Catalytic copyrolysis of torrefied cork oak and high density polyethylene over a mesoporous HY catalyst

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ABSTRACT

The catalytic copyrolysis of torrefied cork oak (TOak) and high density polyethylene (HDPE) over mesoporous HY catalysts was performed using a tandem μ-reactor-gas chromatograph/mass spectrometry/flame ionization detector. Two types of mesoporous HY catalysts with different acidity, MesoHY-1 and MesoHY-2, were prepared by pseudomorphic synthesis with various surfactant ratios. For comparison, a commercial microporous HY was also used as a catalyst. The properties of the catalysts were measured by N_2-sorption, X-ray diffraction, and NH_3-temperature programmed desorption. Compared to the catalytic pyrolysis of cork oak (Oak), that of TOak produced a larger amount of mono aromatic hydrocarbons (MAHs) over all HY catalysts. The catalytic copyrolysis of TOak and HDPE over micropore HY and MesoHY-1 produced a larger amount of MAHs than that over MesoHY-2 due to the higher acidities. Although both micropore HY and MesoHY-1 have similar acidity, MesoHY-1 showed stronger synergy for the formation of MAHs on catalytic copyrolysis than micropore HY owing to its larger pore, which allows the easier diffusion of HDPE reaction intermediates into the pore of the catalysts.

1. Introduction

The value of biomass as a renewable energy source is increasing due to the current issues worldwide, such as fossil fuel shortage, air contamination, and climate change [1–5]. Technical development to utilize biomass has been focusing on the production of value-added fuels or chemicals via various kinds of conversion methods, such as fermentation, pyrolysis, and gasification [6]. Among these techniques, biomass pyrolysis is used for the production of a liquid fuel called bio-oil or pyrolysis oil at intermediate temperatures ranging from 400 to 600 °C. Over last several decades, many types of biomass, such as wood [7], miscanthus [8], fruit peel [9], and algae [10] have been used as feedstock for the production of bio-oil via pyrolysis. Biomass pyrolysis can be divided into thermal pyrolysis and catalytic pyrolysis, depending on the use of a cata-

lyst for the pyrolysis process. The main aim of catalytic pyrolysis is to decompose biomass components and upgrade the pyrolysis products together in a single pot. Owing to the poor stability and low heating value of biomass pyrolysis oil caused by the large oxygen-containing compounds and water, catalytic pyrolysis is being considered as an efficient process to remove oxygen from pyrolysis oil and produce value-added chemicals, such as aromatic hydrocarbons [11–13]. The overall reaction performance on the catalytic pyrolysis of biomass is influenced by not only the type of catalyst but also the lignocellulosic composition of biomass [14]. Therefore, the catalytic pyrolysis of the individual components of biomass was investigated intensively. Wang et al. [15] examined the catalytic pyrolysis of the individual components of biomass and achieved the highest aromatic hydrocarbons yields from cellulose over the HZSM-5 catalyst. Regarding the catalyst development research, Jae et al. [16] and Mihalcik et al. [17] screened a range of catalysts for the production of aromatics via catalytic pyrolysis and concluded that HZSM-5 has the highest aromatic production efficiency than the other zeolites, such as HBeta, HY.

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Although the production of aromatic hydrocarbons is improved by the use of a catalyst on the pyrolysis of biomass, the actual yields of aromatic hydrocarbons are still insufficient for its application to the commercial scale. Recently, the thermal pretreatment of biomass, such as torrefaction, or co-feeding with plastics, such as polyethylene (PE) and polypropylene (PP), was reported to improve the yield of aromatic hydrocarbons from the catalytic pyrolysis of biomass. Biomass torrefaction is the low temperature pyrolysis of biomass normally at temperatures ranging from 200 to 300 °C. The carbon density of biomass was reported to be increased by torrefaction because the hemicellulose in biomass is eliminated, and the structures of cellulose and lignin are modified to a better form for pyrolysis. Neupane et al. [18] examined the effects of the torrefaction conditions on aromatics production from the catalytic pyrolysis of pinewood with the HZSM-5 catalyst and reported the optimal torrefaction conditions for aromatics production. Other researchers also torrefied the lignocellulosic components of biomass and examined the effects of torrefaction on the formation of aromatics via catalytic pyrolysis [19,20].

The main reason for the use of plastics as the co-feeding feedstock on the catalytic pyrolysis of biomass was to increase the effective hydrogen to carbon ratio (H/C_{eff}) of pyrolysis feedstock. Plastics, such as PP and PE, have a much higher H/C_{eff} than that of biomass and the total H/C_{eff} of the pyrolysis feedstock can be increased by mixing plastics together with biomass. The intermolecular catalytic reactions between the specific pyrolyzates of biomass and plastics also resulted in the synergistic formation of aromatic hydrocarbons [21]. Li et al. [22] reported that the Diels-Alder reaction between the furans from biomass and light olefins from plastics is the main synergistic reaction pathway for the formation of aromatic hydrocarbons on the co-pyrolysis of biomass and plastics. Overall, previous studies reported the positive effects of biomass torrefaction and co-feeding of plastics with biomass on the aromatic production. Therefore, it is possible that their combination can be an efficient means for the catalytic pyrolysis of biomass. On the other hand, this has not attracted significant research attention.

The overall reaction efficiency of the catalytic co-pyrolysis of biomass and plastics is strongly related to the pore size, acidity, amount of catalyst together with the reaction temperature. Kim et al. [21] reported that a larger amount of aromatic hydrocarbons was produced over HY than over HZSM-5 when a low catalyst to sample ratio (1–1) was applied to catalytic co-pyrolysis. They indicated that the diffusion of reactant molecules into the pores of HZSM-5 was severely hindered by coke and char, which are formed during the catalytic pyrolysis of biomass. This hindering effect, however, could be reduced by applying a HY catalyst, which has a larger pore size than HZSM-5, resulting in enhanced aromatic production. Mesoporous materials can also be used to minimize the hindering effect of biomass on the catalytic pyrolysis of plastics. On the other hand, mesoporous catalysts, such as Al-MCM-41, were not effective on the catalytic pyrolysis of biomass because the total acidity of Al-MCM-41 is much lower than the microporous catalyst [8,9]. Recently, mesoporous Y, having similar acidity to microporous HY, was synthesized via a simple pseudomorphic synthesis method [23,24], and it can be expected to be a highly efficient catalyst for the catalytic pyrolysis of biomass owing to its high acidity and mesopores. Nevertheless, its actual use in the catalytic co-pyrolysis of biomass and plastics has not been reported.

In this study, the catalytic co-pyrolysis of Oak tree and high density polyethylene (HDPE) over mesoporous HY catalyst was performed using a thermogravimetric (TG) analyzer and tandem μ-reactor-gas chromatography (GC)/mass spectrometry (MS)/flame ionization detector (FID). The effects of torrefaction, co-feeding of HDPE, and the use of a mesoporous HY catalyst on the catalytic pyrolysis of Oak tree were evaluated based on the thermal behavior and aromatic formation efficiency.

2. Materials and methods

2.1. Materials

Cork oak (Oak), which was obtained from a sawmill factory in South Korea, was sieved to make a particle size less than 300 μm, and dried at 80 °C over a day period. HDPE was purchased from a local polymer company in South Korea. Table S1 lists the results of proximate, ultimate analysis, and high heating value measurement of the Cork oak and HDPE used in this study. Torrefied Cork Oak (TOak) was prepared by torrefaction at 250 °C in a fixed bed reactor under a nitrogen atmosphere. The yield of TOak was 84.7 wt.% and those of the gas and liquid products emitted from the Oak during torrefaction were 1.7 and 13.6 wt.%, respectively. The liquid products consisted of a large amount of water (83.5%), acetic acid, and furfural, indicating the elimination of hemicellulose during torrefaction.

2.2. Catalysts

A commercial microporous HY zeolite (CBV 720, $SiO_2/Al_2O_3 = 30$, Zeolyst) was purchased from Zeolyst International. Two types of mesoporous HY catalyst, MesoHY-1 and HY-2, were synthesized from the microporous HY via modified pseudomorphic synthesis by applying different molar ratios of trimethylammonium hydroxide (TMAOH): hexadecyltrimethylammonium bromide (CTAB) = 0.5 and 2.

For example, 1.67 g of the commercial HY zeolite and 0.83 g of CTAB (VWR Co., 99%) were mixed with 50 mL of 0.09 M TMAOH (Sigma-Aldrich, 25 wt.% in water) for the synthesis of MesoHY zeolite with TMAOH:CTAB = 2. The mixture was stirred for 30 min at room temperature, and moved to a Teflon-lined autoclave for hydrothermal treatment at 150 °C for 20 h. The resulting product was cooled to room temperature, filtered, and washed with water. The product was dried at 75 °C and calcined at 550 °C. The MesoHY samples synthesized with TMAOH: CTAB = 0.5 and 2 are designated as "MesoHY-1" and "MesoHY-2", respectively. Both microporous and MesoHY catalysts were calcined at 550 °C in air for 4 h prior to catalytic pyrolysis. All the catalysts were characterized by XRD, N_2-sorption, and NH_3-TPD analysis. Powder X-ray diffraction (XRD) was performed on a Rigaku Multiplex instrument using Cu-Kα radiation (λ = 0.15406 nm), operated at 40 kV and 40 mA (1.6 kW). The nitrogen adsorption isotherms were measured at −196 °C on a Micromeritics Tristar 3000 volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 300 °C in a degassing station. The surface acidity of the catalysts was measured by loading 50 mg of the catalyst in a glass flow-through cell, and carrying out the temperature-programmed desorption of ammonia (NH_3-TPD) using a BEL-CAT TPD analyzer with a TCD detector.

2.3. Thermogravimetric analysis (TGA)

The thermal profiles of the non-isothermal pyrolysis of the individual samples (2 mg), Oak, TOak, HDPE, and their mixtures (2 mg) were obtained by heating the samples from ambient temperature to 700 °C at a heating rate of 10 °C/min under a flowing nitrogen atmosphere at 50 mL/min using a TG analyzer (Pyris 1, PerkinElmer, USA). For the catalytic TGA, 2 mg of catalyst was also added to the sample (Catalyst to sample ratio: 1–1) and mixed manually to perform the in-situ catalytic pyrolysis.