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In-situ hydrodeoxygenation of a mixture of oxygenated compounds with hydrogen donor over ZrNi/Ir-ZSM-5+Pd/C

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ABSTRACT

In-situ hydrodeoxygenation of a mixture of oxygenated compounds from bio-oil with hydrogen donor over supported multi-metal catalysts was investigated. As most previous in-situ hydrodeoxygenation reports focused on phenols, guaiacol, furfural, and acetic acid, this paper extends the scope to a mixture of oxygenated compounds of not only phenols, guaiacol, furfural and acetic acid, but also of lesser reported hydroxyl -propanone, cyclopentanone aiming at obtaining more liquid fuels. The method of incipient wetness impregnation was used to load the three metals (Zr, Ni, Ir) and Pd on the support of ZSM-5 and C, respectively. The conversion of acetic acid, hydroxyl -propanone, cyclopentanone, guaiacol, furfural, and phenol reached 99.7%, 99.3%, 100%, 100%, 100%, and 100%, respectively, including the total deoxygenation ratio of 99.6%, the liquid yield (96.5%), and the hydrocarbon yield (86.7%), under the suitable conditions. The sulfur content, the octane number, and the H/C ratio of bio-oil through in-situ hydrodeoxygenation have been improved, and reached 0, 89 and 1.9, respectively. We also speculated reaction pathways of different oxides according to the product distribution over ZrNi/Ir-ZSM-5 and Pd/C.

1. Introduction

Environmental pollution from fossil fuel consumption, the decreasing petroleum and the growing energy needs of the world make a good prospect for developing renewable resources [1,2]. The fuel derived from biomass has a low nitrogen content, a low sulfur content, and then release less NO_2 and SO_2 on combustion, but it contains high concentrations of phenolic and furanic compounds, and has poor properties as fuels [3,4]. The undesirable characteristics stemmed from a high concentration of oxygenates have a detrimental effect on transportation, storage and combustion of fuels. So it is critical to make bio-oil upgrading through deoxygenation for improving heating value, stability, and physical properties such as acidity and viscosity [5–10]. Bio-oil provides a unique opportunity to use a renewable resource to produce fuels and chemicals from waste materials and plants that do not compete with food production [11]. One common tactic for deoxygenation is hydrodeoxygenation (HDO), which involves adding hydrogen to perform C-O bond cleavage by removal of water [12–14]. Therefore, to upgrade bio-oil using HDO, where hydrogen was used to remove the oxygen in bio-oil, would be a beneficial effect on fuels. However, HDO needs a pressure of 7–20 MPa and a temperature of 473–673 K [15–17], and different reactions occur in hydroprocessing because of many oxygenated species in bio-oil. Phenol and its derivatives are rich in bio-oil, which has been found as one of the more persistent oxygenates to be deoxygenated. Hydrogen for HDO can be supplied by the steam reforming of partial bio-oil using catalysts such as Co-Fe, Ni/Ash, and Ni/Al_2O_3 [18,19]. Catalytic hydrogenation mainly includes hydrodeoxygenation and mild hydrogenation. In general, the deoxygenating of bio-oil to form aliphatic hydrocarbons and water is carried out at a high-pressure, which leads to a harsh need of equipments and high consumption of hydrogen [20,21]. To improve the bio-oil stability, the mild hydrogenation is used to saturate aromatic rings and double bonds at a low-pressure [22]. Typical hydrogenation catalysts are divided into several types: metal phosphides, Mo-based sulfides, noble metals, and other metals. The catalytic aqueous phase hydrogenation of bio-oil was carried out at 10 MPa in a fixed-bed reactor,

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followed by the catalytic cracking of condensation products in another reactor, and the selectivity of olefins and aromatic compounds achieved 43% and 18.3%, respectively [23,24]. Ruddy and Jacobson have reviewed the development of bio-oil upgrading in detail. However, the coke is prone to deposit on the catalyst, which results in deactivation during bio-oil upgrading because of covering the active sites and consuming a large pore volume and superficial area [25–28]. Considering the deactivation in the hydroprocessing, the hydrogenation conditions should be milder than those of the traditional HDO. One can rarely perform the different reaction needed by the deoxygenating of biomass-derived oxygenates. Much attention has been placed on multifunctional catalysts, where the different active materials are used to provide catalytic sites for diverse reactions [29–31]. Here, a bio-oil upgrading technology based on a continuous hydrogenation reaction was proposed. Acetic acid, hydroxypropanone, guaiacol, cyclopentanone, furfural and phenol were mixed with methanol as the model compounds. HDO of the model compounds over ZrNi/Ir- ZSM-5 and Pd/C has been explored with emphasis on the influence of catalyst properties and operating conditions on the hydrogenation and deoxygenation reactions. These studies show the feasibility of ZrNi/Ir-ZSM-5 and Pd/C with multifunctional catalysis needed by hydrogenation and C-O cleavage to perform HDO at reasonable rates.

2. Material and methods

Acetic acid, hydroxypropanone, guaiacol, cyclopentanone, furfural and phenol were bought from Sinopharm Chemical Reagents Co., Ltd. The model compounds were prepared by mixing methanol with acetic acid, hydroxypropanone, guaiacol, cyclopentanone, furfural and phenol. All chemicals were commercially available and used without further treatment.

Samples of ZrNi/Ir-ZSM-5 and Pd/C were prepared, respectively, by the following method.

Seven grams of ZSM zeolite (Si/Al = 180) and 50 mL of 0.5 mol/L NaOH solution were introduced into a 100 mL flask to form a slurry. The samples were separated by vacuum filtration, washed thoroughly with deionized water, dried at 384 K for 12 h, and then calcined in air at 823 K for 4 h. To obtain ZSM-5 zeolite, the samples were ion-exchanged with 0.5 mol/L NH_4NO_3 solution at 358 K three times, dried at 383 K for 12 h, and then calcined in air at 813 K for 4 h. The obtained sample was impregnated with a mixture of hydrochloric acid solution, Zirconium oxychloride (2.8 g), Iridium chloride acid (3.8 g) and nickel nitrate (3.4 g) at 332 K for 1 h, dried at 413 K for 4 h, and calcined at 673 K for 2 h to get ZrNi/Ir-ZSM-5.

The Pd/C catalyst was prepared using the impregnation method coupled with complexation of sodium citrate and reduction of ethylene glycol. A calculated amounts of $PdCl_2$ were added to the sodium citrate solution, and the mixture was stirred until the precursor salt dissolved. The solution was mixed with ethylene glycol, and the mixture was stirred at room temperature for 2 h. A necessary weight of activated carbon powder was added to the mixture solution and dispersed by magnetic stirring, meanwhile NaOH solution was added drop by drop to maintain the pH value of slurry in the range of 9–10. The slurry was heated under flowing N_2 for 4 h and then was cooled to room temperature. The sample obtained was washed with a large amount of hot deionized water to remove chloride anion and sodium citrate. The solid was dried in a vacuum oven for a whole night.

The crystalline was characterized by X-ray diffraction (XRD; D/Max 2500×; worked at 40 kV and 100 mA, Cu Kα source). The morphology and size were characterized by transmission electron microscopy (TEM, A JEOL JEM-2010F). The pore size and volume distribution were measured with nitrogen adsorption-desorption (Quantarome NOVA 4000) at 77 K. The surface areas of the sample were determined according to the Brunauer-Emmett-Teller (BET) equation. The acidity was characterized by the temperature programmed desorption of ammonia (NH_3-TPD) in a dynamic chemisorption analyzer (Micromeritics ASAP 2920). The isothermal reduction measurements applied a TG unit (TG-SDTA 851e). Temperature-programmed reduction (TPR) with H_2 were performed using a TPD51 system (Belsorp, Japan).

The fuel produced from biomass-derived oxygenates was carried out over ZrNi/Ir-ZSM-5 and Pd/C in a fixed-bed reactor. A scheme of the reaction setup is shown in Fig. 1. First, a certain percentage of ZrNi/Ir-ZSM-5 (6 g) and Pd/C (3 g) was installed in the reactor, respectively, the upper stage is ZrNi/Ir-ZSM-5, and activated at 673 K for 30 min. The reaction bed was heated gradually to the reaction temperature of 350–500 K. The methanol as a hydrogen donor (0.4 mL/min) and model compounds (1–16 mL/min) were preheated to 350–500 K and introduced to the fixed reactor. The product was cooled, separated by gas-liquid separator, and then analyzed by gas chromatography or gas chromatography-mass spectrometry.

We calculated the conversion of oxygenates as:

$$\text{Conversion of oxygenates} = \frac{(C_I - C_O)}{C_I} \times 100\%$$

where C_I and C_O are the inlet concentration and outlet concentration of different oxygenates, respectively.

We calculated total deoxygenation ratios as:

$$\text{Deoxygenation ratios} = \frac{C_1 \times M_1 - C_2 \times M_2}{C_1 \times M_1} \times 100\%$$

where C_1 and C_2 are the oxygen content in materials and oxygen content in upgrading bio-oil, respectively. M_1 and M_2 are bio-oil mass and upgraded bio-oil mass, respectively.

3. Results and discussion

3.1. Characterization

XRD patterns of Pd/C, ZSM-5, ZrNi/ZSM-5 and ZrNi/Ir-ZSM-5 are presented in Fig. 2. These patterns of fresh catalysts show weak diffraction peaks at 40.06° (2θ), showing most of Pd is loaded on the carbon in the form of microcrystalline. And the spent catalyst has a strong and sharp diffraction peak at 40.06° (2θ). According to the Scherer formula, the average particle sizes of the fresh and the spent catalyst were 4 nm and 22 nm, respectively. The size of the spent was 5 times larger than those of the fresh because most of the

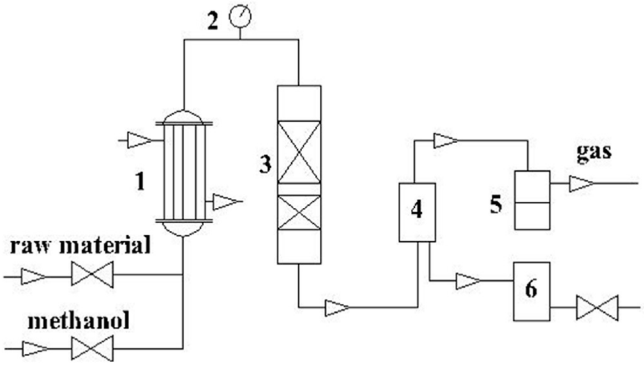

Fig. 1. Schematic diagram of the setup used for hydrocarbon produced from oxygenates (1. preheater, 2. pressure gauge, 3. hydrogenation reactor, 4. condenser, 5. tail gas processor, 6. product tank).