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Breaking the equilibrium limit: synthesis of diethyl carbonate from CO₂ using regenerable bis-/tris-triethoxysilane substrates†

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Breaking the equilibrium limit is necessary to promote the production of diethyl carbonate (DEC) from CO₂ and alkoxy silanes. DEC yields are predicted to overcome the equilibrium limitation when substrates that generate oligomers as byproducts are used. In this study, we explored the catalytic synthesis of DEC using bis-/tris-triethoxysilane substrates over a Zr-based catalyst. Beyond-equilibrium DEC yields (>50% yield) are observed when typical substrates were used as the oligomer is obtained as a byproduct. For example, the isocyanate substrate solidified during DEC synthesis, yielding twice the amount of DEC generated from tetraethoxy orthosilicate. The isocyanate substrate was initially converted into an isocyanurate intermediate prior to polymerization to overcome the equilibrium limitation. The sustainability of this approach is highlighted by the feasibility of substrate regeneration from polymer byproducts. The demonstrated effectiveness of catalysis in promoting DEC from CO₂ can drive scientific and industrial advancements while maintaining sustainability.

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Sustainable spotlight

The advancement of CO₂ utilization technologies is shattering the equilibrium limits and enabling us to transcend beyond previous boundaries, achieving higher yields of valuable products. The results demonstrate that diethyl carbonate (DEC) can be synthesized from carbon dioxide (CO₂). The substrates generate oligomers as byproducts, breaking the equilibrium limitation. The DEC yield exceeded the limit (>50%) because the alkoxy silane by-product is solidified through oligomerization. The monomeric byproduct can be regenerated using ethanol in a circular reactor using a base catalyst. The conversion of CO₂ coupled with byproduct regeneration is a pivotal technology for reducing CO₂ emissions while promoting innovation in chemical manufacturing. This is consistent with global initiatives aimed at achieving SDG 11 (environmental sustainability) and SDG 13 (climate action).

Introduction

CO₂ emissions originating from anthropogenic activities, including coal combustion (43%), and oil (36%) and gas (20%) consumption, have a considerable impact on the elevation of global temperatures.¹ Despite global CO₂ emissions declining by 8.8% (approximately 1.5 Gt CO₂) in the first half of 2020 due to the COVID-19 pandemic, the atmospheric concentration remained high (410 ppm).² Efforts have been made to achieve a continual decline; CO₂ utilization has recently garnered considerable attention as it can either contribute to CO₂ mitigation or produce fine chemicals. However, the utilization of

CO₂ as a C1-building block is challenging due to its high thermodynamic stability. This is attributed to its low standard heat of formation ($\Delta H_f = -394 \text{ kJ mol}^{-1}$) and standard Gibbs energy of formation ($\Delta G_f = -395 \text{ kJ mol}^{-1}$).³ These properties make the activation and conversion of CO₂ into valuable chemicals a significant challenge. Consequently, the use of CO₂ as feedstock for organic reaction needs high energy input or reacts with a high free energy substrate to provide thermodynamically feasible process. As a C-1 chemical feedstock, CO₂ can be converted to carbonates,⁴ carbamates,⁵ urea,⁶ isocyanate,⁷ and carboxylic acid,⁸ some of which have been commercialized. For example, 180 and 250 Mt of urea and carbonates, respectively, were produced from CO₂ in 2016.⁹ The synthesis of dialkyl carbonates from CO₂ has recently attracted significant attention in the chemical industry because of its environmentally friendly nature, and its strong potential for industry.

Diethyl carbonate (DEC), a member of the dialkyl carbonate family, is an important green chemical because of its low toxicity and high biodegradability.¹⁰ It has wide applicability in the chemical, battery, and polymer industry; moreover, it has

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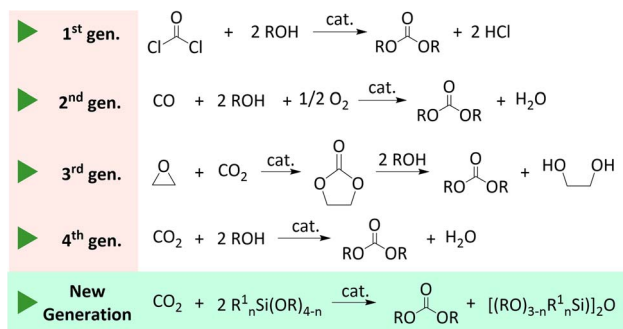


Fig. 1 Various routes for the synthesis of dialkyl carbonates.

the potential to replace methyl *tert*-butyl ether (MTBE) as a fuel additive, which could increase the octane number of gasoline.¹¹ Although several synthetic processes such as phosgenation (Bayer process),¹² alcohol carbonylation (Enichem process),^{13,14} and indirect alcohol *trans*-esterification (Asahi Kasei process) have been industrialized,^{15,16} direct synthesis from the reaction of CO₂ with alcohol seems more favorable for CO₂ mitigation and reutilization of CO₂ (Fig. 1).¹⁷ This direct method also generates water as the only byproduct. However, this reaction is limited by a chemical equilibrium; it is an unspontaneous reaction ($\Delta G_{298K} = 35.85 \text{ kJ mol}^{-1} > 0$).¹⁸ The combination of a catalyst with an appropriate dehydrating agent is required to overcome the limitations associated with equilibrium. Various homogeneous and heterogeneous catalysts, such as Ti(*i*-OPR)₄,¹⁹ Bu₂SnO,^{20,21} Nb(OR)₅,²² CeO₂,^{23–26} and Ti_xCe_{1–x}O₂ (ref. 27) have been extensively utilized for the direct synthesis of dialkyl carbonate from CO₂ and alcohols in combination with dehydrating agents including molecular sieves (MS),²⁸ acetal,^{21,29,30} orthoester,³¹ or 2-cyanopyridine.^{32,33} However, the development of an efficient process to regenerate the dehydrating agent remains challenging.

In our previous report, we identified a new method for direct DEC synthesis from the reaction of CO₂ and ethoxysilane substrate with a Zr(OEt)₄ catalyst.^{34,35} Instead of water, a disiloxane formed as a byproduct, which was regenerated into tetraethyl orthosilicate (TEOS), establishing a new waste-free synthesis method for DEC. The highest yield of DEC was approximately 50% due to the equilibrium (Fig. 2). The subsequent substrate scope investigation showed that the increasing number of ethoxy groups on the substrate gradually improved the DEC yield to the optimum 50% yield (Fig. S1†). Disiloxane was the only byproduct generated from these substrates. Based on these preliminary results, we hypothesized that the use of a substrate with a greater number of ethoxy moieties could promote polymerization. We further postulate that the equilibrium limit may be broken through the use of a substrate that

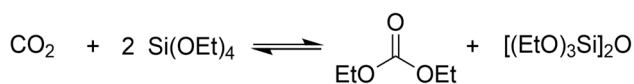


Fig. 2 Direct synthesis of DEC from TEOS and CO₂.

generates not only a dimer but also an oligomer, resulting in a higher DEC yield. Herein, we report a catalytic DEC synthesis using regenerable substrates bearing multiple ethoxy groups, for example, bis-/tris-triethoxysilane or oligomer-generable substrates, to achieve a high DEC yield and present an ideal synthetic process to realize sustainability.

Experimental section

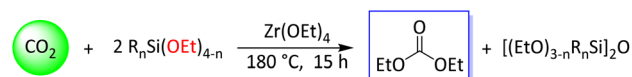
Materials & characterization

All compounds were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Wako, and Gelest Inc. and used without further purification. ¹H NMR spectra were recorded using a Bruker ADVANCE III HD (¹H NMR at 400 MHz and 600 MHz, ¹³C NMR at 100.7 MHz, and ²⁹Si NMR at 79.5 MHz). GC was performed using a Shimadzu GC-2014 instrument equipped with a flame ionization detector and a TC-1 column. Gas chromatography-mass spectrometry (GC-MS) was performed using a Shimadzu QP-2010 spectrometer with a TC-1 column. MALDI-TOF MS of the oligomers were performed using a Bruker Autoflex Speed. Samples for the MALDI-TOF MS were prepared by mixing the oligomer (20 mg mL⁻¹, 10 μL), a matrix (DCTB, 50 mg mL⁻¹, 50 μL), and a cationic agent (sodium trifluoroacetate or silver trifluoroacetate, 25 mg mL⁻¹, 20 μL) in THF. GPC analysis was performed in THF (1.0 mL min⁻¹) at 40 °C using a Shimadzu instrument equipped with a Shodex GPC KF-803 column (molecular weight range 1000–50 000, exclusion limit, 7 × 10⁴). Infrared (IR) spectra were recorded using a JASCO ATRS-100-CIR spectrophotometer. Elemental analyses were performed using a WDXRF Bruker AXS T8 Tiger spectrophotometer.

DEC synthesis

DEC synthesis was carried out in an autoclave with an inner volume of 10 mL in a manner similar to a previous method using TEOS as the substrate.³⁴ Approximately 0.3 g Zr(OEt)₄ catalyst and 15.7 mmol of substrate **1a** (3-(triethoxysilyl)propyl isocyanate) were put in the autoclave with a stirring bar. The reactor was subsequently pressurized and purged with CO₂ to 5 MPa under ambient conditions. After CO₂ insertion, the reactor was heated to 100–180 °C. The mixture was stirred continuously during the reaction. After the specified reaction time, the reactor was cooled to room temperature and 0.1 g of mesitylene was added to the liquid phase as an internal standard for quantitative analysis. Syntheses using other organosilicon substrates were conducted in a similar manner.

The conversion, yield, material balance, and turnover number (TON) are calculated by following manner, when **1a**, TEOS, or other alkoxy silanes were used as substrates.



$$\text{Conv. (\%)} = (1 - (\text{mole of remaining substrate}/(\text{initial mole of substrate})) \times 100\%$$



$$\text{Yield (\%)} = ((\text{mole of detected DEC} \times 2) / (\text{initial mole of substrate})) \times 100\%$$

$$\text{TON} = (\text{mole of DEC}) / (\text{mole of added catalyst})$$

Synthesis of intermediate **1b** from substrate **1a**

Intermediate **1b** was synthesized in an Erlenmeyer flask under a N₂ atmosphere. The isocyanate **1a** (10 mL) was stirred at 180 °C for 96 h without catalysts or other additives. Isocyanate **1b** was subsequently used for DEC synthesis after the addition of Zr(OEt)₄ catalysts. ¹H NMR (400 MHz, C₆D₆): δ 3.68–3.78 (m, 6H + 18H), 1.90–1.78 (m, 6H), 1.16–1.07 (t, *J* = 14 Hz, 27H), 0.65–0.55 ppm (m, 6H). ¹³C NMR (100 MHz, C₆D₆): δ 148.6, 58.1, 45.0, 21.5, 18.1, 7.7 ppm. ²⁹Si NMR (79.5 MHz, C₆D₆): δ –46.7 ppm. IR (ATR): 2973, 2928, 2886, 1698, 1455, 1390, 1313, 1167, 1067, 950, 761, 702, 539 cm⁻¹.

Results and discussion

The DEC formation reaction was initially explored at 140 °C under 5 MPa of initial CO₂ pressure with 3-(triethoxysilyl)propyl isocyanate as substrate **1a**. After screening for the optimum conditions (Table S1†), the highest yield of DEC (6 mmol; 75% yield) was obtained at 140 °C under 5 MPa of initial CO₂ pressure. In Fig. 3A, the time profile of DEC produced from **1a** is compared with the TEOS profile at their respective optimum conditions (**1a** at 140 °C and TEOS at 180 °C, Si/Zr = 14, 5 MPa of CO₂ pressure). Compared with TEOS, substrate **1a** was clearly superior for DEC production. At 6 h of reaction, 5 mmol of DEC was produced from **1a** (Table S1†), which is almost a two-fold increase from the amount of DEC produced from TEOS at the same reaction time (2.9 mmol). The results show that the reaction with substrate **1a** produced more than a 50% yield of DEC, even during the initial 6 h, indicating that this reaction is far beyond the chemical equilibrium. Increasing the reaction time to 96 h increased DEC formation to 7.4 mmol. We observed that polymerization proceeded during the synthesis of DEC, as indicated by the formation of a solid product after the reaction. Compared with TEOS, **1a** produced a higher amount of DEC in the temperature and pressure screening tests (Fig. 3B). Substrate **1a** followed a different trend, as decreasing the temperature from 180 °C to 140 °C resulted in a gradual increase of DEC, while further decreasing the temperature yielded less DEC product. Notably, a solid product was not obtained with the product evidently remaining in the liquid phase when the reaction proceeded at 180 °C. This indicates that polymerization hardly proceeded under harsh conditions, most likely due to a reverse reaction. A lower initial CO₂ pressure (3 MPa) resulted in a lower DEC yield but produced a higher amount of DEC than TEOS. Moreover, these results suggest that the use of substrate **1a** is more effective than previous reports for the direct synthesis of DEC from CO₂ (Table S2†).

The above results led us to the hypothesis that the reaction may proceed through an intermediate product that drives the polymerization process. At the beginning of the reaction,

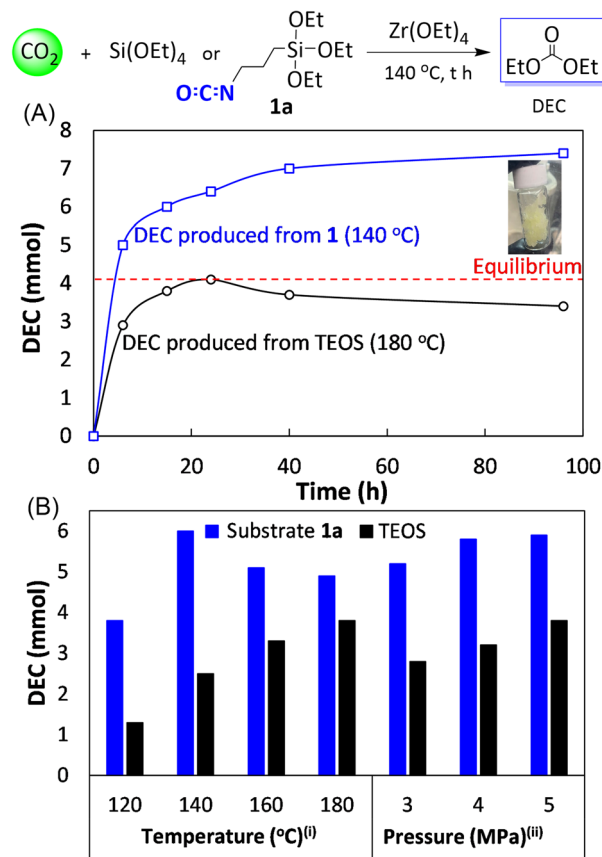


Fig. 3 (A) DEC produced from the reaction of **1a** or TEOS with CO₂. reaction conditions: **1a** or TEOS, 15.7 mmol; CO₂, 5 MPa at room temperature; Zr(OEt)₄, 0.3 g (Si/Zr = 14); 140 °C. DEC yield and **1a** conversion were determined by GC using mesitylene as an internal standard. (B) Profile of DEC produced from **1a** and TEOS in (i) temperature screening (reaction conditions: **1a** or TEOS, 15.7 mmol; CO₂, 5 MPa at room temperature; Zr(OEt)₄, 0.3 g (Si/Zr = 14)); and (ii) initial CO₂ pressure screening (reaction conditions: **1a** or TEOS, 15.7 mmol; Zr(OEt)₄, 0.3 g; 180 °C).

substrate **1a** was completely consumed with a 46% DEC yield (Table S3†). This yield gradually increased with the reaction time, indicating the formation of intermediate products during the reaction (Fig. S2†). Ganachaud *et al.* reported that metal alkoxides promote the trimerization of alkyl isocyanates to produce a cyclic isocyanurate moiety.³⁶ In this reaction, cyclic isocyanurate was likely formed as an intermediate during the DEC synthesis. Assuming that the trimeric cyclic isocyanurate is formed, the nine ethoxy moieties present in isocyanurate raise the possibility of polymerization; thus, the polymer product is most likely the result of this polymerization. To verify the existence of a reaction intermediate in the DEC synthesis, we attempted to synthesize isocyanurate from the corresponding isocyanate **1a**.

Synthesis of the isocyanurate was conducted by heating **1a** at 180 °C under N₂ atmosphere without a catalyst (Fig. 4). The reaction was complete after 96 h to produce tris[3-(trimethoxysilyl)propyl] isocyanurate (**1b**) exclusively. The chemical structure of the product was elucidated by spectroscopic analysis to



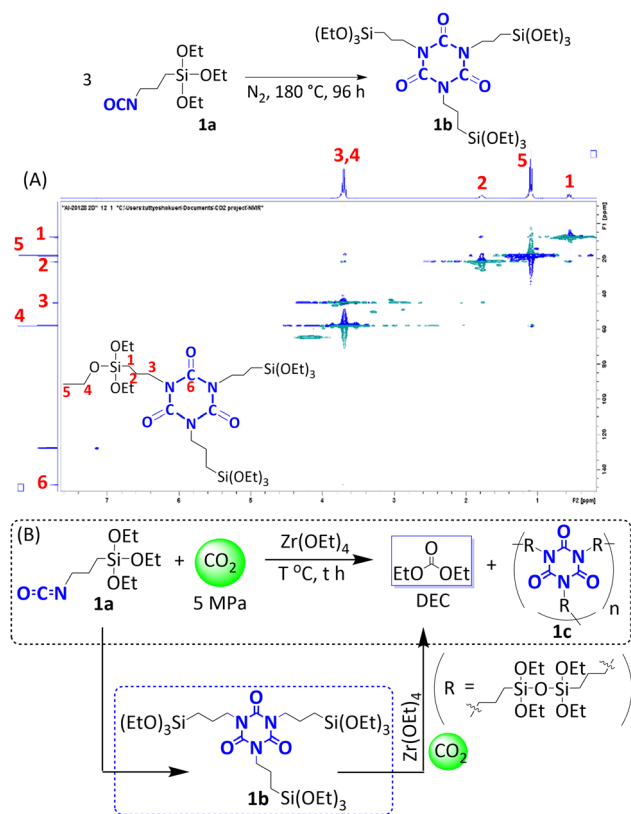


Fig. 4 (A) 2D (HSQC) NMR result of isocyanurate **1b**; (B) reaction pathway of DEC formation from CO_2 and **1a** through **1b** intermediate product. Reaction conditions: **1a**, 10 mL; N_2 , atmosphere; $180\text{ }^\circ\text{C}$; 96 h. Yield was determined by ^1H NMR spectroscopy.

confirm the formation of **1b**. The proton nuclear magnetic resonance (^1H NMR) spectrum showed a triplet at δ 3.23 ppm ($\text{N}-\text{CH}_2$ -3 of **1a**) to δ 3.8 ppm, which overlapped with ($\text{O}-\text{CH}_2$ -4) (Fig. S3 \dagger). The results of carbon nuclear magnetic resonance spectroscopy (^{13}C NMR) suggested that signal-6 at δ 122 ppm ($\text{C}=\text{O}$ of isocyanate **1a**) is shifted to δ 149 ppm (Fig. S4 \dagger). In the silicon nuclear magnetic resonance (^{29}Si NMR) spectrum, the peak showed a slight up field shift from -46.5 to -46.7 ppm (Fig. S5 \dagger). The overlapped signals at δ 3.8 ppm were further confirmed by 2D (COSY) NMR. The signals CH_2 -3 and CH_2 -4 were correlated with CH_2 -2 and CH_3 -5, respectively (Fig. S6 \dagger). The 2D (HSQC) NMR spectrum reveals the correlation of the proton (CH_2 -3) at δ 3.8 ppm with the carbon (CH_2 -3) at δ 46 ppm and the proton (CH_2 -4) at δ 3.8 ppm with the carbon (CH_2 -4) at δ 57 ppm (Fig. 4A). The NMR data confirm the successful formation of tris[3-(trimethoxysilyl)propyl] isocyanurate **1b** from substrate **1a**.

Additionally, attenuated total reflection-FTIR (ATR-FTIR) analysis showed the disappearance of the $-\text{NCO}$ band from isocyanate at 2267 cm^{-1} (Fig. S7 \dagger). In contrast, the new bands assigned as the $\text{C}=\text{O}$ bond of **1b** and DEC were observed at 1698 cm^{-1} and 1746 cm^{-1} , respectively.³⁶ Furthermore, the matrix assisted laser desorption ionization coupled with time of flight mass spectrometry (MALDI-TOF MS) showed a single peak at $m/z = 759$, which closely agrees with the theoretical molecular

weight of **1b** (763; Fig. S8 \dagger). The $\text{Zr}(\text{OEt})_4$ catalyst accelerated the formation rate of **1b**, and the reaction reached completion in 15 h. The spectroscopic ^1H , ^{13}C , and ^{29}Si NMR patterns were identical to those of a previous reaction conducted without a catalyst (Fig. S9–S11 \dagger). These results indicate that **1b** was formed during the synthesis of DEC.^{37,38}

There is a significant ongoing effort to elucidate the formation of intermediate **1b** during DEC synthesis and exploring its capability to produce DEC compared to substrate **1a** is of considerable interest. DEC formation progress from **1b** was observed under identical conditions (5 MPa of CO_2 , $180\text{ }^\circ\text{C}$, and Si/Zr ratio = 14) as in the DEC formation reaction from substrate **1a** (Fig. S12 \dagger). The results showed that the rate of DEC formation from **1b** was slightly higher than that from **1a**, indicating that conversion of **1a** to intermediate **1b** is an initial step in the reaction. No induction period was detected during the early reaction stages, suggesting that **1b** formed quickly. Additionally, **1b** not only served as an important intermediate for triggering polymerization, but the high yield of DEC produced from **1b** demonstrated that it is a promising reagent for the synthesis of DEC (Fig. 4B).

The solid product, referred to as polyisocyanurate **1c**, formed during DEC synthesis was characterized after DEC extraction with tetrahydrofuran (THF) (Fig. S13 \dagger). It was identified by ^{29}Si NMR, gel permeation chromatography (GPC), and MALDI-TOF MS. In ^{29}Si NMR spectrum, two peaks appeared at -54.7 and -46.7 ppm that corresponded to Si–O bridge and terminal Si–O, respectively (Fig. S14 \dagger).³⁹ Data from ^{29}Si NMR analysis were utilized for determining average molecular weight (\bar{M}_w) value of Si-based polymers.⁴⁰ The average value of repeating unit (\bar{n}) of **1c** after DEC synthesis can be estimated from the ratio of terminal-bridge Si–O bonds (Table S5 \dagger) and represents the degree of polymerization of **1c**, which is then correlated with the DEC yield (Fig. S14 \dagger). For example, \bar{n} of **1c** estimated from the reaction at $140\text{ }^\circ\text{C}$ was 4, yielding 5.1 mmol of DEC, whereas the reaction at $180\text{ }^\circ\text{C}$ gave \bar{n} equal to 3 and yielded 4.1 mmol DEC. However, this analysis is limited by the estimation of the

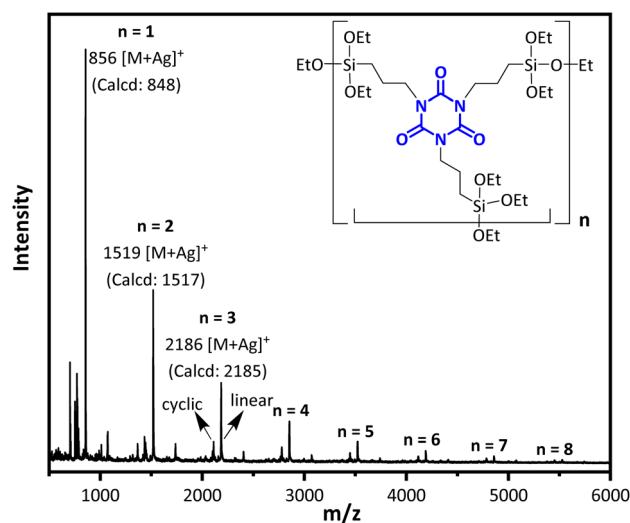


Fig. 5 MALDI-TOF MS of oligomer **1c** produced after DEC synthesis.



average number of polymers dissolved in the deuterated solvent. Future studies could focus on improving solvent systems for ^{29}Si NMR to enhance the accuracy of polymer dissolution and characterization. To overcome this limitation of ^{29}Si NMR analysis, the distribution of M_w was determined by GPC and MALDI-TOF analysis.

The M_w of **1c** was in the range 800–7200, corresponding to the presence of monomers to oligomers with $n > 5$ (Fig. S15 and Table S6†). Monomer **1b** was the dominant component (24%), indicating that **1b** was not fully converted to **1c**. However, the M_n values obtained from GPC did not precisely match the theoretical values that could support this claim. Thus, the M_w was further verified by MALDI-TOF MS measurements (Fig. 5). MALDI-TOF MS was performed using a 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) matrix with Ag as the cation.⁴¹ The M_w of **1c** obtained from MALDI-TOF MS agreed well with the calculated value, for which the structure varied from monomer to octamer ($n = 1-8$) with the mixture of linear and cyclic structures (Table S7†). These results strongly indicate that the reaction at 140 °C produced oligomer **1c** in a broad range of M_w values, resulting in a high yield of the DEC product. Therefore, the use of a substrate that can form oligomers is a key factor in improving DEC yield.

Next, the substrate scope was explored. Other substrates that can produce oligomers, such as bis- and tris-triethoxysilane, were employed in the DEC reaction, and their performances were compared (Fig. 6). Generally, substrates bearing a high

number of ethoxy groups yielded higher amounts of DEC than TEOS. For example, bis-(triethoxysilyl) substrates **2a–7a** yielded 2.2–3.3 mmol DEC, an increase compared to the reaction with TEOS as the substrate. Tris-(triethoxysilyl) substrates (**8a** and **9a**) gave 3.1 and 3.3 mmol of DEC, respectively. Similar to substrate **1a**, the oligomer was observed as a byproduct of the bis- and tris-substrates. DEC synthesized from substrate **3a** resulted in not only dimer by-products, but also monocyclic and bicyclic silsesquioxanes, along with a high DEC yield (Fig. S16†). Previously, the intramolecular condensation of bis-(trialkoxysilyl)alkanes to afford cyclic- and alkane-bridged trialkoxysilsesquioxanes (**3b–3d**) has been investigated extensively for the synthesis of sol-gel materials.^{42,43} Again, these results demonstrate that the utilization of substrates that can produce oligomers as byproducts can improve the yield of DEC. The use of intermediate **1b**, which afforded the highest DEC yield (4.5 mmol), prompted us to explore the regeneration of **1b** from byproduct **1c**.

Finally, to clarify the sustainability and potential industry applicability of this method, the regeneration of **1b** from byproduct **1c** (Fig. 7A) and potential scaling up were investigated. The scaling-up experiment was conducted under 5 MPa

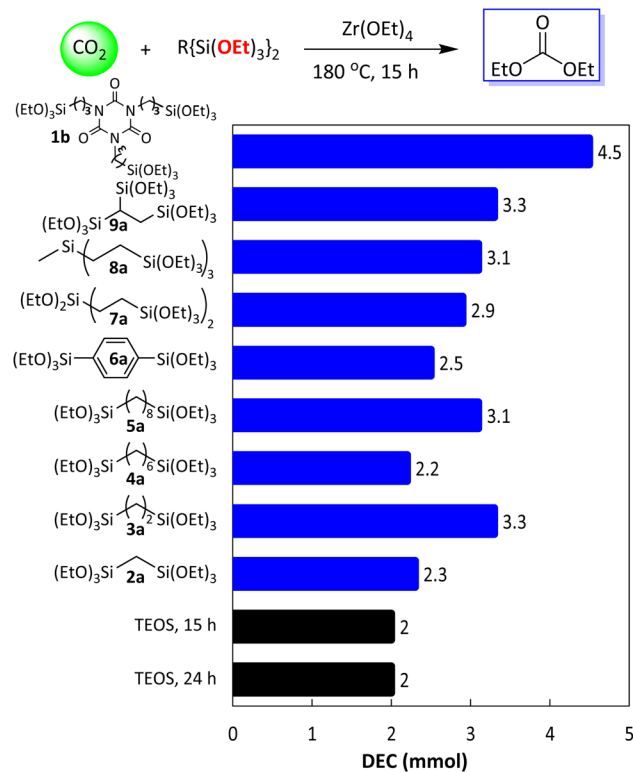


Fig. 6 Substrate scope. Reaction conditions: Si amount = 7.8 mmol, $\text{Zr}(\text{OEt})_4 = 0.3$ g ($\text{Si}/\text{Zr} = 7$); CO_2 , 5 MPa at room temperature. Yield was determined by GC or ^1H NMR analysis using mesitylene as an internal standard.

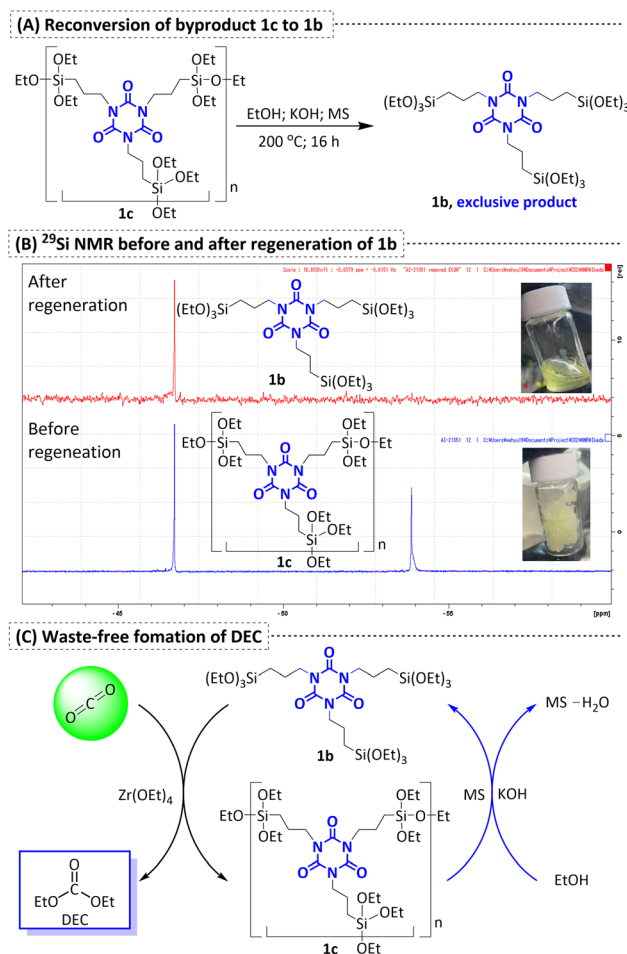


Fig. 7 (A) Reconversion of the oligomer byproduct **1c**; (B) ^{29}Si NMR results of **1b** regeneration; and (C) schematic illustration of waste-free formation of DEC.



of CO₂ at 180 °C using a 200 mL reactor (10 times larger than the normal scale). 96 mmol of DEC (61% yield) was achieved, which was slightly lower than the original scale (5 mmol or 64%) (Table S8 and Fig. S17†). The isolated yield of DEC was found to be identical to the GC yield (64%). The TON was increased to 41 by employing 0.2 g of catalyst over a 69 hours reaction. DEC was subsequently removed from the reaction system, followed by the addition of dry ethanol and potassium hydroxide (KOH) as catalyst to regenerate **1b** from byproduct **1c** (Scheme S1†). An autoclave equipped with MS 3A was installed in the circulating system (Fig. S18†). The successive DEC synthesis and regeneration process were monitored by ²⁹Si NMR measurements to observe the compound **1c** obtained after the DEC synthesis and the regeneration product **1b**, as shown in Fig. 7B. The ²⁹Si NMR spectrum for the product after regeneration exhibited the complete disappearance of the peak derived from bridged silicon at -54.7 ppm, indicating that the solid byproduct **1c** was fully recyclable to liquid **1b** after 16 h of reaction at 200 °C (Fig. 7B and S16†). Liquefaction of the solid of byproduct **1c** indicating the depolymerization of byproduct **1c** effectively proceeded over KOH catalyst. Collectively, these results demonstrate the potential industrial applicability of this method for the waste-free formation of DEC and its capability to achieve catalytic sustainability while producing high yields of DEC (Fig. 7C).

Conclusion

The catalytic synthesis of DEC from CO₂ and alkoxy silane was optimized to overcome equilibrium limitations. Bis-/tris-triethoxysilane substrates produced high amounts of oligomer byproducts that triggered high DEC formation. High DEC yields were obtained using isocyanate **1a** through the intermediate isocyanurate **1b** prior to the formation of solid polyisocyanurate **1c** ranging from a monomer to an octamer. The other bis-/tris-triethoxysilane substrates produced higher amounts of DEC than TEOS. Additionally, the monomeric substrate **1b** can be regenerated by simply reacting the oligomer byproduct **1c** with ethanol. The development of an effective heterogeneous catalyst for this reaction could be ideal for future upcoming step for industrial applicability and sustainability of the process.⁴⁴ Therefore, this method might provide the opportunity to obtain high DEC yields sustainably.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Wahyu S. Putro: conceptualization, investigation, writing, reviewing, and editing the original paper. Akira Ikeda: investigation, data validation, and formal analysis. Toshihide Yamamoto: writing, reviewing, and editing. Satoshi Hamura: writing, reviewing, and editing. Jun-Chul Choi: conceptualization, supervising, reviewing, and editing the original paper. Norihisa

Fukaya: conceptualization, supervising, reviewing, and editing the original paper.

Conflicts of interest

The authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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