy consists of coal, natural gas and fossil fuels, whilst, renewable energy comprises of biomass, biogas, geothermal, water, solar and wind. Biogas is now considered as one of the most promising and long-term solution in energy crisis as it can be transformed into valuable products.

Biogas is generated from anaerobic digestion process of organic materials, such as landfills, sewage-treatment plants, mesophilic and thermophilic digestion of organic waste (Jönsson et al., 2003). In Malaysia, biogas production is dominated from anaerobic digestion of palm oil mill effluent (POME). With increased palm oil plantation in Malaysia, the amount of POME released increases gradually. Moreover, it contains high concentration of biological oxygen demand (BOD) and chemical oxygen demand (COD), whereby disposal without proper treatment is undesirable (Sulaiman et al., 2011). However, anaerobic digestion releases high level of carbon dioxide, CO2 (25%-45%) and methane, CH4 (55%-75%), which are the main contributors to climate change (Serrano-Lotina & Daza, 2013). Therefore, methane reforming technology is one of the most promising reactions in mitigating GHG emissions and full utilisation of the biogas by converting it to syngas provide a key-intermediate product for Fischer-Tropsch reaction (Daza et al., 2010).
Dry reforming of methane (DRM) draws interest of researchers as this reaction can be used to utilise the methane and the carbon dioxide gases to produce syngas as shown in Equation 1.1 (Jang et al., 2013).

$$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO} \quad \Delta H_{298K}^\circ = +247.0 \text{ kJ/mol} \quad (\text{Eq. 1.1})$$

Furthermore, DRM is known for its ability to produce syngas ratio (H$_2$/CO ratio) near to unity, which makes it suitable in Fischer-Tropsch synthesis to produce petrochemicals and chemical energy storage systems (Fan et al., 2010; Kambolis et al., 2010). Besides, the costly and energy intensive process in separating CO$_2$ can be neglected, and eventually reduce the gas treatment cost (Ay & Üner, 2015).

However, the commercialization of DRM in industry is still in debate due to several drawbacks such as high reaction temperature is required to achieve better conversion due to its high endothermic nature. The reaction also suffers from catalyst deactivation due to carbon deposition that caused by unwanted side reactions. There are three main side reactions in DRM; reverse water-gas shift reaction, methane decomposition and Boudouard reaction. Carbon deposition is another problem that is prone to occur, which makes the selection of the catalysts becomes more critical. Therefore, several types of catalysts have been developed for this reaction, these includes, noble metals-based catalyst, nickel-based catalyst and cobalt-based catalyst in order to identify active catalysts with high feedstock conversion and stable catalytic activity by preventing unwanted side reactions (Sutthumporn et al., 2012).

1.2 Problem Statement

Dry reforming of methane with carbon dioxide (DRM) offers great potential for power generation and solving environmental-related problems. Malaysia, the second largest exporter of crude palm oil encounters several problems such as treatment of palm oil mill effluent (POME) via anaerobic digestion that produced huge amount of methane and carbon dioxide gases, which are the main cause of global warming. Thus, there is urgent need to utilize these gases into the valuable products; hydrogen and carbon monoxide gases.

Dry reforming of methane is known as an endothermic reaction which requires high reaction temperature to obtain high conversion. Besides, the formation of carbon (coking), agglomeration and sintering of metal active sites are critical problems as it may cause serious catalyst deactivation. Hence, it is an urge to develop new catalyst that able to operate at lower reaction temperature with high catalytic activity and to prevent catalyst deactivation.

Therefore, cobalt catalyst is synthesized as they are known as the most suitable catalysts for industrial applications due to their high activity, availability and low price (Luisetto et al., 2012; Marcos et al., 2014). Alkaline or alkaline-earth metals are
introduced in the development of catalysts as it helps in the dispersion of active metals to enhance the catalysts activity and suppress the formation of coke due their high basicity (Barroso-Quiroga et al., 2010). Naturally occurring alkaline earth-metal (dolomite) is chosen as the main support for Co catalysts.

1.3 Scope of Study

This work is focused on two studies. The first part of the study is to investigate the influence of single metal Co loading on the dolomite and selection of the optimum Co loading that shows the best catalytic activity. The second part is to develop the bimetallic catalysts by impregnating second dopant to the catalysts that includes Ni, Ce and La. Several characterizations techniques have been done to study the physical and chemical properties of the catalysts. Finally, the catalysts were tested for dry reforming of methane with CO$_2$ at different initial condition in a continuous fixed-bed reactor connected with a mass flow controller and an online GC-TCD system. The deposition of carbon of the used catalyst were analysed using TGA and FESEM-EDX.

1.4 Objectives

The objectives of this study are as follows:

1. To prepare mono (Co/Dol) and bimetallic cobalt based catalysts (Co-La, Co-Ni and Co-Ce) via impregnation method.
2. To evaluate the physical and chemical properties of the synthesized catalysts using XRD, BET, TGA, H$_2$-TPR, CO$_2$-TPD, and FESEM-EDX.
3. To study the catalytic activity between reduced and unreduced catalysts on the production of syngas.
4. To evaluate the effects of second dopant and reaction temperature (750 – 900 °C) in the syngas production.
5. To study the stability of the best catalyst in DRM reaction on the production of syngas.
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