

Electronic Supplementary Information

Tandem μ -reactor-GC/MS for online monitoring of aromatic hydrocarbon production *via* CaO-catalysed PET pyrolysis

Shogo Kumagai^{a,}, Ryota Yamasaki^a, Tomohito Kameda^a, Yuko Saito^a, Atsushi Watanabe^b, Chuichi
Watanabe^b, Norio Teramae^{b,c}, Toshiaki Yoshioka^a*

^a Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki-aza, Aoba-ku,
Sendai, Miyagi 980-8579, Japan

^b Frontier Laboratories Ltd., 4-16-20, Saikon, Koriyama, Fukushima 963-8862, Japan

^c Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai, Miyagi
980-8578, Japan

*Corresponding author: kumagai@env.che.tohoku.ac.jp; Tel & Fax: +81-22-795-7212.

Characterization of the prepared CaO

Prepared CaO were characterized by X-ray diffraction (XRD, Rigaku powder diffractometer RINT-2200VHF+/PC, scanning between 3° and 90° using the CuK α line with a scanning rate 1° min⁻¹). The XRD spectrum of the fresh CaO after calcination at 900 °C for 1 hour are summarized in Figure S1. Only the peaks of CaO (JCPDS No. 00-037-1497) are observed in all prepared CaO. Hence, it was confirmed that calcination at 900 °C for 1 hour is enough to decompose CaCO₃ and Ca(OH)₂ before using to reaction. Lattice parameter, a , was determined by the average of a calculated for (111), (200), (220), (311), (222), (400), and (331) planes. The a of each plane was determined by measured d values (Table S1) using Bragg's equation. Each CaO shows comparable lattice parameter 4.805-4.809 Å as summarized in Table S1. The lattice parameters for the CaO samples were comparable with each other and consistent with those for the pure-phase CaO (JCPDS No. 00-037-1497), which implied that the prepared CaO samples had high purity. The crystallite size of each CaO was determined by Halder-Wagner method,¹ resulting in 432, 528, 557, and 597Å for CaO_A, CaO_B, CaO_C, and CaO_D, respectively.

Scanning electron microscopy (SEM, Hitachi-High-Technologies Corporation, S-4800) was used to observe surface morphology of the prepared CaO. The SEM images are summarized in Figure S2. The BET surface area and pore volume of the prepared CaO were tested by BELSORP-mini II (MicrotracBEL Corp.), which are summarized in Table 1 in the main manuscript. The SEM images clearly indicate that CaO_A has a rugged surface, while the others have a rounded surface because of sintering, consistent with the results of BET surface area and pore volume measurements.

Carbon dioxide temperature-programmed desorption (CO₂-TPD) (Quantachrome Instruments, ChemBET PULSAR™ TPR/TPD) was carried out for evaluating basic sites concentration and basic strength of the prepared CaO. CO₂ adsorption was carried out at 100 °C for 1 hour, and then CO₂ desorption was monitored by following temperature program: 100 °C → 10 °C/min → 200 °C (30 min) → 5 °C/min → 850 °C. First period until 200 °C is to remove physically adsorbed CO₂, which is not considered for further discussion. The measurements were controlled using the software TPRWin

provided by Quantachrome Instruments. The CO₂ desorption area was determined using the software QCfit provided by Quantachrome Instruments. As per the CO₂-TPD profiles (not shown), the CaO samples differ in the strength and number of base sites because CO₂ desorption of CaO_A, CaO_B, and CaO_C and CaO_D occurred at 601, 524, 489, and 489 °C, respectively. The calculated base site density of CaO_A, CaO_B, CaO_C, and CaO_D are 315, 44, 30, and 25 μmol g⁻¹.

Based on these results, CaO_A had the highest base site density and base strength, and the smallest crystallite size and hence was the most active base. CaO_B had a significantly smaller base site density, lower CO₂ desorption temperature, and larger crystallite size than CaO_A. However, the base site density on CaO_B surface is comparable with that on CaO_A. The base site density and CO₂ desorption temperatures of CaO_C and CaO_D were further lowered, and the crystallite size was slightly larger than CaO_B.

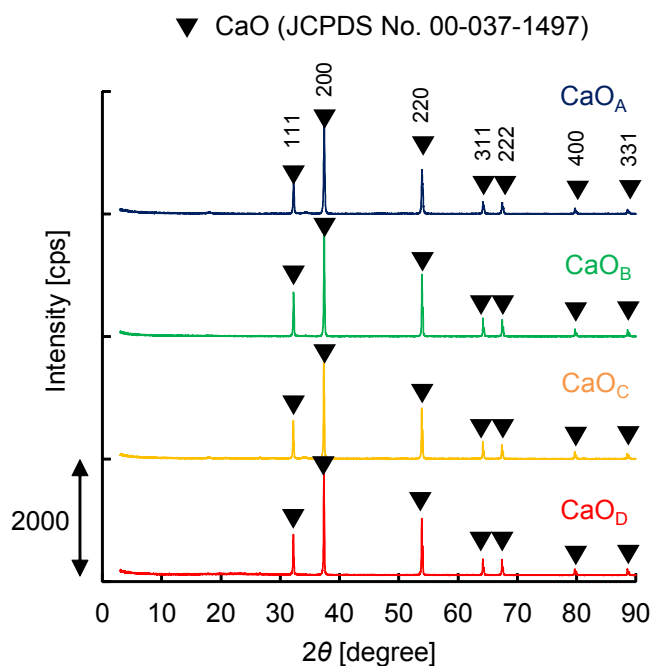
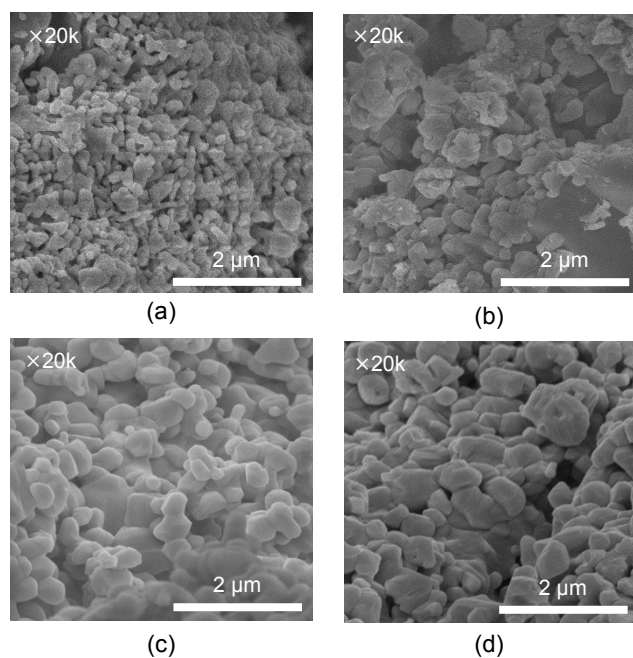


Figure S1 XRD spectrum of fresh CaO after calcination at 900 °C for 1 hour.

Table S1. Measured d values and calculated a values for each CaO

hkl	CaO _A		CaO _B		CaO _C		CaO _D	
	d	a	d	a	d	a	d	a
111	2.772	4.800	2.773	4.803	2.777	4.809	2.777	4.810
200	2.401	4.802	2.402	4.804	2.405	4.811	2.405	4.809
220	1.699	4.806	1.699	4.805	1.700	4.810	1.700	4.809
311	1.449	4.806	1.449	4.807	1.450	4.810	1.450	4.809
222	1.387	4.806	1.387	4.806	1.388	4.809	1.388	4.809
400	1.202	4.808	1.202	4.807	1.202	4.809	1.202	4.809
331	1.103	4.806	1.103	4.807	1.103	4.809	1.103	4.810
<i>Average</i>		<i>4.805</i>		<i>4.806</i>		<i>4.809</i>		<i>4.809</i>



1

2 **Figure S2** SEM images of (a) CaO_A, (b) CaO_B, (c) CaO_C, and (d) CaO_D at 20 k-fold magnification.

3

4 References

5 1. N. C. Halder and C. N. J. Wagner, *Acta Crystallographica*, 1966, 20, 312-313.