

ARTICLE

Production of Low-carbon Light Olefins from Catalytic Cracking of Crude Bio-oil

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Low-carbon light olefins are the basic feedstocks for the petrochemical industry. Catalytic cracking of crude bio-oil and its model compounds (including methanol, ethanol, acetic acid, acetone, and phenol) to light olefins were performed by using the La/HZSM-5 catalyst. The highest olefins yield from crude bio-oil reached 0.19 kg/(kg crude bio-oil). The reaction conditions including temperature, weight hourly space velocity, and addition of La into the HZSM-5 zeolite can be used to control both olefins yield and selectivity. Moderate adjusting the acidity with a suitable ratio between the strong acid and weak acid sites through adding La to the zeolite effectively enhanced the olefins selectivity and improved the catalyst stability. The production of light olefins from crude bio-oil is closely associated with the chemical composition and hydrogen to carbon effective ratios of feedstock. The comparison between the catalytic cracking and pyrolysis of bio-oil was studied. The mechanism of the bio-oil conversion to light olefins was also discussed.

Key words: Crude bio-oil, Low-carbon olefin, Catalytic cracking, Zeolite catalyst

I. INTRODUCTION

Low-carbon light olefins (*i.e.* ethylene, propylene, and butylene) have been widely used as the raw materials of polyolefins and various chemicals in the petrochemical industry [1]. The present cost of light olefin is very high and in the upward trend [2]. While most olefins are currently produced through steam cracking routes and fluid catalytic cracking (FCC) processes using naphtha, light diesel and other petroleum products as feedstocks at present [3, 4]. In recent years, the increase of crude oil price and the limited petroleum resources have made the production of olefins via the non-petrochemical routes more and more attractive. Production of high-grade liquid fuels and chemicals from the most abundant and sustainable lignocellulosic biomass is one of the most promising ways to solve energy and environmental problems caused by our dependence on fossil oil [5–8]. However, this route may be limited by the Anderson-Schulz-Flory (ASF) distribution as well as high-pressure operation [9, 10].

Crude bio-oil, produced from fast pyrolysis of various plant components of lignocellulosic biomass, has been identified as an important renewable feedstock for the production of bio-fuels and chemicals [11, 12]. Com-

pared with solid biomass as the raw material, liquid bio-oil, which can be readily stored and transported, is more suitable for the production of bio-fuels or chemicals on a large scale. Vispute *et al.* has outlined a distinct strategy for bio-oil deoxygenation into C2-C6 alcohols, C6-C8 aromatic hydrocarbons and C2-C4 light olefins [11]. Gayubo *et al.* reported on a two-step (thermal-catalytic) process for the conversion of the crude bio-oil into hydrocarbons with HZSM-5 zeolite [13]. They revealed that the bio-oil conversion and the olefins selectivity were significantly enhanced by co-feeding methanol. The main challenge for catalytic conversion of biomass and its derived feedstocks to light olefins is how to improve catalyst and process conditions to obtain high light olefins yields. The catalytic conversion of biomass or its derived feedstocks has been widely investigated with various zeolite catalysts such as ZSM-5, HZSM-5, Y-zeolite, Beta zeolite, Al-MCM-41, H-USY, SBA-15, and Al-MSU catalysts [14–23]. It should be pointed out that bio-oil possesses some unique characteristic composition such as higher content of oxygen and lower H/C ratio, as compared with the common feedstocks (*e.g.*, naphtha) used for the production of light olefins. Also, the complex reactions are generally involved in the bio-oil catalytic transformation process due to the complexity of bio-oil composition. So far, both the selectivity and yield of light olefins derived from bio-oil are noticeably lower than those from methanol, ethanol and naphtha, and

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thereby need to be improved by optimizing the catalytic transformation process.

In our previous work, attentions have been paid to the production of hydrogen, bio-syngas, and biofuels from bio-oil [24–28]. In this work, light olefins are selectively produced through the catalytic cracking of crude bio-oil using the modified La/HZSM-5 catalyst. La-modified ZSM-5 has been employed for the conversion of methanol to olefins or the methanol aromatization [29–31]. The selectivity and yield of light olefins were significantly improved via adjusting the acid density distribution and reaction conditions. The characteristics and differences in the production of light olefins from different group components in crude bio-oil were also investigated using the selected model compounds. The transformation of bio-oil to light olefins may potentially provide a promising approach to producing the key building blocks in the petrochemical industry from the renewable biomass.

II. EXPERIMENTS

A. Feedstocks

Crude bio-oil was produced by the fast pyrolysis of biomass in a circulating fluidized bed with a capacity of 120 kg/h oil at our Lab [24–28]. The main elemental composition of bio-oil feedstock derived from fast pyrolysis of straw stalk contains 56.6% C, 6.3% H and 37.1% O. Water content in the crude bio-oil is about 37.3%. The chemical formula of the oxygenated organic compounds of the crude bio-oil feed can be expressed as $\text{CH}_{1.33}\text{O}_{0.49}$. Model compounds, including methanol, ethanol, acetic acid, acetone, and phenol, were purchased from Sinopharm Chemical Reagent Company Limited in China (Shanghai, China).

B. Catalysts and characterization

The HZSM-5 zeolite with Si/Al ratio of 25 obtained from Nankai University catalyst Co., Ltd. (Tianjin, China) was calcined in nitrogen atmosphere at 550 °C for 4 h prior before use. The impregnation method was adopted to load lanthanum into the HZSM-5 zeolite. The HZSM-5 zeolite was impregnated in the solution of lanthanum nitrate over a night, followed by rotary-evaporation at 60 °C, drying at 80 °C for 6 h, and calcinating at 550 °C for 5 h.

The elemental content in the catalyst was measured by inductively coupled plasma and atomic emission spectroscopy (ICP-AES, Atomscan Advantage, Thermo Jarrell Ash Co., USA). The catalyst was also investigated by NH_3 -TPD (temperature programmed desorption of ammonia), XRD (X-ray diffraction) and N_2 adsorption/desorption isotherms. For the NH_3 -TPD tests, the catalyst was firstly pretreated at 500 °C in

a helium flow (ultrahigh purity, 100 mL/min) for 2 h, and then adsorption of ammonia was carried out at 120 °C for 1 h. After the catalyst was flushed with He at 120 °C for 1 h, the programmed-desorption of NH_3 was run from 120 °C to 700 °C with a heating rate of 10 °C/min. The amount of desorbed ammonia was measured by a gas chromatograph (GC-SP 6890) with a TCD detector (thermal conductivity detector). XRD patterns of the catalysts were recorded on an X'pert Pro Philips diffractometer, using a $\text{CuK}\alpha$ radiation ($\lambda=0.15418$ nm). The N_2 adsorption/desorption isotherms of the catalysts were measured at -196 °C using the COULTER SA 3100 analyzer.

C. Experimental setup and product analysis

The production of light olefins from the catalytic cracking of bio-oil or its model compounds was carried out in the continuous-flowing systems, using a quartz fixed-bed reactor under atmospheric pressure. This system consists of a quartz tube reactor (inner diameter of 30 mm, length of 400 mm), a gas feed system, a liquid feeding pump, a heater and temperature control system, condensers and an on-line gas analysis unit, which has been described in detail previously [24–28]. For the typical runs, 10 g of the La/HZSM-5 zeolite with a particle size of 40–60 mesh was uniformly filled in the catalyst bed, which was held in the reactor by quartz beads. The liquid reactants were fed into the reactor using a multisyringe pump (TS2-60, Baoding Longer Precision Pump). The steam from a steam generator, which was controlled by the mass flow controller, was used as carrier gas. Before the reactions, the reactor was flushed by argon with the flow rate of 30 mL/min for 2 h at the room temperature, and then was externally heated to a given temperature by the carborundum heater with a programmed temperature controller. The gaseous products were analyzed using an on-line GC equipped with two detectors, a TCD for analysis of H_2 , CO, CH_4 , and CO_2 separated on TDX-01 column, and a flame ionization detector (FID) for gaseous hydrocarbons separated on a Porapak-Q column. The liquid products obtained in each experiment were weighed to calculate their yields, and subsequently stored in sealed glass jars for further analysis. The liquid products were analyzed by a GC-MS (Thermo Trace DSQ (I)) with a TR-5MS fused-silica capillary column. The coke deposited on the catalyst has been studied by combustion with air in the TG/MS arrangement. The performance of production of light olefins via catalytic cracking of crude bio-oil was evaluated by carbon yield (Y_X), selectivity (S_X), light olefins mass yield (Y_{olefins}) as well as the olefins distribution D according to the following equations:

$$Y_X = \frac{x_X}{x_{\text{feed}}} \times 100\% \quad (1)$$

TABLE I List of productions obtained from the catalytic cracking and pyrolysis of crude bio-oil over different La/HZSM-5 catalyst or sand.

	$Y_{\text{olefins}}/$ (kg/kg bio-oil)	Products $S_X/C\%$						$D/\%$			Overall carbon yield/%			
		$C_2=C_4$	CH_4	C2-C4	CO	CO_2	C_5^+	C_2H_4	C_3H_6	C_4H_8	Gas	Liquid	Solid	Total
0%La	0.15	38.8	5.4	2.5	23.7	12.9	14.3	34.3	58.3	7.4	52.1	8.9	30.4	91.4
5.0%La	0.19	46.5	3.8	4.5	20.1	16.1	8.9	31.0	56.6	12.4	56.5	5.5	33.1	95.1
10.0%La	0.17	43.9	3.4	4.3	22.9	15.9	10.2	30.6	55.8	13.6	53.2	5.9	35.0	94.1
Pyrolysis	0.03	11.3	7.4	2.9	19.1	6.8	52.5	44.8	36.5	18.7	18.2	20.1	32.0	70.3

* Reaction conditions: $T=550$ °C, $S/C=10$, $WHSV=0.4$ h⁻¹, and 10.0 g of catalyst.

$$S_X = \frac{x_X}{x_{\text{product}}} \times 100\% \quad (2)$$

$$Y_{\text{olefins}} = \frac{y_{\text{olefins}}}{y_{\text{feed}}} \quad (3)$$

$$D = \frac{C_{C_nH_{2n}}}{C_{\text{olefins}}} \times 100\%, \quad n = 2, 3, 4 \quad (4)$$

where X represents C2-C4 olefins, CO, CO_2 , CH_4 , C2-C4 alkanes or C_5^+ compounds, x_X , x_{feed} , and x_{product} are the moles of carbon in X, feed, and products, y_{olefins} and y_{feed} are mass of light olefins and feed, $C_{C_nH_{2n}}$ and C_{olefins} are carbon moles of C_nH_{2n} ($n=2, 3, 4$) and light olefins. All the tests were repeated three times and the reported data were the mean values of three trials. For the carbon balance analysis, the carbon contents in the gas, liquid and solid products were quantified by gas chromatograph analysis, elemental and composition analysis and TGA analysis, respectively. The carbon content in each feed was also determined by elemental and composition analyses. The carbon balance was evaluated by the overall carbon yields obtained from the gas, liquid and solid products, and the identified carbon in all products was between 82.6% and 108.9% for all tests.

III. RESULTS AND DISCUSSION

A. Influence of La in zeolites on the conversion of crude bio-oil to olefins

Table I presents the influence of the addition of lanthanum with different loadings into the HZSM-5 zeolite on the production of light olefins from crude bio-oil. It was observed that the addition of lanthanum obviously increased both the yield and selectivity of light olefins. The conversion of crude bio-oil over pure HZSM-5 zeolite gives light olefins weight yield of 0.15 kg/kg bio-oil with a 38.8% $C_2=C_4$ olefins selectivity. When the 5.0% lanthanum was added into HZSM-5 zeolite (referred as 5.0%La/HZSM-5), the best performance (0.19 kg/kg bio-oil yield with a 46.5% olefins selectivity.) was obtained. Further increasing La amount over 10% causes a slight decrease in the light olefins yield, which may be attributed to the decrease in the cata-

lyst acidity. The selectivities towards CH_4 and C_5^+ hydrocarbons were effectively depressed, leading to the improvement of the olefins selectivity. With regards to the distribution of light olefins, increasing the La loadings leads to the increase in butylene, accompanied by the decrease in ethylene and propylene. The variation in the production of light olefins with the La-modified HZSM-5 is mainly originated from the changes in acidity and distribution of acid sites of the zeolite catalysts. In addition, the carbon balance was evaluated by the overall carbon yields obtained from gas, liquid and solid products, the carbon in all products was between 91.4% and 95.1% (Table I).

B. Influence of reaction temperature on the production of light olefins

Figure 1 shows the effect of temperature on the production of light olefins from the crude bio-oil over the selected 5.0% La/HZSM-5 catalyst. The overall carbon yield (sum of gas, liquid and solid products) increased with increasing temperature and reached about 95.1% at 550 °C (Fig.1(a)), implying an almost complete conversion of crude bio-oil at high temperatures. With increasing temperature from 450 °C to 650 °C, the total gas yield shows an increase trend along with the decrease in the liquid yield, indicating that high temperature is more favorable to the cracking of the oxygenated compounds in the bio-oil. The main gas product observed at 550 °C was C2-C4 light olefins together with smaller amount of CO, CO_2 and CH_4 and C2-C4 alkanes (Fig.1(b)), which formed from the deoxygenation and catalytic cracking of crude bio-oil. The light olefins selectivity increases with increasing temperature below 550 °C, and goes through a maximum of 46.5% near 550 °C. Further increasing temperature to 650 °C significantly reduced the olefins selectivity to 38.9%. As the temperature increased, accompanied by a decrease in the C_5^+ compounds selectivity, the selectivity towards CH_4 and CO increased. The above results suggest that increasing the reaction temperature enhanced the deoxygenation of bio-oil and the transformation of the heavier compounds to smaller molecular gas prod-

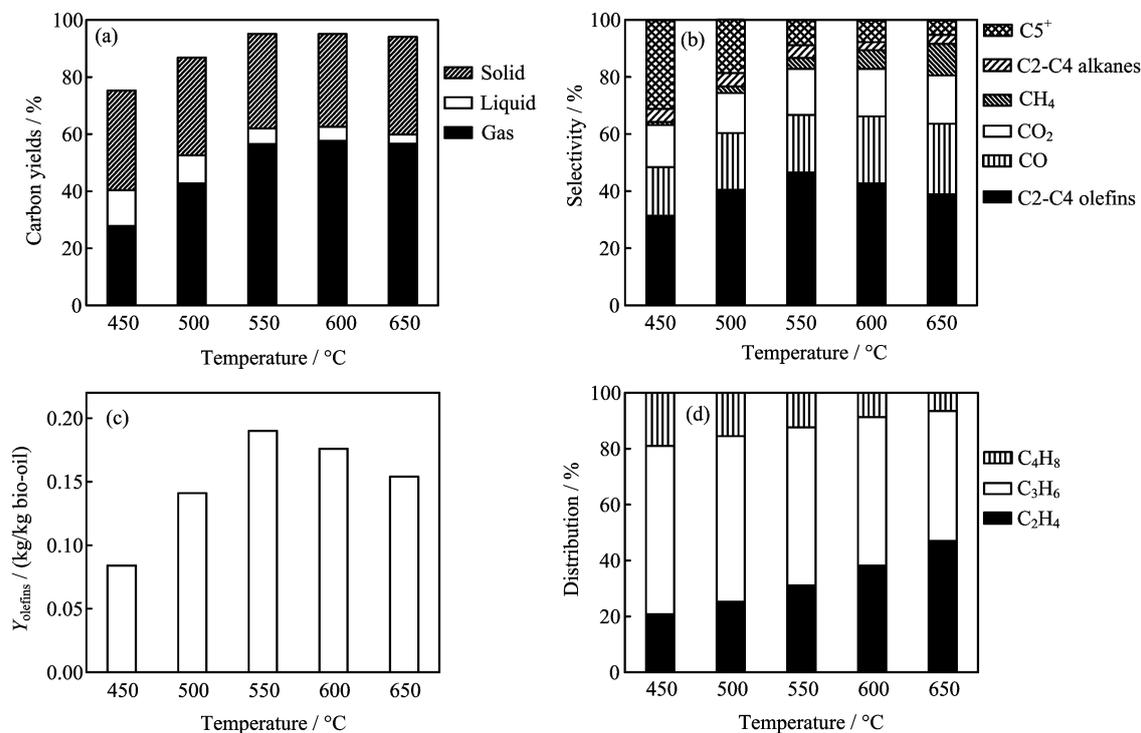


FIG. 1 Effect of temperature on production of light olefins from crude bio-oil over 5%La/HZSM-5 catalyst. (a) Carbon yield, (b) Products selectivity, (c) $\text{C}_2=\text{C}_4$ olefins weight yield, and (d) olefins distribution. Reaction conditions: $T=450-650\text{ }^{\circ}\text{C}$, $S/C=10.0$, $\text{WHSV}=0.4\text{ h}^{-1}$.

ucts by the secondary catalytic cracking reactions.

In addition, the total yield of C2-C4 light olefins presents a maximum value of 19.0% around 550 °C (Fig.1(c)). The rapid reduction in the olefins yield over 550 °C is mainly owed to the decrease in the olefins selectivity and the increase in the CO and CH_4 selectivity. With regards to the olefins distribution, light olefins derived from the bio-oil are dominated by ethylene and propylene together with a smaller amount of butanes (Fig.1(d)). The ethylene yield increased with increasing temperature, and the formation of propylene and butenes decreased at high temperatures, which was attributed to the secondary decomposition reactions.

C. Influence of weight hourly space velocity on the production of light olefins

Figure 2 shows the production of light olefins from the catalytic cracking of crude bio-oil as a function of weight hourly space velocity (WHSV). Increasing WHSV shows a negative impact on the overall gas yield. Increasing WHSV also resulted in the decrease in the C2-C4 olefins selectivity, accompanied by an obvious increase in the C_5^+ hydrocarbons selectivity. Accordingly, the olefins weight yield gradually reduced from 0.19 kg/(kg bio-oil) to 0.07 kg/(kg bio-oil) with the increase of WHSV from 0.4 h^{-1} to 4.0 h^{-1} . Besides, the butylenes amount in the olefins products ascended in

the case of high WHSV. The increase of space velocity generally shortens the reactants residence time in the catalyst bed, leading to the decrease both in the bio-oil conversion and in the olefins yield. The increase of selectivity for the heavier products (*e.g.* C_5^+ hydrocarbons) at a high WHSV may be attributed that a shorter reaction time which will slow down the secondary reactions of these heavier products.

D. Production of light olefins from different oxygenates and reaction pathways

To further illustrate the transformation of bio-oil into light olefins, the pyrolysis of bio-oil was separately investigated with the sand. As shown in Table I the products derived from the bio-oil pyrolysis are quite different from the catalytic cracking of crude bio-oil. The yield of light olefins from the bio-oil pyrolysis is much lower than the catalytic cracking of bio-oil. The results indicated that the pyrolysis of bio-oil is mainly dominated by the gasification to forming CO and methane as well as decomposition of the heavier compounds in the crude bio-oil towards lighter ones. For the production of C2-C4 light olefins, it is required to perform the catalytic cracking of bio-oil through the deoxygenation and catalytic cracking processes.

Crude bio-oil produced through the fast pyrolysis of biomass is a complex mixture of oxygenated organic

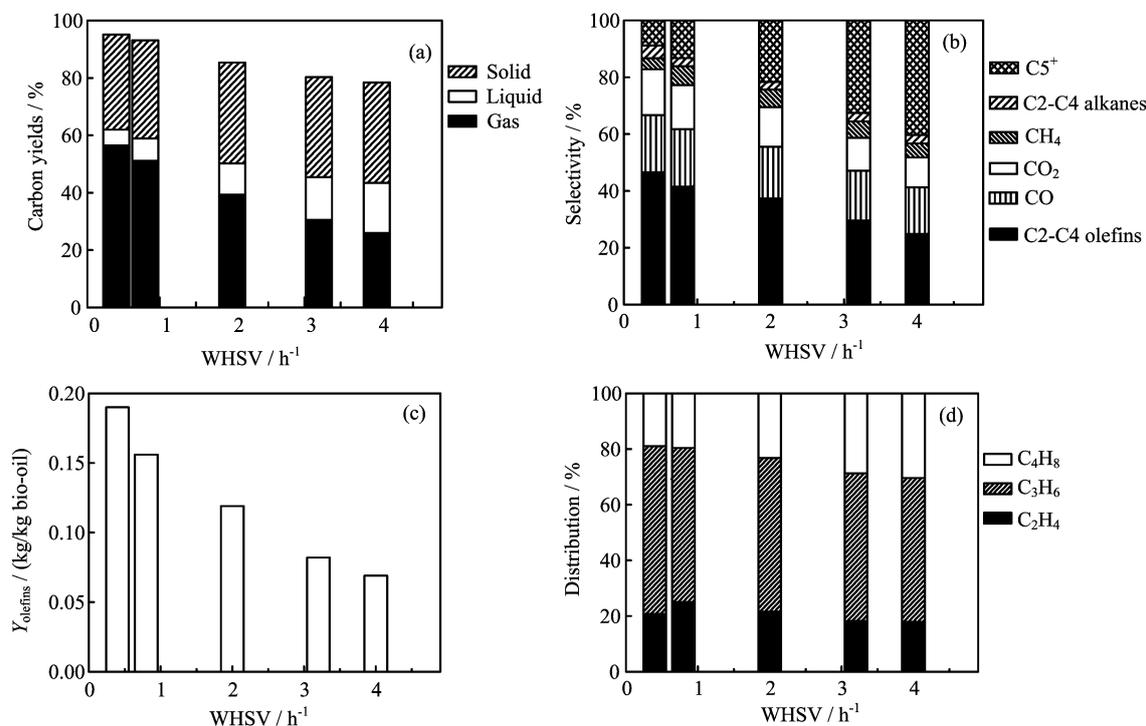


FIG. 2 Effect of WHSV on production of light olefins from crude bio-oil over 5%La/HZSM-5 catalyst. (a) Carbon yields, (b) Products selectivity, (c) C₂=C₄ olefins weight yield, and (d) olefins distribution. Reaction conditions: $T=550\text{ }^{\circ}\text{C}$, $S/C=10.0$, $\text{WHSV}=0.4\text{--}4.0\text{ h}^{-1}$.

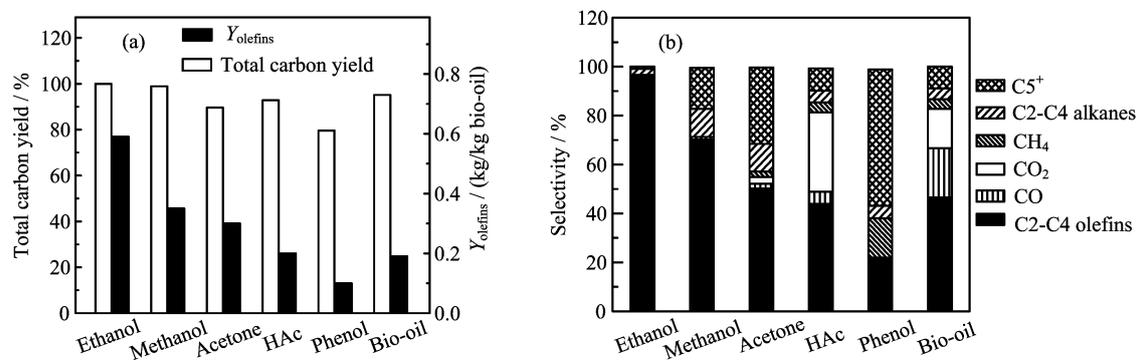


FIG. 3 Performance for production of light olefins using various feedstocks over 5%La/HZSM-5. (a) Total carbon yield and light olefins weight yield and (b) selectivity of products. The optimal reaction temperature was 400, 450, 500, 550, 550, 600 $^{\circ}\text{C}$ for ethanol, methanol, acetic acid, acetone, crude bio-oil, phenol respectively. WHSV was kept at 0.4 h^{-1} .

compounds including acids, alcohols, aldehydes, ketones, substituted phenolics and other oxygenates [13, 27]. To further study the differences of the bio-oil transformation into olefins from the different oxygenates, the catalytic conversion of the selected model compounds (methanol, ethanol, acetic acid, acetone and phenol) were performed. As shown in Fig.3, we found that alcohols are more easily catalytically converted into olefins through the dehydration reaction over the zeolite catalyst, while phenolic compounds produce a higher amount of methane, benzene as well as coke. The differences of light olefins yields among the different feedstocks may be mainly attributed to the differences in

their molecular structures as well as hydrogen to carbon effective (H/C_{eff}) ratios [32]. With regards to the reaction paths, the complex components of bio-oil results in the complex reactions network in the catalytic conversion of bio-oil, mainly including deoxygenation (decarbonylation, decarboxylation, dehydration), cracking, hydrogen transfer, hydride transfer, cyclization, aromatization and oligomerization reactions [32–35].

In present work, the main products observed from the catalytic conversion of bio-oil over the zeolite catalyst are C₂-C₄ olefins, CO and CO₂. According to the study on the catalytic cracking of bio-oil and the model compounds, the following reactions processes are suggested

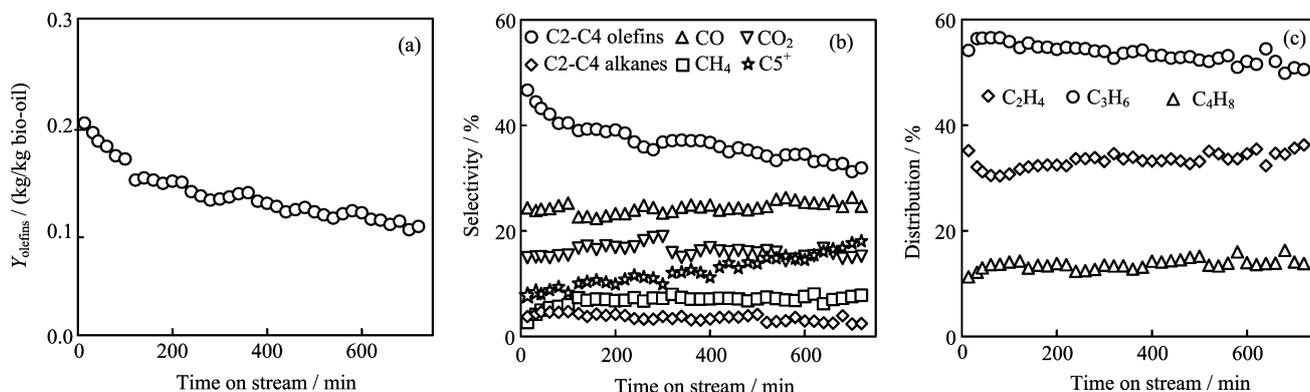
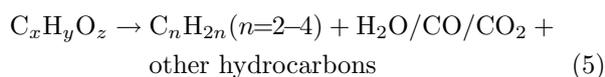


FIG. 4 Catalyst stability in the catalytic cracking of crude bio-oil over 5.0%La/HZSM-5 catalyst. (a) Light olefins yield, (b) products selectivity, and (c) olefins distribution. Reaction conditions: $T=550\text{ }^{\circ}\text{C}$, $S/C=10.0$, $\text{WHSV}=0.4\text{ h}^{-1}$.

to account for the formation of the light olefins. First, the oxygenated organics in the bio-oil can be directly cracked to olefins through the deoxygenation process:



Second, the large molecules in the bio-oil are catalytically cracked to the lighter organics, followed by the secondary reactions to produce light olefins through deoxygenation and hydrogen or hydride transfer processes. Third, the light components in the bio-oil (*e.g.* acetic acid, lower alcohols, aldehydes, ketones) may transform into intermediates via the deoxygenation, and subsequently, these intermediates undergo the catalytic cracking and hydrogen or hydride transfer to form olefins [32, 35]. The main by-products of CO and CO₂ are formed via the decarbonylation and decarboxylation reactions of the oxygen-containing organics over the zeolite catalysts. And the C₅⁺ hydrocarbons products (mainly aromatic hydrocarbons) are probably formed via the cracking of the heavy compositions (such as phenolics) in bio-oil, together with aromatization and oligomerization of the light olefins. In addition, the solid residual derived from the cracking of the bio-oil contains 76.2% C, 5.0% H and 18.8% O under the typical reaction condition ($T=550\text{ }^{\circ}\text{C}$, $S/C=10.0$, $\text{WHSV}=0.4\text{ h}^{-1}$).

E. Catalyst stability in the catalytic cracking of crude bio-oil

As shown in Fig. 4, the catalyst stability in the catalytic cracking of crude bio-oil was tested as a function of the time on stream under the optimized reaction condition ($T=550\text{ }^{\circ}\text{C}$, $S/C=10.0$, $\text{WHSV}=0.4\text{ h}^{-1}$). A gradual decrease in the catalytic activity was observed in our investigated ranges. The yield of the light olefins declined from the initial value of about 20% to 10% for 12 h. The selectivity towards light olefins slightly decreased, and the selectivity towards carbon monoxide

and methane slightly increased. The above results indicate that the impact of thermal decomposition was enhanced over the used catalyst. The decrease in the catalyst activity is mainly attributed to the carbon deposition on the catalysts in the cracking of bio-oil, as well as change in the properties of the catalysts.

F. Catalyst characterization

To understand the properties of the HZSM-5 and La/HZSM-5 catalysts, the typical catalysts were characterized by means of NH₃-TPD, XRD, ICP/AES, and N₂ isothermal adsorption/desorption. Figure 5(a) shows typical XRD of the 5% La/HZSM-5 catalyst that has a typical MFI (Mobil fifth) structure the same as HZSM-5 [21]. It indicates that the framework structure of the zeolite was not destroyed by adding a small amount of La. The intensity of XRD peaks for the used catalyst seems to be weaker as compared with the fresh one (Fig. 5(b)), reflecting a decrease of crystallinity during the bio-oil conversion. As shown in Fig. 5(c) and (d), the NH₃-TPD analyses indicate that the La/HZSM-5 catalysts have strong acid (SA) and weak acid (WA) sites. The total acid sites of the used catalysts, estimated by the Gaussian fitting of the NH₃-TPD profiles, decreased after the catalytic conversion of the crude bio-oil.

Table II summarized main properties of the zeolite catalysts with different La-loadings as well as the used catalysts. The addition of a small amount of La into the HZSM-5 zeolite does not cause an obvious change of the Si/Al ratio in the framework. On the other hand, the Si/Al ratio in the used catalysts observably increased, suggesting that the zeolite has suffered somewhat dealumination process under the hydrothermal condition. The dealumination process usually leads to the decrease in the number of the surface acid sites through the loss of the structural hydroxyl group in the zeolite [36]. These results agree with the acid strength measurements for the used catalysts using the NH₃-TPD

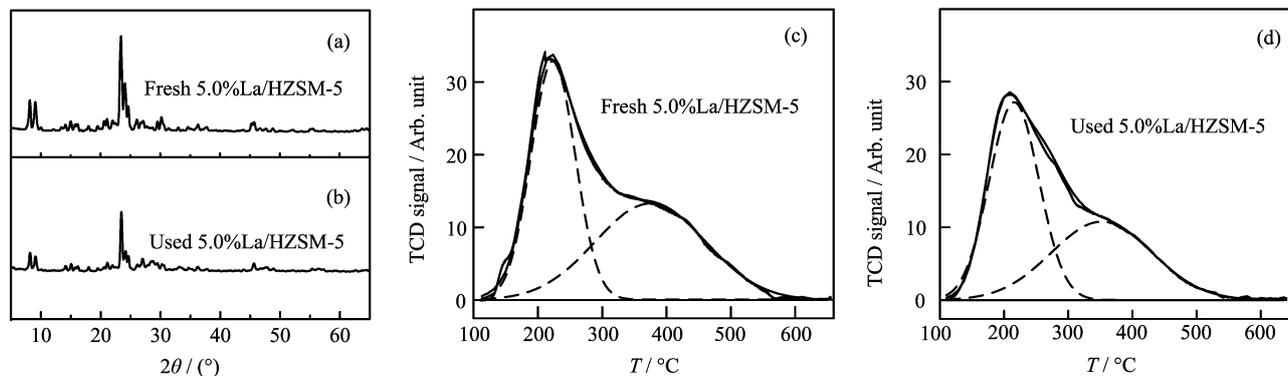


FIG. 5 XRD spectra for (a) fresh 5.0%La/HZSM-5 catalyst and (b) used 5.0%La/HZSM-5 catalyst, and NH_3 -TPD spectra for (c) fresh 5.0%La/HZSM-5 catalyst and (d) used 5.0%La/HZSM-5 catalyst after catalytic conversion of crude bio-oil at $T=550\text{ }^\circ\text{C}$, $S/C=10.0$, and $\text{WHSV}=0.4\text{ h}^{-1}$.

TABLE II Main properties of the zeolite catalysts.

Catalysts	[Si]/[Al]	$S_{\text{BET}}^a/(\text{m}^2/\text{g})$	$V_p^a/(\text{cm}^3/\text{g})$	$d_{\text{xrd}}^a/\text{nm}$	$\text{TA}^b/(\mu\text{mol}/\text{g})$	$\text{SA}^b/(\mu\text{mol}/\text{g})$	$\text{WA}^b/(\mu\text{mol}/\text{g})$
HZSM-5	25	266.3	0.19	18.8	590.0	315.1	274.9
5%La/HZSM-5	23	280.9	0.18	19.2	327.5	162.8	164.7
10%La/HZSM-5	21	291.8	0.16	19.7	191.3	88.4	102.9
Used HZSM-5 ^c	46	157.0	0.15	19.0	272.6	113.9	158.7
Used 5%La/HZSM-5	72	188.0	0.15	19.0	302.5	138.8	163.7

^a Symbols meanings: [Si]/[Al] is the mole ratio of silicon to aluminum in the zeolites, S_{BET} is BET surface area, V_p is pore volume, d_{xrd} is mean particle sizes calculated by the Scherrer equation.

^b The total acid density (TA), strong acid (SA), and weak acid (WA) sites were estimated by the Gaussian fitting of the NH_3 -TPD profiles.

^c The used catalysts of HZSM-5 and 5%La/HZSM-5 after the bio-oil catalytic cracking at $T=550\text{ }^\circ\text{C}$, $S/C=10.0$, and $\text{WHSV}=0.4\text{ h}^{-1}$.

analyses. Especially, the total acid sites of the zeolite catalysts for HZSM-5 was about $590.0\ \mu\text{mol}/\text{g}_{\text{catal}}$ and changed to $327.5\ \mu\text{mol}/\text{g}_{\text{catal}}$ for 5% La/HZSM-5. The percentages of the strong acid and weak acid sites for HZSM-5 were about 53% and 47%, and changed to about 49% and 51% respectively for 5.0% La/HZSM-5. Considering the NH_3 -TPD analysis results (Table II) and the results for the olefins yield in Table I, a moderate acidity with a suitable ratio between the strong acid and weak acid sites is favorable for enhancing the production of olefins from the catalytic cracking of bio-oil.

IV. CONCLUSION

This work reported selective catalytic cracking of crude bio-oil and its model compounds for the production of light olefins over the La-modified HZSM-5 catalyst. The highest olefins yield from bio-oil reached 19% with a nearly complete bio-oil conversion. The reaction parameters including temperature, weight hourly space velocity and the La addition amount into the HZSM-5 zeolite can be used to control both olefins yield and

selectivity. The production of light olefins from crude bio-oil is closely associated with its chemical composition and hydrogen to carbon effective ratios. The conversion of bio-oil to light olefins may potentially provide a promising route for the production of the key petrochemical-light olefins using renewable biomass.

V. ACKNOWLEDGEMENTS

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