



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



Chris M. Marin, Lei Li, Anuja Bhalkikar, James E. Doyle¹, Xiao Cheng Zeng, Chin Li Cheung*

Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, USA

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ABSTRACT

The direct conversion of carbon dioxide (CO₂) 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 CO₂ 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 CO₂ and methanol adsorption occurs in separate reaction steps.

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1. Introduction

The direct synthesis of dimethyl carbonate (DMC) from carbon dioxide (CO₂) and methanol (MeOH) has drawn intense interest because both chemicals are abundant, renewable and relatively inexpensive. CO₂ 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 CO₂ 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 CO₂ to form methanol [5]. Thus, the direct synthesis of DMC from CO₂ and methanol has the potential to remove three moles of CO₂ 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 CO₂ and methanol to DMC has attracted considerable attention for both environmental and commercial reasons.

Numerous catalysts have been explored for the direct conversion of CO₂ and methanol to DMC. These catalysts include Co_{1.5}-PW₁₂O₄₀ [10], K₂CO₃ [11], KOH [11], ZrO₂ [12], and CeO₂ [13–16]. As an excellent catalyst support with both Lewis acid and base properties, ceria in particular has been extensively studied after doping with Al₂O₃ [15], ZrO₂, Ga₂O₃, Ni₂O₃, Fe₂O₃, and other lanthanide elements [17]. Unfortunately, the direct conversion of CO₂ 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 CO₂ [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 CO₂ is generated.

* Corresponding author.

E-mail address: ccheung2@unl.edu (C.L. Cheung).

¹ Current address: Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, USA.

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 CO₂ reactions are difficult because these reactions have a significant activation volume (Δv^\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 CO₂ and methanol into DMC using ceria nanorods and highly crystalline commercial ceria as the catalysts. As the synthesis of DMC from CO₂ 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 (Solvol). 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[®] 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 CO₂ 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 CO₂ (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.

CO₂ 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 CO₂ 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 CO₂. 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 CO₂ is known to be in the supercritical state above 74 bar and 31 °C, and CO₂ is the reaction solvent, we do not expect there to be an issue with mass transport between phases. This lack of a

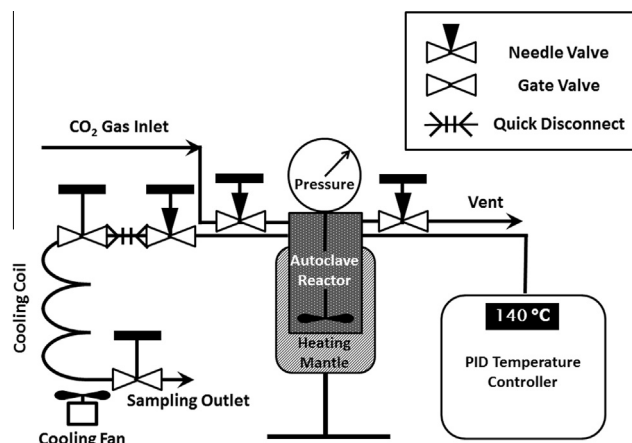


Fig. 1. Schematic diagram of the experimental setup used in this study. Reactor was pressurized with a direct connection to a compressed CO₂ gas tank.

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