

Ring-opening polymerization of trimethylene carbonate to poly(trimethylene carbonate) diol over a heterogeneous high-temperature calcined CeO<sub>2</sub> catalyst

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## Experimentals

### Materials

All the chemicals for organic reactions were purchased from chemical products corporations and were used without further purification. Trimethylene carbonate (Tokyo Chemical Industry Co. Ltd., >98.0%), 1-hexanol (Tokyo Chemical Industry Co. Ltd., >98%), tetrahydrofuran (Kanto Chemical CO., Inc.), acetonitrile (Kanto Chemical CO., Inc. >99.8%), water (FUJIFILM Wako Pure Chemical Corporation), dithranol (Tokyo Chemical Industry Co. Ltd., >95.0%), NaI (FUJIFILM Wako Pure Chemical Corporation, >99.5%), Ar (Tokyo Koatsu CO. Ltd. >99.99999%),  $\text{CDCl}_3$  (Acros Organics, 99.8%, 0.03 vol% TMS).

### Metal oxides

$\text{CeO}_2$  catalysts were prepared by calcining cerium oxide (HS, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) in 3 hours under air at different calcination temperature (873, 1073, 1173, 1273, 1373, 1473 K). Other metal oxides were commercially available or supplied from the Catalysis Society of Japan:  $\text{ZrO}_2$  (Daiichi Kigenso Kogyo Co. Ltd.,  $\text{Zr}(\text{OH})_2$  was calcined under air at 873 K for 3 h.), MgO (Ube Industries, Ltd., MgO 500A, MgO was used after calcining under air at 873 K for 3 h.),  $\text{TiO}_2$  (Nippon Aerosil Co. Ltd., P-25),  $\gamma\text{-Al}_2\text{O}_3$  (Sumitomo Chemical Company Ltd.,  $\gamma\text{-Al}_2\text{O}_3$  was used after calcining under air at 873, 1073, 1273 or 1473 K for 3 h),  $\text{SiO}_2$  (Fuji Silysia Chemical Ltd., G-6,  $\text{SiO}_2$  was used after calcining under air at 973 K for 3 h.),  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (JRC-SAL-2), ZnO (Sakai Chemical Industry Co., Ltd., Finex-50).  $\text{La}_2\text{O}_3$  (Soekawa Chemicals,  $\text{La}(\text{OH})_3$  was calcined under air at 873 K for 3 h),  $\text{Y}_2\text{O}_3$  was prepared by the precipitation method.  $\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  (Pure Chemical Industries Ltd., >99.9%) was used as a precursor. A precursor (25 g) was dissolved in water (100 ml) and  $\text{NH}_3\text{aq}$  (1 M) was dropped with stirring. The pH of the solution was set to 10, resulting in a precipitate. The precipitate was filtered and washed with water, following a drying at 383 K overnight (12 h) and calcined under air at 873, 1073, 1273 or 1473 K for 3 h. The specific surface areas of metal oxides were measured by BET method.

### Typical procedure for ring-opening polymerization of trimethylene carbonate

$\text{CeO}_2$  (1 mmol (0.17 g)) and TMC 10 mmol were put into the autoclave together with a stirrer bar. The reactor was sealed, and then the air content was quickly purged by flushing Ar three times, and was pressurized with Ar to 1.1 MPa at room temperature. Then the autoclave was heated to 333 K. The time when the temperature of the autoclave reached 333 K was defined as 0 h. The mixture was constantly stirred during the reaction. After the reaction, the reactor was cooled in water bath to room temperature. After the gas phase was sampled, 1-hexanol (~0.2 ml) was added to the reaction mixture as an internal standard for

quantitative analysis, and the reaction mixture was collected by using THF (total 15 ml) as a washing solvent. The products were analyzed by a gas chromatograph (GC) equipped with an FID using a CP-Sil5 (Agilent J&W, length = 50 m, I.D. = 0.25 mm) and by high performance liquid chromatography (HPLC) with RI detector using Gemini-NX (Shimadzu GLC, particle size 5  $\mu\text{m}$ , 150 mm $\times$ 4.6 mm, conditions: developing solvent, acetonitrile/water=45/55, 0.2 ml/min, 313 K). The quantitative analyses of TMC and 1,3-propanediol were conducted by GC-FID and HPLC, respectively because polymer can be decomposed to 1,3-propanediol and CO<sub>2</sub> by heating. Produced amount of CO<sub>2</sub> was analyzed by GC with an FID and a methanator using a Porapak N (GL Science, length = 2.0 m, I.D. = 3.0 mm). The produced polymers were analyzed by MALDI-TOF mass (AB Sciex, TOF / TOF™ 5800) using dithranol and NaI as a matrix and ionization agent, respectively, and size exclusion chromatography (SEC, Shimadzu Prominence) with an RI detector (RID-10A) using a KF-805L (Shodex, developing solvent: THF, 1.0 ml/min, 313 K).

The conversion and selectivity were calculated by the following equations.

Conversion / % = 100  $\times$  [1 - (Amount of TMC after reaction (mmol))/(Amount of TMC before reaction (mmol))]

Selectivity / % = 100  $\times$  [(Amount of the product (mmol) $\times$ (carbon number of the products))/(amount of reacted TMC (mmol) $\times$ 4)]

The amount of polymers was determined by subtraction of TMC-derived product amount from reacted TMC amount, and the selectivity was also calculated by the above equation.

The water content of TMC and CeO<sub>2</sub> was determined by the Karl Fischer titration method using a Karl Fischer moisture titrator (899 Coulometer; Metrohm Ltd.). A sample weighed exactly was titrated by using HYDRANAL-Coulomat AG-Oven (Honeywell Fluka™) as the Karl Fischer reagent.

Reusability test was conducted as follows: After the reaction, the used catalyst and the liquid phase were separated by centrifugation, and the collected catalyst was washed with THF (15 ml) three times, and then the collected wet catalyst was dried at 353 K for 12 h. The dried catalyst was heated at 1273 K under air for 3 h, and then used for the next reaction. The reaction scale was decreased based on the collected amount of CeO<sub>2</sub>.

## Characterization

The surface area of metal oxides was measured with BET method (N<sub>2</sub> adsorption) using Gemini (Micromeritics). X-ray diffraction (XRD) patterns were recorded using MiniFlex 600 with Cu K $\alpha$  (40 kV, 15 mA) radiation. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500). The sample for the ICP was obtained by removing the

CeO<sub>2</sub> from the reaction mixture by filtration. Therefore, the sample contained the remaining substrate, polymer and solvent.

**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR analysis**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at ambient temperature on Bruker, AV400 operating at 400 MHz. The sample was prepared by using CDCl<sub>3</sub> solvent.

## Supporting Tables

Table S1 Effect of calcination temperature of CeO<sub>2</sub> in the ring-opening reaction of TMC

Entry	Calcination <i>T</i> /K	<i>S</i> <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>	Conv. /%	Polymer sel. /%	CO <sub>2</sub> amount /mmol	<i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	<i>V</i> <sup>b</sup> / mmol h <sup>-1</sup> g <sup>-1</sup>	<i>V</i> <sub>surf</sub> <sup>c</sup> / mmol h <sup>-1</sup> m <sup>-2</sup>
1	873	84	38	92	0.29	990	1300	1.32	2.8	0.03
2	1073	41	46	98	0.21	2200	2900	1.25	3.3	0.08
3	1173	25	60	95	0.20	2900	3600	1.25	4.3	0.17
4	1273	13	71	98	0.14	7000	9500	1.37	5.1	0.40
5	1373	5	31	96	0.10	3000	3800	1.27	2.3	0.45
6	1473	1	5	91	0.05	460	510	1.12	0.4	0.44

Reaction conditions: CeO<sub>2</sub> 1 mmol, TMC 10 mmol, Ar 1.1 MPa, 333 K, 8 h

<sup>a</sup>Specific surface area determined by BET method

<sup>b</sup>Reaction rate per catalyst amount

<sup>c</sup>Reaction rate per surface area of catalyst

Table S2 Effect of calcination temperature of Al<sub>2</sub>O<sub>3</sub> in the ring-opening reaction of TMC

Entry	Calcination T /K	S <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>	Conv. /%	Polymer sel. /%	CO <sub>2</sub> amount /mmol	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>	V <sup>b</sup> / mmol h <sup>-1</sup> g <sup>-1</sup>	V <sub>surf</sub> <sup>c</sup> / mmol h <sup>-1</sup> m <sup>-2</sup>
1	873	97	61	98	0.14	5800	7700	1.32	15	0.15
2	1073	92	54	98	0.10	7000	10000	1.41	13	0.14
3	1273	90	49	98	0.10	6100	8600	1.41	12	0.13
4	1473	66	38	98	0.09	5100	7400	1.44	9.4	0.14

Reaction conditions: Al<sub>2</sub>O<sub>3</sub> 1 mmol, TMC 10 mmol, Ar 1.1 MPa, 333 K, 8 h

<sup>a</sup>Specific surface area determined by BET method

<sup>b</sup>Reaction rate per catalyst amount

<sup>c</sup>Reaction rate per surface area of catalyst

Table S3 Effect of calcination temperature of  $Y_2O_3$  in the ring-opening reaction of TMC

Entry	Calcination $T/K$	$S^a$ $/m^2 g^{-1}$	Conv. $/\%$	Polymer sel. $/\%$	$CO_2$ amount $/mmol$	$M_n$	$M_w$	$M_w/M_n$	$V^b/$ $mmol h^{-1} g^{-1}$	$V_{surf}^c/$ $mmol h^{-1} m^{-2}$
1	873	43	57	96	0.22	3600	5400	1.49	6.3	0.15
2	1073	31	65	99	0.17	8600	17000	2.04	7.2	0.23
3	1273	14	25	97	0.08	4100	6400	1.55	2.8	0.20
4	1473	5	8	95	0.04	2100	3200	1.54	0.87	0.18

Reaction conditions:  $Y_2O_3$  1 mmol, TMC 10 mmol, Ar 1.1 MPa, 333 K, 8 h

<sup>a</sup>Specific surface area determined by BET method.

<sup>b</sup>Reaction rate per catalyst amount

<sup>c</sup>Reaction rate per surface area of catalyst

Table S4 Effect of water in the ring-opening polymerization of TMC over CeO<sub>2</sub> (1273 K)

Entry	Added water /mmol	Conv. /%	Polymer sel. /%	CO <sub>2</sub> amount /mmol	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>M<sub>w</sub>/M<sub>n</sub></i>
1	0	46	98	0.10	5989	7575	1.26
2	0.2	18	84	0.22	1600	1900	1.24

Reaction conditions: CeO<sub>2</sub> (calcined at 1273 K) 1 mmol, TMC 10 mmol, Ar 1.1 MPa, 333 K, 6 h



Table S5 Comparison of our catalyst system with the previously reported heterogeneous catalyst systems at low conversion level.

Reference	Catalyst	$S^a$ /m <sup>2</sup> g <sup>-1</sup>	Catalyst amount / mg	Substrate amount /mmol	Additive	$t$ /h	$T$ /K	Conv. /%	$M_n$	$M_w/M_n$	$V_{\text{amount}}$ /mmol h <sup>-1</sup> g <sup>-1</sup>	$V_{\text{surf}}$ /mmol h <sup>-1</sup> m <sup>-2</sup>
[20]	CeO <sub>2</sub>	78	20	3	MeI (0.01 mmol)	2	333	27	18000	1.27	15	0.19
[20]	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /CeO <sub>2</sub>	73	20	3	MeI (0.01 mmol)	2	333	20	6200	1.41	15	0.21
This study	CeO <sub>2</sub> calcined at 1273 K	13	170	10	-	4	333	37	2529	1.34	5.4	0.41
						8	333	71	7000	1.37	-	-

<sup>a</sup>Specific surface area determined by BET.

Table S6 Reusability of CeO<sub>2</sub> calcined at 1273 K in the ring-opening polymerization of TMC

Usage time	CeO <sub>2</sub> amount /mol	TMC amount /mmol	Conv. /%	Polymer sel. /%	CO <sub>2</sub> amount /mmol	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
1 (Fresh)	2	20	25	97	0.17	3100	3900	1.26
2	1.78	17.8	23	97	0.11	4000	4900	1.24
3	1.67	16.7	19	97	0.08	3100	3800	1.23
4	1.58	15.8	18	98	0.06	3300	4300	1.32

Reaction conditions: CeO<sub>2</sub> 1.58-2.0 mmol, TMC 20-15.8 mmol (TMC/CeO<sub>2</sub>=10 mmol/mmol), Ar 1.1 MPa, 333 K, 4 h

## Supporting Figures

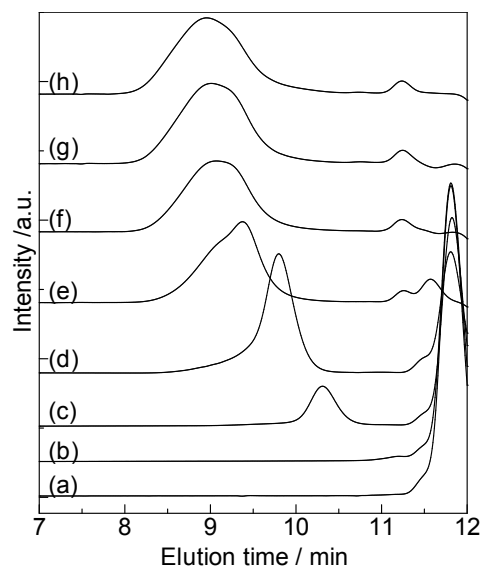


Figure S1. SEC traces of poly(trimethylene carbonate) diol produced by ring-opening polymerization of TMC over  $\text{CeO}_2$  (1273 K) at different reaction times. (a) 0 h, (b) 2 h, (c) 4 h, (d) 8 h, (e) 16 h, (f) 24 h, (g) 48 h, (h) 72 h.



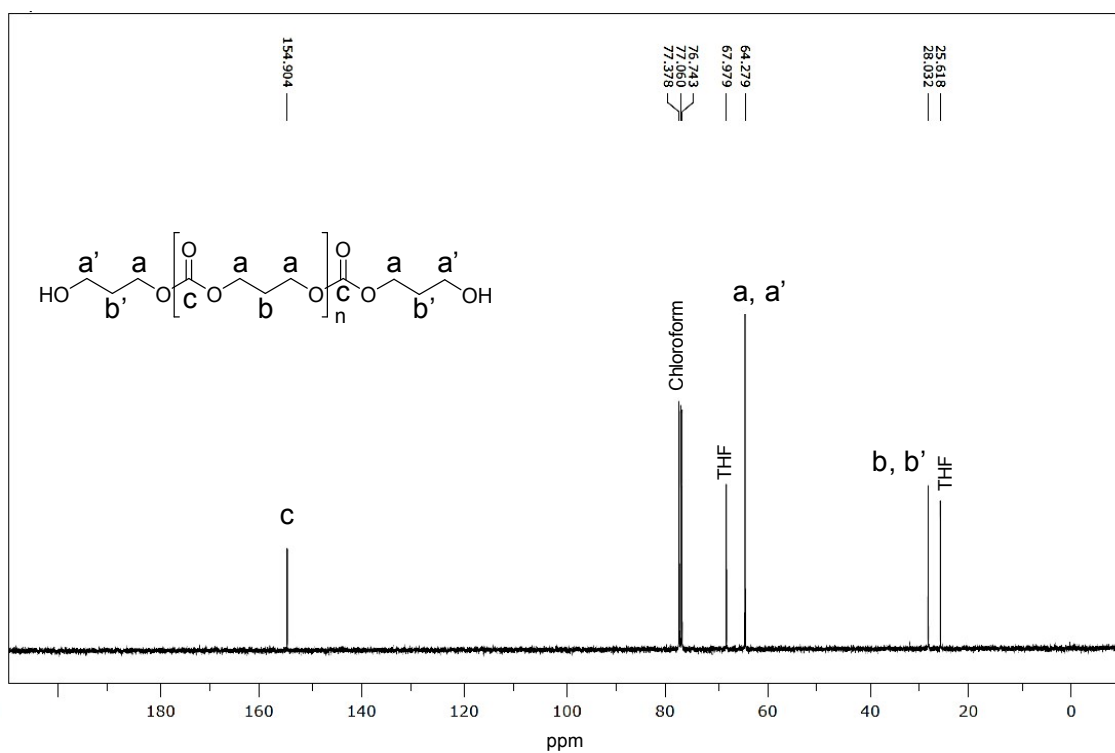


Figure S3  $^{13}\text{C}$ -NMR spectrum of the reaction mixture after 24 h.

Reaction conditions: TMC 10 mmol,  $\text{CeO}_2$  (1273 K) 1 mmol, 333 K, Ar 1.1 MPa, 24 h.

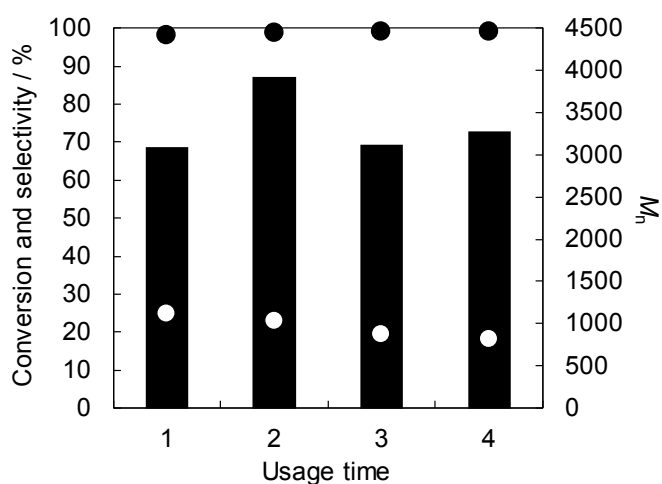


Figure S4 Reusability test of  $\text{CeO}_2$  calcined at 1273 K in the ring-opening reaction of TMC (⊙: conversion, ⊗: selectivity to polycarbonate, black bar: averaged molecular weight). Reaction conditions:  $\text{CeO}_2$  (1273 K) 1.58-2.0 mmol, TMC 20-15.8 mmol ( $\text{TMC}/\text{CeO}_2=10$  mmol/mmol), Ar 1.1 MPa, 333 K, 4 h. Detailed results were shown in Supplementary information (Table S4).

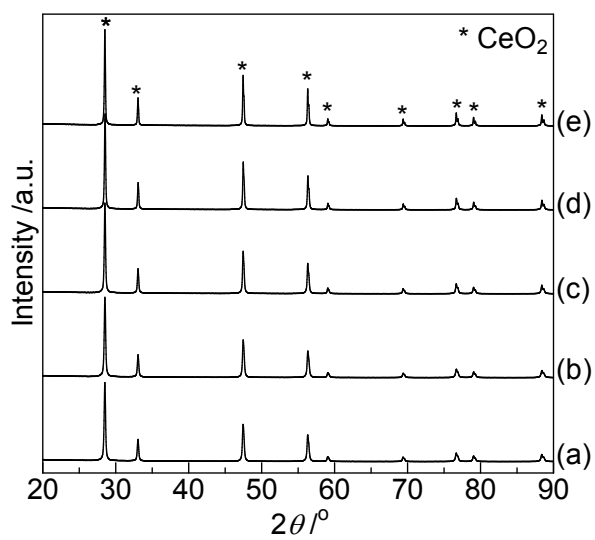


Figure S5. XRD patterns of CeO<sub>2</sub>. (a) fresh CeO<sub>2</sub>, (b) CeO<sub>2</sub> after the first reaction, (c) CeO<sub>2</sub> after the second reaction, (d) CeO<sub>2</sub> after the third reaction, (e) CeO<sub>2</sub> after the fourth reaction.