

Continuous DMC Synthesis from CO₂ and Methanol over a CeO₂ Catalyst in a Fixed Bed Reactor in the Presence of a Dehydrating Agent

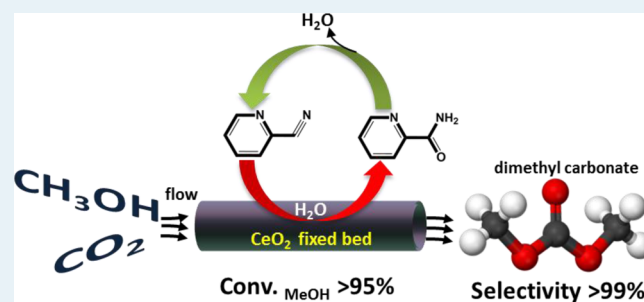
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Supporting Information

ABSTRACT: Methanol and carbon dioxide are continuously and efficiently converted to dimethyl carbonate (DMC) over a CeO₂ catalyst using 2-cyanopyridine as a recyclable dehydrating agent in a fixed bed reactor. The process was operated over a wide range of pressure (1–300 bar) by feeding CO₂ and the stoichiometric amount of methanol and 2-cyanopyridine mixture into the reactor. The study shows a successful demonstration of direct DMC synthesis mediated by a dehydrating agent with outstanding methanol conversion (>95%) and dimethyl carbonate selectivity (>99%) under optimized conditions. Remarkably higher reaction rates were achieved compared to those in batch operation.

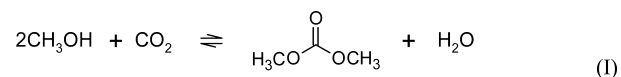
KEYWORDS: heterogeneous catalysis, CO₂ conversion, dimethyl carbonate, dehydrating agent, 2-cyanopyridine, high pressure, methanol conversion, continuous flow, fixed bed reactor



Utilization of carbon dioxide in many industrially relevant chemical reactions has gained considerable attention. This is largely driven by the fact that CO₂ is one of the most suspected greenhouse gases responsible for climate change and also by its increasingly vast availability from the CO₂ capture facilities. One promising strategy to convert a large amount of CO₂ is to produce fundamental and highly demanded chemicals like fuels such as methanol. Recently we reported an almost complete one-pass conversion of CO₂ to methanol via hydrogenation, taking advantage of high pressure reaction conditions.¹ Other pathways have been actively investigated and are considered industrially viable in some cases by making use of this renewable source of carbon to improve the present industrial processes safer and greener.²

Among nonreductive CO₂ transformation pathways, synthesis of organic carbonates, particularly dimethyl carbonate (DMC), is of wide interest due to its attractive chemical characteristics. DMC has been employed as electrolytes in lithium ion batteries and used as aprotic polar solvent.³ Owing to the high octane number, low RVP (Reid vapor pressure), and reduced CO and NO_x emissions, DMC has gained much attention as a fuel additive.⁴ Also, DMC can act as a nontoxic methylating and carbonylating agent or as an intermediate in the production of higher carbonates, polyurethanes, isocyanates, and polycarbonates.⁵ DMC has been produced by reacting methanol, traditionally with phosgene and more recently with carbon monoxide by oxidative carbonylation.⁴ The major drawbacks of the former process are the high toxicity of phosgene and the disposal of the coproduced hydrogen chloride, while that of the latter is catalyst

deactivation at high conversion besides the use of toxic CO. Hence, the direct synthesis of DMC from methanol and CO₂ (Reaction I) is considered one of the most promising routes for future DMC production yielding water as the only byproduct, meeting ecological restrictions as well as economically viability.



Although both homogeneous and heterogeneous catalysts are effective in this reaction,⁶ heterogeneous catalysts are generally preferred for the general advantage of separation and scale up. Among metal oxides, CeO₂ and ZrO₂ were found consistently active in this reaction.⁷ There are several reports where a fixed bed reactor was employed using various types of heterogeneous catalysts, such as carbon supported Cu/Cu–Ni,⁸ Cu–Ni or H₃PO₄ modified V₂O₅,⁹ metal oxide supported Rh,¹⁰ and heteropolyacids.¹¹ The methanol conversion reported in these works was in the range of 5–10% with mild-to-high DMC selectivity (60–90%), although a much lower methanol conversion value should be expected according to thermodynamics.¹² It is very important to realize that thermodynamics plays a decisive and probably more critical role in the synthesis of DMC from CO₂ and methanol, limiting the reactant

Received: August 19, 2014

Revised: September 26, 2014

Published: September 29, 2014

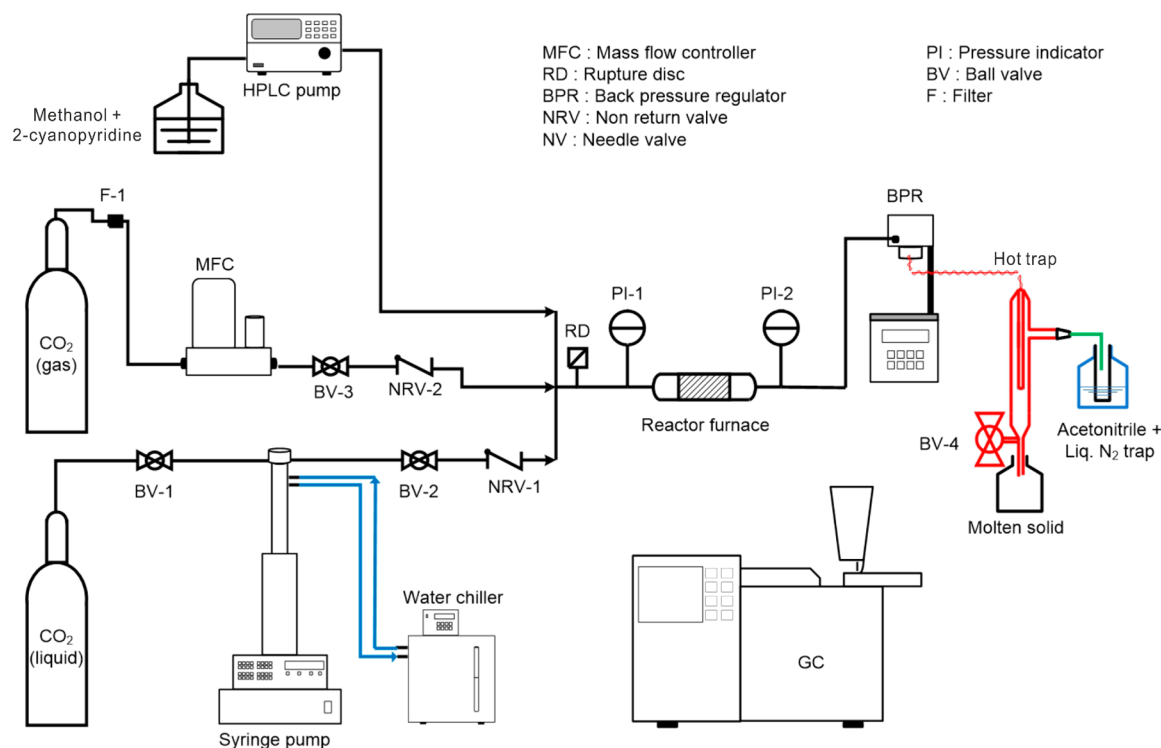


Figure 1. Schematic process flow diagram of the reaction system for the continuous production of DMC.

conversion lower than 1% even at favorable high pressure conditions (150–200 bar).¹²

According to Reactor I, the catalytic activity can be boosted by water removal using an adequate dehydrating strategy or by increasing the CO₂ concentration using a high pressure approach. Among several strategies reported, simple dehydration of methanol before the reaction,¹³ the use of organic molecules as a dehydrating agent,¹⁴ incorporation of a dehydration unit filled with inorganic (zeolite) materials,¹⁵ and the use of a membrane reactor for selective water removal¹⁶ have been attempted. Using a membrane reactor to shift the equilibrium by removing water *in situ*, 10% methanol conversion and 96% DMC selectivity have been achieved.¹⁶

Recently, Tomishige and co-workers examined the use of various dehydrating agents for direct conversion of methanol and CO₂ to DMC over ceria catalyst in a batch system.¹⁷ The use of 2-cyanopyridine as a dehydrating agent resulted in an excellent catalytic activity, by far the highest to the best of our knowledge, 94% DMC yield with 99% selectivity.¹⁷ Importantly, 2-picolinamide, formed from the reaction between 2-cyanopyridine and water, was shown to be recyclable back to 2-cyanopyridine by a dehydration reaction over a catalyst,¹⁷ although the regeneration process was rather slow and further optimization is necessary to evaluate the feasibility of the overall process. The same authors recently reported mechanistic insights into the reaction and also a wider substrate scope (various alcohols) of the dehydration strategy.¹⁸ It was shown that the reaction proceeds with a similar mechanism in the presence and absence of the dehydrating agent.¹⁸

Nevertheless, the studies involving organic dehydrating agents have so far been performed in high pressure batch reactor setups. The major disadvantages of batch versus continuous flow processes are less control over the process variables, frequent catalyst recovery, and associated process complexity. Furthermore, typically required long reaction times

of batch processes could result in secondary reactions, possibly reducing the desired product yield.

In this communication, we report a high pressure catalytic process using a fixed-bed reactor for extremely efficient, continuous production of DMC from CO₂ and methanol over a ceria catalyst in the presence of 2-cyanopyridine as a dehydrating agent.

2-Picolinamide is a solid at room temperature and atmospheric pressure with high melting and boiling points (ca. 105 and 284 °C, respectively), whereas 2-cyanopyridine has relatively low melting and high boiling points (ca. 28 and 213 °C, respectively). The major challenge to perform a continuous reaction forming 2-picolinamide is to avoid blockage of the flow in the reaction system. Moreover, due to the very different melting and boiling points of the reactants and products, obtaining the reaction products in suitable and well separated forms, being ready for the analytical system, brings another challenge. The reaction system used in this study is a modified version of a high pressure CO₂ hydrogenation setup.¹⁹ Figure 1 shows the schematic process flow diagram of the reaction system capable of performing reactions from atmospheric pressure up to 400 bar. It is equipped with a HPLC pump (Jasco, PU-2080) to feed the methanol and 2-cyanopyridine mixture. CO₂ was passed to the system using a thermal mass flow controller (Bronkhorst) or using a high pressure liquid syringe pump (Teledyne Isco, 260D), depending on the desired operating pressure. A back pressure regulator (BPR, Jasco, BP-2060) connected after the outlet of the reactor tube maintained the pressure inside the reactor. All the transfer lines and components after the reactor were heated at 180 °C to avoid solid formation. Especially the heating of the BPR with ensured proper functionality was important, and a modification to the BPR was made to allow sufficient heating at the position where the fluid passed through.

To begin with the reaction, 300 mg of sieved (100–300 μm) CeO_2 catalyst was charged into the reactor tube (ID: 1.74 mm, OD: 3.17 mm) with the catalyst bed length of ca. 7.5 cm. The dehydrating agent, 2-cyanopyridine, was dissolved in methanol at the stoichiometric molar ratio (2-cyanopyridine:methanol = 1:2).¹⁷ First, the reactor was pressurized with CO_2 to a desired reaction pressure, and then CO_2 and the methanol+2-cyanopyridine mixture were passed over the catalyst bed. The flow rate of CO_2 was kept at 6 NmL/min and that of methanol+2-cyanopyridine was at 10 $\mu\text{L}/\text{min}$ at room temperature and atmospheric pressure, giving the molar ratio of methanol: CO_2 of 1:2.5. Estimated space time is described in the Supporting Information. Feed stabilization and the reaction were performed within 12 h. Separation of methanol-derived products (DMC, methyl carbamate, methyl picolinate) was achieved by maintaining the hot trap at 180 $^\circ\text{C}$ where high boiling compounds such as 2-cyanopyridine and 2-picolinamide were trapped. Following the hot trap, the outlet stream was passed to a U shaped glass condenser maintained at ca. -41 $^\circ\text{C}$ (acetonitrile+liquid N_2 mixture). The product analysis was performed by GC (Bruker 450) using ethanol as solvent and 1-hexanol as an internal standard. The error in the quantification of methanol and DMC due to evaporation and condensation was found to be $\pm 10\%$. The product identification was aided by GC-MS analysis. Herein only the products directly or indirectly originated from methanol above the trace level were quantified and discussed; hence the product selectivity was calculated based on methanol.

Figure 2 shows the effect of pressure on methanol conversion and product selectivity at 120 $^\circ\text{C}$. Obviously, the reaction

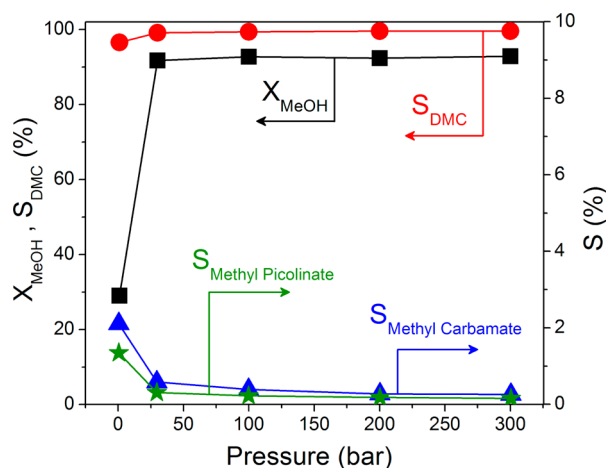


Figure 2. Effect of pressure on methanol conversion and product selectivity at 120 $^\circ\text{C}$.

pressure had a drastic impact on methanol conversion. Thanks to the highly reactive dehydrating agent, even at 1 bar the conversion was 27%, which is excellent as compared to the values obtained for direct conversion of methanol and CO_2 in a fixed bed reactor (without the dehydrating agent the conversion increased with the reaction pressure but at the level of ca. 1% at even 400 bar; results are not shown). DMC selectivity was found to be 96.5% along with formation of methyl carbamate and methyl picolinate at selectivity of 2.1% and 1.3%, respectively. Increase in pressure up to 30 bar resulted in outstanding conversion of 92% with enhanced DMC selectivity of $>99\%$, suppressing the formation of methyl

carbamate and methyl picolinate. Surprisingly, further pressure increase above 30 bar did not improve the conversion values except for a slight suppression of the byproducts. This implies that above 30 bar the conversion is independent of pressure and that the residence time is sufficiently large due to reactants compression under the high pressure conditions.

Figure 3 depicts the effect of reaction temperature on catalytic activity in the presence of 2-cyanopyridine at 200 bar.

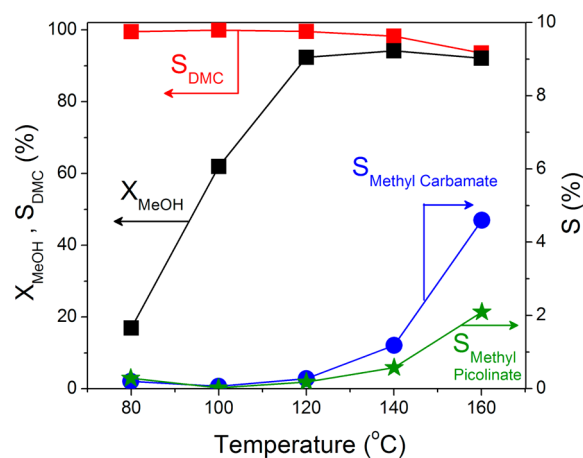
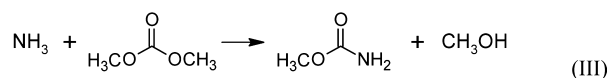
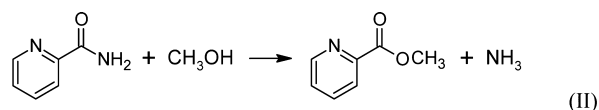


Figure 3. Effect of the temperature on methanol conversion and product selectivity at 200 bar.

With temperature increase, methanol conversion was drastically increased from 17% (80 $^\circ\text{C}$) to 92.4% (120 $^\circ\text{C}$) with DMC selectivity of $>99\%$. The highest methanol conversion of 94% was observed at 140 $^\circ\text{C}$ with DMC selectivity of 98%. At higher temperatures, methanol conversion and DMC selectivity were slightly decreased with considerable formation of methyl picolinate and methyl carbamate with selectivity of 2% and 4.5%, respectively, at 160 $^\circ\text{C}$. In terms of the product distribution and methanol conversion, 120 $^\circ\text{C}$ was found optimum for selective and productive DMC synthesis.

It should be noted that the same byproducts were also identified by Tomishige and co-workers,¹⁷ curiously with almost identical dependency on reaction temperature and pressure.¹⁸ According to their work, the formation of methyl picolinate is attributed to the reaction of 2-picolinamide with methanol, producing ammonia (Reaction II). The formation of methyl carbamate is then attributed to the reaction of ammonia with DMC (Reaction III).



These undesired side reactions are enhanced at low pressure and high temperature conditions (Figures 2 and 3). One possible explanation for this is due to the largely different residence time of the reactants in the reactor influencing the selectivity, but this is unlikely because very similar selectivity trends have been reported using a batch reactor where the

reaction was tested for 12 h.¹⁸ This also indicates that the residence time in our continuous system was sufficiently large for the reactants to be activated to the level achieved under the batch reaction conditions, in spite of the much smaller contact time in the range of 10 s–10 min (Supporting Information). Therefore, the selectivity toward the byproducts is likely more intrinsic to the reaction pressure and temperature than to the residence time.

Instigated by this promising catalytic activity, we also investigated the effect of catalyst weight on the methanol conversion at a relatively mild pressure of 30 bar (Supporting Information, Figure S1). It was found that methanol conversion reaches a maximum value of 95% when the reaction was performed with 500 mg of catalyst with DMC selectivity of >99%. The undesired byproducts formation was slightly enhanced at a higher catalyst amount. This indicates the importance of a balance between the amount of catalyst (i.e., residence time) besides reaction temperature and pressure, although the latter parameters are more decisive in defining product selectivity.

Finally, the catalyst stability was investigated over 200 h at 30 bar with 300 mg of the catalyst. The activity gradually but linearly decreased with time, and ca. 40% methanol conversion was observed after 200 h of the reaction. Interestingly, DMC selectivity was unaltered and remained very high. Elucidating the nature of deactivation and designing catalysts with a high long-term stability are the clear tasks to be investigated for successful implementation of continuous DMC synthesis.

In conclusion, we reported the first dehydrating agent mediated direct synthesis of DMC from CO₂ and methanol in a fixed bed continuous flow reactor over a CeO₂ catalyst with excellent (>95%) methanol conversion and high DMC selectivity (>99%), giving high weight time yield of ca. 1 g_{DMC} g_{cat}⁻¹ h⁻¹. The known role of 2-cyanopyridine as a dehydrating agent for a batch reaction system has been successfully employed in a continuous process. This approach was found effective in maximizing the reactivity of the reaction and dehydration, thus achieving high DMC yield with a much shorter reaction time than in a batch operation. The catalytic activity reported here is by far the highest in the direct DMC synthesis from CO₂ and methanol using a continuous flow fixed bed reactor. A delicate balance between temperature, pressure, and residence time exists to achieve excellent catalytic performance. This study presents new opportunities in heterogeneous catalysis to investigate in a continuous manner the reactions which are generally performed in batch processes and especially limited by equilibrium and the presence of water.

■ ASSOCIATED CONTENT

■ Supporting Information

Materials and methods, Figure S1. Effect of catalyst weight on catalytic activity at 30 bar, 120 °C. Estimation of space time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the ICIQ Foundation and MINECO (CTQ2012-34153) is greatly acknowledged. We also thank MINECO for support through Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319) and DAIICHI KIGENSO KAGAKU KOGYO CO., Ltd. for kindly providing us CeO₂. A.B. is grateful to the AGAUR – Generalitat de Catalunya, Spain, for the FI doctoral grant. Mr. Dragos Stoian is kindly acknowledged for assisting the long-term stability test.

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