



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



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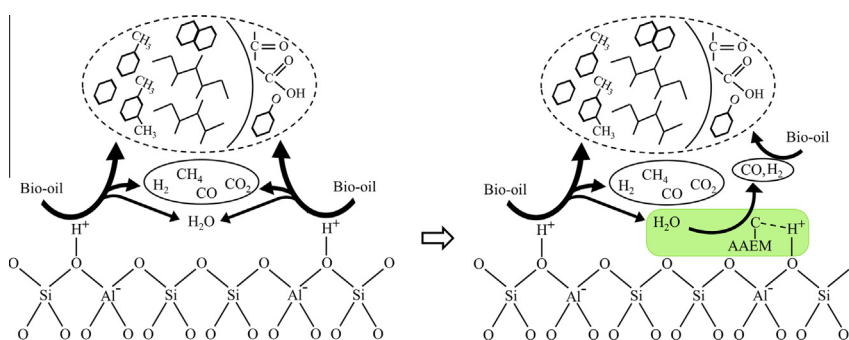
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HIGHLIGHTS

- Selective catalytic conversion of bio-oil over high-silica zeolite were investigated.
- All these zeolites had high deoxygenation ability for the bio-oil.
- The oxygen in the bio-oil was removed mainly in the form of H₂O.
- Beta-type zeolite of HSZ-960 showed high selectivity to hydrocarbons.
- Acid sites in zeolite had great effect on the catalytic activity for deoxygenation.

GRAPHICAL ABSTRACT



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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.

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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 feed-

stock (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 and 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).

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

The acidity of the zeolites were compared by NH₃-Temperature Programmed Desorption method (NH₃-TPD) (Belcat, Japan). The catalyst was heated from room temperature to 500 °C with a heating rate of 10 °C/min in 50 cm³/min of helium stream and held for 1 h. Then it was cooled to 120 °C and stabilized at that temperature for 10 min. After stabilization, NH₃ stream was introduced into the cell for 1 h. To ensure the single layer adsorption of NH₃ on the zeolite surface, the catalyst was then flushed with 50 cm³/min helium stream for 5 h to remove the physically adsorbed NH₃. After stabilization at 120 °C for 10 min, NH₃ desorption was

started by increasing the temperature to 900 °C with a heating rate of 10 °C/min in 30 cm³/min helium stream and held at that temperature for 10 min. The measured thermal conductivity detector (TCD) voltage, which expresses the amount of the desorbed ammonia, was converted using the 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

Table 1
Surface area of as-received zeolite catalysts.

Catalyst	Si/Al molar ratio	As-received surface area (m ² /g)	Surface area after calcined at 650 °C (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

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