SYNTHESIS AND CHARACTERIZATION OF  Ni-Co ON DIFFERENT
COMPOSITION SUPPORT TOWARDS HYDROGEN PRODUCTION FROM
ACETIC ACID STEAM REFORMING

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*Especially to my wonderful wife, who has always been there through the hard times and to my daughter Sarah*

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# ABSTRACT

Hydrogen is being considered as an alternative source for power generation in the future. The development of environmental friendly and cost effective hydrogen production become the main challenge in this area. In this work, the production of hydrogen by steam reforming of acetic acid over nickel-cobalt (Ni-Co) supported on lanthanum oxide ($La_2O_3$), cerium oxide ($CeO_2$) and aluminum oxide ($Al_2O_3$) was studied. The objectives of this study are to prepare the catalyst using an impregnation method, to characterize the catalyst using Temperature Programmed Desorption (TPD-$NH_3$), Brunauer-Emmett-Teller with $N_2$ (BET-$N_2$) and Temperature Programmed Reduction with $H_2$ (TPR-$H_2$) analysis and also to study the effect of reaction temperature on acetic acid conversion. TPR- analysis of the samples indicated that the amount of hydrogen consumed by the catalyst supported with same oxides decreases with increasing amount of $La_2O_3$. Furthermore, Ni-Co/70%$La_2O_3$-20%$CeO_2$ catalyst was reduced at lower temperature compared to other three catalysts. The result of TPD-$NH_3$ also showed that the acidity of the catalysts reduced by reducing the amount of ceria. Meanwhile, steam reforming of acetic acid was conducted in a fixed bed reactor with metal catalysts on different supports metal at temperature of 600 $^o$C, atmospheric pressure, 0.36 ml/min flow rate, acetic acid concentration 10 wt% and the weight of catalyst was 0.2 g. It was found that the mole fraction of hydrogen over Ni-Co/70%$La_2O_3$-20%$Al_2O_3$ catalyst was the highest which is 0.59, while acetic acid conversion over Ni-Co/70%$La_2O_3$-20%$CeO_2$ catalyst was the highest 93%. In addition, the catalyst (Ni-Co/70%$La_2O_3$-20%$CeO_2$ and Ni-Co/80%$La_2O_3$-10%$CeO_2$) performance tests are carried out in a fixed bed reactor at atmospheric pressure and temperature from 500°C to 700°C at increment of 50°C/min, 0.36ml/min flow rate and 10 wt% acetic acid concentration. It was found that the hydrogen production dropped by increasing of temperature and the temperature of 500 to 550$^o$C produce the high amount of hydrogen.

# ABSTRAK

Hidrogen merupakan satu sumber alternatif untuk penjanaan kuasa pada masa hadapan. Pembangunan penghasilan hydrogen yang mesra alam serta efektif dari segi kos merupakan cabaran utama dalam bidang ini. Dalam kajian ini, penghasilan hidrogen melalui proses pembaharuan stim terhadap asid asetik di atas Nikel Kobalt (Ni-Co) disokong pada lantanum oksida ($La_2O_3$), serium oksida ($CeO_2$) dan aluminium oksida ($Al_2O_3$) telah dikaji. Objektif-objektif kajian ini adalah untuk menyediakan pemangkin menggunakan kaedah penyabungan, pencirian mangkin menggunakan analisis-analisis seperti nyahpenyerapan suhu terancang ($TPD-NH_3$), Brunauer-Emmett-Teller dengan nitrogen ($BET-N_2$) dan Penurunan Suhu program dengan $H_2$ ($TPR-H_2$), dan juga untuk mengkaji kesan suhu tindakbalas terhadap penukaran asid asetik. Analisis TPR ke atas sampel menunjukkan bahawa amaun hidrogen yang disunakan oleh pemangkin tersokong atas oksida berkurangan dengan peningkatan amaun $La_2O_3$. Di samping itu, pemangkin (Ni-Co/70% $La_2O_3$-20% $CeO_2$) diturunkan pada suhu yang lebih rendah berbanding dengan tiga jenis pemangkin yang lain. Keputusan $TPD-NH_3$ juga menunjukkan bahawa keasidan pemangin-pemangkin dikurangkan dengan pengurangan amaun serium oksida. Sementara itu, proses pembaharuan stim asid asetik telah dijalankan dalam reaktor terpadat dengan penyokong pemangkin logam yang berbeza pada suhu 600 °C, tekanan atmosfera, kadar aliran sebanyak 0.36 ml/min, kepekatan asetik asid sebanyak 10% mengikut nisbah berat dan berat mangkin adalah 0.2 gram. Didapati bahawa pecehan mol hidrogen dengan penggunaan pemangkin Ni-Co/70%$La_2O_3$-20% $Al_2O_3$ adalah tertinggi iaitu 0.59, manakala penukaran asid asetik dengan penggunaan pemangkin Ni-Co/70% $La_2O_3$-20% $CeO_2$ adalah paling tinggi 93%. Di samping itu, ujian prestasi pemangkin (Ni-Co/70% $La_2O_3$-20% $CeO_2$ and Ni-Co/80% $La_2O_3$-10%$CeO_2$) dijalankan dalam reaktor laisan tetap pada tekanan atmosfera dan suhu dari 500 ° C sehingga 700 °C pada kenaikan 50 °C/min, kadar aliran sebanyak 0.36 ml/min dan kepekatan asid asetik sebanyak 10% mengikut berat. Adalah didapati bahawa penghasilan hidrogen menurun dengan peningkatan suhu dan penghasilan tertinggi didapati pada 500 ke 550°C.

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# LIST OF SYMBOLS

| | | |
|---|---|---|
| A.A | - | Acetic Acid |
| BET | - | Brunaue, Emmett, Teller |
| FID | - | Flame Ignition Detector |
| $CH_4$ | - | Methane |
| $C_2H_4$ | - | Ethylene |
| $C_2H_6$ | - | Ethane |
| CO | - | Carbon monoxide |
| $CO_2$ | - | Carbon dioxide |
| Eq. | - | Equation |
| $H_2$ | - | Hydrogen |
| Ar | - | Argon |
| $N_2$ | - | Nitrogen |
| He | - | Helium |
| XRD | - | X-Ray Diffraction |
| RT | - | Room Temperature |
| SMR | - | Steam Methane Reformation |
| TCD | - | Thermal Conductivity Detector |
| TPD | - | Temperature Programmed Desorption |
| TPR | - | Temperature Programmed Reduction |

# LIST OF ABBREVIATION

| | | |
|---|---|---|
| % | - | Percent |
| $\Delta H$ | - | Enthalpy |
| $KJ$ | - | Kilojoule |
| $mol$ | - | Mole |
| $k^{\circ}$ | - | Kelvin |
| $C^{\circ}$ | - | Centigrade |
| $g$ | - | Gram |
| $m^2$ | - | Square meter |
| $ml$ | - | Milliliter |
| $bar$ | - | Bar |
| $min$ | - | Minute |
| Sccm | - | Standard Cubic Centimeters Per Minute |

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# CHAPTER 1

# INTRODUCTION

## 1.1    Background of Study

The world's energy consumption is heavily dependents on the non-renewable source such as fossil fuels, especially in the transportation sector. This leads to energy tautness and  harms environmental, i.e. release of pollutant and the decrease of fossil fuel reserves. The demands aggregate energy will speed up the overtiredness of the fossil fuel limitation. Combustion of fossil fuels often yields large amount toxic, as well as greenhouse gases such as $SO_2$, NOx, $CH_4$ and $CO_2$ that cause global warming and acid rain (Mohammed *et al.*, 2011). However as oil production declines, coal has found favor not least because of plans to extract from underground coal schemes (Ribeiro, 2010).

Currently,  hydrogen is considered as one of the promising energy sources (Wanga and Cheng, 2012), and will become a significant carrier energy in the future. Large scale of hydrogen application in the fuel cells as well as the internal combustion engines, can be expected if hydrogen can be produced from renewable resources at high efficiency (Yazhong and Hengyong, 2006; Wanga and Cheng, 2012). Currently, hydrogen gas is produced through industrial conversion of fossil fuel such as, natural gas, naphtha and coal, through the catalytic steam reforming, partial oxidation or  gasification processes. However, these processes are

unsustainable due to release of greenhouse gases to the environment during the processes.

Currently, there is an increasing interest on the use of hydrogen to substitute fossil fuel in the energy sector. Hydrogen is a promising energy that potentially plays an important role in future energy systems and replaces fossil energy due to its clean burning qualities, as well as its potential for domestic production and the potential fuel cell vehicles to replace current vehicles that relay on fossil fuel potential for high efficiency. Hence, hydrogen production is a matter of great importance, both in clean fuel production and refinery recently. Therefore, for internal combustion engines, hydrogen can be good fuel cells, good possibility fuel and other applications (Li *et al.*, 2009). The overall reaction is represented by equation (1.1):

$$CH_3COOH + 2H_2O \longrightarrow 2CO_2 + 4H_2 \tag{1.1}$$

Where one mole of acetic acid reacts with two moles of water to product two moles of carbon dioxide and four moles of hydrogen. The steam reforming reaction is an endothermic with enthalpy value of +134.77 kJ/mole at 25$^{\circ}$C. Due to its endothermic nature, the reaction is favored at high temperature.

The improvement of different catalysts like noble metals, Co, Zn, Ni, and Fe was used for the steam reforming of bio-ethanol to produce hydrogen for fuel cells applications. They found out that Ni and noble metals- based catalysts were more active and selective towards hydrogen production. Rioche and Czernik noted the significance for the synthesis gas from the conversion of bio-oil is used by the bi-functional properties of the catalysts. The improvement of the steam activation and those metallic particles because of the ceria/zirconia support are involved in the organic molecules activation was their suggestion. However, the noble metal catalysts are expensive, but it can be decided that the good hydrogen yield in the steam reforming of bio-oil is due to the use of noble metal catalysts. In comparison,

nickel based catalysts are not expensive and promising catalysts for bio-oil and biomass gasification (Bulushev and Ross, 2011).

Nickel and cobalt are the most proper for steam reforming of acetic acid (Freni *et al.*, 2002; Frusteri *et al.*, 2004). Meanwhile, $La_2O_3$ has been reported to be excellent as basic support for industrial use (Mo *et al.*, 2001).The routes for carbon formation include Boudouard reaction, methane decomposition and polymerization of ethane, which later originated from acetic acid dehydration over $La_2O_3$ acidic sites. The direct deactivation of catalysts occurs mostly due to encapsulating of carbon and it impedes the reactivity of catalyst by covering its active sites. In addition, carbon at times deposit over catalysts without deactivation, especially in a mechanism that involve: carbon deposition over metal surface, migration of carbon containing species to the bulk phase of metal, saturation of these species and condensation of carbon. Mechanism of this nature results in the formation of filamentous carbon that does not directly deactivate the catalyst, but its continuous accumulation may block the bed or break the pellets (Alberton *et al.*, 2007).

Previously, Ni and Co based catalysts have been studied broadly in steam reforming and hydrogenation of hydrocarbons (Abdullah, 2009). Nickel and cobalt have the potentials to facilitate C-C bond and disintegration at temperature as low as $400^oC$. $La_2O_3$ and $ZrO_2$ are having weak acidic and basic properties, which make them to be chemically stable. These metal oxides are known for their redox properties (Abdullah, 2009). In most cases the redox properties are directly related to the catalyst active rating, while the acidic-basic nature determines the product selectivity (Zhao *et al.*, 2004). Redox properties and nature of acidity/alkalinity of catalyst depend on the metal compositions. However, the catalyst deactivation resulting from coke formation is a setback in $H_2$ production by steam reforming (Wu and Liu, 2010).

## 1.2 Problem Statement

Acetic acid is used as a model compound for hydrogen for hydrogen production by steam reforming because it is one of the major components of bio- oil (up to 12%). In addition, acetic acid is non-flammable, hence it is a safe hydrogen carrier. Different types of catalyst are used for the reaction of steam reforming (SR) of acetic acid. However, there are some challenges to be overcome before acetic acid can be used for mentioned purpose, and one of the challenges is the high cost of catalyst. Thus, for economic purpose, it is important to catalyst that can be easily obtained at low cost. Another problem is the deactivation of catalyst due to its high acidity. Hence it is important to characterize the catalyst to investigate the effectiveness, acidity, surface area and reducibility temperature of the catalyst, as these factors are significant in predicting and evaluating the performance of catalyst. The characterization can be done using temperature programmed desorption (TPD), temperature programmed reduction (TPR) and brunauer emmelt teller (BET) (Akande *et al.*, 2005).

## 1.3 Objective of This Work

The objectives of the study are:

i. To prepare the catalyst on different composition support.
ii. To characterize the catalyst using brunauer emmelt teller and temperature programmed method of reduction and desorption.
iii. To evaluate the effect of reaction temperature on the acetic acid reforming over Ni/Co supported by $La_2O_3$, $CeO_2$ and $Al_2O_3$.

## 1.4 Scope of Study

The overall scope of this work includes:

i. Prepare the 10%(Ni-Co) on different composition support ($La_2O_3$, $CeO_2$ and $Al_2O_3$) using an impregnation method.

ii. Characterize the chemical and physical properties of the catalyst using temperature programmed reduction-hydrogen (TPR-$H_2$), temperature programmed desorption with $NH_3$ and brunauer emmelt teller with nitrogen (BET-$N_2$).

iii. Study the effect of reaction temperature on the acetic acid reforming in the range of 500-700 $^o$C using bimetallic of 5 wt.% cobalt and 5wt.% nickel supported on lanthanum oxide, aluminum oxide and cerium oxide.

## 1.5 Significant of Research

Currently, there is an increasing interest in the use of hydrogen to substitute fossil fuel in the energy sector. The use of hydrogen may reduce air pollution. Moreover, hydrogen can be produced from numerous sources including methane, gasoline, biomass, coal or water. Therefore, the study on hydrogen ($H_2$) production by steam reforming of acetic acid will create more understanding and opportunity to apply this technology, especially on the area of the catalyst support since there is still limited finding on the use of bimetallic catalysts for hydrogen production. This is an environmental friendly and cost competitive method for hydrogen production. Furthermore, catalyst characterization techniques are significant methods in understanding and evaluating the performance of catalyst towards acetic acid conversion.

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