Catalytic Pyrolysis of Cellulose over SAPO-11 Using Py-GC/MS

In-Gu Lee,[a] Bo Ram Jun,[†,a] Hyeon Koo Kang,[†] Sung Hoon Park,[‡] Sang-Chul Jung,[‡]
Jong-Ki Jeon,[§] Chang Hyun Ko,[#] and Young-Kwon Park[†,¶,*]

Korea Institute of Energy Research, Daejeon 305-343, Korea
[†]*Graduate School of Energy and Environmental System Engineering, University of Seoul, Seoul 130-743, Korea*
[‡]*Department of Environmental Engineering, Sunchon National University, Suncheon 540-950, Korea*
[§]*Department of Chemical Engineering, Kongju National University, Cheonan 330-717, Korea*
[#]*School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea*
[¶]*School of Environmental Engineering, University of Seoul, Seoul 130-743, Korea. *E-mail: catalica@uos.ac.kr*
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The catalytic pyrolysis of cellulose was carried out over SAPO-11 for the first time. Pyrolyzer-gas chromatography/mass spectroscopy was used for the *in-situ* analysis of the pyrolysis products. The acid sites of SAPO-11 converted most levoglucosan produced from the non-catalytic pyrolysis of cellulose to furans. In particular, the selectivity toward light furans, such as furfural, furan and 2-methyl furan, was high. When the catalyst/cellulose ratio was increased from 1/1 to 3/1 and 5/1, the increase in the quantity of acid sites led to the promotion of deoxygenation and the resultant increase of the contents of light furan compounds. Because furans can be used as basic feedstock materials, the augmentation of the economical value of bio-oil through the catalytic upgrading over SAPO-11 is considerable.

Key Words : Cellulose, SAPO-11, Catalytic pyrolysis, Furans, Py-GC/MS

Introduction

Biomass is a promising renewable energy source that can help overcome the future energy crisis. Studies have recently been conducted to produce various biofuels, *e.g.*, biodiesel, bio-oil, bioethanol, *etc.*, from biomass.[1-7] In particular, the production of fuels or chemicals from lignocellulosic biomass, such as grass-type and woody biomass, which is regarded as cheap carbon resource that can replace petroleum-based fuels, is attracting significant attention.[8-13] The production of bioethanol using biological methods and the production of heat, syngas and bio-oil using thermochemical methods are representative ways for the biomass-to-energy conversion of lignocellulosic biomass.[1-7] Bio-oil is produced from the pyrolysis of biomass. Having a typical heating value of about 20 MJ/kg, bio-oil can be used as boiler oil.[14, 15]

Lignocellulosic biomass consists of cellulose, hemicellulose and lignin, among which cellulose takes the largest mass fraction (40-50%). Cellulose is a biopolymer composed of β-D-glucopyranose units connected by β-glycosidic bonds.[16] The production of bio-oil from various lignocellulosic biomass materials has been carried out tremendously. The pyrolysis characteristics of the biomass constituents (cellulose, hemicellulose and lignin) have also been investigated during the recent few years.[17,18] For example, classical simple conversion mechanism was suggested for the pyrolysis of cellulose.[19] According to this mechanism, at first, cellulose is converted to active cellulose (intermediate species) without mass reduction. Then actual decomposition reaction

proceeds along two competing pathways. Cellulose decomposes either to volatiles and tars such as levoglucosan, or to solid residue (char) and gaseous products. Grasping the pyrolysis characteristics of each biomass constituent is important for understanding the thermal decomposition behavior of biomass. The representative structure of lignocellulosic biomass, cellulose, hemicellulose and lignin can be found in the literature.[20]

The bio-oil produced from the pyrolysis of lignocellulosic biomass has several shortcomings as a fuel: high oxygen and moisture contents, low pH (acidic property), and inclusion of highly reactive and unstable species. Catalytic upgrading is frequently used to improve the fuel quality and increase the value-added of the pyrolysis product oil.[4,15] Acid catalysts, such as microporous zeolite materials (HZSM-5, HY, Hβ, *etc*) and mesoporous materials (MCM-41, SBA-15, MCM-48, *etc*), have normally been used for the upgrading of bio-oil. The atmospheric reforming of bio-oil over acid catalysts is an economical process because it does not need the supply of hydrogen gas. Another kind of acid catalysts that are attracting attention are molecular sieve catalysts, called silicoaluminophosphate molecular sieves (SAPO). The SAPO catalysts have been applied to methanol-to-olefin (MTO) conversion process, reforming of plastics, and pyrolysis of biomass, exhibiting high catalytic activity comparable to those of zeolite and mesoporous materials.[21-23] Nevertheless, the application of SAPO catalysts to the catalytic pyrolysis of biomass constituents has hardly been reported. While SAPO-34, which has been known to be an efficient MTO reaction catalyst, has small pores with a diameter of 0.38 nm (0.38 × 0.38 nm), SAPO-11 has an AEL structure

containing pores with a maximum diameter of 0.65 nm (0.65 × 0.40 nm).[24] Therefore, SAPO-11 may be adequate for the pyrolysis reactions because the diffusion of reactant molecules into its pores is expected to be easier.

In this study, the catalytic pyrolysis of cellulose over a SAPO-11 catalyst was performed for the first time. Pyrolyzer-gas chromatography/mass spectroscopy (Py-GC/MS) was employed for the *in-situ* analysis of the product distribution.[18]

Experimental

Cellulose and SAPO-11 were purchased from Sigma-Aldrich and Tianjin Chemist Scientific Ltd., respectively. N_2 adsorption experiment was conducted at –196 °C using a physisorption analyzer (Micromeritics ASAP 2010) to determine the Brunauer-Emmett-Teller (BET) surface area. The acidity of the catalyst was determined by NH_3–temperature programmed desorption (TPD) performed at 100 °C in a 40 mL/min helium flow. The desorption process was monitored by a thermal conductivity detector while temperature was increased from 100 °C to 600 °C at a rate of 20 °C/min. The nature of the acid sites was examined using pyridine Fourier transform infrared (FT-IR, Spectrum GX Perkin Elmer) spectroscopy. A pyrolyzer Py-2020D (Frontier-Lab Co.) was used for the Py-GC/MS analysis. 0.93 mg of cellulose sample was placed on a sample cup, over which a quartz wool layer and a catalyst layer were located successively. In this arrangement, the vapor species produced from the non-catalytic pyrolysis of cellulose was reformed when they passed through the catalyst layer. The mass ratio between the catalyst and cellulose was 1/1, 3/1 or 5/1. Also, the pyrolysis of levoglucosan was carried out to investigate the conversion of reaction intermediates over SAPO-11. The mass of levoglucocan was 0.55 mg and the mass ratio of catalyst/levoglucosan was 1/1, 3/1 or 5/1. The detailed experimental procedure was described in previous publications.[18,21]

Results and Discussion

Because the characteristic data of SAPO-11 were reported already in a previous paper,[21] only a brief summary is provided here. The specific surface area and pore volume of the commercial SAPO-11 used in this study are 121 m^2/g and 0.15 cc/g, respectively. The NH_3-TPD analysis showed that SAPO-11 has weak acid sites and intermediate-strength acid sites appearing at 150 °C and 250 °C, respectively (Figure 1). The pyridine FT-IR spectrum of SAPO-11 (Figure 2) showed the peaks representing Lewis acid (about 1445 cm^{-1}) and Brønsted acid (about 1545 cm^{-1}).[9]

Figure 3 shows the product distributions obtained from the pyrolysis of cellulose with different catalyst doses at 500 °C. In all the cases tested, oxygenates were the main product. The area% of oxygenates, however, was decreased substantially by catalytic upgrading, accompanied by slight increase in the contents of acids, hydrocarbons and aromatics. This result indicates that oxygenates were converted to other
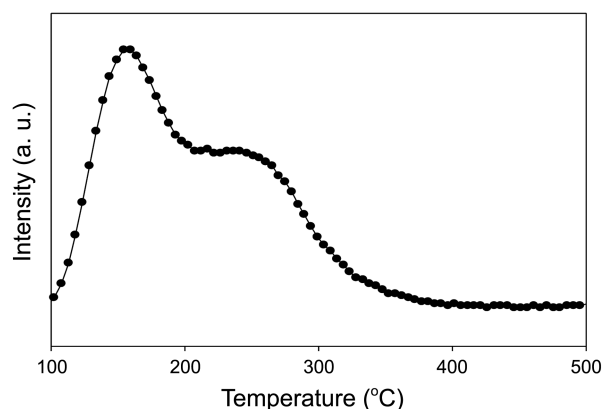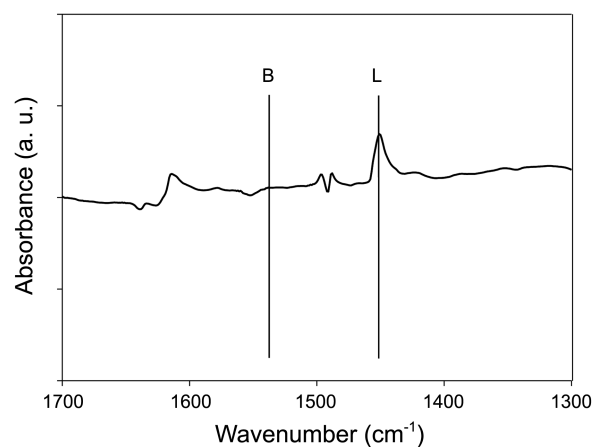

Figure 1. NH_3 TPD of SAPO-11.[21]

Figure 2. Pyridine FT-IR spectra of SAPO-11 (Pyridine desorption at 150 °C).[21]
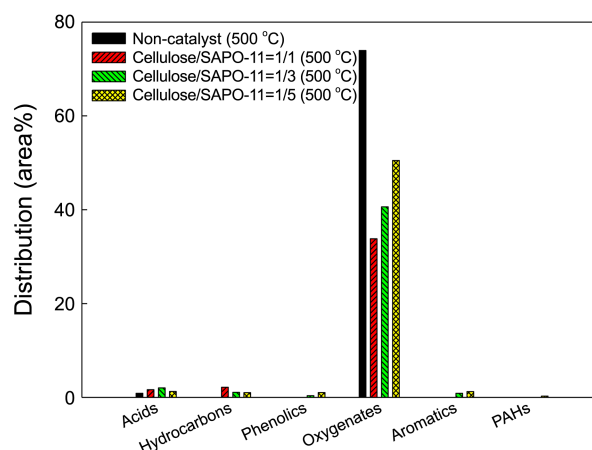

Figure 3. Product distribution of catalytic pyrolysis of cellulose over SAPO-11 at 500 °C with different cellulose/SAPO-11 ratios.

species by catalytic upgrading.

Figure 4 shows the detailed species distribution of oxygenates produced at 500 °C. In the absence of catalyst, levoglucosan was the most abundant oxygenate species. Levoglucosan is known to be produced by depolymerization during the non-catalytic pyrolysis of cellulose.[25] This levoglucosan is converted into other species when it passes
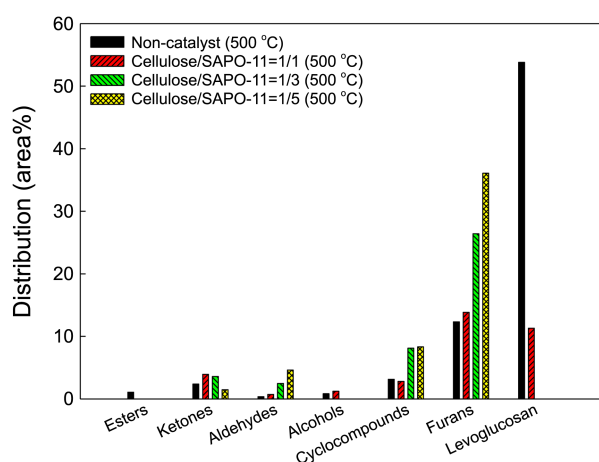
Figure 4. Species distribution of oxygenates.

Figure 5. Detailed species distribution of furans.

through the catalytic layer. A little amount of levoglucosan remained when the catalyst/cellulose ratio was 1/1, while complete conversion of levoglucosan was observed when the catalyst/cellulose ratio increased to 3/1. The drastic decrease of levoglucosan was accompanied by the production of considerable amount of furans (furan, 2-methyl-furan, 2(5*H*)-furanone, furfural, 5-methyl-2-furancarboxyl-aldehyde, *etc.*) and other species, such as cyclocompounds, ketones and aldehydes. Furans are useful organic solvents for the production of medicines, resins, food additives, and fuel additives. Therefore, the enhanced yield of furans is economically beneficial.[18,25] When the catalyst/cellulose ratio was increased further to 5/1, the content of light furan compounds increased even further. The promotion of dehydration and cracking by the increased acid sites is believed to be the reason of the enhanced production of light furan compounds.

Furans are known to be produced by dehydration of cellulose or carbohydrate.[18] Therefore, the presence of a catalyst with appropriate acid sites can promote the production of furans *via* enhanced dehydration reaction. Jeon *et al.*[18] performed the catalytic pyrolysis of cellulose over SBA-15-based catalysts. They reported that Al-SBA-15, which has acid sites, produced much larger amount of furans than SBA-15 with no acid sites and suggested that the presence of acid sites is essential for the production of furans. In addition, increased catalyst dose resulted in enhanced production of furans, which is in good agreement with the result of the present study. Torri *et al.*[26] argued that levoglucosan produced from the pyrolysis of cellulose was converted to other valuable species by dehydration and deoxygenation in the presence of metal-containing MCM-41 catalyst. When the number of acid sites is too big or the sort of acid sites are strong Brønsted acid sites, furans can be converted to aromatics.[17,27] Therefore, appropriate strength and number of acid sites must be needed to maximize the yield of furans. As SAPO-11 has medium-strength acid sites, it may be one of the most suitable catalysts for the production of furans. Figure 5 shows the area% of each species grouped into the furans category. The content of furan was only 0.2% when
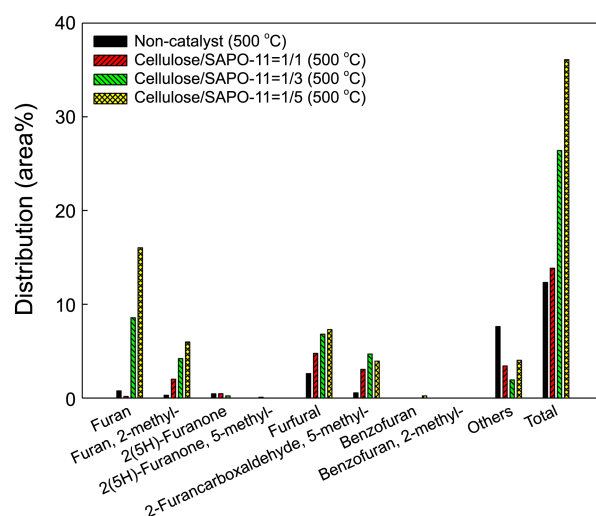
the catalyst/cellulose ratio was 1/1. When the ratio was increased to 3/1 and 5/1, remarkable increase of the furan content was observed. This implies that deoxygenation, such as decarbonylation, took place, in addition to dehydration, on the acid sites under an increased catalyst dose condition. The content of 2-methyl furan, another furan species with no carbonyl group, also increased from 2% to 6% when the catalyst/cellulose ratio increased from 1/1 to 5/1. Considering the reduction of oxygen content in bio-oil leads to the enhancement of oil quality, the promotion of decarbonylation is desirable.

In addition, as shown in Figure 4, aldehydes (mainly acetaldehyde), ketones and alcohols are produced by the ring scission reaction of cellulose.[28] The increase in the contents of these species, though they are still small, by catalytic upgrading is attributed to cracking of large molecules occurring when they pass through the catalyst layer. However, more detailed analyses of these species were not conducted because their yields were very small.
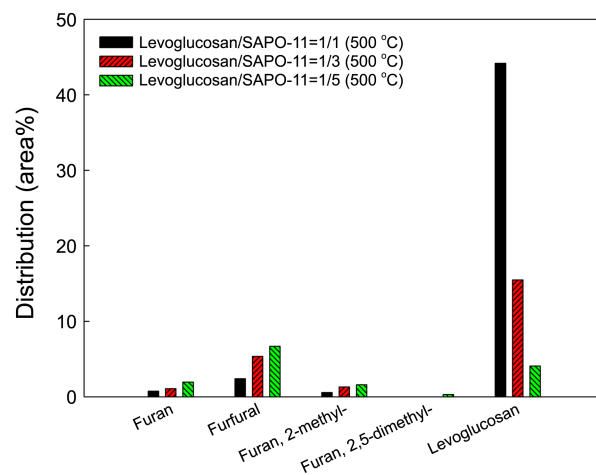
To verify levoglcosan conversion to furan compounds,

Figure 6. Conversion of levoglucosan over SAPO-11 obtained with different levoglucosan/SAPO-11 ratios.

catalytic conversion of levoglucosan was performed over SAPO-11 at 500 ºC (Figure 6). The main products of catalytic conversion of levoglucosna by SAPO-11 were a series of furans and furfurals, which is in good agreement with the result of the pyrolysis of cellulose. Also, the contents of furan and furfural increased with increasing of catalyst.

Conclusion

SAPO-11 was used for the catalytic pyrolysis of cellulose. Most levoglucosan, the main product of the non-catalytic pyrolysis of cellulose, was converted to light furan compounds with higher value-added. Increase of the catalyst dose resulted in the promotion of dehydration and decarbonylation due to the increased quantity of acid sites, leading to huge increase of the yields of light furan compounds, such as furan, 2-methyl furan, and furfural, and significant improvement of the bio-oil quality.

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