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Short communication

Aromatic hydrocarbon selectivity as a function of CaO basicity and aging during CaO-catalyzed PET pyrolysis using tandem μ-reactor-GC/MS

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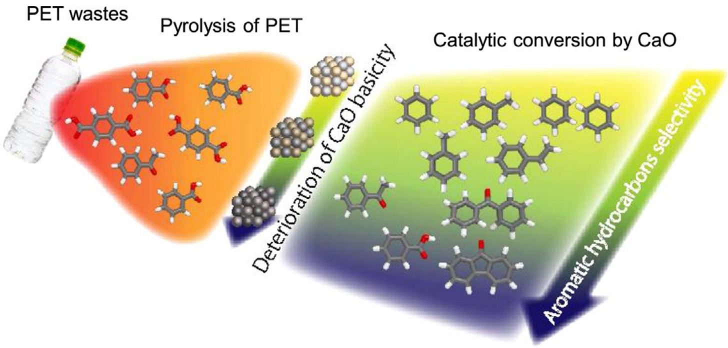
GRAPHICAL ABSTRACT



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ABSTRACT

During the tandem pyrolysis of poly(ethylene terephthalate) (PET) and catalytic conversion of the PET pyrolysates over calcium oxide (PET/CaO process), the relationship between catalyst deterioration and the aromatic hydrocarbon selectivity was elucidated. Using a tandem micro (μ)-reactor-gas chromatography/mass spectrometry (TR-GC/MS) system, PET was pyrolyzed at 450 °C in the 1st μ-reactor and the PET pyrolysates were refined over one of two CaO catalysts with different basicities at 700 °C in the 2nd μ-reactor. Strongly basic CaO enhanced benzene production via decarboxylation, resulting in 83.6% selectivity for aromatic hydrocarbon products. This selectivity decreased with repeated runs over the strongly basic CaO, while oxygen-containing compounds such as benzophenone and benzoic acid increased. The surface morphology changes observed by scanning electron microscopy indicated that CaO was thoroughly sintered with repeated use, which reduced its basicity. The less-basic CaO effected diminished carboxyl-unit surface adsorption and suffered deteriorated deoxygenation ability. Thus, this study clearly demonstrates that CaO deterioration (by sintering during repeated PET/CaO processing) and CaO basicity strongly influence reaction selectivity.

1. Introduction

Pyrolysis is widely applied to decompose polymers into smaller molecules using only heat under an inert atmosphere, and is often combined with various catalysts to obtain useful gas, liquid, and solid products [1–3]. However, in the case of poly(ethylene terephthalate)

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(PET)—the most prevalent polyester worldwide—pyrolysis produces significant amounts of acidic, high-boiling terephthalic acid (TPA, boiling point ~400 °C) [4,5], which causes corrosion and clogs pipes [6,7]. To avoid the negative effects of TPA in recycling systems, a PET recycling protocol that uses a calcium oxide (CaO) catalyst to completely suppress TPA formation and yield a benzene-rich aromatic oil as the final product was developed (PET/CaO process) [8–13]. This process has also been applied for mixed plastics [14,15], metal-PET composites [8,11], and PET-based waste carpets [16]. The addition of FeOOH [17,18], TiO_2/SiO_2 [19], and ZSM-5 [16] catalysts during PET pyrolysis has also been reported to suppress TPA formation. Thus, the catalytic pyrolysis of PET is an attractive topic in the field of plastics recycling, and CaO is one of the least expensive catalysts that converts waste PET into a benzene-rich aromatic oil.

Online analysis is a feasible method for promptly investigating product compositions and emission behaviors. Thermogravimetry-mass spectrometry (TG-MS) and TG-Fourier transform infrared spectrometry (TG-FTIR) are well-known techniques for online product analysis during the pyrolysis of plastics [20–25]. These analyses are often performed by mixing plastics and solid catalysts to evaluate catalyst performance and product emission behaviors [26–29]. However, for PET, such analyses suffer several drawbacks: (1) High-boiling TPA is deposited inside the long transfer tube connecting the TG and MS or FTIR components. (2) Plastics and mixed solids are heated via the same temperature program, while the optimum temperatures for PET pyrolysis and various catalysts including CaO are different [10]. To our knowledge, the online investigation of PET/catalyst pyrolysis processes has never been performed. Furthermore, the behavior and effects of the deterioration of CaO catalytic activity on aromatic hydrocarbon production are also unknown.

In this work, a tandem micro (μ)-reactor-GC/MS (TR-GC/MS) system (Fig. 1) was employed to evaluate a repeatable PET/CaO process for the first time. The TR prevents line obstruction from TPA deposition because of the minuscule sample loading (< 1 mg) and high split-injection ratio (100:1) into the GC/MS system. Strongly and weakly basic CaO catalysts were prepared to investigate the effects of basicity and the deterioration of CaO activity on aromatic hydrocarbon production.

2. Materials and methods

2.1. Materials

Powdered PET pellets (< 250 μm, Shinko Plastics Co., Ltd.) were used for all experiments. The C, H, and O composition of the sample was 62.4, 4.3, and 33.4 wt%, respectively, consistent with theory for PET. Proximate analysis obtained under reported conditions [30] revealed volatile and fixed carbon values for the sample of 83.2 and 16.8 wt%, respectively, with no moisture or ash observed. Other chemicals were obtained from Kanto Chemical Co., Inc. or Tokyo Chemical Industry Co., Ltd.

2.2. CaO preparation and characterization

CaO samples with different basicities, prepared by the calcination of $CaCO_3$ at 900 or 1110 °C under N_2, were kindly supplied from Okutama Industries Co., Ltd. Each CaO sample was ground to a particle size of 0.3–1.0 mm.

The prepared CaO was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area and pore volume analyses, and CO_2 temperature-programmed desorption (CO_2-TPD). Detailed characterization procedures and conditions are summarized in the Supporting Information (SI).

2.3. TR-GC/MS experiments

A TR-GC/MS system (Fig. 1) was used for all experiments. Detailed system information and experimental procedures are summarized in the SI. Briefly, PET (1 mg) was pyrolyzed at 450 °C in the 1st μ-reactor under helium flow, and the pyrolysates passed into the 2nd μ-reactor were reacted with CaO (5.8 mg) at 700 °C. The temperatures of both μ-reactors were maintained for 20 min. Products generated from the TR were trapped at −196 °C using a cryotrap placed between the GC injection port and the separation column. After terminating the reaction, the cryotrap was removed and the contents immediately analyzed by GC (column oven temperature: 40 °C (5 min) → 10 °C min^{-1} → 300 °C (10 min)).

To monitor CaO deterioration over multiple runs, the above procedure was repeated 10 times without CaO regeneration or replacement. Detailed procedures are summarized in the SI.

3. Results and discussion

3.1. Characterization of the prepared strongly/weakly basic CaO

The SEM images presented in Fig. 2(a, d) clearly indicate that CaO_{900} has a rugged surface, whereas CaO_{1110} has a rounded surface

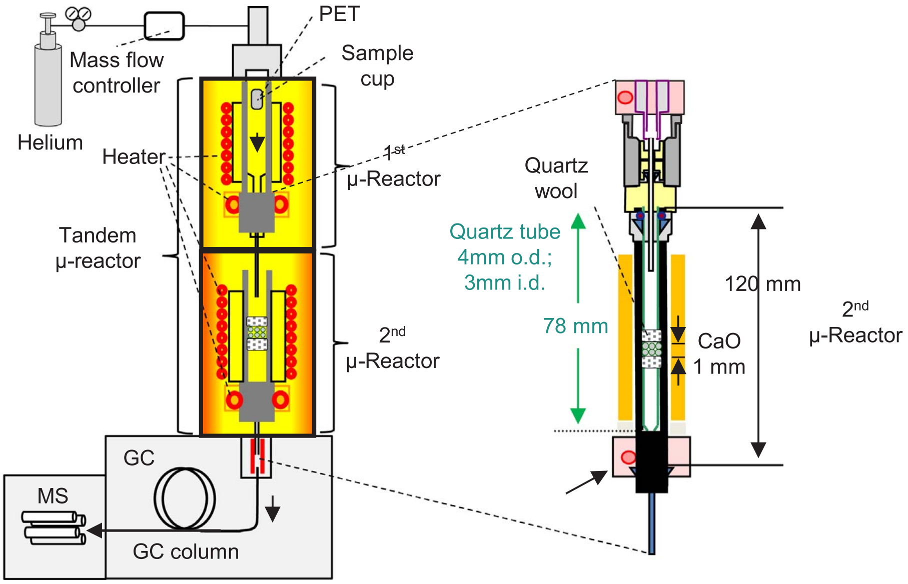

Fig. 1. Tandem μ-reactor-GC/MS system.