Novel route to propylene carbonate: selective synthesis from propylene glycol and carbon dioxide

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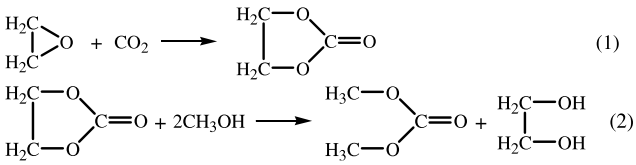
CeO_2–ZrO_2 solid solution catalysts are very effective for the selective synthesis of propylene carbonate (PC) from propylene glycol and carbon dioxide. Dipropylene glycols and poly (PC) are expected to be formed as by-products, however, they were not detected at all in the analysis by gas chromatograph and FTIR.

KEY WORDS: propylene carbonate; CeO_2–ZrO_2 solid solution; propylene glycol; carbon dioxide.

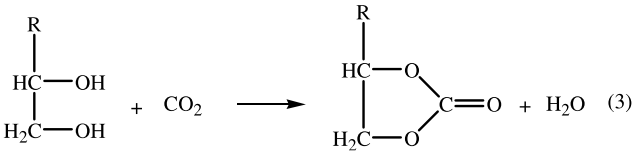
1. Introduction

Propylene carbonate (PC) has been used as both a reactive intermediate and an inert solvent [1,2]. In addition to its biodegradability and high solvency, it has high boiling and flash points, low odor levels and evaporation rate and low toxicities. Furthermore, the use of PC as a solvent in degreasing, paint stripping, and cleaning applications has increased drastically in the past few years. Carbon dioxide insertion into propylene oxide and ethylene oxide is the commercial method for the industrial production of PC and ethylene carbonate (EC) [1,3]. Recently, there have been some researches for the development of catalysts, especially heterogeneous catalysts, such as polymer-supported quaternary onium salts [4], magnesia [5,6], Mg–Al mixed oxide [7], and Cs-loaded zeolite and alumina [8,9], and lanthanide oxychloride [10].

Furthermore, the possible utilization of the cyclic alkylene carbonates such as EC and PC is the transesterification with methanol to form dimethyl carbonate (DMC) and corresponding glycols. This is one of a few industrial synthetic processes utilizing CO_2 as a raw material [11]. The conversion of carbon dioxide to useful industrial compounds has recently raised much interest in view of "Green Chemistry" [12–14]. From this view point, DMC is a promising intermediate for the utilization of CO_2. Especially, DMC is largely utilized as a raw material in chemical industry, for example, for the production of polycarbonate. DMC has also attracted much attention in terms of a non-toxic substitute for dimethyl sulfate and phosgene, which are toxic and corrosive chemicals [15]. In addition, DMC is considered to be an option for meeting the oxygenate specifications for the transportation fuel [16]. The traditional synthesis of DMC used to require phosgene as a reagent. Two processes based on the oxy-carbonylation of methanol have been already successfully developed up to larger scale: (1) the oxidative carbonylation of CH_3OH with carbon monoxide and oxygen catalyzed by cuprous chloride [17], and (2) an oxidative carbonylation process using a palladium catalyst and methyl nitrite promoter [18]. The utilization of carbon dioxide as the raw material of the DMC synthesis process has been developed. The reaction scheme is EC formation from ethylene oxide and CO_2 (equation (1)) [19,20], and the transesterification of EC with methanol (equation (2)) [21–24]:



In this system, ethylene glycol (EG) is always co-produced with DMC. If EC can be synthesized from EG and CO_2, the reaction scheme becomes more valuable since EG can be reused. From this viewpoint, the synthesis of cyclic carbonate such as EC and PC from CO_2 and corresponding glycols can be more important (equation (3)). When this reaction can be realized, DMC can be synthesized from methanol and CO_2 by using a cyclic carbonate as a recyclable intermediate. However, the selective synthesis method has not been reported.



(EG: R=H, PG: R=CH_3)

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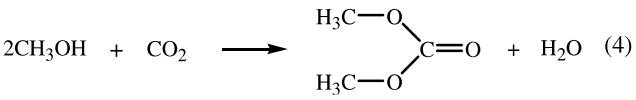
Our group has developed heterogeneous catalysts for selective DMC synthesis from CH_3OH and CO_2 (equation (4)) such as ZrO_2 [25,26], H_3PO_4/ZrO_2 [27–29], and CeO_2–ZrO_2 solid solution [30,31] catalysts.



In this letter, we report that CeO_2–ZrO_2 solid solution can be applied to the reaction between propylene glycol and CO_2 to form PC with high selectivity.

2. Experimental

CeO_2–ZrO_2, CeO_2 and ZrO_2 were prepared by calcining the hydroxides (available from Daiichi Kigenso, Japan) for 3 h under air atmosphere at various temperatures (673–1473 K). The preparation method of the hydroxides was on the basis of the patent [32]. The molar ratios Ce/(Ce + Zr) of the catalysts were 0, 0.2, 0.33, 0.5 and 1.0. The reaction was carried out in a stainless-steel autoclave reactor with an inner volume of 70 mL. The standard procedure is as follows: 7.60 g propylene glycol (PG, 100 mmol, Wako Pure Chemical Industries, 99.5% min, dehydrated), 4.92 g CH_3CN (solvent, 120 mmol, Wako Pure Chemical Industries, 99%, dehydrated) and 0.05 or 0.5 g catalyst were put into an autoclave, and then the reactor was purged with CO_2. After that, the autoclave was pressurized with CO_2 (200 mmol, Takachiho Trading Co. Ltd. 99.99%). The reactor was heated and magnetically stirred constantly during the reaction. After the reaction, 2-propanol was added to the liquid phase as a standard for the quantitative analysis. Products in liquid phase were analysed by a gas chromatograph (GC) equipped with FID. The capillary column TC-WAX was used for the separation column. In the analysis of the liquid phase, PC was observed as a product. Dipropylene glycols (DPGs), which are expected by-products in this reaction, were not detected as the products by means of GC analysis. Furthermore, all the products in the gas phase were below the detection limit of FID-GC. Products are also identified by GC-MS.

The surface area of the catalyst was measured with BET method (N_2 adsorption) using Gemini (Micromeritics). In order to evaluate the formation of PC, FTIR spectra of liquid phase after the reaction test were obtained using a liquid IR cell and Magna 550 (Nicolet) in a transmission mode. FTIR measurement was carried out after the separation of solid catalysts from the liquid phase.

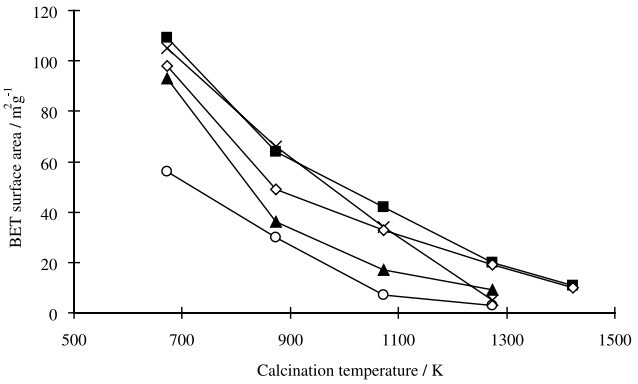


Figure 1. Effect of calcination temperature on BET surface area of various catalysts. ○: CeO_2, ▲: ZrO_2, ◇: CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.20), ■: CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33, ×: CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.5.

3. Results and discussion

Figure 1 shows the calcination temperature dependence of BET surface area of CeO_2–ZrO_2 solid solution with various Ce content (Ce/(Ce + Zr)). BET surface area decreased with increasing calcination temperature. The order of the surface area at the same calcination temperature was as follows: $CeO_2 < ZrO_2 < CeO_2$–ZrO_2. These behaviors agree with the previous reports [33,34]. This indicates that the mixture of Ce with Zr is very effective for maintaining higher surface area. Especially, CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2 and 0.33) had higher surface area than CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.50) at higher calcination temperature such as 1273 K. This pointed out that larger amount of ZrO_2 addition is necessary for the maintaining higher surface area.

Figure 2 shows the calcination temperature dependence of PC formation starting from PG and CO_2 over various catalysts at 423 K. The formation of PC and H_2O from PG and CO_2 is a reversible reaction, and PC yield can be limited by the equilibrium. Under these reaction conditions, the equilibrium yield can be estimated to be 2.0 mmol as shown later. Therefore, the PC amount shown in figure 2 did not reach the equilibrium of PC yield and it corresponded to the catalytic activity. The PC yield was very low over ZrO_2 calcined at various calcination temperatures (673—1273 K), and this indicates that ZrO_2 exhibited almost no activity in this reaction. Regarding CeO_2 catalyst, maximum PC yield was obtained over the catalyst calcined at 873 K. On the other hand, maximum PC yield was obtained on CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.5) calcined at 1073 K and CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2 and 0.33) calcined at 1273 K. From the comparison between the catalytic activity and BET surface area in the dependence of the calcination temperature, the BET surface area of catalyst with high activity can be in the range of 19–34 m^2/g. The catalyst with higher surface area can usually have

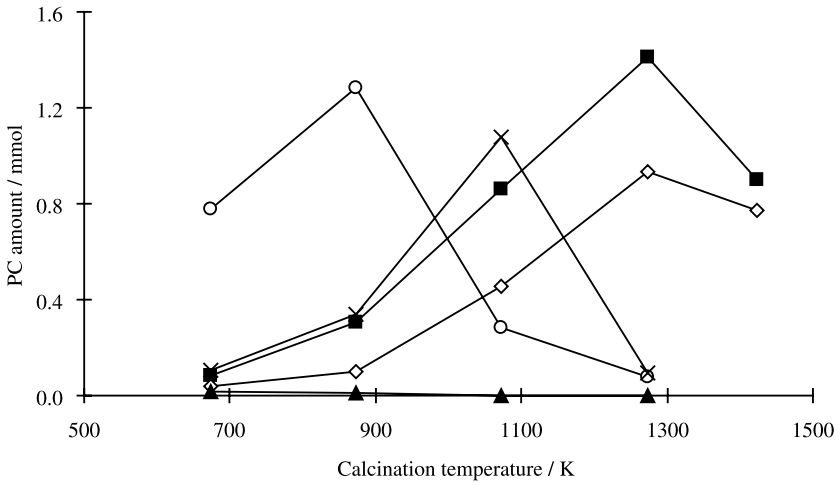
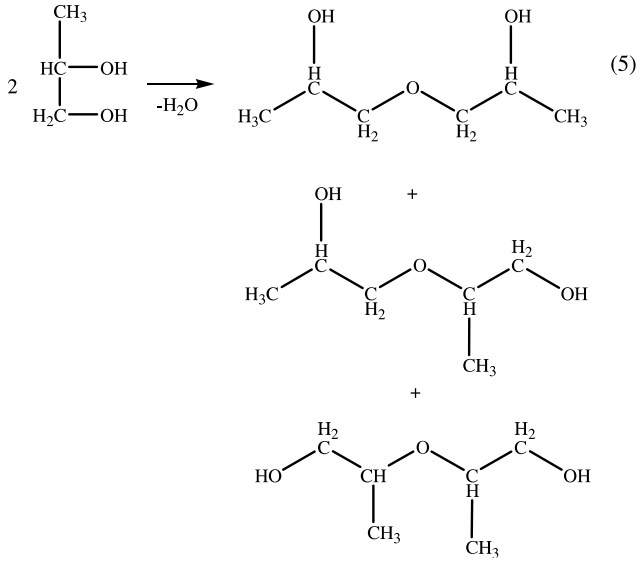


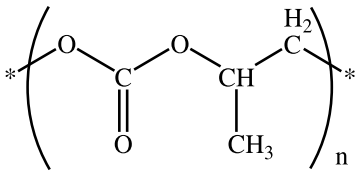
Figure 2. Calcination temperature dependence of the amount of PC formation over the catalysts. ○: CeO_2, ▲: ZrO_2, ◇: CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.20), ■: CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33, ×: CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.5 Reaction conditions: reaction temperature 423 K, PG : CO_2 : CH_3CN = 100 : 200 : 120, reaction time 2 h, catalyst weight 0.05 g.

higher activity. However, on all the catalysts, the calcination temperature range in which the catalytic activity increased with decreasing BET surface area was observed. The crystal growth is promoted by the calcination at higher temperature, therefore, the surface becomes more smooth. At present, it is thought that the catalytic activity is related to smooth surface of the catalysts. Further investigation is necessary for this interpretation and the elucidation of the active site. In addition, the catalysts with very low surface area exhibited low activity, and this is due to the decrease of the number of active site.

Table 1 shows the dependence of the amount of PC formation under various reaction conditions over CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33) calcined at 1273 K. Dipropyleneglycols (DPG) are an expectable by-products in PG + CO_2 reaction (equation (5)). DPGs have three isomers as shown below.



As a result, DPGs were not detected by GC analysis under these reaction conditions as listed in table 1. Furthermore, we measured the FTIR spectra of liquid phase after the reaction in order to recognize the formation of poly (PC). It has been reported that poly (PC) can be synthesized from propylene oxide and CO_2 using chromium salen derivatives as catalysts [35]. According to the reference, it is easy to distinguish between poly (PC) as shown in equation (6) and cyclic PC by means of FTIR measurement.



It is known that the absorbance at 1752 cm^{-1} is due to poly (PC) and that at 1802 cm^{-1} is assigned to PC. Figure 3 shows the FTIR spectra of the liquid phase after the reaction as well as the reference samples. In the case of propylene glycol, no peak was observed near 1800 cm^{-1} (figure 3a). On the other hand, the peak at 1782 cm^{-1} was observed in the reference sample (figure 3b). The sample contained PC and the peak is assigned to PC. Although the peak shift was observed, this is probably because the reference sample consisted of a large amount of PG. Furthermore, the peak at 1790 cm^{-1} was observed in the liquid phase after the reaction. This can be also assigned to PC formed from the reaction of PG and CO_2, which was supported by GC analysis. It should be noted that no peak was observed at 1750 cm^{-1} due to poly (PC) at all, and this indicates that poly (PC) is not formed at all during the reaction. From the analysis of the liquid phase after the reaction by GC and FTIR, it is concluded that the

Table 1
Results of PG + CO_2 reaction over CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33) under various reaction conditions

Reaction temperature	Catalyst weight	Reaction time	Formation amount/mmol	
/K	/g	/h	PC	DPGs
383	0.05	2	0.16	n. d.
383	0.5	2	1.1	n. d.
383	0.5	8	2.0	n. d.
403	0.05	2	0.67	n. d.
403	0.5	2	2.0	n. d.
403	0.5	8	2.0	n. d.
423	0.05	2	1.4	n. d.
423	0.5	2	2.0	n. d.
423	0.5	8	2.0	n. d.
443	0.05	2	1.6	n. d.
443	0.5	2	2.0	n. d.
443	0.5	8	1.9	n. d.
463	0.05	2	1.5	n. d.
463	0.5	2	1.9	n. d.
463	0.5	8	1.9	n. d.

Reaction conditions: PG : CO_2 : CH_3CN = 100 : 200 : 120 mmol. Catalyst : CeO_2–ZrO_2(Ce/(Ce + Zr) = 0.33), calcination temperature 1273 K.
n. d.; not detected by FID–GC.

detected product is PC and the selectivity of PC formation is very high.

Results of PG + CO_2 reaction over CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33) calcined at 1273 K are listed in table 1. The amount of PC formation over the catalyst after 8 h was almost the same as that after 2 h at reaction temperatures higher than 403 K. It is thought that the amount of PC reaches the equilibrium level. Similar phenomenon was also observed in the case of DMC synthesis from methanol and CO_2 (equation 4) [25,31]. These results indicate that the amount of PC over the 0.05 g catalyst after 2 h is controlled by the catalytic activity of PC formation. In 0.05 g CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33), the total amount of Ce and Zr ions is estimated to be about 0.36 mmol, which is smaller than PC formation (1.6 mmol at 443 K). The turnover number (TON) can be calculated to be 4.4, and in fact it must be much higher because the number of surface active site is much smaller than the total amount of Ce and Zr ions judging from the BET surface area. Here, the TON is defined as the ratio of PC amount to the total amount of Ce and Zr contained in the catalyst.

This is supported by the result that CeO_2–ZrO_2 solid solution works as heterogeneous catalysts in DMC formation from methanol and CO_2 [31]. The formation rate of PC at 443 K over CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33) calcined at 1273 K can be calculated to be 16 mmol g cat^{-1} h^{-1}. On the other hand, the formation rate of DPGs is below 0.01 mmol/ 0.5 g/ 8 h (= 0.0025 mmol g cat^{-1} h^{-1}) since the detection limit of DPGs in GC analysis is 0.01 mmol. The selectivity of PC formation on the basis of this estimation is above 99.9%. It can be said that PC can be selectively synthesized from propylene glycol and CO_2 over CeO_2–ZrO_2 solid solution catalysts.

In terms of the productivity, the yield of PC is very low and also limited by the equilibrium since the maximum PG conversion is about 2%. This problem is also pointed in the direct synthesis of DMC from methanol and CO_2 [31,36]. The challenge for higher yield has been carried out, and two successful methods have been reported: one is the removal of H_2O using the molecular sieves [36] and the other is the removal of H_2O through the reaction between H_2O and 2,2-dimethoxy propane [31]. PC formation from PG and CO_2 is also limited by the equilibrium like DMC from methanol and CO_2. It is thought that these methods are also promising in the increase of PC yield in the reaction system since higher yield of PC is available if H_2O is removed from the system in principle.

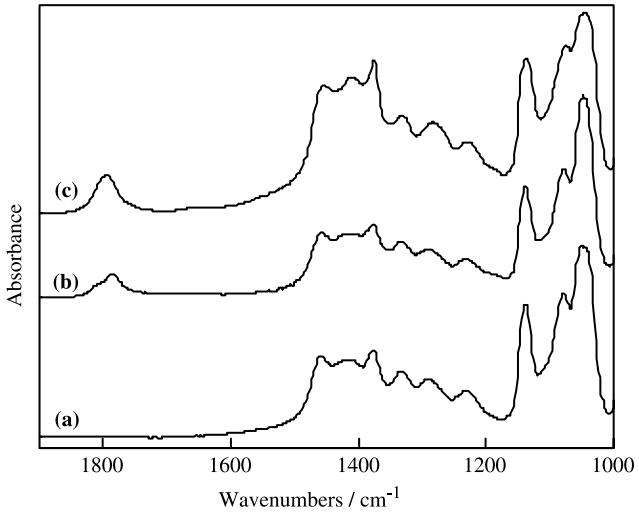


Figure 3. FTIR spectra of liquid phase. (a) PG (b) PG: PC = 100: 2 mmol. (c) After the reaction at 403 K (0.5 g CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.33) calcined at 1273 K, PG : CH_3CN : CO_2 = 100 : 120 : 200 mmol, 2-Propanol (2.6 mmol) was added the liquid phase after the reaction as a standard. The thickness of liquid phase was 0.015 mm for (a) and (b), and 0.045 mm for (c).

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