



# Kinetic and mechanistic investigations of the direct synthesis of dimethyl carbonate from carbon dioxide over ceria nanorod catalysts



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## ABSTRACT

The direct conversion of carbon dioxide (CO<sub>2</sub>) to organic carbonates such as dimethyl carbonate (DMC) is favored only at low temperatures. However, these reactions are typically conducted at high temperatures due to poor reaction kinetics. In this article, the reaction kinetics were experimentally investigated for the direct conversion of CO<sub>2</sub> and methanol to DMC using a ceria nanorod catalyst and were compared with those of a highly crystalline commercial ceria catalyst. The apparent activation energy for this reaction over our nanorod catalyst was determined to be 65 kJ/mol whereas that of a commercial ceria catalyst was measured to be 117 kJ/mol. The reaction rate law was found to be approximately first order with respect to both catalysts, with an apparent negative one reaction order with respect to methanol. These results were found to be consistent with a Langmuir–Hinshelwood type reaction mechanism where CO<sub>2</sub> and methanol adsorption occurs in separate reaction steps.

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## 1. Introduction

The direct synthesis of dimethyl carbonate (DMC) from carbon dioxide (CO<sub>2</sub>) and methanol (MeOH) has drawn intense interest because both chemicals are abundant, renewable and relatively inexpensive. CO<sub>2</sub> is an abundant carbon waste which is produced on the order of billions of metric tons in the U.S. from burning fossil fuels for energy [1]. Methanol is primarily produced from the methane component of natural gas, of which there are over 350 trillion cubic feet of confirmed reserves in the United States alone [2]. In addition, methanol is also commercially produced directly from CO<sub>2</sub> and water or hydrogen [3,4]. As an example, Carbon Recycling International in Iceland generates hydrogen from the electrolysis of water using hydro and geothermal electricity and then catalytically reacts the generated hydrogen with flue gas CO<sub>2</sub> to form methanol [5]. Thus, the direct synthesis of DMC from CO<sub>2</sub> and methanol has the potential to remove three moles of CO<sub>2</sub> for every mole of DMC formed. DMC is of particular interest as it is a ready plug-in commercial chemical used both as an

electrolyte solvent for lithium ion batteries (for which there is a market for ~20 thousand tons per year) [6] and as an attractive green feedstock for polycarbonate plastics (which have a current world demand of ~4.5 million tons) [7–9]. Consequently, the direct conversion of CO<sub>2</sub> and methanol to DMC has attracted considerable attention for both environmental and commercial reasons.

Numerous catalysts have been explored for the direct conversion of CO<sub>2</sub> and methanol to DMC. These catalysts include Co<sub>1.5</sub>-PW<sub>12</sub>O<sub>40</sub> [10], K<sub>2</sub>CO<sub>3</sub> [11], KOH [11], ZrO<sub>2</sub> [12], and CeO<sub>2</sub> [13–16]. As an excellent catalyst support with both Lewis acid and base properties, ceria in particular has been extensively studied after doping with Al<sub>2</sub>O<sub>3</sub> [15], ZrO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and other lanthanide elements [17]. Unfortunately, the direct conversion of CO<sub>2</sub> to DMC reported in the literature remains characterized by low yields (up to 7.2% [12]) at high temperatures (80–200 °C [10,11]) and long reaction times of 3 [17] to 10 h [11], limited by the thermodynamic stability of CO<sub>2</sub> [10,18]. To improve product yields, dehydrating agents such as orthoesters, and molecular sieves have been explored for this synthetic route [19]. However, orthoesters are expensive and difficult to recover. Furthermore, the life time of molecular sieves for dehydration reactions can be short, on the order of hours [20,21]. Such a short life time makes it necessary for molecular sieves to be continuously replaced and regenerated for large scale processes, a costly concern for industry and an environmental concern if net CO<sub>2</sub> is generated.

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Determining the mechanistic kinetics in the direct synthesis of DMC has the potential to inspire improved catalyst design, thereby decreasing the activation energy barrier and mitigating the problems of long reaction times and high reaction temperatures. Unfortunately, such kinetic studies are experimentally difficult due to the very long reaction times, high pressures, and extremely anhydrous conditions involved. Since the initial amount of water on the reactor walls, tubes, catalyst, and gas cylinder cannot be measured before every run, the very low product yields of DMC and water typical for this reaction can result in significant deviation in the equilibrium product yield depending on the initial conditions. As a result, previous kinetic models based on modeling the reaction profile have shown good agreement between the simulation and the experimental data in the initial rate region, but with larger deviations later in the reaction (after 5–25 h) when close to equilibrium conditions [16]. Additionally, experiments and simulations for the kinetics of alcohol and CO<sub>2</sub> reactions are difficult because these reactions have a significant activation volume ( $\Delta v^\ddagger$ ), which describes the impact of pressure on the rate constant similar to how activation energy relates temperature and rate [16]. Hence, a small leak or a slight water contamination will result in a dramatically different reaction profile than had the depressurization not occurred, making reaction rate modeling difficult for this system.

Here we report our detailed study of the kinetics for the conversion of CO<sub>2</sub> and methanol into DMC using ceria nanorods and highly crystalline commercial ceria as the catalysts. As the synthesis of DMC from CO<sub>2</sub> and methanol is a slow reaction, we focus on utilizing the initial rates of conversion in order to determine the reaction order with respect to ceria and methanol concentrations. Provided that care is taken to maintain a constant reaction pressure, a method of initial rates is found to be effective at isolating the parameters that impact the rate from those that affect the equilibrium. Additionally, the high surface area of the ceria nanorods used in this study allowed for a reduced activation energy compared to that used previously for the synthesis of DMC [16], allowing for reasonable rates with small catalyst loading.

## 2. Materials and methods

### 2.1. Synthesis of ceria nanorods

Ceria nanorod catalysts were prepared using a modified, reported hydrothermal method [22] that incorporated a lengthened calcination time to ensure the dryness of the catalysts. Briefly, 0.5 g of cerium (III) sulfate hydrate (Sigma–Aldrich) was mixed with 40 mL of a 10 M sodium hydroxide (Sigma–Aldrich) aqueous solution in a 50 mL Teflon autoclave liner. This Teflon liner was sealed in a stainless steel autoclave bomb (Parr 4744, Moline, IL) and placed in a convection oven for 15 h at 120 °C. The solid product was vacuum-filtered through 3.0 µm polycarbonate membrane filters (EMD Millipore) and dried for 1 h at 50 °C on the membrane. Afterward, the catalyst was separated from the filter membrane, pulverized, and dried for an additional hour at 50 °C. The rods were then mixed with 100 mL of 15% aqueous hydrogen peroxide solution (Macron) and the resulting mixture was sonicated for 30 min. After an additional hour of stirring, the ceria catalyst was again vacuum-filtered through 3.0 µm polycarbonate membrane filters and dried overnight in a convection oven at 50 °C. Finally, the catalyst was calcined under pure oxygen by placing on a quartz boat in the center of a 1"-quartz tube furnace. The system was isolated from atmosphere by a glass double bubbler using Fomblin oil (Solvay). Five hundred SCCM of 99.6% extra dry oxygen (Matheson Tri-Gas) was continuously supplied during calcination. The sample was heated to 400 °C over 30 min, and held for 4 h before being allowed to slowly cool to room temperature.

### 2.2. Commercial ceria preparation

Commercial ceria was utilized for comparison with our synthesized nanorod catalysts. REacton<sup>®</sup> ceria was purchased from Alfa Aesar (99.9% REO). For consistency with our nanorod catalyst, this ceria catalyst was also calcined under 500 SCCM of 99.6% extra dry oxygen with a 30 min ramp to 400 °C and a 4 h hold time.

### 2.3. Evaluation of catalyst performance

Catalyst performance was evaluated based on the conversion of CO<sub>2</sub> and methanol to dimethyl carbonate (DMC) in a high pressure stainless steel reactor (Parr 4560, Moline, IL) (Fig. 1). In a typical reaction, 0.10 grams of previously prepared catalyst was weighed out and placed in an 80 °C drying oven for 1 h of drying. Since water is a byproduct of the formation of DMC, care must be taken to avoid the addition of any additional water. For that reason, the reactor head was purged with CO<sub>2</sub> (99.99% purity Matheson Tri-gas) and heated to 80 °C via a heat gun before each reaction. The steel reactor vessel was likewise heated in a drying oven to at least 80 °C for 1 h prior to the reaction. After heating, the catalyst and reactor vessel were allowed to cool to near room temperature in a DriRite filled glass desiccator. After cooling, 15 mL of anhydrous methanol (DriSolv, EMD Millipore) and the 0.1 g of dried catalyst were combined promptly in the reactor prior to reactor sealing. The methanol utilized had a manufacturer certified water content below 50 ppm. Methanol dryness was maintained by extracting methanol under dry nitrogen and periodically monitored by HPLC.

CO<sub>2</sub> pressurization was optimized such that the reactions took place at a constant 2000 psi reaction pressure regardless of reaction temperature. If the reaction was to be performed at 140 °C, the reactor was pressurized with CO<sub>2</sub> such that the pressure held at 800 psi (55 bar) at 22 °C. If the reaction temperature was below 140 °C, the sealed reactor was chilled using a water–ice slurry to the desired temperature (e.g. 6 °C for a 125 °C reaction temperature) and pressurized with CO<sub>2</sub>. This ensured that the reaction pressure remained a constant 2000 psi (138 bar) regardless of the reaction temperature. The sealed and pressurized assembly was then heated to the reaction temperature with constant stirring. As CO<sub>2</sub> is known to be in the supercritical state above 74 bar and 31 °C, and CO<sub>2</sub> is the reaction solvent, we do not expect there to be an issue with mass transport between phases. This lack of a

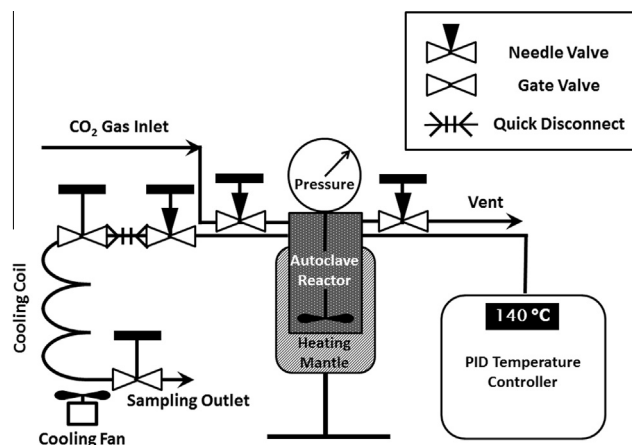


Fig. 1. Schematic diagram of the experimental setup used in this study. Reactor was pressurized with a direct connection to a compressed CO<sub>2</sub> gas tank.

mass transport limitation has been confirmed by previous studies where no apparent reaction profile differences were found with regard to the stirring speed [16,18]. Also, we evaluated the use of a baffle insert to improve the reactant mixing and the insert was found to have no observable effects on the experimental results. The reactor was held at the desired temperature ( $\pm 1$  °C) and  $2000 \pm 100$  psi for the specified reaction time. Afterward, the heating mantle was removed and the reactor was cooled rapidly by a small fan before being carefully vented over  $\sim 20$  min in order to avoid liquid loss. After fully depressurizing the reactor, the liquid product was collected for chemical analysis. The catalyst was separated from the carbonate sample by centrifugation and the liquid product was filtered using  $0.2 \mu\text{m}$  PTFE syringe filters (VWR) prior to analysis.

#### 2.4. GC–MS method for identification of reaction products

The identity of our major reaction product was determined to be DMC by using gas chromatography-mass spectrometry (GC–MS). For GC analysis, the oven (Thermo Scientific Focus with PolarisQ MS, Waltham, MA) temperature was ramped from 80 to 250 °C at 20 °C/min. Inlet temperature was kept at 120 °C and helium was used as the carrier gas. The injection volume was 1  $\mu\text{L}$  carried out in splitless mode. The mass spectrometer detector was operated in electron ionization mode. The presence of DMC in the reaction products was verified via characteristic electron ionization fragments at 45 and 59  $m/z$  in the MS data.

#### 2.5. HPLC method for quantification of reaction products

The methanol and DMC content of our reaction products were analyzed using a high performance liquid chromatography (HPLC) method developed by the National Renewable Energy Laboratory [23,24]. Briefly, 10  $\mu\text{L}$  of filtered analyte was injected into the HPLC instrument (Waters, Milford, MA). The mobile phase used was 0.005 M sulfuric acid (99.999% HPLC grade, Sigma–Aldrich) with a flow rate of 0.6 mL/min. An Aminex HPX-87H (Bio-Rad Laboratories Inc., Hercules, CA) sugars and alcohols column heated at 55 °C was used to separate DMC (retention time 24.7 min) from methanol (retention time 18.6 min). The separated components were detected using a Waters 410 Differential Refractometer (Waters, Milford, MA) held at 35 °C. The assignment of DMC and methanol was confirmed both based on retention time using DMC (99 + % extra dry, Acros Organics) and methanol references. The concentration of DMC in the product mixture was determined by integrating the area of the peak at 24.7 min and comparing the resulting area with external DMC standards.

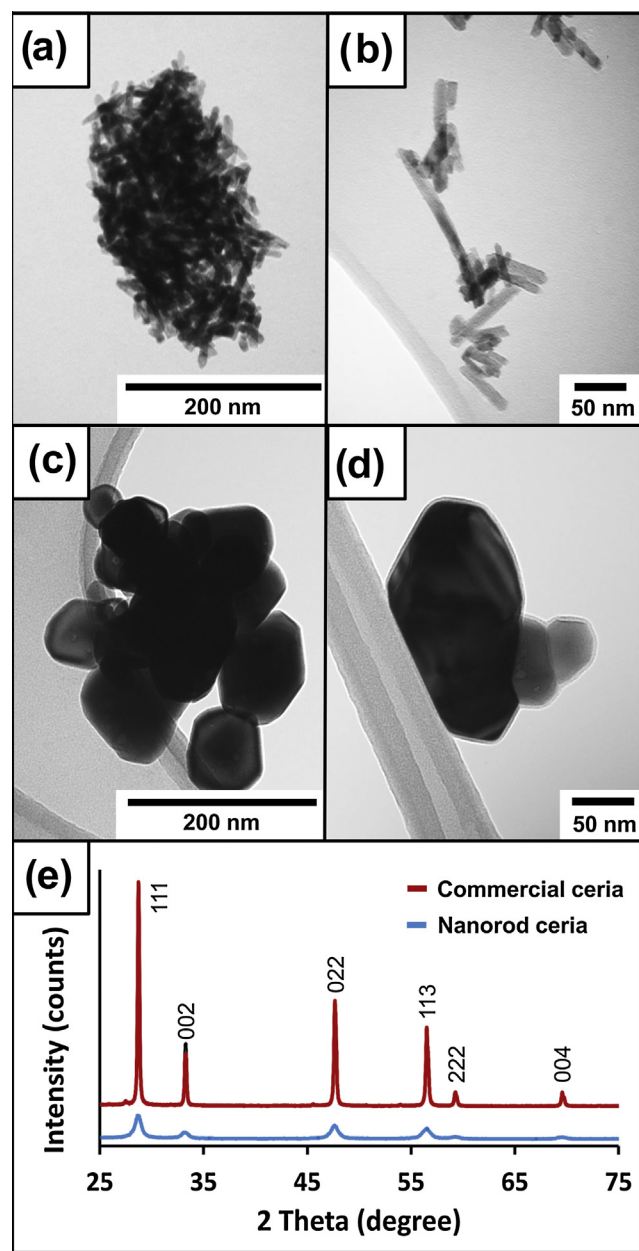
#### 2.6. Physical characterization of the catalysts

The crystal structure of the as-synthesized catalyst samples was determined using powder X-ray diffraction (PANalytical Empyrean, Westborough, MA) using a Cu K $\alpha$  source with an average wavelength of 1.544 Å. Diffraction peak assignments were indexed using the ICDD data card #04-016-6171. The surface area was measured by Brunauer–Emmett–Teller (BET) analysis using a Micromeritics ASAP 2460 surface area and porosity analyzer (Micromeritics, Norcross, GA) and nitrogen. The degasification process was performed at 250 °C for 1000 min and the BET analysis was performed at 77 K. Morphological analysis of the catalyst microscale and nanoscale structure was made by transmission electron microscopy (TEM; Hitachi H7500, Pleasanton, CA) operating at 80 kV.

### 3. Results and discussion

#### 3.1. Structural characterization of the catalysts

The morphological and atomic structure of the as-synthesized ceria nanorods catalyst was studied by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). Our TEM analysis revealed that the synthesized nanorods had a range of lengths from  $\sim 50$  to a few hundred nanometers (Fig. 2a and b). Due to their one-dimensional structures, even when the nanorods stick together, the resulting agglomerate remained porous instead of close packed (Fig. 2a). For comparison, the REacton<sup>®</sup> commercial ceria noticeably agglomerates to large clusters (Fig. 2c). Isolated



**Fig. 2.** (a) TEM image of a typical ceria nanorod agglomerate. Note the large pores that remain present as a consequence of the large aspect ratio of the rods. (b) TEM image of isolated nanorods after sonication for dispersion. (c) TEM image of a typical commercial ceria agglomerate. (d) TEM image of isolated ceria particles. (e) XRD pattern of the nanorod and commercial ceria used in this study. Labeled peaks are for fluorite-structured  $\text{CeO}_2$ .

nanoparticles were observed to have flat facets and displayed a range of particle sizes (Fig. 2d). As shown in the XRD pattern in Fig. 2, the crystal structures of both ceria catalysts are well-matched to that of fluorite-structured  $\text{CeO}_2$ . No diffraction lines due to impurities were detected by XRD for the nanorod samples. However, a very small amount of unidentified impurity (likely another lanthanide) was observed in the commercial ceria as indicated by the small satellite lines. The relatively broad diffraction line widths observed for the nanorod ceria are characteristic of nanoscale crystallites which have an average crystallite size of 13 nm by Rietveld analysis. In contrast, the commercial ceria gave very sharp intense lines, with a Rietveld analysis yielding a 77 nm crystallite size. Note that the 3-dimensional network structures of nanorods allowed them to have a large BET surface area of  $82.3 \pm 0.2 \text{ m}^2/\text{g}$  even after calcining for 4 h at  $400^\circ\text{C}$ . This BET surface area of nanorods only slightly decreased to  $76.6 \pm 0.1 \text{ m}^2/\text{g}$  after their use for catalysis ( $125^\circ\text{C}$  and 2000 psi for 1 h with 15 mL methanol). Such a small decrease of catalyst surface area demonstrates the excellent robustness of the nanorod catalysts to the pressures utilized in this study. For comparison, the commercial ceria particles had a BET surface area of  $8.1 \pm 0.1 \text{ m}^2/\text{g}$ , which decreased to  $4.3 \pm 0.2 \text{ m}^2/\text{g}$  after use as a catalyst.

### 3.2. Effect of temperature on the reaction profile

From a thermodynamic standpoint, the conversion of  $\text{CO}_2$  and methanol to DMC is expected to be unfavorable at high temperatures.



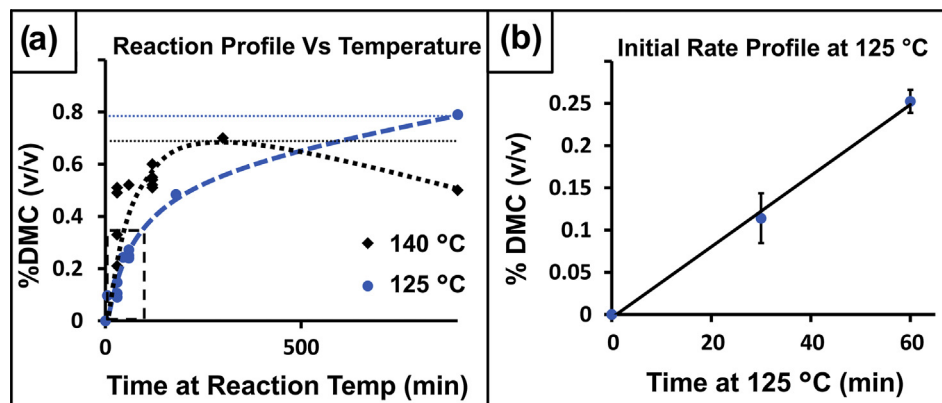
Note that Eq. (1) is a thermodynamic equation showing the phases of the initial and final states of matter of the reactants and products. It does not indicate the phases of reactants during the chemical reaction (which is a supercritical solution). From Eq. (1), the overall reaction results in a large decrease in entropy ( $\Delta S$ ) both in terms of three moles of reactants forming two moles of products, as well as from the overall change from gas and liquid reagents to purely liquid products. This is characteristic of all  $\text{CO}_2$  (gas) to organic carbonate (liquid) reactions. Fortunately, the enthalpy change ( $\Delta H$ ) is also negative ( $-20 \text{ kJ/mol}$  [16]), making the overall direct synthesis of DMC an enthalpy driven process. Although the system is not quite a constant pressure process, it is helpful to think of the system in terms of Gibbs free energy ( $\Delta G$ ) in accordance with Eq. (2):

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Since a reaction is only spontaneous when  $\Delta G$  is negative, a negative  $\Delta H$  and a negative  $\Delta S$  suggest that the reaction only favors products at low temperatures. To examine this deduction, we prepared a series of direct DMC synthesis experiments at two different reaction temperatures ( $125$  and  $140^\circ\text{C}$ ) but with consistent amounts of methanol (15 mL) and ceria nanorod catalyst (0.10 g) in order to compare the reaction profiles with respect to temperature (Fig. 3).

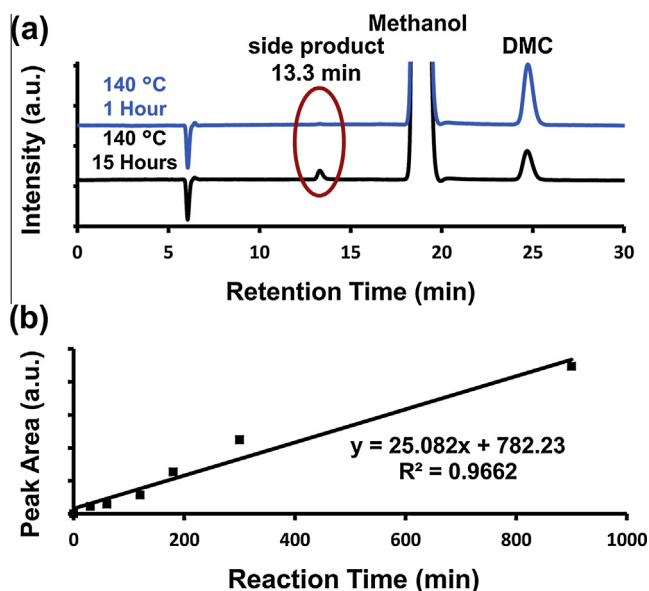
Although our reactor was equipped with a sampling coil, we found that the decrease in pressure with each sampling ( $\sim 100$  psi drop) impacted the overall equilibrium value of DMC. Sampling multiple data points in series would have a drastic impact on the reaction profile because the vented  $\text{CO}_2$  could not be restored. Instead of sampling a series of data points from a single run, the reaction profiles shown in Fig. 3 are reconstructed from the end product concentrations observed from 24 separate experiments. As illustrated in Fig. 3, the reaction profiles at both temperatures show a linear initial region, followed by an apex as the equilibrium DMC concentration is approached. As predicted from thermodynamics, a reduced reaction temperature leads to a higher equilibrium product concentration. However, given enough time at elevated temperatures, the DMC concentration begins to decrease instead of simply plateauing. From our HPLC analysis, this observation was attributed to a slow formation of at least one major side product as seen in Fig. 4. However, it is worth pointing out that our HPLC method cannot detect all possible side products because we are only sampling the liquid remaining after venting off the gaseous chemicals in the reactor. Additionally, the catalytic decomposition of DMC with temperature was previously observed and discussed in the formation of DMC from carbon monoxide and methanol by Anderson et al. [25].

The side product observed at 13.3 min was largely visible as a consequence of the excellent limits of detection (down to 4 ppm for organic carbonates) made possible by the ion-moderated partition high performance liquid chromatography (HPLC) method utilized for the sample analysis [26]. Furthermore, this HPLC method allowed for low ( $55^\circ\text{C}$  column) temperatures for the analysis and thus allowed us a better opportunity to observe volatile or fragile side products than when the samples were analyzed by GC-MS. As shown in Fig. 4, the concentration of the observed side product increased linearly with reaction time, suggesting that its production followed a pseudo-zeroth order reaction. While the formation of this side product was trivial in the initial rate region for the reaction, the continued formation of side products significantly impacts the reaction profile once DMC production slows as equilibrium is neared and leads to a gradual decrease in DMC yield over



**Fig. 3.** (a) Concentration of DMC product in percent by volume versus reaction time at (black diamonds)  $140^\circ\text{C}$  and (blue dots)  $125^\circ\text{C}$ . All 24 reaction runs shown were performed with 0.10 g of ceria nanorods, 15 mL of methanol and a reaction pressure of  $2000 \pm 100$  psi. Each data point is from a separate reaction run. Dashed line box shows the initial rate region used for this study. (b) Reaction profile at  $125^\circ\text{C}$  showing the linear initial rate profile. Data points shown are the average concentrations from reactions of 30 and 60 min long. Error bars are one standard deviation.



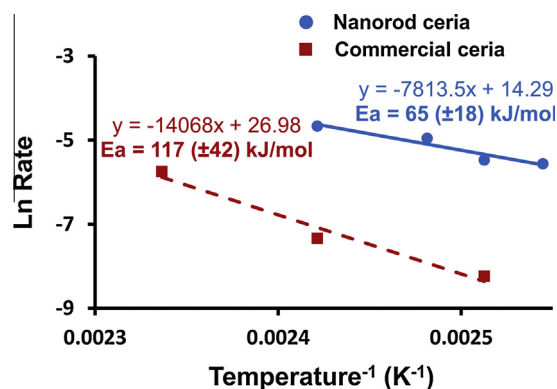


**Fig. 4.** (a) HPLC chromatograms of product mixtures from the direct synthesis of DMC with ceria nanorods catalysts at 140 °C after reaction times of 1 h and 15 h. Note that the increasingly large side product peak is visible at the retention time of 13.3 min. (b) Kinetics for the side product identified at 13.3 min. Peak area increases largely linearly with respect to time at 140 °C.

time. This introduces complexity to the overall reaction profile, again highlighting the importance of acquiring kinetics information from the relatively clean initial rate region. Also, it is worth pointing out that the same trace impurities were observed in the HPLC chromatograms of the products obtained both from using the commercial ceria catalyst and the nanorod catalyst.

From Fig. 3, using the ceria nanorod catalyst, a decrease in temperature of merely 15 °C is enough to half the initial rate for the reaction from 0.0087% DMC/min to just 0.0042% DMC/min. Since the reaction profile at 140 °C stays linear for only the first 30 min and well past 60 min for temperatures below 140 °C, the initial rate was measured at 120, 125, 130, and 140 °C by collecting samples at 30 and 60 min. The results are summarized in the Arrhenius plot in Fig. 5.

A linear fit of the Arrhenius plot shows a slope of  $-7814$ , which indicated an apparent activation energy of  $65 \pm 18$  kJ/mol for the ceria nanorod catalyst, while the y-intercept indicates a pre-



**Fig. 5.** Arrhenius plot composed of initial rate data for the direct synthesis of DMC with (blue solid circles) ceria nanorod catalysts and (red solid squares) commercial ceria. Rates were measured in volumetric % DMC per minute. The apparent activation energy ( $E_a$ ) of this reaction was found to be  $65 \pm 18$  kJ/mol for the ceria nanorod catalyst and  $117 \pm 42$  kJ/mol for the commercial ceria. Error ranges are at the 70% confidence interval.

exponential factor of  $1.6 \times 10^6$ . This value of apparent activation energy is far lower than that previously reported for a non-nanostructured ceria catalyst (106 kJ/mol) [16]. For comparison, initial rate experiments were run using highly crystalline commercial ceria at 125, 140, and 155 °C, with a resulting apparent activation energy of  $117 \pm 42$  kJ/mol, consistent with previous measurements. This strongly suggests that the structure of the ceria nanorods is improving the catalytic activity of ceria beyond the improvements in surface area alone. However, 65 kJ/mol is still a substantial activation barrier. Consequently, reaction conditions have to be chosen as a compromise between low yields at fast rates with high temperatures, or theoretically higher yields at lower temperatures that nonetheless are never obtained due to poor kinetics.

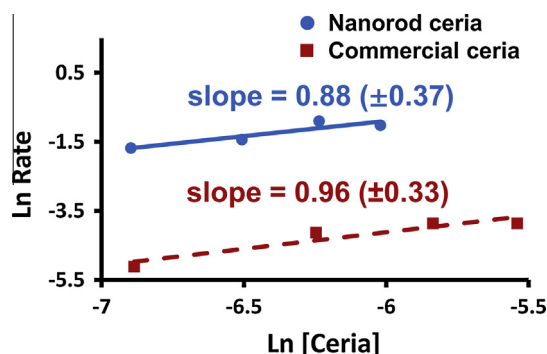
### 3.3. Initial rate kinetic studies

In an effort to improve reaction rates at reduced reaction temperatures, we have attempted to experimentally determine the rate law equation for conversion of  $\text{CO}_2$  and methanol ( $\text{MeOH}$ ) to DMC exclusively using initial rate kinetics for both ceria nanorods and commercial ceria catalysts. The general rate equation takes the form:

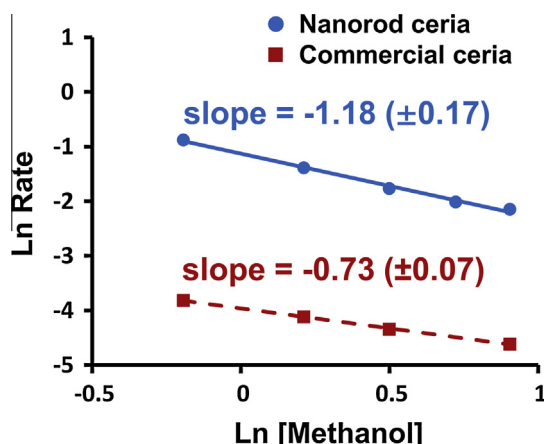
$$\text{Rate} = k[\text{CO}_2]^a [\text{MeOH}]^b [*]_0^c \quad (3)$$

where  $k$  is the experimental rate constant for the overall reaction,  $[*]_0$  indicates the concentration of catalyst active sites, and  $a$ ,  $b$ , and  $c$  are experimentally determined constants. While the rate constant is strictly controlled by the temperature, pressure, activation energy, and activation volume, the overall rate is also a function of the concentration of reactants and catalyst loading. In order to estimate the order of the reaction with respect to each reagent, we conducted a series of initial rate experiments in which the loading of ceria and amount of methanol were varied while maintaining a constant 2000 psi reaction pressure, consistent amounts of  $\text{CO}_2$ , and a consistent reaction temperature of 125 °C. Since the initial rate region remains well behaved and linear for well over 60 min at these conditions, the reaction was stopped at 30 or 60 min for each initial rate experiment and the concentration of DMC in the products was quantified by HPLC. The results of these experiments are shown as log-log plots in Figs. 6 and 7.

As expected, there is a positive direct relationship between the concentrations of catalyst in the reactor versus the initial rate as the catalyst loading is increased from 0.05 g to 0.20 g (Fig. 6). As the increased reaction rate with catalyst loading risked running



**Fig. 6.** Kinetics study of the initial rate of DMC production versus ceria nanorod catalyst loading. All experiments were performed using 15 mL of methanol at 125 °C and 2000 psi. The concentration of DMC was sampled after a one hour reaction for the bulk ceria, and after 30 min for the nanorod ceria. Rates were measured in volumetric % DMC per hour and concentration of ceria is expressed as molarity. Blue solid circles: ceria nanorod catalyst; red solid squares: commercial bulk ceria. Slope errors assuming a 70% confidence interval.



**Fig. 7.** Kinetics study of the initial rate of DMC production versus methanol loading. All experiments used 0.1 g of ceria and were performed at 125 °C and 2000 psi with the concentration of DMC sampled after a one hour reaction. Rates were measured in volumetric % DMC per hour and concentration of methanol is expressed as molarity. Blue solid circles: ceria nanorod catalyst; red solid squares: commercial bulk ceria. Slope error assuming a 95% confidence interval.

the DMC concentration into thermodynamic limits for ceria nanorod loadings greater than 0.1 g, the rate measurements were stopped at just 30 min for the nanorod loading experiments. This ensured that we remained in the initial rate region of the reaction profile. For comparison, we ran these experiments with both the ceria nanorod and commercial ceria catalyst. A log–log plot of the rate versus catalyst concentration (in molarity) reveals a reaction order of +0.88 for the ceria nanorods and +0.96 for the commercial ceria. Within experimental error, this is approximately a +1 reaction order for both catalysts, suggesting that both ceria catalysts are behaving as a heterogeneous catalyst without major mass transport limitations.

Surprisingly, the initial rate had an inverse relationship with the concentration of methanol added, with a log–log plot giving a slope of  $-1.18$  for the nanorod catalyst, and  $-0.73$  for the commercial ceria as methanol loading increased from 10 to 30 mL (Fig. 7).

Approximately, this is a  $-1$  reaction order for both catalysts. This indicates that methanol is competing with the reagents that are involved in the rate controlling step, namely  $\text{CO}_2$ . As a whole, these results suggest that the observed experimental rate equation is roughly:  $\text{Rate} = k[\text{CO}_2]^{a(>0)} [\ast]_0^{-1} [\text{MeOH}]^{b(-1)}$  with the concentration of methanol likely competing for the same surface sites as  $\text{CO}_2$  negatively impacting the reaction rate.

### 3.4. Mechanistic insights

Our kinetics studies provide experimental evidence that helps to clarify the reaction mechanism of the direct synthesis of DMC from  $\text{CO}_2$  and methanol. The fact that the rate of the reaction is strongly impacted by the amount of catalyst present suggests that the rate controlling step in the reaction occurs on the catalyst surface. For methanol to not positively factor into the experimental rate law, the adsorption of  $\text{CO}_2$  on the catalyst surface has to be occurring in a separate elementary step than the adsorption of methanol. This is consistent with a Langmuir–Hinshelwood (LH) type mechanism since it reveals that the  $\text{CO}_2$  and methanol must be interacting with the catalyst in two separate steps with the  $\text{CO}_2$  adsorption rate determining. Fig. 8 compares two typical reaction mechanisms for heterogeneously catalyzed reactions proposed in the literature: the Langmuir–Hinshelwood (LH) mechanism and the Eley–Rideal (ER) mechanism [16,18]. Shown in Fig. 8 are the elementary steps for two previously proposed reaction mechanisms along with the apparent rate law expression that we would expect to observe if the given step were rate determining and the previous steps relatively rapid (see Supplementary Information for the derivations). Note that the concentration of methanol necessarily appears in the apparent rate laws for any of the later reaction steps after the adsorption of  $\text{CO}_2$  in the LH mechanism (Step 1) while also appearing in every apparent rate law derived from the shown ER mechanism. Also note that for simplicity's sake, the rate law is still shown in terms of available catalyst sites  $[\ast]$ . However, changing the catalyst loading directly varies the total catalyst sites  $[\ast]_0$  which is equal to the available catalyst sites plus the occupied catalyst sites.

| Langmuir–Hinshelwood (LH) mechanism |                                                                                                            |                                                  | Eley–Rideal (ER) mechanism                                                                    |                                                |
|-------------------------------------|------------------------------------------------------------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------------------------------------------------|------------------------------------------------|
|                                     |                                                                                                            |                                                  |                                                                                               |                                                |
| Step                                | Elementary reaction step                                                                                   | Rate law if rate determining                     | Elementary reaction step                                                                      | Rate law if rate determining                   |
| 1                                   | $\text{CO}_2 + \ast \rightleftharpoons \text{CO}_2^\ast$                                                   | $R = k [\text{CO}_2] [\ast]$                     | $\text{MeOH} + \ast \rightleftharpoons \text{MeOH}^\ast$                                      | $R = k [\text{MeOH}] [\ast]$                   |
| 2                                   | $\text{MeOH} + \ast \rightleftharpoons \text{MeOH}^\ast$                                                   | $R = k [\text{MeOH}] [\ast]$                     | $\text{MeOH}^\ast + \text{CO}_2 \rightleftharpoons \text{MC}^\ast$                            | $R = k [\text{MeOH}] [\text{CO}_2] [\ast]$     |
| 3                                   | $2\text{MeOH}^\ast + \text{CO}_2^\ast \rightleftharpoons \text{DMC}^\ast + \text{H}_2\text{O}^\ast + \ast$ | $R = k [\text{CO}_2] [\text{MeOH}]^2 [\ast]^3$   | $\text{MC}^\ast + \text{MeOH}^\ast \rightleftharpoons \text{DMC} + \text{H}_2\text{O} + \ast$ | $R = k [\text{CO}_2] [\text{MeOH}]^2 [\ast]^2$ |
| 4                                   | $\text{DMC}^\ast \rightleftharpoons \text{DMC} + \ast$                                                     | $R = k [\text{MeOH}] [\ast] [\text{CO}_2]^{1/2}$ |                                                                                               |                                                |
| 5                                   | $\text{H}_2\text{O}^\ast \rightleftharpoons \text{H}_2\text{O} + \ast$                                     | $R = k [\text{MeOH}] [\ast] [\text{CO}_2]^{1/2}$ |                                                                                               |                                                |

$\ast$  = available catalyst active site

MC = methyl carbonate

**Fig. 8.** Elementary mechanistic steps previously proposed for the formation of DMC from  $\text{CO}_2$  and methanol by a Langmuir–Hinshelwood and an Eley–Rideal mechanism [16,18]. Apparent rate law was shown for each step if the given step was significantly slower than the preceding step(s). See Supplementary Information for rate law derivations.

In order to derive the reaction rate law with respect to the total catalyst sites, a few assumptions must be made. If the adsorption of CO<sub>2</sub> is slow while the adsorption of methanol is fast, then the catalyst surface is likely saturated with adsorbed methanol as the most abundant reactive intermediate (*mari*). This is very similar to what is observed in the Haber process where the reaction between the relatively energetic H<sub>2</sub> molecule is limited by the rate of adsorption of the very stable N<sub>2</sub> molecule on the catalyst surface in a Langmuir–Hinshelwood (LH) mechanism. In the Haber process, such adsorption phenomena results in a positive rate order with respect to N<sub>2</sub>, and a reaction order of  $-1$  with respect to H<sub>2</sub> [27,28]. Similarly, if we assume that methanol is the *mari* in our system, then the total concentration of surface sites  $[*]_0 \approx [\text{MeOH}^*] + [*]$ . Assuming that step 1 of the LH mechanism as shown is the rate determining step, the derived rate law expression for the conversion of CO<sub>2</sub> to DMC is:

$$\text{Rate} = \frac{k_1 [\text{CO}_2] [*]_0}{K_2 [\text{MeOH}] + 1} \quad (4)$$

where  $k_1$  is the rate constant for the first elementary step and  $K_2$  is the equilibrium constant for step 2 (see Supplementary Information for derivations). This rate law is in excellent agreement with our initial rate kinetics with a  $+1$  reaction order with respect to the catalyst and CO<sub>2</sub>, and a reaction order of  $\sim -1$  with respect to methanol. Note that as a consequence of the denominator being a polynomial expression ( $K_2 [\text{MeOH}] + 1$ ), the logarithm of the rate versus methanol loading should vary between 0 and  $-1$ . If the magnitude of  $K_2$  or the molar concentration of methanol is small, the  $+1$  term becomes significant and the  $\ln(1)$  is defined as 0. Conversely, if the product of  $K_2 [\text{MeOH}]$  is much larger than 1, the function approaches a  $-1$  rate order. Consequently, the difference in the observed reaction orders with respect to methanol may be a consequence in the difference in the methanol adsorption equilibrium constants ( $K_2$ ) over the two different catalysts. However, a detailed study of the initial rate with varying CO<sub>2</sub> partial pressures (but constant total pressure) is still recommended for further verification of the derived first reaction order with respect to CO<sub>2</sub>.

The discussed initial reaction rate kinetics experiments strongly suggest that the conversion of methanol and CO<sub>2</sub> to DMC over ceria catalysts follows a Langmuir–Hinshelwood mechanism where the CO<sub>2</sub> and methanol are binding to the catalyst in separate steps, consistent with previous kinetics studies modeling the reaction from the reaction profile [16]. Interestingly, this result contrasts with that shown for the production of DMC from methanol and carbon monoxide over copper zeolite catalysts, which were found to have a non-negative rate order with respect to methanol and are believed to follow an ER mechanism [29]. This suggests that the production of DMC from CO<sub>2</sub> instead of CO may take a very different pathway for the production of DMC despite the apparent similarity of the overall reaction.

#### 4. Conclusions

The reaction profile and kinetics were studied for the direct conversion of CO<sub>2</sub> and methanol into dimethyl carbonate over ceria nanorod catalysts along with a commercial ceria catalyst. The nanorod catalysts were found to have an activation energy barrier of  $65 \pm 14$  kJ/mol, substantially lower than the 106 kJ/mol previously reported for bulk ceria [16], or the  $\sim 117$  kJ/mol that we measured for commercial ceria. Consistent with an enthalpy driven reaction, reduced temperatures were found to favor DMC formation, although the reaction remained limited by slow kinetics. Taking advantage of the slow reaction rates at lower reaction temperatures, a method of initial rates approach was successfully utilized. The rate order with respect to ceria was  $\sim 1$  (experiment:

$+0.88$  ceria nanorods;  $+0.96$  commercial ceria), while that of methanol was  $\sim -1$  (experiment:  $-1.2$  nanorods,  $-0.73$  commercial). These results are consistent with a Langmuir–Hinshelwood type mechanism where the CO<sub>2</sub> and methanol must first interact with the solid catalyst in two separate steps with the CO<sub>2</sub> adsorption step being rate controlling. These results suggest that the kinetics for the conversion of CO<sub>2</sub> and methanol to DMC could best be improved by (1) maximizing the surface area of the ceria nanorod catalysts, (2) reducing the energy barrier required for CO<sub>2</sub> adsorption and activation mechanism step, and (3) conducting the reaction with a low ratio of methanol to CO<sub>2</sub> in the feed gas.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2016.06.003>.

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