



# Hydrogen production from catalytic steam reforming of phenol with bimetallic nickel-cobalt catalyst on various supports

Walid Nabgan<sup>a,b</sup>, Tuan Amran Tuan Abdullah<sup>a,b,\*</sup>, Ramli Mat<sup>b</sup>, Bahador Nabgan<sup>a,b</sup>, Sugeng Triwahyono<sup>c</sup>, Adnan Ripin<sup>a</sup>

<sup>a</sup> Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, UTM Skudai, 81310 Johor, Malaysia

<sup>b</sup> Department of Chemical Engineering, Faculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia, UTM Skudai, 81310 Johor, Malaysia

<sup>c</sup> Centre for Sustainable Nanomaterials (CSNano), Department of Chemistry, Universiti Teknologi Malaysia, UTM Skudai, 81310 Johor, Malaysia

## ARTICLE INFO

### Article history:

Received 3 July 2016

Received in revised form 28 August 2016

Accepted 31 August 2016

Available online 13 September 2016

### Keywords:

Hydrogen production

Steam reforming

Phenol

Bimetallic nickel-cobalt

Various supports

## ABSTRACT

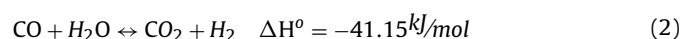
Catalytic phenol steam reforming with the aim of hydrogen production was studied in terms of bimetallic nickel-cobalt supported by CeO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, and α-Al<sub>2</sub>O<sub>3</sub>. The catalysts (each formed of 5% wt. of nickel and 5% wt. of cobalt on the support) were prepared according to the impregnation method. The effect of different supports on the properties and catalytic behaviour with the aim of hydrogen production, phenol conversion, and coke formation on the surface of the catalysts were studied. The physical and chemical properties of the catalysts were characterised in terms of their surface area, acidity, basicity, reducibility, crystallinity, and coke formation (for spent catalysts). The catalysts were tested by using a micro-reactor fixed bed at a temperature range of 500–800 °C. The activity of the catalysts on phenol conversion and hydrogen yield depends on the basic and acidic site of the catalysts as well as the metal interaction with the support. Results of various experiments in catalytic activity confirmed that a higher production of H<sub>2</sub> occurred in the presence of high CO<sub>2</sub> uptake and H<sub>2</sub> consumption which are characterised by basicity and reducibility analysis respectively. The coke analysis results show that the irreducible oxides for the Ni-Co bimetallic catalyst are more favour for coke formation than reducible oxides. All catalysts were active in the reformative reactions but the catalysts supported on the reducible oxides of ZrO<sub>2</sub> showed superiority in activity and stability. The most active catalyst was Ni-Co/ZrO<sub>2</sub> because of having the tetragonal phase structure which is favour in reforming processes, strong metal-support interaction, high surface area, the lowest coke formation, and six days' reformative stability. The catalyst test shows that the phenol conversion achieved at 650 °C is 75.9% and hydrogen yield is 80.7% for Ni-Co/ZrO<sub>2</sub> catalyst. The reaction rate and activation energy with respect to Ni-Co/ZrO<sub>2</sub> catalyst were found to be 11.17 mmol/gs and 102.41 (J/mol), respectively.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogen can be considered an attractive source of carrying energy due to the advanced development of proton exchange membrane fuel cell (PEMFC), a green technology. PEMFC is well-known to be a clean technology for mobile application (such as transportation) and aims to replace fossil fuel combustion engines. Since hydrogen does not exist naturally or is stable in its normal condition, it must be extracted from a renewable source, compound or molecules that contain hydrogen [1]. Phenol, with six hydro-

gen atoms, six carbon atoms, and an oxygen atom, is considered to contain a high level of hydrogen. Interestingly, phenol can be obtained from a side reaction during the pyrolysis of biomass. Phenolic compounds are the main bio-oil components with up to 38% wt. [2,3]. Phenol was further recognized as the main component of tar formed following wood-biomass gasification by steam in a fluidized bed reactor in the low temperature range (600–700 °C) [4–6]. According to the previous research [7], there are two successive reactions that may take place in the steam reforming of phenol. Phenol steam reforming reaction and water gas shift reaction are represented by Eqs. ((1) and (2)).



\* Corresponding author at: Hydrogen and Fuel Cell Lab, N29, Universiti Teknologi Malaysia, Skudai, 81310, Malaysia.

E-mail addresses: [tamran@cheme.utm.my](mailto:tamran@cheme.utm.my), [tuanamran@utm.my](mailto:tuanamran@utm.my) (T.A. Tuan Abdullah).

However, one of the major problems in the phenol steam reforming is the high potential formation for some by-products such as carbon [7–9]. This carbon formation will lead to catalyst deactivation and can make troubles for continuous steam reforming process and sustainable production of hydrogen.

The reaction product of biomass pyrolysis typically contains a high molecular weight of hydrocarbon, phenolic compounds, acid, and water. It can directly convert to highly valuable gas hydrogen via catalytic steam reforming. It has been found that steam reforming is the most effective and convenient method for hydrogen production from hydrocarbons compared to other methods such as auto-thermal reformation, partial oxidation, and dry reformation [10,11].

Many typical active metals such as Ni [8], Rh [12,13], Fe [7], Rh-Fe [6], CaO [14], Pt, Pd, and Rh [15] over irreducible oxide supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [15,16], La<sub>2</sub>O<sub>3</sub> [8,13,16,17] and reducible oxide supports such as ZrO<sub>2</sub> [6,8,12,13,15], MgO [6,7,12], and CeO<sub>2</sub> [6–8,12,13,15] have been studied in terms of phenol reformation. For example, Matas Güell, et al. [8] found that Ni/K-La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts exhibited high activity and good stability in phenol conversion. However, the catalysts suffered in deactivation due to coke formation. Ruthenium (Rh) supported on different composition of CeO<sub>2</sub>, ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> was examined by Constantinou, et al. [13] at a steam to phenol ratio of 67:1. They achieved 80% phenol conversion and 80% hydrogen yield at a low temperature of 450 °C for 5 wt.% Rh supported on 13 wt% Ce, 83 wt% Zr and 4 wt% La catalyst. This shows good performance, but there are drawbacks due to the high price of Ru itself as a precious metal. In general, ZrO<sub>2</sub> exists in three different polymorphs at ambient pressures: monoclinic (m-ZrO<sub>2</sub>), tetragonal (t-ZrO<sub>2</sub>), and cubic (c-ZrO<sub>2</sub>). The t-ZrO<sub>2</sub> phase shows higher stability, performance and metal dispersion for chemical reactions [18–20]. Another important work is that of Polychronopoulou et al. [7], who examined Fe supported on MgO-Al<sub>2</sub>O<sub>3</sub> and MgO-CeO at temperature between 600 and 700 °C and a water to phenol ratio of 8:1. They found that a 5 wt.% Fe/50MgO-50CeO catalyst is more active in terms of H<sub>2</sub> production and has low coke formation on its surface. It is believed that Al<sub>2</sub>O<sub>3</sub> was the main contribution to coke formation and suffered less activity compared to a catalyst supported on MgO-CeO. Other works applied La<sub>2</sub>O<sub>3</sub> support catalysts for phenol [8,13,16], acetic acid [21,22], and ethanol [23,24] reformation. It was found that applying a La<sub>2</sub>O<sub>3</sub> support in the catalyst highly affected the water gas shift reaction and increased H<sub>2</sub> production.

Among the metals, nickel as an active metal has been selected due to its considerably cheaper price compared with precious metals (for example, platinum, rhodium, or ruthenium) at high catalytic activity in terms of the cracking of C–C and C–H bonds [25]. In previous research, in the steam reforming of acetic acid [26,27] and ethanol [28,29], a basic catalyst was found to be highly active in fuel conversion and had good selectivity in terms of hydrogen yield. Cobalt can assist C–C bond cleaving at temperatures as low as 400 °C and this shows high production of H<sub>2</sub> and CO<sub>2</sub> [28]; this is due to the highly favourable water gas shift reaction [10,29,30]. In our previous researches [31,32] we found that the same combination of Ni and Co metals may improve the performance of the catalyst in the acetic acid steam reforming reaction. Zhang, et al. [33] examined the effect of bimetallic Ni-Co for the CO<sub>2</sub> reformation of methane. They found that bimetallic Ni-Co catalysts exhibit highly stable activity with no deactivation and no detectable carbon formation. De Sousa et al. [34] also investigated bimetallic nickel-cobalt catalysts for methane dry reformation. They also reported that a different catalytic support will have an effect on the catalyst's performance. They found that the NiCo dispersed on NiAl<sub>2</sub>O<sub>4</sub> species was highly active in terms of CH<sub>4</sub> conversion. NiAl<sub>2</sub>O<sub>4</sub> species was highly active in terms of CH<sub>4</sub> conversion, whereas Ni<sup>o</sup>

dispersed on either Fe<sub>3</sub>O<sub>4</sub>–Co<sub>3</sub>O<sub>4</sub> or CeO<sub>2</sub>–NiAl<sub>2</sub>O<sub>4</sub> provided lower catalytic performance due to active phase degradation.

According to the above-mentioned information, there have not been systematic studies about the effect of the support on hydrogen production from phenol steam reforming over supported bimetallic Ni-Co catalysts. However, different type of support can have a significant effect on catalytic activity and selectivity toward phenol steam reforming reaction. The metal-support interactions can have a significant effect on catalytic activity and selectivity in phenol steam reforming reaction. Another point is that oxygen mobility of the support is a critical property to favour carbon removal and avoid deactivation. However, during reaction, the morphology and the oxidation state of the metal particles are changed and the actual dispersion under reaction conditions cannot be represented by initial dispersion of the metal catalyst. Therefore, the study of the effect of reducible oxides such as ZrO<sub>2</sub> and CeO<sub>2</sub> and irreducible oxides such as La<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports on the performance of bimetallic Ni–Co catalysts with the aim of hydrogen production from phenol steam reforming is of considerable interest. The overall performance of these supports for bimetallic Ni-Co catalyst will be calculated based on phenol conversion and the hydrogen yield. Thus, the physicochemical properties and activity of bimetallic Ni–Co catalyst in relation to La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports in the steam reforming of phenol with the aim of hydrogen production is reported herewith. In addition, the activation energy (E<sub>a</sub>) and the reaction rate for phenol conversion for every catalyst were carried out.

## 2. Experimental procedure

### 2.1. Catalyst preparation

The bimetallic catalysts of 5 wt.% Ni and 5 wt.% Co supported on La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (all from Sigma-Aldrich) were prepared by using the impregnation method. Previous researched [35–37] were reported that the 5 wt.% Ni in the bimetallic catalysts show high activity in the reforming reaction. The catalysts were prepared by mixing nickel nitrate hexahydrate and cobalt nitrate hexahydrate AR with a metal oxide support in deionised water based on their metal content. This mixture was continuously stirred on a hotplate at 90 °C until it becomes slurry. The slurry was dried in an oven at 110 °C overnight, followed by calcination at 750 °C overnight. The powder catalyst will pass the reactor mesh; therefore, the catalyst's particle size was required to be 1 mm in order that it could hold in the reactor. Thus, the calcined catalyst was crushed and filtered on two layers of 35 mesh and 34 mesh sieves to obtain a particle size of 1.0 to 1.4 mm.

### 2.2. Catalyst characterisation

A chemisorption analyser, Micromeritics Chemisorb 2720, was used to evaluate the reducibility of the bimetallic catalysts on the support by applying a temperature-programmed reduction of hydrogen (TPR-H<sub>2</sub>) method. 25 mg of the catalysts were treated at 300 °C for an hour under a high purity of 20 mL/min helium (99.99%) to remove moisture and other adsorbate impurities. The TPR-H<sub>2</sub> profile was obtained by ramping the temperature at 10 °C/min under 20 mL/min of 10% (vol.) H<sub>2</sub> in argon.

The same apparatus of chemisorption was used to carry out the temperature-programmed desorption of CO<sub>2</sub> and NH<sub>3</sub> to evaluate the basicity and acidity, respectively. 35 mg of the sample was kept under a 30 mL/min argon flow rate at 600 °C for 60 min, then cooled down to 25 °C and kept under a 20 mL/min helium flow rate for 30 min. The CO<sub>2</sub> saturation of the catalyst was carried out for 30 min at 20 mL/min under purified CO<sub>2</sub>. The heating rate was set

Download English Version:

<https://daneshyari.com/en/article/6453335>

Download Persian Version:

<https://daneshyari.com/article/6453335>

[Daneshyari.com](https://daneshyari.com)