Selective catalytic conversion of **bio-oil over high-silica zeolites**

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Abstract

Four high silica zeolites, i.e., HSZ-385, 890, 960, and 990 were utilized for the selective catalytic conversion of bio-oil from *Fallopia Japonica* to certain chemicals in a fixed-bed reactor. The Beta-type HSZ-960 zeolite showed the highest selectivity to hydrocarbons, especially to aromatics as well as PAH compounds with the lowest unwanted chemicals while HSZ-890 showed high selectivity to aromatics. NH₃-Temperature Programmed Desorption (TPD) analysis indicated that different amounts of acid sites in different zeolites determined the catalytic activity for the oxygen removal from bio-oil, in which the acid sites at low temperature (LT) region gave more contribution within the utilized temperature region. The reusability test of HSZ-960 showed the stability of hydrocarbons yield at higher temperature due to the significant contribution of coke gasification which assisted further deoxygenation of bio-oil. These results provide a guidance to select suitable zeolite catalysts for the upgrading of bio-oil in a practical process.

Keywords: Biomass; Bio-oil; High silica zeolite; Selective catalytic conversion; Deoxygenation.

1. Introduction

Nowadays, many concerns on the depletion of fossil fuels encourage researchers to conduct both basic and applied researches on the effective utilization of biomass as alternative energy feedstock (Bi et al., 2013; Gong et al., 2011; Goyal et al., 2008; Lee et al., 2014). Of all the products of biomass conversion, bio-oil from pyrolysis and liquefaction of biomass has received considerable attentions since it could replace fossil fuels or could be used as feedstock for many chemicals production (Cordella et al., 2012; Jacobson et al., 2013; Kanaujia et al., 2014; Li & Suzuki, 2010). The assessment of the potential of bio-oil has been done by many scientists and some strategies and policies have also been proposed for replacing fossil fuel with bio-oil (Demirbas, 2011; Wonglimpiyarat, 2010).

Despite its potential, bio-oil contains various unwanted oxygenated compounds such as acids and aldehydes/ketones which should be removed since their existence could result in the thermal instability of the fuel (Lehto et al., 2014; Oasmaa & Kuoppala, 2003) and mismatching with the standard fossil fuel properties. In order to upgrade the quality of bio-oil, some approaches, such as hydroprocessing / hydrotreatment and catalytic cracking have been investigated and applied. It is found that zeolite can be used for the catalytic pyrolysis of biomass to assist the aromatization of bio-oil (Foster et al., 2012; Mihalcik et al., 2011). These zeolites mainly include

Y-type zeolite (Černý et al., 2013; Mante et al., 2013; Qi et al., 2006), ZSM-5 (Fan et al., 2014; Foster et al., 2012; Vitolo et al., 2001), and Beta-type zeolite (Cheng et al., 2014). However, the relationship between the zeolite properties and product distribution is still unclear. Furthermore, the studies on the stability and reusability of zeolite catalysts after several cycles, which are the main issues for practical use of catalytic pyrolysis, are also not enough. In the present study, four kinds of commercial high silica zeolites were investigated for the upgrading of bio-oil derived from the pyrolysis of biomass in a fixed-bed reactor, and their performances on the deoxygenation of bio-oil and their selectivity to certain chemicals were compared. The reusability of zeolite catalyst with the best performance was then examined at different temperatures to understand the relationship between the reusability and pyrolysis temperature. The mechanism for deoxygenation of bio-oil using the present zeolites was analyzed and discussed. This study is expected to provide a guidance for the selection of zeolite type which can be used for selective conversion of bio-oil to different target products.

2. Materials and Methods

2.1 Catalyst preparation and characterization

High silica zeolites, i.e., Ultrastable-Y (HSZ-385), ZSM-5 (HSZ-890), and Beta-zeolite (HSZ-960 and HSZ-990), were purchased from TOSOH Corporation. Prior

77 to utilization, they were calcined at 650 °C in air for 3h to ensure the remaining
78 impurities is completely removed and stored in vacuum state to avoid moisture
79 adsorption. The surface area of the as-calcined zeolites and the reused zeolites were
80 evaluated using Brunauer-Emmet-Teller (BET) method (NOVA 4200e, Quantachrome
81 Instruments, USA). The zeolites were vacuum-degassed at 250 °C for 2 h prior to the
82 measurement. The results of surface areas of the as-calcined zeolites were shown in
83 Table 1.

84 The acidity of the zeolites were compared by NH₃-Temperature Programmed
85 Desorption method (NH₃-TPD) (Belcat, Japan). The catalyst was heated from room
86 temperature to 500 °C with a heating rate of 10 °C/min in 50 cm³/min of helium stream
87 and held for 1 h. Then it was cooled to 120 °C and stabilized at that temperature for 10
88 min. After stabilization, NH₃ stream was introduced into the cell for 1 h. To ensure the
89 single layer adsorption of NH₃ on the zeolite surface, the catalyst was then flushed with
90 50 cm³/min helium stream for 5 h to remove the physically adsorbed NH₃. After
91 stabilization at 120 °C for 10 min, NH₃ desorption was started by increasing the
92 temperature to 900 °C with a heating rate of 10 °C/min in 30 cm³/min helium stream and
93 held at that temperature for 10 min. The measured thermal conductivity detector (TCD)
94 voltage, which expresses the amount of the desorbed ammonia, was converted using the
95 calibration data and plotted as a function of temperature.

2.2 Catalytic activity and selectivity

Stem part of *Fallopia Japonica* (FJS), a fast-growing biomass in the wild field, was used as biomass feedstock. The details of its properties and pretreatment of it prior to use can be found elsewhere (Widayatno et al., 2014). The experiments were performed in a down-flow fixed-bed reactor (Kaewpanha et al., 2014) with the assistance of 50 cm³/min argon gas. For each experiment, 2 g of zeolite (height of 2.5 cm) was loaded under 0.6 g of biomass layer in a holder, which is made of deactivated stainless steel wire mesh and placed in the center of the reactor. The zeolite layer and biomass layer were separated by a thin layer of quartz wool in the holder. Ar gas was passed through the reactor with a flow rate of 50 cm³/min for about 30 min before the pyrolysis starting. The pyrolysis was conducted at 500 °C respectively with a heating rate of approximately 80 °C/min, and held at final temperature for 30 min. The obtained bio-oil was collected by two ice-cold traps. Here, acetone was used in the second cold trap to trap the light bio-oil. All collected bio-oils were mixed together for the analysis. The non-condensable gases were flowed through a gas dryer chamber and collected in a gas bag.

The gas phase was analyzed by a gas chromatography (GC 7890A, Agilent Technologies USA) using two TCD units. The bio-oil yield was calculated by subtracting the initial mass of biomass (dry ash free, daf) with the mass of remained

char, equivalent mass of gas products, mass of coke, and the water content in bio-oil. The compositions of bio-oil were analyzed by Gas Chromatography (GC-2010 Plus, Shimadzu Japan) and Mass Spectroscopy (GCMS-QP2010 Ultra, Shimadzu Japan) with Ultra ALLOY⁺-5 capillary column. The bio-oil was injected using auto injection mode into the column from a temperature of 50 °C to 300 °C with a ramp rate of 10 °C/min and hold for 10 min. The ionization chamber of MS setup was set at 200 °C. The obtained GC-MS spectra were compared with the built-in NIST database in the GC-MS apparatus to get chemical identity of the assigned peaks. The content of hydrocarbons was determined by summing the peak area percentages of hydrocarbon peaks. The contents of aliphatic, aromatics, phenol and derivatives, carbonyl, carboxyl, polyaromatic hydrocarbon (PAH), and ether were also assessed using the same method as that for hydrocarbon calculation. Water content in the bio-oil was analyzed using Karl-Fischer titration method (MKS-500, KEM Japan). In order to evaluate the reusability of zeolite, HSZ-960 was reused for 3 times at different temperatures (400, 450, 500, and 600 °C), which were denoted as reuse-1, reuse-2, and reuse-3, respectively.

3. Results and Discussion

3.1. Catalytic activity and selectivity of various zeolites

Fig. S1 shows NH₃-TPD profiles of all zeolites and their acid properties are summarized in Table 2. Two desorption peaks, which are defined as low temperature (LT) and high temperature (HT) peaks, were found for all zeolites. Among the 4 kinds of zeolites, HSZ-385 had the lowest amount of acidic sites, shown by the low intensity of ammonia desorption for both temperature regions; HSZ-890 showed the highest amount of acidic sites at HT region. Two Beta-type zeolites, i.e., HSZ-960 and HSZ-990 showed different NH₃-TPD profiles, in which HSZ-960 showed the typical Beta zeolite pattern with the main LT peak and a lower tailing peak at HT region (Miyamoto et al., 2000), while HSZ-990 showed a small LT peak with a much higher HT peak. It is reported that the main peak could shift from LT region to HT region as Si/Al ratio increased (Wang & Xin, 2001). Meanwhile, the number of acidic sites (Lonyi & Valyon, 2001a; Rodríguez-González et al., 2007; Shirazi et al., 2008; Wang & Xin, 2001) and the acidity strength followed the common correlation with Si/Al ratio. Some researchers mentioned that the maximum desorption temperature could not simply correlated with the acidity strength of zeolite and the enthalpy of ammonia desorption, which also includes the operational parameters during ammonia desorption, should be considered (Miyamoto et al., 2000; Niwa et al., 1995; Rodríguez-González et al., 2007). However, in general, it can be used as a rough estimation since the measurement used the same operational parameters and the difference of the maximum

desorption temperature is quite significant in many cases (Camiloti et al., 1999; Lonyi & Valyon, 2001a; Lonyi & Valyon, 2001b; Wang & Xin, 2001). Since the reactions were conducted at LT regions, the acid sites indicated in LT regions could be considered to explain the catalytic activity of zeolite. Thus, considering the number of acidic site and acidity strength, the order of catalytic activity should be HSZ-960 > HSZ-890 > HSZ-990 > HSZ-385 in this study.

Fig. S2 in the supplementary material shows the mass balance of the products (left axis) and the distribution of gaseous products (right axis) from the catalytic conversion over various zeolites at 500 °C. All of the gas yields were expressed in mmol per gram of dry ash free biomass (mmol/g.daf). For expressing the mass balance, the molar yields of gaseous products were converted into the equivalent mass yields. Gas yields increased only a little by using the catalyst. However, it is obvious that water yield in the liquid products increased while oil yield decreased to a great extent, indicating that H₂O should come from the catalytic conversion of bio-oil by the zeolite and the oxygen in the bio-oil was mainly removed in the form of H₂O. It should be noted that Beta-type zeolites of HSZ-960 and HSZ-990 and ZSM-5 type zeolite of HSZ-890 resulted in more H₂O generation. In case of HSZ-960, more CO₂ was produced, suggesting that more oxygen in the bio-oil were also removed in the form of CO₂. In addition, it should be noted that more coke was formed on HSZ-890. Due to its lower acidity strength at LT

region and much smaller channel than those of Beta-type zeolites, some compositions such as benzene derivatives, and polynuclear aromatics could be cracked on the surface of HSZ-890, and led to higher coke deposition (Bartholomew, 2001).

Fig. 1(a) shows the hydrocarbon yields with and without zeolite at 500 °C. In the oils shown in Fig. S2, the highest and the lowest hydrocarbon composition were found to be existed in the oil obtained by using HSZ-960 and HSZ-385, respectively, suggesting that HSZ-960 has much higher selectivity for the production of hydrocarbon from original bio-oil. This may be attributed to its more porous structure, higher surface area, and higher acid sites amongst the 4 zeolites. Herein, the yield of total hydrocarbons seemed to have great correlation with the amount of acid sites at LT region rather than the total amount of acid sites in whole temperature region.

Fig. 1(b) shows the chemical distribution in the obtained bio-oil without and with zeolite. The complete chemical distribution and GC-MS spectra of bio-oil can be seen in Table S1 and Fig. S3 in the supplementary material. One can see that HSZ-385 showed poor selectivity to certain chemicals compared with other zeolites. Especially, some unwanted chemicals such as carboxyl were also generated when using HSZ-385. In contrast, HSZ-960 showed much higher selectivity to aromatics as well as PAH compounds with only a small amount of carbonyl, while HSZ-890 gave the highest selectivity to aromatics (more than 50%). It should be noted that except for HSZ-960,

other zeolites induced the generation of significant amount of carboxyl (e.g. acetic acid), suggesting that HSZ-960 is a good catalyst for upgrading of bio-oil. Herein, the selectivity to aromatic compounds seemed to have strong correlation with the total amount of acid sites, giving the order of aromatics selectivity of HSZ-890 > HSZ-960 > HSZ-990 > HSZ-385.

3.2. Effect of zeolite bed temperature on chemical distribution and reusability of the catalyst

Fig. S4 in the supplementary material shows the effect of zeolite bed temperature on the hydrocarbons yield in the oil obtained with (a) and without (b) zeolite HSZ-960. It can be seen that for the non-catalytic system, the maximum yields of hydrocarbons and BTX compounds were obtained at 500 °C and xylene was only generated at 600 °C. In the case of the catalytic system, the yields of hydrocarbons and BTX compounds increased to a great extent at each temperature and reached the maximum at 450 °C, but the difference was not so significant.

Fig. 2 shows the chemical distribution in bio-oil obtained with (a) and without (b) zeolite HSZ-960 at different reaction temperatures. In the non-catalytic system, no selectivity was shown for certain kind of chemical since the decomposition reaction of biomass and the interactions amongst the decomposition products are very complex. In

contrast, for the catalytic system, it is obvious that the amount of aromatics in the obtained oil decreased as temperature increased up to 500 °C, and then increased slightly at 600 °C. However, the maximum yield of PAHs was obtained at 500 °C. Meanwhile, phenolic compounds increased obviously in the range between 450 - 500 °C.

Fig. 3 shows the reusability of zeolite HSZ-960 used at different temperatures. One can see that for the fresh zeolite, the highest yield of hydrocarbon (84%) was achieved at 450 °C. However, after it was reused without regeneration for 3 times, the yield of hydrocarbons including BTX compounds decreased to 61%. At 500 °C, the yield of hydrocarbons remained almost unchanged until the second reuse (84%), but for the third reuse, the yield of hydrocarbons decreased to 67%. In contrast, when the reaction temperature was increased to 600 °C, the zeolite still had good selectivity to hydrocarbon and gave high yield of hydrocarbon after being reused for 3 times, suggesting that a higher reaction temperature is necessary for maintaining the reusability of zeolite HSZ-960.

Fig. S5 in the supplementary material shows the mass balances of the products obtained after several reuses of zeolite HSZ-960 at 600 °C. One can see that coke deposited on the zeolite increased to a great extent after the first reuse, but the coke decreased gradually while the gaseous products of CO₂, CO and H₂ increased to some

extent after the second and third reuses, indicating that some coke could be gasified and moved out of the zeolite surface. The water produced from the dehydration of cellulose part in the earlier stage of biomass pyrolysis (Carlson et al., 2009) and the deposited coke could react with each other with the catalytic assistance of alkali and alkaline earth metals (AAEMs) (Guan et al., 2012; 2013a,b) in the bio-oil, producing H₂ and CO which served as reducer to react with oxygenates in bio-oil for removing out more oxygen from the bio-oil. The simultaneous decrease of coke and water content in Fig. S5 proved that the additional production of reduction gases was also come from the gasification of coke, not only from auto thermal reforming of bio-oil. The BET surface area (209 m²/g) of the zeolite reused at 600 °C for 3 times was also found to have no significant difference with that (289 m²/g) the zeolite reused at 450 °C for 3 times, indicating that severe coke deposition at higher temperature can be minimized due to coke gasification. The similar phenomenon was not observed at lower temperatures, suggesting that higher temperature is necessary for the occurring of this phenomenon in this study.

Fig. 4 shows the chemical distributions in the bio-oil obtained by reusing zeolite HSZ-960 at different temperatures. The complete chemical distributions and GC-MS spectra of the bio-oil are summarized in Table S2-S5 and shown in Figs. S6-S9 of the supplementary material. It can be seen that at lower temperatures (400 and 450 °C) the

selectivity to aromatics tended to decrease as the zeolite bed was reused for several time while the selectivity to PAHs also increased at first and then decreased to some extent. At 500 °C, the selectivity to aromatics showed a slight decrease after reused while the selectivity to PAHs remained relatively stable. In contrast, at 600 °C, the selectivity to PAHs increased while that to aromatics remained relatively stable after several reused. It indicated that zeolite HSZ-960 can maintain its high selectivity to PAHs as well as aromatics at relatively high temperatures.

4. Conclusions

4 high silica zeolites, i.e., HSZ-385, 890, 960, and 990 were investigated for the selective catalytic conversion of bio-oil to certain chemicals. It is found that all these zeolites had high deoxygenation ability for the bio-oil and the oxygen in the bio-oil was removed mainly in the form of H₂O. Beta-type zeolite of HSZ-960 showed the highest selectivity to hydrocarbons, especially to aromatics as well as PAH compounds with the lowest yield of unwanted chemicals while HSZ-890 showed high selectivity to aromatics. These results provide a guidance to select suitable zeolite catalysts for the upgrading of bio-oil in practical processes.

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384 **Table captions**

385 **Table 1.** Surface area of as-received zeolite catalysts

386 **Table 2.** Acid properties of zeolite catalysts

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388 **Figure captions**

389 **Fig. 1** Hydrocarbons yields (a) and chemical distribution of bio-oil (b) at 500 °C.

390 **Fig. 2** Chemical distribution in bio-oil obtained with (a) and without (b) zeolite
391 HSZ-960 at different reaction temperatures.

392 **Fig. 3** The reusability of zeolite HSZ-960 used at different temperatures.

393 **Fig. 4** The chemical distributions in the bio-oil obtained by reusing zeolite HSZ-960 at
394 different temperatures.

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Table 1.

Catalyst	Si/Al molar ratio	As-received surface area (m ² /g)	Surface area after calcined at 650 (m ² /g)
HSZ-385 (USY)	100	600	580
HSZ-890 (ZSM-5)	1500	310	312
HSZ-960 (Beta)	100	560	410
HSZ-990 (Beta)	1500	470	505

Table 2.

Catalyst	LT peak		HT peak	
	Temp.	Desorbed NH ₃	Temp.	Desorbed NH ₃
	(°C)	(mol/kg)	(°C)	(mol/kg)
HSZ-385 (USY)	251.6	0.04	639.9	0.03
HSZ-890 (ZSM-5)	334.9	0.02	703.7	0.31
HSZ-960 (Beta)	333.8	0.22	607.5	0.01
HSZ-990 (Beta)	291.9	0.02	636.0	0.15

Figure-1

Figure-2

Figure-3

Figure-4