

Catalytic pyrolysis of Japanese larch using spent HZSM-5

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Abstract—The direct catalytic upgrading of the pyrolytic vapor of Japanese larch was carried out in a fixed catalyst bed reactor installed at the upper part of a bubbling fluidized bed reactor. The catalytic performance of spent HZSM-5 in the catalytic upgrading of bio-oil in terms of the product distribution and chemical composition was compared with that of fresh HZSM-5. The spent HZSM-5 showed comparable activity for the deoxygenation of oxygen in bio-oil and selectivity to higher value chemicals to fresh HZSM-5.

Key words: Biomass, Pyrolysis, Spent HZSM-5, Upgrading

INTRODUCTION

Recently, there has been increasing interest in renewable energy due to the environmental concerns over greenhouse gases generated through the use of fossil fuels. In particular, among the variety of alternative energy resources available, biomass is considered to be capable of playing a very important role as a chemical feedstock and as an alternative to fossil fuels. Therefore, thermo-chemical and biochemical conversion technologies employing biomass have been investigated worldwide. The large amount of biomass research recently focused on the recovery of high-value-added compounds or the use of biomass as a fuel from a fast pyrolysis process with a high bio-oil yield [1-5]. It is important to eliminate oxygen from bio-oil, which results in high acidity (low pH), poor heating value, corrosion, instability and high viscosity, in order to use it as a regular fuel. A typical upgrading method is catalytic deoxygenation using zeolite catalysts. In contrast to traditional hydro-treatment methods, catalytic deoxygenation has two advantages: mild reaction conditions, such as atmospheric pressure, are required; no requirement for hydrogen consumption. Until now, catalytic cracking with different fresh catalysts, such as microporous zeolites and mesoporous materials, has been examined to improve the quality of bio-oil [6-12]. Among the fresh catalysts, HZSM-5 or Ga/HZSM-5 can be an effective catalyst for cracking or reforming bio-oil on account of their unique solid acid characteristics [6]. However, there are no reports of the use of spent HZSM-5 catalyst for bio-oil upgrading.

HZSM-5 catalysts are normally disposed of after use in various petrochemical processes in Korea. Styrene Monomer (SM) is synthesized from an alkylation reaction between ethylene and benzene over an HZSM-5 catalyst. Approximately 2,420,000 tons/year of SM are manufactured in Korea, with almost 40,000 kg of HZSM-5 catalyst used in the aforementioned process. The lifetime of the

catalyst in the alkylation process is approximately 2 years. Therefore, approximately 20,000 kg of spent HZSM-5 catalyst is consumed per year. It would be valuable if this spent catalyst could be re-used in the pyrolysis process of biomass.

In this study, the catalytic upgrading of bio-oil with spent HZSM-5 catalyst was first attempted by using a fixed catalyst bed installed consecutively at the latter part of a bubbling fluidized bed. The catalytic performance of the spent catalyst on the product distribution and composition was also compared with that of the fresh one.

EXPERIMENTAL

1. Woody Biomass

Japanese larch is a wood species used in construction and furniture materials in Korea. The sawdust used in these experiments was sieved to obtain a size range of 0.425-1.0 mm, and dried in an oven (J-NDS1, JISICO) at 105 °C for 24 h to minimize the water content in the product oil. After drying, the water content in the Japanese larch sawdust was <1 wt%. The characteristics of the Japanese larch are described in detail elsewhere [1].

2. Catalysts

In this study, fresh and spent HZSM-5 with an Si/Al ratio of 15 and a pellet shape, 7 mm in length and 2 mm in diameter, were used. The spent HZSM-5 catalyst was used after 2 years use in the alkylation process of ethylene and benzene, which is one of the styrene manufacturing processes at Hyundai Petrochemical Co. Ltd. The catalysts were calcined in air at 500 °C for 5 hrs.

3. Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained at room temperature with a Rigaku D/MAX-III instrument with a Cu K α X-ray source. The acidity was examined by an NH $_3$ -temperature-programmed desorption (TPD) method on a TPD/TPR 2900 analyzer (Micromeritics Instrument Co.). The N $_2$ adsorption/desorption isotherms were obtained at -196 °C using a Micromeritics ASAP 2000, and the Brunauer-Emmett-Teller (BET) surface areas were calcu-

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lated from the linear part of the BET plot. After catalytic upgrading, the coke amount deposited on the catalyst was determined with thermogravimetric analysis (TGA) using a thermogravimetric analyzer (TGA, [TGA 2050, TA Instruments]), in the presence of air, at a heating rate of 5 °C/min.

4. Reaction Procedure and Product Analysis

The experimental apparatus and procedure, as well as the analytical methods are described in detail elsewhere [6]. The non-catalytic pyrolysis and catalytic upgrading were carried out at 500 °C, at which the maximum bio-oil yield could be obtained. The weight of the catalysts in the experiments was 6 g.

RESULTS AND DISCUSSION

1. Catalyst Characterization

The surface area of the spent HZSM-5 was 310 m²g⁻¹ and the pore volume was 0.44 cm³g⁻¹. On the other hand, the surface area and pore volume of the fresh HZSM-5 were 330 m²g⁻¹ and 0.46 cm³g⁻¹, respectively. An approximately 6% decrease in surface area was observed in the spent HZSM-5, compared to the fresh one. XRD of the fresh and spent HZSM-5 (data not shown) showed that the spent HZSM-5 had only slightly lower peak intensities than the fresh one, indicating that the crystallinity of the spent HZSM-5 was conserved. Fig. 1 shows the NH₃-TPD curves of the fresh and spent HZSM-5. There were lower acid sites of the spent HZSM-5 than the fresh one, particularly strong acid sites, indicating that the cracking ability of spent HZSM-5 was reduced.

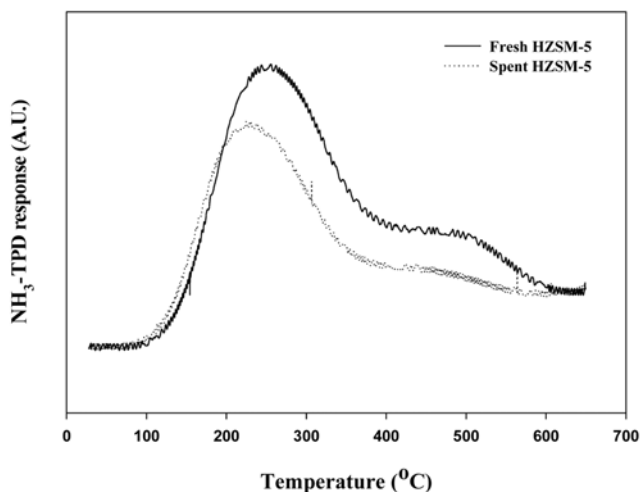


Fig. 1. NH₃-TPD curves of catalysts.

Table 1. Product distribution

Yield (wt%)	Non-catalytic	Fresh HZSM-5	Spent HZSM-5
Bio-oil	58.2	42.9	45.8
Water ^a	28.3	41.3	42.5
Gas	20.6	35.6	32.1
Char	21.2	21.5	22.1
Coke	-	<1	<1

^aon bio-oil basis

Table 2. Composition of gas products

Component	Yield (wt%)		
	CO	CO ₂	C ₁ -C ₄
Non-catalytic	7.0	10.9	2.7
Fresh HZSM-5	12.9	18.7	4.0
Spent HZSM-5	11.7	17.1	3.3

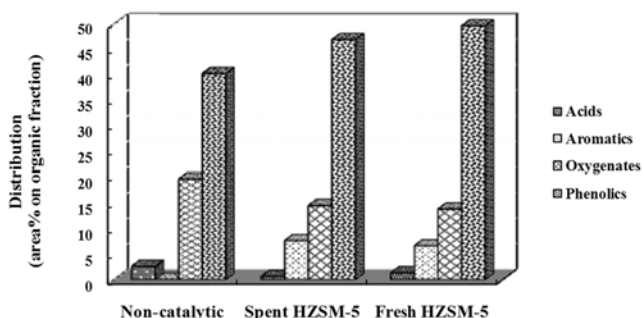


Fig. 2. Chemical composition of bio-oils after catalytic upgrading.

2. Catalytic Pyrolysis

Table 1 shows the effect of the catalysts on the product distribution. After catalysis, the bio-oil yields decreased significantly due to cracking of the pyrolytic vapors, followed by an increase in gases. Table 2 shows that after catalytic upgrading, the water content in the bio-oils was higher than that produced from non-catalytic pyrolysis, indicating the production of a more stable bio-oil by deoxygenation. Despite the decreased acidity, the catalytic activity of the spent HZSM-5 was comparable to that of the fresh one. The amount of carbon deposited on the catalysts was <1 wt% due to their steric constraint.

Generally, bio-oil contains a large amount of oxygenated compounds with carbonyl and carboxyl groups. These compounds are responsible for the instability of bio-oil during the aging process. Accordingly, removing oxygen from bio-oil is essential for various applications, particularly as a fuel in internal combustion engines, such as gas turbines and engine. As shown in Fig. 2, there was no difference between the catalytic performances of the two types of catalyst materials used. Both catalysts induced a decrease in the content of acid and other oxygenated compounds, which is associated with the increase in water in bio-oil, as mentioned previously. In addition, the catalysts showed high selectivity for highly valuable chemicals, such as aromatics and phenolics. Consequently, the spent HZSM-5 is a promising catalyst for the catalytic upgrading of bio-oil.

3. Gaseous Product

The uncondensable gaseous products were analyzed quantitatively by GC-TCD and GC-FID (Table 2). The main products were CO, CO₂ and low molecular hydrocarbons within the range of C₁-C₄. The amount of hydrogen was negligible (<0.2 wt%). The amount of CO and CO₂ increased significantly with the use of the catalysts. This suggests that the oxygen in bio-oil can react to form CO and CO₂ as well as H₂O. As shown in Table 2, the compositions of the gas products of both catalysts are similar, suggesting that the upgrading ability of spent HZSM-5 is comparable to that of the fresh

one.

CONCLUSION

The applicability of the spent HZSM-5 as a catalyst for the upgrading of bio-oil was examined using the combination system of a fluidized bed and fixed catalyst bed. The spent HZSM-5 showed both excellent activity for deoxygenation and high selectivity for highly valuable chemicals, which was comparable to the fresh catalyst. Overall, the use of the spent HZSM-5 catalyst in the catalytic upgrading of bio-oil may be a preferable choice in eco-friendly and economic catalyst based systems.

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