Acetic acid-phenol steam reforming for hydrogen production: Effect of different composition of La_2O_3-Al_2O_3 support for bimetallic Ni-Co catalyst

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ABSTRACT

Hydrogen production from a mixture of side products of pyrolysis oil through the catalytic steam reforming was carried out. Acetic acid and phenol were considered as side products in the bio-oil derived from the pyrolysis of biomass. The performance of bimetallic Nickel-Cobalt (Ni-Co) catalyst supported on different ratios of Lanthanum (III) Oxide (La_2O_3) and gamma-aluminum oxide (γ-Al_2O_3) was evaluated. The catalytic properties of the prepared catalysts were characterized for the total acidity, basicity, catalyst total surface area, crystallinity and the reducibility of active metal. The results of the characterization shows that presence of γ-Al_2O_3 as a support decreased the reducibility, acidic and basic site of the catalyst but increased its performance due to high surface area. By increasing the γ-Al_2O_3 metal oxide content in the catalyst, the coke deposits are increased because of the weak interaction of metal-support of high γ-Al_2O_3 contents catalysts. Catalyst dilution was found to increase the performance of the steam reforming reaction by changing the catalyst bed height. The results show that the ~100% conversion for acetic acid and 95.7% for phenol at 800 °C over the undiluted catalyst while 97% of phenol conversion was achieved while SiC dilution applied.

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1. Introduction

The exploration for alternative energy sources has become a necessity due to the reduction of worldwide fossil fuel resources coupled with the endless rise in energy demand. The use of biomass is considered as a clean alternative energy resource due to its renewability and relatively low CO_2 and low sulfur value levels. In many areas, the operation of biomass energy has been widely improved. Through thermo-chemical processes, it can be converted into hydrogen and hydrogen-rich gas. Thermo-chemical conversion methods generally includes steam reforming, pyrolysis, gasification, and high-pressure supercritical conversion [1]. There are lots of components in bio-oil derived from biomass which comprises of ketones, alcohols, carboxylic acids, aldehydes, acetic

acid and phenols [2,3]. A complete study on bio-oil derived from diverse biomass remains reveals that acids, phenols and ketones are the major ones with 19 wt.%, 30 wt.% and 21 wt.% weight percentages respectively. Hence, in studies on catalytic steam reforming phenol, acetic acid (HOAc) and hydroxyacetone are mostly employed as generic model combinations for each group [4]. The phenols, acetic acids and phenolic compounds are not considered as fuels and they are corrosive to combustion engines. A typical bio-oil generation results in 30 wt.% acetic acids [5] and 38 wt.% phenols [6] as unwanted components of pyrolysis oil. The methods used for hydrogen production from biomass are catalytic steam reforming of biomass pyrolysis oil and gasification. Among the economic advantages of bio-oil steam reforming process includes its easy operation and high yield of hydrogen [7,8]. For more than two decades, significant research efforts have been dedicated towards improving the process for hydrogen production.

Ketonization, water shift reaction, methanation, and thermal analysis reaction are possible reactions which may occur through acetic acid-phenol steam reforming [9–11]. Phenols contain an —OH group, which is bonded to one of the sp^2 carbon atoms of a

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benzene ring. The phenol family includes the parent compound as well as a wide variety of other compounds having additional substituent attached to the phenol ring [12,13]. Moreover, steam reforming requires the lowest process temperature and produces higher H_2/CO_2 ratio in product compared to other possible methods like dry reforming (DR), partial oxidation (POX) and coal gasification [9–11,14].

Nickel-based catalyst has been commonly used for steam reforming of bio-oil due to its high selectivity and activity towards hydrogen production [15–17]. In particular, Ni-based catalysts were found to be effective for tar destruction, thereby producing high yields of synthesis gas [18,19]. Due to their low attrition resistance, these catalysts are generally placed down-stream in the gasifier in a separate fixed-bed reactor [19,20]. On the other hand, Cobalt-based catalyst is an appropriate catalyst for steam reforming of bio-oil due to its advantages of having no catalyst inventory cost and low temperature towards high hydrogen yield. Cobalt has the capability to promote C—C bond rupture at temperatures as low as 400 °C and supported cobalt catalysts show higher production of H_2 and CO_2 with lower ethylene production [21]. The activity and selectivity properties of La_2O_3 are the reasons for the selection of rare-earth oxides as supports. It is used to develop ferroelectric and optical materials [22]. The chemical and hydrothermal stabilities of γ-Al_2O_3 are critical points for catalytic applications [23]. Studies on hydrogen production with Ni as active species supported on SiO_2, Al_2O_3 and Fe_2O_3 resulted in 98.4% and 83.5% conversion of acetic acid and phenol respectively [3]. Sun et al. [24] studied hydrogen production from ethanol at low temperature using Ni/Y_2O_3,Ni/La_2O_3 and Ni/Al_2O_3 catalysts for fuel-cell application. It was found that the Ni supported on Al_2O_3 exhibited lower relative activity and selectivity. The low feed conversion, low activity of Ni-Al_2O_3 catalyst were the obstacles of previous researches. This is due to coke formation behavior of alumina support during the steam reforming. In another research by Kan et al. on crude bio oil reforming using Ni-Cu-Zn-Al catalyst, the hydrogen yield and feed conversion were found to be 64% and 74%, respectively [25]. These low conversion and low hydrogen yield could be attributed to the high complexity of real bio-oil [3].

To improve the catalyst activity towards hydrogen production and phenol and acetic acid conversion, Nickel/Cobalt supported on different series of gamma-aluminum oxide and Lanthanum (III) Oxide could be applied in the reforming process. The advantage of the investigation of different series of La_2O_3 and γ-Al_2O_3 supports is to avoid the coke formation after steam reforming which is mostly favorable for γ-Al_2O_3 support. The active metal of Ni and noble-based catalysts used in hydrogen production are more energetic and effective and offer good hydrogen incomes in acetic acid and phenol steam reforming. In the present work, the Ni-Co catalyst employed has a lower cost compared to noble metals such as ruthenium (Ru), rhodium (Rh), platinum (Pt), palladium (Pd) and iridium (Ir) [26–29]. Moreover, Ni catalysts used in bio-oil and biomass gasification are highly promising. In addition to different series of La_2O_3 and γ-Al_2O_3 supports, diluting agents such as Glass, quartz, alumina, and silicon carbide (SiC) can play an important role in catalyst activity because of their good heat transfer properties [30] and difference in catalyst bed height [31]. Moreover, catalyst dilution can increase the performance of complex successive reaction schemes over undiluted catalyst [32] and can significantly reduce the overall cost of the catalyst [33]. The recent work aims to evaluate the catalytic efficiency of this low cost and high performance bimetallic Ni-Co catalyst supported on La_2O_3 and γ-Al_2O_3 for steam reforming of the mixture phenol and acetic acid with silicon carbide (SiC) as dilution agent.

2. Experimental work

2.1. Catalyst preparation

Cobalt and nickel supported on γ-Al_2O_3 and La_2O_3 were prepared using impregnation technique. The advantage of impregnation method is that it produce high concentration of active materials on the catalyst surface [34]. The procedure of this method was reported by Athanasios et al. [9]. For the first catalyst sample, 5 wt.% Ni and 5 wt.% Co as the active metals were deposited on 45 wt.% La_2O_3 and 45 wt.% γ-Al_2O_3 supports. The weight percentages of Ni and Co were btained from $Ni(NO_3)_2 \cdot 6H_2O$ (nickel nitrate hexahydrate with 98.5% purity, the 1.5% impurities are the presence of other chemical elements) and $Co(NO_3)_2 \cdot 6H_2O$ (cobalt nitrate hexahydrate with 99.999% purity) respectively as shown in Eq. (1).

$$\text{Amount of } X(g) = 0.5\, \text{gram Ni(or)Co} \times \frac{1\text{m o1N i(or)Co}}{58.7\ gr} \times \frac{1\text{m o1X}}{1\text{m o1N i(or)Co}} \times \frac{291\ grX}{1\text{m o1X}} =$$

$2.47 g$ of $(Co(NO_3)_2 \cdot 6H_2O)(or)(Ni(NO_3)_2 \cdot 6H_2O)$ (1)

0.5 g nickel, 0.5 g cobalt with 9 g supports, and 250 ml de-ionized water were mixed in order to prepare the catalyst, which consisted of 5% Ni-5% Co/90% supports. In a similar way, the weight percentages of various other catalysts were computed, as shown in Table 1.

The mixture was stirred with a magnetic stirrer and heated to 90 °C until it turned into a highly viscous paste. The paste was put into an oven at 110 °C and dried overnight. Subsequently, the catalyst was calcined at 750 °C overnight in a furnace. It was pelletized and sieved on two layers of 35 and 34 mesh to obtain particles size between 1.0 mm and 1.4 mm.

2.2. Catalyst characterization

Crystalline structure of the reduced catalyst was determine by X-ray diffraction (High Resolution X-Ray Diffractometer brand Bruker D8 Advance) using a Cu Kα radiation at 40 kV and 30 mA. The total surface area of the catalysts was measured using the multipoint BET-N_2 on a surface area analyzer (Micromeritics, Gemini 2360). Prior to the analysis, the samples were degassed at 200 °C for 2 h to remove unwanted components on the surface before outgassing the samples. A chemisorption analyzer (Micro-meritics Chemisorb 2720) was used to evaluate the reducibility of the active metals (nickel and cobalt) on the support by applying temperature-programmed reduction of hydrogen (TPR-H_2). Before the reduction, 25 mg of the catalyst was treated at 300 °C under high purity 99.99% helium with the flow rate of 20 ml/min for an hour to remove moisture and other gas impurities. The TPR-H_2 profile was obtained by ramping the temperature at 10 °C/min, 20 ml/min of 10% (vol.) H_2/Ar between 50 °C and 800 °C. The same apparatus (Micromeritics Chemisorb 2720 Chemisorption) was used for CO_2 TPD. Prior to adsorption, 35 mg of the sample was kept under 30 ml/min of argon flow rate at 600 °C for 60 min, then cooled down to 25 °C and kept under 20 ml/min of helium flow rate for 30 min so as to remove the adsorbed impurities completely. The CO_2 saturation of the catalyst was carried out for 30 min under

Table 1
Weight percentages of active species and supports for the various catalysts.

Catalysts	Nickel (wt.%)	Cobalt (wt.%)	La_2O_3 (wt.%)	γ-Al_2O_3 (wt.%)
NC/La_1Al_1	5.0	5.0	45.0	45.0
NC/La_1Al_2	5.0	5.0	29.7	60.3
NC/La_1Al_3	5.0	5.0	22.5	67.5
NC/La_1Al_4	5.0	5.0	18.0	72.0
NC/La_1Al_5	5.0	5.0	15.3	74.7