Supplementary Material

Mechanochemical Methanolysis of Polyethylene Terephthalate Using Calcium Oxide as Solid Base Catalyst

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Experimental

1. Chemicals

Polyethylene terephthalate used was a powder of SKYPET BR8040 (M_w 18900, M_n 8700, M_w/M_n 2.2, SK Chemical) sieved to about 100 microns. Methanol (99.8%, Kanto Chemical), dimethyl terephthalate (DMT; 99.0%, Tokyo Chemical Industry), 2-hydroxyethyl methyl terephthalate (2-HEMT; 97.0%, Tokyo Chemical Industry), monomethyl terephthalate (MMT; 99.0%, Fujifilm Wako), disodium terephthalate (Na_2TPA; 99.0%, Tokyo Chemical Industry), toluene (99.5%, Kanto Chemical), phenol phthalein (98.0%, Kanto Chemical) and benzoic acid (99.5%, Kanto Chemical) were used for the reactions and analysis. CaO (99.9%, Fujifilm Wako), MgO (98.0%, Fujifilm Wako), SrO (95%, nacalai tesque), BaO (99.9%, Sigma-Aldrich), ZnO (99.0%, Fujifilm Wako), TiO_2 (99.0%, Fujifilm Wako), Nb_2O_5 (99.9 %, Fujifilm Wako), WO_3 (99.5%, Fujifilm Wako), MoO_3 (99.0%, Fujifilm Wako), $Ca(OH)_2$ (96.0%, Kanto Chemical), $CaCO_3$ (99.5%, Kanto Chemical), $Ca(OCH_3)_2$ (95.0%, Tokyo Chemical Industry), K_2CO_3 (99.5%, Kanto Chemical), $NaHCO_3$ (99.5%, Fujifilm Wako) and NaOH (Granular, 98.0%, Wako) were used as catalysts.

2. Methanolysis of PET

The mechanochemical methanolysis of PET was carried out with a planetary ball mill

(pulverisette 7 classic line, Fritsch) at room temperature. Appropriate amount of PET powder, catalyst, methanol and six 10 mm diameter zirconia balls were placed in a 12 mL zirconia milling vessel. Ball milling was conducted for 2-20 cycles, in which each cycle was carried out for 30 min with 5 min intervals. The rotation direction was reversed each cycle. After ball milling, methanol was added to the milled powder and the slurry was centrifuged at 3000 rpm. The resultant liquids in the supernatant were analyzed by using high-performance liquid chromatograph (HPLC; pump PU-2089, JASCO) equipped with UV detector (UV-2075 Plus, JASCO) using a Shodex Silica C18P 4E column (flow rate: 0.6 mL min^{-1}; eluent: MeOH-H_2O (70/30)) . Retention times of DMT, 2-HEMT, MMT and Na_2TPA were identified as 11.1, 6.9, 4.4 and 6.8 min, respectively.

3. Characterization

The crystal structure of the sample was investigated by X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu Kα radiation (λ = 0.15418 nm) at a voltage of 40 kV and a current of 20 mA. Scans were obtained at a speed of 5^o min^{-1} with a step width of 0.05 for 2θ values of 10^o to 80^o. The particle size and its morphology were evaluated by a scanning electron microscopy (SEM; VE-8800, Keyence). The detection of radical species was carried out by electron spin resonance spectroscopy (ESR; JES-FA200, JEOL). The analysis was performed at room temperature in air. The amount of base of catalysts was estimated by a titration method. 0.15 g of sample was suspended and stirred for 30 min in 2 mL of toluene solution including phenolphthalein (0.1 g L^{-1}) followed by the titration of 0.01 M toluene solution of benzoic acid.

Table S1. Amounts of base sites on various metal oxides

Metal oxides	Base amount / mmol g^{-1}
BaO	0.45
SrO	0.053
CaO	0.12
MgO	0.067
ZnO	0.020
TiO_2	0
Nb_2O_5	0
Ta_2O_5	0
WO_3	0
MoO_3	0

Table S2. Experimental design matrix and DMT yields.

No.	CaO (g)	PET (g)	MeOH (mL)	Corded variable			DMT yield (%)
	X_1	X_2	X_3	x_1	x_2	x_3	
1	0.0025	0.1000	0.5	-1	-1	-1	74.6
2	0.0175	0.1000	0.5	1	-1	-1	73.6
3	0.0025	0.2000	0.5	-1	1	-1	34.6
4	0.0175	0.2000	0.5	1	1	-1	61.8
5	0.0025	0.1000	2.5	-1	-1	1	46.2
6	0.0175	0.1000	2.5	1	-1	1	30.4
7	0.0025	0.2000	2.5	-1	1	1	63.3
8	0.0175	0.2000	2.5	1	1	1	51.4
9	0.0025	0.1500	1.5	-1	0	0	65.0
10	0.0175	0.1500	1.5	1	0	0	78.1
11	0.0100	0.1000	1.5	0	-1	0	68.5
12	0.0100	0.2000	1.5	0	1	0	49.8
13	0.0100	0.1500	0.5	0	0	-1	55.8
14	0.0100	0.1500	2.5	0	0	1	63.1
15	0.0100	0.1500	1.5	0	0	0	82.6
16	0.0100	0.1500	1.5	0	0	0	79.8
17	0.0100	0.1500	1.5	0	0	0	79.9
18	0.0100	0.1500	1.5	0	0	0	78.3

Table S3. ANOVA results for DMT yields evaluating amounts of catalyst, PET and methanol as factors.[a]

	Coefficients	Standard error	F value	p value
Intercept	75.46	3.55	452.27	<0.0001
X_1	1.16	2.85	0.165	0.695
X_2	-3.24	2.85	1.291	0.289
X_3	-4.6	2.85	2.601	0.145
X_1X_2	4.013	3.19	1.583	0.244
X_1X_3	-6.738	3.19	4.464	0.068
X_2X_3	11.24	3.19	12.42	0.008
X_1^2	0.786	5.48	0.020	0.900
X_2^2	-11.61	5.48	4.493	0.067
X_3^2	-11.31	5.48	4.264	0.073

[a] R^2 = 0.845, adj R^2 = 0.671, sum of squares = 3558, means square = 395.3

Fig. S1 Photographic images of two zirconia vessels with temperature indicator labels following the ball milling reaction at 600 rpm for 4h. The ball milling reactions were performed with temperature labels on the bottom of the vessel that irreversibly turned black above 40, 43, 49 and 54 °C, respectively, but no such color changes were observed.

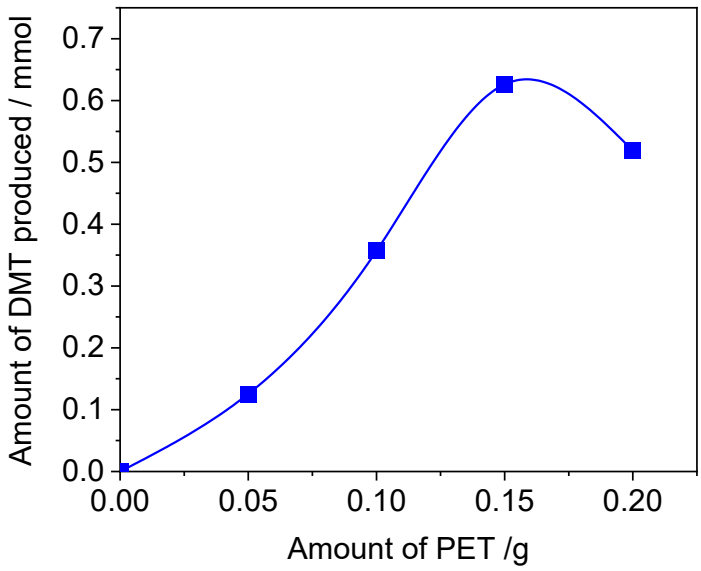

Fig. S2 Amount of DMT produced as a function of quantity of PET used for reaction.

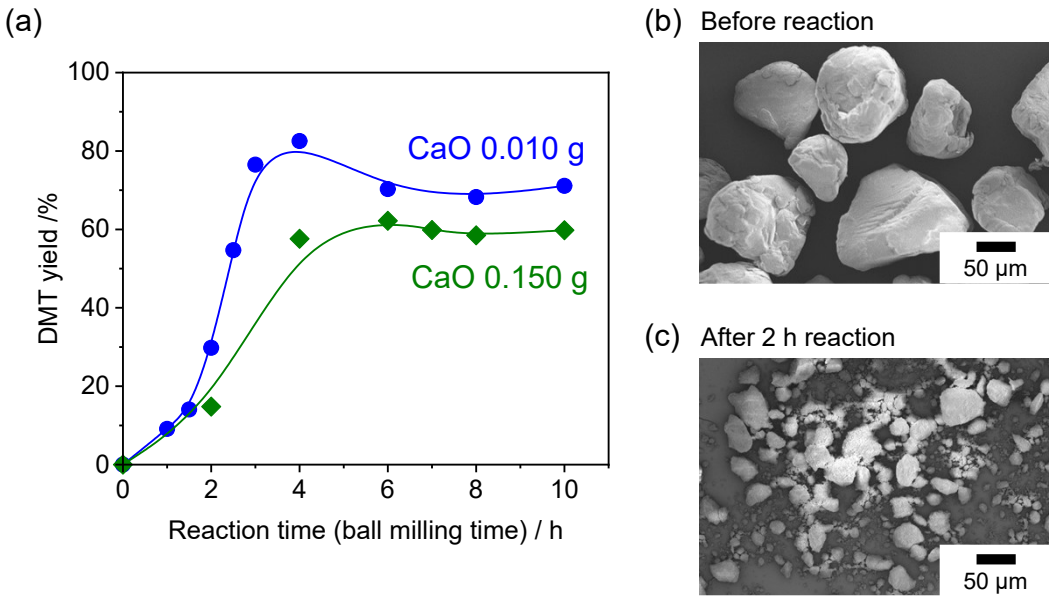

Fig. S3 (a) DMT yields during mechanochemical methanolysis of PET using various quantities of CaO as functions of time, and SEM images of (b) PET powder before reaction and (c) resulting powder after 2 h.

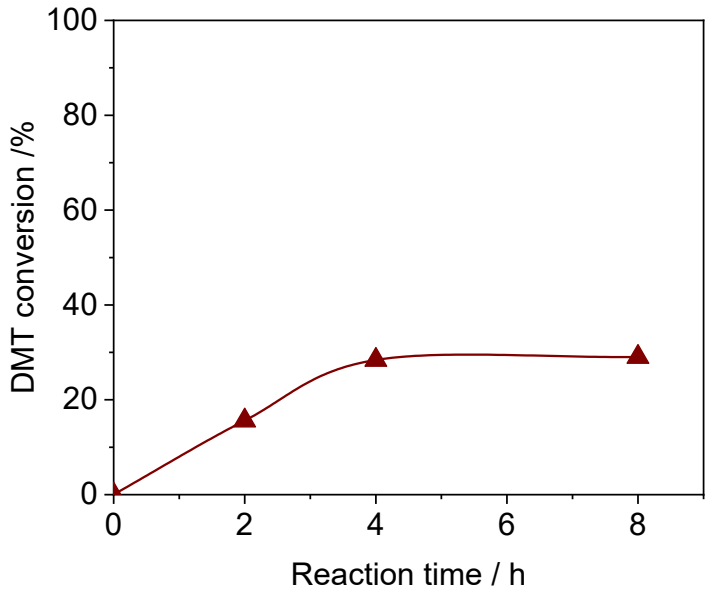

Fig. S4 DMT conversion during ball milling with ethylene glycol and CaO in methanol. Reaction conditions: DMT (0.150 g), ethylene glycol (1.00 eq.), CaO (0.010 g), methanol (1.5 mL), 600 rpm.

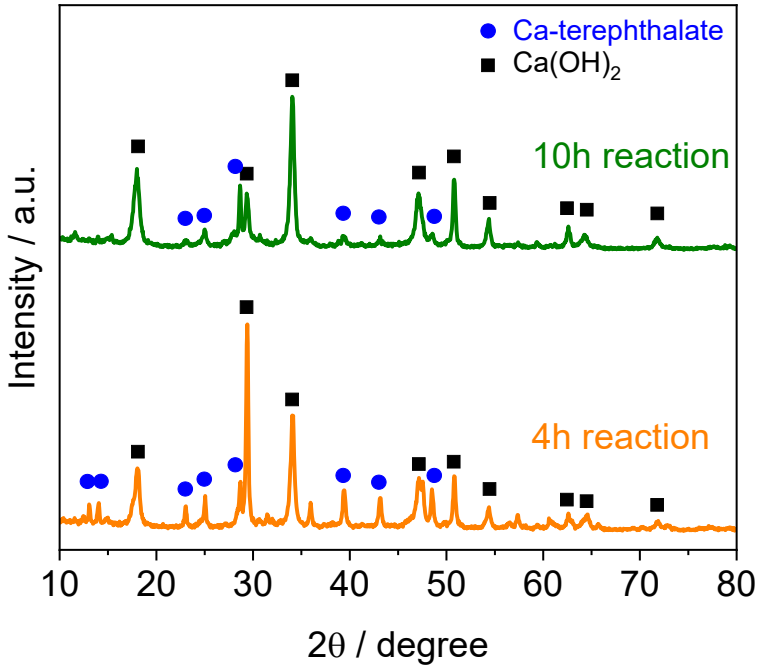

Fig. S5 XRD patterns for the solid residue after 4 h and 10 h reaction.

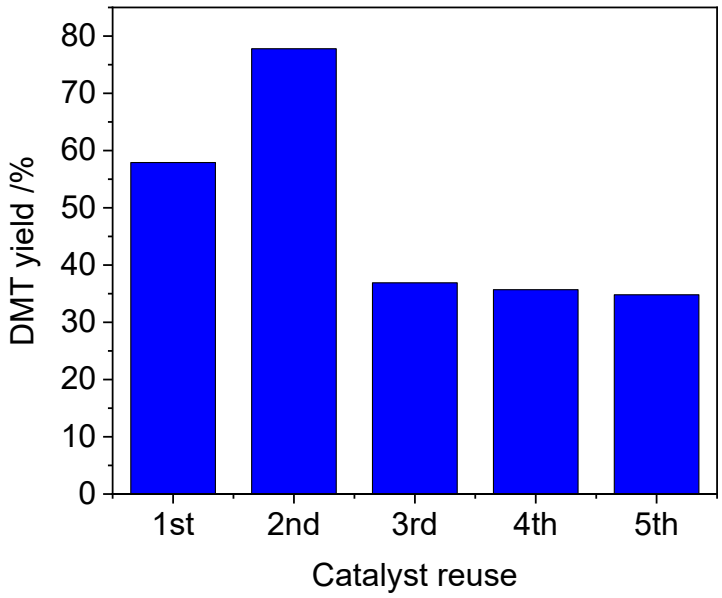

Fig. S6 Recycling of the CaO catalyst. Reaction conditions: PET (0.150 g), CaO (0.150 g), methanol (1.5 mL), 600 rpm, 4h.