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Sustainable Catalytic Synthesis of Diethyl Carbonate

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Abstract: New sustainable approaches should be developed to overcome equilibrium limitation of dialkyl carbonate synthesis from CO₂ and alcohols. Using tetraethyl orthosilicate (TEOS) and CO₂ with Zr catalysts, we report the first example of sustainable catalytic synthesis of diethyl carbonate (DEC). The disiloxane byproduct can be reverted to TEOS. Under the same conditions, DEC can be synthesized using a wide range of alkoxysilane substrates by investigating the effects of the number of ethoxy substituent in alkoxysilane substrates, alkyl chain, and unsaturated moiety on the fundamental property of this reaction. Mechanistic insights obtained by kinetic studies, labeling experiments, and spectroscopic investigations reveal that DEC is generated via nucleophilic ethoxylation of a CO₂-inserted Zr catalyst and catalyst regeneration by TEOS. The unprecedented transformation offers a new approach toward a cleaner route for DEC synthesis using recyclable alkoxysilane.

Exponential increase in atmospheric CO₂ levels has forced the research community to seek sustainable ways to reduce and transform CO₂ into useful chemicals and/or fuels.^[1] Among the various carbon capture technologies available.^[2] the use of CO₂ as a C-1 feedstock for chemical synthesis such as dialkyl carbonates could be an important method to mitigate CO₂ emissions. Owing to increasing use of dialkyl carbonates growing in chemical synthesis (as solvents and reagents), batteries (as electrolytes), and polymer industries,^[3] the search for newer and safer synthesis methods is highly desired to substitute the harmful phosgene route (Scheme 1.A.(1)). Conversion of CO₂ into dialkyl carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC) is one of the most attractive methods from the viewpoint of green chemistry.^[4] Recently, Asahi Kasei Chemical, Japan has constructed a plant for synthesizing dialkyl carbonates via an indirect route, which is cycloaddition of epoxides followed by trans-esterification with alcohols (Scheme 1.A.(2)).^[3a] Direct route for dialkyl carbonate synthesis seems promising because of its nontoxicity and the use of abundantly available reactants, i.e. alcohols; however, the reaction is limited by chemical equilibrium (Scheme 1.A.(3)). An effective combination of the catalyst and dehydrating agent is necessary to counteract the equilibrium limitation.^[5] For example, Bu₂SnO-acetal,^[6] Bu₂Sn(OMe)₂molecular sieves (MS),^[7] CeO₂-butylene oxide,^[8] CeO₂-2cyanopyridine,^[9] Nb(OR)₅-dicylohexylcarbodiimide (DCC)^[10] have been reported to be effective in producing DMC or DEC in high yields. Regeneration of the dehydrating agent is another problem that should be addressed to realize sustainability.



Scheme 1. Examples of linear carbonate synthesis.

To address this issue, we envisioned an alternative system where water is not generated as a byproduct because it inhibits the reaction progress. We report here a solution to this challenge, a sustainable synthesis of DEC from CO_2 and ethoxysilane derivatives using $Zr(OEt)_4$. We also discuss previous studies that shed light on the mechanisms of DEC formation. Regeneration of TEOS from the disiloxane byproduct is also demonstrated (Scheme 1.B)

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Table 1. Reaction optimization									
CO ₂ + 2 Si(OEt) ₄ 3.5 mL (15.67 mmol) Catalyst (W (g)) EtO OEt + {(EtO) ₃ Si} ₂ O									
Na	Cataluat	Т	Р	t	w	Yield	TON		
NO	Catalyst	(°C)	(MPa) ^a	(h)	(g) ^b	(%)°	ION		
1	Ti(OEt) ₄	160	5	15	0.3	22	1.3		
2	Zr(OEt) ₄	160	5	15	0.3	42	3.0		
3	Hf(OEt) ₄	160	5	15	0.3	38	2.8		
4	Zr(OEt) ₄	180	5	15	0.3	48	3.5		
5	Zr(OEt) ₄	200	5	15	0.3	38	2.7		
6	Zr(OEt) ₄	180	4	15	0.3	40	2.9		
7	Zr(OEt) ₄	180	5	40	0.3	46	3.4		
8	Zr(OEt) ₄	180	5	15	0.1	41	8.7		
9	Zr(OEt) ₄	180	5	72	0.01	21	43.0		
10 ^e	Zr(OEt) ₄	180	5	15	0.3	41	3.0		
11 ^f	Zr(OEt) ₄	180	5	24	6.0	58	3.8		
Reaction condition: TEOS, 3.5 mL (15.7 mmol); a CO2 pressure at room									
temperature, ^b Catalyst weight (g), ^c DEC yield was calculated by GC using									
mesitylene as an internal standard based on TEOS conversion into DEC, $^{\rm d}$									
TON (turnover number) = mole DEC / mole catalyst, ^e 1.5 mL of ethanol was									
added; ^f TEOS, 70 mL (313 mmol).									

Catalytic synthesis of DEC using TEOS under CO2 was initially chosen as a model system. DEC was confirmed by GC and NMR (Figure S1). A series of metal ethoxide catalysts listed in Table S1, showed that group 4 metals, i.e. Ti, Zr, and Hf ethoxides are the most prominent catalysts for DEC synthesis (Table 1, entries 1-3). Among them, Zr(OEt)₄ was selected for further studies because of its superior activity (42%) (Table 1, entry 2). Heating at 180 °C improved the yield to 48% (Table 1, entry 4); however, when the temperature was increased to 200 °C, the DEC yield decreased to 38% (Table 1, entry 5). The DEC yield also reduced on decreasing the initial CO₂ pressure (Table S3; Table 1, entry 6). The reaction time was prolonged to 40 h, no yield improvement was observed, which remained at 46% (Table 1, entry 7), presumably because of the deactivation of the catalyst or equilibrium. Decreasing the catalyst loading to 0.1 g suppressed the DEC yield to 41%, but the TON number increased to 8.7 (Table 1, entry 8). The TON number reached 43 when 0.01 g of the Zr(OEt)₄ catalyst was used (Table 1, entry 9). To the best of our knowledge, this is the highest TON number for DEC synthesis ever reported in the literature (Table S6). This result suggests a small extent of catalyst deactivation. To study the possibility of the equilibrium process, the probability of the reverse reaction using disiloxane and DEC as reactants under CO₂ or Ar atmosphere was investigated (Table S7). The results showed that the disiloxane reverted to TEOS in 78% and 84% yields under CO₂ and Ar, respectively. This clearly implies that the equilibrium led to a steady increase in the DEC yield after 15 h (Table S4). The DEC or DMC can reportedly convert SiO₂ into the corresponding alkoxysilane.[11] Therefore, the subsequent reaction of DEC with disiloxane to regenerate TEOS hampered the DEC production. The addition of ethanol did not increase the DEC yield (41%) because the formed water might inhibit DEC formation (Table 1, entry 10). The addition of acetonitrile, benzonitrile, and 2-cyanopyridine enhanced the DEC yield, but not more than 50% (Table S8). Prolonging the reaction time using acetonitrile showed the same tendency with the maximum yield of 50% (Figure S7). The large-scale experiment using 200-mL



reactor (Fig. S8) indicated that 58% yield of DEC was achieved

with TON of 3.8 (Table 1, entry 11).

Scheme 2. Scope and limitations. *Reaction conditions*: substrate 15.7 mmol, $Zr(OEt)_4$ 7 mol%, CO_2 5 MPa, 180 °C, 15 h. DEC yield was calculated by GC using mesitylene as an internal standard based on substrate conversion into DEC. ^a DEC yield from **3** was determined by ¹H NMR using mesitylene as an internal standard.

Next, we focused on the scope and limitations of the Zr(OEt)₄ catalysts to gain fundamental information about DEC synthesis under the optimized reaction conditions. Herein, we classified the scope into four categories: effect of the number of ethoxy groups, length of the R1-substituent, presence of unsaturation in R1 and miscellaneous (Scheme 2). When the number of ethoxy groups on the substrate is increased the DEC yield gradually improved, with the order 4 (12%) < 3 (30%) < 2(41%) < 1 (48%). Time-on-stream results of these substrates showed the same tendency (Figure S9), indicating the importance of the ethoxy groups for DEC synthesis. Substrates bearing longer alkyl chains decreased the DEC yield (2 > 6 > 7), probably owing to steric hindrance. In contrast, hydrosilane 5 afforded a low DEC yield of 7% because it underwent disproportionation during the catalytic reaction (Scheme S1).^[12] Substrates with unsaturated moieties, i.e. vinyl 8, allyl 9, and phenyl 10 showed no considerable effect on DEC formation (Figure S11). The alkyl length of alkyl halide substrates (11 and 12) strongly influenced the DEC yield and decreased it to 7% and 38%, respectively. When 11 was used, the yield of DEC was 20% in the initial reaction (6 h); however, when the reaction time was prolonged to more than 15 h, the DEC yield decreased to 7% (Figure S12). The 1,2-Cl rearrangement might probably take place due to thermal decomposition during the reaction (Scheme S2).^[13] However, the decomposition of the chloro-propyl substrate (12) was not observed; therefore, the DEC yield gradually increased to 50% when the reaction time was extended to 40 h. Substrate-bearing nitrile (13) facilely synthesized DEC, 48% at 15 h, with no decomposition.

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To elucidate the possible reaction pathway, several control experiments were performed. No DEC was obtained in the absence of Zr(OEt)₄ catalysts (Scheme 3(A)); however, DEC was stoichiometrically produced with Zr(OEt)₄ (Scheme 3(B)), indicating the importance of Zr(OEt)₄. Under Ar, the Zr(OEt)₄ catalyst was inactive (Table S10), but the CO₂-inserted Zr(OEt)₄ catalyst was active for DEC synthesis and the yield of DEC catalyzed by Zr(OEt)₄-CO₂ (42%) was slightly higher than that catalyzed by Zr(OEt)₄ (37%) (Scheme 3(C)). It is likely that the CO₂-inserted Zr(OEt)₄ species is the first reaction intermediate, i.e., CO2 insertion into the Zr-OEt bond proceed prior to DEC formation. Therefore, DEC formation presumably occurs via an intramolecular pathway involving CO2-inserted Zr(OEt)4, similar to Sn complex catalysis.^[6a, 6c] We observed that CO₂ insertion is fast and reversible,^[14c] because CO₂ uptake takes place under ambient conditions and CO₂ is completely released under vacuum, as confirmed by attenuated total reflection (ATR) analysis (Figure S13). New bands were observed at 1600 and 1327 cm⁻¹, which were assigned to the asymmetric (vas(C=O)) and symmetric stretching $v_s(C=O)$ of the carbonyl group, respectively, indicating that CO₂ was inserted via η^2 -coordination, because the value of Δv of 273 cm⁻¹ matches those reported for bridging or chelating the OCOO moieties (Scheme S3).^[14] The ¹³C NMR results also confirmed two new peaks, at 161.6 and 166.8 ppm, which might be assigned to the hemicarbonate moieties (Figure S14). Heating the CO₂-loaded Zr(OEt)₄ catalyst at 180 °C led to the appearance of a new peak at 155.6 ppm as the C=O bond of DEC, with the disappearance of the peak at 166.8 ppm (Figure S15). The DEC

yield mediated by TEOS was significantly higher than that obtained using other reagents (Table S11), revealing that TEOS probably acts as a catalyst regenerator. This is validated by the fact that DEC could be formed with a TON of 3 using $[ZrO(OEt)_2]$ (Scheme S4). Accordingly, the $[ZrO(OEt)_2]$ species was reconverted by TEOS to the initial $Zr(OEt)_4$ catalyst species, thereby closing the catalytic cycle of DEC synthesis.



Scheme 4. Proposed mechanism for DEC synthesis from TEOS

Next, isotope-labeling experiments were performed using both ${}^{13}CO_2$ and $C{}^{18}O_2$ to determine the fate of the CO_2 atoms during the catalytic reaction. The mass number (m/z) of unlabeled DEC is 119 (Figure S16), whereas that of DEC resulting from ¹³CO₂ was 120 (Figure S17), revealing that the C atom of the DEC carbonyl moiety was derived from CO₂. In addition, the ¹³C NMR results showed that ¹³CO₂ was initially inserted into Zr(OEt)₄-¹³CO₂ prior to DEC (with the ¹³C=O moiety) formation owing to heat treatment (Figure S18). Previously, alkyl carbonate synthesis from metal alkoxides has been reported to be formed through two possible pathways: (i) nucleophilic alkoxylation or (ii) electrophilic alkylation (Scheme S5).[9a,15] To confirm which pathway is followed during the reaction, C¹⁸O₂ was employed. If electrophilic ethylation is the main route, the intensity of m/z = 123would be greater than that of 121. In contrast, the nucleophilic ethoxylation process should give the opposite result. The GC-MS data showed that the m/z of DEC generated by C18O2 was 121 (Figure S19). A similar result was obtained when TEOS was used for DEC synthesis (Figure S21). Hence, we can claim that DEC was generated via a nucleophilic attack of the ethoxy group on the hemicarbonate moieties of the [Zr(OEt)₄-CO₂] intermediate. Interestingly, the m/z of disiloxane was mainly 344 (Figure S22), which is two units higher than that of disiloxane resulting from unlabeled CO₂ (342) (Figure S20). This result indicates that TEOS incorporates an O atom from CO₂ during catalyst regeneration. Therefore, it is spectroscopically confirmed that the two O atoms of CO₂ are distributed between DEC and disiloxane.

The spectroscopic results from the control experiments demonstrated that the reaction initially underwent a reversible insertion of CO_2 into $Zr(OEt)_4$ (Step 1), followed by DEC formation via nucleophilic ethoxylation of $[Zr(OEt)_4-CO_2]$ (Step 2) (Scheme

COMMUNICATION

4). The [ZrO(OEt)₂] intermediate formed after DEC elimination was converted by TEOS to the starting Zr(OEt)₄ and also produced disiloxane (Step 3). To verify the validity of this proposed mechanism, kinetic studies of DEC synthesis from TEOS and CO₂ with the Zr catalysts were also performed. At the beginning of reaction, the rate of DEC was independent of the TEOS concentration, which confirms the pseudo-zero-order on TEOS under this experimental condition (Figure S23). In addition, the slope values for the straight line over various CO₂ (Figure S24) and Zr(OEt)₄ (Figure S25) concentration reveal that DEC synthesis follows the first-order reaction kinetics for both CO2 and Zr(OEt)₄. Overall, the DEC synthesis follows second-order reaction kinetics. These experimental kinetic results are consistent with the kinetic model derived from the proposed mechanism (Scheme S6). Activation energy of 72.6 kJ/mol was calculated from the Arrhenius plot for DEC formation (Figure S27).



Scheme 5. TEOS regeneration and catalytic sustainability of DEC formation

Finally, to clarify the potential sustainability of this reaction system, regeneration of the disiloxane byproduct was investigated. Based on previous studies on the direct synthesis of alkoxysilanes from SiO_2 ,^[16] we postulate that the disiloxane could be reverted to the corresponding alkoxysilane. Hence, TEOS was regenerated from disiloxane by ethanol using MS as a dehydrating agent in an autoclave. In the presence of KOH as a catalyst and excess ethanol, the disiloxane was converted to TEOS with 74% yield at 240 °C in 3 h (Scheme 5(A)). A combination of these cyclic protocols allows the realization of catalytic sustainability for DEC synthesis using regenerable TEOS (Scheme 5(B)).

In conclusion, we have presented the first example of a unified catalytic cycle for sustainable synthesis of DEC. Use of $Zr(OEt)_4$, one of the most prominent catalysts and the optimized reaction conditions showed that the DEC yield strongly depends on the number of ethoxy groups and organic functional groups of the substrates. Combined studies involving spectroscopic monitoring, kinetic profiling, and isotopic labeling helped delineation of the catalytic cycle. The evidence that the disiloxane byproduct was regenerable offers a new promising direction for the development of waste-free synthesis of DEC.

Experimental Section

DEC Synthesis: In a typical procedure, 3.5 mL of TEOS (15.7 mmol) and 0.3 g of $Zr(OEt)_4$ were loaded into an 10 mL autoclave. At ambient condition, the reactor was pressurized with 5 MPa CO₂ and heated to 180 °C for 24 h. After reaction, mesitylene was added to the reaction mixture for a quantitative analysis by gas chromatography (GC) or nuclear magnetic resonance (NMR). **TEOS regeneration:** The disiloxane (1.8 mmol), KOH (5mol%)

and excess amount of ethanol (8 mL, 137 mmol) were added to the 10 mL autoclave. 8 g of MS 3A was added to the joint and connected with the autoclave and condenser so that the reaction mixture can be circulated. The autoclave was subsequently heated to 240 °C for 3 h. After reaction, mesitylene was added to the liquid phase for GC analysis.

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Keywords: Sustainable catalytic synthesis • CO₂ • alkoxysilane • diethyl carbonate • Zr catalysts

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The first example of a sustainable catalytic synthesis of diethyl carbonate (DEC) from CO_2 and alkoxysilane substrate with $Zr(OEt)_4$ catalysts is herein reported. The result that the disiloxane byproduct was regenerable offers a new promising direction for the development of waste-free synthesis of DEC.



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1

Page 1 – Page 4

Sustainable Catalytic Synthesis of Diethyl Carbonate