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Direct Cyclic Carbonate Synthesis from CO_2 and Diol over Carboxylation/Hydration Cascade Catalyst of CeO_2 with 2-Cyanopyridine

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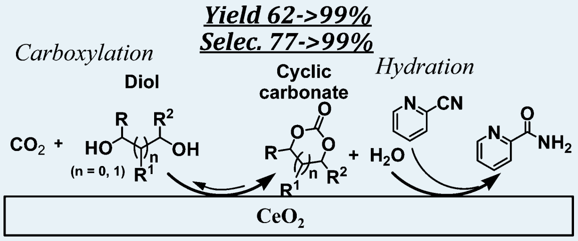
S *Supporting Information*

ABSTRACT: We first achieved direct synthesis of propylene carbonate from CO_2 and 1,2-propanediol in excellent yield (>99%) using a carboxylation/hydration cascade catalyst of CeO_2 with 2-cyanopyridine. The catalyst system can be applied to syntheses of various cyclic carbonates, including 6-membered ring carbonates that are difficult to synthesize in high yields (62−>99%).



KEYWORDS: *Cerium oxide, carbonate, CO_2, hydration, carboxylation*

INTRODUCTION

The direct syntheses of chemicals and fuels from CO_2 have drawn much interest because CO_2 is an abundant, nontoxic, nonflammable, and inexpensive carbon source.[1] However, the scope of transformation methods of CO_2 is limited because of its inert nature. Therefore, the development of effective catalytic methods for transformation of CO_2 by low energy input is an important and urgent matter.

Among various target chemicals, cyclic carbonate is a promising one and has been widely used as a starting material for polycarbonate resin,[2] an electrolyte for lithium ion batteries,[3] and an inert solvent.[4] Conventionally, cyclic carbonates have been produced by using phosgene or its derivatives;[5] however, this process has considerable drawbacks, such as use of highly toxic phosgene, and coproduction of a large amount of salts by the neutralization. Various alternative methodologies with catalysts,[6] such as oxidation of olefins with CO_2, cycloaddition of CO_2 to epoxides, oxidative carbonylation of diols, transesterification of diols with dialkyl carbonate, and the reaction of diols with urea, have been proposed. Among these methodologies, cycloaddition of CO_2 to epoxides has been the most investigated owing to its green process, and many effective catalysts have been reported.[1] However, this process has problems that starting materials such as epoxides and oxetanes demand peculiar handling techniques because of their high reactivity or toxicity,[7] and oxetanes are prepared by the perplexing method.[8]

On the other hand, carboxylation of diols with CO_2 can be regarded as an alternative green method because this reaction gives only water as a byproduct, and diols can be manufactured from biomass.[9] Therefore, various homogeneous[10] and heterogeneous[11] catalysts have been developed. However, these catalysts have suffered from high CO_2 pressure (generally >10.0 MPa)[6b] and/or low yield (maximum yield of propylene carbonate and ethylene carbonate is 42% and 62%, respectively)[6b] because of a severe equilibrium limitation. To overcome the equilibrium limitation, removal of H_2O from the reaction mixture was one of the most promising strategies and was performed only by a benzonitrile hydration system using K_2CO_3 as the catalyst,[10b] which, however, resulted in low yield (20%) and low selectivity (45%) because of byproducts derived from benzonitrile. On the other hand, for dimethyl carbonate (DMC) synthesis from CO_2 and methanol, various dehydrating agents have been reported, such as 2,2-dimethoxypropane,[12] trimethyl orthoacetate,[13] trimethoxymethane,[14] benzonitrile,[15] acetonitrile,[10d,11c,16] butylene oxide,[17] and DCC (dicyclohexylcarbodiimide).[18] Therefore, development of an effective catalyst system for both carboxylation of diol and removal of water is desired.

Recently, CeO_2 has attracted much attention in the field of organic synthesis because of its unique acid−base and redox properties,[19] and various reactions over CeO_2 have been reported, such as a selective dehydration of alkanediols into unsaturated alcohols[19b] or transformations of nitriles and amides.[19c] We have reported the effective carboxylation/hydration cascade catalyst of CeO_2 with nitrile in DMC synthesis from CO_2 + methanol,[20] in which CeO_2 simultaneously catalyzes both carboxylation of methanol and hydration of nitrile with the produced water.

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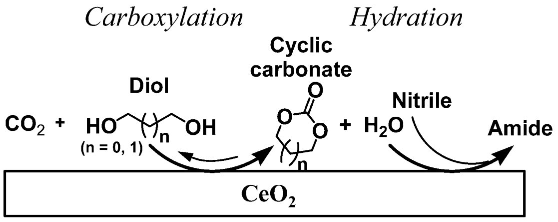
We envisioned that this catalyst system could enable us to obtain various cyclic carbonates in high yield (Scheme 1) if activation of two hydroxyl groups of diol and suppression of side reactions, such as transformation of nitriles or polymerization, are possible. In this communication, we report that the cascade catalyst of CeO_2 with 2-cyanopyridine is the most efficient catalyst system for direct synthesis of various cyclic carbonates from CO_2 and diols.

Scheme 1. Carboxylation/Hydration Cascade Catalyst of CeO_2 with Nitrile



RESULTS AND DISCUSSION

First, propylene carbonate (PC) synthesis from 1,2-propanediol (1,2-PrD) and CO_2 was examined using various metal oxides with 2-cyanopyridine (Table 1). 2-Cyanopyridine was selected because of its reactivity for hydration over CeO_2.[21] The reaction was carried out with an autoclave reactor containing 0.03 mmol of CeO_2 calcined at 873 K, 1,2-PrD (10 mmol), and 2-cyanopyridine (100 mmol) under 5 MPa CO_2. Products in gas and liquid phases were analyzed by FID−GC, GC/MS, and NMR. The results of hydration of 2-cyanopyridine are shown in Supporting Information (SI) Table S1. Yields were calculated on the basis of 1,2-PrD. Without a catalyst, no product was obtained. In contrast, CeO_2 shows the highest activity among the metal oxides tested, and the initial PC formation rate is more than 2 orders of magnitude higher than those of the other metal oxides. The produced water was stoichiometrically transformed to 2-picolinamide by hydration of 2-cyanopyridine. After the reaction, CeO_2 was removed from the reaction mixture, and the filtrate was analyzed by coupled plasma atomic emission spectroscopy (ICP−AES), which indicates that no Ce species was in the filtrate (<0.1 ppm). Moreover, $Ce(NO_3)_3 \cdot 6H_2O$, a homogeneous catalyst, showed no activity. These results suggest that CeO_2 acts as a truly heterogeneous catalyst. Therefore, CeO_2 is the most effective heterogeneous catalyst for PC synthesis from CO_2 and 1,2-PrD among the metal oxides tested. The optimization of CeO_2 was examined in this reaction by changing the calcination temperatures from 673 to 1273 K (SI Figure S1), which revealed that CeO_2 calcined at 873 K is the best catalyst from the viewpoint of product yield.

Table 1. Activity Tests of Various Metal Oxides in Formation of PC from CO_2 and 1,2-PrD

catalyst	S_{BET}[a]/ m^2 g^{-1}	yield/%	select./%	V[b]/ mmol g^{-1} h^{-1}
CeO_2[c]	89	9.4	>99	188
MgO	41	0.9	1.4	1.1
ZrO_2	116	0.5	38	0.2
ZnO	4	0	0	0
SnO_2	35	0	0	0
TiO_2	48	0	0	0
γ-Al_2O_3	97	0	0	0
α-Al_2O_3	11	0	0	0
La_2O_3	28	0	0	0
Pr_6O_{11}	30	0	0	0
Sm_2O_3	41	0	0	0
Y_2O_3	72	0	0	0
SiO_2−Al_2O_3	334	0	0	0
SiO_2	419	0	0	0
none		0	0	0
$Ce(NO_3)_3 \cdot 6H_2O$		0	0	0

[a] Specific surface area determined by BET method. [b] V: initial PC formation rate. Conditions: catalyst (metal = 2 mmol), 1,2-PrD/2-cyanopyridine =10 mmol/100 mmol, CO_2 5 MPa, 423 K, 1 h. [c] Conditions: catalyst (CeO_2 0.03 mmol), 1,2-PrD/2-cyanopyridine =10 mmol/100 mmol, CO_2 5 MPa, 423 K, 1 h.

Table 2 lists the effect of reaction conditions in the reaction of 1,2-PrD and CO_2 over CeO_2. Without the addition of 2-cyanopyridine, PC yield was as low as 0.3%, which is due to the equilibrium limitation (entry 1). In contrast, addition of 30 mmol of 2-cyanopyridine drastically improved the PC yield up to 92% (entry 2), which suggests that 2-cyanopyridine is essential for progression of the reaction. Moreover, 100 mmol of 2-cyanopyridine provided an excellent yield of >99% in 1 h under the conditions of 403 K and 5 MPa CO_2 (entry 3). This is the highest yield in PC synthesis from CO_2 and 1,2-PrD (SI Table S3). To estimate the efficiency of CeO_2-catalyzed hydration at a low concentration of water, hydration of 2-cyanopyridine was examined (the details are shown in SI Figures S2 and S3), which resulted in a higher reaction rate for hydration (1.1×10^3 mmol g^{-1} h^{-1}) than that for carboxylation of diols (91 mmol g^{-1} h^{-1}). Therefore, carboxylation and hydration can simultaneously and efficiently proceed over CeO_2, leading to a high yield of PC. In addition, this catalyst system can be applied under milder reaction conditions: PC was obtained in >99% yield at 363 K in 48 h (entry 4) and 90% under 0.8 MPa CO_2 in 24 h (entry 5). From an industrial viewpoint, this catalyst system is quite promising.

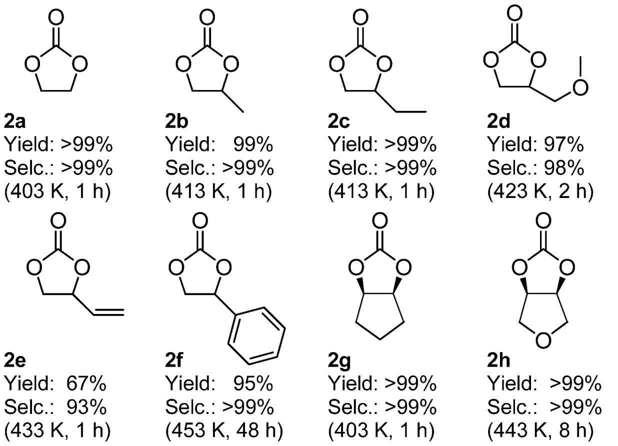
Table 2. Effect of Reaction Conditions in Formation of PC from CO_2 and 1,2-PrD[a]

entry	2-cyanopyridine/ mmol	P_{CO_2}/ MPa	T/K	t/h	yield/%	select./%
1	0	5	413	24	0.3	99
2	30	5	413	1	92	>99
3	100	5	403	1	>99	>99
4	100	5	363	48	>99	>99
5[b]	200	0.8	423	24	90	93

[a] Conditions: CeO_2 2 mmol, 1,2-PrD 10 mmol. [b] CeO_2 5 mmol.

Scheme 2 shows the results of various 5-membered ring carbonate syntheses from CO_2 and diols by the catalyst system. The hydration of 2-cyanopyridine proceeded stoichiometrically (SI Table S4). Linear vicinal diols, including ones with an allyl group and a phenyl group (**2a**−**f**), reacted to afford the corresponding 5-membered ring carbonates in high yields (67−>99%) with high selectivity (93−>99%). Cyclic diols (**2g**,**h**) were also transformed in high yields (>99%). Syntheses of **2d**,**e**,**g**,**h** are the first report, and the yields of the other carbonates are much higher than those of reported catalysts in the same reaction (The details are shown in SI Table S3), indicating that the carboxylation/hydration cascade catalyst of

Scheme 2. Synthesis of 5-Membered Ring Carbonates from CO_2 + Diols

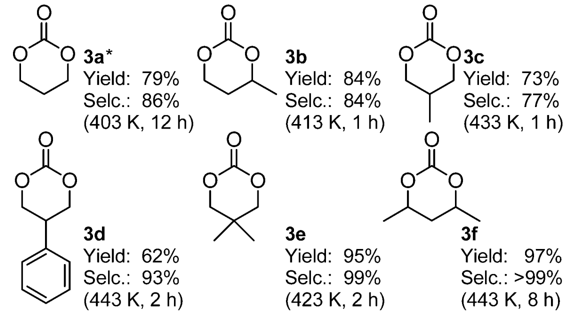


Conditions: CeO_2 2 mmol, diol/2-cyanopyridine = 10 mmol/100 mmol, CO_2 5 MPa.

CeO_2 is the most effective for direct cyclic carbonate synthesis from CO_2 and diols.

To expand the potential of this catalyst system, synthesis of 6-membered ring carbonates was carried out (Scheme 3).

Scheme 3. Synthesis of 6-Membered Ring Carbonates from CO_2 + Diols



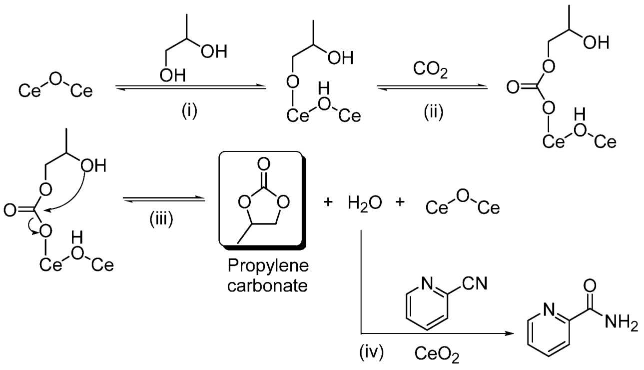
Conditions: CeO_2 2 mmol, diol/2-cyanopyridine = 10 mmol/100 mmol, CO_2 5 MPa, $^*CeO_2$ 1 mmol.

Various 1,3-diols with monoalkyl, dialkyl, and phenyl substituents were converted to the corresponding 6-membered ring carbonates in high yields (62−97%). The ester that is produced by the reaction of diol with 2-picolinamide is detected as a main byproduct. In general, syntheses of 6-membered ring carbonates, particularly ones bearing substituents, are difficult in any methodology,[22] although they are useful chemicals and intermediates[23] for biodegradable polymers of drug delivery vehicles,[23a] a repair of open inguinal hernia,[23b] and a histological membrane.[23c] Recently, Kleij et al. reported that an Al complex catalyst based on amino triphenolate ligands produces a 6-membered trimethylene carbonate from oxetane and CO_2 with high yield (95%); however, the yield of 6-membered ring carbonate with dimethyl substituents is rather low (26%), even after 66 h of reaction time.[22a] To the best of our knowledge, the syntheses of 6-membered ring carbonates of **3b,d,f** have never been reported by any methodologies, including cycloaddition of CO_2 into oxetanes, and the other results except trimethylene carbonate were also better than those of the reported literature (SI Table S5). From these results, the cascade catalyst of CeO_2 with 2-cyanopyridine is a superior system and can be applied to a wide range of 5- and 6-membered ring carbonate syntheses.

The catalytic performance and properties of used CeO_2 were studied (SI Table S6). The recovered catalyst was reused at least three times without loss of its high selectivity and yield. In addition, the BET surface area and XRD pattern of CeO_2 were almost unchanged from before to after the reaction, which indicates that CeO_2 is highly stable under the reaction conditions.

The reaction mechanism is proposed in Scheme 4. Considering the reaction mechanism of previous reports for carbonate, carbamate, and urea formations over CeO_2,[15,24] the reaction begins with (i) the adsorption of one OH group of diol to Lewis acid sites of CeO_2 to form cerium alkoxide adspecies; (ii) CO_2 insertion into the Ce−O bond and to give alkyl carbonate species; (iii) nucleophile attack of the other OH group to the carbonyl carbon in carbonate species, leading to the production of cyclic carbonate and H_2O, and CeO_2 being regenerated; and (iv) H_2O is successively removed by 2-cyanopyridine hydration over CeO_2. High yields of cyclic carbonates in the present system can be due to the high activity of CeO_2 for carboxylation of diols and for hydration of 2-cyanopyridine.

Scheme 4. Proposed Reaction Mechanism



CONCLUSIONS

The cascade catalyst of CeO_2 with 2-cyanopyridine is effective for the direct synthesis of propylene carbonate from 1,2-PrD and CO_2, even at a low CO_2 pressure of 0.8 MPa. Versatile cyclic carbonates, especially a 6-membered ring carbonate, which is difficult to synthesize, can be obtained in high yields (62−>99%) from CO_2 and diols with the catalyst system. This is the first report of achieving high yields of cyclic carbonates from CO_2 and diols, and the catalyst system could be applied to various transformation reactions of CO_2.

EXPERIMENTAL METHODS

All the reactions were carried out in an autoclave reactor with an inner volume of 190 mL. A typical procedure of the reaction of diol and CO_2 with 2-cyanopyridine was as follows: 2 mmol of the CeO_2 catalyst, 10 mmol of diol, and 100 mmol of 2-cyanopyridine were put into the autoclave together with a spinner, and then the reactor was purged and pressurized with CO_2. Then the reactor was heated to the reaction temperature. After the reaction time, the reactor was cooled to room temperature, and 30 mL of ethanol and 0.2 mL of 1-hexanol were added to the liquid phase as a solvent and an internal standard substance for a quantitative analysis, respectively. Products in liquid and gas phases were analyzed by using a gas chromatograph equipped with an FID (Shimadzu GC-2014) and GC/MS (Shimadzu QP2010 Ultra) using a CP-Sil5 (length 50 m, i.d. 0.25 mm, film thickness 0.25 μm) or TC-WAX (length 30 m, i.d. 0.25 mm, film thickness 0.25 μm) capillary column.

■ ASSOCIATED CONTENT

Supporting Information

Details of Tables 1 and 2 (Tables S1 and S2), reported yields for the synthesis of cyclic carbonates from CO_2 and corresponding alcohols (Table S3), details of Schemes 2 and 3 (Table S4), reported yields of 6-membered ring carbonate from CO_2 and corresponding oxetane (Table S5), catalyst recycle test (Table S6), effect of calcination temperature of the catalyst (Figure S1), and the reaction rates of 2-cyanopyridine hydration (Figure S2) and PC formation (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365−2387. (b) Quadrelli, E. A.; Centi, G.; Duplan, J. L.; Perathoner, S. *ChemSusChem* **2011**, *4*, 1194−1215. (c) Aresta, M., Ed.; *Carbon Dioxide as Chemical Feedstock*; Wiley-VCH: New York, 2010. (d) Song, C. *Catal. Today* **2006**, *115*, 2−32.

(2) Fukuoka, S.; Fukawa, I.; Tojo, M.; Oonishi, K.; Hachiya, H.; Aminaka, M.; Hasegawa, K.; Komiya, K. *Catal. Surv. Asia* **2010**, *14*, 146−163.

(3) Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. *Energy Environ. Sci.* **2011**, *4*, 3243−3262.

(4) Shaikh, A. A.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951−976.

(5) Davies, A. G.; Hua-De, P.; Hawari, J. A.-A. *J. Organomet. Chem.* **1983**, *256*, 251−260.

(6) (a) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975−2992. (b) Tamura, M.; Honda, M.; Nakagawa, Y.; Tomishige, K. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 19−33. (c) Dibenedetto, A.; Angelini, A. *Adv. Inorg. Chem.* **2014**, *66*, 25−81.

(7) Wuitschik, G.; Carreira, E. M.; Wagner, B.; Fischer, H.; Parrilla, I.; Schuler, F.; Rogers-Evans, M.; Müller, K. *J. Med. Chem.* **2010**, *53*, 3227−3246.

(8) Ye, Y.; Zheng, C.; Fan, R. *Org. Lett.* **2009**, *11*, 3156−3159 and references therein.

(9) (a) Nakagawa, Y.; Tomishige, K. *Catal. Surv. Asia* **2011**, *15*, 111−116. (b) Nakagawa, Y.; Tamura, M.; Tomishige, K. *ACS Catal.* **2013**, *3*, 2655−2668.

(10) (a) George, J.; Patel, Y.; Pillai, S. M.; Munshi, P. *J. Mol. Catal. A* **2009**, *304*, 1−7. (b) Da Silva, E.; Dayoub, W.; Mignani, G.; Raoul, Y.; Lemaire, M. *Catal. Commun.* **2012**, *29*, 58−62. (c) Zhao, X.; Sun, N.; Wang, S.; Li, F.; Wang, Y. *Ind. Eng. Chem. Res.* **2008**, *47*, 1365−1369. (d) Huang, S.; Liu, S.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. *J. Fuel Chem. Technol.* **2007**, *35*, 701−705. (e) Huang, S.; Ma, J.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. *Catal. Commun.* **2008**, *9*, 276−280. (f) Du, Y.; Kong, D. L.; Wang, H. Y.; Cai, F.; Tian, J. S.; Wang, J. Q.; He, L. N. *J. Mol. Catal. A* **2005**, *241*, 233−237.

(11) (a) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B.; Kunimori, K. *Catal. Lett.* **2004**, *95*, 45−49. (b) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B.; Kunimori, K. *Green Chem.* **2004**, *6*, 206−214. (c) Huang, S.; Liu, S.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. *Catal. Lett.* **2007**, *118*, 290−294.

(12) (a) Fan, B.; Li, H.; Fan, W.; Zhang, J.; Li, R. *Appl. Catal., A* **2010**, *372*, 94−102. (b) Sakakura, T.; Choi, J.-C.; Saito, Y.; Masuda, T.; Sako, T.; Oriyama, T. *J. Org. Chem.* **1999**, *64*, 4506−4508. (c) Tomishige, K.; Kunimori, K. *Appl. Catal., A* **2002**, *237*, 103−109.

(13) Sakakura, T.; Saito, Y.; Okano, M.; Choi, J.-C.; Sako, T. *J. Org. Chem.* **1998**, *63*, 7095−7096.

(14) Zhang, Z.-F.; Liu, Z.-W.; Lu, J.; Liu, Z.-T. *Ind. Eng. Chem. Res.* **2011**, *50*, 1981−1988.

(15) Honda, M.; Kuno, S.; Sonehara, S.; Fujimoto, K.; Suzuki, K.; Nakagawa, Y.; Tomishige, K. *ChemCatChem.* **2011**, *3*, 365−370.

(16) Honda, M.; Suzuki, A.; Noorjahan, B.; Fujimoto, K.; Suzuki, K.; Tomishige, K. *Chem. Commun.* **2009**, 4596−4598.

(17) Eta, V.; Mäki-Arvela, P.; Leino, A.; Kordas, K.; Salmi, T.; Murzin, D. Y.; Mikkola, J.-P. *Ind. Eng. Chem. Res.* **2010**, *49*, 9609−9617.

(18) Aresta, M.; Dibenedetto, A.; Fracchiolla, E.; Giannoccaro, P.; Pastore, C.; Pápai, I.; Schubert, G. *J. Org. Chem.* **2005**, *70*, 6177−6186.

(19) (a) Vivier, L.; Duprez, D. *ChemSusChem* **2010**, *3*, 654−678. (b) Sato, S.; Sato, F.; Gotoh, H.; Yamada, Y. *ACS Catal.* **2013**, *3*, 721−734. (c) Tamura, M.; Shimizu, K.; Satsuma, A. *Chem. Lett.* **2012**, *41*, 1397−1405.

(20) Honda, M.; Tamura, M.; Nakagawa, Y.; Sonehara, S.; Suzuki, K.; Fujimoto, K.; Tomishige, K. *ChemSusChem* **2013**, *6*, 1341−1344.

(21) Tamura, M.; Wakasugi, H.; Shimizu, K.; Satsuma, A. *Chem.—Eur. J.* **2011**, *17*, 11428−11431.

(22) (a) Whiteoak, C. J.; Kielland, N.; Laserna, V.; Escudero-Adán, E. C.; Martin, E.; Kleij, A. W. *J. Am. Chem. Soc.* **2013**, *135*, 1228−1231. (b) Darensbourg, D. J.; Horn, A., Jr.; Moncada, A. I. *Green Chem.* **2010**, *12*, 1376−1379.

(23) (a) Amsden, B. G. *Macromol. Biosci.* **2010**, *10*, 825−835. (b) Symeonidis, D.; Efthimiou, M.; Koukoulis, G.; Mamaloudis, I.; Ioannou, M.; Tzovaras, G. *Hernia* **2013**, *17*, 791−794. (c) Van Leeuwen, A. C.; Van Kooten, T. G.; Grijpma, D. W.; Bos, R. R. M. *J. Mater. Sci: Mater. Med.* **2012**, *23*, 1951−1959.

(24) (a) Tamura, M.; Honda, M.; Noro, K.; Nakagawa, Y.; Tomishige, K. *J. Catal.* **2013**, *305*, 191−203. (b) Honda, M.; Kuno, S.; Noorjahan, B.; Fujimoto, K.; Suzuki, K.; Nakagawa, Y.; Tomishige, K. *Appl. Catal., A* **2010**, *384*, 165−170. (c) Tamura, M.; Noro, K.; Honda, M.; Nakagawa, Y.; Tomishige, K. *Green Chem.* **2013**, *15*, 1567−1577. (d) Yoshida, Y.; Arai, Y.; Kado, S.; Kunimori, K.; Tomishige, K. *Catal. Today* **2006**, *115*, 95−101.