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Short Communication

NiFe/γ-Al_2O_3: A universal catalyst for the hydrodeoxygenation of bio-oil and its model compounds

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ABSTRACT

NiFe bimetallic catalyst shows an excellent activity and selectivity for the hydrodeoxygenation (HDO) of three typical model compounds of bio-oil. The conversion of furfuryl alcohol, benzene alcohol and ethyl oenanthate is 100, 95.48 and 97.89% at 400 °C and the yield to 2-methylfuran, toluene and heptane is 98.85, 93.49 and 96.11% at 0.1 ml/min flow speed and atmospheric pressure. It indicates that the major reaction pathway is the cleavage of C–O rather than C–C. After the catalytic HDO of bio-oil over NiFe/Al_2O_3 catalyst, the heating value changes from 37.8 to 43.9 MJ/kg, the pH changes from 6.65 to 7.50.

1. Introduction

Due to the consumption of fossil sources and increasing of energy requirements, the search for the alternative energy has caused economic, political and academic concerns [1]. Different from other alternative energy (solar, wind and nuclear energy), biomass, which includes lignocellulose and algae, is the only resource for the production of fuels, chemicals and hydrocarbons. Bio-oil, obtained from biomass by fast pyrolysis or high-pressure liquidation under inert gas atmosphere, has an irresistible trend applied for transportation fuel economically and technologically. The bio-oil components are complex, containing mainly oxygenated compounds as furans, ketones, carboxylic acids, ethers, esters and alcohols [2,3]. Due to the high content of oxygen, bio-oil has a low heating value and high viscosity, limiting the application to transportation fuels [4].

The catalytic hydrodeoxygenation (HDO) is one of the efficient ways to remove oxygen in upgrading bio-oil to fuel. The noble metal catalysts, such as supported Pt, Pd, Rh, Ru [5–10], have high activities. The sulfided NiMo and CoMo, as the industrial hydrodesulfurization catalysts, have been investigated in HDO reactions. However, they may cause the contamination of bio-oil. Therefore, reduced supported transition metals catalysts, such as Ni, Mo, Co, Fe, Cu [11–14], have attracted much attention due to their good catalytic performances. Recent studies have shown that the bimetallic catalysts always have superior catalytic properties than single metallic catalysts [15–17]. The study by Heeres et al. found that 16 *wt*%–2 *wt*% NiCu/δ-Al_2O_3 had the best activity for HDO of anisole and the hydrotreatment products were cyclohexane and benzene via demethoxy reaction [15]. The study by Resasco et al. showed the primary products of furfural hydrogenation were furfuryl alcohol and furan over monometal Ni/SiO_2 catalyst while 2-methylfuran over NiFe/SiO_2 [18]. Wang et al. used non-sulfided Ni/HZSM-5 to catalyze phenol and got a high conversion (91.8%) [19]. The study by Tomishige et al. showed that Ni–Pd/SiO_2 (Ni/Pd = 7) performed a good yield to 2, 5-bis (hydroxymethyl) tetrahydrofuran (96%) for the hydrogenation of 5-hydroxylmethyl furfural, which was super to Raney Ni and Pd/C [20].

Due to the complex of bio-oil, the catalysts used in HDO must be universal for all of model compounds. To the best of our knowledge, very few studies have been conducted on bimetallic catalysts used in different model compounds under the same reaction conditions. In this work, the catalytic activity of NiFe bimetallic catalyst was evaluated by the HDO of furfuryl alcohol, benzyl alcohol (model compounds of lignocellulose) and ethyl oenanthate (model of algae and proper carbon chain length for jet fuel). Our study shows that NiFe performs excellent catalytic activities on dehydration rather than decarbonation or decarboxylation. Finally, higher heating value and pH fuel are obtained by catalytic HDO of bio-oil, which confirm the universality of NiFe catalyst.

2. Experimental

2.1. Catalyst synthesis and characterizations

The NiFe/Al_2O_3 catalyst was prepared by incipient wetness co-impregnation, using an aqueous solution (20 ml de-iron water) containing both metal precursors, $Ni(NO_3)_2 \cdot 6H_2O$ (AR, Aladdin) and

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$Fe(NO_3)_3 \cdot 9H_2O$ (AR, Aladdin). Then, the aqueous solution was added to the γ-Al_2O_3 support (20–40 mesh, Wuke Biochemical Co. Ltd).The loading of Ni was kept constant at 15.0 wt. %, while the Fe loading was 5.0 wt. %. After impregnation, the catalyst was first dried overnight at 80 °C and then calcined for 4 h at 600 °C in the muffle furnace.

Several physical techniques were employed to characterize the structure of the NiFe/Al_2O_3 catalysts. X-ray powder diffraction pattern (XRD) for the sample was collected on an X'Pert PRO X-ray Diffract meter (PANalytical), using Cu Ka radiation generated at 40 kV and 40 mA. The scans covered the range from 10 to 80°. Morphology and size of the Ni–Fe clusters were characterized by transmission electron microscopy (TEM, Tecnai G2 F30).

2.2. Catalytic activity measurements

The vapor-phase conversions of furfuryl alcohol, benzyl alcohol, ethyl oenanthate and bio-oil over the Ni–Fe catalyst were evaluated in a tubular quartz reactor, which was heated by electricity. In each run, a catalyst sample (size range: 40–60 mesh, 5 ml) was placed at the center of the reactor tube (diameter = 7 mm, length = 400 mm) between two layers of quartz wool and pre-reduced in H_2 flow (40 ml/min, 99.999%,Shanghai) for 3 h at 400 °C. After reduction, a 0.03 ml/min flow of liquid (benzyl alcohol was pure, furfuryl alcohol was diluted 10 times by benzene, ethyl oenanthate was diluted 10 times by n-decane) was preheated at 230 °C and purged onto the catalyst bed. The liquid feed was fed continuously from a peristaltic pump (Baoding Lead Fluid Tech. Co. Ltd.) and vaporized into a H_2 stream of 40 ml/min. The reaction products were analyzed by GC out-line (Zhejiang Fuli Analytical Instrument Co. Ltd., 9790), using a PEG-20 M capillary column and a FID detector. The product conversion for each product was calculated as follows:

$$\text{Conversion} = \frac{\text{mol of the inget feed} - \text{mol of the outget feed}}{\text{mol of the inget feed}} \times 100\%$$

3. Results

3.1. Catalyst characterizations

The physical properties of Al_2O_3 and oxidized and reduced NiFe/Al_2O_3 were shown in Table 1. The specific surface area of the γ-Al_2O_3 support and NiFe/Al_2O_3 determined by Barrett–Joyner–Halenda adsorption method (ASAP 2020, America) is 245, 184 and186 m^2/g. H_2 consumption, determined from H_2-TPR (HIDEN QIC-20), was only 1.4 mmol $gCat^{-1}$. Based on TEM observation, the average particle size for NiFe particles was 4.8 nm (Fig. 1). It is seen that the uniform NiFe particles were well dispersed on the support. The zoom-in image was depicted in Fig. 1 (b). The energy spectrum analysis of one randomly chosen particle (red circle) showed that it was composed with 16 wt% Ni and 2 wt% Fe, which is nicely agreement with the experimental loading ratio. But a little aggregation of metals was observed for the used catalyst from TEM observations (Fig. 1 c, d). Due to high dispersion, there were no peaks of Ni and NiFe for fresh catalyst [21] (Fig. 2), while for used catalyst, the peaks of Ni and NiFe alloy were detected, which was agree with TEM.

Table 1
Physical properties of support and catalysts.

Support and catalyst	Metal loadings (mmol $gCat^{-1}$)		H_2 consumption from H_2-TPR (mmol $gCat^{-1}$)	Diameter (nm)	BET (m^2/g)
	Ni	Fe			
Support	–	–	–	–	245
Oxidized 15Ni–5Fe	2	0.625	1.40	–	184
Reduced 15Ni–5Fe	2.10	0.656	–	4.8	186

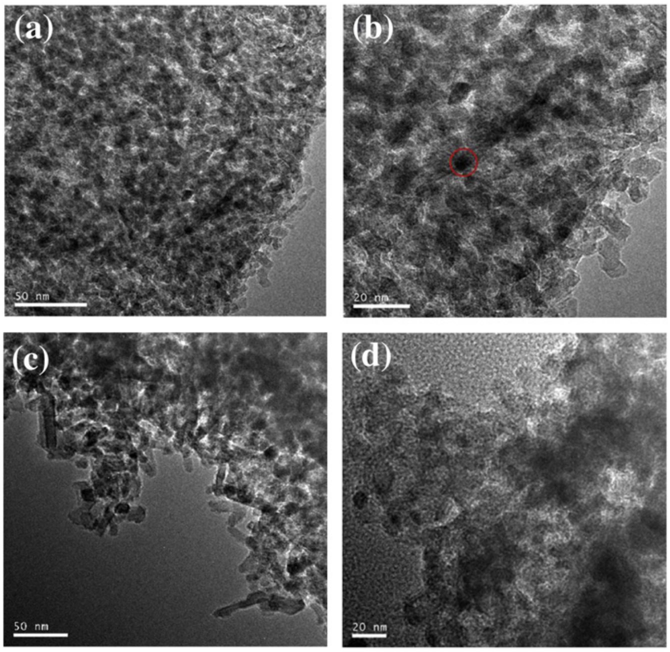


Fig. 1. TEM images of fresh (a, b) and used (c, d) catalyst.

3.2. HDO of model systems over NiFe/γ-Al_2O_3 catalyst

In this study, three different model systems were chosen to evaluate the HDO over NiFe/γ-Al_2O_3 catalyst. These supports (γ-Al_2O_3, active carbon) alone do not catalyze three substrates. The conversions over NiFe catalyst were higher than monometal ones probably due to the synergistic effect of bimetallic active phases [21]. Through the optimization of Ni/Fe ratio and loadings of metals supported on γ-Al_2O_3, we found Ni/Fe = 3 and the loading of 15% Ni – 5% Fe were the optimum values. The effect of temperature on conversions and yields of these systems were shown in Fig. 3. At 300 °C, the conversion of both furfuryl alcohol and benzyl alcohol was more than 85%, while only about 15% for ethyl oenanthate. Therefore, the influence of temperature on the conversion and yield of ethyl oenanthate is much bigger than furfuryl alcohol and benzyl alcohol. The conversion of furfuryl alcohol was all above 90% when the temperature is

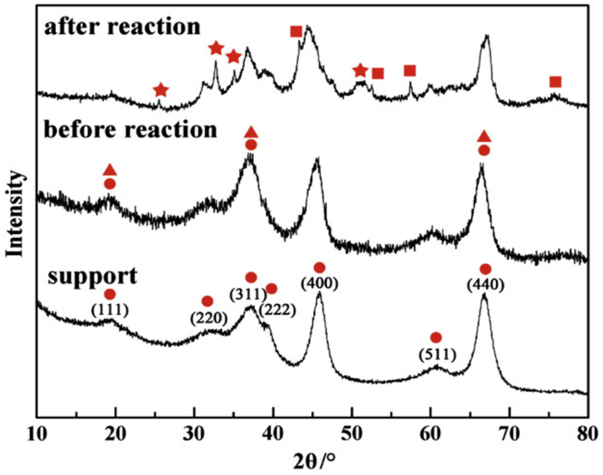


Fig. 2. XRD characterizations of support, fresh catalyst and used catalyst. ● —— γ-Al_2O_3 ▲ —— $NiAl_2O_4$ ■ —— Ni ★ —— NiFe alloy

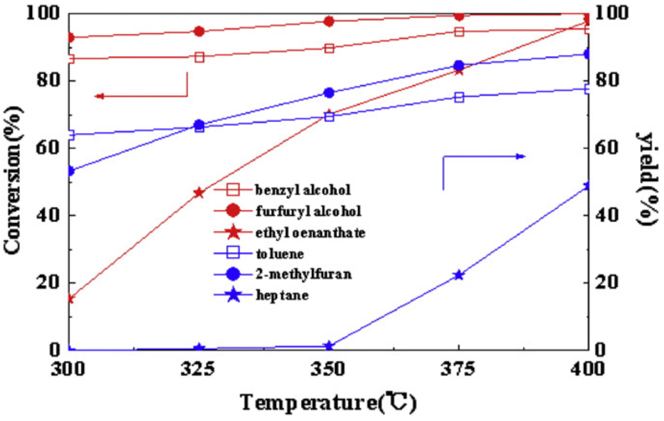


Fig. 3. Conversions and target product yields over NiFe catalyst at different temperature, atmosphere.

higher than 350 °C. However, the conversion of ethyl oenanthate changes from 70.2% at 350 °C to 97.9% at 400 °C. From GC analysis of tail gas, the main products of three different model compounds are toluene, 2-methylfuran, and heptane. The yield of 2-methylfuran increased from 53% to 88%, for toluene from 64 to 78% at the temperature range from 300 to 400 °C, while for heptane was even larger, from 0 to 49%. The conversions of ethyl oenanthate, benzene alcohol and furfural alcohol over fresh NiFe catalyst are higher than the sulphided CoMo [22], Ru-based [23] and Cu-based [24] catalysts, respectively. In order to obtain good catalytic performance for each compound in bio-oil, 400 °C was set as the proper reaction temperature for catalytic HDO of bio-oil.

The conversions and yields over NiFe bimetallic catalyst under different flow speeds at 400 °C were shown in Fig. 4. At a low flow speed (<0.10 ml/min), all the conversions were high (above 90%) and stable. But when the flow speed was up to 0.15 ml/min, the conversion of benzene alcohol still kept at a high value (>90.4%), while conversions of the other two declined dramatically, at the edge of inactivation (the deactivation rate exceeding 30%). The influence of flow speeds on the yields showed the same rule with the conversions. The bigger of flow speed, the lower conversions and yields. Therefore, 0.1 ml/min was set as the proper flow speeds for catalytic HDO of bio-oil.

From the product analysis of the catalytic HDO of three different model compounds of bio-oil, it was found that the main products were deoxidized ones, resulted by C–O cleavage rather than C–C cleavage (see Scheme 1). Independent on the groups (furan ring, benzene ring and straight-chain paraffin), the C–O bond was easier activated than C–C one under the investigated reaction conditions. Of course, dependent on the specific oxygen-containing group, the activation temperatures were different. The C–O in the carboxyl group was activated more difficult than C–OH group, which can explain the effect of temperature on the conversion and yields of ethyl oenanthate is much bigger than furfuryl alcohol and benzyl alcohol. Therefore, NiFe bimetallic catalyst shows excellent catalytic properties for removing oxygen in three typical model compounds of bio-oil. A more general model was shown that –OY group was displaced by H atom actually.

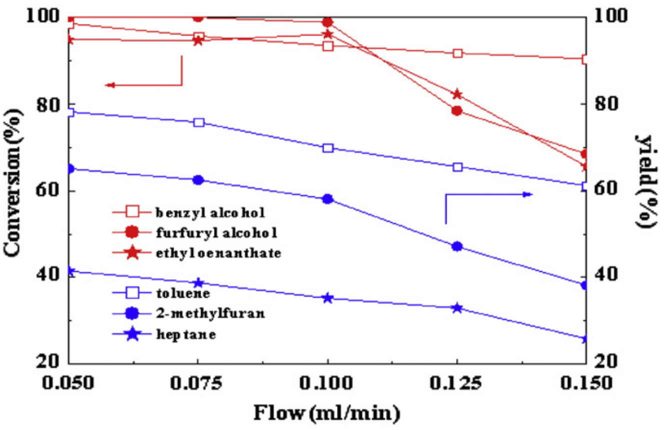
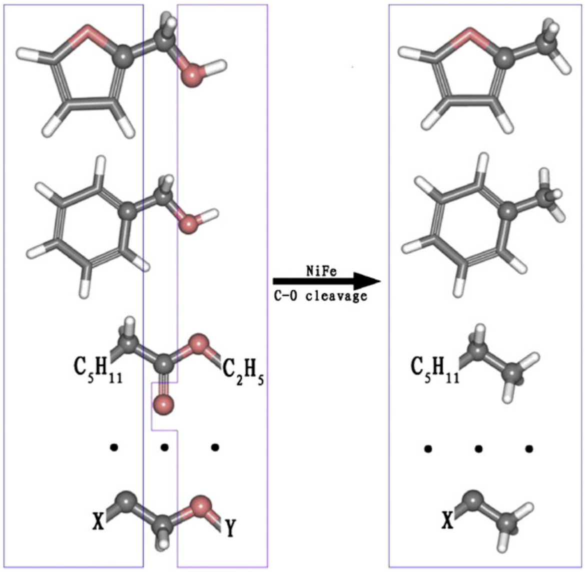


Fig. 4. Conversions and target product yields over NiFe catalyst under different flows at 400 °C, atmosphere.



Scheme 1. Proposed pathways of three substrates.

3.3. HDO of bio-oil over NiFe catalyst

The NiFe catalysts have been further used in catalytic HDO bio-oil obtained from straw. The atomic H/C ratio is up to 2.15, but the oxygen content is 47.59 *wt %* determined by element analysis. The heating value of this bio-oil is 37.8 MJ/kg determined on a XRY-1A oxygen bomb calorimeter, which is lower to fossil fuel (46.04 MJ/kg) and mainly used in kitchens as liquefied gas. The pH of bio-oil was about 6.65(±0.05). After HDO of bio-oil on over NiFe bimetallic catalyst at 400 °C and atmospheric pressure, the pH was 7.5 and the heating value was 43.9 MJ/kg close to the value of fossil diesel (46.04 MJ/kg).

4. Conclusions

NiFe bimetallic catalyst has an excellent catalytic HDO property of three typical model compounds of bio-oil. The excellent catalytic properties of NiFe bimetallic catalysts were attributed to the formation NiFe alloy confirmed from XRD and TEM characterizations. From the product analysis, we proposed that the major reaction pathway is the cleavage of C–O cleavage rather than C–C under the investigated reaction conditions. After the catalytic HDO of bio-oil over NiFe bimetallic catalyst, the heating value changes from 37.8 to 43.9 MJ/kg, the pH changes from 6.65 to 7.50.

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