

Conversion of Kraft Lignin Over Hierarchical MFI Zeolite

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Catalytic pyrolysis of kraft lignin was carried out using pyrolysis gas chromatography/mass spectrometry. Hierarchical mesoporous MFI was used as the catalyst and another mesoporous material Al-SBA-15 was also used for comparison. The characteristics of mesoporous MFI were analyzed by X-ray diffraction patterns, N₂ adsorption–desorption isotherms, and temperature programmed desorption of NH₃. Two catalyst/lignin mass ratios were tested: 5/1 and 10/1. Aromatics and alkyl phenolics were the main products of the catalytic pyrolysis of lignin over mesoporous MFI. In particular, the yields of mono-aromatics such as benzene, toluene, ethylbenzene, and xylene were increased substantially by catalytic upgrading. Increase in the catalyst dose enhanced the production of aromatics further, which is attributed to decarboxylation, decarbonylation, and aromatization reactions occurring over the acid sites of mesoporous MFI.

Keywords: Kraft Lignin, Mesoporous MFI, Catalytic Pyrolysis, Py-GC/MS.

1. INTRODUCTION

Production of alternative energy using biomass has become an important issue of energy research. In particular, pyrolysis is attracting significant attention because it can be carried on most kinds of biomass materials, producing biogas, biochar, and bio-oil.^{1–15} Biogas can be used as a fuel in the pyrolysis process, while biochar can be used as heat source, soil conditioner, or adsorbent.^{13–15} Bio-oil can also be used as a liquid fuel in the industry, e.g., as boiler oil. To improve the oil quality and enhance its economic value, however, adequate post-treatment is required. Physical treatment, such as hot filtration, and chemical treatment using catalysts are generally used for the post-treatment of the pyrolysis bio-oil. The catalytic (chemical) post-treatment, which, in combination with non-catalytic pyrolysis, composes catalytic pyrolysis, is known to produce a bio-oil with a higher economic value than physical post-treatment.^{16–23} Also, catalytic pyrolysis is a very economical process because it can be operated under atmospheric pressure without using hydrogen. Acid catalysts,

such as zeolite and mesoporous materials, are usually used for catalytic pyrolysis.^{16,17}

Pyrolysis of the constituents of lignocellulosic biomass, cellulose, hemicellulose, and lignin, has recently been investigated extensively.^{24–26} In particular, lignin, composed of a chain network of aromatic compounds, is difficult to be pyrolyzed and, if pyrolyzed, it is converted to large-molecular-mass species such as tar because of its structural characteristics. Therefore, it is required to find adequate catalysts for effective pyrolytic conversion of lignin.

Thus far, microporous zeolite materials, e.g., HZSM-5, have been reported to be effective for pyrolysis of lignin.^{27,28} Because the primary products of the pyrolysis of lignin are large-molecular-mass species, however, mesoporous catalysts may be more advantageous than microporous ones because large molecules can diffuse easily into the mesopores. Based on this reasoning, Al-SBA-15 was recently applied to the catalytic pyrolysis of lignin, producing mainly phenolic compounds.¹⁸ Besides, hierarchical catalysts, which have both micro- and mesopores, were recently applied to various catalytic reactions. In particular,

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mesoporous MFI catalyst exhibited excellent performance for catalytic pyrolysis of various biomass materials, such as wood and miscanthus.^{20–23} However, mesoporous MFI catalyst has never been applied to the pyrolysis of lignin. Therefore, it is urgently required to evaluate the catalytic performance of mesoporous MFI for the conversion of lignin to extend our understanding of catalytic pyrolysis process of lignin.

In this study, mesoporous MFI was applied, for the first time, to the catalytic pyrolysis of lignin using pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). A representative mesoporous catalyst Al-SBA-15 was also used for comparison.

2. EXPERIMENTAL DETAILS

2.1. Kraft Lignin

Kraft lignin (product number: 370959) was purchased from Sigma-Aldrich.

2.2. Preparation of Catalyst

Mesoporous MFI zeolite was synthesized using the method described in the Refs. [21–23]. Al-SBA-15 was also synthesized using the method reported previously.^{18, 29, 30}

2.3. Characterization of Catalyst

X-ray diffraction patterns (XRD) were collected between 2θ angles of 5 and 35° with a Rigaku Multiflex diffractometer using Cu $K\alpha$ radiation (30 kV, 40 mA). Nitrogen adsorption isotherms were obtained at the liquid nitrogen temperature (−196 °C) using a volumetric Micromeritics Tristar-II instrument. Prior to the measurements, the sample was degassed for 12 h at 300 °C. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation using the adsorption data obtained in the pressure range $P/P_0 = 0.05–0.2$. The pore size distributions were converted from the entire adsorption branch according to the Barrett–Joyner–Halenda (BJH) algorithm. The surface acidity of the catalysts was measured by temperature programmed desorption of ammonia (NH₃-TPD) using a TPD analyzer (BELCAT-M, BEL Japan) equipped with a thermal conductivity detector (TCD). Samples were heated to 500 °C under helium flow (30 mL min^{−1}) prior to the NH₃ adsorption to remove the compounds adsorbed in the sample. After cooling down to 100 °C, NH₃ adsorption was carried out. Subsequently, samples were exposed to a helium flow at 100 °C to remove NH₃ adsorbed weakly. The TPD profile was obtained while rising the temperature from 100 °C to 650 °C at a rate of 100 °C min^{−1} under a helium flow (30 mL min^{−1}).

2.4. Py-GC/MS Analysis

Catalytic pyrolysis was conducted using Py-GC/MS to evaluate the performance of the catalyst for upgrading the bio-oil produced from the lignin.

Experiments were carried out in a vertical-furnace-type pyrolyzer (Py-2020D, Frontier-Lab. Ltd., Fukushima, Japan). For the non-catalytic pyrolysis, 0.7 mg of kraft lignin was only placed on the metal sample cup floor. For the catalytic pyrolysis, two lignin:catalyst mass ratios of 1:5 and 1:10 were used. The pyrolysis products were analyzed using the method reported previously.¹⁸

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalyst

Figure 1 shows the XRD pattern of the mesoporous MFI synthesized in this study. The typical structural characteristics of MFI are revealed well by this figure. Figure 2 shows the nitrogen adsorption isotherms. Mesoporous MFI catalyst exhibited type-IV isotherms, having a sharp nitrogen capillary condensation step at $P/P_0 \approx 0.95$. As is shown in Table I, the specific surface area, pore volume, and pore size of the mesoporous MFI were 496 m²/g, 0.41 cm³/g, and 2.8 nm, respectively. The Si/Al ratio was 20.

Figure 3 shows the NH₃ TPD results. Mesoporous MFI was shown to have both a weak acid site peak appearing

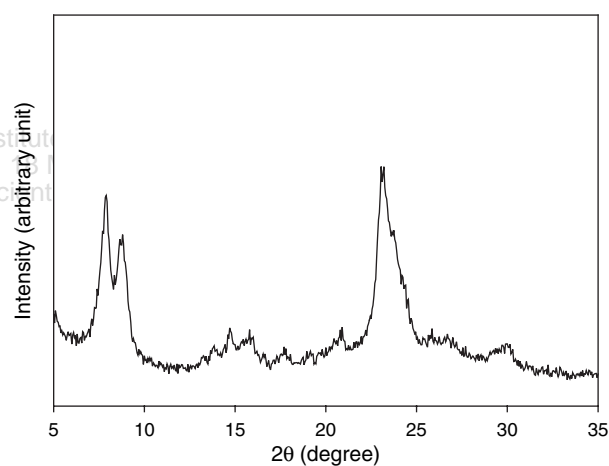


Figure 1. XRD pattern of mesoporous MFI.

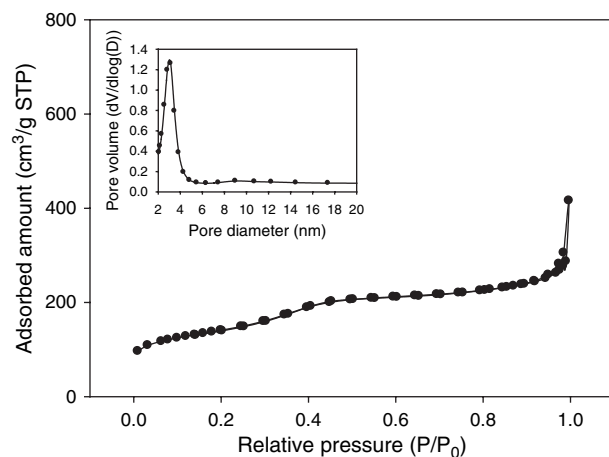


Figure 2. N₂ adsorption–desorption isotherm of mesoporous MFI.

Table I. Physical characteristics of catalysts.

Catalyst	Si/Al	BET surface area (cm ² /g)	BJH pore size (nm)	Pore volume (cm ³ /g)
Mesoporous MFI	20	496	2.8	0.41
Al-SBA-15	20	429	10.7	1.1

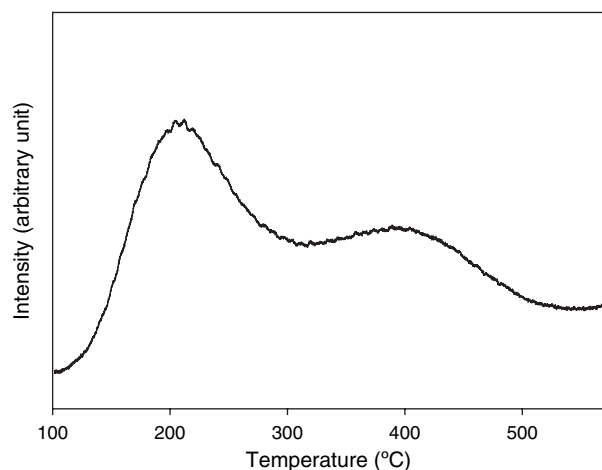
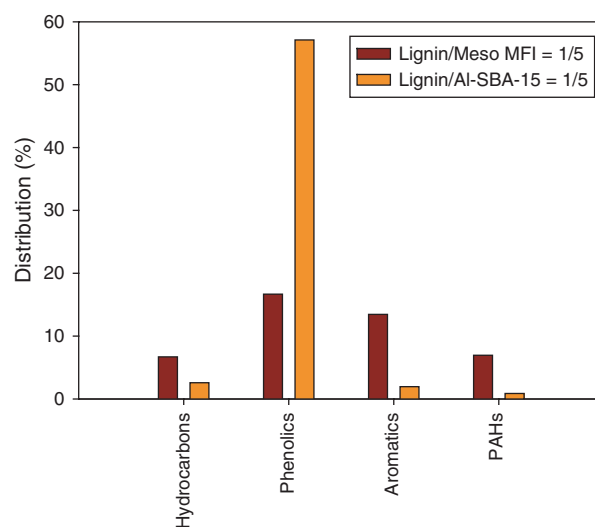
at 210 °C and a strong acid site peak appearing at 400 °C. Because high acidity is known to play a more important role for the pyrolysis of lignin,^{18,27,28} the result shown in Figure 3 implies a high potential of mesoporous MFI for the pyrolysis of lignin.

3.2. Catalytic Conversion of Lignin

When Py-GC/MS chromatograms obtained with and without catalyst were compared (data not shown), a number of large-molecular-mass peaks were observed in the case of non-catalytic pyrolysis. In the case of catalytic pyrolysis, however, the intensities of small-molecular-mass peaks, appearing over the small retention time range, increased at the cost of large-molecular-mass peaks. In particular, in the case of mesoporous MFI, most large-molecular-mass peaks disappeared. This indicates that mesoporous MFI is superior to Al-SBA-15 for lowering the average molecular mass of the product of pyrolysis of lignin.

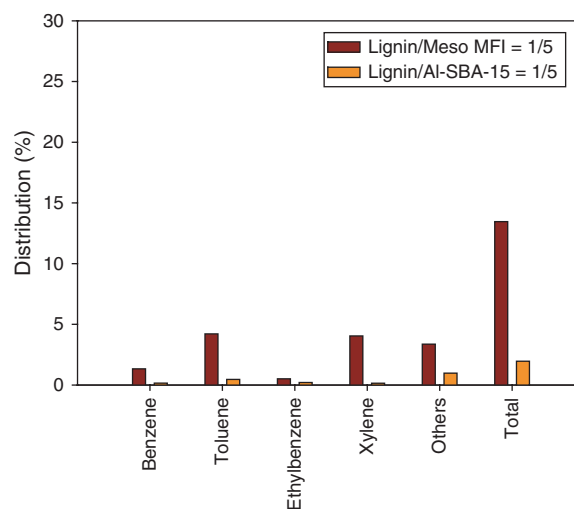
The non-catalytic pyrolysis product was composed mainly of phenolics (> 60 area%) and oxygenates (aldehydes, ketones, esters and furans: c.a. 10 area%), while the fractions of other species including acids, hydrocarbons, aromatics, polyaromatic hydrocarbons (PAHs) were negligible (data not shown). In the case of catalytic pyrolysis (Fig. 4), however, hydrocarbons, phenolics, aromatics, and PAHs were the main species, while oxygenates disappeared completely.

Hydrocarbons produced over mesoporous MFI were 2-methyl-1-propene, 1,3-cyclopentadiene, cyclopentene, isopropenylcyclopropane, 1,4-cyclohexadiene, 1-hexen-3-yne and cyclohexene. Al-SBA-15 also produced 2-methyl-1-propene, 1,3-cyclopentadiene, 1,4-cyclohexadiene,

**Figure 3.** NH₃ TPD of mesoporous MFI.**Figure 4.** Product distribution of catalytic pyrolysis of lignin.

1-hexen-3-yne and cyclohexene. Meanwhile, the product of catalytic pyrolysis over Al-SBA-15 was mostly phenolics. On the other hand, mesoporous MFI increased the production of aromatics considerably. This difference in the product distribution is attributed to the acid properties of the catalysts.

Production of aromatics from phenolics is generally known to be difficult. In the presence of adequate acid sites, however, it is possible to produce aromatics from phenolics. Ma et al.²⁷ reported that they could produce aromatics from phenol on acid sites. As was shown in the NH₃-TPD (Fig. 3), mesoporous MFI has strong acid sites. Under a high enough catalyst/lignin ratio of 5/1, therefore, phenolics could be converted to aromatics over strong Brønsted acid sites via cracking, oligomerization, and aromatization reactions. In the case of Al-SBA-15, however, formation of aromatics was not significant despite the high

**Figure 5.** Distribution of mono-aromatics produced from catalytic pyrolysis of lignin.

catalyst/lignin ratio. This is attributed to the weak acidity of Al-SBA-15.¹⁸ Therefore, the high strength and large quantity of the Brönsted acid sites present in mesoporous MFI seems to be the reason for the active production of aromatics in this study. In particular, it was encouraging that the contents of mono-aromatics such as benzene, toluene, ethylbenzene, and xylene, which are important feedstock species in the petroleum chemical industry, rather than poly aromatic hydrocarbons, were high (Fig. 5). The selectivity toward toluene and xylene, among the mono-aromatics, was particularly high. The MFI structure of the mesoporous MFI, which has been reported to have shape selectivity toward mono-aromatics, is believed to have contributed, in part, to the production of mono-aromatics.

Figure 6 shows the phenolics distribution obtained from catalytic pyrolysis. Alkyl phenols (phenol, methyl

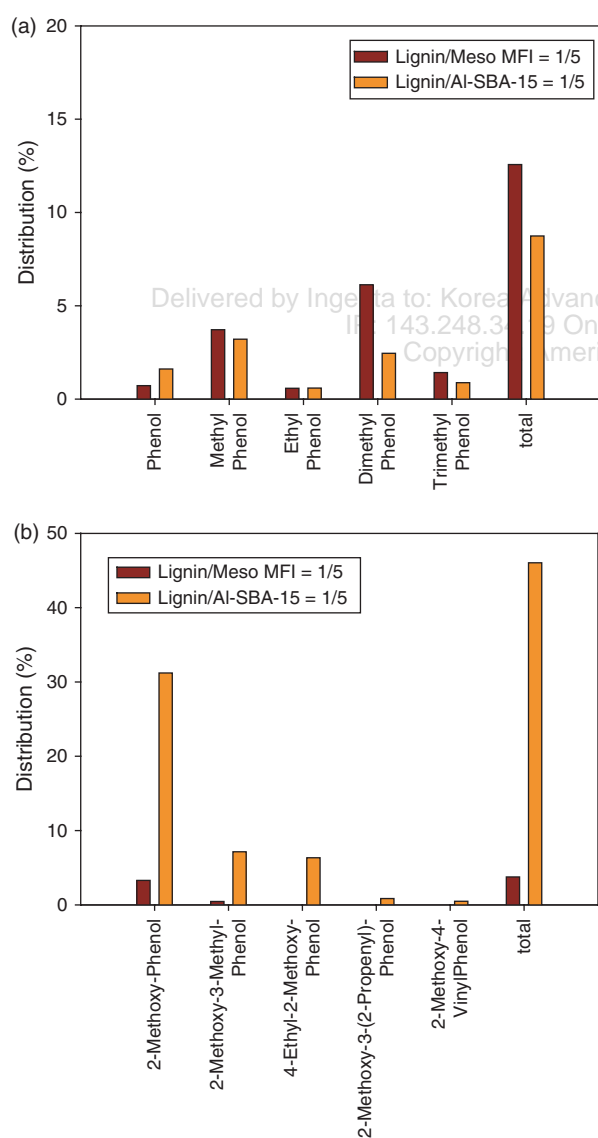


Figure 6. Distribution of (a) alkyl phenolics (b) alkoxy phenolics obtained from catalytic pyrolysis of lignin.

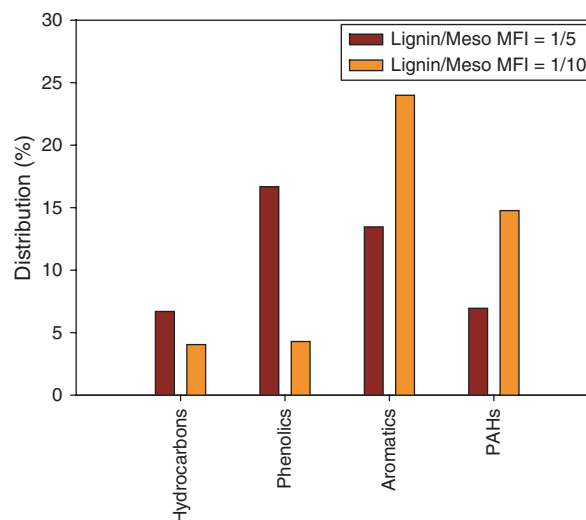


Figure 7. Effect of catalyst/lignin ratio on the product distribution of catalytic pyrolysis of lignin.

phenol, ethyl phenol, dimethyl phenol, trimethyl phenol, etc.) were mainly produced by mesoporous MFI, whereas Al-SBA-15 led to more production of alkoxy phenols such as 2-methoxy phenol. This difference is attributed to the strong acid sites of mesoporous MFI, which promotes deoxygenation reaction, such as decarbonylation and decarboxylation, of phenolics.

Increase of the catalyst/lignin ratio from 5/1 to 10/1 promoted further the conversion of phenols to aromatics because of the increase in the quantity of acid sites (Fig. 7). In particular, the amount of alkyl phenols decreased substantially (Fig. 8), most of which has seemingly been converted to aromatics. Alkoxy phenols were converted to other species completely because the increase in the acid sites promoted deoxygenation.

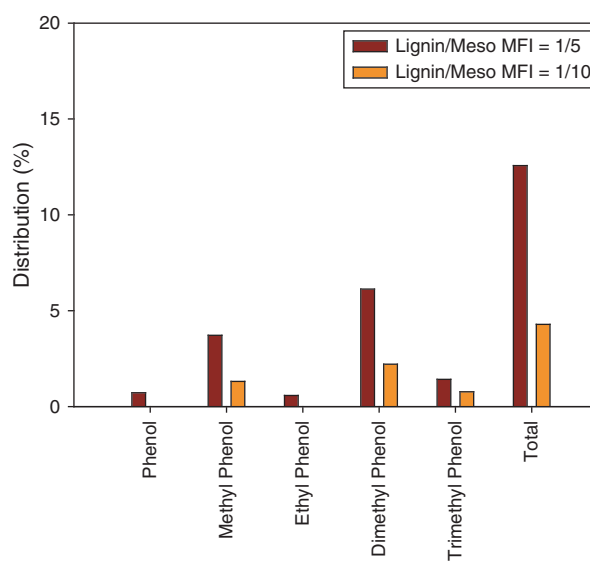


Figure 8. Effect of catalyst/lignin ratio on the distribution of alkyl phenolics obtained from catalytic pyrolysis of lignin.

4. CONCLUSIONS

Catalytic pyrolysis of lignin was carried out over mesoporous MFI using Py-GC/MS. The main products of catalytic pyrolysis were alkyl phenols (phenol, methyl phenol, ethyl phenol, dimethyl phenol, trimethyl phenol, etc.) and mono-aromatics (benzene, toluene, ethylbenzene, and xylene) because the strong Brønsted acid sites of mesoporous MFI could convert phenolics to aromatics. The acid sites of mesoporous MFI were also very active for deoxygenation reaction, such as decarbonylation and decarboxylation, of alkoxy phenols.

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