

# Sustainable Synthesis of Dimethyl- and Diethyl Carbonate from CO<sub>2</sub> in Batch and Continuous Flow—Lessons from Thermodynamics and the Importance of Catalyst Stability

Matthew F. O'Neill, Meenakshisundaram Sankar,\* and Ulrich Hintermair\*



Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 5243–5257



Read Online

ACCESS |



Metrics & More



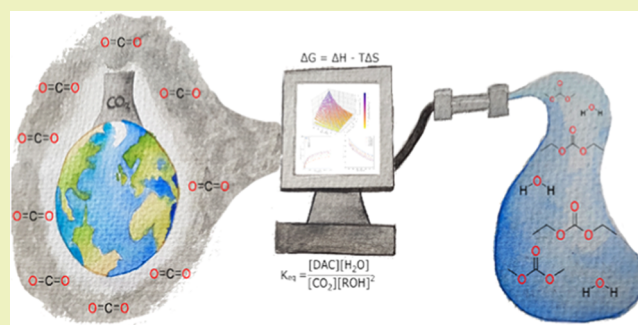
Article Recommendations



Supporting Information

**ABSTRACT:** Equilibrium conversions for the direct condensation of MeOH and EtOH with CO<sub>2</sub> to give dimethyl- and diethyl carbonate, respectively, have been calculated over a range of experimentally relevant conditions. The validity of these calculations has been verified in both batch and continuous flow experiments over a heterogeneous CeO<sub>2</sub> catalyst. Operating under optimized conditions of 140 °C and 200 bar CO<sub>2</sub>, record productivities of 235 mmol/L·h DMC and 241 mmol/L·h DEC have been achieved using neat alcohol dissolved in a continuous flow of supercritical CO<sub>2</sub>. Using our thermodynamic model, we show that to achieve maximum product yield, both dialkyl carbonates and water should be continuously removed from the reactor instead of the conventionally used strategy of removing water alone, which is much less efficient. Catalyst stability rather than activity emerges as the prime limiting factor and should thus become the focus of future catalyst development.

**KEYWORDS:** direct synthesis of dialkyl carbonates, CO<sub>2</sub> utilization, thermodynamics, continuous flow processing, supercritical fluids



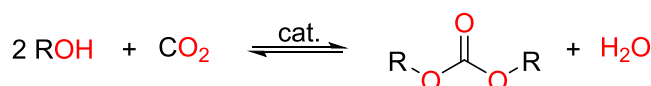
## INTRODUCTION

CO<sub>2</sub> emissions are one of the biggest global issues affecting humanity due to their role in the warming of the earth's atmosphere. A total of 37 billion tonnes were emitted globally in 2018, and the trend points upward.<sup>1</sup> CO<sub>2</sub> accounts for 65% of all greenhouse gas emissions,<sup>2</sup> with transport and industry combined being responsible for 35%.<sup>2</sup> Although unintentional, this vast production of CO<sub>2</sub> is a consequence of our linear take-use-dispose exploitation of our planet's fossil carbon reserves. More sustainable ways of fuel and chemical production and use are therefore pressing areas of research, and utilizing CO<sub>2</sub> as a chemical feedstock is an integral part of realizing a more circular economy.<sup>3</sup> Chemical valorization of CO<sub>2</sub> is a key topic in this context,<sup>4</sup> but is faced with a number of technological and fundamental (i.e., kinetic and thermodynamic) challenges.<sup>5–8</sup> The redox-neutral incorporation of CO<sub>2</sub> into organic carbonates (linear, cyclic, or polymeric) represents one of the most viable approaches to chemical CO<sub>2</sub> utilization. Monomeric dialkyl carbonates (DACs) are useful compounds for a number of applications, from electrolyte solvents in Li-ion batteries, reagents in organic transformations, fuel additives, and green solvents.<sup>9–11</sup> Dimethyl carbonate (DMC) is listed by the GSK solvent selection guide as a potential replacement for chlorinated solvents due to its low eco-toxicity, a property that diethyl carbonate (DEC) shares.<sup>12</sup> The industrial production of DACs has historically used condensation of the corresponding alcohol with phosgene as a carbonyl source,

although alternative methods such as urea alcoholysis<sup>13</sup> and oxidative carbonylation of alcohols<sup>13,14</sup> are more attractive due to the avoidance of chloride waste and handling of hazardous phosgene. The oxidative carbonylation of alkenes has also been investigated for the production of cyclic carbonates.<sup>15,16</sup> The utilization of CO<sub>2</sub> in DAC synthesis via double condensation with alcohols (Scheme 1) is an appealing alternative,<sup>17</sup> specifically for the production of DMC<sup>18–21</sup> and DEC.<sup>13,22–25</sup>

A number of homogeneous and heterogeneous catalysts have been reported for this direct synthesis. Among the heterogeneous catalysts reported, CeO<sub>2</sub> is by far the most common,<sup>18,26–37</sup> with attempts to increase its effectiveness

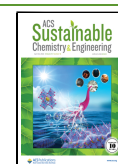
**Scheme 1. : General Reaction Scheme for the Catalytic Direct Synthesis of Linear Dialkyl Carbonates (DACs) from CO<sub>2</sub>**



**Received:** January 17, 2022

**Revised:** March 25, 2022

**Published:** April 12, 2022



through surface modification.<sup>38</sup> Mixed metal oxides such as  $\text{Fe}_x\text{Zr}_{1-x}\text{O}_y$ ,<sup>39</sup>  $\text{Ce}_x\text{Al}_{1-x}\text{O}_y$ ,<sup>28</sup> and even supported metal oxides such as  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_y/\text{C}$ <sup>40</sup> have also been investigated, and homogeneous catalysts based on tin alkoxides<sup>25,41</sup> have been tested with some success. The major difficulty with the direct DAC synthesis however is not the kinetics but the thermodynamics of the reaction. The redox-neutral double-condensation reaction is exothermic in the formation of the DAC, but overall the reaction is endergonic under typical reaction conditions (see below). Thus, for catalyst development, it has become customary to add dehydrating agents such as trimethoxy methane,<sup>25,40</sup> 2-cyanopyridine,<sup>30,37,42–45</sup> nitriles,<sup>29,46,47</sup> epoxides,<sup>48,49</sup> alkyl iodides,<sup>50,51</sup> or carbodiimides<sup>52</sup> to increase the driving force for DAC formation so that kinetic accelerations may be quantified more easily. Such conditions are less relevant to real-world application of course, as post-reaction regeneration of the dehydrating agent used would require at least the same amount of energy they add to the DAC synthesis, in addition to the difficulties of their separation, recovery, and reuse. It is also worth pointing out that all dehydrating agents used are synthetic products with significant carbon footprints from their own manufacturing, and their cost typically exceeds the value of the target DAC product by several orders of magnitude. More easily regenerable water removal approaches based on physical separation, such as membranes and molecular sieves, are thus more appealing from an applied perspective but, unfortunately, also much less effective in shifting the equilibrium position inside the reactor than chemical dehydration agents. Typically repeated reaction-removal cycles with long equilibration times are required<sup>25</sup> due to the low quantities of water removed per cycle. Thus, while many stable<sup>28</sup> and active<sup>34</sup> catalysts have been reported for this important reaction under conditions rather irrelevant for application, the key process challenge of limiting equilibrium position under realistic conditions has received little attention so far.<sup>24</sup> Here, we report thermodynamic equilibrium data for the free condensation of MeOH and EtOH with  $\text{CO}_2$  over a range of reaction conditions to provide a basis for comparing experimental results from catalytic reactions in batch and continuous flow. We demonstrate a productive continuous flow system with the ability to monitor catalyst stability, and propose a new process model based on repeated separation of both reaction products.

## EXPERIMENTAL SECTION

**General.** All reagents were purchased from major commercial suppliers in the highest purity available. Methanol was distilled from magnesium turnings under inert atmosphere, and absolute ethanol was stored over molecular sieves under inert atmosphere. Methanol water content was determined to be 25 ppm by Karl Fischer titration (Mettler Toledo DL32). Commercial nanocrystalline cerium oxide (Alfa Aesar, 99.5%, 15–30 nm, BET surface area 30–50  $\text{m}^2/\text{g}$ ) and industrial-grade  $\text{CO}_2$  (99.8%) were used as received.

**Analysis.** NMR spectra were recorded in standard 5 mm glass tubes at room temperature on a 400 MHz instrument. Quantitative analysis of samples from catalytic experiments without dehydrating agents was performed on a Shimadzu GC-2010 plus equipped with a FID detector at 300 °C with a  $\text{H}_2$  flow rate of 40 mL/min, an air flow rate of 400 mL/min, and an argon makeup flow rate of 30 mL/min. Helium was used as a carrier gas at a constant linear velocity of 39.4 cm/s through a BP20 capillary column from SGE analytical science (30 m length, 0.25 mm ID, 0.5  $\mu\text{m}$  film thickness). The sample (1  $\mu\text{L}$ ) was injected with a split ratio of 50 and an injector temperature of 250 °C. The column was held at 50 °C for 1 min, then the temperature ramped up to 70 °C at 3 °C/min, then to 180 °C at 7 °C/min, and

finally up to 240 °C at 23 °C/min. For reactions with dehydrating agents, analysis was performed on a Varian 3900 GC equipped with a FID detector at 300 °C with a  $\text{H}_2$  flow rate of 40 mL/min, an air flow rate of 400 mL/min, and an argon makeup flow rate of 30 mL/min. Helium was used as a carrier gas at a constant linear velocity of 39.4 cm/s through a CP-Sil 5CB column from Agilent (50 m length, 0.32 mm ID, 5  $\mu\text{m}$  film thickness). The sample (0.5  $\mu\text{L}$ ) was injected with a split ratio of 100 and an injector temperature of 300 °C. The column was held at 50 °C for 5 min, then the temperature ramped up to 70 °C at 3 °C/min, then to 180 °C at 7 °C/min, and finally up to 300 °C at 23 °C/min.

**Direct Batch Synthesis of DMC and DEC.** Batch experiments were conducted in custom-made stainless steel autoclaves with a total volume of 20 mL. For reactions with dehydrating agents, 1 g of dry MeOH was added to a glass liner containing 0.03 g of  $\text{CeO}_2$ , along with 0.5 mol equivalents of diisopropyl carbodiimide, 2-cyanopyridine, or trimethoxy methane and a Teflon-coated magnetic stirrer bar. The glass liner was inserted into a preheated autoclave, sealed, and pressurized with 50 bar  $\text{CO}_2$  at 40 °C. For reactions without dehydrating agents, 5 mL of dry alcohol was added to 0.3 g of nanocrystalline  $\text{CeO}_2$  in a glass liner containing a Teflon-coated magnetic stir bar. The glass liner was inserted into a preheated autoclave, which was then sealed and pressurized with 70 bar  $\text{CO}_2$  at 40 °C. The autoclaves were then placed into aluminum heating blocks set to the desired reaction temperature with stirring at 400 rpm. At the end of the reaction, the autoclaves were cooled to room temperature before being slowly depressurized. The liquid remaining in the glass liner was filtered, internal standard solutions were added, and the mixtures were analyzed by GC-FID. Yield is based on alcohol as the limiting reagent and is calculated using the following equation

$$\% \text{ yield} = \frac{2n(\text{DAC})}{n(\text{ROH})} \times 100 \quad (1)$$

where  $n(\text{DAC})$  denotes the final moles of dialkyl carbonate and  $n(\text{ROH})$  denotes the starting moles of alcohol.

**Continuous Flow Synthesis of DMC and DEC.** A 10 cm piece of 1/2 inch stainless steel tubing was packed with 0.3 g of cerium oxide between two beds of glass wool. This was attached to a preheated continuous flow rig as described elsewhere.<sup>53</sup> The reactor was wrapped in resistive heating tape (200 W, 120 cm) and temperature-controlled using a Eurotherm 2216 PID control box. The system was purged with 2 mL/min  $\text{CO}_2$  at 200 bar and 40 °C for 10 min. Then, the reactor containing the catalyst bed was heated up to the desired reaction temperature, and the reaction was started by the addition of liquid alcohol from an inert reservoir at room temperature pumped at 0.2 mL/min. A back-pressure regulator (JASCO BP-2080 Plus) was connected to an autosampler (GE Frac920). The degassed liquid (6 mL) eliminated by the back-pressure regulator (see Figure S6) was collected in 30 min intervals for 0.2 mL/min. Aliquots (1 mL) of these samples were taken, 0.12 mmol mesitylene was added to each, and the mixtures were analyzed by GC-FID. Productivity was calculated via eq 1, where  $p$  is the productivity,  $n(\text{DAC})$  is the number of moles of dialkyl carbonate formed,  $v$  is the volume of the catalyst bed, and  $t$  is the reaction time.

$$p = \frac{n(\text{DAC})}{vt} \quad (2)$$

**DMC Hydrolysis.** Hydrolysis experiments of DMC were performed using a stock solution consisting of 1 mL of DMC, 0.236 mL of  $\text{H}_2\text{O}$  (adjusted to pH 3 with 1 M  $\text{HNO}_3$ ), 1 mL of DMSO (to homogenize the mixture), and 0.05 mL of  $d_6$ -DMSO. Sealed J-Young's NMR tubes were then loaded with 1 mL of the homogeneous solution and placed into an aluminum heating block set to the desired hydrolysis temperature. The mixture was periodically analyzed by quantitative  $^1\text{H}$  NMR (zg30, D1 = 1 s, NS = 16), and the MeOH peak area at 3.18 ppm was monitored to calculate DMC conversion.

**Thermodynamic Calculations.** Values for  $\Delta H_f^\circ$  and  $S^\circ$  for DEC and DMC were obtained from the literature (see Table S3).<sup>13,23</sup>

$\Delta H_r^0$  and  $\Delta S_r^0$  were calculated using eq 3A,B, respectively

$$\begin{aligned} \text{(A)} \Delta H_r^0 &= \sum n \Delta H_{f(\text{products})}^0 - \sum n \Delta H_{f(\text{reactants})}^0 \\ \text{(B)} \Delta S_r^0 &= \sum n S_{(\text{products})}^0 - \sum n S_{(\text{reactants})}^0 \end{aligned} \quad (3)$$

where  $n$  is the stoichiometry.

Using the Gibbs equation,  $\Delta G^0$  was calculated at 298 K (eq 3)

$$\Delta G = \Delta H_r - T \Delta S_r \quad (4)$$

$\Delta G^0$  was then calculated for a temperature range of 40–160 °C relying on the Van't Hoff approximation. Using eq 4, the equilibrium constant  $K_{eq}$  was calculated for each temperature as

$$\ln(K_{eq}) = -\frac{\Delta G}{RT} \quad (5)$$

Equation 5 was used to calculate product equilibrium concentrations from  $K_{eq}$

$$K_{eq} = \frac{[\text{DAC}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{alcohol}]^2} \quad (6)$$

A numerical optimization of eq 5 was implemented in python, and the code is freely available on GitHub.<sup>54</sup>

$\text{CO}_2$  densities were obtained from Pease Software,<sup>55</sup> and concentrations were determined calculated using the following equation

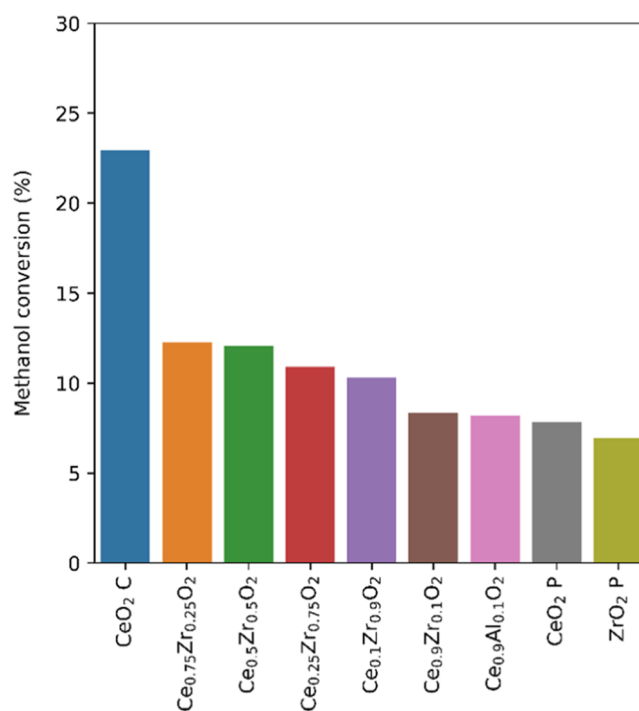
$$[\text{CO}_2] = \frac{d_{\text{CO}_2}}{M_r} \quad (7)$$

where  $d_{\text{CO}_2}$  is the  $\text{CO}_2$  density and  $M_r$  is the molecular mass of  $\text{CO}_2$ .

## RESULTS AND DISCUSSION

**Catalyst Benchmarking with Dehydrating Agents.** As reaction conditions and catalyst performance metrics reported for the formation of DMC from  $\text{CO}_2$  vary in the literature, we started with a side-by-side comparison of some prominent catalyst materials<sup>28,56</sup> to provide a basis for further investigations. This initial activity benchmarking was performed at 3 wt % catalyst loading in batch mode using diisopropyl carbodiimide (DIC) as a dehydrating agent at 120 °C. Figure 1 shows the level of MeOH conversion achieved by the various ceria and zirconia catalyst materials investigated (including a commercial  $\text{CeO}_2$  sample) after 2 h reaction time to gauge initial activity rather than final conversion.

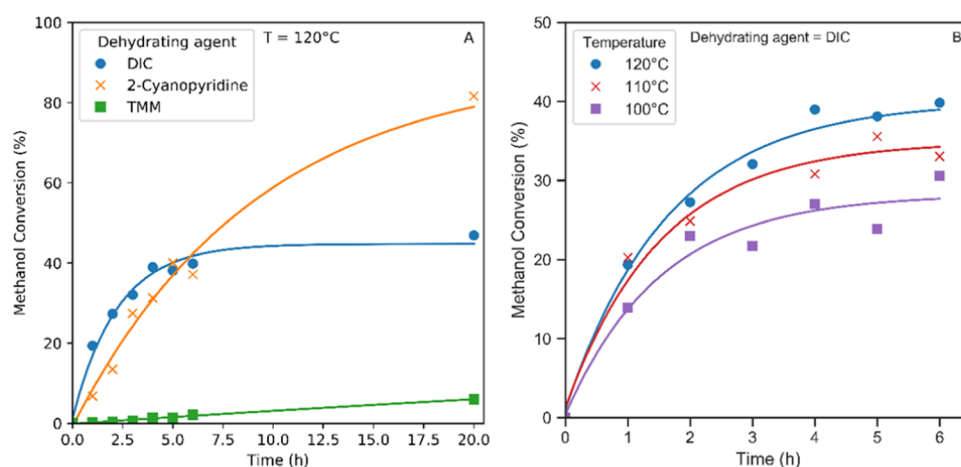
All metal oxides synthesized via standard precipitation-calcination routes (for details, see the Supporting Information) gave conversions in the range of 7–13% after 2 h, with mixed Ce/Zr materials being slightly more effective than the pure oxides. This has previously been reported in DMC formation reactions without dehydrating agents and has been correlated to the favorable acid–base properties of the mixed metal oxides.<sup>56–58</sup> A commercial  $\text{CeO}_2$  sample proved to be about twice as active as any other material tested, 23% compared to 12%, and was thus selected for all further experiments. This commercial sample had less than half of the BET surface area of the other catalysts used (Table S2), and it has been previously shown that factors such as calcination temperature, precursor, and surface acidity/basicity have more pronounced effects on activity in DAC synthesis than surface area.<sup>33</sup> We briefly investigated its effectiveness with different dehydrating agents including the most commonly used diisopropyl carbodiimide (DIC), 2-cyanopyridine, and trimethoxy methane (TMM)<sup>40,43,59</sup> in a 1:2 ratio with MeOH, giving a maximum achievable conversion of 100%. Figure 2A shows the



**Figure 1.** Comparison of metal oxide catalysts for effectiveness in catalytic DMC formation. Reaction conditions: 0.03 g of catalyst, 1 g of MeOH, 2:1 mol ratio of MeOH/DIC, pressurized to 50 bar  $\text{CO}_2$  at 40 °C prior to heating to 120 °C for 2 h (C = commercial, P = synthesized via precipitation).

profile of these reactions in batch mode sampled over time. At 120 °C, TMM achieved a conversion of only 3% after 6 h, which is greater than equilibrium with no dehydrating agent (see below) but much less than what was seen with the other reagents tested. As DMC yields of up to 33% have been reported under similar conditions with a 10 wt % loading of a mixed ceria/zirconia catalyst material supported on graphene,<sup>40</sup> we suspect that the hydrolysis kinetics of TMM are unfavorable under our reaction conditions using the commercial  $\text{CeO}_2$  catalyst. Consistent with this assumption, other work successfully utilizing orthoesters used a more acidic catalyst for the orthoester hydrolysis to alcohols.<sup>38,60</sup> 2-Cyanopyridine was more effective under our reaction conditions and gave a rather linear reaction profile, achieving >40% conversion after 6 h and continuing to produce 80% conversion after 20 h. With 15.6 mmol of 2-cyanopyridine used, the rates observed (78 mmol/g<sub>cat</sub>·h) are comparable to previous reports<sup>30</sup> but about half of the highest activities reported.<sup>29</sup> Like TMM, 2-cyanopyridine also requires an oxide catalyst to facilitate its reaction with water, which may lead to competition for active sites during the catalysis. Previous reports have also shown 2-cyanopyridine to be capable of promoting the reaction of an alcohol with  $\text{CO}_2$  in the absence of a catalyst,<sup>44</sup> as well as assisting the formation of strongly basic sites, which can enhance the performance of the metal oxide catalyst.<sup>61</sup> The activity shown is therefore likely to be a combination of the additional driving force provided by the dehydration as well as a kinetic acceleration of the reaction. DIC, which spontaneously reacts with water, gave the highest initial rates but began to plateau after 4 h and stalled at a maximum of 47% after 20 h. This behavior is ascribed to the precipitation of the corresponding urea that progressively coats the catalyst and noticeably thickens the reaction mixture (see





**Figure 2.** (A)  $\text{CeO}_2$ -catalyzed MeOH conversion to DMC at 120 °C in the presence of different dehydrating agents. (B)  $\text{CeO}_2$ -catalyzed MeOH conversion to DMC in the presence of DIC at different reaction temperatures (reaction conditions: 0.03 g of  $\text{CeO}_2$ , 1 g of MeOH, 2:1 mol ratio of MeOH/dehydrating agent, pressurized to 50 bar  $\text{CO}_2$  at 40 °C prior to heating to reaction temperature).

Figure S1). The 104 mmol/g<sub>cat</sub>·h observed for DIC with commercial ceria compares favorably to other dehydrating agents used for this reaction.<sup>62</sup>

Using the effective  $\text{CeO}_2$ -C material combined with DIC, we investigated the lower temperature limit of the catalysis in view of the unfavorable entropic term that bedevils the free condensation reaction without dehydrating agents. As shown in Figure 2B, the commercial  $\text{CeO}_2$  catalyst remained active down to 100 °C, with a decrease in both the initial rate and final conversion levels. The latter effect is ascribed to the lower solubility of the diisopropyl urea at lower temperatures, leading to a more pronounced inhibitory effect under reaction conditions. Temperatures below 100 °C gave much lower MeOH conversions (less than 10% after 3 h), showing 100 °C to be the onset temperature of catalytic activity of  $\text{CeO}_2$ .

**Thermodynamics of the Free Condensation Reaction without Dehydrating Agents.** As the use of dehydrating agents is clearly impractical for large-scale DAC production, we sought to apply the active  $\text{CeO}_2$  catalyst in the free condensation reaction under various conditions. To our surprise, we did not find precise equilibrium data for this widely studied reaction in the literature, so we set out to calculate equilibrium positions of the free condensation reaction over a range of reaction conditions (for details, see the Experimental Section). Standard heats of formation were available for all reagents and products, however with some variations depending on the source (Table S3). After testing a range of different scenarios and comparing them with experimental results (see below), we concluded the data in Table 1 to be the most accurate.

**Table 1. Thermodynamic Values for Each Component Investigated in This Work at 298 K in Standard State**

component	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)	refs
MeOH <sub>(l)</sub>	−238.4	127.2	63, 64
EtOH <sub>(l)</sub>	−277.0	159.9	63, 64
CO <sub>2(g)</sub>	−393.5	213.8	63, 64
DMC <sub>(l)</sub>	−613.8	218.7	13, 65
DEC <sub>(l)</sub>	−681.6	293.3	63, 65
H <sub>2</sub> O <sub>(l)</sub>	−285.8	70.0	63, 64

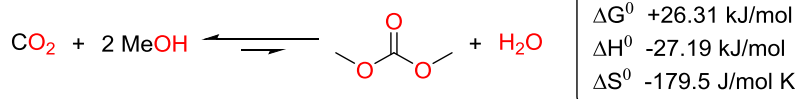
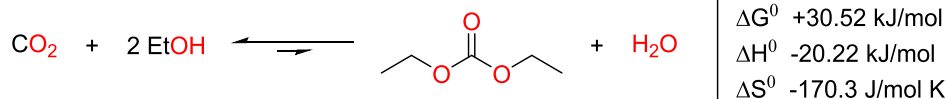
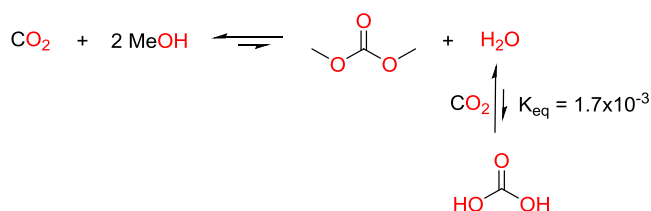
Using these values,  $\Delta H_r$  and  $\Delta S_r$  can then be calculated for the formation of DMC and DEC, respectively (Schemes 2 and 3).

From these values, it can be seen that the formation of both DACs is exothermic ( $\Delta H^\circ = -27.2$  kJ/mol for DMC and  $-20.2$  kJ/mol for DEC) along with a strongly endotropic term of  $-180$  and  $-170$  J/mol·K, respectively, making the reaction endergonic by more than 25 kJ/mol at room temperature already. Higher temperatures (as typically needed for catalysis to occur) will lead to even less favorable equilibrium positions. At a typical reaction temperature of 413 K,  $K_{eq}$  has a value of  $1.16 \times 10^{-6}$ , which increases to  $1.72 \times 10^{-6}$  at 393 K, corresponding to DMC equilibrium concentrations of 55 and 85 mM, respectively.

For the larger ethanol molecule, the entropic change of the condensation reaction is slightly lower than that for methanol due to the higher number of degrees of freedom, but the enthalpic term for DEC formation is much lower than for DMC so that the Gibbs free energy for DEC formation is 4.2 kJ/mol higher than for DMC formation.

We also considered the additional effect of the carbonic acid equilibrium that could potentially shift the DAC equilibrium position by consumption of water from the reaction mixture (Scheme 4). Due to the small equilibrium constant for the formation of carbonic acid, the latter has a negligible effect on the position of the DAC equilibrium ( $<0.01\%$ ) and is thus not considered in our following thermodynamic calculations. However, we note that the acidification of the reaction mixture, via both  $\text{CO}_2$  solvation (physisorption) and carbonic acid formation (chemisorption), may have kinetic implications for the catalysis such as exerting an accelerating effect for DAC formation or perhaps playing a role in catalyst deactivation pathways.

Using the values shown in Table 1, a multivariate equilibrium calculation was carried out to translate the thermodynamic data into product yields over a range of reaction conditions (details can be found in the Supporting Information, including a link to the code used which is freely available). Figure 3a shows the equilibrium conversions of MeOH to DMC across a range of relevant temperatures and  $\text{CO}_2$  densities in a closed system. As expected from the negative reaction entropy term, DMC yield decreased with increasing temperature. Increasing  $\text{CO}_2$  density (pressure)

Scheme 2. Reaction of CO<sub>2</sub> and Methanol to Form DMC and Water, with Thermodynamic Data at 298 KScheme 3. Reaction of CO<sub>2</sub> and Ethanol to Form DEC and Water, with Thermodynamic Data at 298 KScheme 4. Reaction of CO<sub>2</sub> and Water to Form Carbonic Acid, with Equilibrium Constant at 298 K<sup>66</sup>

increased the conversion of MeOH to DMC due to higher CO<sub>2</sub> concentrations. The model showed that DMC yields up to 4.5% are possible in liquid CO<sub>2</sub> at room temperature (56 bar), whereas only about 1% conversion can be achieved at more typical reaction temperatures of 100–140 °C where CO<sub>2</sub> densities are much lower, even when going to very high pressures of 1000 bar. For EtOH conversion to DEC a similar trend was seen (Figure 3b), but due to its lower  $\Delta G_r$ , DEC equilibrium yields were about half of those of DMC under the same conditions, giving a maximum DEC yield of 2% in liquid CO<sub>2</sub> at room temperature which declines to about 0.6% at higher reaction temperatures.

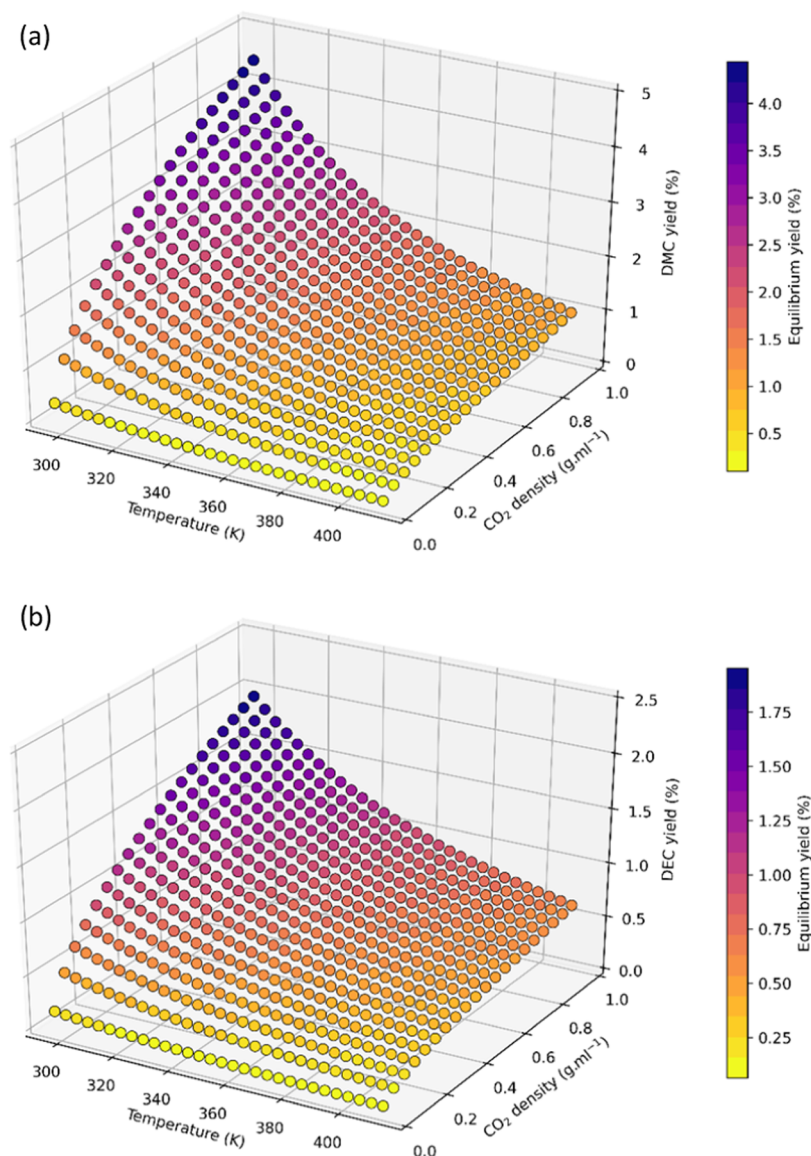
The model can also be used for determining what effect residual moisture in the starting materials has on the equilibrium conversion of the alcohol (Figure S5). This allows for the calculation of upper and lower limits of the equilibrium conversions given a range of moisture expected within the starting materials used. Most importantly though, these thermodynamic limits under the reaction conditions applied allow assessing the effectiveness of catalytic reactions without dehydrating agents in terms of absolute rates, conversion levels, and space-time yields rather than the often-used normalized metrics of activity per catalyst mass or surface area.

**Catalytic Batch Reactions without Dehydrating Agents.** With this information in hand, the direct synthesis of DMC from MeOH and CO<sub>2</sub> over a few CeO<sub>2</sub>-based catalysts was assessed, without any dehydrating agents, in a batch reactor. Following some initial catalyst testing (Table S1), the commercial CeO<sub>2</sub> catalyst was selected for further reactions. Both the forward reaction to give DMC and the reverse reaction (hydrolysis of DMC back to MeOH and CO<sub>2</sub>) were investigated to test the accuracy of our equilibrium calculations. Figure 4a shows that the commercial CeO<sub>2</sub> catalyst was active at 140 °C, with MeOH conversion progressing rapidly over the first 2 h with an initial rate of approximately 58.4 mM/h to converge to 0.4% DMC yield after about 6 h. The reverse reaction starting with 1% water and DMC mixture converged on the calculated equilibrium

with an initial rate of approximately 64.8 mM/h, plateauing at 0.55% MeOH conversion (reverse reactions at 120 and 100 °C are shown in Figure S13). The equilibrium value for MeOH conversion under these conditions predicted by the above calculations was 0.45%, showing the model to be valid and indicating that the observed plateau was indeed caused by the system reaching equilibrium. When the reaction temperature was lowered to 120 °C, the initial rate decreased to 10.8 mM/h (Figure 4b), and a conversion of 0.32% was reached after 6 h. Decreasing the reaction temperature further to 100 °C gave a much lower initial rate of 2.24 mM/h, and the CeO<sub>2</sub> catalyst only achieved 0.1% MeOH conversion after 6 h. By 30 and 20 h, respectively, reactions at 120 and 140 °C had reached their predicted equilibrium conversions. By 30 h at 100 °C, only 56% of the calculated equilibrium had been reached (MeOH conversion of 0.38%) due to the consistently lower rate at this temperature. For the reaction of EtOH with CO<sub>2</sub> to give DEC at 140 °C, the initial rate of reaction was approximately 21.7 mM/h, with the conversion profile approaching the calculated equilibrium position of 0.29% after 6 h (Figure 5).

**Hydrolytic Stability of DMC.** It has been previously observed in DMC synthesis that the product readily hydrolyzes back to CO<sub>2</sub> and methanol,<sup>67</sup> and our above experiments (Figure 4a) indeed showed the CeO<sub>2</sub> catalyst to be equally active in the forward and backward reactions. This potentially presents a challenge for *in situ* separation strategies targeted at increasing productivity by continually removing the product from the reactor. With a view to continuous flow operation with integrated downstream separations, we investigated the stability of aqueous DMC solutions in the absence of CeO<sub>2</sub>. When the 1% DMC/water/MeOH mixture used for the catalytic reverse reaction shown in Figure 4a was heated to 140 °C in the absence of a catalyst, less than 10% hydrolysis of DMC back to MeOH and CO<sub>2</sub> occurred over 20 h, indicating promising stability of DMC in the presence of moisture. A more detailed investigation following DMC hydrolysis at lower temperatures over longer timescales (Figure S14) yielded surprisingly long half-lives of DMC even under mildly acidic conditions (Table 2 and Scheme 4). A solution pH of 3 was used for these experiments as this has previously been determined to be the lower limit of aqueous solutions under 100 bar CO<sub>2</sub>.<sup>68</sup>

At a 5.2 M concentration with equimolar quantities of water, the half-life of DMC was found to be ~9 months at 80 °C and ~6 months at 100 °C assuming a zero-order hydrolysis reaction (Figure S12). Applying the same rates to more typical reaction conditions of 87 mM DMC, we calculated zero-order  $t_{1/2}$  for DMC to be 4 and 3 days at 80 and 100 °C, respectively.



**Figure 3.** Calculated equilibrium conversions for the condensation of CO<sub>2</sub> with (a) MeOH (Scheme 2) and (b) EtOH (Scheme 3) across multiple temperatures and CO<sub>2</sub> densities.

These results show the product mixture to be quite stable even at reaction temperature when no longer in contact with the catalyst, opening the door for *in situ* enrichment strategies that increase yields beyond the values calculated in the homogeneous equilibrium system shown in Figure 3.

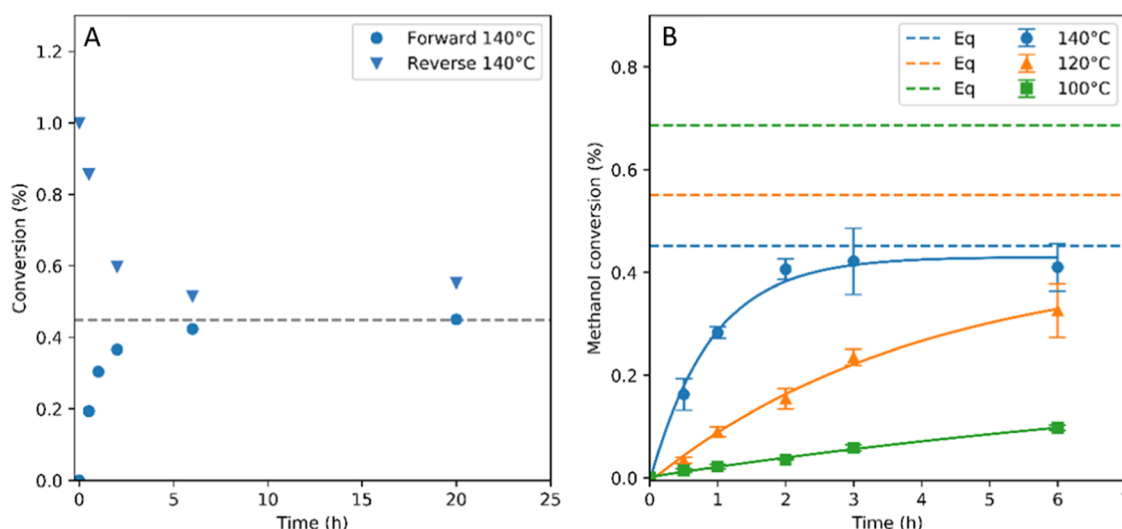
**Catalytic Continuous Flow Reactions without Dehydrating Agents.** While batch reactions enable convenient screening for activity and scoping of reaction parameters,<sup>13,30,34,56,69</sup> they typically have lower productivity than continuous flow processes due to nonproductive downtimes associated with charging/cleaning, heating/cooling, etc.<sup>24,70</sup> The tight control of reaction conditions in a steady-state continuous flow reactor is another advantage over batch testing that may be exploited to accurately screen a range of reaction conditions on the same catalyst bed.<sup>24</sup> Finally, catalyst stability tests in continuous flow are more realistic than batchwise recycling experiments that may be influenced by the repeated change in conditions. For the synthesis of DACs from short-chain alcohols and CO<sub>2</sub>, the use of compressed (near- or supercritical) CO<sub>2</sub> as the carrier in a flow system is particularly

appealing, as such media are known to combine gas-like diffusivity with solution-like solubility.<sup>71</sup> In addition, the option of tunable phase behavior by modulation of temperature and pressure offers interesting possibilities for separations of the product mixture obtained.<sup>72–74</sup> We thus investigated the performance of the CeO<sub>2</sub> catalyst for DAC formation as a fixed bed in a continuous flow reactor<sup>53</sup> using neat, dry alcohol dissolved in scCO<sub>2</sub> (for experimental details, see the Supporting Information).

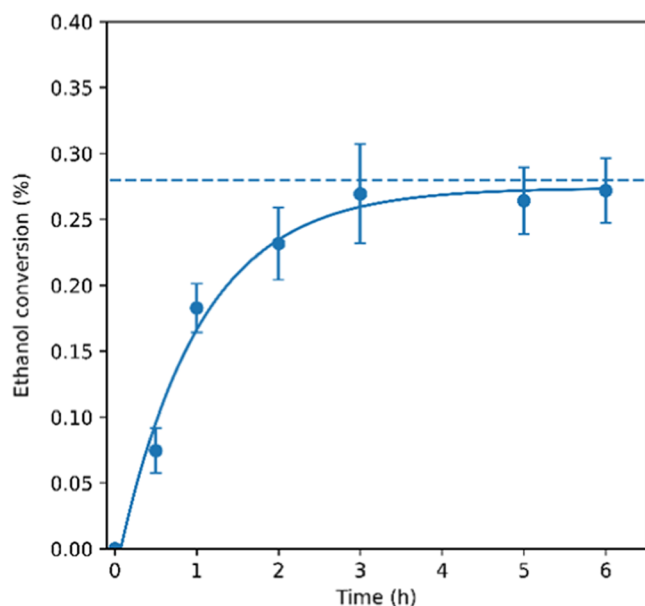
When the temperature was varied from 80 to 140 °C at 200 bar and a constant flow rate of CO<sub>2</sub> through a fixed bed of CeO<sub>2</sub> at a contact time of 4.2 min, steady-state conversions increased progressively for both MeOH and EtOH due to the activity of the catalyst increasing with temperature (Figure 6). As expected from the thermodynamics, equilibrium conversions calculated under these conditions followed the opposite trend due to the enthalpy of the reaction (Figure 3) as seen before in batch (Figure 4B).

While the activity of CeO<sub>2</sub> for DAC formation was low below 100 °C, DMC yields of >50% of the equilibrium value





**Figure 4.** (A) DMC formation from MeOH and CO<sub>2</sub> catalyzed by CeO<sub>2</sub> (forward reaction) as well as DMC hydrolysis from twice the equilibrium conversion (reverse reaction) at 140 °C. (B) DMC formation from MeOH and CO<sub>2</sub> catalyzed by CeO<sub>2</sub> at different temperatures over time. Dashed lines indicate calculated equilibrium conversions, with [MeOH] = 24.7 M and [CO<sub>2</sub>] = 4.5 M. Reaction conditions: 0.3 g of CeO<sub>2</sub>, 70 bar CO<sub>2</sub> at 40 °C (0.2 g/mL), 5 mL of dry MeOH (errors derived from triplicates).



**Figure 5.** DEC formation from EtOH and CO<sub>2</sub> catalyzed by CeO<sub>2</sub>. Dashed lines indicate calculated equilibrium conversion, with [EtOH] = 17.1 M and [CO<sub>2</sub>] = 4.5 M. Reaction conditions: 0.3 g of CeO<sub>2</sub>, 70 bar CO<sub>2</sub> at 40 °C (0.2 g/mL), 5 mL of dry EtOH, 140 °C (errors derived from triplicates).

**Table 2. Rate of DMC Hydrolysis in Aqueous Solution<sup>a</sup>**

temperature (°C)	rate (mol/L·h)	<i>t</i> <sub>1/2</sub> (days)
80	$3.94 \times 10^{-4}$	275
100	$5.85 \times 10^{-4}$	185

<sup>a</sup>Conditions: 1 mL of DMC (5.2 M), 0.236 mL of H<sub>2</sub>O (acidified to pH 3 with HNO<sub>3</sub>) in DMSO, analyzed by quantitative <sup>1</sup>H NMR in a sealed J-Young tube.

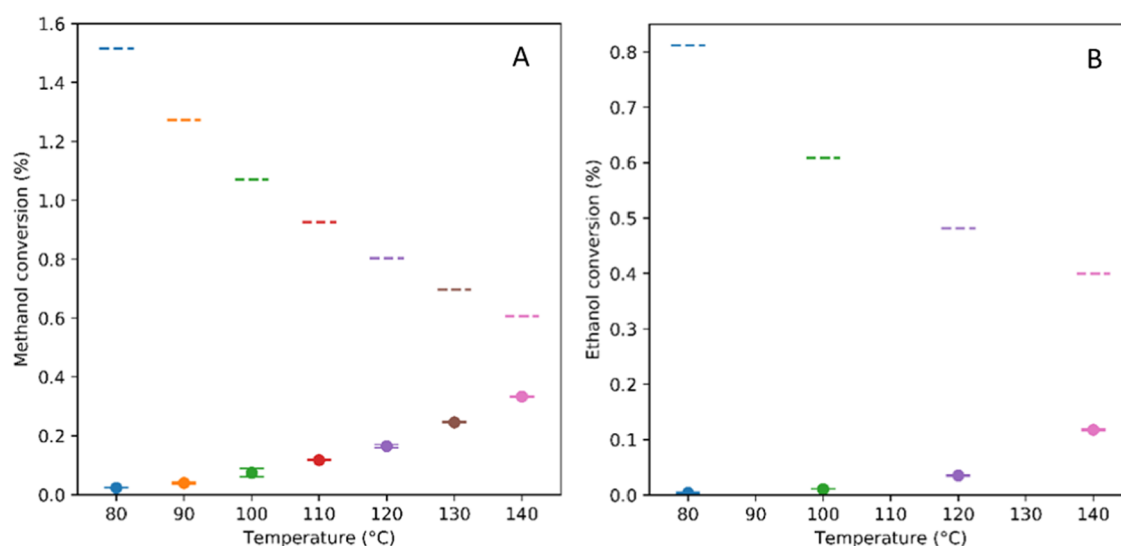
could be obtained at 140 °C with a contact time of less than 5 min. As seen in batch before, DEC formation levels were about half those of DMC across all temperatures. Comparing rates and productivities of batch versus flow experiments under

consideration of the different reaction conditions (Table 3), we can see that DMC formation is about 8 times more efficient in flow (entries 7 and 3) and DEC formation about 7 times more efficient in flow than in batch (entries 8 and 4), notably all with the same CeO<sub>2</sub> catalyst.

When the methanol feed rate was increased at constant CO<sub>2</sub> flow and pressure at 140 °C, DMC conversions decreased progressively further away from the equilibrium value of 0.6% (Figure 7). Note that the higher amount of substrate did not significantly alter the total flow rate (and thereby contact time with the catalyst) due to it remaining a single phase,<sup>75</sup> but merely increased MeOH concentration in the scCO<sub>2</sub>.

Although the percentages of substrate converted decreased with increasing MeOH content in the feed, the absolute number of moles of substrate converted increased, producing more DMC over the same period. Plotting DMC productivity of the system over MeOH flow rate indeed showed a maximum DMC output of 235 mmol/L·h at intermediate feed rates of around 0.5 mL/min MeOH (at 140 °C and 200 bar CO<sub>2</sub>). This value is among the highest DMC productivity for the direct catalytic condensation of MeOH with CO<sub>2</sub> (without water removal) reported to date.<sup>18</sup> The conditions giving maximum productivity were found at a 1.5:1 ratio of CO<sub>2</sub> to MeOH at 25% reaction progress in steady state (0.2% conversion vs. 0.8% equilibrium), which appeared to be the optimum balance of rate and conversion level that resulted in maximum productivity per unit time. Increasing the CO<sub>2</sub> flow rate at 1 mL/min MeOH feed decreased the catalyst contact time without increasing the number of moles converted, leading to both lower conversions and lower DMC productivities (Figure S7).

Performing the same feed ratio variation in continuous flow with EtOH gave similar results (Figure 8). At 140 °C and 200 bar, we found peak productivity of the catalytic process at ~50% steady-state reaction progress (0.4% conversion vs. 0.8% equilibrium) around a 2:1 CO<sub>2</sub> to EtOH ratio as the optimum compromise between rate and conversion. Again, the DEC space-time yield of 240 mmol/L·h achieved under these conditions is one of the highest values reported to date.<sup>24,76</sup>



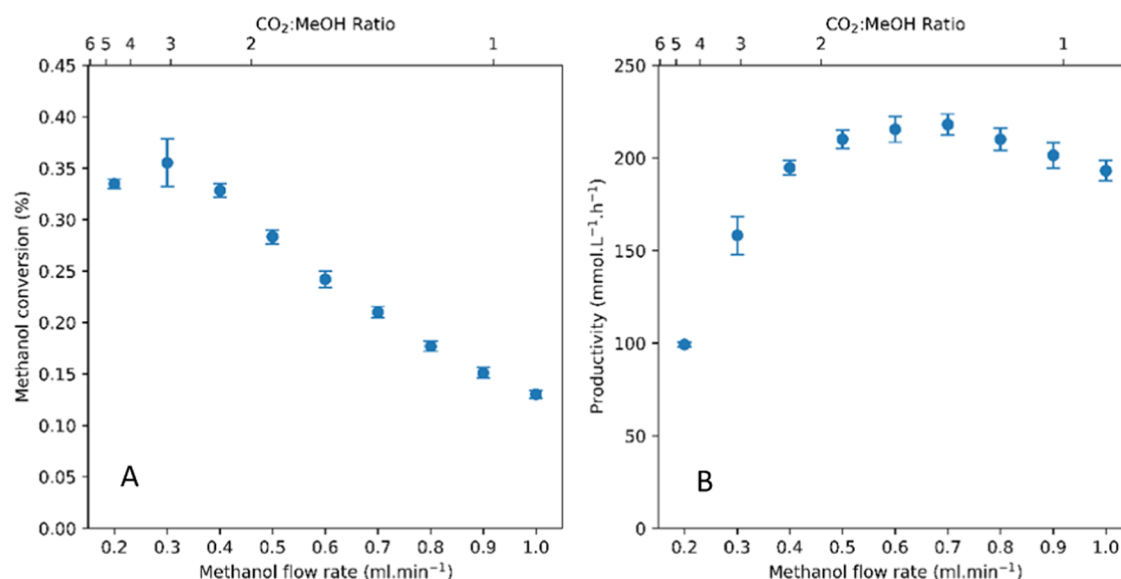
**Figure 6.** Steady-state alcohol conversions (A = MeOH, B = EtOH) to DAC in continuous flow mode with CO<sub>2</sub> over a fixed bed of CeO<sub>2</sub> at different temperatures (dots) including calculated equilibrium values (dashed lines). Reaction conditions: 1 mL/min CO<sub>2</sub>, 200 bar, 0.2 mL/min alcohol, 0.3 g of catalyst, 5 mL of bed volume, contact time 4.2 min.

**Table 3.** Comparison of Productivity Metrics between Batch and Flow Experiments

entry	reaction	temperature (°C)	substrate/cat ratio (mol/mol)	observed rate (mM/h)	normalized rate (mM/h·g <sub>cat</sub> )	TOF (h <sup>-1</sup> ) <sup>c</sup>	productivity (mmol/(L·h))
1	DMC batch	100	71	2 <sup>a</sup>	7	0.020	0.89
2	DMC batch	120	71	11 <sup>a</sup>	36	0.063	2.76
3	DMC batch	140	71	58 <sup>a</sup>	195	0.231	10.1
4	DEC batch	140	49	27 <sup>a</sup>	72	0.436	3.78
5	DMC flow	100	12	87 <sup>b</sup>	290	0.059	18.6
6	DMC flow	120	12	205 <sup>b</sup>	683	0.125	39.3
7	DMC flow	140	12	417 <sup>b</sup>	1390	0.279	87.6
8	DEC flow	140	8	193 <sup>b</sup>	644	0.100	20.5

<sup>a</sup>Observed rate calculated from tangent at  $t = 0$  of the fitted curve. <sup>b</sup>Observed rate calculated as concentration change in 4.2 min residence time.

<sup>c</sup>TOF calculated from total moles of product formed/total moles of catalyst per time.

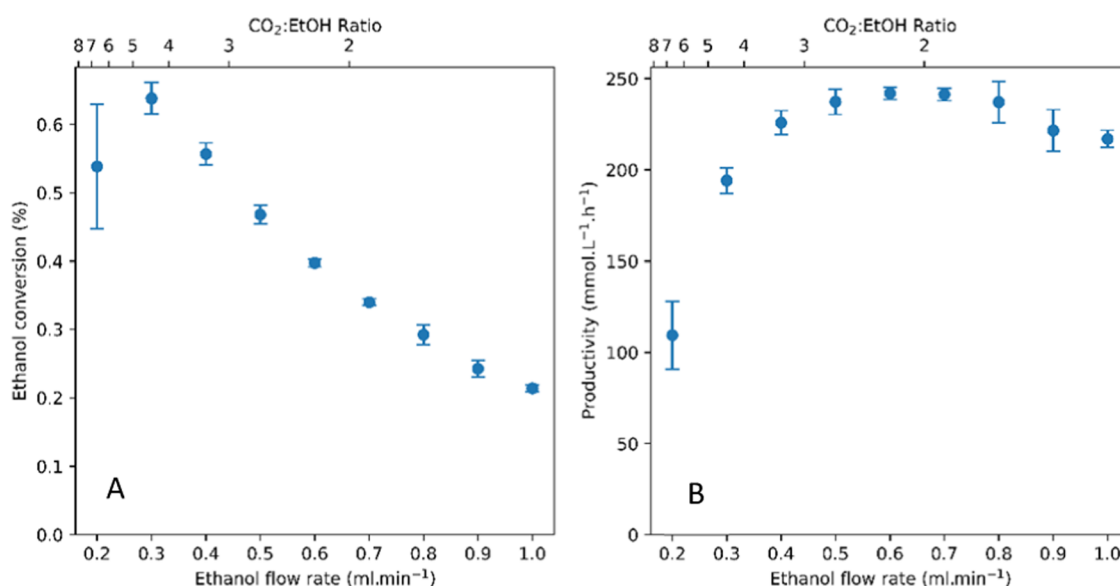


**Figure 7.** MeOH conversion at various feed rates (A) and corresponding DMC productivity values (B). Reaction conditions: 140 °C, 1 mL/min CO<sub>2</sub>, 200 bar, 3 g CeO<sub>2</sub>, 5 mL bed volume.

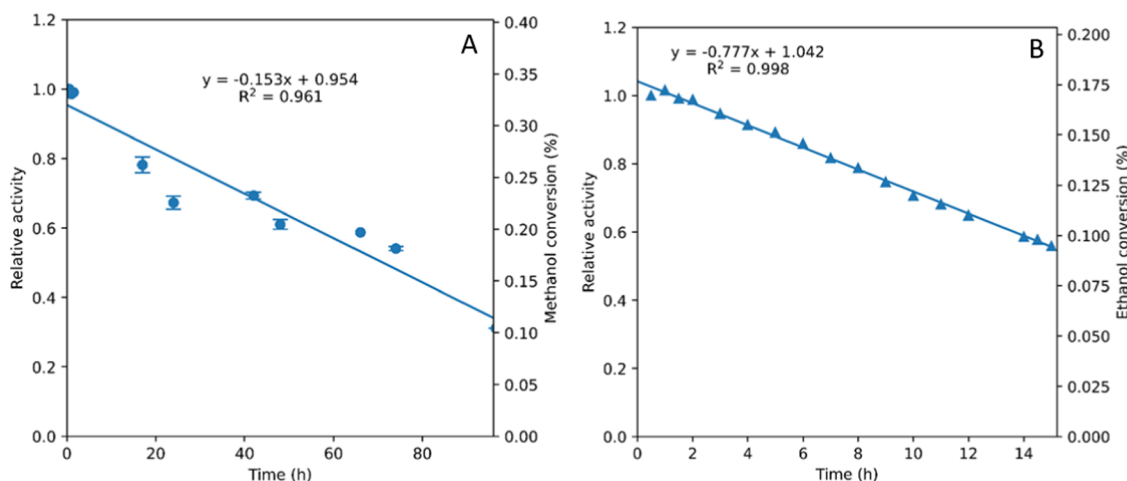
**Catalyst Stability in Continuous Flow.** While having an active catalyst and productive reactor system is important, stability of the catalyst is a key criterion for industrial

application. One of the advantages of using a flow system is that it negates the need for catalyst recovery between batchwise recycling experiments and allows for a more





**Figure 8.** EtOH conversion at various feed rates (A) and corresponding DEC productivity values (B). Reaction conditions: 140 °C, 1 mL/min CO<sub>2</sub>, 200 bar, 3 g CeO<sub>2</sub>, 5 mL bed volume.



**Figure 9.** Stability of commercial CeO<sub>2</sub> in catalytic DAC formation in continuous flow (A = MeOH, B = EtOH). Reaction conditions: 0.2 mL/min alcohol, 1 mL/min CO<sub>2</sub>, 200 bar, 140 °C, 0.3 g CeO<sub>2</sub>, contact time 4.2 min.

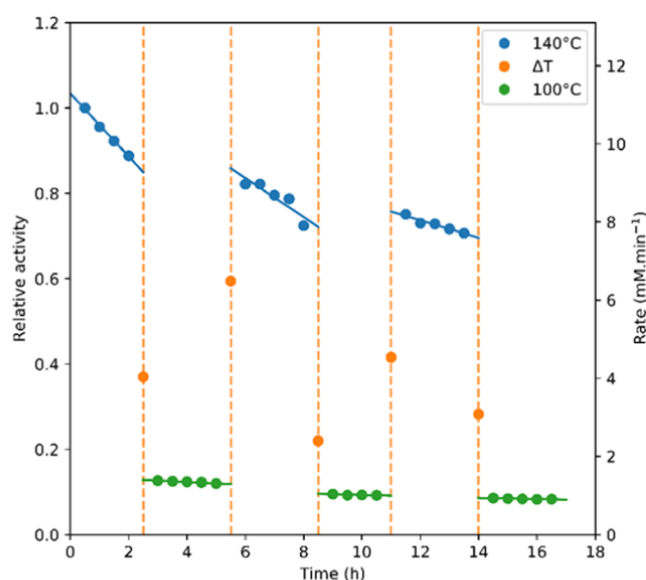
meaningful assessment of its intrinsic stability toward sustained reaction conditions.<sup>77</sup> In previous work, different types of CeO<sub>2</sub> have been investigated for their stability in the reaction of MeOH with CO<sub>2</sub> under various conditions, and several studies have reported modification procedures to combat some of the deactivation seen in repetitive batch experiments with different types of ceria.<sup>28</sup> As good activity and no obvious signs of deactivation were observed in our initial experiments, the long-term stability of commercial, unmodified CeO<sub>2</sub> was assessed for the condensation of MeOH and EtOH with CO<sub>2</sub> in continuous flow mode at 140 °C and 200 bar, respectively.

Figure 9 shows the formation of DMC (A) and DEC (B) over extended times on stream with no change in reaction conditions. In the methanol reaction, the catalyst lost 68% of its activity over the course of 96 h, corresponding to a zero-order  $k_{d(obs)}$  of 0.15/day, or a catalyst half-life of 6.6 days. The reaction of ethanol with CO<sub>2</sub> caused a more pronounced deactivation, with the catalyst losing around 44% of its activity over 15 h corresponding to a  $k_{d(obs)}$  of 0.77/day or a catalyst half-life of 1.3 days. This corresponds to a 5 times faster

deactivation with EtOH than with MeOH. Attempts to regenerate the catalyst by heating the bed to 120 °C under reduced pressure failed to restore activity.

To gain more insight into the deactivation behavior of CeO<sub>2</sub> under sustained reaction conditions in continuous flow, accelerated aging experiments were carried out with MeOH. Repeatedly cycling the catalyst bed between 140 and 100 °C (Figure 10) showed CeO<sub>2</sub> deactivation to be about 16 times slower at 100 °C. The initial  $k_{d(obs)}$  observed were larger than those derived from the long-term experiments shown in Figure 9 but decreased with each cycle, suggesting the most active sites to quickly deactivate before slower progressive catalyst deactivation takes over linearly (Table 4).

Areata proposed the main mode of catalyst deactivation for ceria in catalytic DMC formation to be a progressive reduction of active Ce(IV) sites to inactive Ce(III).<sup>28</sup> Analyzing our partially deactivated CeO<sub>2</sub> by X-ray photoelectron spectroscopy after conversion had just begun to decrease after a short amount of time on stream showed no discernible levels of reduction to Ce(III) (Figure 11). Instead, an increased level of



**Figure 10.** Relative activity of commercial cerium oxide when cycled between 140 and 100°C; dashed lines indicate the 30 min for temperature stabilization. Conditions: 0.2 mL/min MeOH, 1 mL/min CO<sub>2</sub> at 200 bar, 0.3 g of CeO<sub>2</sub>, contact time 4.2 min.

**Table 4.** Deactivation Rates at Each Temperature and Cycle for Commercial Cerium Oxide

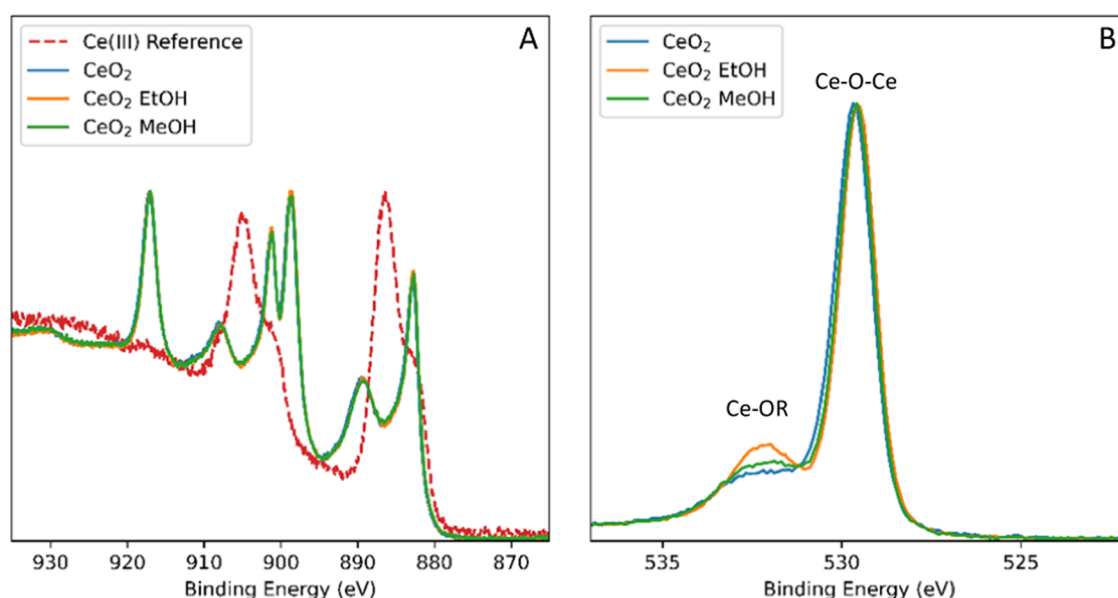
temperature cycle	140 °C $k_{d(ops)}$ (d <sup>-1</sup> )	100 °C $k_{d(ops)}$ (d <sup>-1</sup> )
1	-1.77	-0.078
2	-1.10	-0.040
3	-0.49	-0.031

oxygen defects was observed in the material post-reaction that is indicative of a decrease in the number of O<sup>2-</sup> sites on the surface of the material. The anionic defect sites thus created may be occupied by hydroxides, alkoxides, or carboxylates, implying the first step leading to catalyst deactivation to involve a loss of basic Ce–O–Ce sites that are required for

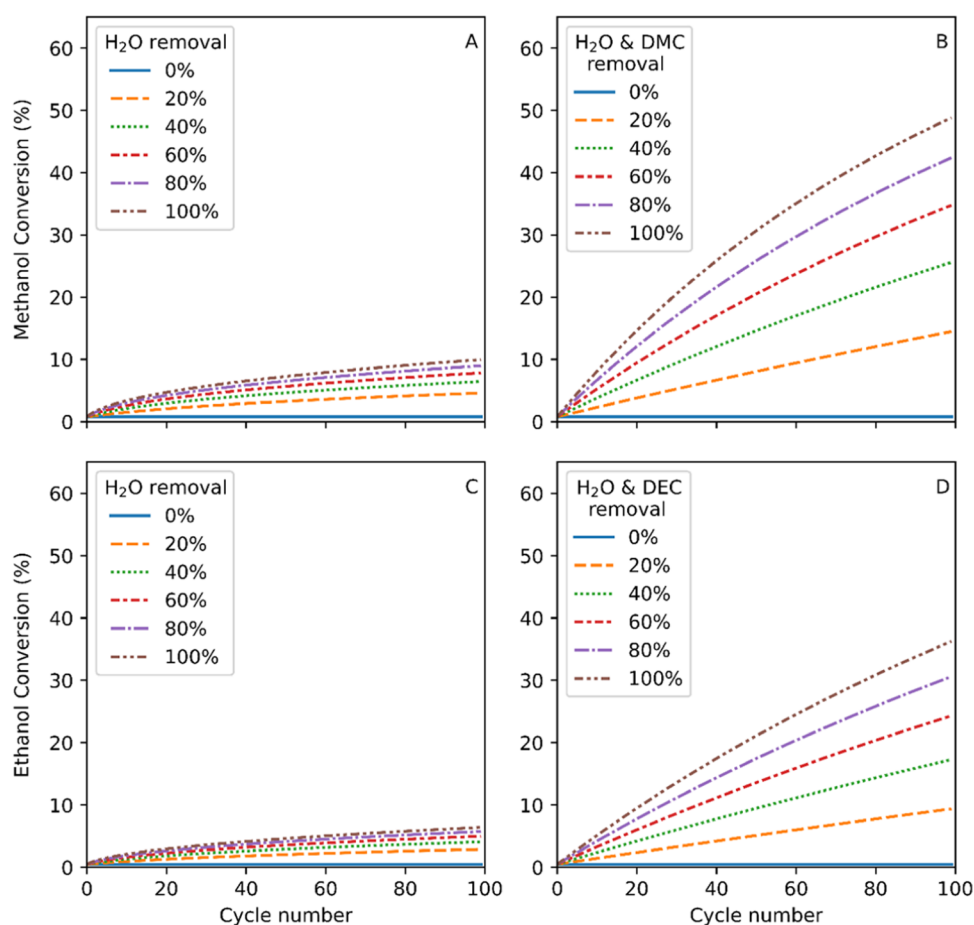
CO<sub>2</sub> binding and activation.<sup>20,35</sup> This is most likely caused by hydrolysis to acidic Ce–OH hydroxyls (possibly facilitated by carbonic acid formed *in situ*), Ce–OR alkoxides, or Ce–OOR carboxylates that are difficult to regenerate to Ce–O–Ce sites required for catalytic DAC formation. As significant degrees of reduction to Ce(III) have been detected in CeO<sub>2</sub> catalysts by XPS after more pronounced deactivation,<sup>28,36</sup> the hydrolysis of surface Ce–O–Ce units observed here after a low number of catalytic turnovers likely represents an entry point into catalyst deactivation that subsequently entails irreversible cerium reduction. Ethanol being more reducing than MeOH ultimately leads to faster catalyst deactivation, and more robust catalyst materials will be needed for DEC synthesis in particular.

**Effect of Product Removal.** A number of publications have pursued strategies to remove water from the reaction via nonreactive (physical) separation strategies to shift the unfavorable equilibrium position of DAC formation from alcohol and CO<sub>2</sub>.<sup>24,76,78</sup> While this represents a more realistic approach than adding synthetic, high-energy water scavengers that change the thermodynamics of the reaction (see above), these approaches have met with limited success so far. Typically, absorber beds are added as a separate unit downstream of the catalyst bed, and the dried DMC/MeOH/CO<sub>2</sub> mixture fed back into the reactor to re-establish equilibrium.

With our thermodynamic model we can calculate the efficiency of such approaches that iteratively shift the equilibrium position to higher DAC concentrations by stepwise removal of water from the mixture.<sup>a</sup> Figure 12 shows a thermodynamic prediction of how effective these stepwise, nonreactive water removal strategies may be. This is achieved by calculating the initial equilibrium position of the alcohol to DAC reaction as above (in this case at 140 °C and 200 bar) and then removing a percentage of the H<sub>2</sub>O byproduct from the mixture. The system is then allowed to re-equilibrate via repeated contact with the catalyst and the cycle repeated. The varying percentages of water removal reflect



**Figure 11.** XPS spectra of unused catalyst (CeO<sub>2</sub>) and following a 6 h reaction with ethanol and methanol: (A) cerium region with a Ce(III) reference and (B) oxygen region.



**Figure 12.** Calculated methanol and ethanol yields with iterative product removal at various drying efficiencies. (A) Cumulative DMC yields with water removal. (B) Cumulative DMC yields with equal water and DMC removal. (C) Cumulative DEC yields with water removal. (D) Cumulative DEC yields with equal water and DEC removal. Model parameters: 140 °C, 0.358 g/mL CO<sub>2</sub> (200 bar). Starting concentrations: 13.36 M CO<sub>2</sub>, 10.19 M MeOH, 7.05 M EtOH, 0 M DAC, and 0 M H<sub>2</sub>O.

different degrees of drying efficiency, with a theoretical 100% efficiency representing the thermodynamic best-case limit.

For the MeOH to DMC reaction (Figure 12a), we can see that 100 cycles with complete water removal would allow us to accumulate a DMC yield of around 7%. Previously, Choi et al.<sup>25</sup> reported >40% DMC yield using a loop reactor including a drying column packed with 3 Å molecular sieves under similar (supercritical) flow conditions. We calculate that over 2000 drying cycles at 100% efficiency are necessary to achieve this result, and the system reported indeed required 15 g of drying agent to push 3.2 g of MeOH to 40% DMC conversion over the course of three days (corresponding to a peak productivity of 90 mmol/L·h, decreasing to 16 mmol/L·h after 70 h).

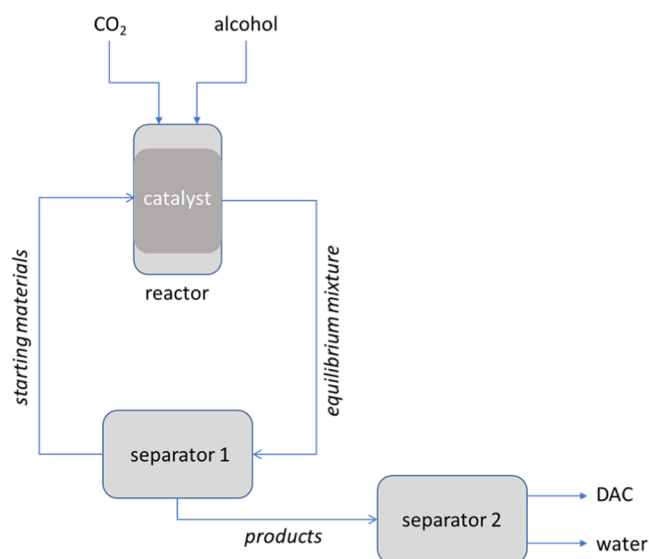
For the equivalent EtOH-to-DEC reaction, we find similar results (Figure 11c), with 100 cycles of perfect drying efficiency increasing the yield from 5 to 38%. Separation of water and DEC using membranes has recently been demonstrated for DEC synthesis by Wang et al.,<sup>24</sup> where a 30% enrichment of DEC and water was observed in their permeate at 0.02% conversion. Similarly, Dibenedetto et al.<sup>76</sup> demonstrate an improvement in ethanol conversion from 0.9% up to 3% with pervaporation membranes.

These results show that water removal alone is unlikely to improve the efficiency of DAC production from alcohols and CO<sub>2</sub> to the point where it may become economically viable, as

either marginal gains in yield are obtained or large amounts of drying agent and cycle numbers are required. From a process perspective, it is thus worth considering alternative separation schemes.

The removal, recovery, and reuse of excess CO<sub>2</sub> from the reaction is straightforward due to it forming a separate gas phase upon depressurization. The remaining liquid phase composed of excess alcohol with <1% water and DAC is stable in the absence of a catalyst (see above) but difficult to purify due to the low product concentration and azeotrope formation. It has previously been reported that a complete separation of this ternary mixture by way of fractional distillation becomes economically viable from DAC contents of >6%.<sup>79</sup> An alternative approach would be to only recover unreacted alcohol and CO<sub>2</sub> in the first instance, recycling this substrate mixture over the catalyst, and thereby accumulating more 1:1 DAC/H<sub>2</sub>O product mixture for later separation (Figure 13). The latter promises to be relatively facile due to the absence of alcohol that forms an azeotrope with aqueous DAC.<sup>80</sup>

If this approach could be coupled to or even built into the reactor similar to the use of drying beds, much larger gains than for water removal alone are to be expected, as thermodynamically both DAC and H<sub>2</sub>O limit the equilibrium position of the system. This can be seen mathematically in eq 6 where both products form the numerator of the fraction. Figure 12B,D illustrates the gains in productivity achievable by



**Figure 13.** Continuous flow process schematic with the DAC reactor coupled to a series of two separation units (pumps and process controls not shown). Liquid  $\text{CO}_2$  and alcohol are equilibrated with DAC and water over a packed catalyst bed in the reactor, and the pressurized mixture passed through a separator that removes the product mixture (water + DAC). Unconverted starting materials ( $\text{CO}_2$  and alcohol) are recycled back into the reactor where they are continuously topped up with fresh reagents. The liquid DAC/ $\text{H}_2\text{O}$  product mixture (which is stable in the absence of a catalyst) is further separated by fractionation. Segregating all three units would allow for optimum conditions to be applied at each operation (high  $T$  and high  $p$  in the reactor, low  $T$  and high  $p$  in separator 1, low  $p$  and high  $T$  in separator 2).

this approach compared to water removal only (A and C), all relative to a single batch reaction as the first data point in each plot. By removing both products from the catalyst bed in the reactor, we calculate that up to 5 times greater MeOH conversion can be achieved over the same number of reaction/separation cycles than for water removal alone. Importantly, even with a mere 20% removal efficiency of both products, we calculate a 2-fold increase in MeOH conversion over water removal alone. The thermodynamic data for DEC show similar results: 20% removal of both products would accumulate close to 10% yield over 100 cycles (sufficient for distillative separation), whereas removal of water alone, even if 100% effective, would yield less than 5% yield (insufficient for distillative separation) over the same cycle number.

A variety of separation technologies may be evaluated to achieve this task, including  $\text{CO}_2$ -induced phase splits,<sup>72,73,81</sup> supercritical extraction,<sup>82</sup> or pervaporation membranes. The latter have been used successfully for DMC/MeOH separations<sup>83</sup> as well as two-step distillation–pervaporation separations in DEC synthesis from EtOH.<sup>76</sup> Of course, all of these separation methods will have an associated energy cost for each cycle that will depend on the method chosen, concentration of the components, separation efficiency, and scale applied as previously investigated.<sup>84–86</sup> Which of these technologies may prove viable for application will depend on a number of additional factors that are beyond the scope of this work (cost, lifetime, etc.), and a careful evaluation of compatibility with the reaction conditions and kinetics which are not considered in this thermodynamic analysis.

## CONCLUSIONS

Although dehydrating agents are widely used additives for the evaluation of catalyst materials in the formation of dialkyl carbonates from alcohol and  $\text{CO}_2$ , they suffer from limitations such as complex hydrolysis kinetics and/or precipitation that make comparisons across different reports difficult. Most importantly, however, their use is nonsensical from thermodynamic, economic and environmental points of view, and as such, they do not contribute to an advancement of chemical  $\text{CO}_2$  utilization. A range of active catalysts have been developed for DAC formation, with commercial ceria remaining one of the most effective materials. Arguably, faster catalysts are not necessarily needed to advance this area, although catalysts with lower onset temperatures would allow for higher equilibrium yields that increase process productivity and facilitate product isolation. We have produced an accurate thermodynamic model that allows calculating equilibrium yields of DMC and DEC over a wide range of reaction conditions and predicting the effects of residual moisture as well as various product removal strategies. While water is widely considered the limiting byproduct in this reaction, removal of DAC product and water byproduct, which have been shown to be stable enough as a mixture on typical process timescales, is far more effective in accumulating practically useful DAC concentrations. We have demonstrated one of the most productive continuous flow systems for DMC and DEC formation from alcohol and  $\text{CO}_2$  to date and identified progressive surface M–O–M hydrolysis as the entry point into catalyst deactivation that is a major hurdle for process development. A new process model based on the continuous removal of both water and DAC product from the pressurized reactor effluent has been proposed, which along with sufficiently stable catalysts of perhaps also lower onset temperatures may make the direct carboxylation of alcohols an economically viable process as a meaningful contribution to practical  $\text{CO}_2$  utilization in the future.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c00291>.

Details of the experimental setup (incl. photographs), catalyst characterization (XRD, SEM, EDX data), analytical details and GC calibration, additional thermodynamic data, catalyst testing results and DMC hydrolysis experiments, and Arrhenius analysis of DMC formation (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Meenakshisundaram Sankar – Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom; [orcid.org/0000-0002-7105-0203](https://orcid.org/0000-0002-7105-0203); Email: [sankar@cardiff.ac.uk](mailto:sankar@cardiff.ac.uk)

Ulrich Hintermair – Centre for Sustainable and Circular Technologies, University of Bath, Bath BA2 7AY, United Kingdom; [orcid.org/0000-0001-6213-378X](https://orcid.org/0000-0001-6213-378X); Email: [u.hintermair@bath.ac.uk](mailto:u.hintermair@bath.ac.uk)

### Author

Matthew F. O'Neill – Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, United



Kingdom; Centre for Sustainable and Circular Technologies,  
University of Bath, Bath BA2 7AY, United Kingdom

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acssuschemeng.2c00291>

## Notes

The authors declare no competing financial interest.  
All data supporting this study is provided as Supporting Information accompanying this paper.

## ACKNOWLEDGMENTS

This work was supported by the EPSRC Centre for Doctoral Training in Catalysis (EP/L016443/1; studentship to M.F.O'N.) and the Royal Society (UF160458; fellowship to U.H.). The authors thank Dr. David Morgan of the Cardiff Catalysis Institute for XPS analysis.

## ADDITIONAL NOTE

“Note that these calculations do not give any indication of kinetics, i.e., the time required for each of these separation steps to proceed and the reactor content reequilibrate to reach these conversions.

## REFERENCES

- (1) Tollefson, J. Global Industrial Carbon Emissions to Reach All-Time High in 2018. *Nature* **2018**, *10*, No. 3.
- (2) Intergovernmental Panel on Climate Change. *Climate Change 2014 Mitigation of Climate Change*, 2014.
- (3) Keijer, T.; Bakker, V.; Slootweg, J. C. Circular Chemistry to Enable a Circular Economy. *Nat. Chem.* **2019**, *11*, 190–195.
- (4) Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81.
- (5) Sakakura, T.; Choi, J.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365–2387.
- (6) Kumar, K.; Das, D.; Baciocchi, R.; Costa, G.; Zingaretti, D. Transformation and Utilization of Carbon Dioxide. *Transform. Util. Carbon Dioxide* **2014**, 268–299.
- (7) Poliakov, M.; Leitner, W.; Streng, E. S. The Twelve Principles of CO<sub>2</sub> CHEMISTRY. *Faraday Discuss* **2015**, *183*, 9–17.
- (8) Aresta, M.; Dibenedetto, A.; Quaranta, E. State of the Art and Perspectives in Catalytic Processes for CO<sub>2</sub> Conversion into Chemicals and Fuels: The Distinctive Contribution of Chemical Catalysis and Biotechnology. *J. Catal.* **2016**, *343*, 2–45.
- (9) Selva, M.; Perosa, A.; Fiorani, G. Dimethyl Carbonate: A Versatile Reagent for a Sustainable Valorization of Renewables. *Green Chem.* **2018**, *20*, 288–322.
- (10) Sakakura, T.; Kohno, K. The Synthesis of Organic Carbonates from Carbon Dioxide. *Chem. Commun.* **2009**, *10*, 1312–1330.
- (11) Sakakura, T.; Kohno, K. The Synthesis of Organic Carbonates from Carbon Dioxide. *Chem. Commun.* **2009**, *10*, 1312–1330.
- (12) Alder, C. M.; Hayler, J. D.; Henderson, R. K.; Redman, A. M.; Shukla, L.; Shuster, L. E.; Sneddon, H. F. Updating and Further Expanding GSK's Solvent Sustainability Guide. *Green Chem.* **2016**, *18*, 3879–3890.
- (13) Leino, E.; Mäki-Arvela, P.; Eta, V.; Murzin, D. Y.; Salmi, T.; Mikkola, J. P. Conventional Synthesis Methods of Short-Chain Dialkylcarbonates and Novel Production Technology via Direct Route from Alcohol and Waste CO<sub>2</sub>. *Appl. Catal., A* **2010**, *383*, 1–13.
- (14) Davies, B. J. V.; Šarić, M.; Figueiredo, M. C.; Schjødt, N. C.; Dahl, S.; Moses, P. G.; Escudero-Escribano, M.; Arenz, M.; Rossmeisl, J. Electrochemically Generated Copper Carbonyl for Selective Dimethyl Carbonate Synthesis. *ACS Catal.* **2019**, *9*, 859–866.
- (15) Engel, R. V.; Alsaiani, R.; Nowicka, E.; Pattison, S.; Miedziak, P. J.; Kondrat, S. A.; Morgan, D. J.; Hutchings, G. J. Oxidative Carboxylation of 1-Decene to 1,2-Decylene Carbonate. *Top. Catal.* **2018**, *61*, 509–518.
- (16) Aresta, M.; Dibenedetto, A. Carbon Dioxide as Building Block for the Synthesis of Organic Carbonates Behavior of Homogeneous and Heterogeneous Catalysts in the Oxidative Carboxylation of Olefins. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 399–409.
- (17) Huang, S.; Yan, B.; Wang, S.; Ma, X. Recent Advances in Dialkyl Carbonates Synthesis and Applications. *Chem. Soc. Rev.* **2015**, *44*, 3079–3116.
- (18) Zhang, M.; Xiao, M.; Wang, S.; Han, D.; Lu, Y.; Meng, Y. Cerium Oxide-Based Catalysts Made by Template-Precipitation for the Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol. *J. Clean. Prod.* **2015**, *103*, 847–853.
- (19) Kabra, S. K.; Turpeinen, E.; Keiski, R. L.; Yadav, G. D. Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide: A Thermodynamic and Experimental Study. *J. Supercrit. Fluids* **2016**, *117*, 98–107.
- (20) Jung, K. T.; Bell, A. T. An in Situ Infrared Study of Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over Zirconia. *J. Catal.* **2001**, *204*, 339–347.
- (21) Chen, L.; Wang, S.; Zhou, J.; Shen, Y.; Zhao, Y.; Ma, X. Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over CeO<sub>2</sub> versus over ZrO<sub>2</sub>: Comparison of Mechanisms. *RSC Adv.* **2014**, *4*, 30968.
- (22) Zhang, X.; Jia, D.; Zhang, J.; Sun, Y. Direct Synthesis of Diethyl Carbonate from CO<sub>2</sub> and Ethanol Catalyzed by ZrO<sub>2</sub>/Molecular Sieves. *Catal. Lett.* **2014**, *144*, 2144–2150.
- (23) Leino, E.; Mäki-Arvela, P.; Eränen, K.; Tenho, M.; Murzin, D. Y.; Salmi, T.; Mikkola, J. P. Enhanced Yields of Diethyl Carbonate via One-Pot Synthesis from Ethanol, Carbon Dioxide and Butylene Oxide over Cerium (IV) Oxide. *Chem. Eng. J.* **2011**, *176–177*, 124–133.
- (24) Wang, J.; Hao, Z.; Wohlrab, S. Continuous CO<sub>2</sub> Esterification to Diethyl Carbonate (DEC) at Atmospheric Pressure: Application of Porous Membranes for in-situ H<sub>2</sub>O Removal. *Green Chem.* **2017**, *19*, 3595–3600.
- (25) Choi, J.-C.; He, L.-N. N.; Yasuda, H.; Sakakura, T.; Yasudaa, H.; Sakakura, T. Selective and High Yield Synthesis of Dimethyl Carbonate Directly from Carbon Dioxide and Methanol. *Green Chem.* **2002**, *4*, 230–234.
- (26) Tomishige, K.; Kunimori, K. Catalytic and Direct Synthesis of Dimethyl Carbonate Starting from Carbon Dioxide Using CeO<sub>2</sub>-ZrO<sub>2</sub> Solid Solution Heterogeneous Catalyst: Effect of H<sub>2</sub>O Removal from the Reaction System. *Appl. Catal., A* **2002**, *237*, 103–109.
- (27) Chen, Y.; Wang, H.; Qin, Z.; Tian, S.; Ye, Z.; Ye, L.; Abroshan, H.; Li, G. Ti<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub> Nanocomposites: A Monolithic Catalyst for the Direct Conversion of Carbon Dioxide and Methanol to Dimethyl Carbonate. *Green Chem.* **2019**, *21*, 4642–4649.
- (28) Aresta, M.; Dibenedetto, A.; Pastore, C.; Cuocci, C.; Aresta, B.; Cometa, S.; De Giglio, E. Cerium(IV)Oxide Modification by Inclusion of a Hetero-Atom: A Strategy for Producing Efficient and Robust Nano-Catalysts for Methanol Carboxylation. *Catal. Today* **2008**, *137*, 125–131.
- (29) Honda, M.; Tamura, M.; Nakagawa, Y.; Sonehara, S.; Suzuki, K.; Fujimoto, K. I.; Tomishige, K. Ceria-Catalyzed Conversion of Carbon Dioxide into Dimethyl Carbonate with 2-Cyanopyridine. *ChemSusChem* **2013**, *6*, 1341–1344.
- (30) Honda, M.; Tamura, M.; Nakagawa, Y.; Nakao, K.; Suzuki, K.; Tomishige, K. Organic Carbonate Synthesis from CO<sub>2</sub> and Alcohol over CeO<sub>2</sub> with 2-Cyanopyridine: Scope and Mechanistic Studies. *J. Catal.* **2014**, *318*, 95–107.
- (31) Fu, Z.; Zhong, Y.; Yu, Y.; Long, L.; Xiao, M.; Han, D.; Wang, S.; Meng, Y. TiO<sub>2</sub>-Doped CeO<sub>2</sub> Nanorod Catalyst for Direct Conversion of CO<sub>2</sub> and CH<sub>3</sub>OH to Dimethyl Carbonate: Catalytic Performance and Kinetic Study. *ACS Omega* **2018**, *3*, 198–207.
- (32) Liu, B.; Li, C.; Zhang, G.; Yan, L.; Li, Z. Direct Synthesis of Dimethyl Carbonate from CO<sub>2</sub> and Methanol over CaO-CeO<sub>2</sub> Catalysts: The Role of Acid-Base Properties and Surface Oxygen Vacancies. *New J. Chem.* **2017**, *41*, 12231–12240.

- (33) Yoshida, Y.; Arai, Y.; Kado, S.; Kunimori, K.; Tomishige, K. Direct Synthesis of Organic Carbonates from the Reaction of CO<sub>2</sub> with Methanol and Ethanol over CeO<sub>2</sub> Catalysts. *Catal. Today* **2006**, *115*, 95–101.
- (34) Liu, B.; Li, C.; Zhang, G.; Yao, X.; Chuang, S. S. C.; Li, Z. Oxygen Vacancy Promoting Dimethyl Carbonate Synthesis from CO<sub>2</sub> and Methanol over Zr-Doped CeO<sub>2</sub> Nanorods. *ACS Catal.* **2018**, *8*, 10446–10456.
- (35) Chen, L.; Wang, S.; Zhou, J.; Shen, Y.; Zhao, Y.; Ma, X. Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over CeO<sub>2</sub> versus over ZrO<sub>2</sub>: Comparison of Mechanisms. *RSC Adv.* **2014**, *4*, 30968–30975.
- (36) Al-Darwish, J.; Senter, M.; Lawson, S.; Rezaei, F.; Rownaghi, A. A. Ceria Nanostructured Catalysts for Conversion of Methanol and Carbon Dioxide to Dimethyl Carbonate. *Catal. Today* **2020**, *350*, 120–126.
- (37) Stoian, D.; Bansode, A.; Medina, F.; Urakawa, A. Catalysis under Microscope: Unraveling the Mechanism of Catalyst de- and Re-Activation in the Continuous Dimethyl Carbonate Synthesis from CO<sub>2</sub> and Methanol in the Presence of a Dehydrating Agent. *Catal. Today* **2017**, *283*, 2–10.
- (38) Tamura, M.; Hiwataishi, D.; Gu, Y.; Nakayama, A.; Nakagawa, Y.; Tomishige, K. Organic Compound Modification of CeO<sub>2</sub> and 2-Cyanopyridine Hybrid Catalyst in Carbonate Synthesis from CO<sub>2</sub> and Alcohols. *J. CO<sub>2</sub> Util.* **2021**, *54*, No. 101744.
- (39) Li, A.; Pu, Y.; Li, F.; Luo, J.; Zhao, N.; Xiao, F. Synthesis of Dimethyl Carbonate from Methanol and CO<sub>2</sub> over Fe-Zr Mixed Oxides. *J. CO<sub>2</sub> Util.* **2017**, *19*, 33–39.
- (40) Saada, R.; Kellici, S.; Heil, T.; Morgan, D.; Saha, B. Greener Synthesis of Dimethyl Carbonate Using a Novel Ceria-Zirconia Oxide/Graphene Nanocomposite Catalyst. *Appl. Catal., B* **2015**, *168–169*, 353–362.
- (41) Choi, J. C.; Kohno, K.; Ohshima, Y.; Yasuda, H.; Sakakura, T. Tin- or Titanium-Catalyzed Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol: Large Promotion by a Small Amount of Triflate Salts. *Catal. Commun.* **2008**, *9*, 1630–1633.
- (42) Wang, S. P.; Zhou, J. J.; Zhao, S. Y.; Zhao, Y. J.; Ma, X. Bin. Enhancements of Dimethyl Carbonate Synthesis from Methanol and Carbon Dioxide: The In Situ Hydrolysis of 2-Cyanopyridine and Crystal Face Effect of Ceria. *Chinese Chem. Lett.* **2015**, *26*, 1096–1100.
- (43) Bansode, A.; Urakawa, A. Continuous DMC Synthesis from CO<sub>2</sub> and Methanol over a CeO<sub>2</sub> Catalyst in a Fixed Bed Reactor in the Presence of a Dehydrating Agent. *ACS Catal.* **2014**, *4*, 3877–3880.
- (44) Su, X.; Lin, W.; Cheng, H.; Zhang, C.; Wang, Y.; Yu, X.; Wu, Z.; Zhao, F. Metal-Free Catalytic Conversion of CO<sub>2</sub> and Glycerol to Glycerol Carbonate. *Green Chem.* **2017**, *19*, 1775–1781.
- (45) Tomishige, K.; Tamura, M.; Nakagawa, Y. CO<sub>2</sub> Conversion with Alcohols and Amines into Carbonates, Ureas, and Carbamates over CeO<sub>2</sub> Catalyst in the Presence and Absence of 2-Cyanopyridine. *Chem. Rec.* **2019**, *19*, 1354–1379.
- (46) Honda, M.; Kuno, S.; Begum, N.; Fujimoto, K. I.; Suzuki, K.; Nakagawa, Y.; Tomishige, K. Catalytic Synthesis of Dialkyl Carbonate from Low Pressure CO<sub>2</sub> and Alcohols Combined with Acetonitrile Hydration Catalyzed by CeO<sub>2</sub>. *Appl. Catal., A* **2010**, *384*, 165–170.
- (47) Honda, M.; Kuno, S.; Sonehara, S.; Fujimoto, K. I.; Suzuki, K.; Nakagawa, Y.; Tomishige, K. Tandem Carboxylation-Hydration Reaction System from Methanol, CO<sub>2</sub> and Benzonitrile to Dimethyl Carbonate and Benzamide Catalyzed by CeO<sub>2</sub>. *ChemCatChem* **2011**, *3*, 365–370.
- (48) Eta, V.; Mäki-Arvela, P.; Wärn, J.; Salmi, T.; Mikkola, J. P.; Murzin, D. Y. Kinetics of Dimethyl Carbonate Synthesis from Methanol and Carbon Dioxide over ZrO<sub>2</sub>-MgO Catalyst in the Presence of Butylene Oxide as Additive. *Appl. Catal., A* **2011**, *22*, 39–46.
- (49) Tian, J. S.; Miao, C. X.; Wang, J. Q.; Cai, F.; Du, Y.; Zhao, Y.; He, L. N. Efficient Synthesis of Dimethyl Carbonate from Methanol, Propylene Oxide and CO<sub>2</sub> Catalyzed by Recyclable Inorganic Base/Phosphonium Halide-Functionalized Polyethylene Glycol. *Green Chem.* **2007**, *9*, 566–57.
- (50) Honda, M.; Tamura, M.; Nakagawa, Y.; Tomishige, K. Catalytic CO<sub>2</sub> Conversion to Organic Carbonates with Alcohols in Combination with Dehydration System. *Catal. Sci. Technol.* **2014**, *4*, 2830.
- (51) Faria, D. J.; Moreira dos Santos, L.; Bernard, F. L.; Selbach Pinto, I.; Carmona da Motta Resende, M. A.; Einloft, S. Dehydrating Agent Effect on the Synthesis of Dimethyl Carbonate (DMC) Directly from Methanol and Carbon Dioxide. *RSC Adv.* **2020**, *10*, 34895–34902.
- (52) Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W. Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment. *Chem. Rev.* **2018**, *118*, 434–504.
- (53) Hintermair, U.; Roosen, C.; Kaever, M.; Kronenberg, H.; Thelen, R.; Aey, S.; Leitner, W.; Greiner, L. A Versatile Lab to Pilot Scale Continuous Reaction System for Supercritical Fluid Processing. *Org. Process Res. Dev.* **2011**, *15*, 1275–1280.
- (54) O'Neill, M. Thermodynamics\_class, *GitHub*, 2019.
- (55) Wischnewski, B. Peace Software, [http://www.peacesoftware.de/einigewerte/co2\\_e.html](http://www.peacesoftware.de/einigewerte/co2_e.html) (accessed Jan 14, 2019).
- (56) Lee, H. J.; Park, S.; Jung, J. C.; Song, I. K. Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide over H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> Catalysts: Effect of Acidity of the Catalysts. *Korean J. Chem. Eng.* **2011**, *28*, 1518–1522.
- (57) Lee, H. J.; Park, S.; Song, I. K.; Jung, J. C. Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide over Ga<sub>2</sub>O<sub>3</sub>/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> Catalysts: Effect of Acidity and Basicity of the Catalysts. *Catal. Lett.* **2011**, *141*, 531–537.
- (58) Lee, H. J.; Joe, W.; Song, I. K. Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide over Transition Metal Oxide/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> Catalysts: Effect of Acidity and Basicity of the Catalysts. *Korean J. Chem. Eng.* **2012**, *29*, 317–322.
- (59) Aresta, M.; Dibenedetto, A.; Fracchiolla, E.; Giannoccaro, P.; Pastore, C.; Pápai, I.; Schubert, G. Mechanism of Formation of Organic Carbonates from Aliphatic Alcohols and Carbon Dioxide under Mild Conditions Promoted by Carbodiimides. DFT Calculation and Experimental Study. *J. Org. Chem.* **2005**, *70*, 6177–6186.
- (60) Chang, T.; Tamura, M.; Nakagawa, Y.; Fukaya, N.; Choi, J. C.; Mishima, T.; Matsumoto, S.; Hamura, S.; Tomishige, K. An Effective Combination Catalyst of CeO<sub>2</sub> and Zeolite for the Direct Synthesis of Diethyl Carbonate from CO<sub>2</sub> and Ethanol with 2,2-Diethoxypropane as a Dehydrating Agent. *Green Chem.* **2020**, *22*, 7321–7327.
- (61) Tamura, M.; Kishi, R.; Nakayama, A.; Nakagawa, Y.; Hasegawa, J. Y.; Tomishige, K. Formation of a New, Strongly Basic Nitrogen Anion by Metal Oxide Modification. *J. Am. Chem. Soc.* **2017**, *139*, 11857–11867.
- (62) Tomishige, K.; Gu, Y.; Chang, T.; Tamura, M.; Nakagawa, Y. Catalytic Function of CeO<sub>2</sub> in Non-Reductive Conversion of CO<sub>2</sub> with Alcohols. *Mater. Today Sustainable* **2020**, *9*, No. 100035.
- (63) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899.
- (64) Domalski, E. S.; Hearing, E. D. Condensed Phase Heat Capacity Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899.
- (65) Design Institute for Physical Properties. *DIPPR Project 801 - Full Version*; Design Institute for Physical Property Research/AICHE, <https://app.knovel.com/hotlink/toc/id:kpDIPPRPF7/dippr-project-801-full/dippr-project-801-full>.
- (66) Sadhukhan, T.; Latif, I. A.; Datta, S. N. Solvation of CO<sub>2</sub> in Water: Effect of RuBP on CO<sub>2</sub> Concentration in Bundle Sheath of C<sub>4</sub> Plants. *J. Phys. Chem. B* **2014**, *118*, 8782–8791.

- (67) Tamboli, A. H.; Chaugule, A. A.; Kim, H. Catalytic Developments in the Direct Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol. *Chem. Eng. J.* **2017**, *323*, 530–544.
- (68) Roosen, C.; Ansorge-Schumacher, M.; Mang, T.; Leitner, W.; Greiner, L. Gaining PH-Control in Water/Carbon Dioxide Biphasic Systems. *Green Chem.* **2007**, *9*, 455–45.
- (69) Cui, H.; Wang, T.; Wang, F.; Gu, C.; Wang, P.; Dai, Y. Kinetic Study on the One-Pot Synthesis of Dimethyl Carbonate in Supercritical CO<sub>2</sub> Conditions. *Ind. Eng. Chem. Res.* **2004**, *43*, 7732–7739.
- (70) Hintermair, U.; Franciyò, G.; Leitner, W. Continuous Flow Organometallic Catalysis: New Wind in Old Sails. *Chem. Commun.* **2011**, *47*, 3691–3701.
- (71) Foster, N. R.; Luden, F.; Mammucari, R. Basic Physical Properties, Phase Behavior and Solubility. *Handbook of Green Chemistry - Green Solvents: Volume 4 - Supercritical Solvents*; 2010; Vol. 29, pp. 77–99.
- (72) Abbott, A. P.; Hope, E. G.; Mistry, R.; Stuart, A. M. Controlling Phase Behaviour on Gas Expansion of Fluid Mixtures. *Green Chem.* **2009**, *11*, 1536–1540.
- (73) Pollet, P.; Hart, R. J.; Eckert, C. A.; Liotta, C. L. Organic Aqueous Tunable Solvents (OATS): A Vehicle for Coupling Reactions and Separations. *Acc. Chem. Res.* **2010**, *43*, 1237–1245.
- (74) Hintermair, U.; Leitner, W.; Jessop, P. Expanded Liquid Phases in Catalysis: Gas-Expanded Liquids and Liquid-Supercritical Fluid Biphasic Systems *Handb. Green Chem.* 2010, *11*, DOI: 10.1002/9783527628698.hgc037.
- (75) Reighard, T. S.; Lee, S. T.; Olesik, S. V. Determination of Methanol/CO<sub>2</sub> and Acetonitrile/CO<sub>2</sub> Vapor-Liquid Phase Equilibria Using a Variable-Volume View Cell. *Fluid Phase Equilib.* **1996**, *123*, 215–230.
- (76) Dibenedetto, A.; Aresta, M.; Angelini, A.; Ethiraj, J.; Aresta, B. M. Synthesis, Characterization, and Use of Nb V/Ce<sup>IV</sup>-Mixed Oxides in the Direct Carboxylation of Ethanol by Using Pervaporation Membranes for Water Removal. *Chem. - A Eur. J.* **2012**, *18*, 10324–10334.
- (77) Yakabi, K.; Milne, K.; Buchard, A.; Hammond, C. Selectivity and Lifetime Effects in Zeolite-Catalysed Baeyer–Villiger Oxidation Investigated in Batch and Continuous Flow. *ChemCatChem* **2016**, *8*, 3490–3498.
- (78) Li, C. F.; Zhong, S. H. Study on Application of Membrane Reactor in Direct Synthesis DMC from CO<sub>2</sub> and CH<sub>3</sub>OH over Cu-KF/MgSiO Catalyst. *Catal. Today* **2003**, *82*, 83–90.
- (79) Aresta, M.; Dibenedetto, A.; Dutta, A. Energy Issues in the Utilization of CO<sub>2</sub> in the Synthesis of Chemicals: The Case of the Direct Carboxylation of Alcohols to Dialkyl-Carbonates. *Catal. Today* **2017**, *281*, 345–351.
- (80) Bauer, K.; Sy, J.; Lipmann, F. Verfahren zur Abtrennung von Dimethylcarbonat aus seinem Azeotrop mit Methanol. EP0581115 B11973.
- (81) Ablan, C. D.; Hallett, J. P.; West, K. N.; Jones, R. S.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. Use and Recovery of a Homogeneous Catalyst with Carbon Dioxide as a Solubility Switch. *Chem. Commun.* **2003**, *3*, 2972–2973.
- (82) Zosel, K. Separation with Supercritical Gases: Practical Applications. *Angew. Chem. Int. Ed. Eng.* **1978**, *17*, 702–709.
- (83) Wang, L.; Han, X.; Li, J.; Zhan, X.; Chen, J. Separation of Azeotropic Dimethylcarbonate/Methanol Mixtures by Pervaporation: Sorption and Diffusion Behaviors in the Pure and Nano Silica Filled Pdms Membranes. *Sep. Sci. Technol.* **2011**, *46*, 1396–1405.
- (84) Lee, C.-T.; Tsai, C. C.; Wu, P. J.; Yu, B. Y.; Lin, S. T. Screening of CO<sub>2</sub> Utilization Routes from Process Simulation: Design, Optimization, Environmental and Techno-Economic Analysis. *J. CO<sub>2</sub> Util.* **2021**, *53*, No. 101722.
- (85) Ohno, H.; Ikhlal, M.; Tamura, M.; Nakao, K.; Suzuki, K.; Morita, K.; Kato, Y.; Tomishige, K.; Fukushima, Y. Direct Dimethyl Carbonate Synthesis from CO<sub>2</sub> and Methanol Catalyzed by CeO<sub>2</sub> and Assisted by 2-Cyanopyridine: A Cradle-to-Gate Greenhouse Gas Emission Study. *Green Chem.* **2021**, *23*, 457–469.
- (86) Yu, B. Y.; Wu, P. J.; Tsai, C. C.; Lin, S. T. Evaluating the Direct CO<sub>2</sub> to Diethyl Carbonate (DEC) Process: Rigorous Simulation, Techno-Economical and Environmental Evaluation. *J. CO<sub>2</sub> Util.* **2020**, *41*, No. 101254.