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Bio-gasoline production from co-cracking of hydroxypropanone and ethanol

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ABSTRACT

Hydroxypropanone was selected as the model compound of bio-oil ketones to study its cracking behavior for bio-gasoline production. The cracking of pure hydroxypropanone generated inferior oil phase which had a content of high oxygenated compounds. The quality of oil phase was obviously improved when ethanol was adopted as the co-reactant. Furthermore, increasing cracking pressure also benefited the yield and quality of the oil phase. The conversion yield of the reactants reached 100% and the selectivity of the oil phase reached 31.9 wt.% in the co-cracking process under 400 °C and 2 MPa. The oil phase also had an outstanding quality with a hydrocarbon content of 100% and mainly contained hydrocarbons with carbon numbers ranging from 7 to 10, which are also important components in commercial gasoline. Based on the results, a co-cracking mechanism was proposed to illustrate the role of ethanol in promoting hydroxypropanone cracking.

1. Introduction

Bio-oil produced from the fast pyrolysis of biomass is regarded as a promising substitute for traditional transportation fuel in the future. However, crude bio-oil has inferior properties such as high water and oxygen content, high viscosity, strong acidity, and low heating value, which prevent it from being applied directly in current engines. Therefore, it is very necessary to transform bio-oil to a liquid fuel that is similar to gasoline or diesel by upgrading [1,2]. Currently, hydrodeoxygenation and zeolite cracking are two efficient ways for upgrading bio-oil. Compared with hydrodeoxygenation, which should be operated under high hydrogen pressure, zeolite cracking is also able to convert bio-oil to hydrocarbon fuels with no hydrogen consumption, which is considered more economical [3].

Although early research on crude bio-oil cracking achieved partial conversion of bio-oil to hydrocarbons, the yield of carbon deposits reached 20 wt.%, which led to rapid deactivation of catalysts and the experiments were usually terminated in less than half an hour [4,5]. Because bio-oil has a complex composition that includes acids, aldehydes, ketones, alcohols, phenols, esters, ethers, and sugars, researchers studied the cracking behaviors of model compounds of bio-oil. It was found that some alcohols, acids and ketones could be converted to aromatic hydrocarbons at moderate temperatures, while some compounds with a high oxygen content and a high degree of unsaturation such as phenols, were easily coked and resulted in the deactivation of the catalyst [6–8]. In view of the possible influence on cracking characteristics by oxygen content and unsaturated degree, the concept of an effective hydrogen to carbon ratio ($(H/C)_{eff}$) was introduced, as shown in Eq. (1), with H, O, N, C and S being the mole percents of hydrogen, oxygen, nitrogen, carbon and sulfur present in the compound. [3,9]. In the cracking test of model compounds with different $(H/C)_{eff}$ ratios, catalysts tended to deactivate during the cracking of compounds with low $(H/C)_{eff}$ ratios [9]. Thus, it can be inferred that the deactivation of catalysts during crude bio-oil cracking is mainly caused by the low $(H/C)_{eff}$ ratio owing to its high oxygen content and unsaturated degree.

$$(H/C)_{eff} = \frac{H-2\cdot O-3\cdot N-2\cdot S}{C} \qquad (1)$$

To improve the stability of the cracking process, compounds with higher $(H/C)_{eff}$ ratios were used to increase the integral $(H/C)_{eff}$ ratio of the reactants. Some aliphatic alcohols are considered to be the ideal co-reactant because they have a relatively high $(H/C)_{eff}$ ratio of 2, which makes their conversion under similar operating conditions stable and, on the other hand, both polar and nonpolar molecules can be dissolved in alcohols. Methanol can be synthesized by syngas produced from biomass gasification and ethanol can be obtained by biomass fermentation, so the production of these two alcohols is sustainable [10,11]. Compared with the conversion of methanol and ethanol to gasoline, if the bio-oil obtained from the biomass waste can be co-cracked with alcohols to produce liquid fuels rich in hydrocarbons, the high-value integral utilization of biomass could be achieved and it would be more economical. Recently, there has been some research on the co-cracking of methanol and bio-oil or its model compounds, and the results have shown that the selectivity of hydrocarbons was increased and the lifetime of the catalyst was prolonged [9,12].

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Hydroxypropanone is a typical ketone in bio-oil. It is commonly considered to be largely produced by the pyrolysis of cellulose. In the research by Luo et al. [13], hydroxypropanone was found to be formed from the decomposition of active cellulose and it had a content of 4.5 wt.% in anhydro-bio-oil when the temperature of the radiation source was above 900 °C. Lin et al. [14] proposed that cellulose first underwent depolymerization to form levoglucosan, which subsequently underwent fragmentation and retroaldol condensation reactions to produce hydroxypropanone. Oasmaa and Meier [15] reported that hydroxypropanone was identified in three of the four studied bio-oils from different laboratories and its amount could be as much as 7.82 wt.% on a wet liquid basis. In another quantitative analysis of hydroxypropanone on a dry biomass basis by Demirbas [16], the highest yield of 13.5 wt.% was obtained.

Due to the complexity in the crude bio-oil composition, it is difficult to directly catalytic convert crude bio-oil to high-grade fuels. Because the hydroxyl and carbonyl groups in hydroxypropanone are representative in bio-oil, the study of the cracking characteristics of hydroxypropanone not only investigates the cracking performance of ketones, but also has high reference value for compounds containing C═O bonds, such as acids and aldehydes. Unfortunately, hydroxypropanone has a low $(H/C)_{eff}$ ratio of only 0.667, which is much lower than that of alcohols, so it is very important to maintain the activity of the catalyst during cracking. In this work, we selected ethanol as the co-cracking solvent and investigated the influence of the HPO (hydroxypropanone)/EtOH (ethanol) ratio in feed and the reaction temperature and pressure on the selectivity and composition of cracking products. Finally, some possible reaction pathways are proposed.

2. Experimental section

2.1. Materials

The hydroxypropanone was purchased from Alfa Aesar with the purity of 95% and the ethanol was purchased from Sinopharm Chemical Reagent Co. with the purity of 99.7%.

The HZSM-5 catalyst (Si/Al = 25, purchased from the Catalyst Plant of Nankai University), was calcined in the air for the activation at 550 °C for 6 h and then sieved to 40–60 mesh.

2.2. Catalyst characterization

The total acidity and acid strength distribution of HZSM-5 catalyst were determined by measuring the adsorption of NH_3 at 100 °C and the subsequent temperature-programmed desorption (TPD) of the adsorbed NH_3 with a temperature ramp of 10 °C/min up to 800 °C.

The BET specific surface areas of blank HZSM-5 and spent catalysts were measured by N2 adsorption–desorption at 77 K, using an Autosorb-1 Quantachrom apparatus.

2.3. Catalytic run

Catalytic experiments were performed in a fixed-bed reactor with a catalyst loading of 2 g. The reaction pressure was regulated with a back pressure valve, using the carrier gas nitrogen with the flow rate of 30 mL/min. The weight hourly space velocity (WHSV) of the reactants was kept at 3 h^{-1}. The outlet gases from the reactor passed through a condenser and were separated into liquid products and incondensable gases. Each experimental run lasted 3 h. The reaction temperature and pressure studied were set within the range of 340–430 °C and 0.1–3 MPa, respectively. The influences of $(H/C)_{eff}$ on the reactant conversion and the product distribution were also studied by varying the hydroxypropanone to ethanol ratios (HPO/EtOH) in the feed. The feed $(H/C)_{eff}$ were 2, 1.6, 1.33, 1.07 and 0.67, corresponding to the HPO concentration of 0, 30%, 50%, 70% and 100%, respectively.

Both the gaseous and liquid products were analyzed. Gaseous products were quantified by an online gas chromatograph (Agilent 7890A). The liquid products obtained consisted of an easily separable oil phase and an aqueous phase. The oil phase was determined by a gas chromatography–mass spectrometry system and its fractions were quantified by the area normalization method. The residual reactants in the collected liquids were quantified by gas chromatography with the external reference method, thereby allowing calculation of the conversion of the reactants based on the feed mass.

The conversion of the reactants (X_i) and the selectivity (S_i) for the liquid components are defined by Eqs. (2)–(5). The mass of HPO and EtOH was calculated by gas chromatography with the external reference method. In the calculation of selectivity, the unconverted reactants were excluded from the received liquid products. The symbol “m” in the following equations represents the mass of the corresponding substances.

$$X_{HPO} = \frac{(m_{HPO})_{in} - (m_{HPO})_{out}}{(m_{HPO})_{in}} \times 100\% \tag{2}$$

$$X_{EtOH} = \frac{(m_{EtOH})_{in} - (m_{EtOH})_{out}}{(m_{EtOH})_{in}} \times 100\% \tag{3}$$

$$S_{Oil\,phase} = \frac{\left(m_{Oil\,phase}\right)_{collected}}{(m_{Reactants})_{in} - (m_{Reactants})_{out}} \times 100\% \tag{4}$$

$$S_{Aqueous\,phase} = \frac{\left(m_{Aqueous\,phase}\right)_{collected}}{(m_{Reactants})_{in} - (m_{Reactants})_{out}} \times 100\% \tag{5}$$

The mass balance of each catalytic run was checked in terms of carbon balance, based on the carbon content in the feed and the products. The results showed that each catalytic run had a carbon balance error within ±5%.

3. Results and discussion

3.1. NH_3-TPD characterization of HZSM-5

The NH_3-TPD profile of HZSM-5 catalyst is shown in Fig. 1. Two broad peaks at low and high temperatures are corresponding to weak and medium/strong acid sites, and the maximum desorption temperatures are 190 °C and 388 °C, respectively. The total acidity of catalyst calculated based on the NH3-TPD profile is 0.45 (mmol of NH3)/(g of catalyst).

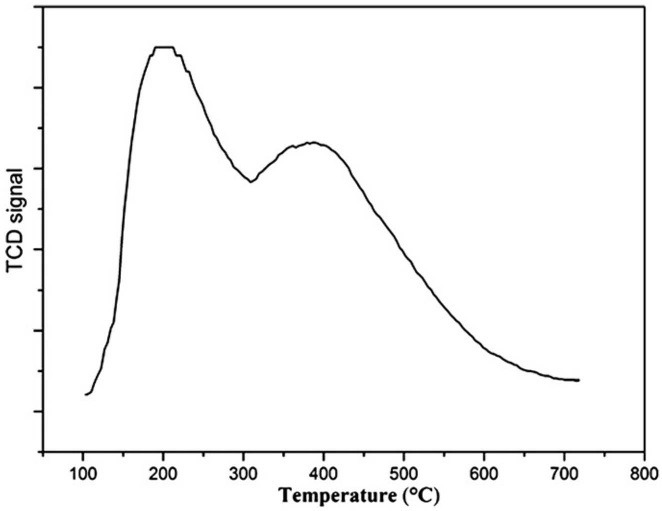

Fig. 1. NH_3-TPD profile of HZSM-5 catalyst.