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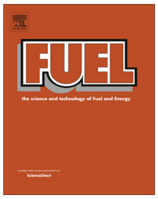

Catalytic transformations of acids, aldehydes, and phenols in bio-oil to alcohols and esters

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HIGHLIGHTS

- A method to convert acids, aldehydes, and phenols to alcohols and esters was proposed.
- C-supported catalysts gave complete conversion of phenol and *n*-butanal.
- Esterification was mainly catalyzed by weak and medium acid sites.
- Yields of desired products (alcohols and esters) as high as 95% could be achieved in OHE.

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ABSTRACT

Acids, aldehydes, and phenols have negative effects on the properties of bio-oil. In this paper, *n*-butanal, acetic acid, and phenol were selected as model compounds of aldehydes, acids, and phenols, respectively. To convert these compounds into stable and combustible oxygenated organics (alcohols and esters), separate hydrogenation–esterification (SHE) of *n*-butanal, phenol, and acetic acid was carried out. 100% conversions of *n*-butanal and phenol were achieved over C-supported catalysts (Ru/C, Pt/C, and Pd/C) with high selectivity to desired products. With the catalysis of $SO_4^{2-}/ZrO_2/SBA\text{-}15$, the yields of butyl acetate and cyclohexyl acetate were 75.89% and 30.97% respectively, which were higher than those over HZSM-5. Based on the results, one-pot hydrogenation–esterification (OHE) of *n*-butanal, phenol and acetic acid was tested. In OHE, yields of desired products (alcohols and esters) reached 95%, which were higher than those in SHE. Hydrogenation–esterification is a promising method to convert aldehydes, phenols, and acids in bio-oil to stable and combustible organics.

1. Introduction

With the depleting of oil reserves, the demand for an alternative liquid transportation fuel is becoming increasingly apparent [1]. Biomass is the only renewable source of energy that can be converted into liquid fuels. Lignocellulosic biomass is abundant, and it has the potential to significantly replace petroleum in the production of fuels for the transportation sector [2]. Multiple conversion routes for biomass conversion to liquid transportation fuels have been considered [3]. Fast pyrolysis of biomass is a feasible route to convert biomass into liquid fuels [4]. Depending on the biomass composition and operational condition, the yield of bio-oil from fast pyrolysis varied in the range of 60–80 wt% [5]. However, unlike petroleum, bio-oil exhibited undesirable properties such as high viscosity, high corrosiveness, low heating value, and instability. It is widely accepted that bio-oil from fast pyrolysis of biomass cannot be considered as a realistic candidate for large scale liquid transport fuel substitution unless it is upgraded [6].

The oxygen content of bio-oil can be as high as 40%, which was once considered as the main reason for its undesirable properties [7]. Two catalytic upgrading methods including hydrodeoxygenation [8] and catalytic cracking [9,10] have been applied to remove the oxygen from bio-oil. However, these two upgrading methods were characterized by low liquid yield and severe catalysts deactivation. On the other hand, the oxygen content in bio-oil does not necessarily to be completely removed. Some oxygenated organics such as ethanol, butanol, and bio-diesel have been applied as

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Abbreviations: SHE, separate hydrogenation–esterification; OHE, one-pot hydrogenation–esterification; SZr, $SO_4^{2-}/ZrO_2/SBA\text{-}15$; TPD, temperature programmed desorption; $X(i)$, conversion of reactant i; $Y(i)$, yield of i; $S(i)$, selectivity to i; BTA, *n*-butanal; POH, phenol; BTO, *n*-butanol; CYO, cyclohexanol; BTE, butyl acetate; CAE, cyclohexyl acetate.

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transportation fuels. Besides, the cost can be reduced by converting bio-oil into stable and combustible oxygenated organics as less H_2 was consumed. Therefore, alcohols and esters, which are stable and combustible oxygenated organics, were regarded as the desired products in this paper.

Due to the complexity of bio-oil, most of the work focused on the conversion of model compounds. Bio-oil is composed of more than 400 compounds, including acids, aldehydes, alcohols, ketones, esters, phenols, and ethers [11]. The undesirable properties of bio-oil are correlated with certain types of compounds. Acids contribute to the corrosiveness of bio-oil, and the instability of bio-oil is mainly caused by aldehydes and phenols. Hence, acids, aldehydes, and phenols should be removed in the final product.

Aldehydes and phenols can be converted into stable oxygenated organics by hydrogenation [12]. Esterification is an effective method to convert acids in bio-oil into more stable esters [13,14]. However, in previous papers, most of the studies focused on single model compound, while the simultaneous conversions of different types of compounds were still to be studied. Zheng et al. [15–18] combined hydrogenation of aldehydes and esterification of acids to convert aldehydes and acids into alcohols and esters. However, in their work, aldehydes, phenols, and acids could not be simultaneously converted.

In this paper, *n*-butanal, phenol, and acetic acid were selected as representatives of aldehydes, phenols, and acids, respectively. Four different groups of reactions: hydrogenation of *n*-butanal to *n*-butanol, hydrogenation of phenol to cyclohexanol, esterification of *n*-butanol and acetic acid, and esterification of cyclohexanol and acetic acid were carried out separately to verify the possibility of hydrogenation–esterification of aldehydes, phenols, and acids. Pt/C, Pd/C, and Ru/C were used for hydrogenation as they were generally known as hydrogenation catalysts [19,20]. Acid catalysts SO_4^{2-}/ZrO_2/SBA-15 and HZSM-5 with different Si/Al ratios (25, 50, and 100) were employed in the esterification reactions. Based on the results of SHE, one-pot hydrogenation–esterification reactions (OHE) of *n*-butanal, acetic acid, and phenol were carried out. Physically mixed catalysts and bifunctional catalysts were tested and a comparison was made between OHE and SHE.

2. Experimental

2.1. Materials

SBA-15, sulfuric acid, zirconium nitrate pentahydrate ($Zr(NO_3)_4$ $5H_2O$), cetyltrimethylammonium bromide (CTAB) were purchased to prepare acid catalyst SO_4^{2-}/ZrO_2/SBA-15 (denoted as SZr). SZr and HZSM-5 (acid catalysts) with different Si/Al ratios were employed as the catalysts for esterification, while commercial Ru/C, Pt/C, and Pd/C were used as hydrogenation catalysts. $RuCl_3 \cdot 3H_2O$ was used as the Ru precursor of bifunctional catalysts. Phenol (99.0%), acetic acid (99.5%) and *n*-butanal (98.0%) were used as reactants and *n*-hexane (97.0%) was employed as the reaction solvent. Cyclohexanol (99.0%), *n*-butanol (99.9%), butyl acetate (99.7%), and cyclohexyl acetate (99.0%) were employed as standards. All chemicals were commercially available and used without further treatment.

2.2. Catalysts preparation and characterization

SO_4^{2-}/ZrO_2/SBA-15 (designated as SZr) was prepared via a two-step impregnation method according to Li [21]. Bifunctional catalysts 5 wt% Ru/SZr and 5 wt% Ru/HZSM-5 (Si/Al = 50) were prepared by incipient impregnation method.

The characterizations of Ru/SZr and Ru/HZSM-5 were conducted prior to activation. X-ray diffraction (XRD) analysis was conducted on an X'Pert PRO X-ray diffractometer using Cu Kα radiation over 2θ in the ranges of 10–70°. N_2 adsorption–desorption isotherms were measured by a Micromeritics ASAP 2020 system. All samples were pretreated in vacuum at 200 °C for 2 h. 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 $p/p_0 = 0.97$.

Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted to determine the acidity of acid catalysts and bifunctional catalysts. In a typical run, 0.1 g of sample was treated in a flow of NH_3 (10% in He, 30 mL/min) at 60 °C for 1 h after pretreatment at 500 °C in a flow of He (40 mL/min) for 1 h. The physically absorbed NH_3 was removed by flushing the catalyst with He (50 mL/min) at 100 °C for 90 min before starting the TPD analysis. Experimental runs were recorded with a mass spectrometry (QIC20) system by heating the sample from 100 °C to 700 °C at a ramp of 10 °C/min under He flow (40 mL/min). The mass number of 17 was used to track NH_3 desorption.

2.3. Experimental procedure and products analysis

All the reactions were conducted in a sealed 100 mL stainless steel batch reactor. The reactor was equipped with an electrical heating jacket and a mechanical stirrer. Prior to the reaction, the self-made bifunctional catalysts (Ru/HZSM-5 and Ru/SZr) were activated in flowing hydrogen at 400 °C for 3 h. In the SHE reactions, four different groups of reactions were carried out: *n*-butanal hydrogenation, phenol hydrogenation, esterification of acetic acid and *n*-butanol, and esterification of acetic acid and cyclohexanol. For hydrogenation reactions, the feedstock was 0.01 mol of reactant dissolved in 20 mL of solvent (*n*-hexane). For esterification reactions, the feedstock was composed of 0.01 mol of *n*-butanol or cyclohexanol and 0.01 mol of acetic acid dissolved in 20 mL of *n*-hexane. The feedstock and 0.5 g of catalysts were added into the reactor. In a typical run of OHE reactions, the feedstock consisted of 0.01 mol of *n*-butanal, 0.01 mol of phenol and 0.01 mol of acetic acid dissolved in 20 mL of *n*-hexane. The feedstock and a certain amount of catalyst (0.5 g of bifunctional catalysts or 0.5 g of Ru/C + 0.5 g of acid catalysts) were added into the reactor.

Before each run, the reactor was flushed five times with N_2 and H_2 respectively to exclude the remaining air, followed by filled with H_2 to 4.0 MPa. Then the reactor was heated to the reaction temperature (150 °C) in 1 h, and the isothermal reaction proceeded for 3 h with a stirring speed of 700 rpm. Afterwards, the reactor was cooled down to room temperature and the products were recovered after the reaction. The mass balance was about 95% for all the reactions. The liquid and solid products were separated. The liquid products were analyzed by GC-FID (Agilent 7890) with an HP-5 column (30 m × 0.25 mm × 0.25 μm) using the external standard method. The GC 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. Every sample was analyzed three times and the deviation was within 5%. The conversion rate (*X*), yield (*Y*), and the selectivity (*S*) were calculated according to the following equation.

$$X(\text{Reactant}) = \frac{n(\text{Reactant, in}) - n(\text{Reactant, out})}{n(\text{Reactant, in})} \quad (1)$$

$$Y(i) = \frac{n(i, \text{out})}{n(\text{Reactant, in})}, \quad i = \text{Products} \quad (2)$$

$$S(i) = \frac{Y(i)}{X(\text{Reactant})} \quad (3)$$