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Biogasoline production by co-cracking of model compound mixture of bio-oil and ethanol over HSZM-5

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ABSTRACT

Acids and ketones in biomass pyrolysis oil (bio-oil) can be readily cracked to produce hydrocarbons. They can also be enriched in the distilled fraction using molecular distillation techniques. To simulate the actual composition of the distilled fraction, the co-cracking performance of mixtures of hydroxypropanone, cyclopentanone, and acetic acid with ethanol in a fixed-bed reactor over an HZSM-5 catalyst was studied. The influences of reaction temperature and pressure on the reactant conversion, selectivity, and composition of the oil phase were investigated. At a low reaction temperature of 340 °C, the conversions of acetic acid and ethanol were as low as 67.9% and 74.4%, respectively, and the oil phase had a low hydrocarbon content of 59.8%, with large amounts of oxygenated byproducts. Cracking under atmospheric pressure also generated a low-quality oil phase with a very low selectivity of only 10.8%. Increasing the reaction temperature promoted reactant conversion and improved the deoxygenation efficiency, whereas increasing the reaction pressure significantly promoted hydrocarbon production. The optimum conditions for biogasoline production were 400 °C and 2 MPa. Under these conditions, the reactant conversion reached 100% and the oil phase selectivity was 31.5 wt%. This oil phase consisted entirely of hydrocarbons, 91.5 wt% of which were aromatic hydrocarbons, indicating that the HZSM-5 catalyst had high activity for deoxygenation and aromatization reactions during cracking. In addition, characterization of the spent catalysts and stability tests showed that the catalyst was deactivated after a long reaction time. However, the catalytic activity was recovered by catalyst regeneration.

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1. Introduction

With the growing fossil fuel crisis and increasingly severe environmental pollution, the use of renewable and clean biomass is receiving global attention [1–3]. Among methods of using biomass, fast pyrolysis has great potential, because it can efficiently convert solid biomass to liquid bio-oil [4–6]. However, the inferior properties of bio-oil, such as high oxygen content, high water content, and instability, limit its use as a fuel

for vehicles [7]. It is therefore necessary to upgrade bio-oil for such high-grade uses.

At present, the main bio-oil upgrading techniques are catalytic cracking, catalytic hydrogenation, catalytic esterification, catalytic steam reforming, and emulsification [8]. Catalytic cracking, using a zeolite catalyst, is a promising bio-oil upgrading technique, which can remove oxygen from the bio-oil in the form of H₂O, CO, and CO₂ and convert the bio-oil to high-grade hydrocarbon fuels [9–12].

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The composition of bio-oil is very complicated. It has a high content of oxygenated components such as carboxylic acids, ketones, alcohols, aldehydes, phenols, ethers, esters, and sugars [13,14]. Although direct cracking of crude bio-oil produces some liquid hydrocarbon fuel, serious catalyst deactivation by coking occurs [15]. To investigate the detailed cracking mechanism of each component in bio-oil, the cracking behavior of different model compounds in bio-oil has been studied. It was found that some small-molecule compounds such as alcohols, acids, and ketones have high reactivities, whereas phenols have low reactivities [16,17]. In addition, macromolecules such as sugars and phenols in bio-oil easily form coke deposits on catalysts [18].

To improve the efficiency of bio-oil cracking, it is therefore necessary to enrich components with high cracking activities. Thermosensitive bio-oil can be efficiently separated into the corresponding distilled fraction and a residual fraction using the molecular distillation technique. In our previous studies on the molecular distillation of bio-oil, it was found that the distilled fraction had a high content of small-molecule ketones and acids such as hydroxypropanone (HPO), cyclopentanone (CPO), and acetic acid (HOAc), whereas macromolecules such as sugars and phenols were enriched in the residual fraction [19–21]. The cracking properties of the distilled fraction of bio-oil were therefore better than those of crude bio-oil.

Although the cracking properties of the distilled bio-oil fraction are better than those of crude bio-oil, direct cracking may still cause coking problems because of the high oxygen content and high degree of unsaturation. To evaluate the influence of oxygen content and degree of unsaturation of bio-oil on the cracking performance, some researchers have introduced the concept of the effective hydrogen to carbon ratio, $(H/C)_{\text{eff}}$ [14,22], as expressed in equation $(H/C)_{\text{eff}} = (H - 2O - 3N - 2S)/C$. Mentzel et al. [14] found that catalyst deactivation occurred more easily in the cracking of low $(H/C)_{\text{eff}}$ compounds.

According to the equation, the $(H/C)_{\text{eff}}$ values for HPO, CPO, and HOAc are only 0.67, 1.2, and 0, respectively, suggesting that the catalyst is easily deactivated during cracking of these compounds. The addition of compounds with relatively high $(H/C)_{\text{eff}}$ values as coreactants to increase the overall $(H/C)_{\text{eff}}$ may therefore be an efficient way to improve the stability of the cracking process. Aliphatic alcohols are ideal cracking coreactants because they have a relatively high $(H/C)_{\text{eff}}$ value of 2. In the study of co-cracking of methanol and bio-oil model compounds by Mentzel et al. [14], it was found that the catalyst lifetime was significantly increased and the conversion capacity increased tenfold. Valle et al. [18] used thermally treated bio-oil and then methanol for co-cracking, and the reaction stability was improved. Our previous study of the co-cracking of ketones (HPO or CPO) with alcohols also showed that the addition of alcohols enhanced the deoxygenation of ketones and the production of hydrocarbons [23,24]. In this work, mixtures of HPO, CPO, and HOAc were selected as model compounds to study the co-cracking behavior with ethanol (EtOH). The influences of reaction temperature and pressure on reactant conversion, selectivity, and composition of the oil phase were investigated to determine the most suitable reaction conditions.

2. Experimental

HPO was purchased from Alfa Aesar (Ward Hill, MA, USA), CPO was purchased from Aladdin Industrial Corporation (Shanghai, China), and HOAc and EtOH were purchased from the Sinopharm Chemical Reagent Co. (Beijing, China). In our previous studies, it was found that 70 wt% alcohols mixed with ketones efficiently generated oil phase products [23]. Therefore, mixtures containing 70 wt% EtOH and 30 wt% model compound mixture were again used in this work. Based on the HPO, CPO, and HOAc contents of crude bio-oil and their separation characteristics during molecular distillation [19–21], the weight ratio of HPO, CPO, and HOAc in the model compound mixture was set at 6:1:5, i.e., 15 wt% HPO, 2.5 wt% CPO, and 12.5 wt% HOAc. The HZSM-5 (Si/Al = 25) zeolite catalyst used in the experiments was activated at 550 °C for 6 h and then sieved to 40–60 mesh.

Catalytic cracking experiments were performed in a fixed-bed reactor. The catalyst (about 2 g) was supported on quartz wool in the reactor, which was a stainless-tube with an inner diameter of 8 mm. The mixed reactants were pumped using an HPLC pump and entered the reactor after vaporization with N₂. The reaction pressure was regulated using N₂ at a flow rate of 30 mL/min. The weight hourly space velocity of the reactants was kept at 3 h⁻¹. The outlet gases from the reactor were cooled by a condenser to separate them into liquid products and non-condensable gases. Each experimental run lasted 3 h, and the reaction temperature and pressure were set within the ranges 340–430 °C and 0.1–3 MPa.

The gaseous products were quantified using an online gas chromatograph (Agilent 7890A, Agilent Technologies, Palo Alto, CA, USA). The liquid products had an obviously separable oil phase and an aqueous phase. The oil phase was analyzed using a gas chromatography-mass spectrometry system and quantified using the area normalization method. Finally, the residual reactants in the liquid products were quantified by gas chromatography using the external reference method to calculate the conversion of the reactants based on the feed mass. The selectivities of the liquid products were calculated based on the mass of oil phase and aqueous phase collected (excluding unconverted reactants) and the mass of converted reactants.

The Brunauer-Emmett-Teller (BET) specific surface areas of blank HZSM-5 and spent catalysts were measured by N₂ adsorption-desorption at -196 °C, using an Autosorb-1 Quantachrome apparatus.

3. Results and discussion

3.1. Effects of reaction temperature and pressure

3.1.1. Reactant conversion

The effect of temperature on the conversion of the model compound mixture and EtOH at 2 MPa is shown in Fig. 1(a). At 340 °C, HPO and CPO were almost completely converted, but the conversions of HOAc and EtOH were low, 67.9% and 74.4%, respectively. This might be a result of the low catalytic capacity of the catalyst at low temperature and the low activities of

Fig. 1. Conversion of reactants using different conditions: (a) 2 MPa; (b) 400 °C.

HOAc and EtOH molecules, whereas HPO and CPO showed higher activities. However, the converted HPO molecules mainly underwent intermolecular dehydration reactions to form ketones and other oxygenated byproducts at low reaction temperatures [23]. In a study of CPO conversion over acidic zeolites by Huang et al. [25], it was also found that CPO tended to form oxygenated polymers by condensation at low temperatures. Therefore, although the conversion of ketones is very high at low temperatures, the products may not be the desired hydrocarbons. The conversion of HOAc at low temperatures has been proved by Gayubo et al. [17] to be very difficult. They found that acetone, which is produced by ketonization of HOAc

during cracking, was generated in large amounts when the temperature was above 400 °C. As the temperature was reduced to 370 °C, the conversion of EtOH clearly increased to 89.5%, and the conversion of HOAc also increased to 72.8%, but the conversions of HPO and CPO decreased slightly. The main reason for this phenomenon might be that increasing the reaction temperature leads to an increase in the molecular activities of HOAc and EtOH, but the catalytic capacity is not sufficiently high. Consequently, competition occurs among the reactants, leading to an increase in HOAc and EtOH conversions, but has little effect on the HPO and CPO conversions. At 400 °C or above, the catalytic capacity improved further, and not only were the high conversions of HPO and CPO maintained, but HOAc and EtOH were almost completely converted.

Figure 1(b) shows the conversion of the model compound mixture and EtOH at 400 °C at different reaction pressures. HPO, CPO, HOAc, and EtOH all showed conversions of 97% or more under these pressurized conditions and were almost completely converted when the pressure was increased to above 2 MPa. At atmospheric pressure, HPO was also almost completely converted, but the conversions of CPO, HOAc, and EtOH were low, 83.6%, 85.6%, and 93.1%, respectively.

3.1.2. Liquid-product selectivity

The liquid product obtained by cracking consisted of two separable layers. The upper layer was an oil phase product, and the bottom layer was a clear aqueous-phase product, as shown in Fig. 2(a). In addition, the oil phases obtained under different conditions were different colors, as shown in Fig. 2(b), indicating that the compositions of the oil phases were distinct.

Figure 3(a) shows the liquid product selectivities at 2 MPa and different temperatures. At 340 °C, although the oil phase selectivity was 33.1%, the oil phase was brown in appearance, suggesting that it contained many oxygenated byproducts. When the reaction temperature rose to 370 °C, the color of the oil phase changed to fawn. So, although the oil phase selectivity decreased to 27.6%, the actual selectivity for hydrocarbons might be higher. At 400 °C or above, the oil phase selectivity remained above 31%, and the oil phase was light yellow. Based

Fig. 2. (a) Photographs of liquid products showing two separable phases at 400 °C/2 MPa; (b) Oil phases obtained under different reaction conditions.

Fig. 3. Reactant selectivities under different reaction conditions: (a) 2 MPa; (b) 400 °C.

on these selectivity variations, we conclude that reaction temperatures above 400 °C are not only conducive to complete conversion of the reactants but also favor oil phase formation. A comparison of the oil phase selectivity in co-cracking of individual ketones (HPO or CPO) with alcohols, which was around 31.8% [23,24], showed that the addition of HOAc did not affect the oil phase selectivity. This showed that HOAc also has good capacity for oil phase generation. This is because HOAc is first cracked to produce acetone, followed by acetone condensation and deoxygenation to produce hydrocarbons [17].

The liquid product selectivities at 400 °C and different reaction pressures are shown in Fig. 3(b). At atmospheric pressure, the oil phase selectivity was only 10.8%, and the product was dark brown, whereas the aqueous phase selectivity was 47.5%. Under pressurized conditions, the oil phase selectivities

reached 27.1%, 31.5%, and 32.2% at 1, 2, and 3 MPa, respectively. This demonstrated that pressurized conditions could also promote oil phase formation.

3.1.3. Oil phase composition

The oil phase composition at 400 °C and 2 MPa is shown in Fig. 4. This oil phase consisted mainly of aromatic hydrocarbons with carbon numbers in the range 7–10; these are also important components of commercial gasoline. To enable a clear comparison of the compositions of the oil phases obtained under different conditions to be made, the compounds in the oil phase are classified into aromatics, aliphatics, ketones, ethers, and esters. The results are summarized in Fig. 5; “340 °C/2 MPa” refers to co-cracking of the model compound mixture and EtOH at 340 °C and 2 MPa.

Figure 5(a) shows the oil phase compositions at different temperatures. At 400 and 430 °C, the oil phase contained high contents of hydrocarbons, greater than 99%. The hydrocarbons were mainly C₇–C₁₀ aromatic hydrocarbons, including toluene, xylene, and methyl-ethyl-benzenes. When the reaction temperature was lower than 400 °C, oxygenated byproducts were generated. Under the conditions 340 °C/2 MPa, the content of oxygenated compounds in the oil phase was 40.2%, and the content of oxygenated byproducts reached 18.2% using the conditions 370 °C/2 MPa. The main oxygenated byproducts were ketones, ethers, esters, and other alcohols. The molecular structures of these oxygenated byproducts suggest that the large-molecule ketones were mainly derived from aldol condensation reactions between HPO, CPO, and acetone [23,26]. The ether content was also high, mainly produced by EtOH etherification. Esters, in particular ethyl acetate, were typical products of the esterification of HOAc and EtOH. To ensure complete deoxygenation of the model compound mixture and EtOH, a reaction temperature above 400 °C is necessary. As the reaction temperature increased, the aromatic hydrocarbon content in the oil phase also increased. This indicates that raising the reaction temperature could promote aromatization reactions; this has also been observed by other researchers [17].

Fig. 4. Oil phase composition at 400 °C and 2 MPa.

Fig. 5. Oil phase compositions under different reaction conditions: (a) 2 MPa; (b) 400 °C.

The oil phase from co-cracking of the model compound mixture and EtOH had a high content of aromatic hydrocarbons, implying that the reactants might be converted by a double-route transformation mechanism, as proposed in our previous study [23,24]. In the first direct-cracking route, HPO, CPO, and acetone from the primary cracking of HOAc undergo aldol condensation and subsequent decarbonylation, decarboxylation, and dehydration reactions to form olefins, H₂O, and CO_x, and then the olefins undergo further polymerization to form hydrocarbon products [17,26]. The second mechanism, the “hydrocarbon pool” mechanism, is associated with active intermediates such as methyl-substituted benzenes (such as toluene and xylene) [27,28]. HPO, CPO, and the intermediate acetone first undergo hydrogen transfer and molecular reforming on the zeolite acidic sites to form enol intermediates containing hydroxyl groups [25]. The enol intermediates and EtOH then react with the active intermediates and are deoxygenated, forming H₂O and olefins, which ultimately undergo aromatization to generate aromatic hydrocarbons [27,28].

The oil phase compositions at different reaction pressures are shown in Fig. 5(b). The total hydrocarbon contents in the oil phase at 400 °C/1 MPa, 400 °C/2 MPa, and 400 °C/3 MPa were above 97%, and the contents of the corresponding aromatics reached 89.5%, 91.5%, and 92.4%, respectively. However, the hydrocarbon content in the oil phase using conditions 400 °C/0.1 MPa decreased significantly, to 66.3%. Along with low oil phase selectivity, the yield of liquid hydrocarbons was very low. The influence of pressure is related to the reaction equilibrium. Light olefins such as C₂H₄ are important intermediates in bio-oil cracking [19,29]. In the aromatization reac-

tions, where light olefins are converted to liquid hydrocarbons, the total stoichiometric number of the products is smaller than that of the reactants. When the pressure increases, the reaction equilibrium therefore moves to the right, which facilitates the conversion of light olefins to liquid hydrocarbons. When the reaction pressure is increased to 2–3 MPa, as a result of limitation of the catalytic capability of the catalyst, the effect of pressure on the reaction equilibrium is not so obvious, so the hydrocarbon selectivity remains constant.

3.1.4. Vent gas composition

The vent gas compositions under different conditions are shown in Table 1. The general distribution of gaseous products shows that the vent gases generated using good reaction conditions (400 °C/2 MPa, 430 °C/2 MPa, 400 °C/1 MPa, and 400 °C/3 MPa) all had high contents of CO_x and C₃H₈. A high concentration of CO_x in the vent gas indicates extensive decarbonylation and decarboxylation reactions, which are beneficial for the removal of oxygen; C₃H₈, a saturated light hydrocarbon, might come from an aromatization reaction, in which light olefins are converted to highly unsaturated aromatics. As the reaction temperature or pressure decreased, the concentration of CO_x in the vent gas decreased, indicating that deoxygenation reactions such as decarbonylation and decarboxylation were suppressed, and more oxygenated byproducts were produced. In addition, the concentration of C₂H₄ in the vent gas increased significantly when the reaction temperature or pressure dropped, suggesting that a lower temperature or pressure suppressed aromatization reactions, and intermediate olefins were released instead of being involved in aromatization reactions to form liquid hydrocarbons. This is in good agreement with the lower oil phase selectivity at lower reaction temperature or pressure.

3.2. Characterization of spent catalysts

Catalyst stability is important in catalytic cracking processes, and the main cause of catalyst deactivation is coke formation. The spent catalysts were characterized by N₂ physical adsorption and thermogravimetric analysis. The textual properties and coke analysis of the spent catalysts are listed in Table 2.

After reaction for 3 h, the specific surface areas of the spent catalysts all decreased compared with the blank HZSM-5 catalyst, which has a high specific surface area of 340.0 m²/g. Gen-

Table 1
Vent gas compositions under different conditions (%).

Conditions	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀
340 °C/2 MPa	1.6	1.8	0.1	89.1	0.4	3.1	3.4	0.1	0.5
370 °C/2 MPa	4.5	5.4	0.5	69.0	2.3	5.1	11.3	0.6	1.3
400 °C/2 MPa	16.4	15.3	1.8	3.4	8.5	1.8	40.5	10.1	2.2
430 °C/2 MPa	19.7	15.2	4.1	0.2	10.5	0.2	38.4	8.2	3.5
400 °C/0.1 MPa	1.2	1.1	0.1	88.6	0.8	7.8	0.0	0.1	0.4
400 °C/1 MPa	12.7	13.3	1.9	2.9	8.0	2.4	38.4	14.4	5.9
400 °C/3 MPa	19.5	15.4	3.0	0.5	9.4	0.4	38.9	9.2	3.8

Table 2

Textural properties and coke analysis of catalyst.

Conditions	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	C/Cat
400 °C/2 MPa	95.5	0.11	5.42	0.15
430 °C/2 MPa	101.9	0.12	5.21	0.15
370 °C/2 MPa	75.9	0.08	5.89	0.16
340 °C/2 MPa	70.6	0.08	6.02	0.18
400 °C/3 MPa	103.0	0.14	5.32	0.14
400 °C/1 MPa	89.4	0.09	5.66	0.14
400 °C/0.1 MPa	40.9	0.07	6.38	0.18
Blank	340.0	0.26	3.09	—

erally, under conditions that gave gasoline phases of higher selectivity and quality, the corresponding catalyst specific surface areas were higher. For example, the specific surface of the catalyst from 400 °C/2 MPa was 95.5 m^2/g , whereas those from 340 °C/2 MPa and 400 °C/0.1 MPa were 70.6 and 40.9 m^2/g , respectively, showing that the catalytic activity was better maintained under the conditions 400 °C/2 MPa. The coke:catalyst ratio (C/Cat), calculated based on the thermogravimetric analysis, showed the same tendency. The C/Cat was 0.15 for the conditions 400 °C/2 MPa, but those for 340 °C/2 MPa and 400 °C/0.1 MPa both reached 0.18.

In our previous study of co-cracking of HPO and EtOH, the spent catalysts after reaction for 3 h were characterized, and the catalyst from co-cracking of 30% HPO and 70% EtOH under the conditions 400 °C/2 MPa had a specific surface area of 129.3 m^2/g and a C/Cat of 0.12. Compared with these results, the catalyst from co-cracking of the model compound mixture and EtOH had a lower specific surface area but a higher C/Cat, indicating that the decrease in the catalytic activity was more severe. The model compound mixture has only a small proportion of CPO, which might have a similar cracking performance to that of HPO, because they both have carbonyl groups, therefore it can be concluded that the more obvious deactivation tendency was the result of the presence of HOAc. As mentioned above, the $(\text{H}/\text{C})_{\text{eff}}$ values of HOAc, HPO, and CPO are 0, 0.67, and 1.2, respectively. Cracking of HOAc, which has a low $(\text{H}/\text{C})_{\text{eff}}$, would therefore favor production of compounds with low $(\text{H}/\text{C})_{\text{eff}}$ values, such as coke. In the study carried out by Mentzel et al. [14], in which 10% HOAc and 10% acetone, respectively, were cocracked with methanol the catalyst conversion capacities during co-cracking of acetone and methanol were found to be much higher than that of HOAc, indicating that the catalyst lifetime was longer for the co-cracking of acetone and methanol. Coking and catalyst deactivation were therefore higher for cracking of the model compound mixture containing HOAc than those for cracking of individual ketones.

3.3. Catalyst stability tests

The catalyst characterization described in Section 3.2 showed that the specific surface area of the catalyst decreased after reaction for 3 h, and some coke formed on the catalyst surface, indicating that the catalytic activity decreased during cracking. The catalyst stability was therefore tested under the conditions 400 °C/2 MPa.

Fig. 6. Reactant conversion as a function of time on stream at 400 °C/2 MPa.

3.3.1. Reactant conversion

The changes in reactant conversion as a function of time on stream are presented in Fig. 6. Before 240 min, the four reactants, i.e., HPO, HOAc, CPO, and EtOH, were all converted almost completely. As the reaction continued, the conversion of HOAc began to decrease, from 76.7% at 240 min to 7.2% at 330 min, but the conversions of the other three reactants were still close to 100%. This showed that the decrease in the catalytic activity had a stronger effect on the primary conversion of HOAc than on those of the other reactants, which led to decreased conversion.

3.3.2. Liquid product selectivity

Figure 7 shows the changes in liquid product selectivity as a function of time on stream. In the primary stage of cracking, the oil phase selectivity remained at about 31%. It started to drop at 210 min and reached 3.5% at 330 min. Compared with the changes in reactant conversion, in which only the HOAc conversion decreased, the decrease in oil phase selectivity occurred earlier, and the changes were greater, showing that the decrease in the catalytic activity had a greater effect on the formation of oil phase products. The main components in the oil phase, i.e., aromatic hydrocarbons, were generated by aromatization, so it can be concluded that the aromatization ca-

Fig. 7. Liquid product selectivity as a function of time on stream at 400 °C/2 MPa.

capacity of the catalyst was first affected when catalyst deactivation started, and the primary conversion capacity of the reactants was affected to a lesser extent. Unlike the case for the oil phase, the aqueous phase selectivity continued to increase slightly even when the catalyst was deactivated; this also indicated that the primary conversion of reactants involving dehydration was not significantly affected.

3.3.3. Oil phase composition

The changes in the oil phase composition as a function of time on stream are shown in Fig. 8. Prior to 180 min, the oil phase had a stable composition consisting of about 90% aromatic hydrocarbons, 9% aliphatic hydrocarbons, and few oxygenated byproducts. As the reaction continued, accompanied by catalyst deactivation, the aromatic hydrocarbon content decreased, and the aliphatic hydrocarbon and oxygenated by-product contents both increased. At a reaction time of 330 min, the aromatic hydrocarbon content was only 50%, and the contents of aliphatic hydrocarbons and oxygenated byproducts reached 31.6% and 18.4%, respectively. The decrease in the aromatic hydrocarbon content reflected the lower aromatization capacity of the catalyst, and the production of larger amounts of oxygenated byproducts, mainly alcohols and ketones, showed a reduction in the deoxygenation efficiency.

3.3.4. Vent gas composition

The changes in vent gas composition as a function of time on stream are shown in Fig. 9. In general, the concentrations of the gaseous products except C_2H_4 all decreased. In the primary cracking period, the main gaseous products were C_3H_8 , CO, and CO_2 , with concentrations of about 40%, 16%, and 15%, respectively. As the catalytic activity decreased, the concentrations decreased to 33.6%, 13.9%, and 12.3% at 210 min. The concentration of C_2H_4 increased greatly, from 3% to 17.9%, at this time. The discussion of the oil phase selectivity in section 3.3.2 showed that the decrease in the oil phase selectivity also began at 210 min, further proving that this decrease was a result of the weaker aromatization capacity of the catalyst, and the intermediate C_2H_4 was released instead of participating in the subsequent aromatization reaction. When the reaction time

Fig. 8. Oil phase composition as a function of time on stream at 400 °C/2 MPa.

Fig. 9. Vent gas composition as a function of time on stream at 400 °C/2 MPa. (a) Light hydrocarbons; (b) CO_x .

was 330 min, the concentrations of C_3H_8 , CO, and CO_2 declined to 1.9%, 2.4%, and 2.7%, respectively; the concentrations of other gaseous products were lower than 1%, whereas the concentration of C_2H_4 was 90.8%. This indicated the low extent of the aromatization reaction, in good agreement with the very low oil phase selectivity of 3.5% at this point.

3.4. Catalyst regeneration

In the catalyst stability tests, the catalytic activity was found to decrease as the reaction proceeded. Catalyst deactivation was mainly caused by coke formation on the catalyst surface, which would cover the active sites and block the inner pores. The spent catalyst after reaction for 4 h under the conditions 400 °C/2 MPa was regenerated by burning the coke, and the extent of recovery of the catalytic activity was studied. The regeneration temperature was 550 °C based on the study by Valle et al. [18], and the catalyst was regenerated four times.

3.4.1. Reactant conversion

The changes in reactant conversions before and after catalyst regeneration are shown in Fig. 10. During the reaction stage using the fresh catalyst, the conversions of HPO, CPO, and EtOH were close to 100%, but the conversion of HOAc declined to 76.7% at 240 min. After the first regeneration of the catalyst, the conversion of HOAc returned to above 99%, and the conversions of the other three reactants remained above 99%. Similarly, in the subsequent continuous reaction, the regenerated catalysts all achieved good recovery of catalytic activity.

3.4.2. Liquid product selectivity

The changes in liquid product selectivities before and after catalyst regeneration are shown in Fig. 11. Before the first re-

Fig. 10. Reactant conversions before and after catalyst regeneration at 400 °C/2 MPa.

Fig. 11. Liquid-product selectivity before and after catalyst regeneration at 400 °C/2 MPa.

generation, the oil phase selectivity dropped from about 31% at the primary stage to only 19.3%. After catalyst regeneration, the oil phase selectivity was again above 30%. In the subsequent continuous reaction, the catalytic activity recovered well in the regeneration steps and maintained steady generation of the oil phase. In general, the catalyst regeneration extended the catalyst lifetime.

3.4.3. Oil phase composition

Figure 12 shows the changes in the oil phase composition before and after catalyst regeneration. Compared with those in the primary stage, the content of aromatic hydrocarbons declined from 92.0% to 79.1% at 240 min, and the contents of aliphatic hydrocarbons and oxygenated byproducts rose to 15.2% and 5.7%, respectively. After catalyst regeneration, the content of aromatic hydrocarbons returned to above 90%, indicating that the aromatization capacity of the catalyst was well recovered by regeneration.

3.4.4. Vent gas composition

The catalyst stability tests showed that the concentrations of CO, CO₂, C₂H₄, and C₃H₈ changed significantly when the catalyst was deactivated. The concentrations of these four gaseous products before and after catalyst regeneration were therefore monitored; the results are shown in Fig. 13. When the catalyst

Fig. 12. Oil phase composition before and after catalyst regeneration at 400 °C/2 MPa.

Fig. 13. Vent gas composition before and after catalyst regeneration at 400 °C/2 MPa.

was deactivated, the concentrations of CO and CO₂ decreased, and the concentration of C₃H₈ decreased greatly from 43% to 22.6%, whereas the concentration of C₂H₄ increased significantly from 2.6% to 32.6%. After regeneration, the concentration of C₂H₄ was below 5% again, suggesting good recovery of the aromatization capacity, which favored conversion of the intermediate C₂H₄ to liquid hydrocarbons.

4. Conclusions

The co-cracking performance of mixtures of bio-oil model compounds (HPO, CPO, and HOAc) with EtOH was investigated in a fixed-bed reactor. Higher temperatures and pressures promote conversion of the reactants and generation of liquid hydrocarbons. The optimum reaction conditions were found to be 400 °C and 2 MPa. Under these conditions, acids and ketones were converted completely, and the oil phase selectivity

Graphical Abstract

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Biogasoline production by co-cracking of model compound mixture of bio-oil and ethanol over HZSM-5

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Co-cracking with ethanol using an HZSM-5 catalyst is an efficient method for converting a bio-oil model compound mixture to hydrocarbon fuels.

reached 31.5 wt%. This oil phase had a high hydrocarbon content, greater than 99%, and mainly contained C₇–C₉ aromatic hydrocarbons such as toluene, xylene, and methyl- and ethyl-substituted benzenes. Characterization of the spent catalysts showed that the specific surface area decreased after cracking, and some coke formed on the catalyst surface. Stability tests also showed that the catalyst was deactivated after 330 min. The catalyst was regenerated by burning the coke and the regeneration achieved good recovery of the catalyst. Because the bio-oil distilled fraction was rich in small-molecule ketones and acids, the successful conversion of ketones and acids to hydrocarbons proves that the co-cracking of actual bio-oil distilled fractions and EtOH is feasible.

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生物油酸酮类模化物与乙醇在HZSM-5上共裂化制备生物汽油

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摘要: 生物油中酸类和酮类化合物具有较高的裂化活性, 而使用分子蒸馏技术能将这些组分富集到蒸出馏分中, 因此蒸出馏分相比原始生物油具有更好的裂化特性. 为了模拟实际蒸出馏分的组成, 本文将生物油模化物(羟基丙酮(HPO)、环戊酮和乙酸)进行配

比混合,在固定床反应器上对其与乙醇的共裂化行为进行了研究,考察了不同反应温度和压力对混合反应物的转化率、粗汽油相的选择性和组成的影响。研究发现,当反应温度在340 °C时,乙酸和乙醇的转化率分别仅为67.9%和74.4%,同时得到的油相产物中烃类含量仅为59.8%,并含有大量的含氧副产物。常压裂化同样生成了低品质的油相产物,同时油相选择性仅为10.8%。提高反应温度能促进反应物的转化,提高裂化过程中的脱氧效率,而提高反应压力对液体烃类的生成有明显的促进作用。在400 °C和2 MPa时,酸类和酮类都有良好的裂化表现,反应物接近完全转化,粗汽油相选择性达到31.5%,且全部由烃类组成,其中芳香烃含量高达91.5%。此外,反应后催化剂表征和稳定性测试结果表明,催化剂在较长时间反应后会失活,但通过催化剂再生能够很好地恢复催化剂活性。

关键词: 生物油; 分子蒸馏; 混合模化物; 催化裂化; 生物汽油

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1. 前言

随着化石能源日渐短缺和环境问题日趋严重,生物质以其可再生和低污染等特性而备受关注^[1-3]。在众多生物质利用技术中,快速热裂解具有较大潜力,它能高效地将固态生物质转化为能量密度高、易运输、易储存的液态生物油^[4-6]。但是生物油的低热值、高含氧量、高水分含量和热不稳定性等燃料特性上的不足阻碍了其高品位利用^[7]。

品位提升工艺是克服生物油以上不足的一个重要环节,它包括催化加氢、催化裂化、水蒸气催化重整、催化酯化和乳化等^[8]。其中,催化裂化^[9-12]可通过催化剂将生物油中的氧元素以H₂O、CO和CO₂等形式脱除,使生物油转变为高品位液体烃类产物,大大降低生物油含氧量和粘度,同时提高生物油稳定性和热值,是未来较有潜力的生物油品位提升方法。

生物油组成复杂,富含酸、醛、酮、醇、酚、酯、醚和糖等各种含氧化合物^[13,14]。因此,以全组分生物油为原料进行裂化时,虽能得到一定品质的液体烃类燃料,但是在裂化过程中存在较为严重的结焦堵塞及催化剂失活问题^[15]。为了深入探究生物油中各组分裂化机理,研究者对生物油不同族类模化物的裂化行为进行了研究,发现醇、酸和酮等小分子物质具有较高的裂化活性,而酚类等反应活性较低^[16,17]。同时,生物油中大分子的糖类和酚类聚合物在进入催化床层后很容易沉积并形成焦炭^[18]。

因此,为了提高生物油组分的裂化效率,首先要实现生物油中适宜裂化组分的富集。结合分子蒸馏技术,可以实现热敏性生物油的高效分离,获得相应的生物油蒸出馏分和残余馏分。在我们前期对生物油的分子蒸馏特性研究中发现,蒸出馏分富集了生物油中的酮类和酸

类等小分子化合物,如羟基丙酮(HPO)、环戊酮(CPO)和乙酸(HOAc)同时大分子的糖类和酚类得到了良好脱除^[19-21]。因此,生物油蒸出馏分与原始生物油相比具有更好的裂化表现。

尽管生物油蒸出馏分的裂化特性优于原始生物油,但其直接裂化仍存在结焦问题,主要原因是蒸出馏分仍具有较高的含氧量和不饱和度。在生物油催化裂化的研究中,一些研究者通过引入有效氢碳比(H/C)_{eff}的概念来评估生物油中含氧量和不饱和度对催化剂寿命的影响^[14,22],公式为(H/C)_{eff}=(H-2O-3N-2S)/C。Mentzel等^[14]发现催化剂更容易在低(H/C)_{eff}化合物裂化过程中失活。因此,可以推断生物油中较高含氧量和不饱和度导致的较低的(H/C)_{eff},是导致裂化过程中催化剂失活的主要原因。

通过上式计算生物油馏分油典型模化物的(H/C)_{eff}发现,羟基丙酮仅为0.67,环戊酮仅为1.2,乙酸为0。故这几种生物油模化物在反应过程中较容易形成积炭造成催化剂失活。因此,需要加入一些具有相对较高(H/C)_{eff}的化合物进行共裂化,通过提高裂化过程反应物的整体(H/C)_{eff}来提高反应的稳定性。醇类具有相对较高的(H/C)_{eff}、良好的稳定性和溶解性,是一种理想的共裂化溶剂。Mentzel等^[14]研究了甲醇和生物油模化物的共裂化,发现催化剂寿命明显提高,其转化能力达到原来的10倍以上。Valle等^[18]使用热处理后的生物油与甲醇共裂化,同样使反应稳定性得到提高。我们之前研究了生物油酮类模化物(环戊酮和羟基丙酮)与醇类的共裂化,获得了高品质的汽油相产物,同时催化剂的稳定性较好^[23,24]。本文沿用前期的共裂化思路,以羟基丙酮、环戊酮与乙酸为主要研究对象,将它们按照在生物油蒸出馏分中的分布进行配比来模拟实际蒸出馏分,并以乙醇为共裂化反应物,研究它们的共裂化行为,考察温度和压力

对裂化产物选择性和组成的影响, 寻找反应最适宜工况。

2. 实验部分

羟基丙酮购自阿法埃莎公司, 环戊酮购自阿拉丁公司, 乙酸和乙醇购自国药化试公司买。前期研究发现, 使用70%乙醇掺混到酮类模化物中进行共裂化能高效生成汽油相产物^[24]。因此, 本实验继续采用70%乙醇和30%混合模化物配比。同时, 基于羟基丙酮、环戊酮和乙酸在原始生物油中的含量及其分子蒸馏分离特性^[19–21], 混合模化物中羟基丙酮:环戊酮:乙酸 = 6:1:5, 即15%羟基丙酮, 2.5%环戊酮和12.5%乙酸。使用的催化剂为HZSM-5(Si/Al = 25)分子筛。HZSM-5催化剂在反应前以5 °C/min的速率升温至550 °C活化6 h, 并筛分至40–60目。

裂化实验在固定床反应器上进行, 装填2 g的催化剂到内径为8 mm的不锈钢管里, 用石英棉支撑。反应物通过HPLC泵输送给料, 经汽化后与载气N₂一起进入反应器中, 反应压力由N₂维持, 其流量为30 mL/min。反应物的质量空速(WHSV)恒定为3 h⁻¹。反应器出口气体经冷凝器冷却, 得到液体产物和不可冷凝的气体。单次工况运行3 h, 研究的反应温度为340–430 °C, 反应压力为0.1–3 MPa。

实验获得的产物包括气体和液体产物。气体产物通过在线气相色谱(安捷伦7890A)进行定量分析。裂化液体产物存在明显的分层, 包括粗汽油相与水相。粗汽油相采用气相色谱与质谱联用仪器(GC-MS)进行定性与面积归一法定量分析。液体产物(包括粗油相和水相)中的残余反应物采用气相色谱外标法进行定量, 用于计算反应物转化率。液体产物的选择性根据收集到的粗油相和水相(不包括未转化的反应物)和转化的反应物质量进行计算。

空白和反应后HZSM-5催化剂的比表面积通过–196 °C下的N₂物理吸附测定, 使用的设备为Autosorb-1 Quantachrome全自动比表面与孔径分布分析仪。

3. 结果与讨论

3.1. 反应温度与压力的影响

3.1.1. 反应物转化率

不同反应温度下模化物混合物与乙醇的转化率如图1(a)所示。在340 °C时, 羟基丙酮和环戊酮趋于完全转化, 而乙酸和乙醇的转化率分别仅有67.9%和74.4%。这可能是由于低温下催化剂的催化裂化能力较弱, 同时乙

酸和乙醇分子活性也较低, 导致它们难以完全转化。在我们之前对羟基丙酮与乙醇的共裂化研究中也发现, 在较低的反应温度下羟基丙酮就有良好的反应活性, 而乙醇反应活性较低, 但羟基丙酮低温下主要发生的是分子间脱水缩合生成酮类等含氧副产物^[23]。Huang等^[25]对环戊酮在酸性分子筛上的转化研究中也发现低温下环戊酮同样也容易发生缩合形成含氧多聚物。因此, 尽管酮类在低温下转化率较高, 但反应可能不是生成目标产物。低温下乙酸的转化较为困难, Gayubo等^[17]发现乙酸裂化的中间产物丙酮需要在400 °C左右的反应温度下才开始大量生成。当温度增大至370 °C时, 乙醇转化率大幅提高到89.5%, 乙酸转化率也增加到72.8%, 而羟基丙酮和环戊酮的转化率则略有降低。这可能是由于温度上升时乙酸和乙醇的分子活性增加, 但受370 °C时催化剂催化能力限制, 与羟基丙酮和环戊酮在催化剂上的转化发生一定竞争, 使得自身转化率增加而羟基丙酮和环戊酮的转化率降低。当反应温度进一步升高至400 °C及以上时, 催化剂催化能力提高实现了乙酸和乙醇的顺利活化, 不仅羟基丙酮和环戊酮继续保持较高的转化率, 乙醇和乙酸也同时接近完全转化。因此, 为了实现模化物混合物与乙醇的完全转化, 反应温度需要控制在400 °C以上。

不同反应压力下模化物混合物与乙醇的转化率如图1(b)所示。在400 °C的反应温度下, 加压时反应物羟基丙酮、环戊酮、乙酸和乙醇的转化率都达到97%以上, 且当压力增加到2 MPa以上时反应物均接近于完全转化; 在常压时, 羟基丙酮转化率达到100%, 但环戊酮、乙酸和乙醇转化率却偏低, 分别为83.6%, 85.6%和93.1%。因此, 保持一定的压力对促进反应物转化是有利的。

3.1.2. 液体产物选择性

反应收集到的液体存在着明显的分层现象, 上层为粗汽油相, 下层为澄清的水相(图2(a)); 且不同工况下汽油相的颜色也不同(图2(b))。

不同反应温度下液体产物的选择性如图3(a)所示。当反应温度为340 °C时, 尽管有33.1%的粗汽油相选择性, 但粗汽油相外观呈黄褐色, 即其中可能含有较多的含氧副产物。当反应温度升高至370 °C时, 粗汽油相颜色开始呈现淡黄褐色, 因此尽管370 °C时粗汽油相选择性比340 °C时有所降低, 为27.6%, 但实际烃类选择性可能较高。当反应温度升高至400 °C及以上时, 粗汽油相的选择性稳定在31%以上, 且收集到的粗汽油相为淡黄色, 说明400 °C以上的反应温度不仅有利于反应物的完全转化, 还能促进汽油相的有效生成。与400 °C时酮类

(羟基丙酮和环戊酮)分别单独与醇类裂化的粗汽油相产率(31.9%和31.6%)相比,乙酸的添加并未明显影响汽油相的产率^[23,24]。这说明乙酸也有很好的裂化制备汽油相的能力,即乙酸能顺利通过丙酮等中间产物进一步按照酮类的裂化机理产生烃类^[17]。

不同反应压力下液体产物的选择性如图3(b)所示。常压下粗汽油相的选择性仅为10.8%,且汽油相为深褐色,而水相的选择性则高达47.5%。而在加压条件下(1, 2和3 MPa),粗汽油相的选择性分别可达27.1%, 31.5%和32.2%。这说明加压对粗汽油相的生成有明显的促进作用。

3.1.3. 粗汽油相组成

400 °C/2 MPa工况下粗汽油相的组成如图4所示,该汽油相主要由C₇–C₁₀的小分子芳香烃组成,而这些小分子芳香烃同时也是市售汽油的主要成分。为了清楚比较不同工况下粗汽油相的组成,对这些裂化产物按照芳香烃、脂肪烃、酮类、醚类和酯类等进行归类分析,获得了如图5所示的组成信息。其中“340 °C/2 MPa”表示模化物混合物与乙醇在340 °C和2 MPa下的裂化实验工况。

图5(a)给出了不同反应温度下粗汽油相的组成。当反应温度为400和430 °C时,获得的粗汽油相基本上由烃类组成,芳香烃含量分别达到91.5%和94.1%,组成上主要是以C₇–C₁₀的小分子液体烃类为主,包括甲苯、二甲苯和甲基乙基苯等汽油中的重要组分。当反应温度低于400 °C时,粗汽油中含氧副产物开始生成,粗汽油品质下降。340 °C/2 MPa工况下得到的粗汽油相中含氧副产物含量高达40.2%,而在370 °C/2 MPa工况时得到的粗汽油相中含氧副产物含量也达到18.2%。生成的含氧副产物主要包括酮类、醚类、酯类及其他醇类等。从这些副产物的组成和分子结构来看,羟基丙酮、环戊酮及乙酸的中间产物丙酮可能在裂化过程中发生羟醛缩合等反应形成醚类、醇类、呋喃类和新的结构复杂的酮类^[23,26];乙酸和乙醇则可能发生典型的酯化反应生成酯类。这些副产物的产生主要是由于较低的反应温度影响了反应物的活性和催化剂的催化能力,使得脱氧过程不能完全进行。因此,400 °C以上的反应温度是保证裂化反应完全进行所必需的。同时,随着反应温度升高,粗汽油相中的芳香烃含量不断增大,表明反应温度与芳构化程度成正相关,这也被其他研究者所证实^[17]。

模化物混合物与乙醇共裂化反应的汽油相中富含芳香烃的现象恰好符合了我们在之前研究中提出的反应物双路径转化(直接裂化和烃池转化)机理^[23,24]。对于

直接裂化反应路径,反应物羟基丙酮、环戊酮和乙酸初步裂化生成的丙酮可能发生缩合以及后续的脱羰基、脱羰基和脱水反应得到烯烃、H₂O, CO和CO₂,再由烯烃进一步聚合得到烃类产物^[17,26]。而烃池转化路径则可能与汽油相中的甲基取代苯这类活性中间体(如甲苯、二甲苯和三甲苯等)有关^[28,29]。羟基丙酮、环戊酮和乙酸裂化中间产物丙酮首先在分子筛酸性位上通过氢键转移和分子重整转变为含有羟基的烯醇类中间结构^[26]。随后,这些含羟基的中间产物以及共裂化反应物乙醇与活性中间体发生作用,并以H₂O的形式脱氧生成烯烃,并最终发生芳构化得到芳香烃等产物,进一步丰富烃类^[27,28]。

不同反应压力下粗汽油相组成如图5(b)所示。400 °C/1 MPa、400 °C/2 MPa和400 °C/3 MPa这三个加压工况下得到了很好的粗汽油相品质,烃类含量在97%以上,其中400 °C/2 MPa和400 °C/3 MPa更是达到99.5%以上;相应的芳香烃含量分别为89.5%、91.5%和92.4%。而常压裂化得到的粗汽油相烃类含量降至66.3%,由于实验中该工况下粗汽油相的选择性很低,故实际的烃类产率相当低,同时还存在一定的酮类和醚类等含氧化合物。在生物油含氧化合物裂化反应中,轻质烯烃例如C₂H₄是一种重要的反应中间体^[19,29],在裂化过程中这些轻质烯烃会在催化剂作用下转变为液体烃类产物,而且反应后气体的分子数减少。由于增加压力时化学平衡向气体分子数减小的方向移动,故增加压力将有利于轻质烯烃向液体烯烃转变。当压力增加到2–3 MPa时,受到催化剂催化能力的限制,压力对反应平衡的影响已经不明显,故烃类的选择性基本保持稳定。

3.1.4. 气体产物组成

不同工况下尾气组成如表1所示。从总的气体产物分布来看,裂化效果较好的400 °C/2 MPa、430 °C/2 MPa、400 °C/1 MPa、400 °C/3 MPa工况尾气中CO_x和C₃H₈的浓度大多比较高。较高的CO_x浓度说明裂化过程中发生了高效的脱羰基和脱羰基作用,这样有利于更多的氢元素保留在产物中,提高产物品质和反应过程的稳定性;而C₃H₈为饱和烃,可能来自于烯烃等中间产物转化为不饱和度较高的芳香烃的芳构化过程。随着反应温度和反应压力降低,尾气中的CO_x浓度也开始降低,说明脱羰基和脱羰基等脱氧过程受到抑制,因此在粗汽油相中观察到较多含氧化合物的存在。此外,随着温度和压力的降低,C₂H₄的浓度显著增加,说明较低的温度和压力导致催化剂表面的芳构化反应强度较低,使得这些烯烃中间产物被释放而不继续参与芳构化等反应形成液体烃类,

这与低温与低压工况下观察到的较低的液体烃类选择性相符。

3.2. 反应后催化剂表征

对于催化裂化过程, 最重要的问题是催化剂的稳定性, 导致催化剂失活的主要原因是积炭的形成。因此, 针对实验过程中几个典型工况, 我们采用 N_2 物理吸附方法对反应后的催化剂进行表征, 同时根据热重分析结果计算了催化剂表面的积炭量, 结果如表2所示。

经过3 h的催化裂化反应, 相比原始空白HZSM-5催化剂(比表面积为 $340.0\text{ m}^2/\text{g}$), 各个工况反应后的催化剂比表面积都有不同程度的下降。总的来看, 对于油相选择性和品质较高的工况, 如 $400\text{ }^\circ\text{C}/2\text{ MPa}$, 其反应后的催化剂具有相对较高的比表面积($95.5\text{ m}^2/\text{g}$), 而 $340\text{ }^\circ\text{C}/2\text{ MPa}$ 和 $400\text{ }^\circ\text{C}/0.1\text{ MPa}$ 反应后催化剂的比表面积分别仅为 70.6 和 $40.9\text{ m}^2/\text{g}$, 说明 $400\text{ }^\circ\text{C}/2\text{ MPa}$ 工况更利于维持催化剂的活性。反应后催化剂表面的焦炭与催化剂的质量比(C/Cat)通过热重分析得到。经过计算发现, $400\text{ }^\circ\text{C}/2\text{ MPa}$ 工况反应后的催化剂积炭量相对较小, C/Cat为 0.15 , 而 $340\text{ }^\circ\text{C}/2\text{ MPa}$ 和 $400\text{ }^\circ\text{C}/0.1\text{ MPa}$ 反应后催化剂的C/Cat都达到 0.18 。

在我们过去对羟基丙酮单独与乙醇共裂化的研究中, 也对 $400\text{ }^\circ\text{C}/2\text{ MPa}$ 工况反应3 h后的HZSM-5催化剂进行了表征, 结果显示该催化剂比表面积为 $129.3\text{ m}^2/\text{g}$, C/Cat值为 0.12 。对比羟基丙酮单独与乙醇共裂化的催化剂, 混合模化物与乙醇共裂化后的催化剂比表面积较低, 同时积炭量略高, 即催化剂的活性相对下降得更为明显。考虑到混合模化物中环戊酮量很少, 并且裂化特性与同族类的羟基丙酮较为类似, 可以推断混合模化物裂化过程中催化剂呈现更明显的积炭趋势主要是由于酸性组分乙酸的存在。前面已经提到, 乙酸、羟基丙酮和环戊酮这三种模化物的有效氢碳比分别为 0 , 0.67 和 1.2 , 因此低有效氢碳比的乙酸更容易在裂化过程中生成低H/C的最终产物, 如焦炭等, 从而导致催化剂活性下降。Mentzel等^[14]在对浓度 10% 的乙酸和丙酮分别与甲醇共裂化的研究中也发现, 在丙酮与甲醇共裂化的过程中催化剂在失活前的转化能力更高, 即在酮类和甲醇的共裂化过程中催化剂具有更长的使用寿命。因此, 相比于单独羟基丙酮与乙醇的共裂化, 引入酸性组分乙酸的模化物混合物具有更为明显的积炭和催化剂失活趋势。

3.3. 催化剂稳定性测试

前面的催化剂表征结果显示, 3 h反应后的催化剂比表面积下降, 同时催化剂表面有积炭形成, 表明催化剂

在裂化过程中活性会不断降低。因此, 在 $400\text{ }^\circ\text{C}/2\text{ MPa}$ 条件下通过连续实验对催化剂的稳定性进行了测试。

3.3.1. 反应物转化率

反应物转化率随反应时间的变化如图6所示。在 210 min 以前, 乙酸、羟基丙酮、环戊酮和乙醇这四种反应物都基本实现了完全转化。随着反应进行, 乙酸转化率开始下降, 从 240 min 时的 76.7% 降至 330 min 时的 7.2% , 而其他三种反应物仍然保持了接近 100% 的转化率。这说明催化剂活性的降低对乙酸在催化剂表面的初步分解影响更为明显, 导致其转化率下降。

3.3.2. 液体产物选择性

液体产物选择性随反应时间的变化如图7所示。初始阶段油相产物的选择性稳定在 31% 左右, 并从 210 min 开始出现下降, 到 330 min 时仅为 3.5% 。与反应物的转化率相比, 液体产物选择性的下降不仅更早发生, 而且下降趋势也更为明显(反应物中仅有乙酸出现了转化率下降)。这说明催化剂的活性降低对油相产物的形成影响更大, 考虑到油相产物中的主要组分芳香烃是通过芳构化作用形成的, 因此推断催化剂的活性降低首先影响了其芳构化能力, 而对反应物在催化剂表面的初步转化影响相对较小。与油相产物相比, 即使催化剂活性下降, 裂化获得的水相产物的选择性随着反应的进行仍然呈现一个缓慢增大的趋势。这也说明催化剂表面一些涉及脱水反应的初步转化未受到明显影响。

3.3.3. 油相产物组成

油相产物组成随反应时间的变化如图8所示。在 180 min 以前, 油相产物的组成较为稳定, 芳烃含量在 90% 左右, 脂肪烃含量在 9% 左右, 其余为微量的含氧副产物。随着反应的进行, 伴随着催化剂失活加剧, 芳香烃含量开始降低, 而脂肪烃和含氧副产物的含量则明显升高。当反应进行到 330 min 时, 芳香烃含量降至 50.0% , 同时脂肪烃和含氧副产物的含量分别增大至 31.6% 和 18.4% 。芳香烃含量的降低反映了催化剂芳构化能力的下降。同时, 更多的以醇类和酮类为主的含氧副产物的生成说明催化剂整体脱氧效率下降, 即催化剂虽然实现了羟基丙酮、环戊酮和乙醇的完全转化, 但发生的很多反应是不完全脱氧。

3.3.4. 气体产物组成

尾气组成随反应时间的变化如图9所示。总的来看, 除了 C_2H_4 , 其他气体产物的浓度均呈下降趋势。在反应初期, 主要气体产物是 C_3H_8 , CO 和 CO_2 , 其浓度分别约为 40% , 16% 和 15% 。随着催化剂活性下降, 到 210 min 时,

这三种气体产物的浓度分别降至33.6%, 13.9%和12.3%, 与此同时, C_2H_4 浓度由初期的3%左右显著增大至17.9%。在前面对液体产物选择性的分析中也发现, 油相产物的选择性是在210 min时开始明显降低的, 这进一步证明了此时油相选择性的降低主要是由于催化剂芳构化能力的下降, 导致中间产物 C_2H_4 未发生芳构化形成液体芳烃即被释放出来。当反应进行到330 min时, C_3H_8 , CO和 CO_2 的浓度分别降至1.9%, 2.4%和2.7%, 同时其他气体产物浓度都在1%以下, 而 C_2H_4 浓度已高达90.79%, 这说明此时芳构化反应强度已经很弱, 与此时极低的油相产物选择性(3.5%)相对应。

3.4. 催化剂再生

前面对催化剂稳定性的研究结果表明, 催化剂活性随着反应的进行逐渐降低。催化剂活性的降低主要是由于催化剂表面积炭, 覆盖了表面活性中心, 堵塞了孔道。因此, 我们通过燃烧积炭对240 min反应后的催化剂进行再生, 研究再生后催化剂是否能恢复活性, 反应工况为400 °C/2 MPa。再生的燃烧温度为550 °C^[18], 总共再生4次。

3.4.1. 反应物转化率

反应物转化率如图10所示。在使用新鲜HZSM-5催化剂进行共裂化的过程中, 羟基丙酮、环戊酮和乙醇保持了接近100%的转化率。乙酸的转化率在240 min出现下降, 达到76.7%。在240 min反应后对催化剂进行第一次再生, 继续反应后乙酸的转化率又重新达到99%以上, 而其他三种反应物的转化率仍然接近100%。在后续连续实验中, 催化剂的再生也都很好恢复了催化剂对乙酸的转化能力, 使乙酸的转化率由失活时的80%左右重新回到99%以上, 同时其他反应物保持接近100%的转化率。

3.4.2. 液体产物选择性

液体产物选择性如图11所示。在第一次再生之前, 油相选择性已由初始阶段的31%左右降至19.3%。催化剂经再生后, 油相选择性重新达到30%以上。在后续实验中, 催化剂再生也都使原本芳构化能力明显下降的催化剂基本恢复了活性。总的来看, 催化剂再生使催化剂寿命得到了有效延长。

3.4.3. 油相组成

油相组成如图12所示。相比于初始反应阶段, 240 min时油相中的芳烃含量由92%降至79.1%, 而脂肪烃和含氧副产物的含量分别由7.6%和0.3%增大至15.2%和5.7%。经再生后, 芳烃含量恢复到90%以上, 这也说明催化剂的芳构化能力在再生后得到了良好的恢复。

3.4.4. 尾气组成

在前面的连续实验中发现, 尾气中CO, CO_2 , C_2H_4 和 C_3H_8 浓度随着催化剂失活变化较大。因此, 对这四种气体在再生前后的浓度进行了监测, 结果如图13所示。在催化剂开始失活以后, CO和 CO_2 的浓度出现下降, 而 C_3H_8 的浓度由初始阶段的43%降至22.6%, 相应的 C_2H_4 的浓度由2.6%显著增大至32.6%。催化剂经过再生后, C_2H_4 的浓度重新降至5%以下, 证明催化剂的芳构化能力得到了较好的恢复, 使得大部分中间产物 C_2H_4 都参与到后续的芳构化反应中。

4. 结论

本文在固定床上考察了生物油中典型模化物羟基丙酮、环戊酮、乙酸与乙醇的共裂化特性。研究发现, 较高的反应温度和压力能够促进反应物的完全转化和液体烃类的生成, 同时改善粗汽油相的组成。考虑到较高的反应温度会增加能耗, 较高的反应压力会增加操作的复杂性, 400 °C和2 MPa是较为合适的反应工况。在400 °C和2 MPa时, 生物油的酮酸混合模化物呈现良好的裂化特性, 反应物接近完全转化, 产生高品质的汽油相产物, 粗汽油相的选择性达到31.5%, 且全部由烃类组成, 其中芳香烃含量高达91.5%, 且主要包含苯、二甲苯等 C_7 – C_{10} 的小分子芳香烃。反应后催化剂的表征结果表明, 催化剂反应后会出现比表面积下降和表面积炭。催化剂稳定性测试结果表明, 催化剂会在330 min的反应后出现失活。催化剂再生实验结果表明, 通过燃烧积炭的方法对催化剂进行再生, 能够很好地恢复催化剂活性, 延长了催化剂寿命。由于小分子酮类和酸类是生物油分子蒸馏蒸出馏分的主要组分, 酮酸混合模化物在最佳工况下的顺利转化也证明了生物油实际馏分与乙醇共裂化的可行性。