Hydrogen production by steam reforming of bio-oil aqueous fraction over Co-Fe/ZSM-5

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Abstract: A series of Co-Fe/ZSM-5 catalysts were prepared by impregnation method and their catalytic performance under steam reforming bio-oil aqueous fraction (SRBAF). The as-prepared catalysts were characterized by XRD, BET, and SEM. The characterization results revealed the Co-Fe alloy phase was formed in Co\textsubscript{0.5}Fe\textsubscript{0.5}/ZSM-5 catalyst, and this catalyst exhibited unique pore volume (0.28 cm\textsuperscript{3}/g) and pore size (8.4 nm). The results of experiment demonstrated the addition of Fe species could significantly increase C conversion and H\textsubscript{2} yield, and the formation of Co-Fe alloy effectively inhibited methanation reaction and improved water-gas shift (WGS) reaction. The highest H\textsubscript{2} yield (81\%) and C conversion (85\%) was obtained at the following reaction conditions: 2.5 g of Co\textsubscript{0.5}Fe\textsubscript{0.5}/Z catalyst, T= 700 °C, S/C = 10-14, feed flow rate was 10.0 g\textsubscript{bio-oil}/h, N\textsubscript{2} flow rate was 0.16 L/min.

1. Introduction

A general attention on the world energy issue stresses the importance of fostering the energy production from nontraditional sources. The producing energy through sustainable processes is always focused on hydrogen as an energy carrier. Since hydrogen energy has been regarded as an ideal energy on account of its high efficiency, clean and environmental pollution-free. Last few decades, hydrogen production via the steam reforming bio-oil aqueous fraction (SRBAF) has gained widely attention.

Bio-oil is the liquid produced by pyrolysis and gasification of biomass, which has been considered as extensive reserves, carbon-neutral and eco-friendly renewable sources [1-7]. Bio-oil contains various organic compounds and can be separated into two fractions by adding water [2, 5, 6]. The fraction that is not soluble in water derived from lignin has features similar to those of diesel oil and possesses high economic value. The other fraction is water-soluble and composed of acids, aldehydes, ketones, etc. This fraction lacks specific applications and is always discarded. Consequently, SRBAF to produce hydrogen is one possible application for the aqueous fraction of bio-oil [1-4]. Resende et al. [2] performed a thermodynamic study for SRBAF to obtain the most favorable operating conditions, such as suitable steam/carbon molar ratio (S/C) and operating temperature.

However, for the sake of obtain the higher C conversion and H\textsubscript{2} yield, the way of employing excellent catalyst becomes predominant during the experimental process of ARBAF. Various noble- and non-noble- metal catalysts have been widely applied into this process [3-12]. Ru-based and Ni-based catalysts, as the representative of noble-metal and non-noble-metal catalysts respectively, exhibited outstanding C conversion and H\textsubscript{2} yield, due to their unique ability for breaking C-C, C-H,
and C-O bonds in bio-oil aqueous fraction. Nevertheless, the high-cost for Ru-based catalyst makes it difficult to be employed in industrial application. Additionally, Ni-based catalyst is easily inactive caused by the serious sintering and coking, although it has lower cost. According to the literatures [13-15], the Co-based catalyst is considered as another promising catalyst for the steam reforming ethanol, which is regarded as one of representative bio-oil models. This is attributed to supported Co catalysts could effectively cut off the C-C bonds and inhibit carbon deposition. Meanwhile, the supports are also played an important role during this process, which is because of the support could prevent the sintering of active metal species and affect the reaction paths under high temperature and hydrothermal condition. Among them, the ZSM-5 attracted more attentions in the field of steam reforming due to its high surface area, unique mesoporous structure properties and thermal and mechanical stability [16-18]. Besides carrier material, the dopants (other metal promoters) also play an important role for catalytic performance in steam reforming. Addition of several transition metals and rare earth metals for instance Mo, La, Mg, Ca, Sr, Ba, and Fe forming bimetallic catalyst has been acted as promoters for catalysts in the reforming reaction. Iron used as a promoter exhibit excellent performance for enhancing the catalytic performance [19, 20]. This is attributed to iron oxide enhanced the mobile oxygen contented in catalyst to improve the gasification of coking and formed Fe-content alloy to inhibit the active metal sinter.

In the paper, we investigated the catalytic performance of Co-Fe bimetallic supported ZSM-5 during SRBAF in fixed bed reactor. A series of bimetallic Co-Fe loading on ZSM-5 catalysts via impregnation method and they were characterized by X-ray diffraction (XRD), N\textsubscript{2} adsorption-desorption, scanning electron microscope SEM. In addition, the effects of catalysts, reaction temperatures, times-on-steam and steam/carbon (S/C) ratios on the C conversion and H\textsubscript{2} yield were evaluated in this study.

2. Experimental

2.1 Catalysts preparation and characterization

A series of Co-Fe bimetallic catalysts contained different mass ratio of Co:Fe (which can be labelled as C\textsubscript{x}F\textsubscript{y}/Z, C and F stand for Co and Fe, respectively, x and y were the mass fraction of Co and Fe, where x=0,0.25,0.5,0.75,1 and x+y=1; Z was representative of ZSM-5) supported on ZSM-5 (Si/Al ratio = 1) were prepared by impregnation method. The Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O and Co(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O as Fe and Co precursor, respectively. Typically, a set amount of nitrate precursor was dissolved into absolute ethyl alcohol to form solution and then 5.00 g of ZSM-5 (purchased Fudan University) was added into this solution under intense stir at 80 °C for 4 h to produce slurry. After the slurry was placed at indoor temperature condition for 24 h and then evaporated residual alcohol by using rotary evaporators. The obtained solid was dried at 110 °C for 12 h and then crushed, sieved, calcined at 600 °C for 4 h with a ramp of 2 °C/min. After these processes the fresh catalysts were prepared. The active metal species content was set at about 8 wt.% in every catalyst.

2.2 Catalysts characterizations

X-ray diffraction (XRD) analysis was measured on Shimadu AS-6000. The data was obtained at 2θ = 10-70° with a step width of 0.02° by using Cu K\textalpha radiation (λ= 0.154 nm) operated at 40 mA and 45 kV. Brunauer-Emmett-Teller (BET) surface area, pore volume and pore-size distribution of samples were determined from N\textsubscript{2} adsorption-desorption isotherms at liquid nitrogen temperature in a Micromeritics ASAP 2020 apparatus. Prior to the analysis, the samples were dried for 2 h at 200 °C. Scanning electron microscope (SEM) was performed on Hitachi S-4800N to determine the morphologies of fresh catalysts.

2.3 Experimental apparatus and processes

The SRBAF test were carried out in fixed-bed reactor, as reported in our previous papers [5,6]. The bio-oil aqueous fraction was obtained as describe in reference [3]. Typically, catalyst (2.5 g) was
placed in central section of the reactor. Prior to reaction, the calcined catalyst was reduced at 600 °C for 2 h under H2/N2 (10%/90%, v/v, flow rate: 0.16 L/min) flow. The data about C conversion, H2 yield and the selectivity to C-contained product were calculated according to the equations in references [3-7].

3. Results and discussion

3.1 XRD characterization
As compared, the reduced catalysts after reaction under H2/N2 (10 vol.% of H2) flow at 600 °C for 2 h and fresh catalysts were all detected by XRD and the results were shown in Fig. 1. The diffraction peaks at 2θ = 31.25°, 36.82°, 44.76°, 59.30° and 65.19° for all contained Co and Fe species samples in Fig. 1a were attributed to the overlapping of characteristic peaks that ascribed to Fe2O3 and Co3O4 phases. The other peaks (Fig. 1a) were assigned to the characteristic peaks of ZSM-5. It is worth mentioning that the intensities of characteristic peaks of ZSM-5 were weakened and even disappeared after the induction of cobalt and iron species, which mainly due to cobalt and iron oxides interacted with ZSM-5 lead to cover the surface of ZSM-5 or form some amorphous compounds beyond the detection limitation of XRD. After reduction, the characteristic peaks of ZSM-5 in Fig. 1b had no obvious changes, implying ZSM-5 possessed unique hydrothermal stability. Obviously, the peaks of Fe2O3 and Co3O4 phases were disappeared and there was a weak and broad peak at about 44° that attributed to Co-Fe alloy phase arose in bimetallic catalysts. This demonstrated that the Co and Fe species effectively supported on ZSM-5 and the Co-Fe alloy phase could be easily formed during reaction condition, which was beneficial for improving the catalytic performance.

3.2 N2 adsorption-desorption
Table 1 illustrates catalysts textural properties. The surface area was calculated based on BET method and the pore volume and size were obtained according to the BJH desorption isotherm. The pore sizes for all samples were ranged from 2-10 nm, suggesting these samples all had mesoporous structure. Adding Co and/or Fe oxides into ZSM-5, the surface area of ZSM-5 decreased considerably, while its pore volume and size slightly increased. In addition, the surface area for bimetallic catalysts was reduced with the increasing of iron content, from 341.0 m²/g for C0.75F0.25/Z reduced to 241.9 m²/g C0.25F0.75/Z. The pore volume and size of all catalysts showed a volcano value with the decrease of Co/Fe mass ratio. For C0.5F0.5/Z catalyst, it had the highest pore volume (0.28 cm³/g) and pore size (8.4 nm). The decrease of surface area with the addition of Co and Fe species mainly attributed to the cobalt and iron oxides deposited on the surface of ZSM-5 and wall of pore. The optimum of pore volume and size could lead to C0.5F0.5/Z catalyst exhibited excellent catalytic performance.

![Fig. 1 The XRD patterns of all fresh and reduced catalysts](image-url)
Table 1 - Textural properties of all developed catalysts

| Samples          | Surface Area (m²/g) | Pore Volume (cm³/g) | Pore Size (nm) |
|------------------|---------------------|---------------------|----------------|
| Z                | 448.6               | 0.11                | 2.5            |
| C/Z              | 431.3               | 0.16                | 3.4            |
| C₀.₇₅Fe₀.₂₅/Z    | 341.0               | 0.22                | 7.7            |
| C₀.₅Fe₀.₅/Z      | 326.9               | 0.28                | 8.4            |
| C₀.₂₅Fe₀.₇₅/Z    | 241.9               | 0.21                | 5.3            |
| F/Z              | 201.0               | 0.23                | 4.8            |

### 3.3 SEM characterization

The surface morphologies for selected samples were measured by SEM and the images were presented in Fig. 2. It can be found that the ZSM-5’s accumulation state was cube form and it contained a large number of mesoporous, as displayed in Fig. 2(a) and 2(b). After introduction of Co and Fe species, the surface of ZSM-5 became rough and had some small particles (Fig. 2(c)), implying some amount of cobalt and iron oxides supported on ZSM-5. After reduction, there was some surface was exposed for C₀.₅F₀.₅/Z catalyst, which may due to the formation of Co-Fe alloy phase according to XRD results.

### 3.4 The effect of various catalysts on SRBAF

The effect of various catalysts on SRBAF reaction was conducted under the following condition: 2.5 g of catalyst, T = 700 °C, S/C ratio = 10, feed flow rate was 10.0 g_bio-oil/h, N₂ flow rate was 0.16 L/min. Fig. 3 presented the C conversion (C_conv.), H₂ yield (y) and selectivity to C-contained products. The C_conv. and y on C/Z catalyst were slightly higher than those on F/Z catalyst, suggesting the Co-based catalyst’s performance for breaking C-C, C-H, and C-O bonds was superior to Fe-based catalyst. While the selectivity to CO and CH₄ for F/Z catalyst was significantly lower than C/Z catalyst, implying Fe-based catalyst was positive to improve water-gas shift reaction (WGS, a major side-reaction to increase H₂ yield) and CH₄ steam reforming reaction (the by-product CH₄ was regarded as a disgusting product for enhancing H₂ production). Consequently, the selectivity to CH₄ was reduced with the increase of Fe addition for bimetallic catalysts. Nevertheless, the C₀.₅F₀.₅/Z catalyst exhibited the highest C_conv. (85%) and y (81%), as well as the lowest CO selectivity (10%). This was attributed the formed Co-Fe alloy phase (as demonstrated by XRD) effectively enhanced the ability for breaking chemical bonds of reactant and WGS reaction. Therefore, C₀.₅F₀.₅/Z catalyst had the most excellent catalytic performance than other catalysts.

Fig. 2. SEM images of ZSM-5 (a) and (b), calcined (c) and (d) reduced C₀.₅F₀.₅/Z.
3.5 The effect of reaction temperatures on SRBAF

The effect of reaction temperatures on SRBAF reaction was conducted under the following condition: 2.5 g of $C_{0.5}F_{0.5}/Z$ catalyst, S/C ratio = 10, feed flow rate was 10.0 g$_{bio-oil}$/h, N$_2$ flow rate was 0.16 L/min. Fig. 4 displayed the influence of reaction temperatures on conversion, yield and selectivity. It can be found that the C conv. increased with the increase of temperature, while the selectivity to CH$_4$ exhibited an opposite tendency, which mainly because higher temperature was beneficial to break chemical bonds of reactant (which was regarded as an endothermic reaction) and suppressed the methanation reaction (which was a exothermic reaction). While the H$_2$ yield was not as our expectation obviously raised with the decreasing of CH$_4$ selectivity, due to WGS reaction was reversible reaction and higher temperature was negative for WGS reaction. Consequently, the higher C conversion (85%) and highest H$_2$ yield (81%) were obtained over $C_{0.5}F_{0.5}/Z$ catalyst at 700 °C.

3.6 The effect of S/C ratios on SRBAF

The influence of S/C ratio on SRBAF reaction was performed under the following condition: 2.5 g of $C_{0.5}F_{0.5}/Z$ catalyst, T= 700 °C, feed flow rate was 10.0 g$_{bio-oil}$/h, N$_2$ flow rate was 0.16 L/min. Fig. 5
showed the changes of C conversion, H\textsubscript{2} yield and products selectivity with the increase of S/C ratios. S/C ratio mainly affected the WGS reaction and the gasification of coke deposited on catalyst surface during SRBAF process. As a consequence, the H\textsubscript{2} yield exhibited an obvious increase with the S/C ratios at the range of 2 - 10, along with the increase of C conversion. The selectivity to CO and CH\textsubscript{4} displayed monotone decreasing tendency and that to CO\textsubscript{2} showed only increase during the whole range of 2 - 22. At S/C ratio < 10, the H\textsubscript{2} yield increase rapidly was attributed to the controlling step for improving WGS reaction. When S/C > 10 the effect of S/C on H\textsubscript{2} yield became un-predominant, while the selectivity to CO\textsubscript{2} kept increase rate owing to the gasification reaction of coke became predominant. Considering higher S/C ratio would lead to consume more energy to gasify water, the optimal S/C ratio was 10 - 14.

![Graph showing the effect of S/C ratios on SRBAF](image)

**Fig. 5** The effect of S/C ratios on SRBAF

4. Conclusions

As a summary, Co-Fe/ZSM-5 bimetallic catalysts exhibited promising catalytic performance for steam reforming bio-oil aqueous fraction to produce hydrogen. Especially for Co\textsubscript{0.5}Fe\textsubscript{0.5}/ZSM-5 catalyst, owing to it had unique pore volume (0.28 cm\textsuperscript{3}/g) and pore size (8.4 nm) and the formation of Co-Fe alloy phase. The highest H\textsubscript{2} yield (81\%) and C conversion (85\%) was obtained at the following reaction conditions: 2.5 g of Co\textsubscript{0.5}Fe\textsubscript{0.5}/Z catalyst, T= 700 °C, S/C = 10 - 14., feed flow rate was 10.0 g\textsubscript{bio-oil}/h, N\textsubscript{2} flow rate was 0.16 L/min.

Acknowledgments

The authors thank the National Natural Science Foundation of China (21376007) and National Science and Technology Support Project of China (2014BAD02B03) for the financial support

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