Aromatic hydrocarbon selectivity in CaO-catalyzed PET pyrolysis using Tandem μ-Reactor-GC/MS

[Background] Pyrolysis of waste plastics is often conducted over various catalysts to obtain useful gases and oils. However, in the pyrolysis of polyethylene terephthalate (PET), significant amounts of high-boiling terephthalic acid (TPA, bp ca. 400 ºC), which causes corrosion and clogging of pipes, are produced. To avoid the formation of TPA in recycling systems, a new PET recycling protocol was developed to suppress the TPA formation and yield a benzene-rich aromatic oil by using a calcium oxide (CaO) catalyst. In this report, a Tandem μ-Reactor-GC/MS (TR-GC/MS) system (Fig. 1) was used to investigate the effects of basicity of CaO on the aromatic hydrocarbon production using strongly and weakly basic CaO catalysts.

[Experimental] CaO catalysts with different basicities were prepared by the calcination of $CaCO_3$ at 900 or 1110 ºC under nitrogen atmosphere (CaO_{900} or CaO_{1110}), followed by grinding to a particle size of 0.3-1.0 mm. A TR-GC/MS system (Fig. 1) was used for all experiments. PET (1 mg) was pyrolyzed at 450 ºC in the 1st Reactor under helium flow, and the pyrolyzates flowed into the 2nd Reactor and were converted by a catalytic reaction with CaO (5.8 mg) at 700 ºC. The reaction products were temporarily trapped at the head of the separation column using a MicroJet Cryo-Trap, and the trapped products were separated and detected by GC/MS.

[Results] As shown in Fig. 2, in the presence of strongly basic CaO_{900} (900 ºC) the benzene-rich aromatics are produced selectively. In the presence of weakly basic CaO_{1110}, oxygen-containing compounds such as vinyl benzoate, benzoic acid, benzophenone, etc. are drastically increased. Deoxygenated compounds such as benzene, toluene, and styrene are also detected, but their selectivity is lower than that in the case of CaO_{900}. Thus, the CaO basicity strongly affects the product distribution: highly basic CaO selectively produces aromatic hydrocarbons, while weakly basic CaO enhances the formation of aldehydes and ketones. Repeated use of CaO promoted the formation of oxygen-containing compounds (65 % after 10 times repetitions). SEM analysis revealed that CaO was sintered upon repeated use, leading to its lowered basicity. Thus, this study has demonstrated that the reaction selectivity is strongly affected by CaO deterioration and CaO basicity.

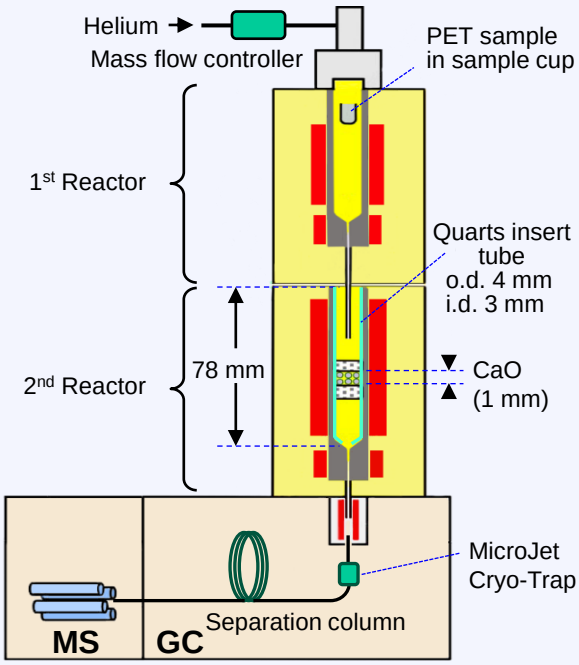

Fig. 1. Tandem μ-Reactor-GC/MS system.

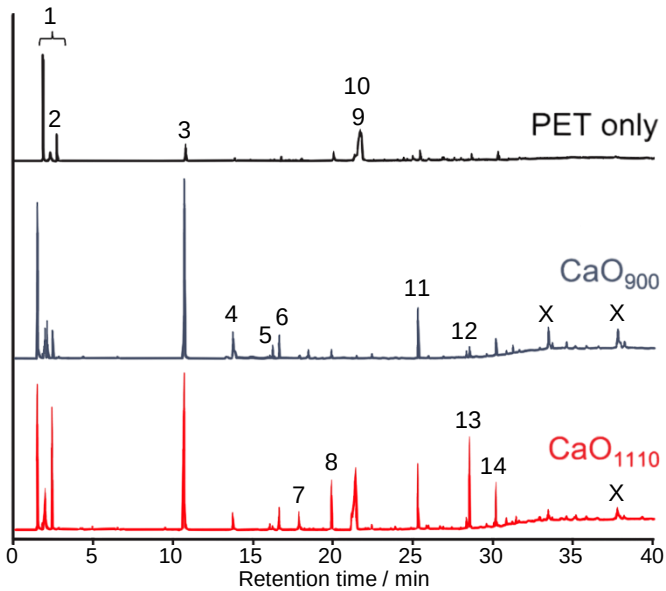

Fig. 2. Chromatograms of major pyrolyzates of PET obtained without and with CaO catalysts having varied basicities.

GC oven temp.: 40 ºC (5 min hold) - 10 ºC /min - 300 ºC (10 min hold).

1: Gases, 2: Acetaldehyde, 3: Benzene, 4: Toluene, 5: Acetyl benzene, 6: Styrene, 7: Benzaldehyde, 8: Acetophenone, 9: Vinyl benzoate, 10: Benzoic acid, 11: Biphenyl, 12: Fluorenylinene, 13: Benzophenon, 14: Fluorenone, x: Column bleed.

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Keywords : CaO catalyst, PET, Aromatic hydrocarbons, Selectivity

Products used : Tandem μ-Reactor, MicroJet Cryo-Trap

Applications : Waste plastics conversion, Catalyst screening

Related technical notes : RXA-003E

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