

Catalytic Conversion of Cellulose Over Mesoporous Y Zeolite

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Mesoporous Y zeolite (Meso-Y) was applied, for the first time, to the catalytic pyrolysis of cellulose which is a major constituent of lignocellulosic biomass, to produce high-quality bio-oil. A representative mesoporous catalyst Al-MCM-41 was also used to compare its catalytic activity with that of Meso-Y. Pyrolysis-gas chromatography/mass spectrometry was used for the experiments. Meso-Y, with higher acidity, led to larger yields of aromatics and furans with high value-added than Al-MCM-41, resulting in the production of bio-oil with higher quality. The effect of temperature on the catalytic pyrolysis was not significant within the range of 400–500 °C. When the Meso-Y to cellulose ratio was increased from 1/1 via 2/1 to 3/1, the deoxygenation efficiency increased, leading to increased yield of aromatics.

Keywords: Cellulose, Mesoporous Y, Bio-Oil, Catalytic Pyrolysis.

1. INTRODUCTION

Replacement of fossil fuels with renewable energy has become a major topic of the energy research.^{1–7} Biomass is a renewable energy source that is carbon-neutral. Pyrolysis of biomass provides bio-oil, which has potential to replace petroleum-derived liquid fuels in the future.^{7–10} The use of crops, among a variety of biomass materials, for bio-energy production can cause food supply shortage. Therefore, the use of non-food lignocellulosic biomass, such as woody biomass, for bio-energy production is attracting increasing attention. Cellulose, a polymer composed of chains of six-carbon sugars (primarily glucose with 1–4 glycosidic bond), accounts for a substantial fraction (40–80%) of lignocellulosic biomass. The molecular linkages in cellulose form linear chains that are rigid, highly stable, and resistant to chemical attack. Therefore, understanding the pyrolysis characteristics of

cellulose is important in grasping the pyrolysis characteristics of biomass.

Thus far, pyrolysis of various biomass materials, including wood, rice straw, miscanthus, switch grass, and sewage sludge, has been investigated. The bio-oils produced from the pyrolysis of these biomass materials exhibited inferior fuel properties, e.g., high oxygen content, low pH, and low heating value, to those of petroleum-derived liquid fuels. Catalytic pyrolysis was employed to improve the quality of bio-oil. Upgrading of bio-oil upon acid catalysts, such as zeolite, reportedly reduced the oxygen content and enhanced the heating value.

On the other hand, reports on (either catalytic or non-catalytic) pyrolysis of cellulose are relatively rare. In addition, most researches on the pyrolysis of cellulose employed microporous zeolite, such as HZSM-5, HY, and HBeta.^{8–10} Bio-oil components produced by the pyrolysis of cellulose has so large molecular size that mesoporous materials with large pore diameter could be beneficial

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for the diffusion of pyrolyzed components. Nevertheless, application of mesoporous materials to the pyrolysis of cellulose was seldom reported. Al-MCM-41 and Al-SBA-15 are the only two mesoporous materials that were reportedly used for the pyrolysis of cellulose. Mesoporous catalysts converted from microporous zeolite has never been used for the pyrolysis of cellulose. Therefore, studying the pyrolysis of cellulose over zeolite-derived mesoporous catalysts can help enhance our understanding of the pyrolysis of cellulose over mesoporous catalysts.

In this study, mesoporous Y zeolite (Meso-Y) synthesized from Y zeolite using pseudomorphic synthesis method⁸ was applied, for the first time, to the catalytic pyrolysis of cellulose. A representative mesoporous material Al-MCM-41 was also used for comparison.

2. EXPERIMENTAL DETAILS

2.1. Biomass

Commercial pure cellulose was purchased from Sigma-Aldrich.

2.2. Preparation of Catalysts

Meso-Y was prepared using the pseudomorphic synthesis method, a zeolite recrystallization process combining partial destructure and constructure of zeolite frameworks. For the detailed procedure of this method, one can refer to a previous study.¹¹

Al-MCM-41 catalyst was prepared using the method reported in the literature.^{12–14}

2.3. Py-GC/MS Analysis

A vertical furnace type pyrolyzer Py-2020D (Frontier-Lab Co.) was used for the pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis. The detailed method was described in the literature.¹¹

3. RESULTS AND DISCUSSION

The characteristics of the catalysts used in this study were reported in the literature.¹¹ In summary, the average size of the mesopores of Meso-Y was 3.1 nm. The BET surface areas of Al-MCM-41 and Meso-Y zeolite were 998 and 755 m²/g, respectively. The pore size of Al-MCM-41 was 2.8 nm. The acidity (strength and quantity of acid sites) of Al-MCM-41 was much lower than that of Meso-Y.

The product distribution obtained from the pyrolysis of cellulose is shown in Figure 1. The catalyst/cellulose ratio shown in the figure legend is the weight ratio. In the absence of catalyst, acids and oxygenates were the two main categories of the product species. On the other hand, catalytic pyrolysis over Meso-Y and Al-MCM-41 resulted in significant change in the product distribution; the fraction of oxygenates was reduced considerably, while that of acids increased and hydrocarbons, phenolics, aromatics, and poly aromatic hydrocarbons (PAHs), which

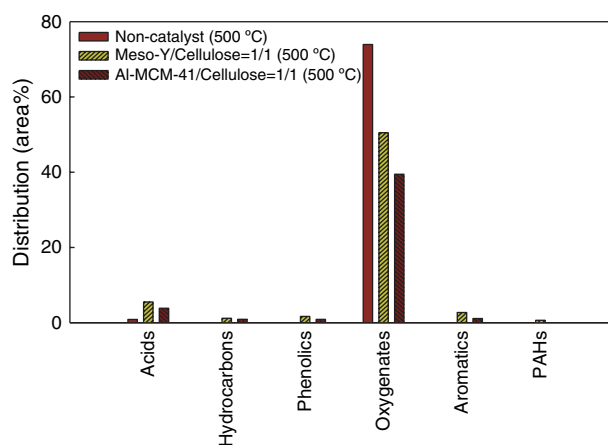


Figure 1. Product distributions obtained from the pyrolysis of cellulose over Meso-Y and Al-MCM-41.

were not detected in the non-catalytic pyrolysis product, were produced. This change is attributed to the conversion of oxygenates to other species, which occurs when the product vapor passes through the catalyst layer. The product distributions obtained with two mesoporous catalysts were a little different. On the whole, the product yields obtained with Meso-Y was higher than those obtained with Al-MCM-41. In particular, the difference for the aromatic yield was large. This is ascribed to the higher acidity of Meso-Y than that of Al-MCM-41. Strong acidity of the catalyst is advantageous for dehydration, decarboxylation, decarbonylation, cracking, oligomerization, and aromatization of pyrolyzed vapor because these reactions typically take place in the presence of acid sites.

Among the product components, acids need to be removed because they cause corrosion of engines and equipments. Acetic acid appeared to be the main acid component, which increased upon catalytic upgrading. The increased production of acetic acid by the use of a mesoporous catalyst was previously reported by Jeon et al.¹⁵ An additional process for removing acids is required to use the bio-oil as a fuel. The oxygenate species contained in the product bio-oil were grouped into 6 categories: esters, ketones, aldehydes, cyclocompounds, furans, and levoglucosan (Fig. 2). The main oxygenate product of non-catalytic pyrolysis was levoglucosan, while it was converted completely to other species by catalytic upgrading over Meso-Y and Al-MCM-41. In particular, furans appeared to be the main oxygenate species of the catalytic pyrolysis bio-oil. This can be attributed to conversion of levoglucosan to furans over the acid sites of the catalyst by dehydration reaction.¹⁶ Meso-Y, which has a larger quantity of acid sites than Al-MCM-41,¹¹ led to a higher furan yield. Jeon et al.¹⁵ investigated the catalytic pyrolysis of cellulose over SBA-15-based catalysts and reported that acid sites played an important role in the conversion of levoglucosan. For example, Al-SBA-15 with many acid sites converted levoglucosan completely, while Si-SBA-15 without acid

sites led to considerable amount of levoglucosan remaining unconverted. The main species produced by the conversion of levoglucosan over Al-SBA-15 were furans.

Meanwhile, increase in the yields of furan (11.7%), 2-methyl furan (7.5%), and furfural (7.9%) by catalytic upgrading over Meso-Y was more significant than that of other species such as furanone (0.9%) and benzofuran (1.5%). This implies that cracking by catalyst promoted production of light furans. Production of furan and 2-methyl furan indicates enhanced decarbonylation reaction. Therefore, deoxygenation, such as dehydration and decarbonylation, appeared to be promoted over catalyst. Because furans are used as important feedstock in the chemical industry, enhanced production of furans can increase the economic value of the bio-oil.

Among the species that can deteriorate the stability of bio-oil, esters were completely removed by both catalysts. On the other hand, the yield of ketones was almost constant, while that of aldehydes increased considerably. Aldehydes were volatile, mostly being acetaldehyde. These species should also be removed before using the bio-oil as a fuel.

Aromatic compounds are very important chemicals used in the petroleum chemical industry. Promotion of the production of aromatics using catalysts is therefore important in economic aspect. As shown in Figure 1, aromatics, which were not produced in the non-catalytic pyrolysis of cellulose, were observed in the catalytic pyrolysis product. On the whole, Meso-Y led to a larger yield of aromatics than Al-MCM-41 by a factor of more than 2. This was attributed to the higher acidity of Meso-Y than that of Al-MCM-41¹¹ because the formation of aromatics is promoted on the strong Brønsted acid sites. PAHs, composed mostly of naphthalene, were observed only upon the upgrading over Meso-Y (Fig. 1).

The effect of temperature on the catalytic pyrolysis was also examined. The results obtained by using the cellulose to catalyst ratio of 1/1 at 400 °C, 450 °C, and

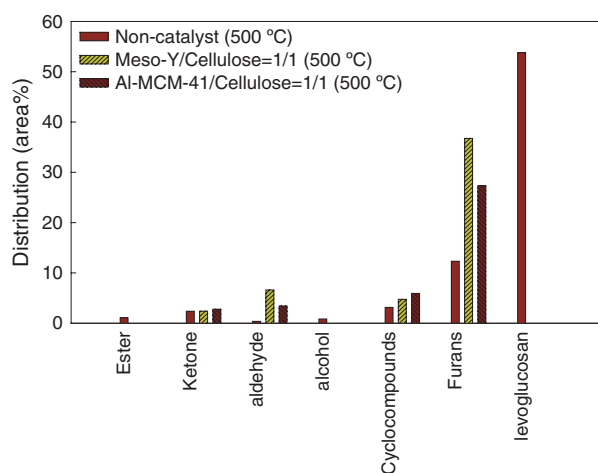


Figure 2. Oxygenates distributions obtained from the pyrolysis of cellulose over Meso-Y and Al-MCM-41.

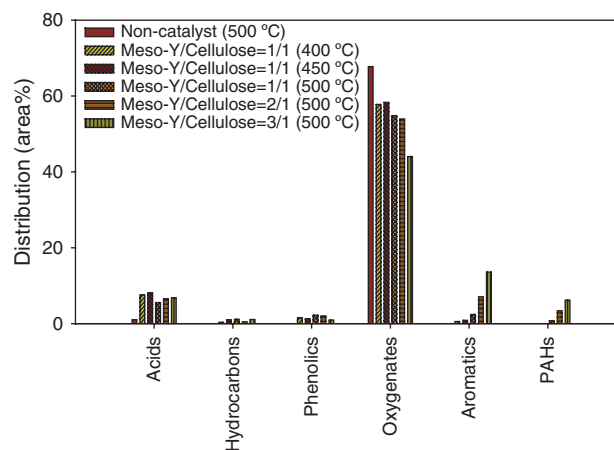


Figure 3. Product distributions obtained from the pyrolysis of cellulose with various Meso-Y/cellulose ratios.

500 °C are shown in Figure 3. The difference among the results were not large although the difference between the results obtained at 450 °C and 500 °C was larger than that between 400 °C and 450 °C and the reduction of oxygenates was the most significant. Therefore, we conclude that the temperature effect was not very important in the temperature range of 400–500 °C although we cannot rule out the potential temperature effect beyond the temperature range tested in this study.

The effect of catalyst dose appeared to be more significant than that of temperature. In particular, reduction of oxygenates and increased production of aromatics and PAHs were observed with increased catalyst dose. As was mentioned above, the effect of the quantity of acid sites on the conversion of cellulose is huge. Increasing the catalyst dose is a direct way to increase the quantity of acid sites that promote dehydration, decarbonylation, decarboxylation, cracking, oligomerization, and aromatization, converting cellulose effectively.

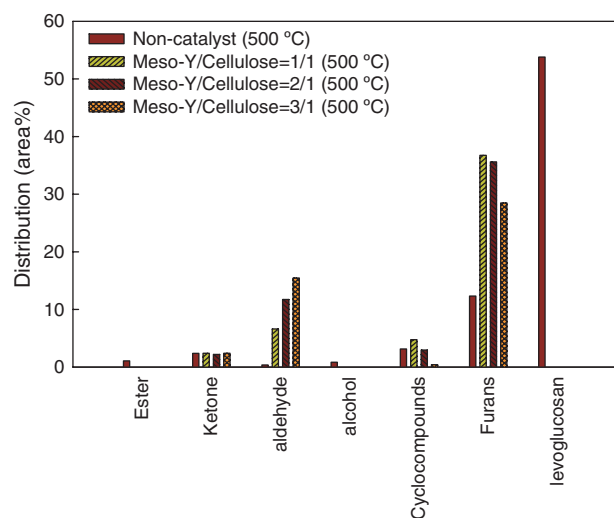


Figure 4. Oxygenate distributions obtained from the pyrolysis of cellulose with various Meso-Y/cellulose ratios.

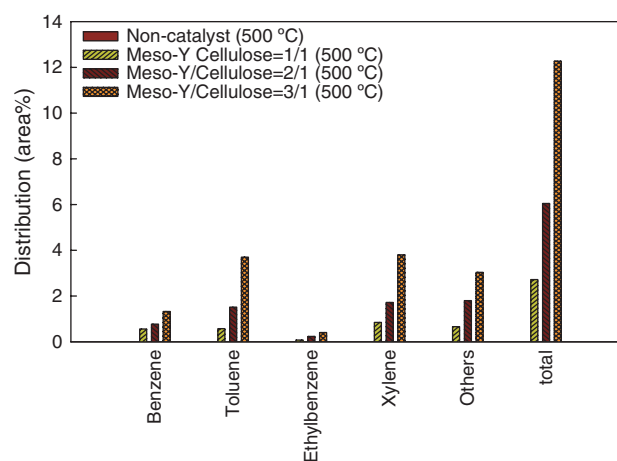


Figure 5. Monoaromatics distributions obtained from the pyrolysis of cellulose with various Meso-Y/cellulose ratios.

The distributions of oxygenates obtained with different catalyst doses are compared in Figure 4. Levoglucosan was produced only from the non-catalytic pyrolysis. The yield of furans increased, compared to the non-catalytic pyrolysis, by catalytic upgrading but the furan yield was highest with the Meso-Y to cellulose ratio of 1/1. When the distributions of furans obtained with different catalyst doses were compared, the furan production decreased as the Meso-Y to cellulose ratio increased from 1/1 to 3/1. This can be attributed to the conversion of produced furans to other species on the acid sites. Huber et al.¹⁷ reported the conversion of furans to aromatics over an acid catalyst. In this study, the aromatics yield also increased with increasing catalyst dose (Figs. 3 and 5) implying the conversion of furans to aromatics by increased acid sites.

Figure 5 compares the distributions of aromatics obtained with different catalyst doses. The aromatics yield increased dramatically with increasing Meso-Y dose. As was explained above, cracking, oligomerization of lower olefins, and aromatization, which take place in the presence of acid sites, are important for the formation of aromatic compounds. Therefore, increase of the acid sites can promote the production of aromatics. Enhanced production of aromatics increases the economic value of the product bio-oil.

4. CONCLUSIONS

Catalytic pyrolysis of cellulose was performed over Meso-Y for the first time. The catalytic activity of Meso-Y

was compared with that of Al-MCM-41. Owing to the stronger acidity of Meso-Y than that of Al-MCM-41, catalytic upgrading over Meso-Y resulted in larger yields of aromatics and furans with high value-added, compared to the upgrading over Al-MCM-41. The effect of catalyst dose on the product distribution was huge, while the effect of temperature was not significant within the range of 450–500 °C. As the catalyst dose increased, the quantity of acid sites increased, promoting the formation of aromatics.

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