

ARTICLE

Transformation of Bio-oil into BTX by Bio-oil Catalytic Cracking

Jiu-fang Zhu, Ji-cong Wang, Quan-xin Li*

Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on April 11, 2013; Accepted on May 13, 2013)

Production of benzene, toluene and xylenes (BTX) from bio-oil can provide basic feedstocks for the petrochemical industry. Catalytic conversion of bio-oil into BTX was performed by using different pore characteristics zeolites (HZSM-5, HY-zeolite, and MCM-41). Based on the yield and selectivity of BTX, the production of aromatics decreases in the following order: HZSM-5>MCM-41>HY-zeolite. The highest BTX yield from bio-oil using HZSM-5 reached 33.1% with aromatics selectivity of 86.4%. The reaction conditions and catalyst characterization were investigated in detail to make clear the optimal operating parameters and the relation between the catalyst structure and the production of BTX.

Key words: Bio-oil, BTX, Catalytic cracking**I. INTRODUCTION**

Biomass conversion into benzene, toluene and xylenes (BTX) can provide the basic feedstocks for the petrochemical industry, and these aromatics also serve as the most important aromatic platform molecules for the development of high-end chemicals [1–3].

Bio-oil, produced from fast pyrolysis of lignocellulosic biomass, has been identified as an important renewable feedstock for the production of bio-fuels and chemicals [4–6]. Compared 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.* outlined a unique route for bio-oil deoxygenation into chemicals including aromatic hydrocarbons, light olefins and mixed alcohols with an about 60% overall carbon yield, in which a cascade process including hydroprocessing of bio-oil over the Ru/C or Pt/C catalysts followed by catalytic conversion of the refined bio-oil to the hydrocarbons over the zeolite catalyst [4]. Zhang *et al.* recently investigated the catalytic conversion of bio-oil and hydrogenated bio-oil with different H/C ratios over the ZSM-5 catalyst, and showed that the yields of aromatics and olefins increased and the coke yield decreased with increasing H/C ratio [7]. Gayubo and co-workers proposed a thermocatalytic two-step process for the conversion of the crude bio-oil into hydrocarbons with a HZSM-5 zeolite, and showed that bio-oil conversion and the light olefins selectivity are significantly enhanced by co-feeding methanol [8–10]. More recently, our group investigated the production of light olefins via catalytic cracking of the water-soluble bio-oil

as well as different biomass feedstocks (husk, sawdust, sugarcane bagasse, cellulose, hemicellulose and lignin) with a lanthanum modified zeolite [11, 12]. Moreover, 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 [13–23]. The remaining challenges for the transformation of biomass or bio-oil to light olefins include improving the selectivity and yield of target products along with suppressing catalyst deactivation.

The bio-oil can be separated by distillation treatment into two components, (lighter and heavier fractions). Lighter fractions can be used as a useful feedstock for the production of light olefins, hydrogen, and other bio-fuels or chemicals. The heavy components, mainly consisting of substituted phenols and aromatic oligomers produced by depolymerization of lignin constituent in lignocellulosic biomass, can serve as a raw material for production of BTX or other high value aromatic chemicals. Our previous work showed that the heavy components of the bio-oil (bio-oil tar) were difficult to be transformed into light olefins or hydrogen as compared with its light components [11, 12, 24–28]. Considering the composition characteristics, the heavier fractions are more suitable for use as a feedstock for production of high value aromatic chemicals. In this work, we investigate the catalytic transformation of the bio-oil to BTX. The study on the transformation of bio-oil to BTX should be useful for the production of high value chemicals using renewable biomass feedstocks.

II. EXPERIMENTS**A. Feedstocks**

Bio-oil was produced by the fast pyrolysis of biomass in a circulating fluidized bed with a capacity of 120 kg/h

* Author to whom correspondence should be addressed. E-mail: liqx@ustc.edu.cn

TABLE I Main organic compounds (ethyl acetate extraction) in the bio-oil. t_{GC} in min and x is the content of an organic compound.

t_{GC}	Formula	Compounds	$x/\%$
6.16	C ₄ H ₈ O ₂	2-Butanone, 4-hydroxy	0.11
6.62	C ₇ H ₈ O ₂	(2-Oxo-3-cyclopenten-1-yl)acetaldehyde	5.20
7.85	C ₅ H ₈ O ₃	2-Oxopropyl acetate	2.44
12.33	C ₆ H ₆ O	Phenol	5.75
13.75	C ₆ H ₈ O ₂	Methyl cyclopentenolone	6.89
16.00	C ₇ H ₈ O ₂	Mequinol	9.40
19.16	C ₁₀ O ₈	Naphthalene	0.89
19.65	C ₈ H ₁₀ O ₂	2-Methoxy-6-methyl phenol	5.60
20.97	C ₁₂ H ₂₄ O ₃	3-Hydroxy dodecanonic acid	3.33
27.01	C ₂₅ H ₃₂ O ₈	6,7-Epoxypregn-4-ene-9,11,18-triol-3,20-dione-11,18-diacetate	4.62
29.35	C ₃₉ H ₇₈ O ₃	3-Octadecoxypopyl octadecanoate	1.28
31.35	C ₁₈ H ₃₂ O ₁₆	α -Maltotriose	0.99
34.33	C ₃₀ H ₄₂ O ₁₀	Sarreroside	1.87
37.58	C ₁₄ H ₁₀	Phenanthrene	0.29
38.50	C ₂₅ H ₃₆ O ₅	12-Acetyloxy-20-oxopregn-16-en-3-yl-acetate	0.18
41.22	C ₁₈ H ₂₄ O	17-Desoxyestradiol	1.56
43.12	C ₂₅ H ₂₆ O ₅	(3-Acetyloxy-4,4,10,13-tetramethyl-7-oxo-2,3,8,9,11,12,14,15,16,17-decahydro-1H-cyclopenta[a]phenanthren-17-yl) acetate	1.11
44.63	C ₂₇ H ₄₂ O ₄	2-(3-Acetyloxy-4,4,10,13,14-pentamethyl-2,3,5,6,7,11,12,15,16,17-decahydro-1H-cyclopenta[a]phenanthren-17-yl)propanoic acid	0.81
45.42	C ₄₁ H ₆₄ O ₁₃	Digitoxin	0.14

oil at our Lab [24–28]. The density of bio-oil is 1.160 Mg/m³, LHV is 17.77 MJ/kg, and pH is 3.3. And the main organic compounds (ethyl acetate extraction) in the bio-oil are shown in Table I. The main elemental composition of bio-oil feedstock derived from fast pyrolysis of straw stalk contains 46.1%C, 7.1%H, 1.6%N, 45.2%O, and 0.07%ash. Water content in the crude bio-oil is about 40.2%. The chemical formula of the oxygenated organic compounds of the crude bio-oil feed can be expressed as CH_{1.85}O_{0.74}.

B. Catalysts and characterization

Different zeolites (such as HZSM-5, HY-zeolite, and MCM-41) were supplied by Nankai University catalyst Co., Ltd. (Tianjin, China) and calcined in nitrogen atmosphere at 550 °C for 4 h prior to use. The elemental contents of the catalysts were measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The catalysts were investigated by NH₃-TPD (temperature programmed desorption of ammonia) and BET (Brunauer-Emmett-Teller surface area) analyses. For the NH₃-TPD tests, the catalysts were at 500 °C under helium flow (ultrahigh purity, 100 mL/min) for 2 h, and adsorption of ammonia was carried out at 120 °C for 1 h. After the catalysts were

flushed with He at 120 °C for 1 h, the programmed-desorption of NH₃ was run from 120 °C to 700 °C with a heating rate of 10 °C/min. The desorbed ammonia was measured by a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou China) with a thermal conductivity detector (TCD). The N₂ 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 BTX from the catalytic cracking of bio-oil was carried out in a fixed-bed flow reactor under atmospheric pressure. This system consists of a quartz tube reactor (inner diameter: 30 mm, length: 400 mm), a gas feed system, a liquid feed pump, a heater and temperature control system, a condenser and an off-line gas analysis unit. For the typical runs, 10 g of the catalyst crushed to 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). Before the reactions, the reactor was flushed by nitrogen with the flow rate of 200 mL/min for 2 h at the room temperature, and then was externally heated to a given temperature by the fur-

TABLE II Performance of production of BTX from bio-oil over different catalysts.

Catalyst	Overall carbon yield/%			Aromatics carbon yield/%						
	Organic liquid	Coke	Gas	Benzene	Toluene	Xylenes	Ethylbenzene	Phenols	N/I ^a	Others
HY	16.3	33.3	44.8	1.3	6.0	3.9	1.6	1.0	1.5	0.9
HZSM-5	36.0	23.8	36.8	8.1	15.5	6.8	2.2	0.5	1.7	1.2
MCM-41	22.3	20.5	48.3	3.5	6.1	5.2	1.7	1.1	1.4	3.3

Catalyst	Gas carbon yield/%			Aromatics selectivity/%						
	CO, CO ₂	Alkanes ^b	C ₂ ⁼ -C ₄ ⁼	Benzene	Toluene	Xylenes	Ethylbenzene	Phenols	N/I ^a	Others
HY	26.1	10.5	8.2	8.0	36.9	23.9	9.9	6.3	9.2	5.6
HZSM	20.8	9.4	6.6	22.6	43.0	18.9	6.1	1.4	4.7	3.3
MCM-41	28.1	14.6	5.6	15.7	27.4	23.3	7.6	4.9	6.3	14.8

Reaction conditions: $f(\text{N}_2)=200 \text{ cm}^3/\text{min}$, $T=500 \text{ }^\circ\text{C}$, and 10 g bio-oil.

^a N/I means naphthalenes/indenes.

^b Gas alkanes.

nace heater with a programmed temperature controller. For gas product analysis, the entire gas in each run was collected with air bags, weighed, and analyzed using a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) with two detectors, a TCD (thermal conductivity detector) for analysis of H₂, CO, CH₄, and CO₂ separated on TDX-01 column, and a FID (flame ionization detector) for gas hydrocarbons separated on Porapak Q column. The moles of a gas product were determined by the normalization method with standard gas. The liquid products (oil and water) in each test were collected by two liquid nitrogen/ethanol bath condensers. Condensed products from the condensers were weighed to obtain the mass of liquid products. The total carbon contents in the liquid organics were measured by a Vario EL III elemental analyzer, and the water content was analyzed by a moisture analyzer (Model ZSD-1, Shanghai, China). The main components of the liquid organic products were further analyzed by a GC-MS (Thermo Trace DSQ (I)) with a TR-5MS fused-silica capillary column. The absolute moles of most of liquid components were determined by the calibrated GC-MS peak area with the standard samples. The solid residues after each experiment were immediately removed from the heating zone and cooled to room temperature in a N₂ flow. The solid residues in each experiment were weighed and measured by the TGA analysis (Q5000IR thermogravimetric analyzer, USA).

Overall carbon yields (Y_j , C-mol%) of the gas, liquid and solid products, carbon yield (Y_l , C-mol%) of a specific product, and aromatic selectivity (S_A , C-mol%) were calculated based on Eq.(1)–(3) as previously described [12]. All tests were repeated three times and the data reported are the mean values of three trials.

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

$$Y_l = \frac{x_l}{x_{\text{feed}}} \times 100\% \quad (2)$$

TABLE III Main characteristics of the catalysts used in this work*.

Catalyst	Si/Al	S_{BET}	V_p	d_{xrd}	Total acid/($\mu\text{mol/g}$)
HZSM-5	25	282.4	0.20	18.8	580.6
HY	6.2	620.0	0.35	22.0	2206.3
MCM-41	157	932.5	0.79	3.7	280.0

* Si/Al is the ratio of silicon to aluminum in the zeolites, S_{BET} in m^2/g , V_p (pore volume) in cm^3/g , and d_{xrd} (average granule size) in nm.

$$S_A = \frac{x_a}{x_{\text{Ar}}} \times 100\% \quad (3)$$

where x_j means carbon moles in gas, liquid or solid products. x_{feed} and x_l are carbon moles fed in and in a products, respectively. x_a and x_{Ar} are carbon moles in an aromatic product and aromatics, respectively. Moreover, the catalyst stability was tested with five samplings, obtained three liquid samples for 150 min of TOS (time of stream). Each sampling took about 30 min.

III. RESULTS AND DISCUSSION

A. Catalytic performance over different pore characteristics zeolites

The comparison of the transformation of the bio-oil into BTX was first carried out using different pore characteristics zeolites (HZSM-5, HY-zeolite, and MCM-41) as catalysts. As shown in Table II, the carbon yields of benzene, toluene and xylenes (BTX) derived from the catalytic cracking of bio-oil with different zeolites decreased in the following order: HZSM-5>MCM-41>HY-zeolite. It was also found that the aromatic selectivity of benzene, toluene and xylenes using the HZSM-5 were about 22.6%, 43.0%, and 18.9% respectively,

TABLE IV Effect of temperature on production of BTX from the bio-oil.

$T/^\circ\text{C}$	Overall carbon yield/%			Aromatics carbon yield/%						
	Organic liquid	Coke	Gas	Benzene	Toluene	Xylenes	Ethylbenzene	Phenols	N/I ^a	Others
500	36.0	23.8	36.8	8.1	15.5	6.8	2.2	0.5	1.7	1.2
550	35.2	22.3	45.0	8.8	15.3	3.3	3.3	0.4	2.5	1.6
600	31.0	21.2	50.5	10.8	13.0	3.0	0.8		2.4	1.0
$T/^\circ\text{C}$	Gas carbon yield/%			Aromatics selectivity/%						
	CO, CO ₂	Alkanes ^b	C2 ⁼ -C4 ⁼	Benzene	Toluene	Xylenes	Ethylbenzene	Phenols	N/I ^a	Others
500	20.8	9.4	6.6	22.6	43.0	18.9	6.1	1.4	4.7	3.3
550	25.2	12.1	7.7	25.0	43.5	9.4	9.4	1.1	7.1	4.5
600	28.2	13.8	8.5	34.8	41.9	9.6	2.6		8.0	3.2

Conditions: $f(\text{N}_2)=200\text{ cm}^3/\text{min}$ and 10 g bio-oil.

^a N/I means: naphthalenes/indenes.

^b Gas alkanes.

which were obviously higher than the levels using HY-zeolite or MCM-41 catalyst. On the other hand, the coke yields using HZSM-5, MCM-41 and HY-zeolite are about 23.8%, 20.5%, and 33.3%, respectively (reaction condition: $T=500\text{ }^\circ\text{C}$, $f(\text{N}_2)=200\text{ cm}^3/\text{min}$, reaction time=0.5 h). The transformation of the bio-oil over the Y-types zeolite produced more coke than that using HZSM-5, leading to a decrease in the BTX yield. Table III summarizes the main characteristics of the catalysts used in this work. The different performance of the transformation of the bio-oil into BTX using different zeolite catalysts should be mainly attributed to the differences in pore topology and acidities.

B. Effect of temperature on transformation crude bio-oil

Table IV shows the effect of temperature on the catalytic transformation of the bio-oil with the selected HZSM-5 catalyst. The overall carbon yields of liquid organic products decreased with increasing the reaction temperature. A higher temperature will lead to the second cracking of liquid organics and the formation of gas hydrocarbons such as gaseous alkanes and olefins. Based on the component analysis, the bio-oil fed consisted of a complex mixture of oxygenated organic compounds mainly including acids, ketones, alcohols, aldehydes, esters, substituted phenols together with levoglucosan, aromatic oligomers and other oxygenates (Table I). It should be pointed out that a large amount of oxygen (45.2%) is contained in the bio-oil. Catalytic conversion of these oxygenated organic compounds in the bio-oil over a zeolite catalyst generally involves complex reactions, mainly including deoxygenation (decarbonylation, decarboxylation, dehydration), cracking, hydrogen transfer, cyclization, aromatization and oligomerization reactions. The above observation suggests an increasing impact on the transformation of oxygenates into hydrocarbons at higher temperature.

The products observed were divided into the following categories: liquid organic compounds (mainly BTX), gaseous products (CO, CO₂, CH₄, C2-C4 alkanes and C2⁼-C4⁼ olefins) and coke (Table IV). At higher reaction temperature ($>500\text{ }^\circ\text{C}$), the liquid organic products primarily consist of benzene, toluene and xylenes (BTX), which are expected to mainly result from the deoxygenation of oxygenated organic compounds along with the removal of groups such as methyl, hydroxyl and methoxy groups in the aromatic rings with the zeolite catalyst. The bio-oil contained acids, alcohols, aldehydes, ketones, levoglucosan and esters, these compounds were almost completely converted to the hydrocarbons (such as BTX) through deoxygenation, cracking and aromatization reactions at the reaction temperature of $550\text{ }^\circ\text{C}$. Increasing the temperature from $500\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$, the carbon yield of BTX slightly decreased from 30.4% to 26.81% due to the secondary cracking of the aromatic hydrocarbons. The selectivity of BTX reaches a highest value of about 86.3% at $600\text{ }^\circ\text{C}$. The overall by-products like phenols, ethylbenzene, naphthalenes and indenes were reduced with increasing the reaction temperature. The above results show that the BTX yield decreased with increasing the reaction temperature, causing by the gasification of bio-oil at high temperature. However, when the temperature was lower than $500\text{ }^\circ\text{C}$, the bio-oil conversion decreased, leading to the decrease in the production of BTX.

On the other hand, the distribution of the aromatics derived from the catalytic cracking of the bio-oil was also sensitive to the operation temperature (Table IV). The order of different aromatics (based on carbon yield) obtained at $500\text{ }^\circ\text{C}$ is as follows: toluene>benzene>xylenes>ethylbenzene>C9⁺ aromatics>phenols. With increasing reaction temperature, the formation of benzene and toluene significantly increased, accompanied by an obvious decrease in C9⁺ aromatics, phenols and xylenes. These changes in the

TABLE V Effect of WHSV on production of BTX from the bio-oil.

WHSV/h ⁻¹	Overall carbon yield/%			Aromatics carbon yield/%						
	Organic liquid	Coke	Gas	Benzene	Toluene	Xylenes	Ethylbenzene	Phenols	N/I ^a	Others
1.0	38.2	24.2	44.8	11.4	14.5	7.2	1.0	0.6	1.8	1.6
2.0	36.0	23.8	36.8	8.1	15.5	6.8	2.2	0.5	1.7	1.2
3.0	46.6	31.7	22.7	5.7	16.5	8.5	5.2	4.9	2.6	3.0

WHSV/h ⁻¹	Gas carbon yield/%			Aromatics selectivity/%						
	CO, CO ₂	Alkanes ^b	C2 ⁼ -C4 ⁼	Benzene	Toluene	Xylenes	Ethylbenzene	Phenols	N/I ^a	Others
1.0	24.4	11.1	9.3	29.8	37.9	18.7	2.6	1.6	4.7	4.2
2.0	20.8	9.4	6.6	22.6	43.0	18.9	6.1	1.4	4.7	3.3
3.0	13.7	4.3	4.7	12.2	35.4	18.2	11.3	10.7	5.6	6.4

Reaction conditions: $f(\text{N}_2)=200 \text{ cm}^3/\text{min}$, $T=500 \text{ }^\circ\text{C}$, and 10 g bio-oil.

^a N/I means naphthalenes/indenes.

^b Gas alkanes.

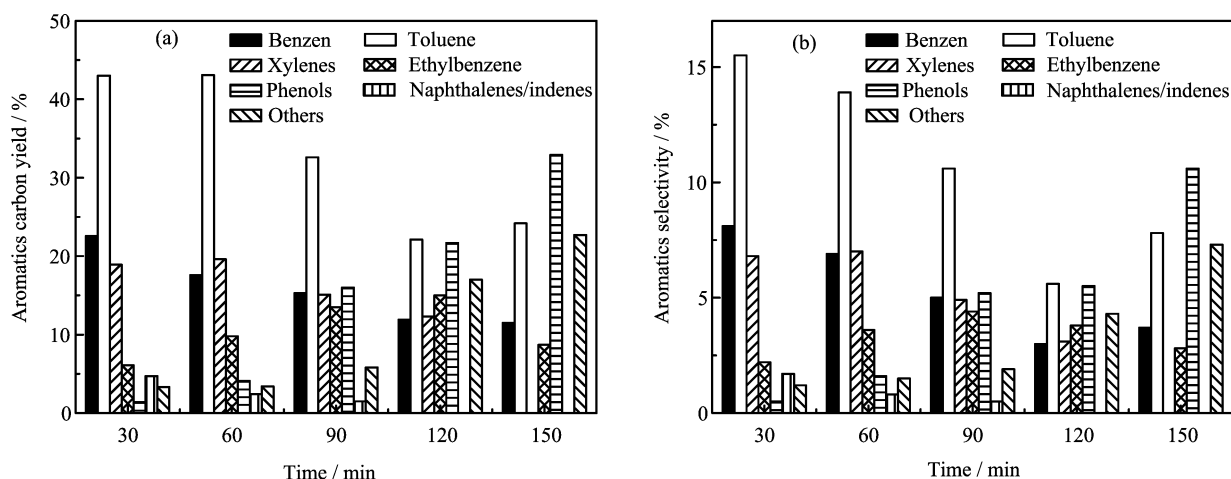
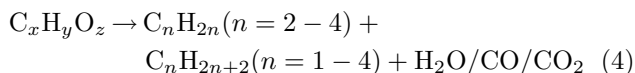


FIG. 1 Catalyst stability in the catalytic cracking of bio-oil. Aromatics carbon yield (a) and aromatics selectivity (b) over HZSM-5 catalyst, respectively. Reaction conditions: $T=500 \text{ }^\circ\text{C}$, $\text{WHSV}=2.0 \text{ h}^{-1}$.

aromatics distribution suggests that higher temperature is favorable for further removal of groups from the initial heavier aromatics (for example demethylation of xylenes), resulting in the increase in the benzene and toluene yields.

Moreover, the gas products mainly consisted of CO, CO₂, C1-C4 alkanes and C2⁼-C4⁼ olefins, and increased with the temperature increasing from 500 °C to 600 °C. CO and CO₂ are formed via the decarbonylation and decarboxylation reactions of the oxygen-containing organics over the zeolite catalyst. For the gaseous alkanes and light olefins, the oxygenated organics in the bio-oil can be directly cracked to these smaller hydrocarbons through the deoxygenation and cracking processes *i.e.*,



Also, the larger molecules in the bio-oil may be catalytically cracked to the lighter organics, and subse-

quently, followed by the secondary reactions to produce gas hydrocarbons through deoxygenation, cracking and hydrogen transfer processes.

C. Effect of WHSV on the transformation of crude bio-oil

Table V shows the production of BTX from the catalytic cracking of bio-oil as a function of weight hourly space velocity (WHSV). WHSV is defined as the mass flow rate of the feed divided by the mass of the catalyst in the reactor. With the increase of WHSV from 1 h⁻¹ to 6 h⁻¹, the BTX carbon yield gradually reduced from 33.1% to 30.7%. Increasing WHSV also resulted in the decrease in the BTX selectivity, accompanied by an increase in the hydrocarbons selectivity of ethylbenzene and phenol. Especially, the formation of benzene decreased with the increasing WHSV, accompanied by the increase in the production of toluene and xylenes. In addition, the gaseous alkanes and light olefins were

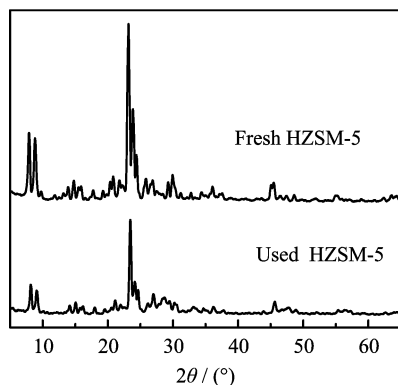


FIG. 2 XRD spectra for the fresh HZSM-5 catalyst and the used HZSM-5 catalyst after catalytic conversion of bio-oil at $T=500\text{ }^{\circ}\text{C}$ and $\text{WHSV}=2.0\text{ h}^{-1}$.

remarkably reduced at higher WHSV. The increase of space velocity generally shortens the reactants residence time in the catalyst bed, leading to the decrease both in the deoxygenation, the gasification, cracking and the secondary processes such as removal of groups from the initial heavier aromatics.

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

As shown in Fig.1, the catalyst stability in the catalytic cracking of bio-oil was tested as a function of the time on stream over the HZSM-5 catalyst under the typical reaction condition ($T=500\text{ }^{\circ}\text{C}$, $\text{WHSV}=2.0\text{ h}^{-1}$). An obvious decrease in the BTX yield had been observed for 150 min (time on stream period). The yields of benzene, toluene and xylenes decreased to about 1/2 of the initial levels. The selectivity of phenol over the used catalyst markedly enhanced, followed by the decrease in the BTX selectivity. The catalyst deactivation should be mainly caused by the carbon deposition on the catalyst during the transformation of bio-oil into BTX, considering that the activity of the catalysts can be almost recovered by the coke burn-off method (not shown here).

E. Catalyst characterization

Figure 2 shows the XRD spectra for the pristine and the used catalysts of HZSM-5. The structure of the HZSM-5 zeolite remained after operating the cracking of the bio-oil. However, the XRD peak intensity for the used catalyst was reduced as compared with the fresh one, indicating that the crystallinity decreased during the bio-oil cracking process. Figure 3 presents the NH_3 -TPD profiles for the fresh and used HZSM-5 catalysts. All tested catalysts showed three acid sites with different acid strength. One strong profile around

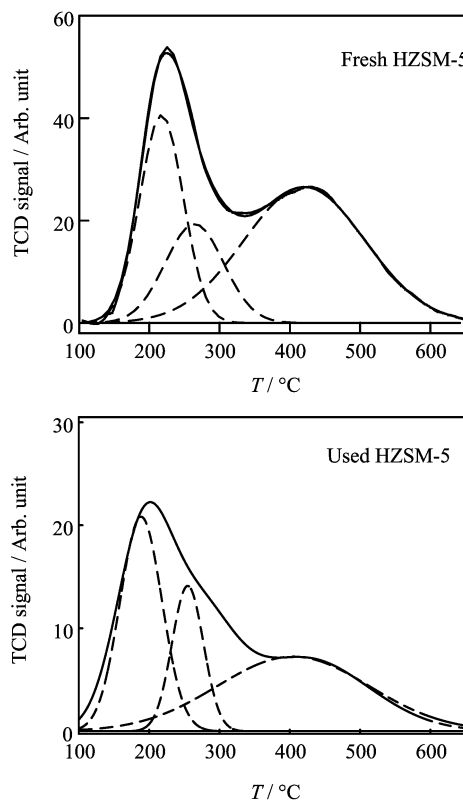


FIG. 3 NH_3 -TPD spectra for the fresh HZSM-5 and the used catalysts after the catalytic conversion of bio-oil at $T=500\text{ }^{\circ}\text{C}$ and $\text{WHSV}=2.0\text{ h}^{-1}$.

$220\text{ }^{\circ}\text{C}$ was assigned to the desorption of NH_3 from the weak acid sites and another weak profile around $430\text{ }^{\circ}\text{C}$ corresponded to the desorption of NH_3 from the strong acid sites. The intersection between the strong and weak acid sites can be deconvoluted into another Gaussian component, referring to NH_3 desorption from the medium acid sites (around $260\text{ }^{\circ}\text{C}$). After the bio-oil cracking, the total acid sites of the zeolite catalyst obviously decreased from $580.6\text{ }\mu\text{mol/g}_{\text{cata}}$ to $241.7\text{ }\mu\text{mol/g}_{\text{cata}}$. The decrease in the total acid sites on the used HZSM-5 catalyst may partly cause the decrease in the production of BTX (Fig.1).

IV. CONCLUSION

Catalytic pyrolysis of bio-oil for the production of BTX was performed by different pore characteristics of zeolites. The highest BTX yield from bio-oil using HZSM-5 reached 33.1% with aromatics selectivity of 86.4%. The reaction parameters and the types of molecular sieve catalysts have an important impact both on the BTX yield and its selectivity. Production of BTX are expected to mainly result from the deoxygenation, cracking and aromatization reactions of oxygenated organic compounds in the bio-oil. The conversion of bio-oil to BTX may potentially provide an alternative

route for the production of the key basic feedstocks for the petrochemical industry using renewable biomass resource.

V. ACKNOWLEDGEMENTS

This work was supported by the National Key Basic Program of China (No.2013CB228105) and the National Natural Science Foundation of China (No.51161140331).

- [1] F. G. Calvo-Flores and J. A. Dobado, *ChemSusChem* **3**, 1227 (2010).
- [2] P. Sannigrahi, Y. Pu, and A. Ragauskas, *Curr. Opin. Environ. Sustainability* **2**, 383 (2010).
- [3] J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius, and B. M. Weckhuysen, *Chem. Rev.* **110**, 3552 (2010).
- [4] T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, and G. W. Huber, *Science* **330**, 1222 (2010).
- [5] T. R. Carlson, Y. T. Cheng, J. Jae, and G. W. Huber, *Energy Environ. Sci.* **4**, 145 (2011).
- [6] G. W. Huber and A. Corma, *Angew. Chem. Int. Ed.* **46**, 7184 (2007).
- [7] H. Zhang, Y. T. Cheng, T. P. Vispute, R. Xiao, and G. W. Huber, *Energy Environ. Sci.* **4**, 2297 (2011).
- [8] B. Valle, A. G. Gayubo, A. T. Aguayo, M. Olazar, and J. Bilbao, *Energy Fuels* **24**, 2060 (2010a).
- [9] B. Valle, A. G. Gayubo, A. Alonso, A. T. Aguayo, and J. Bilbao, *Appl. Catal. B* **100**, 318 (2010b).
- [10] B. Valle, P. Castaño, M. Olazar, J. Bilbao, and A. G. Gayubo, *J. Catal.* **285**, 304 (2012).
- [11] W. W. Huang, F. Y. Gong, M. H. Fan, Q. Zhai, C. G. Hong, and Q. X. Li, *Bioresour. Technol.* **121**, 248 (2012).
- [12] F. Y. Gong, Z. Yang, C. G. Hong, W. W. Huang, S. Ning, Z. X. Zhang, Y. Xu, and Q. X. Li, *Bioresour. Technol.* **102**, 9247 (2011).
- [13] M. Olazar, R. Aguado, J. Bilbao, and A. Barona, *AIChE J.* **46**, 1025 (2000).
- [14] T. Q. Hoang, X. Zhu, T. Danuthai, and L. L. Lobban, *Energy Fuels* **24**, 3804 (2010).
- [15] F. A. Agblevor, S. Beis, O. Mante, and N. Abdoulmoumine, *Ind. Eng. Chem. Res.* **49**, 3533 (2010).
- [16] E. Putun, B. B. Uzun, and A. E. Putun, *Energy Fuels* **23**, 2248 (2009).
- [17] P. Wang, S. Zhan, H. Yu, X. Xue, and N. Hong, *Bioresour. Technol.* **101**, 3236 (2010).
- [18] H. Zhang, R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Energy Fuels* **23**, 6199 (2009).
- [19] K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, and H. Schnitzer, *Bioresour. Technol.* **101**, 3209 (2010).
- [20] T. R. Carlson, T. R. Vispute, and G. W. Huber, *ChemSusChem* **1**, 397 (2008).
- [21] J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo, and G. W. Huber, *J. Catal.* **279**, 257 (2011).
- [22] R. Rinaldi and F. Schüth, *Energy Environ. Sci.* **2**, 610 (2009).
- [23] D. M. Alonso, J. Q. Bond, and J. A. Dumesic, *Green Chem.* **12**, 1493 (2010).
- [24] L. X. Yuan, Y. Q. Chen, C. F. Song, T. Q. Ye, Q. X. Guo, Q. S. Zhu, Y. Torimoto, and Q. X. Li, *Chem. Commun.* 5215 (2008).
- [25] F. Y. Gong, T. Q. Ye, L. X. Yuan, T. Kan, Y. Torimoto, M. Yamamoto, and Q. X. Li, *Green Chem.* **11**, 2001 (2009).
- [26] T. Hou, L. X. Yuan, T. Q. Ye, L. Gong, J. Tu, M. Yamamoto, Y. Torimoto, and Q. X. Li, *Int. J. Hydrogen Energy* **34**, 9095 (2009).
- [27] T. Kan, J. X. Xiong, X. L. Li, T. Q. Ye, L. X. Yuan, Y. Torimoto, M. Yamamoto, and Q. X. Li, *Int. J. Hydrogen Energy* **35**, 518 (2010).
- [28] Y. Xu, T. Q. Ye, S. B. Qiu, S. Ning, F. Y. Gong, Y. Liu, and Q. X. Li, *Bioresour. Technol.* **102**, 6239 (2011).