



Upgrading of bio-oil in supercritical ethanol: Catalysts screening, solvent recovery and catalyst stability study



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ABSTRACT

Supercritical upgrading of bio-oil is an effective method to upgrade bio-oil. In this paper, upgrading of bio-oil was carried out in supercritical ethanol with the aim of catalyst selection, reducing solvent consumption and catalyst stability study. Compared with Ru/HZSM-5, C-supported catalysts (Pt/C, Pd/C, and Ru/C) gave better catalytic performance. Over the C-supported catalysts, the heating value increased from 21.45 MJ/kg to about 30 MJ/kg and the pH value increased from 3.13 to about 5.5. The relative content of desired products reached as high as 80% over Ru/C. The ratio of ethanol to bio-oil was further reduced to about 1:1 by solvent recovery and reutilization. The relative content of desired products particularly that of esters increased with the recovered solvent. Catalytic stability study of Ru/C showed that the relative content of desired products decreased gradually with the number of catalyst recycle times while the consumption of hydrogen decreased mainly in the first recycle. Coke deposition and sintering of metal particles were the main reasons for the deactivation of Ru/C.

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1. Introduction

Bio-oil from fast pyrolysis of biomass is an attractive alternative for fossil-derived transportation liquid fuels. However, bio-oil is unsuitable for direct application in internal combustion engines due to its undesirable properties such as low heating value, high corrosiveness, and high viscosity [1]. To be used as a transportation fuel, it is widely accepted that bio-oil must be upgraded.

Catalytic hydrodeoxygenation has been widely studied as a process to upgrade bio-oil [2–5]. However, high hydrogen consumption, low liquid yield hampered the industrialization of this upgrading process [5,6]. With respect to the high hydrogen consumption in hydrodeoxygenation, catalytic cracking which operates without hydrogen seems attractive. Unfortunately, this method is characterized by high coke deposition and severe catalyst deactivation [6–8].

A new method to convert unstable and corrosive oxygenated components into stable and combustible oxygenated organics was proposed by Zheng et al. [9]. In this regard, alcohols were used in the upgrading of bio-oil. Zhang et al. [10] upgraded bio-oil by esterification with ethanol over solid base and solid acid catalyst. The results showed that the viscosity and the density of bio-oil

lowered markedly while its heating value and stability increased. Li et al. [11] illustrated that acids, the corrosive components, and aldehydes, the unstable compounds were converted into esters and acetals respectively utilizing alcohols over solid acid catalysts.

Researchers further developed this method (upgrading bio-oil with the addition of alcohols) by upgrading of bio-oil in supercritical alcohols. Supercritical fluids exhibit gas-like diffusivity and liquid-like dissolving capability, which reduce heat and mass transfer resistance during reaction. Peng et al. [12] compared bio-oil upgrading in supercritical and subcritical ethanol. The results showed that the supercritical upgrading process performed more efficiently than the subcritical upgrading process. Li et al. [13,14] separated bio-oil into low-boiling and high-boiling fraction by distillation. Both parts were significantly upgraded in supercritical methanol. Tang et al. [15] combined hydrogenation, esterification, and cracking in supercritical upgrading. Zhang et al. [16] compared the effects of solvents (methanol and ethanol), catalyst supports (HZSM-5 and $\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-15}$), and active metals (Pd and Pt) in supercritical upgrading. Dang et al. [17] studied the effects of ethanol to bio-oil ratio, reaction temperature and initial hydrogen pressure on upgrading of bio-oil in supercritical ethanol over $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-15}$.

However, there are still several issues to be addressed before the scaling up of this process. The first issue is the high ratio of solvent to bio-oil adopted in this upgrading method. In previous papers, the mass ratio of solvent to bio-oil was as high as 10:1,

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which implied a large amount of solvent was consumed. To reduce the consumption of ethanol, in this paper, 2:1 of ethanol to bio-oil ratio was used. The recovery and reutilization was carried out as an attempt to further reduce the consumption of ethanol, which was neglected by almost all of these papers. Another issue is the stability of the catalyst. In most of the previous papers, acid or acid-metal bifunctional catalysts were used to couple different reactions in supercritical upgrading while the performance of catalysts with neutral supports was rarely reported. In our previous studies [16,17], we employed bifunctional catalysts (Pt/HZSM-5, Pd/HZSM-5, Pt/SO₄²⁻/ZrO₂/SBA-15, Pd/SO₄²⁻/ZrO₂/SBA-15) to upgrade bio-oil. C-supported catalysts (Pt/C, Pd/C, and Ru/C) were widely used in upgrading of bio-oil for their high hydrogenation activity [3,18,19]. In this paper, carbon-supported catalysts (Ru/C, Pd/C, and Pt/C) were employed and as a comparison an experiment with bifunctional Ru/HZSM-5 (Si/Al = 50) was also conducted. In particular, the stability of catalyst in supercritical upgrading was also studied as it was essential for the industrialization of this process.

2. Experimental

2.1. Materials

RuCl₃·3H₂O and HZSM-5 (Si/Al = 50) were purchased to prepare bifunctional catalyst Ru/HZSM-5. In this work, commercial catalysts 5 wt% Ru/C, 5 wt% Pd/C, and 5 wt% Pt/C and self-made catalyst 5 wt% Ru/HZSM-5 were employed as catalysts. Ethanol was used as the reaction solvent. All chemicals were commercially available and used as received without further treatment (Table S3). The crude bio-oil used in this work was supplied by the University of Science and Technology of China, and was prepared from rice husk by fast pyrolysis.

2.2. Catalyst preparation and characterization

Bifunctional catalysts Ru/HZSM-5 was prepared by incipient wetness impregnation method. The detailed description of the preparation method was provided in our previous papers [16,17]. The characterization of Ru/HZSM-5 was conducted prior to activation. X-ray diffraction (XRD) analysis was conducted on an X'Pert PRO X-ray diffractometer using CuK α radiation over 2θ in the ranges of 10–70°. Scanning transmission electron microscope (STEM) images were obtained on a Tecnai G2 F30 S-Twin electron microscope with an accelerating voltage of 300 kV. N₂ adsorption–desorption isotherms were measured by a Micromeritics ASAP 2020 system. All samples were pretreated in vacuum at 200 °C for 2 h before physisorption. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. The total pore volume was determined from the adsorption and desorption branches of the nitrogen isotherms at $P/P_0 = 0.97$.

2.3. Experimental procedure

All the experiments were carried out in a 300 mL stainless steel batch reactor equipped with an electrical heating jacket and a mechanical agitator. In a typical experiment, the reactor was filled with 40 g of crude bio-oil, 80 g of ethanol together with 3.0 g of catalyst. Subsequently, the leakage test was conducted, followed by flushing the reactor five times with N₂ and H₂, respectively. The reaction was carried out at 300 °C and 2.0 MPa initial hydrogen pressure for 5 h. The stirring speed of the agitator was 700 rpm throughout the whole process. After the reaction, the reactor was cooled to room temperature.

After the reactor was cooled down, the pressure of the reactor was recorded and the gas product was sampled with a gas bag.

The upgraded bio-oil and spent catalyst were recovered and separated by vacuum filtration. The recovered catalyst was washed with ethanol until the filtration was colorless. In the catalyst recycling experiment, the catalyst was reused for another upgrading reaction without a pre-activation step. The mass of gas product was neglected and the mass balance was about 95% for all the experiments. The mass difference between the feed and the liquid product was mainly due to the gas product and unavoidable losses during the collection of products.

2.4. Products analysis

The gas product was analyzed by gas chromatography (GC, Agilent 7820A) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) detector. The chemical compounds in crude bio-oil and upgraded bio-oil were analyzed by gas chromatography–mass spectrometry (GC–MS, Thermo Fisher) with a DB-wax capillary column (30 m × 0.25 mm × 0.25 μ m). The injector temperature was 260 °C in split mode and the carrier gas was nitrogen. The GC–MS operating conditions were as followed: the oven temperature was 40 °C for 3 min, heated to 180 °C at 4.0 °C/min, then to 260 °C at 10 °C/min and held at 260 °C for 10 min. Compounds were identified by the National Institute of Standards and Technology (NIST) library with similarities higher than 70% and the peak area normalization method was used to determine the relative content of a specific compound. The content of ethanol in upgraded bio-oil was measured by the external standard method using an Agilent 7890A GC-FID with an Hp-5 column (30 m × 0.25 mm × 0.25 μ m). The operational conditions of the GC-FID were the same with that of the GC–MS. The physical properties such as heating value, water content and pH value of crude bio-oil and upgraded bio-oil were measured by bomb calorimeter, Karl Fischer moisture titrator and automatic potentiometric titrator, respectively.

Prior to thermogravimetric analysis, the recovered catalysts were pretreated at 300 °C under N₂ atmosphere for 30 min to remove absorbed ethanol and products. The coke deposition of spent catalyst was determined by thermogravimetric (TG) analysis using a TGA/SDTA 851 thermogravimetric analyzer over the range of 25–1000 °C at a temperature ramp of 10 °C/min in flowing O₂ (50 mL/min). The spent catalyst was characterized by N₂ adsorption–desorption, XRD and STEM as well.

3. Results and discussion

3.1. Catalyst characterization

As shown in Fig. 1, fresh C-supported catalysts exhibited a type-I isotherm with an H4-type hysteresis loop, indicating the existence of micropores and mesopores in C-supported catalysts. 5 wt% Ru/HZSM-5 showed a type-I isotherm without hysteresis loop, which is typical for microporous catalysts. The textural characteristics including BET surface area, total pore volume, pore diameter, and t-plot micropore area are given in Table 1. It was clear that C-supported catalysts had larger BET surface area and pore volume than Ru/HZSM-5.

The XRD patterns of catalysts are exhibited in Fig. 2. No diffraction peaks of metals were identified in the profiles of C-supported catalysts, suggesting the metals were highly dispersed in C support (average particle size < 5 nm). There were three diffraction peaks at $2 = 28.0^\circ$, 35.1° , and 54.3° indexed as (1 1 0), (1 0 1), and (2 1 1) reflections of RuO₂, in the profile of Ru/HZSM-5. The average particle size of RuO₂ on Ru/HZSM-5 determined according to the XRD patterns using the Scherrer Equation was 19 nm. The metal particle size in Ru/HZSM-5 was much larger than those in

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