UNIVERSITI PUTRA MALAYSIA

METAL OXIDE MODIFIED LIMESTONE CATALYSTS FOR GASIFICATION OF RICE STRAW IN HYDROGEN PRODUCTION

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FS 2016 55

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By

SURAHIM BIN MOHAMAD @ MAHMUD

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

May 2016

DEDICATED

To my beloved parents

Mohamad @ Mahmud Bin Tahir
Almarhumah Aminah Binti Harun (7.3.1955 – 8.1.2014) *(may Allah grants her the highest Jannah)*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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

Hydrogen has great potential for energy and environmental sustainability. Hydrogen is considered as a secondary source of energy, commonly referred to as an energy carrier which is used to store and transport energy in a form that can be easily used. Hydrogen does not exist freely in nature, it only produced from other sources. The potential of utilization of biomass as renewable and sustainable energy resources have attracted researchers to produce hydrogen from cheap and highly available resources such as lignocellulosic biomass waste. Biomass gasification of rice straw using modified natural limestone based catalysts has been studied to promote the production of hydrogen. This study is aimed to develop natural calcined limestone (CL) based catalysts with high activity and selectivity. Modification with addition of mono and bimetallic metal dopants (Ni, Fe, Co, NiCo, NiFe and CoFe) on CL were performed for gasification of rice straw biomass for hydrogen conversion. The catalysts were synthesized through wet impregnation method and characterized by using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area, Thermogravimetry analysis (TGA), Field emission scanning electron microscopy - Energy dispersive X-ray (FESEM-EDX) and Temperature programmed desorption of carbon dioxide (TPD-CO_2) to determine the structure, physical and chemical properties of the catalysts. Temperature programmed gasification (TPG) was conducted to investigate the gasification reaction of rice straw and the product gases were analysed using online mass spectrometer. The gasification process was carried out in partial oxygen (5% O_2/Helium) environment heating from 50 to 900 °C with mass ratio of biomass to catalyst of 2:1. The results revealed that the addition of metal dopants on CL significantly improves the activity and selectivity towards hydrogen production. For monometallic doped catalysts, Ni-CL was found to give the highest H_2 conversion followed by Co-CL and Fe-CL. Moreover, The CL had shown to act both as catalyst and CO_2 sorbent thus enhanced the production of hydrogen. The additions of bimetallic dopant have shown a further increment of hydrogen yield. The NiCo-CL catalyst exhibit highest hydrogen selectivity compared to other catalysts due to improvement in catalytic activity that enhanced gasification of rice straw and promoted hydrogen favoured reactions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

MANGKIN LOGAM OKSIDA MODIFIKASI BATU KAPUR BAGI PENGEGASAN JERAMI PADI DALAM PENGHASILAN HIDROGEN

Oleh

SURAHIM BIN MOHAMAD @ MAHMUD

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Hidrogen mempunyai potensi yang besar untuk kelestarian tenaga dan alam sekitar. Hidrogen dianggap sebagai sumber tenaga sekunder yang biasanya dirujuk sebagai pembawa tenaga yang digunakan untuk menyimpan dan mengangkut tenaga dalam bentuk yang mudah digunakan. Hidrogen tidak wujud secara bebas dalam alam semulajadi, ia hanya dihasilkan daripada sumber-sumber yang lain. Potensi penggunaan biojisim sebagai sumber tenaga boleh diperbaharui dan mapan telah menarik penyelidik untuk menghasilkan hidrogen dari sumber yang murah dan mudah didapati seperti daripada sisa biojisim lignoselulosa. Pengegasan biojisim daripada jerami padi dengan mnggunakan mangkin berasaskan batu kapur semula jadi yang diubahsuai telah dikaji untuk menggalakkan pengeluaran hidrogen. Kajian ini adalah bertujuan untuk membangunkan mangkin yang berasaskan batu kapur asli terkalsin (CL) yang mempunyai aktiviti dan kepilihan yang tinggi. Pengubahsuaian mangkin dengan penambahan bahan dop mono dan dwilogam (Ni, Fe, Co, NiCo, NiFe dan CoFe) ke atas CL telah digunakan dalam proses pengegasan biojisim jerami padi untuk penukaran hidrogen. Mangkin telah disintesis dengan menggunakan kaedah pengisitepuan basah dan dicirikan dengan menggunakan kaedah pembelauan sinar-X (XRD), analisis luas permukaan menggunakan kaedah Brunauer-Emmett-Teller (BET), analisis terma gravimetri (TGA), mikroskop imbasan elektron pancaran medan – Tenaga penyerakan sinar-X (FESEM-EDX) dan aturcara suhu nyahjerapan karbon dioksida (TPD-CO_2) bagi menentukan struktur serta sifat-sifat fizik dan kimia mangkin. Program-suhu-pengegasan (TPG) telah dijalan bagi menyiasat tindak balas pengegasan biojisim jerami padi dan gas yang terhasil daripada porses pengegasan ini dianalisis dengan menggunakan spektroskopi jisim secara dalam talian. Proses pengegasan dijalankan dalam keadaan separa oksigen (5 % O_2/helium) dan pemanasan pada suhu 50 - 900 ° C dengan nisbah biojisim/mangkin adalah 2:1. Hasil kajian menunjukkan bahawa penambahan bahan dop logam pada CL meningkatkan aktiviti dan kepilihan yang ketara ke atas pengeluaran hidrogen. Bagi mangkin dop monologam, Ni-CL didapati memberikan kadar penukaran hidrogen tertinggi diikuti oleh Co-CL dan Fe-CL. Selain bertindak sebagai mangkin, CL juga bertindak sebagai bahan penjerap bagi gas karbon dioksida di mana ianya telah meningkatkan lagi

pengeluaran hidrogen. Penambahan bahan dopan dwilogam telah menunjukkan peningkatan dalam penghasilan hidrogen. Mangkin NiCo-CL mempamerkan kepilihan yang tinggi terhadap hidrogen berbanding dengan mangkin yang lain. Hal ini disebabkan oleh pengingkatan dalam aktiviti mangkin tersebut yang meningkatkan lagi kadar tindak balas pengegasan biojisim jerami padi sekaligus menggalakkan tindak balas penukaran hidrogen.

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and the Most Merciful

I wish to express my outmost gratitude to Allah SWT for the strength and patience He bestowed on me to complete this study.

I would like to express my greatest gratitude to my main supervisor, Professor Dr. Taufiq Yap Yun Hin, for his guidance, suggestion, patience, support and encouragement throughout my study in Universiti Putra Malaysia. His valuable advices and humanitarian values have giving significant impact towards my morale and skills in conducting my research and my life. I am also grateful to my co-supervisor, Professor Dr. Mohd Zobir Hussein for his guidance and help during the study. I express my special thanks to our post-doc, Dr. Aminul Islam and research officer, Tengku Sharifah Marliza Tengku Azmi and to all the PutraCAT members for their support, expertise and valuable friendship during the period. I sincerely thanks to all staffs in Chemistry Department, Faculty of Science and Institute of Bioscience,UPM for their prompt assistant in technical issue, opinion that has helped me to complete my research.

Lastly, my deepest gratitude goes to my parents and all my family members for their endless love, prayers and continuous support throughout my study. May Allah bless all of us.

I certify that a Thesis Examination Committee has met on 13 May 2016 to conduct the final examination of Surahim bin Mohamad @ Mahmud on his thesis entitled "Metal Oxide Modified Limestone Catalysts for Gasification of Rice Straw in Hydrogen Production" 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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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement of the degree of Master of Science. The members of Supervisory committee were as follows:

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This is to confirm that:

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LIST OF ABBREVIATIONS

BET	Brunauer Emmett Teller
BJH	Barret-Joyner-Halenda
CHNS/O	Carbon Hydrogen Nitrogen Sulfur and Oxygen
TCD	Thermal Conductivity Detector
TGA	Thermal Gravimetry Analysis
Tmax	Temperature at maximum peak
TPD	Temperature Programmed Desorption
XRD	X-Ray Diffraction
JCPDS	Joint Committee on Powder Diffraction Standards

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Nowadays, human mankind on the earth is facing serious threats for their life sustainability which of energy crisis and climate change. Currently the global consumption of primary energy is still dominated by fossil fuel energy resources by 35%. It is predicted that the energy demand would be escalated significantly due to the constant growing of population and modern human activities. With the introduction of fossil fuels in the forms of coal, petroleum and natural gas, the world increasingly became dependent on these fossil fuel sources. This automatically led to much more exploitation and utilisation of fossil fuels. Thus the reserves of fossil fuel sources is being depleted in the near future and a massive increase of pollutants is being released to the atmosphere, water and soil, causing harmful effects on the environment and human health due to the fossil fuel combustion. Carbon dioxide (CO_2) as the main gas emission from the fossil fuel combustion is being known as greenhouse gas (GHG) which is considered as the main factor of global warming and climate change. Beside CO_2, methane (CH_4) easily produced in the nature is considered as the second GHG and contribute about 20% of GHG in the atmosphere respectively (Tondeur & Teng, 2008). Other consequences associated with fossil fuel use are the fossil fuel resources are not distributed evenly around the globe which makes many countries heavily dependent on imports. These tremendous increases have led to many concerns. Although it is not known how much fossil fuel is still available, it is generally accepted that it is being depleted and is non-renewable. Given these circumstances, searching for other renewable forms of energy sources is reasonable. Hence, various research fields regarding to the generation of renewable and sustainable energy sources with efficient and environmental friendly characteristic and reduction program of greenhouse gas is gaining great attention from scientist, engineers and government (Effendi *et al.*, 2005). The example of several sources of renewable energy are solar, hydropower, wind, geothermal, biomass and biofuel energies (Ma & Hanna, 1999; Huber, 2006a).

One of the most promising and long-term solution to the future energy crisis is the production of energy from biomass. Due to wide spread availability in nature, biomass became the primary energy resource after oil and coal and has contributes about 10–14% of the world's energy supply today (McKendry, 2002). The energy utilization from biomass resources has received considerable attention since the energy crisis in the mid-1970s. The energy obtained from agricultural wastes or agricultural by-products can be recognized as a potential source of renewable energy based on benefits of both energy recovery and environmental protection (Tsai *et al.*, 2006). In develop countries, the economy is largely based on the agricultural and forestry, so utilizations of biomass for energy purpose in these countries has a great potential to be done.

Florin & Harris (2008) defined biomass as contemporary organic matter formed by the photosynthetic capture of solar energy, which is stored as chemical energy. The main compositions in biomass are cellulose, hemicellulose, lignin and small amount of other material. Generally, cellulose is the main component (Table 1.1) which represents 40-50% from biomass weight whereas hemicellulose represents 20-40% (Zhang *et al.*, 2010).

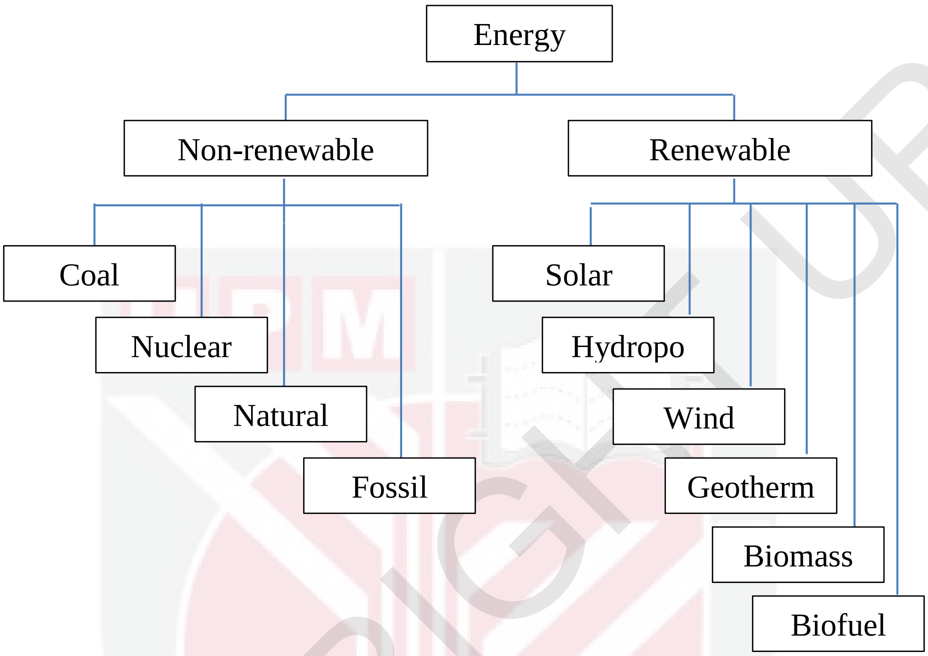

Figure 1.1: Non-renewable energy and renewable energy

Biomass can be converted into useful products including biosynthesis gas or syngas which is a mixture of CO and H_2 gases. Syngas is believed to be critical for the energy, chemical and environmental sustainability. It is very important intermediate, used as a feedstock for various fuel and chemical synthesis such as Fisher Tropsch, oxygenated compound, polycarbonate and other hydrocarbon (Gao *et al.*, 2008; Asami *et al.*, 2003). Hydrogen itself is a clean and efficient energy source which can be used for transportation and stationary power generation. It is widely used as a feedstock for the production of chemicals, hydrogenation of fats and oils in food industry, production of electronic devices, processing steel and also for desulfurization and re-formulation of gasoline in refineries.

In a large manufacture, syngas is produced via several methods include steam reforming of methane (SRM), dry reforming, partial oxidation of fossil fuels (POX) and auto-thermal reforming which combines SRM and POX. Among other methods developed to improve the existing technologies are the membrane processes, selective oxidation of methane and oxidative dehydrogenation. The detail information regarding syngas production will be discussed in Chapter 2. However, syngas is still not readily available in sufficient quantities and the production cost is still high especially for transportation purposes. (Tanksale *et al.*, 2010).

Table 1.1 : Typical level of cellulose, hemicellulose and lignin (Adapted from Mckendry, 2002)

Component	Percent dry weight (%)	Description
Cellulose	40-60	A high-molecular weight (10^6 or more) linear chain of glucose linked by β-glycosidic linkage. This chain is stable and resistant to chemical attack
Hemicellulose	20-40	Consist of short, highly branched chains of sugars (five-carbon sugars such as t-arabinose, ρ-xylose and six-carbon sugars such as ρ-glucose, ρ-galactose and ρ-mannose). Lower molecular weight than cellulose. Relatively easy to be hydrolysed into basic sugar.
Lignin	10-25	A biopolymer rich in three-dimensional, highly branched polyphenolic constituents that provide structural integrity to plant. More difficult to be dehydrated than cellulose and hemicellulose.

Due to increasing need of syngas, development of cost-effective and efficient hydrogen production technologies has gained significant attention in recent years. The technical challenges to achieve a stable syngas economy include improving process efficiencies, lowering the cost of production and harnessing renewable resources.

The production of syngas from biomass is expected to be particularly significant especially by using waste biomass such as rice straw as it is offer a great benefit to environment including utilizing two greenhouse gases (CO_2 and CH_4), and producing highly valuable syngas for a feedstock for other chemical and fuel processes. Besides that, it also can minimize the problem in term of waste management and health issue which related to air pollution.

A possibly good route to produce syngas is by using cheap biomass as a source through thermochemical conversion technology (Chen *et al.*, 2003).Gasification process is more attractive when the interest product is in the gaseous form. The gasification of biomass results in a high production of gaseous products and small quantities of char and ash and considered to be more environmentally friendly because of the lower emissions of toxic gases into the atmosphere. Gasification is basically a thermochemical process that converts lignocellulosic materials such as cellulose, hemicellulose and lignin into gaseous products. It consists of a number of elementary chemical reactions, beginning with the partial oxidation of a lignocellulosic fuel with a gasifying agent such as air, oxygen and steam (Tanksale *et al.*, 2010). Gasification of solid fuels to yield a mixture of H_2 and CO (syngas), followed by water-gas shift reaction to produce H_2 and CO_2, is a well-established process (Ramzan *et al.*, 2011).

One of the objectives in green chemistry principle as published by United State Environmental Protection Agency (USEPA) can be achieved by using a catalyst which effective for particular reaction. Generally, catalyst is defined as any material or substance that speeds up the rate of chemical reaction by lowering it activation energy. It is added in a little amount in comparison to the quantities of the reactant and not been consumed in the chemical transformation. However, in some cases the catalyst effects the reaction by being consumed and regenerated. Related to this work, the role of catalyst (heterogeneous catalyst) is crucial for producing the syngas effectively. There are lot of studies reported that some specified catalyst can enhance the production of syngas with high activity and stability. The detail of catalyst usage in syngas production will be discussed in Chapter 2.

Limestone is a sedimentary rock composed mainly of calcium carbonate ($CaCO_3$), usually in the form of calcite or aragonite. It may contain considerable amounts of magnesium carbonate as well; minor constituents also commonly present include clay, iron carbonate, and quartz.

Limestone has been used in many sector including construction, chemical, agriculture and even pharmaceutical industry. For example, powdered limestone is used as filler in paper, paint, rubber and plastics and crushed limestone is used as a filter stone in on-site sewage disposal systems. Powdered limestone is also used as a sorbent (a substance that absorbs pollutants) at many coal-burning facilities. In catalytic applications, limestone is a promising heterogeneous catalyst since it promotes a non-toxic, basic catalyst which important for the reaction processes.

Similar to the other natural sources of $CaCO_3$ such as dolomite and seashell, the active phases of the limestone were obtained by thermal decomposition of limestone into CaO as shown in Eq. 1 below:

$$CaCO_{3\ (s)} \longrightarrow CaO_{\ (s)} + CO_{2\ (g)} \qquad \text{[Eq.1]}$$

In Malaysia, since it is abundant and easy to get, the price of limestone is just around US$20 - 35 per metric ton. Comparing to the price of commercial calcium oxide (CaO) which around US$1000 - 1600 per metric ton with purity of ~95% , therefore, the application of limestone in syngas production have a high commercial prospect as the cost of material used in the reaction will be reduced.

1.2 Problem Statement

Due to dilemmas in increasing energy demand and fuel price, depletion of petroleum oil, national security and environmental problems have encouraged researchers around the world to find a new energy resources especially renewable energy which can be sustain in the future. According to Food Outlook Global Analysis in 2010, the world's production of rice straw is more than 500 million tonnes per year in last five years and expecting to be increase annually. Therefore, the use of lower-cost and non- food based feedstock of this lignocellulosic waste biomass has been taken into consideration for syngas production.

The products gas from biomass gasification enriched mainly with H_2, CO, CO_2 and CH_4 and also some other components such as H_2O, tar, and inorganic impurities. However, the present of PAH (PolyAromatic Hydrocarbon) in the process reduced the H_2 production and become a great challenge to deal with this tar formation to ensure the product gases is highly concentrate with H_2 at the same time minimizing the emission of CO_2 during gasification process. Thus, this study focuses on catalyst development especially from limestone based catalyst, and the influences of this limestone based catalyst with or without dopants towards the quality of syngas production.

1.3 Objectives

The objectives of this study are:

1. To synthesize various metal oxide modified limestone catalysts via wet impregnation method with addition of mono and bimetallic metal dopants (Ni, Fe, Co, NiCo, NiFe and CoFe).
2. To characterize the physico-chemical of the synthesized catalysts by various techniques such as X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area, Thermogravimetry analysis (TGA), Field emission scanning electron microscopy – Energy dispersive spectroscopy (FESEM-EDX) and Temperature programmed desorption of carbon dioxide (TPD-CO_2).
3. To carried out gasification reaction of rice straw with and without catalysts for the production of hydrogen.

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