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Catalytic synthesis of dialkyl carbonate from low pressure CO_2 and alcohols combined with acetonitrile hydration catalyzed by CeO_2

Masayoshi Honda [a], Shintaro Kuno [b], Noorjahan Begum [b], Ken-ichiro Fujimoto [c], Kimihito Suzuki [c], Yoshinao Nakagawa [a], Keiichi Tomishige [a,b,*]

[a] Tohoku University, Graduate School of Engineering, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan
[b] University of Tsukuba, Graduate School of Pure and Applied Sciences, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8573, Japan
[c] Nippon Steel Corporation, Advanced Technology Research Laboratries, 20-1, Shintomi, Futtsu, Chiba 293-8511, Japan

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ABSTRACT

Dialkyl carbonates have attracted much attention from the viewpoint of sustainable chemistry because they are useful intermediates and solvents and can be synthesized from renewable resources. One promising synthesis method of the dialkyl carbonates is the reaction of CO_2 with the corresponding alcohols. Direct synthesis of diethyl carbonate and dipropyl carbonate from ethanol + CO_2 and 1-propanol + CO_2 was promoted remarkably by the combination of acetonitrile hydration. The yield based on CO_2 reached 42 and 33% for diethyl carbonate and dipropyl carbonate, respectively. All the reactions were catalyzed by CeO_2 as a heterogeneous catalyst. It is characteristic that the combination with *in situ* dehydration enabled the conversion of low pressure CO_2 to dialkyl carbonate.

1. Introduction

Utilization of CO_2 as a raw material for the production of chemicals is limited [1], while the continuous increase of CO_2 concentration in the atmosphere causes global warming. In order to solve the global warming problem, the technology for the separation and purification of CO_2 from the exhaust gases, for example at thermal power stations, has been making progress [2]. While the separation of CO_2 is now aimed at the CO_2 storage, the separation technology will help the utilization of CO_2 as a raw material in the future. Since CO_2 is the most oxidized state of carbon and the energy level of CO_2 is very low, the reductive transformation of CO_2 generally requires a large energy input [1]. Therefore, one of the strategies of CO_2 conversion is to employ a transformation which does not need the reduction of the carbon atom in CO_2. Based on this concept, the synthesis of organic carbonate from CO_2 and alcohols will be a target, since organic carbonates are useful [3]. When methanol is applied as the alcohol, dimethyl carbonate (DMC) is obtained. DMC is the simplest dialkyl carbonate and it has attracted much attention as an environmentally benign substitute for phosgene and dimethyl sulfate, which are highly toxic and corrosive carbonylating and methylating agents [4]. DMC is used as a starting material for polycarbonate resin [5] and as an electrolyte of lithium ion batteries [6,7]. A higher dialkyl carbonate is diethyl carbonate (DEC), which is an excellent solvent in the mid-boiling range, for example, for cellulose nitrate, and finds applications where a pure neutral/aqueous solvent is required [8]. DEC is also used as an intermediate for the pharmaceutical production [9]. In addition, it has been proposed that DMC and DEC can be used as fuel additives [10]. Moreover, the applications of dipropyl carbonate (DPrC) are also expected [11].

Several synthetic routes to DEC and DPrC have been developed, such as the phosgene process, oxidative carbonylation [12–14], transesterification reaction of DMC [15], and reaction of urea [9]. The synthetic routes of DEC and DPrC need ethanol and 1-propanol. It is promising that ethanol and 1-propanol will be derived from biomass in the biorefinery [16,17]. Ethanol is produced by the fermentation of starch at present and that of cellulose in the future. It will be possible to synthesize 1-propanol by the hydrogenolysis of glycerol, which is a major by-product in the biodiesel production from vegetable oils [16,18,19]. The synthesis of DMC from methanol and CO_2 has been proposed since CO_2 is regarded as an environmentally friendly chemical reagent, especially as a phosgene substitute [3,15,20–22]. Another merit of this DMC synthesis is that the only by-product is H_2O. It has been reported that the direct reaction of CO_2 with methanol and ethanol to DMC and DEC is catalyzed by CeO_2 as a heterogeneous catalyst [23–26]. The reactions proceeded selectively; however, a problem of the reaction is low conversion because of the equilibrium limitation [25,27]. The reactions for DMC and DEC synthesis have been carried out in the

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[*] Corresponding author at: Tohoku University, Graduate School of Engineering, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan.
Tel.: +81 22 795 7214.
E-mail address: tomi@tulip.sannet.ne.jp (K. Tomishige).

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presence of high pressure CO_2 [15,20–22,24–26,28,29] and supercritical CO_2 [23,30–32] in order to increase the methanol-based DMC yield. However, high pressure and supercritical CO_2 demands energy for the pressurization. On the other hand, dehydration can be the most powerful methodology to shift the reaction to the carbonate side [3,31]. In particular, *in situ* dehydration of the reaction system using the hydration reaction of organic molecules such as 2,2-dimethoxypropane [21,28,30,32] and acetonitrile [29,33,34] has been attempted. Recently, it has been reported that the direct formation of DMC from methanol and CO_2 catalyzed by CeO_2 is well promoted by *in situ* dehydration using the hydration reaction of acetonitrile to acetamide under a much lower CO_2 pressure, where the DMC yield at the equilibrium was very low without *in situ* dehydration [29,35]. This paper reports that *in situ* dehydration using the acetonitrile hydration reaction over CeO_2 enables the direct synthesis of diethyl carbonate and dipropyl carbonate by the reaction of low pressure CO_2 with ethanol and 1-propanol over CeO_2.

2. Experimental

Preparation of a CeO_2 catalyst was carried out by calcining cerium oxide HS (Daiichi Kigenso, Japan) for 3 h under air atmosphere at 873 K. The preparation conditions were optimized on the basis of the results on the DMC synthesis from methanol and CO_2 [25,29]. All the reactions were carried out in an autoclave reactor with an inner volume of 190 mL. The standard procedure for diethyl carbonate synthesis was as follows: 0.17 g of the CeO_2 catalyst, 4.6 g of C_2H_5OH (100 mmol, Wako Pure Chemical Industries, 99.8% min.), and an appropriate amount of acetonitrile (Wako Pure Chemical Industries, 99.8% min.) were put into the autoclave together with a spinner, and then the reactor was purged with CO_2. After that, it was pressurized with CO_2 (Takachiho Trading Co. Ltd., 99.99%). The experiments under lower CO_2 pressure than 0.1 MPa was carried out using the CO_2 diluted with He (CO_2:He = 20:80) and the partial pressure of CO_2 was adjusted. The reactor was then heated and the mixture was constantly stirred by a magnetic stirrer during the reaction. After the reaction time, the reactor was cooled to room temperature and tetrahydrofuran was added to the liquid phase as an internal standard substance for a quantitative analysis. The reaction tests for the synthesis of dipropyl carbonate from CO_2 and 1-propanol (Wako Pure Chemical Industries, 99.5% min.) combined with acetonitrile hydration were also carried out in the way similar to the case of ethanol. For comparison, dimethyl carbonate synthesis from methanol, CO_2 and acetonitrile were also tested by similar methods.

The activity test of the acetonitrile hydration in the presence of ethanol, 1-propanol and methanol was also carried out by the same procedures as described above, except that 0.18 g of H_2O was added. Products in liquid and gas phases were analyzed using a gas chromatograph equipped with a FID and a quadrupole mass spectrometer using a TC-WAX capillary.

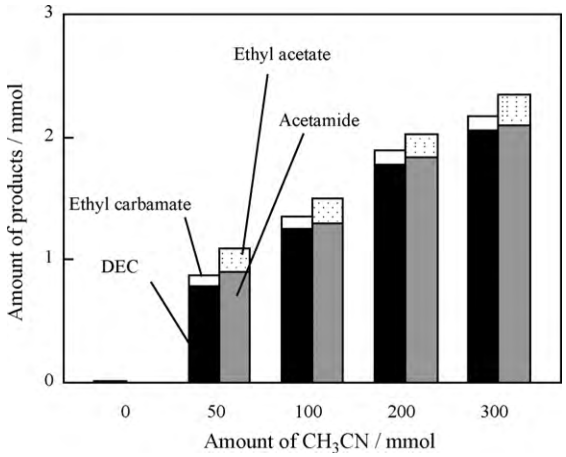
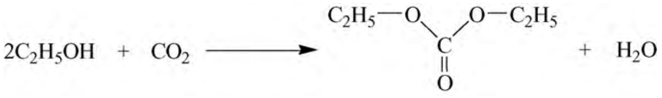


Fig. 1. Effect of the acetonitrile amount of products in the reaction of $C_2H_5OH + CO_2 + CH_3CN$. Reaction conditions: CeO_2 0.17 g, C_2H_5OH 100 mmol, CO_2 pressure 0.2 MPa, reaction temperature 423 K, reaction time 4 h.

3. Results and discussion

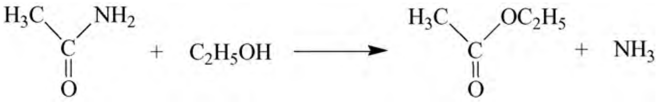
3.1. Diethyl carbonate synthesis from ethanol and CO_2

Fig. 1 shows the dependence of the acetonitrile amount on the diethyl carbonate (DEC) from ethanol and CO_2 in the presence of acetonitrile, which is denoted as $C_2H_5OH + CO_2 + CH_3CN$ at 423 K. As well as DEC, ethyl carbamate, acetamide and ethyl acetate were produced. The DEC and H_2O were formed by the reaction between ethanol and CO_2 (Eq. (1)). The hydration reaction of acetonitrile gives acetamide (Eq. (2)), and a part of acetamide reacts with ethanol to produce ethyl acetate and NH_3 (Eq. (3)).

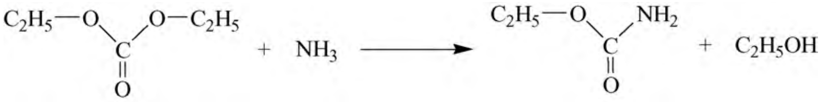


$$2C_2H_5OH + CO_2 \longrightarrow C_2H_5{-}O{-}C({=}O){-}O{-}C_2H_5 + H_2O \quad (1)$$

$$CH_3CN + H_2O \longrightarrow H_3C{-}C({=}O){-}NH_2 \quad (2)$$



$$H_3C{-}C({=}O){-}NH_2 + C_2H_5OH \longrightarrow H_3C{-}C({=}O){-}OC_2H_5 + NH_3 \quad (3)$$



$$C_2H_5{-}O{-}C({=}O){-}O{-}C_2H_5 + NH_3 \longrightarrow C_2H_5{-}O{-}C({=}O){-}NH_2 + C_2H_5OH \quad (4)$$

The surface area of CeO_2 was measured by BET method (N_2 adsorption) using a Gemini (Micromeritics) instrument. X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (Philips X'pert MRD) with Cu K_α (40 kV, 40 mA) radiation. Transmission electron microscope (TEM) images were taken using an instrument (JEM 2010; JEOL) operated at 200 kV. The catalysts before and after the reaction were used as samples for the TEM observation. Supersonic waves dispersed the sample in ethanol. The samples were placed on Cu grids under air atmosphere.

In addition, ethyl carbamate can be formed by the reaction of DEC with NH_3 given by Eq. (3) (Eq. (4)).

Based on these reaction schemes, ethyl carbamate is derived from DEC, on the other hand, acetamide and ethyl acetate are derived from acetonitrile. Therefore, when H_2O reacts with acetonitrile stoichiometrically, the sum of DEC + ethyl carbamate can agree with the sum of acetamide and ethyl acetate. In Fig. 1, it is possible to compare between the sum of DEC + ethyl carbamate and acetamide + ethyl acetate. When acetonitrile was not added, DEC