



Research article

In-situ catalytic upgrading of bio-oil derived from fast pyrolysis of lignin over high aluminum zeolites



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ABSTRACT

Bio-oil derived from the fast pyrolysis of lignin contains a range of chemicals including a lot of oxygenated chemical components which should be selectively upgraded to improve the oil quality. In this study, *in-situ* catalytic upgrading of bio-oil during the fast pyrolysis of lignin over five types of high aluminum zeolites, *i.e.*, H-Ferrierite, H-Mordenite, H-ZSM-5, H-Beta and H-USY zeolites, were performed. It is found that the channel structure, pore sizes and acidity of zeolite had great effect on the product distribution, coke formation, and deoxygenation. The highest yield of light oil was obtained by using H-ZSM-5 zeolite and the highest selectivity towards monoaromatic hydrocarbons was achieved by H-Beta zeolite. This study could provide a guidance for the selection of suitable zeolite for the *in-situ* catalytic deoxygenation of bio-oil derived from fast pyrolysis of lignin.

1. Introduction

Lignin is considered as the abundance of renewable aromatic resource in the world. It is mainly produced in pulp and paper industry as by-product [1]. Unlike cellulose and hemicellulose, the use of lignin has no effect on food supply since it is non-edible [2]. Nowadays, the depletion of fossil fuels and its impact on environment make lignin as a promising aromatic platform resources for the production of aromatic hydrocarbons [3].

Pyrolysis is one of classical thermochemical process for cleavage of lignin to liquid products, *i.e.*, bio-oil [4]. However, such a bio-oil contains a large amount of oxygenated aromatic functional groups so that it cannot be directly used as fuel and must be upgraded prior to use [5,6]. Catalytic upgrading of bio-oil is one of processes to remove oxygen in the oxygenated compounds and improve its quality [7]. Zeolite catalyst is widely applied for the upgrading of bio-oil by deoxygenation, in which the strong acid sites in zeolites are responsible for the dehydration, decarboxylation, demethoxylation, and so on to convert oxygenated components to aromatic hydrocarbons [8]. It is reported that the Si/Al molar ratio determined the number of Brønsted acid sites, and H-ZSM-5 zeolite with high Al/Si molar ratio exhibited high performance for the catalytic pyrolysis of various lignin feedstock such as alkaline lignin [9], milled wood lignin [10], Chinese fir lignin, and rice straw

lignin [11]. Zhao et al. [12] found that the framework and pore size distribution in the zeolite also had great effect on the conversion of glucose to aromatic chemicals after testing 13 different kinds of zeolites. To date, H-ZSM-5, H-USY, H-Mordenite, and H-Beta zeolites, silica, γ -Al₂O₃, macropore materials such as MCM-41, SBA-15, MSU-J have been investigated for the fast pyrolysis of lignin by using pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS), in which the catalyst was mixed with lignin [9–11,13,14]. Py-GC–MS is a pyrolysis process performed in microreactor and the obtained volatile products are directly analyzed by GC–MS. It is a convenient way for the catalyst screening. However, the ratio of catalyst-to-biomass in Py-GC–MS was too high and the coke and char products cannot be distinguished since they were mixed with the catalyst together in the final product [15].

Thring et al. [16] reported that the highest yield of liquid from pyrolysis of Alcell® lignin was 43 wt% by using H-ZSM-5 zeolite at 550 °C and the main products were benzene, toluene, and xylene (BTX) with toluene dominating. Ma et al. [9] claimed that the liquid yield reached 74.9 wt% by using a H-USY zeolite, but a high catalyst-to-lignin ratio was used. However, the composition distribution of liquid product, including water and bio-oil (heavy oil and light oil), were unknown in these work. To solve this problem, *in-situ* catalytic upgrading of bio-oil in which the catalyst was separately placed with biomass and only contacted with pyrolysis vapors was suggested [17].

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As such, the real amount of coke on the catalyst and the product distribution, *i.e.*, char, coke, gas, bio-oil and water, can be easily determined [18–20].

In this work, in order to find suitable high aluminum zeolites for the deoxygenation of bio-oil derived from the fast pyrolysis of lignin, *in-situ* catalytic upgrading of bio-oil during the fast pyrolysis of lignin over five types of high aluminum zeolites, *i.e.*, H-Ferrierite, H-Mordenite, H-ZSM-5, H-Beta and H-USY zeolites, were performed in a fixed bed reactor placed in a rapid heating infrared furnace. The zeolite was characterized by BET, XRD and NH₃-TPD, and the upgraded bio-oil was analyzed by GC–MS and Karl-Fisher analyzer. It is expected to provide a guidance for the selection of a suitable zeolite for the *in-situ* catalytic deoxygenation of bio-oil derived from fast pyrolysis of lignin with more information than Py-GC–MS, especially the amounts of light-oil, coke, gas, and water for scaling up the catalytic upgrading process. Moreover, it is expected to clarify mechanism of deoxygenation of bio-oil derivatives from pyrolysis of lignin over different framework structures in high aluminum zeolites *via in-situ* catalytic upgrading method.

2. Materials and methods

2.1. Materials

Dealkaline lignin from Tokyo Chemical Industry Co., Ltd., Japan (TCI) was used as the feedstock, which was dried overnight at 110 °C prior to use. As shown in Table 1, the dried lignin had a moisture content of 0.3 wt% determined by moisture balance and an ash content of 15.2 wt% determined from the residual weight after calcination at 800 °C for 2 h in air with an elemental composition of C (63.0 wt%), H (5.5 wt%), O (24.9 wt%), S (6.4 wt%) and N (0.2 wt%).

High aluminum zeolites with cation type-H, *i.e.*, H-USY (HSZ-330; Si/Al 6), H-Mordenite (HSZ-620; Si/Al 15), H-Ferrierite (HSZ-722; Si/Al 18), H-ZSM-5 (HSZ-822; Si/Al 24) and H-Beta (HSZ-931; Si/Al 28) were purchased from TOSOH Corp., Japan. These selected zeolites had the highest aluminum content for each type. All zeolites were calcined at 650 °C for 2 h in air with a heating rate of 10 °C/min to remove the remaining impurities, and thereafter pressed to tablet form and then crushed and sieved to a 0.1–1.0 mm of particle size.

2.2. Lignin characterization

Thermal degradation of the dried lignin was analyzed by thermogravimetric analyzer (DTG-60H, Shimadzu, Japan). Less than 10 mg of dried lignin was heated with a heating rate of 20 °C/min in a temperature range of 50–700 °C ($\Delta T = 50$ °C) [21]. High purity of nitrogen was used as carrier gas with a flow rate of 50 cm³/min.

2.3. Zeolite characterization

Surface area and pore distribution of the zeolites were determined by nitrogen adsorption measurement (Nova 4200e, Quantachrome, USA). Before measurement, the calcined zeolite was vacuum-degassed at 200 °C for 2 h. Brunauer-Emmet-Teller method (BET) was used for determination of the total surface area and t-plot method was used for determination of micropore volume. Distribution of acid sites on the

zeolite was analyzed by ammonia desorption measurement (NH₃-TPD) (BELCAT, Japan). The crystalline structure of the zeolite was characterized by using X-ray diffractometry (Smartlab, Rigaku, Japan) in the 2 θ -range of 10–70°.

2.4. *In-situ* catalytic upgrading of bio-oil

Fig. 1 shows the equipment configuration of *in-situ* catalytic upgrading of bio-oil from the fast pyrolysis of lignin. A quartz fixed bed reactor was set in an infrared furnace (RHL-E210P, Ulvac-Rico, Inc., Japan), by which the heating rate can be set as high as 1000 °C/min so that the feedstock is rapidly heated up. The weight ratio of zeolite to the dried lignin was 1:1 [18], which were separated by a thin layer of quartz wool. Nitrogen was passed through the reactor with a flow rate of 100 cm³/min for about 15 min before pyrolysis starting. For the *in-situ* catalytic upgrading of bio-oil during the fast pyrolysis, the reactor was rapidly heated up to 650 °C with a heating rate of 1000 °C/min and then held at 650 °C for 5 min, in which the generated bio-oil was carried by nitrogen gas from the lignin layer to the catalyst layer and deoxygenated. The upgraded bio-oil was collected by acetone in a bottle with cold bath. The non-condensable gases were passed through a gas dryer and collected in a gas bag. Each experiment was performed at least 2 times with an error less than 10%.

The collected bio-oil was analyzed by GC–MS (GC-2010 Plus for GC, QP-2010 Ultra for MS, Shimadzu Japan) with an Ultra ALLOY + – 5 capillary column. One microlitre of the bio-oil in acetone was injected into GC–MS using an auto-injector with an injection temperature of 300 °C. The column temperature was increased from 50 to 300 °C with a heating rate of 10 °C/min and hold at 300 °C for 10 min. In this analysis, only the light bio-oil with boiling point below 300 °C can be detected. For identification of the compositions of the light bio-oil, all mass spectra were compared with those data in the NIST 08 mass spectrum library. As shown in Fig. 2 and Table S1, the light oil in this study was classified into seven groups: monoaromatic hydrocarbons (MAHs), polyaromatic hydrocarbons (PAHs), aromatic oxygenated, phenol, phenol ether, thiol & sulfur, and furan & other. Moreover, for quantitative analysis, aromatic hydrocarbons were classified into six groups: benzene, monosubstituted benzene, disubstituted benzene, trisubstituted benzene, indene and naphthalene groups. The amount of aromatic hydrocarbons was determined by curve fitting of similar backbone structure of standard chemicals, *i.e.*, benzene, toluene, *p*-xylene, mesitylene, indene and naphthalene, which were purchased from Wako Chemicals Co., Ltd., Japan.

The non-condensable gases were analyzed by GC-TCD (GC-TCD, Agilent 7890, USA). To quantify non-condensable gases, GC-TCD was also calibrated by the standard gas CO₂, CH₄, CO, and H₂, which were provided by Japan Fine Product Co., Ltd., Japan. The amount of deposited coke on zeolite was determined by measuring the weight loss of the spent zeolite calcined at 650 °C for 2 h in air. Karl-Fisher titration (MKS-500, KEM, Japan) was applied to determine the water content in the bio-oil. In this study, since the lignin and zeolite were separately placed in the reactor for the catalytic upgrading of bio-oil, the yield of char can be assumed as the same as that obtained by pyrolysis of lignin without catalyst [18–20].

3. Results and discussion

3.1. Characteristics of lignin

In this work, the dried lignin was used as a feedstock in order to avoid the effect of moisture content on the pyrolysis of lignin. Table 1 shows the proximate and ultimate properties of the dried dealkaline lignin. One can see that a high amount of fixed carbon (42.5 wt%) and a high mass ratio of carbon-to-hydrogen, and a high oxygen content were contained in the lignin. As shown in Fig. 3, thermal decomposition of lignin occurred in a wide range of temperature. It is reported that the

Table 1
Proximate and ultimate analysis of dried lignin.

Feedstock	Proximate analysis (wt%)				Ultimate analysis ^a (wt%)				
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	O
Dried lignin	0.3	42	42.5	15.2	63.0	5.5	0.2	6.4	24.9

^a Dry basis.

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