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CATALYTIC CONVERSION OF WOOD WASTE TO BIO-OIL USING MESOPOROUS SBA-15 CATALYST

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Abstract. The catalytic pyrolysis of waste particle board was carried out over mesoporous Si-SBA-15 and Al-SBA-15 catalysts using pyrolysis gas chromatography/mass spectrometry. The Al-SBA-15 exhibited the highest yield of valuable products such as phenolics and furans. In addition, the yields of aromatics also increased due to higher acidity of Al-SBA-15 catalayst.

1. INTRODUCTION

The importance of alternative energy development has increased rapidly due to high international crude oil prices. Bio-oil has been recognized as a representative renewable energy source and chemical feedstock [1-5]. On the other hand, the stability of bio-oil was not good. To enhance the value of bio-oil, several studies have examined the upgrading of bio-oil over solid acid catalysts [6-10]. Among them, zeolites and mesoporous materials have been investigated as pyrolysis catalysts in various types of biomass [6-12].

The use of municipal wood waste including particle board, however, has never been considered in previous catalytic pyrolysis researches. Because the significant amount of municipal wood waste has been generated in Korea, it is much desirable to study catalytic pyrolysis of municipal wood waste. The objective of this study was to investigate the performance of Si-SBA-15 and Al-SBA-15 catalysts for the catalytic cracking of waste particle board. To test the catalytic activity of mesoporous Si-SBA-15 and Al-SBA-15 catalysts, the pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) experiment was carried out because it allowed direct analysis of catalytic products.

2. EXPERIMENTAL

A representative sample of waste particle board was obtained from Korea Electric Power Research Institute. The detailed characterization methods are available elsewhere [1-5] including the proximate analysis, elemental composition and heating values. The carbon content, hydrogen content, oxygen content and nitrogen content was 49.5 wt.%, 5.6 wt.%, 44.6 wt.%, and 0.3 wt.%, respectively. Its calorific value was 17.7 MJ/kg.

The synthesis of Si-SBA-15 was performed using the method in literature [9,13]. Aluminum incorporation of mesoporous materials was carried out using the post-synthetic grafting method [9]. Before baking, the prepared mesoporous material was

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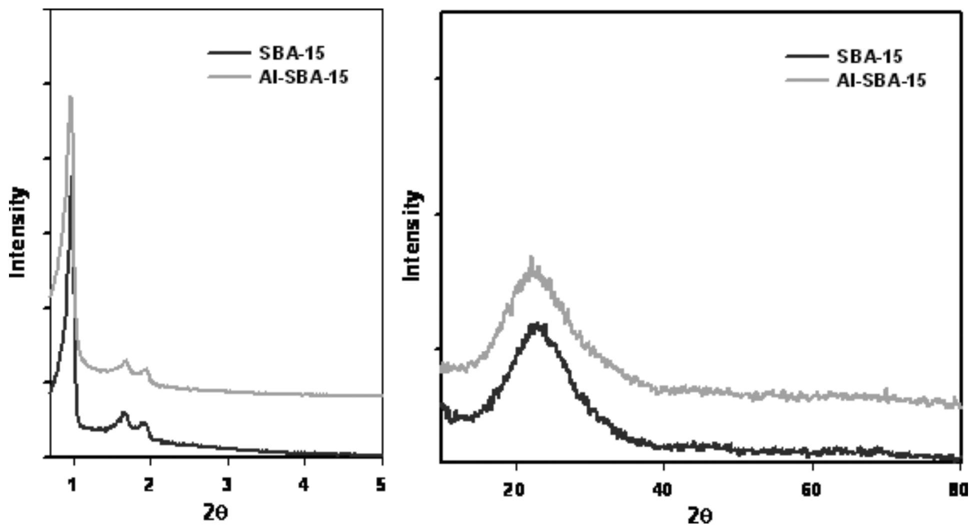

Fig. 1. XRD patterns of Si-SBA-15 and Al-SBA-15 catalysts.

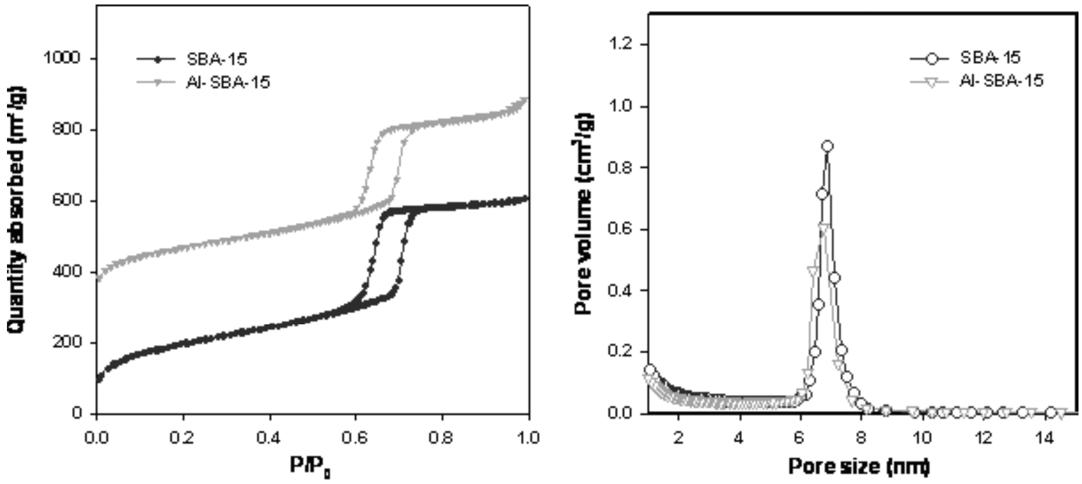

Fig. 2. Nitrogen adsorption-desorption isotherms of Si-SBA-15 and Al-SBA-15 catalysts.

put into a solution prepared by dissolving $AlCl_3$ in 100 mL of ethanol according to the Si/Al ratio of 20. It was then stirred for 24 h, washed with ethanol, filtered, dried for 24 h, and calcined at 550 °C for 4 h.

The characterization methods of catalysts such as XRD, BET, N_2 adsorption-desorption and NH_3 TPD have been described elsewhere [9,13].

A double-shot pyrolyzer (Frontier-Lab Co., Py-2020iD), coupled directly to GC/MS, was used for identification of the catalytic pyrolysis products of waste particle board. Detailed experimental procedures have been described elsewhere [1].

Table 1. Physical properties of Si-SBA-15 and Al-SBA-15 catalysts.

	S_{BET}(m^2/g)	V_p (cm^3/g)	Pore size (nm)
Si-SBA-15	718	0.94	6.9
Al-SBA-15	614	0.90	6.7

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

The XRD patterns of the Si-SBA-15 and Al-SBA-15 catalysts are shown in Fig. 1. The XRD patterns of the Si-SBA-15 and Al-SBA-15 exhibit typical characteristic peaks of SBA-15 [13], representing a 2D hexagonal mesostructure with space group *p6mm*. The nitrogen adsorption-desorption isotherms show that SBA-15 catalysts satisfy the type IV hysteresis loop in accordance with IUPAC classification (Fig. 2). In addition, as shown in Table 1, the physical properties of the synthesized mesoporous SBA-15 catalyst are as follows. The BET surface area of Si-SBA-15 and Al-SBA-15 is 718 and 614 m^2/g, respectively. The pore sizes of Si-SBA-15 and

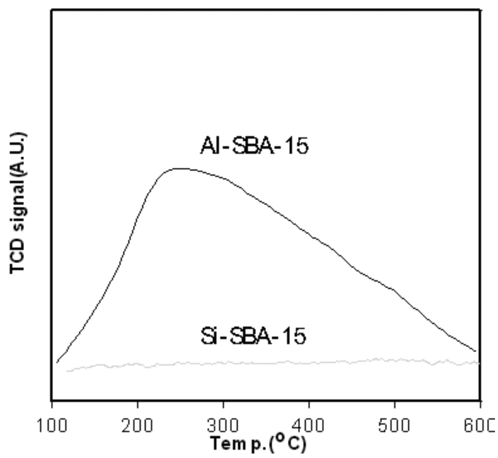

Fig. 3. NH_3 TPD of Si-SBA-15 and Al-SBA-15 catalysts.

Al-SBA-15 is 6.9 and 6.7 nm, respectively. Also, the pore volume of Si-SBA-15 and Al-SBA-15 is 0.94 and 0.90 cm^3/g, respectively. The Si/Al ratio of the Al-SBA-15 catalyst was 20. NH_3-TPD was obtained in order to characterize the amount and strength of acid sites, which are useful for the interpretation of the catalytic activity over those of solid acid catalysts (Fig. 3). Al-SBA-15 was weakly acidic because the peak at approximately 250 °C was attributed to NH_3 desorption from the weak acid sites [1,9,14]. Meanwhile, the acid sites of Si-SBA-15 were negligible.

3.2. Catalytic pyrolysis

The waste particle board was pyrolyzed using Py-GC/MS instrument to allow the direct analysis of the pyrolytic products. Several Py-GC/MS studies have been carried out using different catalysts [1,11,12]. The product distribution after the catalytic pyrolysis was compared to reveal the catalytic effects of different catalysts. For each catalyst, the experiments were repeated at least three times to reduce the errors. Because it has been reported that the peak area of Py/GC-MS can be compared to reveal the change of its content, the corresponding peaks areas of the compounds can be compared to reveal the changing of their yields [1-5,11,12].

As the pyrolysis products were a mixture of a number of species, these species were roughly grouped into following categories: gases (CO, CO_2, and hydrocarbons up to C_4), acids, aldehydes, esters, ketones, furans, sugars, phenolics, aromatics, nitrogen compounds, and others. As shown in Fig. 4, the yield of gas increased with Si-SBA-15 and Al-SBA-15 catalysts. Especially, highest yield of gas was obtained for the Al-SBA-15 due to its highest amount of acid sites [1,9,15]. Acid sites can crack waste particle board with large molecules more easily, resulting in higher gas yields. Therefore, the use of Al-SBA-15 having a greater number of acid sites resulted in a larger gas yield.

Si-SBA-15 and Al-SBA-15 catalysts enhanced the yields of phenolics. For Al-SBA-15, the yield of phenolics was highest and the yields of light phenolics such as phenol and 2-methoxy phenol increased greatly (data not shown). This implied that Al-SBA-15 could promote the cracking of heavy phenols from waste particle board into light phenols. Adam *et al.* [11] also found that Al-SBA-15 broke

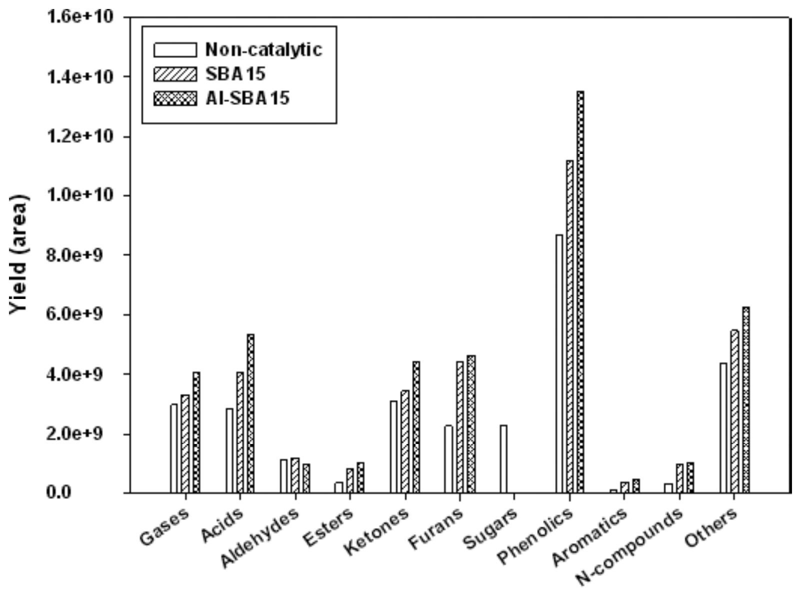

Fig. 4. Yields of products after pyrolysis of waste particle board.

down the heavy phenols greatly for the pyrolysis of different biomass such as sawdust. In this study, phenolics are considered to be valuable products because they can be used for production of the phenolic resins and other petrochemical products. Therefore, Al-SBA-15 can be a good catalyst for production of phenolics via pyrolysis of waste particle board.

The effects of catalysts on furan yield are also shown in Fig. 4. By applying catalysts, the yields of furan increased. Previous studies also have demonstrated that furans are dehydrated products of carbohydrates, and their yields can be increased in the acid-catalyzed conditions [12]. Therefore it can be thought that Al-SBA-15 produced furans mainly by acid-catalyzed reaction. Because furans have significant chemical application values, Al-SBA-15 catalyst would enhance the value of bio-oil.

Catalytic pyrolysis also increased the yields of aromatics. Because it has been reported that acidity increased the production of aromatics [1,8,14], the increase of aromatic yield for Al-SBA-15 can be ascribed to its high acidity.

On the other hand, Si-SBA-15 and Al-SBA-15 catalysts increased the yields of acids. Because acids are undesirable products in bio-oil due to its corrosiveness, high yields of acids make bio-oil difficult to be used as a fuel. The yields of ketones, esters and N-containing compounds also increased for the catalytic pyrolysis of SBA-15.

4. CONCLUSIONS

Mesoporous Si-SBA-15 and Al-SBA-15 catalysts were used for the catalytic pyrolysis of waste particle board using Py-GC/MS. Bio-oil was converted to valuable products such as phenolics, furans and aromatics over mesoporous Si-SBA-15 and Al-SBA-15 catalysts. In particular, Al-SBA-15 showed highest yields of valuable products due to its high acidity. On the other hand, the use of Si-SBA-15 and Al-SBA-15 catalysts increased the yield of acids which are undesirable products due to their corrosiveness.

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