Catalytic Upgrading of Geodae-Uksae 1 over Mesoporous MCM-48 Catalysts

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Catalytic pyrolysis of Geodae-Uksae 1, a kind of miscanthus found in Korea, was carried out over mesoporous MCM-48 catalysts. For rapid product analysis and catalyst evaluation, pyrolysis-gas chromatography/mass spectrometry was used. X-ray diffraction, nitrogen sorption, pyridine adsorbed Fourier transform infrared, and NH_3 temperature programmed desorption were utilized to analyze the properties of the catalysts. Compared to non-catalytic reaction, catalytic upgrading over mesoporous Al-MCM-48 catalysts produced a higher-quality bio-oil with a high stability and low oxygen content. Al-MCM-48 exhibited higher deoxygenation ability than Si-MCM-48 due to its higher acidity.

Key Words : Geodae-Uksae 1, Catalytic pyrolysis, MCM-48, Bio-oil

Introduction

Since industrial revolution, the demand for fossil fuel such as coal and oil has greatly increased accompanied by the development of the chemical industry. Because the continuous supply and utilization of fossil fuel inhibits the sustainable growth of living environment, a large attention is paid to the renewable energy. At this moment, biomass conversion process is a strong candidate due to the capability of large energy production.[1] Bioenergy from biomass can provide 30% of global energy demand in 2020. Especially, the pyrolysis of biomass is the most suitable for the production of a lot of bioenergy among the various biomass conversion processes. Pyrolysis is a thermal process to produce bio-oil in an oxygen-free atmosphere.[2-10] Fast pyrolysis is an optimized process for bio-oil production because its yield is over 50%. However, there is a difficulty for its commercial utilization due to the low heating value and high acidity of the product bio-oil. Therefore, bio-oil should be reformed with catalyst to use it in transport fuel applications. Also, it is essential to use catalyst in order to enhance the yield of valuable products such as furans, phenolics and mono-aromatics from bio-oil.[1,11,12] Mesoporous materials like Al-SBA-15 and Al-MCM-41 have been proved to be effective for the catalytic pyrolysis of biomass.[13-16]

Among various biomass materials, energy crops refer to the plants that are cultivated for dedicated energy production. Geodae-Uksae 1 (giant miscanthus found in Korea) is a sort genotype of *Miscanthus sacchariflorus* (Amur silvergrass) recently discovered Korea.[17,18] It grows as tall as 4 m with an average stalk diameter of 1 cm, which produces dry mass of approximately 30 ton/ha/yr. Due to the doubled yield compared to the common miscanthus, Geodae-Uksae 1 is now cultivated for bioenergy in large scale. Various conversion methods for this crop is being investigated, including biological fermentation, thermal combustion, and thermal fast pyrolysis.[17] However, few papers were reported about the catalytic pyrolysis of miscanthus, especially none with Geodae-Uksae 1.

In this study, the catalytic pyrolysis of Geodae-Uksae 1 was carried out. Al-MCM-48, which is known to be effective for the conversion of large-molecular-mass biomass to bio-oil due to its large pore size, was applied as the catalyst. Al-MCM-48 was more effective than Al-MCM-41 for the pyrolysis of miscanthus in a previous study.[1] An *in-situ* analysis of the product of the catalytic pyrolysis was done using pyrolysis gas chromatography/mass spectroscopy (Py-GC/MS). To investigate the effect of acid sites, Si-MCM-48 without acidity was also used.

Experimental

Geodae-Uksae 1 which was obtained from Korean Rural Development Administration was ground into powders and it was dried at 110 °C in an oven for at least 24 h before experiment. The proximate analysis result of Geodae-Uksae1 was moisture (7.3 wt %), volatile matter (73.2 wt %), fixed carbon (15.9 wt %), and ash (3.6 wt %).[17] The elemental composition analysis of Geodae-Uksae1 on the dry-ash-free basis reveals 47.6%, 5.5%, 46.1% and 0.8% of carbon, hydrogen, oxygen, and nitrogen, respectively.[17] The cellulose, hemicellulose and lignin contents of Geodae-Uksae 1

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were 40.8%, 31.4% and 23.0%, respectively.

Si-MCM-48 and Al-MCM-48 were prepared following the procedure suggested in previous studies.[19,20] After synthesis, the catalysts were calcined for 3 h in air at 550 °C. Before each experiment, catalysts were dried in a 110 °C oven for at least 2 h.

Sorption analysis, X-ray diffraction (XRD), NH_3-temperature-programmed desorption (NH_3-TPD), and pyridine Fourier transform infrared (FT-IR) spectroscopy techniques were used to analyze the properties of catalysts. The N_2 adsorption isotherms were obtained using a volumetric adsorption analyzer (Micromeritics Tristar 3000) at −196 °C. Apparent specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Total pore volume was calculated from the quantity of nitrogen adsorbed at $P/P_0 = 0.95$. Pore size distribution was deduced based on the Barret–Joyner–Halenda method.

The crystalline structure of the catalyst powder samples were examined by Rigaku Multiplex X-ray diffractometer equipped with Cu Kα radiation at 40 kV and 40 mA (1.6 kW). The catalyst surface acidity was determined by NH_3-TPD analysis using a BEL-CAT TPD analyzer equipped with a thermal conductivity detector. The characteristics of the acid sites were examined using pyridine FT-IR. The detailed characterization procedure can be shown in the literature.[1]

Py-GC/MS (Py-2020D, Frontier-Lab Co.) was used to analyze the characteristics of pyrolysis of Geodae-Uksae 1. In non-catalytic pyrolysis experiments, 1 mg of Geodae-Uksae1 was placed in a metal sample cup. On the other hand, for catalytic pyrolysis, 1 mg of biomass sample was placed on the metal sample cup with a small quantity of quartz wool on it. Above the quartz wool bed, 1 mg of catalyst was placed. Pyrolysis was allowed to take place for 3 min at 550 °C and the product gas analysis was conducted by GC (Agilent 7890A Gas Chromatography)/MS (Agilent 5975C inert Mass Spectral Detector). Another set of experiments were performed to examine the effects of the catalyst dose by varying the quantity of catalyst. The detailed Py-GC/MS analysis procedure can be shown in the literature.[13,15]

Results and Discussion

Table 1 shows physical properties of the catalysts used in this study. From the results of N_2 sorption analysis, the BET surface area, pore volume, and pore size of Si-MCM-48 were 1025 m²/g, 0.83 cm³/g and 2.8 nm, respectively. The surface area and pore volume of Al-MCM-48 were 848 m²/g and 0.80 cm³/g, respectively, which were slightly lower than

Table 1. N_2 sorption analysis results of MCM-48 samples

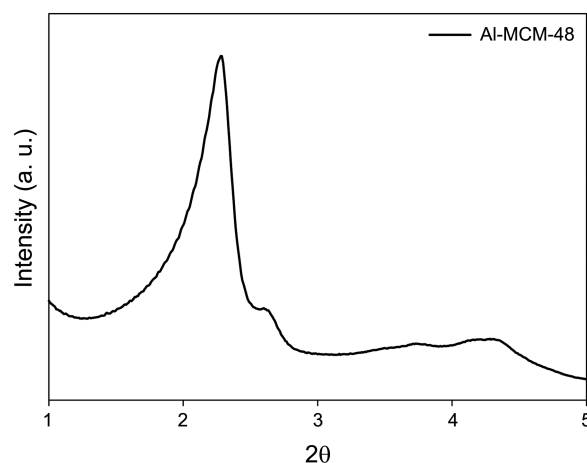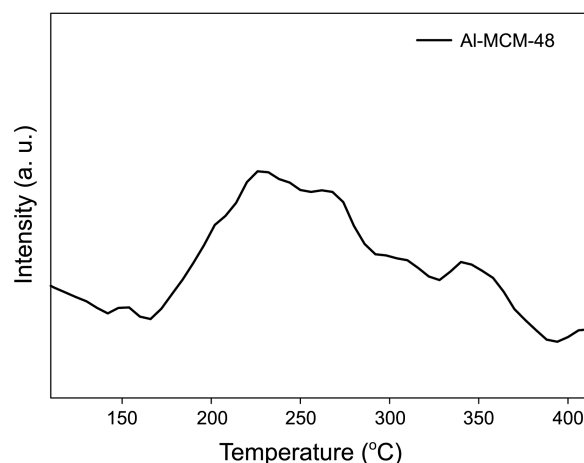| Catalyst	S_{BET} (m²/g)	V_p (cm³/g)	Pore size (nm)	Si/Al ratio
Si-MCM-48	1025	0.83	2.9	-
Al-MCM-48	848	0.80	2.9	40

Figure 1. XRD pattern of Al-MCM-48.

Figure 2. NH_3 TPD of Al-MCM-48.

those of Si-MCM-48, while the pore size was almost the same. The ratio of Si/Al of Al-MCM-48 was 40.

Figure 1 shows the XRD pattern of Al-MCM-48 and it agrees well with the patterns reported in previous studies, which confirms that Al-MCM-48 was well synthesized.[19]
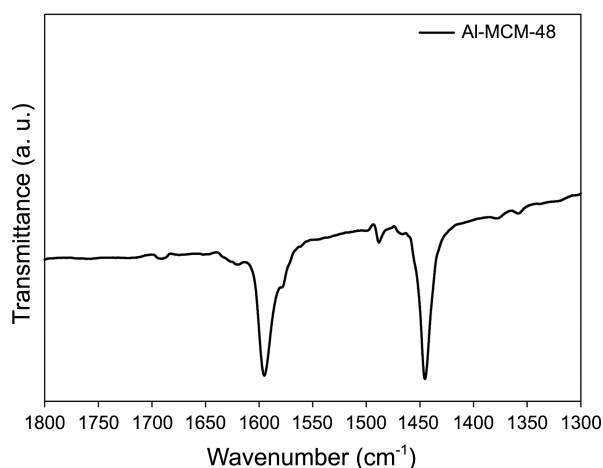
Figure 2 shows the NH_3-TPD profile of Al-MCM-48

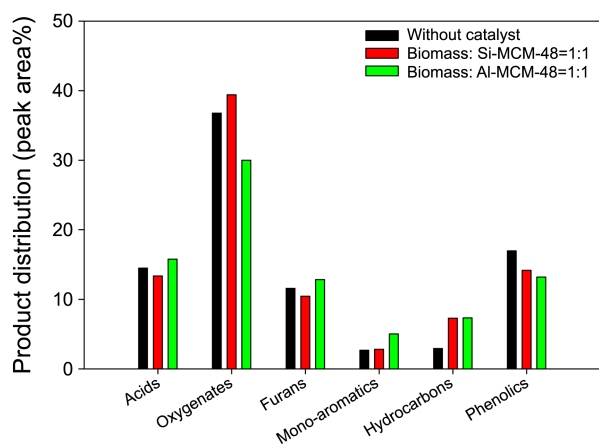**Figure 3.** Pyridine FT-IR spectrum of Al-MCM-48.

Figure 4. Product distribution from non-catalytic pyrolysis and catalytic pyrolysis.

Figure 5. Main product distribution of oxygenates from non-catalytic pyrolysis and catalytic pyrolysis.

indicating its acidic property. A peak which was observed at 200 °C indicates presence of significant number of weak acid sites in the catalyst.

The pyridine FT-IR spectrum of Al-MCM-48 was obtained in the range of 1,300-1800 cm^{-1} to investigate further the property of its acid sites and it is shown in Figure 3. According to previous reports, the strong bands at 1,450 and 1,596 cm^{-1} indicate the existence of Lewis acid sites. The weak band at 1,495 cm^{-1} signifies the co-existence of both Brønsted and Lewis acid sites.[21,22] Al-MCM-48 showed marked bands only at 1,450 cm^{-1} and 1,596 cm^{-1}, implying that it has only Lewis acid sites.

Figure 4 shows the product distribution of the pyrolysis of Geodae-Uksae 1 without and with catalyst. In all the cases compared here, oxygenates, acids, furans, aromatics, hydrocarbons, and phenolics were formed. In the case of catalytic pyrolysis over Si-MCM-48, only hydrocarbons and phenolics were affected significantly by catalyst in its fraction in bio-oil. Because Si-MCM-48 has only very weak acid sites due to terminal silanol group and does not have Brønsted and Lewis acid sites,[23] the conversion efficiency on Si-MCM-48 of pyrolytic vapors which were produced from non-catalytic pyrolysis may be not good. In contrast, by Al-MCM-48, the formation of oxygenates was decreased and those of mono-aromatics and furans were increased due to the reaction of deoxygenation, cracking and aromatization on the acid sites of Al-MCM-48.[1,21,24,25] In addition, fraction of hydrocarbons was increased and fraction of phenolics was decreased for Al-MCM-48.

For the oxygenates, the fractions of levoglucosan (5.42%), ketones (13.26%), aldehydes (3.44%), cyclic compounds (8.28%) and alcohols (3.86%) produced from non-catalytic pyrolysis were changed to levoglucosan (0%), ketones (9.02%), aldehydes (2.48%), cyclic compounds (7.89%) and alcohols (9.02%) for Al-MCM-48 (Figure 5). Levoglucosan was totally decomposed by catalytic pyrolysis which may indicate that levoglucosan was converted to other compounds such as aromatics and furanic compounds on the acid sites. Ketones and aldehydes, which degrade the quality of oil, were also reduced by deoxygenation, such as decarbon-
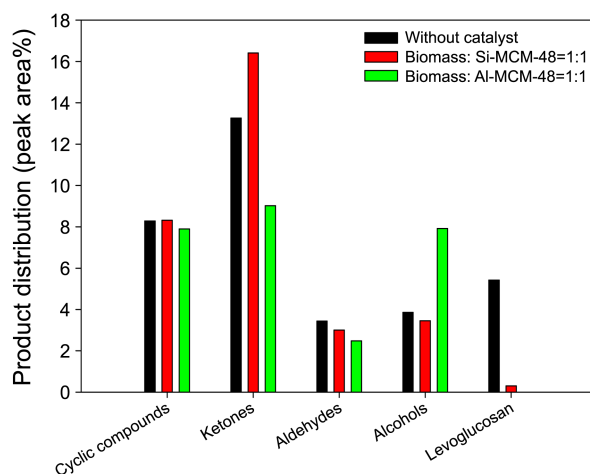
ylation or decarboxylation, on acid sites. Meanwhile, the fraction of alcohols was increased by the catalytic effect of Al-MCM-48. Because alcohols increase the heating value and economic value of the bio-oil, the enhanced alcohol production on Al-MCM-48 was desirable. For Si-MCM-48, too, the fraction of levoglucosan was very low as 0.3%. This suggests that silanol group of Si-MCM-48 was also able to participate in the elimination of levoglucosan.

The content of acids, mainly acetic acid, increased slightly for the catalytic pyrolysis over Al-MCM-48. Because acetic acid induces corrosion of pipe or engine, it should be separated from bio-oil. Meanwhile, hydrocarbon increases the heating value of bio-oil and reduces the oxygen content of bio-oil. Therefore, production of hydrocarbon *via* catalytic pyrolysis helps to upgrade the quality of bio-oil.

The furanic compounds have been used in various fields of chemical industry (*e.g.*, furan resin, fuel additives, medicines), so large production of furanic compounds is needed from bio-oil to prove its quality. Figure 6 shows the detailed analysis of furanic compounds. While heavy 2,3-dihydrobenzofuran was the dominant furanic compound for non-
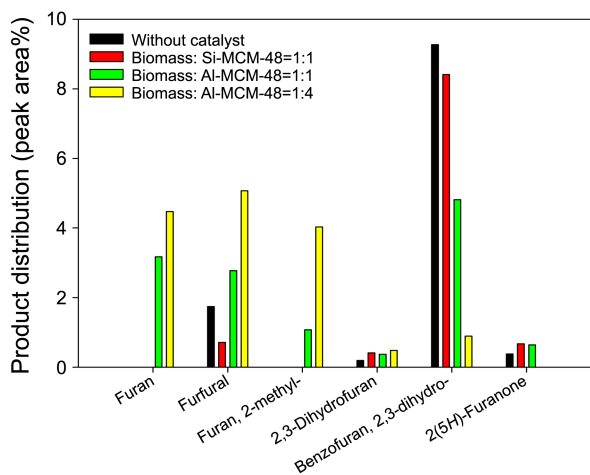

Figure 6. Distribution of furans from non-catalytic pyrolysis and catalytic pyrolysis.
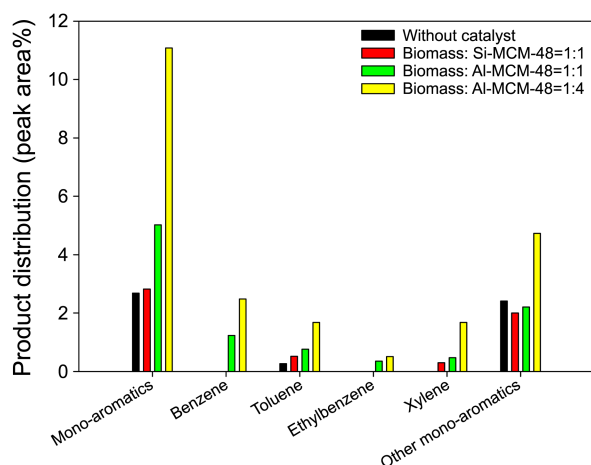
Figure 7. Distribution of aromatics from non-catalytic pyrolysis and catalytic pyrolysis.

Figure 8. Distribution of phenolics from non-catalytic pyrolysis and catalytic pyrolysis.

catalytic pyrolysis and catalytic pyrolysis over Si-MCM-48, catalytic pyrolysis over Al-MCM-48 produced substantially more fraction of light furanic compounds such as furan, alkyl furan, and furfural. This may imply that deoxygenation such as decarbonylation was enhanced on the acid sites of Al-MCM-48. Because reduction of oxygen content was necessary for the increased bio-oil stability and quality, enhanced production of alkyl furans on Al-MCM-48 was encouraging. It was reported that furanic compounds could be synthesized easily by dehydration of cellulose or carbohydrate on acid sites.[26] Therefore, to obtain more light furanic compounds, more acid sites which can enhance deoxygenation should be supplied. As shown in Figure 6, increasing the ratio of catalyst to biomass from 1/1 to 4/1 enhanced the removal of 2,3-dihydrobenzofuran and the production of light furanic compounds.

Monocyclic aromatics, including benzene, toluene, xylene, and ethyl benzene (BTXE), are important basic petrochemicals and fuel additives. The large production of mono-aromatics could contribute to the production of bio-oil with enhanced quality. As shown in Figure 7, mono-aromatics were also increased considerably by Al-MCM-48. The acid sites of Al-MCM-48 may have promoted the cracking, oligomerization and aromatization for the production of mono-aromatics. Therefore, increasing the ratio of catalyst to biomass from 1/1 to 4/1 promoted the production of aromatics significantly.

Figure 8 shows the distribution of phenolics contained in the pyrolysis products, grouped according to the number of methoxy groups in the molecule. A lower phenolic yield was obtained with Al-MCM-48 compared to the results obtained from non-catalytic pyrolysis or catalytic pyrolysis over Si-MCM-48. Phenolics might have been converted to aromatics on Al-MCM-48. Lee *et al.*[16] performed the catalytic pyrolysis of lignin with Al-MCM-48 and reported that phenolics were converted to aromatics on the acid sites of Al-MCM-48. These results agree with the results of the present study. In the present study, much less phenolics with methoxy group were produced from the catalytic pyrolysis over Al-MCM-
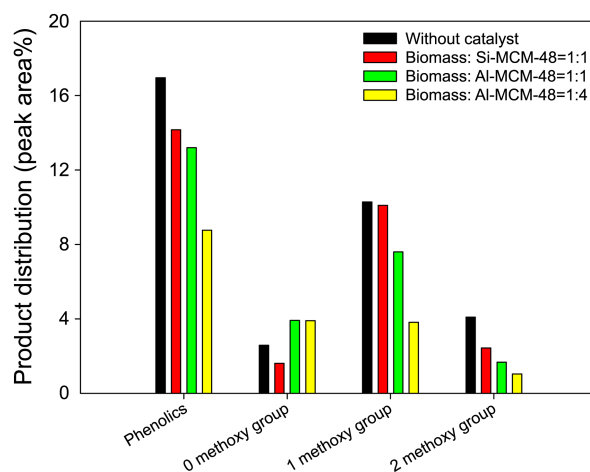
48 because Al-MCM-48 promoted the demethoxylation of phenolics. Jeon *et al.*[13] reported that the demethoxylation of phenolics produced from lignin was enhanced by acid catalysts. The effects of Al containing mesoporous catalysts on promoting decarbonylation and decarboxylation of phenolics were suggested.[13,16] From the above papers, it could be inferred that Al-MCM-48 could promote the deoxygenation (decarbonylation and decarboxylation), demethoxylation, and aromatization of phenolics. This also implied that more stable bio-oil with a lower content of oxygen could be produced using Al-MCM-48 rather than Si-MCM-48. Increased amount of Al-MCM-48 also promoted above reactions.

Conclusion

In this study, the first trial for catalytic pyrolysis of Geodae-Uksae 1 was carried out. Two mesoporous materials, Si-MCM-48 and Al-MCM-48, were tested as catalysts. Si-MCM-48 without acid sites showed the similar product distribution compared to non-catalytic pyrolysis. By using Al-MCM-48 with acid sites, hydrocarbons, the high value-added BTXE compounds, and light furanic compounds, such as furan, alkyl furan, and furfural, were produced. Also, the formation of light phenolics like alkyl phenolics was increased. When the amount of catalyst was increased, the yields of aromatics and furanic compounds were also increased.

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