

HYDROGEN PRODUCTION FROM STEAM REFORMING OF PHENOL OVER
SUPPORTED NICKEL-COBALT CATALYST

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HYDROGEN PRODUCTION FROM STEAM REFORMING OF PHENOL OVER
SUPPORTED NICKEL-COBALT CATALYST

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To my beloved parents and brothers

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ABSTRACT

This thesis presents the results of a study of catalytic phenol steam reforming with the aim of hydrogen production using bimetallic nickel-cobalt (Ni-Co) supported on cerium oxide, zirconium dioxide (ZrO_2), lanthanum oxide, gamma alumina, and alpha alumina catalysts. Phenol has been selected as a reactant due to the high amount of phenol in bio-oil and is a potential renewable feedstock for hydrogen production. The high cost of noble based catalysts, low activity and performance of non-noble based catalysts, deactivation of catalysts by coke formation, and high temperature requirements for complete phenol conversion are the problems of the previous research. The aim of this research is to develop a highly active and stable catalyst for hydrogen production from the steam reforming of phenol. The physical and chemical properties of the catalysts were characterized in terms of their surface area, crystallinity, reducibility, acidity, basicity, and coke formation. Five prepared catalysts were screened by using a micro-reactor fixed bed at a temperature of 650 °C and atmospheric pressure. The effect of Ni to Co ratio on hydrogen production from phenol steam reforming reaction was then investigated. This was followed by parametric study on the process involving five factors, namely temperature (A), feed flow rate (B), catalyst amount (C), presence of Ni and Co (D), as well as concentration of phenol (E), and the two responses were phenol conversion (Y_1) and hydrogen (Y_2). The optimum catalytic performance was found to be for the Ni-Co/ ZrO_2 catalyst with 81.9% of phenol conversion and 80.7% of hydrogen yield at 650 °C. The effect of Ni to Co metal ratio study showed that the 75 wt.% Ni-25 wt.% Co supported on ZrO_2 catalyst displayed a superior catalytic activity among all the ratios. The parametric analysis showed that five variables (A, B, C, D and E) and interactions among AE, BE and DE produced significant effects on Y_1 and Y_2 . In the kinetic study, the results suggested that the surface reaction was the rate limiting step by assuming non-dissociative adsorption of phenol and steam using this catalyst. Hence, it is concluded that bimetallic Ni-Co supported on ZrO_2 catalyst is able to produce high hydrogen yield and has the potential to tackle the catalyst deactivation by coke.

ABSTRAK

Tesis ini membentangkan hasil kajian pembentukan semula stim bermangkin bagi fenol yang bertujuan untuk menghasilkan hidrogen dengan menggunakan pemangkin dwilogam nikel-kobalt (Ni-Co) yang disokong pada serium oksida, zirkonium dioksida (ZrO_2), lantanum oksida, gamma alumina, dan alfa alumina. Fenol telah dipilih sebagai bahan tindak balas kerana terdapat jumlah fenol yang tinggi dalam bio-minyak dan ia merupakan bahan mentah yang boleh diperbaharui dan berpotensi untuk penghasilan hidrogen. Kos tinggi pemangkin logam adi, aktiviti dan prestasi yang rendah pemangkin yang bukan logam adi, penyahaktifan pemangkin oleh pembentukan kok, dan keperluan suhu tinggi untuk penukaran lengkap fenol merupakan masalah penyelidikan sebelumnya. Tujuan kajian ini adalah untuk membangunkan satu pemangkin yang sangat aktif dan stabil untuk penghasilan hidrogen daripada tindak balas pembentukan semula stim bagi fenol. Sifat-sifat fizikal dan kimia pemangkin seperti keluasan permukaan, penghabluran, keterturunan, keasidan, kebesan, dan pembentukan kok telah dicirikan. Lima pemangkin yang disediakan telah disaring menggunakan reaktor mikro lapisan terpadat pada suhu $650\text{ }^\circ\text{C}$ dan tekanan atmosfera. Kesan nisbah Ni kepada Co terhadap penghasilan hidrogen untuk tindak balas pembentukan semula stim bagi fenol telah dikaji. Ini diikuti dengan kajian parametrik mengenai proses yang melibatkan lima faktor, iaitu suhu (A), kadar aliran suapan (B), jumlah pemangkin (C), kehadiran Ni dan Co (D), serta kepekatan fenol (E), terhadap penukaran fenol (Y_1) dan penghasilan hidrogen (Y_2). Prestasi pemangkin terbaik dalam tindak balas ialah pemangkin Ni-Co/ ZrO_2 yang menukarkan 81.9% fenol dan 80.7% penghasilan hidrogen pada suhu $650\text{ }^\circ\text{C}$. Kajian terhadap kesan nisbah logam Ni terhadap Co menunjukkan bahawa pemangkin 75 wt.% Ni-25 wt.% Co yang disokong pada ZrO_2 mempamerkan aktiviti pemangkin yang terbaik di kalangan semua nisbah. Analisis berparameter menunjukkan lima pembolehubah (A, B, C, D dan E) dan interaksi antara AE, BE dan DE menghasilkan kesan yang besar ke atas Y_1 dan Y_2 . Dalam kajian kinetik, dapatan kajian menunjukkan bahawa tindak balas permukaan adalah langkah mengehadkan kadar dengan menganggap penjerapan fenol dan stim yang tidak terpisah menggunakan pemangkin ini. Oleh itu, dapat disimpulkan bahawa pemangkin dwilogam Ni-Co yang disokong pada pemangkin ZrO_2 mampu menghasilkan hidrogen yang tinggi dan mempunyai potensi untuk menangani penyahaktifan pemangkin oleh kok.

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LIST OF ABBREVIATIONS

S/C	–	Steam to carbon ratio
FPS	–	Fuel processing system
ATR	–	Auto thermal reforming
O ₂ /C	–	Oxygen to Carbon ratio
TCD	–	Thermal conductivity detectors
FID	–	Flame ionization detectors
SEM	–	Scanning electron microscopy
TPR	–	Temperature-programmed reduction
TPD	–	Temperature-programmed desorption
TPO	–	Temperature-programmed oxidation
XRD	–	X-ray diffraction
HPLC	–	High performance liquid chromatography
WGS	–	Water gas shift reaction
BET	–	Brunauer, Emmett and Teller
OSC	–	Oxygen storage capacity
TOS	–	Time on stream
LH	–	Langmuir–Hinshelwood
ER	–	Eley–Rideal
RDS	–	Rate-determining step
EPA	–	Environmental protection agency

LIST OF SYMBOLS

$^{\circ}\text{C}$	–	Degree celsius
K	–	Kelvin
g	–	Gram
mL/min	–	Milliliter per minute
C_A	–	Concentration of phenol
C_B	–	Concentration of water
a	–	Reaction order with respect to phenol
b	–	Reaction order with respect to water
k_{rxn}	–	Kinetic constant of reaction
$k_{A(p)}$	–	Kinetic constant corresponding to phenol
$k_{B(w)}$	–	Kinetic constant corresponding to water
R^2	–	Coefficient of determination
r_{ph}	–	Reaction rate
E_a	–	Activation energy
R	–	Gas constant
Q_{ph}	–	Phenol flow rate
mmol	–	Millimole
μmol	–	Micromole
W_{cat}	–	Catalyst weight
X_{ph}	–	Phenol conversion
J	–	Joule
Wt. %	–	Weight percent

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Vehicular pollution from the combustion of fossil fuels poses a great danger to human health in urban societies and contribute to green house gases which are linked to climate change. The damage to the environment is witnessed through the impacts of such pollution through global warming and eventually climate change. These are irreversible changes in magnitude of order but could be mitigated. The low-emission demands of modern automobile industries as well as aviation, mining and electricity generation are the greatest environmental sustainability concerns in the 21st century. Highly efficient vehicles are the simplest key to decreasing emissions. Whereas internal combustion engines in vehicles causes pollution, the introduction of catalytic devices and filters have only slightly help to reduce the emission of particulates such as SO₂ and NO_x[1]. These greenhouse emissions have a great environmental impact, as such are considered not tolerable in the future due to their negative consequences to health of humans and other lives [2-4].

Hydrogen as an energy carrier on board for transportation was recognized long ago. The matter raised up for management includes hydrogen production, storage and transmission, as well as the use of hydrogen, especially as fuel for fuel cells [5]. Hydrogen is a promising energy to replace fossil energy and plays a significant role in future energy systems, because the final product of hydrogen combustion is pure water [6]. Therefore, hydrogen production is a matter consequential, both in refinery and clean fuel production [7]. Present fuel cell

expenses are way above direct cost practicality, and development in fuel cell performance, durability and manufacture thus these serious developments itemizes for allowing the penetration of hydrogen as a general energy carrier [8].

Pure hydrogen gas does not exist as a natural resource like natural gas and oil. Hydrogen can be produced from a variety of sources such as fossil fuels, biomass, water and bio-oil [9, 10]. Bio-oil is a preferred hydrogen resource because of its renewable source and has environmental benefit characteristics. Among various renewable feedstocks alternatives for hydrogen production, bio-oil is very attractive because of its relatively high hydrogen content, availability, non-toxicity, storage, ease of handling and safety. In the present study, only the unwanted and non fuel component of bio-oil which is phenol, a source of hydrogen production is chosen. Phenol, with six hydrogen atoms, six carbon atoms, and an oxygen atom, is considered to contain high level of hydrogen. Interestingly, phenol can be obtained from a side reaction during the pyrolysis of biomass. According to the previous research, there are two successive reactions that may take place in the steam reforming of phenol. Phenol steam reforming reaction and water gas shift reaction is represented by Equations 1.1 and 1.2 respectively [11].



Due to the presence of the hydrogen ions, phenol is considered as an acid compound. Phenol has high stability in the form of phenoxide ($C_6H_5O^-$) ion, as such it is considered as a weak acid via the release of H^+ ion [12, 13].

Steam reforming (SR), coal gasification, auto-thermal reforming (ATR), dry reforming (DR), partial oxidation (POX), thermolysis and electrolysis are effective routes for producing hydrogen [14-17]. Among these, steam reforming is the most studied since it produces the highest hydrogen yield compare to other methods such

as ATR, POX, and DR [18, 19]. Steam reforming of phenol to produce hydrogen has been investigated over a wide variety of supported metal catalysts such as Ni, Rh, Fe, Rh-Fe, CaO, Pt, Pd, and Pt[20-23]. Meanwhile, numerous studies have shown that support such as γ -Al₂O₃, La₂O₃, ZrO₂, MgO, and CeO₂ also plays a critical role in the catalytic performance for hydrogen production from phenol steam reforming [20, 23, 24]. Among the metals, Ni as an active metal has considerably cheaper price compared with precious metals (for example, platinum, rhodium, or ruthenium) and high catalytic activity in terms of the cracking of C-C and C-H bonds [25]. Previous studies show that the process of steam reforming of acetic acid and ethanol, a basic catalyst was found to be highly active in fuel conversion and had good selectivity in terms of hydrogen yield [26-29]. Co can assist C-C bond cleaving at temperatures of 450°C and this showed 100% ethanol conversion and 73.8% of hydrogen selectivity [28].

Matas Güell *et al.* found that Ni/K-La₂O₃-ZrO₂ and Ni/CeO₂-ZrO₂ catalysts exhibited high activity in hydrogen production and good stability in phenol conversion [20]. However, the catalysts suffered in deactivation due to coke formation. Garbarino *et al.* studied ethanol and phenol steam reforming over Ni-La/Al₂O₃ catalyst under temperatures between 500 and 750 °C, GHSV = 54000 h⁻¹ of a gaseous mixture with the following composition: 39.3% He, 54.6% water, 4.1% ethanol and 2% phenol [30]. Operating at 750 °C, 82% hydrogen yield was achieved with phenol conversion of 88%. Wand *et al.* used Ni/Ash catalyst in steam reforming of phenol [31]. They found that this catalyst resulted in 83.5% conversion of phenol and the corresponding hydrogen yields were kept at 79%.

Zhang *et al.* examined the effect of bimetallic Ni-Co for the CO₂ reformation of methane [32]. They found that bimetallic Ni-Co catalysts exhibit highly stable activity with no deactivation and no detectable carbon formation. De Sousa *et al.* also investigated bimetallic Ni-Co catalysts for methane dry reformation [33]. They reported that different catalytic support would affect the catalysts performance. They found that the Ni dispersed on NiAl₂O₄ species were very active in terms of CH₄ conversion. NiAl₂O₄ species were highly active in terms of CH₄ conversion, whereas

Ni⁰ dispersed on either Fe₃O₄-Co₃O₄ or CeO₂-NiAl₂O₄ provided lower catalytic performance due to active phase degradation.

In retrospect of the above research findings, there is an evident research gap on the systematic studies on the effect of the supports and active metal ratio on hydrogen production from phenol steam reforming over supported bimetallic Ni-Co catalysts. Different type of support can have a significant effect in determining catalytic activity and selectivity toward phenol steam reforming reaction.

1.2 Problem Statement

The high cost of catalyst is a major constrain to hydrogen production from phenol steam reforming process [21, 34-37]. Noble metals such as ruthenium, rhodium, palladium, iridium, platinum, and gold provide high hydrogen yield in the reforming reaction. However, the high cost of noble metals limited their further application. Accordingly, the search for non-noble metal catalysts with good activity and selectivity in the phenol steam reforming reaction has receive considerable attention. This will undoubtedly contribute towards making the process more economical, especially when reflected in terms of high and stable hydrogen production [14, 15, 38]. Among non-precious transition metals which have shown good performances in steam reforming reaction are Co and Ni. They are supported on various oxide systems (La₂O₃, ZrO₂, Al₂O₃, CeO₂) [18, 20, 39-42]. Mattos *et al.* reported that oxygen mobility and oxygen storage capacity (OSC) of the support is a critical property to favour carbon removal and avoid deactivation [43]. In specific terms, Ni has been revealed from a number of studies as a very active metal for the reforming reaction, even though it is highly vulnerable to deactivation by coking process [30, 44]. Co displayed better ability in deactivation resistance and stability under different conditions of operation than Ni. The metal-support interactions can have a significant effect in determining catalytic activity and selectivity in phenol steam reforming reaction.

Another major problem with hydrogen production from phenol steam reforming is the high-potential of coke formation[20]. Takanabe *et al.* and Djinović *et al.* reported that alloying Ni with Co breaks the integrity of surface Ni ensembles, which decreases the apparent Ni particle size to the extent that it is too small for carbon nucleation and growth [45, 46]. Additionally, formation of NiCo alloy is reported to improve catalyst stability by improving resistance of active metal oxidation and creating highly active sites for the reforming at the boundary between metal and support.

Factors that affect the performance of hydrogen production from phenol steam reforming reaction are the steam to phenol (S/P) ratio, catalyst composition, the flow rate of carrier gas, operating temperature, reactant feed rate and space-time, preparation method, the catalyst particle size, the amount of catalyst, and ratio of metal in multiple active metal catalysts. It is hard to investigate the effect of each variable at a time using different range towards hydrogen production from phenol steam reforming. The design of experiments (DOE) methods is more suitable than the one-factor-at-a-time techniques because by studying multiple factors at the same time, high efficiency can be obtained. These techniques have the following common benefits: (1) more information per experiment than accidental methods, (2) a decrease on the number and cost of experiments, (3) make the calculation of the interaction among variables possible within the series studied, leading to better facts about the process and (4) simplifies the description of the significant operation conditions in the scale-up process [47]. Therefore, these techniques have been considered as powerful tools for process examination [48].

1.3 Objectives of This Work

The objectives of the study are divided into four, these are:

- a) to prepare and characterize Ni and Co supported on various supports for phenol steam reforming reaction;

- b) to investigate the effect of Ni to Co ratio on the best support;
- c) to determine the effects of different factors towards phenol conversion and hydrogen yield; and
- d) to determine the reaction kinetics for hydrogen production from phenol over Ni-Co/ZrO₂ catalyst.

1.4 Scope of Study

The overall scope of this work can be divided into four focus scope as listed below.

- a) Screening was carried out using Ni-Co on various supports (La₂O₃, CeO₂, ZrO₂, γ -Al₂O₃ and α -Al₂O₃) to determine the best support for hydrogen production from phenol steam reforming reaction. According to literature, metal loadings of 3.5 wt.%-10 wt.% is often used by researchers in this field [20, 44, 49, 50]. Metal loading of 10 wt.% was selected for this research. 10 wt.% (Ni-Co) on various supports, La₂O₃, CeO₂, ZrO₂, γ -Al₂O₃ and α -Al₂O₃ were prepared using an impregnation method. Characterizations of the catalysts were carried out using Brunauer, Emmett and Teller (BET) analysis method, X-Ray diffraction (XRD), temperature-programmed reduction of hydrogen (TPR-H₂), temperature-programmed desorption of ammonia (TPD-NH₃), temperature-programmed desorption of carbon dioxide (TPD-CO₂) and thermogravimetric analysis (TGA) under nitrogen. The screening of the catalyst was performed at the temperature of 650 °C, 10 wt.% phenol, 0.36 mL/min of flow rate in a fixed bed reactor operated at atmospheric pressure due to the equipment limitation.
- b) Catalysts with various Ni-Co ratios on ZrO₂ were prepared by impregnation method. In order to clarify the relationship between catalytic performance and the catalyst structural properties, the Ni_x-Co_y/ZrO₂ (x=0, 1, 2, 3, 4 where

x+y=4) catalysts were characterized extensively using the techniques of XRD, BET, TPR, TPD-CO₂, TPD-NH₃ and TGA. The reaction was carried out under the following conditions: temperature at 600 °C, 0.2 g catalyst, and 0.36 mL/min feed flow rate.

- c) A parametric study was carried out on hydrogen production from phenol steam reforming reaction in a fixed bed reactor. Two-level full factorial design was generated using Minitab® for this purpose. The factors studied were temperature (500-800 °C), amount of catalyst (0.1-0.3 g), feed flow rate (0.16-0.46 mL/min), presence of Ni and Co, and concentration of phenol (2-10 wt.%), while the responses are phenol conversion and hydrogen yield.
- d) An in-depth study in varying reaction parameters such as reaction temperature (500 to 800 °C), amount of catalyst (0.1 to 0.3 g), feed flow rate (0.16 to 0.46 ml/min) and phenol concentration (2 to 10 wt.%) were carried out in order to investigate the catalyst performance for kinetic study. POLYMATH software (version 6.1) was used to solve nonlinear regression. The reaction rate, activation energy, and the reaction order were calculated through a power law kinetic model. Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) models were used to study the possible reaction mechanism.

1.5 Significant of Research

The study is beneficial in a number of particular areas by contributing to the body of knowledge available in fields of hydrogen production from renewable source, lower reaction temperature achieved compared to previous researches and development of highly efficient catalyst towards hydrogen production with less coke formation, useful processing for industry experts, and kinetic study. It is important to look for alternative and renewable hydrogen source. The present work highlights hydrogen production from a model component in bio-oil via steam reforming as an alternative energy source with great potentials. Phenolic compound is an unwanted material from pyrolysis product. However, it has a high value of hydrogen in its

structure. Literature reviewed in this research include works that discussed hydrogen production from catalytic phenol reforming reaction. Furthermore, this study explored the catalytic performance of different supported Ni and Co catalysts in phenol reforming reactions in detail.

Another importance to this study is the catalyst development. Co and Ni are widely used transition metals for various steam reforming reactions, and both are suggested as appropriate materials because of their maximum catalytic performances and has lower cost compared to the noble metals. The detailed comparisons of Co and Ni over M (M= La_2O_3 , ZrO_2 , CeO_2 , $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$) catalysts in terms of catalytic behaviors in phenol reforming reactions have not yet been officially published anywhere. Thus, catalytic behaviors of this different supported metal catalyst in steam reforming of phenol are aimed in this study. Besides, the advantages of steam reforming technique for hydrogen production are low temperature and higher H_2/CO_2 ratio condition in comparison to dry reforming (DR), and partial oxidation (POX). These are considered as other significant issues in the current work.

In addition, this study provided a proposed kinetic model for the steam reforming of phenol using the promising catalyst based upon the methodology of different kinetic models that were reported. Influence of different experimental conditions at the reaction rate which can possibly yield vital information about how quickly or slowly a reaction takes place, as well as the development of mathematical models that can describe the behavior of the reaction were investigated.

1.6 Thesis outline

The materials presented in this thesis address the objectives outlined in the preceding section. The thesis was organized in the following manner: Chapter 1 contains the research background, research objectives and scopes, as well as the significance of research. In Chapter 2, the theoretical background and literature

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