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Hydrogen Production From Steam Gasification of Palm Kernel Shell Using Sequential Impregnation Bimetallic Catalysts

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Abstract—Zeolite β supported bimetallic Fe and Ni catalysts have been prepared using sequential impregnation method and calcined at temperatures between 500-700 ºC. The catalytic activity of these catalysts in a steam gasification of palm kernel shell was tested in a fixed-bed quartz micro-reactor at 700 ºC. Both Fe and Ni active metals present in FeNi/BEA and NiFe/BEA catalysts are corresponding to Fe_2O_3 and NiO. Different calcination temperatures and different sequence in metal addition have a significant effect to the catalytic activity where FeNi/BEA (700) shows the highest hydrogen produced than other catalysts.

Keywords—bimetallic catalyst; sequential impregnation method; hydrogen production; palm kernel shell

I. INTRODUCTION

The development on biomass gasification system is an important strategy for future green technology to protect the environment from CO_2 emission. The conversion of biomass to hydrogen is the promising route since it can be used as an alternative fuel for transportation and power generation. On the other hand, if the process produces syngas, it may be utilized to produces methanol and Fisher-Tropsch oil. [1-2]. Generally, the gasification of biomass at high temperatures yield a product gas composed of CO, CO_2, H_2O, H_2, CH_4, higher hydrocarbons, tars, char, and ash [2-3]. The formation of tar and char are undesirable because the components could limit the hydrogen production and reduce the efficiency of the gasification process [4]. The nature of the tar produced is principally affected by the type of biomass, gasification process, gasifying agent and the operating conditions [3].

The application of metal based catalysts such as nickel (Ni), Cobalt (Co), Iron (Fe), Ruthenium (Ru) and Platinum (Pt) in biomass gasification is an effective method in reducing tar content. Among these catalysts, supported Rhodium (Rh) catalyst showed the best performance in steam gasification whereby catalyst having Rh loading of 1.2×10^{-4}Rh atom for each g of catalyst can convert 98-99% of the carbon in biomass to products at 873K [5]. However, Ni and Fe based catalysts are the preferred choice due to their wide availability and cheapness [4, 6-7]. Moreover, Ni and Fe based catalyst allows both methane reforming and water gas shift activity during the gasification process thus provide adjustment of the H_2/CO ratio in the product gas [8-9].

Nevertheless, the activity of the Ni based catalyst is influence by Ni loading and Ni dispersions [4]. This is due to migration of metallic particles to form larger aggregates thus, reducing the dispersion of catalyst and consequently reducing the catalyst activity [10]. Some studies have demonstrated that the nickel sintering could be limited when nickel oxide has strong interaction with promoter [9] or support [11] and have well defined structure like perovskite [10]. Dolomite and olivine which contains Fe helps stabilize Ni in the support and gives an important effect on precursor reducibility as well as catalytic properties [6]. Chaiprasert and Vitidsant [9] also verified that the addition of metallic noble metals as promoter may help to improve the metallic dispersion, decrease sintering and enhance the thermal stability.

In this study, zeolite β (BEA) supported Fe and Ni catalysts with different sequence in addition of the second metal have been proposed for steam gasification of palm kernel shell (PKS) for hydrogen production. The effects of second metal and calcination temperatures of the catalysts on the composition of gaseous product were investigated.

II. METHODOLOGY

A. Biomass Preparation

The biomass considered in this study is PKS, collected from palm plantation industry at Felda Nasaruddin, Perak. The PKS was dried at 110 ºC before they were crushed and sieved to 500 µm.

B. Catalyst Preparation

The bimetallic catalysts were prepared via a sequential impregnation method. First, BEA was calcined at 500 °C for 16 hrs. First, 5% Ni/BEA and 5% Fe/BEA catalysts were prepared [Anita et al. 2013]. The second metal was introduced in the second impregnation step using another 5 wt% of Fe and Ni metal, yielding 5%Fe5%Ni/BEA and 5%Ni5%Fe/BEA which are designated as FeNi/BEA (T) and NiFe/BEA (T). In general the catalysts are YX/BEA (T) where metal X was impregnated first followed by metal Y and T is the calcination temperature in ºC.

C. Catalyst Characterization

N_2 adsorption-desorption isotherm (Quantachrome ASAP 2000) was used to determine the surface properties of the bimetallic catalysts. Powder X-ray Diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffractometer using Cu-Kα radiation to identify the crystalline phases of FeNi/BEA and NiFe/BEA catalysts. Temperature Programmed Reduction (TPR) experiments were performed on Thermo Finnigan TPDRO 1100 to determine the reducibility of the metal present on the catalyst surface and to investigate the interaction between the metals and support.

D. Catalyst Testing

Experiments were performed in a fixed bed quartz micro reactor (15 mm i.d.) in an electric furnace. The mixture of PKS and catalyst bed was held in place by quartz wool in the tubular reactor. The steam gasification reaction was performed at 700 ºC temperature with catalyst/PKS ratio of 1:3, steam/PKS ratio of 4:1 and steam/Argon ratio of 1:6 (vol.). Two thermocouples were used to measure the temperature; one is placed at the centre of the bed in the tubular reactor and the other is placed on the outer surface of the reactor. Helium and Nitrogen were used as diluents gases and its flow was regulated by mass flow meter. Mass flow meter adjusted the gas flow in the range of 20-30 ml min^{-1}. Water is introduced by liquid pump, where they were quickly evaporated at elevated temperature and then carried to the tubular reactor by inert flow.

The outlet gas was passed through iced water condenser to substantially condense the water before it entered the gas chromatograph (GC). The gaseous product were analysed using an online gas chromatograph (VARIAN CP-3800) equipped with thermal conductivity detector (TCD) and fitted with TDX-01 column with Argon as a carrier gas. This analysis only focuses on the main product which is H_2, CH_4, CO_2 and CO gases.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

The physicochemical properties of the FeNi/BEA catalysts have been reported in our previous works [13]. Therefore, this section will only be discussed in general in order to understand better the comparison between FeNi/BEA and NiFe/BEA as well as the effect in the biomass steam gasification. Based on N_2 adsorption-desorption, the textural properties like BET surface area, pore volume and pore diameters of the catalysts prepared are summarized in Table 1 where all the bimetallic catalysts have lower surface area and smaller pore volume as compared to the bare BEA. An increase in calcinations temperature does not have a significant effect on the surface area of the bimetallic catalysts. However, the average pore diameter of the bimetallic catalysts is bigger than that of bare BEA.

Table 1. Surface properties of the catalysts

Catalysts	**BET Surface Area (m^2 g^{-1})**	**Pore Volume (cm^3 g^{-1})**	**Average Pore Diameter (nm)**
BEA (500)	529	0.15	4.30
FeNi/BEA (500)	445	0.12	5.71
NiFe/BEA (500)	447	0.13	5.88
FeNi/BEA (600)	441	0.12	5.83
NiFe/BEA (600)	454	0.13	5.61
FeNi/BEA (700)	449	0.09	5.34
NiFe/BEA (700)	434	0.09	6.23

Fig. 1 shows the diffraction patterns displayed by FeNi/BEA and NiFe/BEA catalysts. The presence of both Ni and Fe were detected in the prepared catalysts with the diffraction peaks corresponding to NiO phase and α-Fe_2O_3 phase, respectively. The peaks for NiO phase are represented by the appearance of Ni(111) and Ni(200) planes at the $2\theta = 37.3^{\circ}$ and 43.3° while the diffraction peaks corresponding to α-Fe_2O_3 phase are represented with the appearance of Fe(104) and Fe(110) planes positioned at the $2\theta = 33.1^{\circ}$ and 35.6°. These planes are in agreement with data reported in the JCPDS card and those reported in previous studies [14-15].

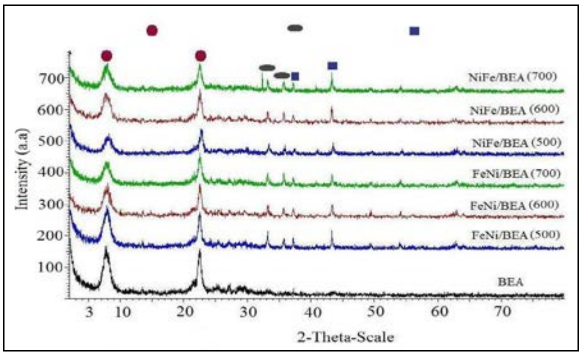


Fig. 1. The diffraction patterns of the bimetallic catalysts

Furthermore, presence of NiO and α-Fe_2O_3 phase in the bimetallic catalysts affects the diffraction peaks of BEA where the diffraction peaks are shifted to slightly higher 2θ value and the intensity is reduced. This may be due to the formation of interacted species between Fe and Ni with Al_2O_3 or SiO_2 in BEA. However, nickel aluminate ($NiAl_2O_4$) and iron aluminate ($FeAl_2O_4$) phase were not present, which could be due to lack of crystallinity as formerly observed by by Salagre *et al.* [16].

The variation in the TPR profile of FeNi/BEA and NiFe/BEA catalysts (Fig. 2) shows the combination of nickel and iron phases' reduction. The reduction of free NiO was observed at 400 - 500 ºC [17]. On the other hand, the reductions of nickel and iron phase at 500 - 800 ºC region were overlapped into a broad peak, which suggests the stabilization of Fe^{3+} and Ni^{2+} ions in the lattice. The reduction process transforms Fe_2O_3, $FeAl_2O_4$ and $NiAl_2O_4$ [17-18].

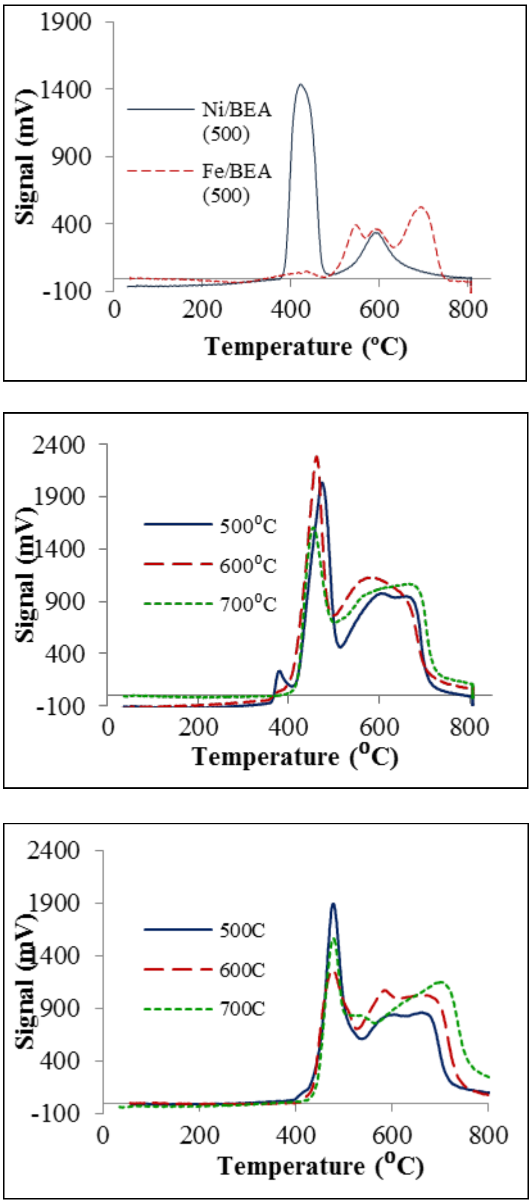


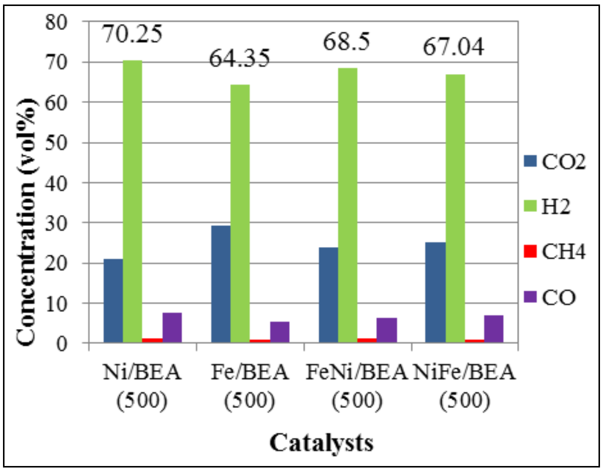
Fig. 2. TPR profile of (a) Ni/BEA and Fe/BEA as a reference (b) FeNi/BEA and (c) NiFe/BEA at different calcination temperatures

The presence of free Fe_2O_3 is noticeable with a small peak at 380 °C from TPR profile of FeNi/BEA (500). However, due to strong interaction of Fe and Ni at high temperature, the reduction peak of free Fe_2O_3 is significantly intensified and disappeared. This type of oxide is easily reduced and its existence can cause several difficulties during reaction such as sintering and carbon deposition on the catalyst surface which will lead to catalyst deactivation [19]. Apart from that, the reduction peak associated to the reduction of free NiO to Ni^o shifted towards lower temperature as the calcination temperatures increases. While, the reduction peak represents the reduction of several phases were shifted to higher temperature.

In the case of NiFe/BEA catalysts (Fig. 2c), the reduction peak representing reduction of several phases are divided into two peaks particularly after the catalyst was calcined at 700 °C. For NiFe/BEA (700), the peak represent the reduction of Fe^{3+} is shifted to lower temperature while the peak having strong interaction with support ($NiAl_2O_4$ and $FeAl_2O_4$) is shifted to higher temperature. This indicates that addition of Ni as a second metal in this catalyst results in higher reducibility of Fe_2O_3 phase where it is reducible at lower temperature and active for the reaction. It is also observed that the reduction temperature of free NiO does not change even though the calcinations temperature of the catalyst was increased; however the intensity of the reduction peak is different.

B. Catalytic Steam Gasification

Fig. 3 shows the concentration of gases evolved from the steam gasification of PKS in the presence of BEA supported bimetallic catalysts. The results on monometallic Ni/BEA and Fe/BEA catalysts from previous work [12] are also reported for comparison. Addition of Fe to the Ni/BEA (500) to form FeNi/BEA (500) resulted in slight decrease in H_2 and CO gas produced, which in turn increases the concentration of CO_2 while there is no significant change in the CH_4 evolved (Fig. 3a). This indicates that FeNi/BEA (500) is slightly less reactive in steam gasification, thus promoting combustion of PKS to CO_2. This could be due to the presence of both fixed nickel oxide ($NiAl_2O_4$) and fixed iron oxide ($FeAl_2O_4$) as seen in Fig. 4b which suppresses the reduction of Fe_2O_3 and NiO with different state of interaction with BEA. Furthermore, presence of ‘free iron oxide’ at reduction temperatures between 380 - 400 °C in the catalyst could also be the reason in low catalytic activity of FeNi/BEA (500) catalyst since it promotes the formation of CO_2 as well as loss of active phase during the reaction [8, 19]



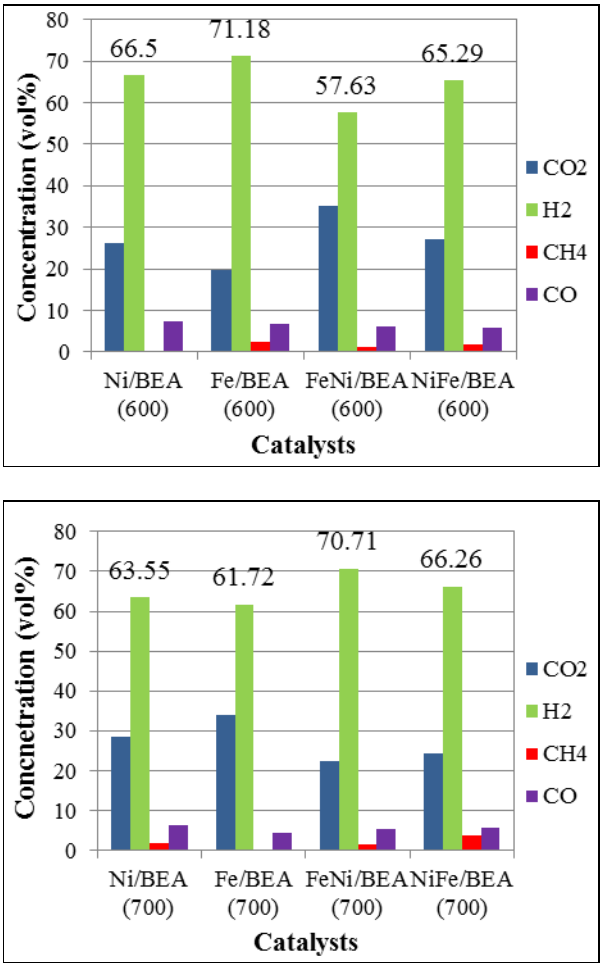


Fig. 3. Performance of the catalysts calcined at (a) 500 ºC (b) 600 ºC (c) 700 ºC in steam gasification of PKS

Addition of Ni to Fe/BEA (500) to form NiFe/BEA (500) on the other hand, enhances the steam methane reforming whereby it leads to an improvement in the concentration of H_2 produced and reduction of CO_2 concentration in the product gas although there is slight increase in CO concentration. This could be due to reaction between CH_4 and H_2O in a 1:1 molar ratio on the catalyst active site to form a 1:3 molar ratio of CO and H_2 during the steam methane reforming [2-3]. High performance of this catalyst may be attributed to bigger reduction peak at 500-700 ºC in H_2-TPR profile as compared to Fe/BEA (500) whereby this peak is attributed to reduction of Fe_2O_3. Bigger reduction peak means more H_2 consumption which means more Fe_2O_3 available within the catalyst system thus, the catalyst becomes more active for steam gasification due to availability of more active sites for the reaction to take place [20].

Addition of Fe to Ni/BEA (600) to form FeNi/BEA (600) follows the same trend as the catalyst calcined at 500 ºC whereby it becomes no longer effective to promote steam gasification of PKS to produce H_2. Instead, the FeNi/BEA (600) promotes oxidation of CO or combustion of PKS which is shown by an increase in CO_2 concentration. FeNi/BEA (600) also promotes the formation of CH_4, presumable via reduction of CO as CH_4 concentration slightly increases while CO concentration slightly decreases. This may be due to insufficient presence of steam content during the reaction and presence of metallic Fe from over reduction of Fe_2O_3 which resulted in reduction of CO with H_2 to produce CH_4 [21]. Indeed, Chaiprasert and Vitidsant [22] have studied the effect of steam during the gasification of biomass and found that increasing of steam feed resulted in higher H_2 evolved, lower CO_2 formation and slightly decrease in CH_4 because of water-gas shift reaction and methane reforming.

Furthermore, addition of Ni to Fe/BEA (600) to from NiFe/BEA (600) resulted in reduction of H_2, CO, and CH_4, evolved. This trend is similar as FeNi/BEA (600) whereby the concentration of CO_2 increases indicating that NiFe/BEA (600) is less reactive in steam gasification, thus promoting PKS to undergo oxidation of CO to produce more $CO_{2.}$

Addition of Fe to Ni/BEA (700) to form FeNi/BEA (700) in contrast, exhibited higher concentration of H_2. A slight decrease in CO concentration indicates that FeNi/BEA (700) promotes the water gas shift reaction even though slight decrease in concentration of CO_2 was observed. However, there is no significant difference in the concentration of CH_4 evolved. As stated in the H_2-TPR analysis, the addition of Fe as the second metal and calcined at 700 ºC significantly improves the reducibility of NiO phase by reducing at low temperature. As a result, more active metals react with PKS to produce H_2 gas and facilitate the water gas shift reaction. Therefore, this indicates that FeNi/BEA (700) is active in steam gasification reaction; hence it is able to prevent the PKS from undergoing oxidation. The results are consistent with the work reported by Chaipraset and Vitidsant [9] whereby the presence of Fe as the second metal in Ni based catalyst enhances the water-gas shift reaction and amplified the H_2 production.

Addition of Ni to Fe/BEA (700) to form NiFe/BEA (700) also results in an increase in concentration of H_2 and reduction of CO_2 in the product gas. A slight increase in CO concentration indicates that NiFe/BEA (700) follows the same trend as the NiFe/BEA (500) catalyst whereby it facilitates the reduction of Fe^{3+} and enhances the steam methane reforming. However, high concentration of CH_4 was observed may be due to NiFe/BEA (700) also promotes the formation of CH_4 through methanation. This possibly attributed to majority of Ni metals on the surface of the catalyst whereby Ni is the first component to be reduced at 450 ºC as reported in H_2-TPR. Hence, this favours the methane steam reforming and methanation reaction on Ni surface [8] as opposed to water gas shift reaction on Fe surfaces [9].

The variations in the trends indicate that the concentration of H_2 gas for FeNi/BEA decreases in the order of calcination temperatures: FeNi/BEA (700) > FeNi/BEA (500) >

FeNi/BEA (600). This is because doping of Fe into Ni/BEA at different calcination temperatures resulted in slightly higher surface area for FeNi/BEA (700) followed by FeNi/BEA (500) and FeNi/BEA (600) as observed in N_2 adsorption-desorption. According to Chaipraset and Vitidsant [9], the catalyst with high surface area can provide large contact area for reactants and consequently enhance the reaction activity. However, FeNi/BEA (700) has less reducibility as compared to FeNi/BEA (500) and FeNi/BEA (600).

The order of the H_2 formation for NiFe/BEA catalysts is NiFe/BEA (500) > NiFe/BEA (700) > NiFe/BEA (600), whereby the catalytic activity decreases with increasing in calcination temperatures. This behaviour is expected since NiFe/BEA (500) shows higher reducibility as compared to NiFe/BEA (600) and NiFe/BEA (700). This can be explained by integration of Ni and Fe in the BEA structure as observed in TPR analysis. The strong interaction of Ni and Fe at higher calcination temperatures (700) causes the stabilization of Fe^{3+} and Ni^{2+} ions in the lattice resulting in less reduction of metals. It is notable that the BET surface area of NiFe/BEA catalysts is in order NiFe/BEA (600) > NiFe/BEA (500) > NiFe/BEA (700). Even though calcination at 600 ºC leads to a bigger surface area, NiFe/BEA (500) still shows a higher catalytic activity due to its reducibility at lower temperature.

IV. CONCLUSION

It can be inferred that different sequence of Fe and Ni as a second metal in bimetallic catalysts resulted in deviation in the catalyst properties and interaction between the active metals with support as well as the catalytic activity. Furthermore, both Fe and Ni are active for the steam gasification of PKS when they act as a second metal if the precursors were calcined at a suitable calcination temperature. The highest concentration of H_2 evolvement in the steam gasification of PKS achieved in the presence of FeNi/BEA (700) and NiFe/BEA (500). Incorporation of Fe as the second metal in the bimetallic catalyst and calcined at 700 ºC improves the reducibility of NiO phase and enhances the water-gas shift reaction. While addition of Ni as the second metal facilitates the reduction of Fe_2O_3 phase and exhibits steam methane reforming. Hence, the second metal plays an important role and may act as a promoter to amplify the steam gasification reaction.

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