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## Transesterification of Cyclic Carbonates to Dimethyl Carbonate Using Solid Oxide Catalyst at Ambient Conditions: Environmentally Benign Synthesis

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Dimethyl carbonate (DMC) is used for a variety of applications in the chemical industries owing to its low toxicity, high oxygen content, and versatile chemical nature.<sup>[1,2]</sup> DMC is a safe and environmentally acceptable alternative for phosgene and dimethyl sulfate as carbonylating and methylating agents, because of the higher reactivity of DMC towards nucleophilic molecules, such as amines and phenols.<sup>[3]</sup> DMC is traditionally produced from phosgene and CO routes that are environmentally hazardous and rigorous safety measures are involved with these processes.<sup>[4,11]</sup> Thus, synthesis of DMC through non-toxic and environmentally benign routes has received considerable attention in recent years.<sup>[4]</sup> Two alternate green routes are available for the synthesis of DMC. One is through the direct reaction of methanol with CO<sub>2</sub> where the DMC yield is restricted by thermodynamics.<sup>[4]</sup> The other route is transesterification of cyclic carbonates with methanol (Scheme 1).<sup>[5]</sup> Cyclic carbo-



Scheme 1. Transesterification of ethylene carbonate using methanol.

nates can be produced quantitatively by  $CO_2$  insertion into epoxides.<sup>[6]</sup> Recently, Asahi Kasei commercialized a process for the transesterification of ethylene carbonate (EC) to produce DMC though at an elevated temperature range.<sup>[7]</sup>

Many homogeneous and heterogeneous catalytic systems have been reported for the transesterification of cyclic carbonates with methanol, which resulted in high selectivity to DMC.<sup>[5,6,8]</sup> Although homogeneous catalyst systems are more active, downstream catalyst separation is usually an issue.

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Many basic metal oxide-based heterogeneous catalysts have been reported for the synthesis of DMC from cyclic carbonates.<sup>[5]</sup> However, these reactions need severe reaction condition like high temperature and/or high CO<sub>2</sub> pressure.<sup>[5,9]</sup> It is rare to see reports on catalyst systems that are active at ambient conditions especially in a continuous operation.<sup>[10]</sup> A continuous process for the synthesis of DMC from EC at room temperature is attractive from an industrial point of view. Thus, the objective of the present work was to develop an efficient heterogeneous catalytic system for the above transformation at ambient conditions with a flexibility of operating in both batch and continuous reactors.

Herein, we report CaO-ZnO-based catalysts with varying Ca/ Ca+Zn ratios for the synthesis of DMC at ambient conditions both in batch and continuous processes. These catalysts were prepared by a wet impregnation method.[11] These catalysts were tested, initially in a batch reactor, for the transesterification of EC by methanol under an atmospheric pressure and the reaction conditions were optimized systematically. In order to optimize the catalyst loading, the reaction was carried at ambient conditions with varying catalyst weight in the range 0.05-0.5 g for 0.05 mol of EC. The Ca/Ca+Zn ratio of the catalyst was 0.5 and the EC:MeOH ratio was 10. The products at the end of 1 h reaction time were analyzed by GC (see the Supporting Information). The DMC yield increased steeply up to 0.25 g catalyst loading and then reached near plateau thereafter. Thus, the catalyst weight of 0.25 g was found to give maximum DMC yield of ca. 84 mol %. Even at the lowest catalyst loading of 0.05 g, the DMC yield was 55 mol%, indicating the efficiency of the catalyst. In the absence of catalyst, the DMC yield was negligible even after 10 h. In order to understand the effect of the reaction temperature on the DMC yield, the reactions were carried out at different temperatures in the range of 283-313 K and the resultant kinetic data are shown in Figure 1.

The experiments were carried with the catalyst having a low Ca/(Ca+Zn) ratio of 0.2 in order to collect sufficient data points over a wider range of temperatures. As seen in Figure 1, the catalyst was active and efficient for the entire temperature range employed. In general, the DMC yield increased steeply at the beginning and then reached the chemical equilibrium. At 300 K, the DMC yield reached around 80% within 4 h. Although the DMC yield increased slightly at higher temperatures up to 313 K, the temperatures higher than that did not improve the DMC yield further. In fact, slight decomposition of cyclic carbonates occurred at higher temperatures.

Transesterification of EC with methanol was carried out with catalysts with different Ca/(Ca+Zn) ratios at room temperature for a fixed amount of time. The catalytic activity increased in a nearly linear fashion with the Ca content, indicating that CaO



**Figure 1.** Kinetic plots for various temperatures ( $\blacksquare$ : 283 K,  $\bullet$ : 293 K,  $\blacktriangle$ : 303 K, and  $\forall$ : 313 K); batch reaction; EC=0.05 mol, Ca/Ca+Zn ratio=0.2, MeOH=0.5 mol, catalyst wt=0.25 g.

is the active component in the present reaction. A similar reaction with pure ZnO showed no trace of DMC (Table 1, entry 1), which substantiates that CaO is the active component. Howev-

<b>Table 1.</b> Catalytic performance of the present catalytic systems, catalyst reusability, and efficiency for different substrates <sup>[a]</sup> .							
Entry	Catalyst	Substrate	Time [h]	DMC yield [%]			
1	ZnO	EC	4.0	0			
2	CaO-ZnO (0.4) (fresh)	EC	4.0	83			
3	CaO-ZnO (0.4) (1st recovery)	EC	4.0	82			
4	CaO-ZnO (0.4) (2nd recovery)	EC	4.0	83			
5	CaO-ZnO (0.4)	PC	4.0	47			
[a] Substrate = 4.4 g, p-xylene = 1 g, MeOH = 16 g, $T$ = 300 K, catalyst wt =							
0.25 g. The values in parentheses represent the ratio of Ca/Ca+Zn.							

er, a difficulty encountered in the catalyst separation, when the reaction was carried out with pure CaO, supports the binding effect of ZnO to CaO in facilitating the catalyst separation in the present system.

The reusability of the catalyst was demonstrated as follows: the present CaO–ZnO catalyst was filtered after the reaction, washed with methanol to remove organic reactant and products, dried at 373 K for 5 h, and then reused for a fresh batch of reactants. The cycle was repeated twice and the activity of the catalyst was retained without loss in activity (Table-1, entries 3 and 4). To the best of our knowledge, the DMC yield of 84% obtained with the present catalyst system is the highest yield produced by any reported heterogeneous catalyst systems at ambient conditions. A table is presented in the Supporting Information, which compares the activity of the present catalytic system with some of the known catalytic systems. To prove the tolerance of the present catalyst system for higher homologous of EC, transesterification reaction of propylene carbonate (PC) with methanol was also tested. With the CaO–ZnO catalyst (Ca/(Ca+Zn) ratio=0.4), the transesterification reaction of propylene carbonate yielded 47 mol% DMC in 4 h at room temperature (Table 1). The DMC yield from the PC reaction was less than that of the EC reaction. As proposed in other literature, the low activity with propylene carbonate may be due to the steric hindrance associated with the PC.<sup>[5]</sup>

A possible continuous operation of a reaction with a heterogeneous catalyst is not only highly desirable to increase the productivity but also shows the efficiency of the solid catalyst. The versatility of the present catalyst system was demonstrated with a continuous DMC production from EC using a simple fixed-bed continuous-flow reactor setup (Figure 2). Reactant



**Figure 2.** Schematic representation of the reactor used for the continuous synthesis of DMC. A: reservoir for reactants; B: liquid feed pump; C: catalyst bed; D: product collection point;  $T_1$ :water inlet from thermostat to maintain reactor temperature;  $T_2$ : water outlet;  $W_1$  and  $W_2$ : cooling water circulation for condensing the products; solid arrows indicate the flow of reactants and products (upward flow).

mixture containing MeOH and EC was taken in the reservoir with a required molar ratio and was pumped by a feed pump in an up-flow manner. The results showed that the catalyst was active and efficient at ambient conditions even with the continuous mode of operation. Experiments to study the effect of MeOH:EC molar ratio (2 to 10) on the DMC yield were carried out at ambient conditions at a liquid hourly space velocity (LHSV) of 2 h<sup>-1</sup>. EC conversion increased with increase in the MeOH:EC molar ratio. The DMC yield of 70 mol% was obtained at the MeOH:EC ratio of 2 and it increased gradually on increasing the MeOH:EC ratio (reached 88% mol when the ratio was 10). This shift towards a higher DMC yield at higher MeOH:EC was expected for any equilibrium controlled reaction in which higher MeOH:EC ratio shifts the equilibrium towards the synthesis of DMC.<sup>[12,13]</sup> Higher the LHSV, larger the productivity for a given catalyst amount. Hence, experiments were carried out to monitor the DMC yield with 6 g catalyst loading at different LHSVs and the results were plotted (Figure 3).

It is interesting to find that the DMC yield is more or less the same even up to a LHSV of  $16 h^{-1}$ . To the best of our knowledge, this value is the highest space velocity reported for the



**Figure 3.** Catalytic performance of the catalyst (Ca/Ca+Zn=0.4) at 300 K in the continuous reaction for various LHSVs (2  $h^{-1}$  to 16  $h^{-1}$ ); MeOH vs EC molar ratio=10; catalyst wt=6 g.

cyclic carbonate transesterification reaction for the production of DMC at ambient conditions. The commercial production of DMC by the transesterification of EC by Asahi Kasei is being carried out at 353–393 K, however, the present catalytic system is effective even at 300 K. Time-on-stream study for the system with 6 g catalyst loading was carried out at ambient conditions at a LHSV of 2 h<sup>-1</sup> for several hours (Figure 4).



**Figure 4.** Stability of catalyst in the continuous reaction for the catalyst (Ca/Ca+Zn = 0.4) at 300 K for LHSV of 2 h<sup>-1</sup>; MeOH vs EC molar ratio = 10; catalyst wt = 6 g.

The catalyst was found to retain its activity up to 60 h and thereafter, a slight decrease in the activity was detected. This observation could be due to the disintegration of the catalyst into finer particles of  $Ca(OH)_2$  which leaches out along the product stream. Clear downstream products turned into a milky solution at the end of 60 h of operation of time-on-stream experiments, which confirmed the catalyst disintegration. The reason for the reduced activity of the catalyst after 60 h of continuous reaction was also analyzed by powder X-ray diffraction (XRD) of fresh and spent catalysts (recovered after 60 h of reaction). As seen in Figure 5, the fresh catalyst



**Figure 5.** XRD pattern of Ca/Ca+Zn = 0.4 catalyst: a) fresh catalyst, b) spent (deactivated) catalyst, and c) catalyst calcined at 1173 K for 5 h (active). O: peaks corresponding to CaO.

showed the reflections corresponding to CaO, which are totally absent in the spent catalyst. This deactivated catalyst was calcined at 1173 K for 5 h; the XRD spectrum of this recalcined sample showed CaO peaks but with much lower intensities (Figure 5).

The reappearance of CaO peaks in the XRD pattern indicates that part of the CaO has been transformed into another amorphous phase (as it is seen in the XRD pattern, Figure 5) over the reaction time of 60 h. The Ca contents of the catalysts were estimated using atomic absorption spectroscopy; deactivated catalyst showed less amount of Ca compared to the fresh catalyst. Thus, it is concluded that the deactivation process may be due to the combination of leaching and formation of dispersed CaCO<sub>3</sub> or Ca(OH)<sub>2</sub>.

In conclusion, we report CaO–ZnO-based catalysts for the synthesis of DMC by the transesterification of cyclic carbonates using methanol with DMC yields up to 84% at ambient reaction conditions. The superiority of the present catalyst systems is demonstrated by both batch and continuous reactions. With the continuous reactor system, the catalyst was found to be active for more than 60 h and the reaction could be carried out up to a LHSV of more than 16 h<sup>-1</sup>. CaO was found to be the active phase for the transesterification reaction and ZnO provided the binding effect to make the present catalyst an efficient solid catalyst. In the case of the batch reaction, the catalyst was recovered at least twice without losing activity and with the continuous mode of operation, the catalyst was stable for more than 60 h.

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## CHEMSUSCHEM

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