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Research article

Improved catalytic upgrading of simulated bio-oil via mild hydrogenation over bimetallic catalysts

upgrading for liquid fuel production.



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ARTICLE INFO	A B S T R A C T		
Keywords: Bio-oil Catalytic upgrading Mild hydrogenation Bimetallic catalyst Reaction mechanism	The bio-oil, produced via fast pyrolysis of biomass, can be used as substitute for transportation fuels after its subsequent upgrading. However, conventional upgrading of bio-oil faces serious problems of rapid catalyst deactivation and low conversion efficiency, due to the high unsaturation degree of bio-oil. In this study, the mild hydrogenation of simulated bio-oil over monometallic catalysts (Pd and Pt) and bimetallic catalysts (Pt-Fe, Pd-Fe, Pt-Ni and Pd-Ni) was performed, in order to increase the saturation degree. It was found that the addition of Ni could significantly facilitate the conversion of phenols. The maximum conversion of guaiacol and phenol over Pt-Ni/SiO ₂ catalyst reached 97.8% and 99.6%, respectively. The introduction of Fe improved the conversion of AcOH by promoting the protonation of carbonyl group. Complete conversion of AcOH was achieved over Pt-Fe/SiO ₂ catalyst. The upgraded product, of which the activity was significantly improved, was ready for subsequent		

1. Introduction

Biomass can be converted into bio-oil via fast pyrolysis to substitute conventional fossil fuels [1]. However, the inferior properties of crude bio-oil, such as high oxygen content, high water content, low heating value and strong corrosiveness, severely limit its utilization [2, 3]. Galle et al. [4] performed the combustion test of crude bio-oil and observed serious corrosion and clogging of injectors. The properties of crude biooil could be significantly improved via catalytic upgrading to produce clean, renewable and high-quality liquid fuels. Recently, several upgrading technologies, such as catalytic hydrogenation, catalytic cracking, catalytic reforming and catalytic esterification, etc., have been developed to obtain hydrocarbon fuels, hydrogen and improved bio-oil [3, 5-10]. However, the integral and efficient conversion of crude bio-oil could not be achieved by single upgrading technology due to its complicated composition. Previous studies on the catalytic upgrading of model compounds of bio-oil revealed that ketones and acids could be converted into hydrocarbons, whereas sugars and large-molecular-weight phenolic oligomers tended to produce coke via condensation reaction, leading to rapid catalyst deactivation [11-13]. Therefore, the removal of sugars and phenolic oligomers in bio-oil is of great importance.

Molecular distillation is an efficient separation technology, through which acids and ketones are enriched in the distilled fraction while sugars and phenolic oligomers are reserved in the residual fraction [14,

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15]. Wang et al. [5, 16–18] carried out the studies on the co-cracking of distilled fraction of bio-oil (and model compounds) with ethanol, and a high yield of liquid hydrocarbons was achieved. However, catalyst deactivation may occur during long-term operation, because of the high unsaturation degree of the remaining monophenol in the distilled fraction.

The saturation degree of bio-oil can be increased via mild hydrogenation under a relatively low pressure [19, 20]. Various catalysts have been used for hydrogenation, including noble metal catalysts, Mobased sulfide catalysts, metal phosphide catalysts and other metal catalysts (Cu, Ni, Mg, etc.) [21]. Pd and Pt have been widely used for biooil hydrogenation because of their high catalytic activity [19, 22]. However, considering the complexity of bio-oil components, some oxygenated compounds cannot be efficiently converted over monometallic catalysts. Some previous studies revealed that phenols and carboxylic acids showed low activity and conversion capacity under hydrotreatment conditions compared with ketones, aldehydes, etc. [23, 24]. Therefore, high-performance catalysts are urgently required for efficient conversion of phenols and acids. Recently, the development of bimetallic catalysts has attracted extensive attentions, since the introduction of a second metal can increase catalyst activity, modify catalyst selectivity or improve catalyst stability [25]. Sun et al. [26] performed hydrodeoxygenation of guaiacol and revealed that the addition of Fe significantly enhanced the hydrodeoxygenation activity of Pd/C with a higher yield of oxygen-free aromatic compounds up to

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83.2% at 450 °C. Cai et al. [27] investigated the hydrogenation behaviors of furfural over several catalysts and found that Ni-Cu/SiO₂ bimetallic catalyst exhibited superior performance to Ni/SiO₂ and Cu/SiO₂ catalysts. The presence of Ni could catalyze the saturation of ring and further hydrodeoxygenation. However, the studies on the catalytic hydrogenation of model compound mixture over bimetallic catalysts are still limited.

In this study, some typical compounds, including acetic acid (AcOH), guaiacol (G-OH), phenol (PhOH), furfural (FF) and hydroxyacetone (HAO), were chosen as the simulated bio-oil. Various metals (Pt, Pd, Pt-Fe, Pt-Ni, Pd-Fe, Pd-Ni) supported on SiO₂ were adopted for mild hydrogenation. The hydrogenation behaviors over different catalysts were investigated in the temperature ranging from 240 to 330 °C. Finally, the reaction mechanism over bimetallic catalysts was proposed based on the quantitative analysis of products.

2. Experimental section

2.1. Catalyst preparation

The hydrogenation catalysts were prepared by incipient wetness impregnation, using Pd(NO₃)₂, Pt(NH₃)₄(NO₃)₂, Fe(NO₃)₃·9H₂O and Ni (NO₃)₂·6H₂O as metal precursors. The loading amounts of Pt and Pd were both 2 wt%, while that of Ni and Fe were 10 wt%. The preparation procedure of Pd-Fe/SiO₂ catalyst was as follows: a requisite amount of Pd(NO₃)₂ and Fe(NO₃)₃·9H₂O were dissolved in the deionized water simultaneously. The pretreated SiO₂ was then added in the aqueous solution. After stabilization of 12 h, the sample was dried in the oven at 110 °C overnight, and then calcined at 550 °C for 6 h. Finally, the catalyst was sieved to 40–60 mesh. The other catalysts were all prepared using the same procedure.

2.2. Catalyst characterization

The BET surface areas and pore sizes of the catalysts were determined by N₂ adsorption-desorption using the automated surface area and pore size analyzer (Quantachrome; Autosorb-1). The particle sizes and their distribution were determined by high resolution transmission electron microscopy (TEM, JEOL, JEM-2100F). Powder X-ray diffraction (XRD) analysis was carried out on a PANalytical X'Pert PRO X-ray diffractometer with Cu K α radiation, operating at 40 kV and 40 mA. The scanning regions of the diffraction angle were $2\theta = 10-80^{\circ}$. Temperature programmed reduction (TPR) was performed on a Micromeritics AutoChem II 2920 instrument. The sample was pretreated with He at 250 °C for 60 min and then cooled to 40 °C. The reduction was carried out with a mixture of 10% H₂/He at a ramp rate of 10 °C/min up to 800 °C.

2.3. Catalytic activity test

AcOH, G-OH, PhOH, FF and HAO were chosen as the simulated biooil, because they are typical bio-oil components and the dominant compounds of corresponding chemical families in the distilled fraction of bio-oil produced by walnut shell pyrolysis. Their functional groups including carboxyl group, phenolic hydroxyl group, methoxyl group, benzene ring, aldehyde group, furan ring, aliphatic hydroxyl group and carbonyl group, are representatives of oxygen-containing characteristics of bio-oil. According to the composition of distilled fraction, the weight ratio of AcOH, G-OH, PhOH, FF and HAO was set at 40:15:15:15:15. Ethanol was introduced as solvent and co-reactant, and the ratio of model compounds and ethanol was 1:1. Consequently, the composition of feedstock was 20 wt% AcOH, 7.5 wt% G-OH, 7.5 wt% PhOH, 7.5 wt% FF, 7.5 wt% HAO and 50 wt% ethanol.

Catalytic hydrogenation experiments were performed in a fixed-bed system. The reactor was a stainless steel tube with an inner diameter of 8 mm. The catalyst (2 g) was placed in the reactor and supported on the quartz wool. The catalyst was reduced at a H₂ flow of 30 mL/min at 500 °C for 3 h before the reaction. The reactants were introduced by a high-performance liquid chromatography pump and then were nebulized with H₂ and fed into the reactor. The outlet gas was cooled by a condenser and separated into noncondensable gases and liquid products. The weight hourly space velocity (WHSV) of reactants was 1 h⁻¹. The reaction temperature ranged from 240 to 330 °C and the pressure was set at 4 MPa.

2.4. Product analysis

An online gas chromatograph (GC, Huaai GC 9560), a gas chromatograph-mass spectrometer (GC–MS; TraceDSQ II) system, and a gas chromatograph (Agilent 7890A) were used to identify the chemical structure of compounds and quantify the unconverted reactants and products. The details about the analysis were mentioned in our previous study [28].

The liquid product yield (Y), reactant conversion (Xi) and product carbon selectivity (Sj) are defined by Eqs. (1)–(3). The symbols "m" and "n" in the equation represent the mass of corresponding substances and the mole number of carbon, respectively. When calculating the product carbon selectivity, the unconverted reactants were excluded. Considering the complicated composition of liquid products, it is reasonable to quantify some typical products although some compounds could not be identified [29].

As determined by TG analysis of spent catalysts, the selectivity of coke in each reaction ranged from 1.1 to 1.9 wt%. Based on the determination of gaseous products, liquid products and coke, the mass balances were calculated and all above 94 wt% for each reaction.

$$Y = m_{\text{liquid products}} / (m_{\text{reactants}})_{\text{in}} \times 100\%$$
⁽¹⁾

$$X_{i} = [(m_{i})_{in} - (m_{i})_{out}]/(m_{i})_{in} \times 100\%$$
⁽²⁾

 $S_{j}(j=liquid \text{ products}) = n_{j}/[(n_{reactants})_{in} - (n_{reactants})_{out}] \times 100\%$ (3)

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Textural properties of catalysts

The textural properties of the support and catalysts are shown in Table 1. The specific surface area declined from $152.1 \text{ m}^2/\text{g}$ to $129.6 \text{ m}^2/\text{g}$ and $120.9 \text{ m}^2/\text{g}$ after the loading of Pt and Pd, respectively. The decline of pore volume was also observed. Further addition of Fe and Ni slightly decreased the specific surface area and pore volume of catalysts. According to the previous study, the decrease of specific surface area and pore volume could be attributed to the dilution effect caused by the active components during the impregnation process [30].

3.1.2. XRD

Fig. 1 shows the XRD patterns of the catalysts. The diffraction peaks detected at $2\theta = 39.8^{\circ}$, 46.2°, 67.5° and 81.2° were assigned to Pt, while

Table 1			
Textural	properties	of	catalysts.

Support/catalysts	$S_{BET} (m^2/g)$	Pore volume (cm ³ /g)	Average particle size ^a (nm)
SiO ₂	152.1	0.716	/
Pt/SiO ₂	129.6	0.481	4.2
Pt-Fe/SiO ₂	113.1	0.449	15.8
Pt-Ni/SiO ₂	109.4	0.450	9.5
Pd/SiO ₂	120.9	0.593	15.7
Pd-Fe/SiO ₂	112.2	0.504	5.1
Pd-Ni/SiO ₂	100.2	0.404	9.4

^a Determined by TEM.

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