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A rapid and effective synthesis of propylene carbonate using a supercritical CO_2–ionic liquid system

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The synthesis of propylene carbonate from propylene oxide and carbon dioxide under supercritical conditions in the presence of 1-octyl-3-methylimidazolium tetrafluoroborate was achieved in nearly 100% yield and 100% selectivity within 5 minutes, whose TOF value is 77 times larger than those so far reported.

From the standpoint of the protection of environment, development of green processes based on chemical fixation of carbon dioxide (CO_2) has been drawing much interest in industrial chemistry, because there are a lot of possibilities that carbon dioxide can be used as a safe and cheap C1 building block to produce useful organic compounds.

The chemical fixation of CO_2 to cyclic carbonates has been investigated, since it is one of the most well-known successful example of CO_2 fixation to produce the carbonates which are widely used as a starting monomer of polymers, and much more environmentally benign process compared to that using poisonous phosgene.[1] To synthesize such cyclic carbonates effectively, quite numerous homogeneous catalytic processes have so far been reported;[2] however, its production has suffered from serious disadvantages of the separation of catalysts.[2] Hence solid catalysts that possess high thermostability and easy catalyst–product separation leading to their recycling look promising, but the time taken to achieve the reactions in the presence of their catalysts was more than 6 h even at higher temperatures than 140 °C,[2] and so the activity was not so high.

Recently, we have demonstrated a remarkable promotion of CO_2 chemical fixation in supercritical CO_2,[3,4,5] especially at the near-critical pressure in the presence of small amount of DMF even without any catalysts.[3] This is due to the function of DMF as a $scCO_2$ soluble acid–base catalyst. However, a reaction time longer than 12 hours was required for the CO_2 fixation to obtain cyclic carbonate, because of the poor catalytic activity of DMF.

For the sake of further improvement in the activity and selectivity, we attempted to apply a $scCO_2$–ionic liquid (IL) biphasic system[6] to the CO_2 fixation, because IL can be used as a prominent acid–base catalyst[7,8] as well as a suitable reaction media.[9] Although in gaseous CO_2 below 5 MPa, the introduction of IL into propylene carbonate synthesis from propylene oxide led to high yields, the reaction times longer than 6 hours were required for the complete fixation even at 110 °C (density < 0.08 g cm^{-3}), and so the rate of reaction remains low.[10] Such a low reaction rate might be attributable to the relatively lower density of gaseous CO_2, since this type of CO_2 fixation proceeds in S_N2 reaction.[3] In addition, apolar organic compounds such as epoxides and carbonates are more highly soluble in higher density $scCO_2$ than in gaseous CO_2, whereas their solubilities in a polar IL are negligibly small. Therefore we first demonstrate that the application of $scCO_2$ to this CO_2 fixation achieves nearly 100% yield at reaction time shorter than 5 minutes even at the temperature of 100 °C as that previously reported.[10]

The carboxylation of propylene oxide **1a** with CO_2 into propylene carbonate **2a** in the presence of the ionic liquid based on 1-methylimidazolium salt (Figure 1) was conducted in a batchwise operation under various conditions as shown in Table 1.[11] Under supercritical conditions, NO_3^-, $CF_3SO_3^-$, BF_4^- and PF_6^- were examined as counter ions of the 1-ethyl-3-methylimidazolium ionic liquid ($[C_2\text{-mim}]^+[X]^-$ salt) for the synthesis of **1a** (runs 1 to 4). Of these, the BF_4^- was found to be the most effective at promoting the chemical fixation and to give a 61% yield with 87% selectivity. Furthermore, this IL can be re-used at least 2 times more with almost the same yield (run 5); however, the time taken to obtain a reasonable yield was as long as 2 h.

A series of the imidazolium ionic liquid with different alkyl chain length from C_2 to C_8 was further investigated. The yield of **2a** is increased with lengthening alkyl chain (runs 4, 6 to 8). It is quite note worthy that the presence of $[C_8\text{-mim}]^+[BF_4]^-$ achieves nearly 100% yield and 100% selectivity for propylene carbonate production even at shorter reaction times around 5 minutes at the same temperature and pressure (runs 8 to 11), whose TOF value ($= 517$ h^{-1}) is 77 times larger than that of previous reported ($= 6.7$ h^{-1}).[10] This could be due to an increase in the solubilities of CO_2 and **1a** in IL phase with lengthening alkyl chain of IL.[12] To our surprise, lowering the temperature from 100 °C to 60 °C can also effect the 100% yield though time-consuming for a period of 120 minutes (runs 8 and 12). However, further decrease in temperature to 40 °C was not allowed to proceed under the same pressure and time-consuming conditions (run 13). Furthermore, decreasing the pressure up to 6 MPa around a subcritical pressure of 6 MPa at a constant temperature of 100 °C led to a remarkable decrease in yield (run 14), and so this chemical fixation process was favored by the supercritical conditions. We thus demonstrate

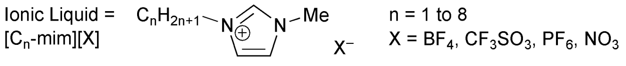

Fig. 1 Ionic liquid for the $scCO_2$–ionic liquid reaction system.

Table 1 Synthesis of propylene carbonate from propylene oxide with 3-methylimidazolium-based ionic liquid in supercritical carbon dioxide

Run	Ionic liquid	Pressure/ MPa	Temp./ °C	Time/ min	Yield/ %	Select./ %
1	$[C_2\text{-mim}]^+[NO_3]^-$	14	100	120	31	59
2	$[C_2\text{-mim}]^+[CF_3SO_3]^-$	14	100	120	25	45
3	$[C_2\text{-mim}]^+[PF_6]^-$	14	100	120	30	37
4	$[C_2\text{-mim}]^+[BF_4]^-$	14	100	120	61	87
5	$[C_2\text{-mim}]^+[BF_4]^-$	14	100	120	64[a]	71
6	$[C_4\text{-mim}]^+[BF_4]^-$	14	100	120	75	100
7	$[C_6\text{-mim}]^+[BF_4]^-$	14	100	120	95	100
8	$[C_8\text{-mim}]^+[BF_4]^-$	14	100	120	97	100
9	$[C_8\text{-mim}]^+[BF_4]^-$	14	100	30	99	100
10	$[C_8\text{-mim}]^+[BF_4]^-$	14	100	15	99	100
11	$[C_8\text{-mim}]^+[BF_4]^-$	14	100	5	98[b]	100
12	$[C_8\text{-mim}]^+[BF_4]^-$	14	60	120	99	100
13	$[C_8\text{-mim}]^+[BF_4]^-$	14	40	120	–[c]	–
14	$[C_8\text{-mim}]^+[BF_4]^-$	6	100	120	71	78

[a] The ionic liquid, that is used in run 4, was re-used. [b] TOF ($= 516$ h^{-1}) is 77 times larger than that of former report (TOF $= 6.7$ h^{-1}, ref. 10). [c] No reaction. Propylene oxide was recovered completely.

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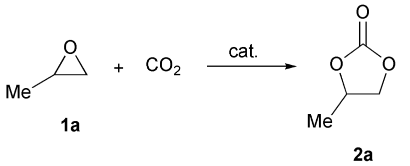


Scheme 1

that the $scCO_2$–IL reaction system can synthesize propylene carbonates by chemical fixation of carbon dioxide in satisfactory yields even a lower temperature of 60 °C or shorter reaction time around 5 minutes.

Fig. 2 shows the pressure dependence of the yield of **2a** in CO_2 in the presence of $[C_2\text{-mim}]^+[BF_4]^-$ or $[C_8\text{-mim}]^+[BF_4]^-$. In the case of $[C_2\text{-mim}]^+[BF_4]^-$ (open circles), one can see the maximum yield of 94 % at a lower pressure of 7 MPa, and then a significant decrease in yield till 10 MPa. Such a decrease with increasing pressure was also reported previously.[10] The epoxide **1a** is soluble more highly in $scCO_2$ than in gaseous CO_2, and this decrease in yield in higher-pressure $scCO_2$ region could be due to less epoxide concentration in IL phase at which the reaction occurs. The yield of **2a** in the presence of $[C_8\text{-mim}]^+[BF_4]^-$ was at best about 70% at lower pressures, but increasing the pressure resulted in the improvement in yield, giving 96% at the near critical pressure, and ultimately nearly 100% in the range above 11 MPa. Visual observation of phase behavior through high-pressure view cell indicates that the solubility of CO_2 in $[C_8\text{-mim}]^+[BF_4]^-$ would be significantly larger compared to that in $[C_2\text{-mim}]^+[BF_4]^-$ under the same pressure and temperature conditions. It is further known that such an epoxide compound can be dissolved more sufficiently in $[C_8\text{-mim}]^+[BF_4]^-$ than in $[C_2\text{-mim}]^+[BF_4]^-$, and therefore a marked increase in the concentrations of CO_2 and epoxide in $[C_8\text{-mim}]^+[BF_4]^-$ phase under $scCO_2$ region above 11 MPa is considered to achieve nearly 100% yield even at shorter reaction times.

A series of epoxide substrates was examined for the synthesis of the corresponding carbonates in the presence of $[C_8\text{-mim}]^+[BF_4]^-$ at 14 MPa and 100 °C (Table 2). Carbonates with alkyl side chain groups (runs 1, 2) were successfully synthesized from each epoxide in nearly 100% yield and 100% selectivity at reaction times shorter than 2 h, whereas the carbonates were obtained in approximately 100% selectivity but low yields around 62% when the phenyl substituted epoxide were used. This is due to the low reactivity of the β-carbon atom that would be activated by the basic site of the ionic liquid (BF_4^- anion). Moreover, the yields of carbonate **2d** and **2e** at a higher pressure of 14 MPa (runs 3, 5), are much higher than those at a lower pressure of 7 MPa (runs 4, 6) in the presence of the ionic liquid. This pressure dependence of the yield was found to be similar to that of propylene carbonate as shown in Table 1, in which the yield decreased with decreasing pressure.

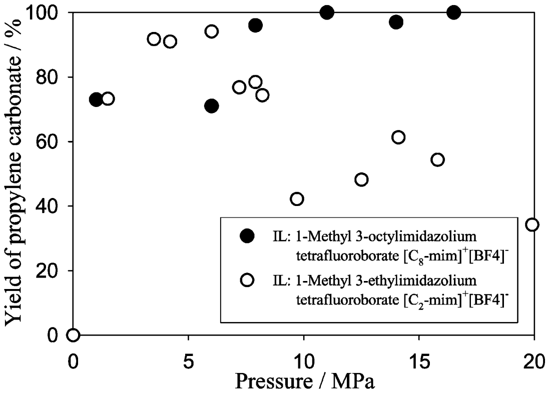
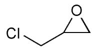
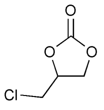
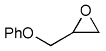
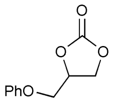
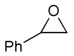
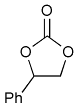
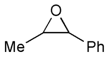
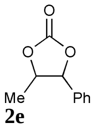


Fig. 2 Pressure dependence of the yield of propylene carbonate in the presence of $[C_8\text{-mim}]^+[BF_4]^-$ and $[C_2\text{-mim}]^+[BF_4]^-$ at 100 °C in CO_2. Reaction time is 2 h.

Table 2 Synthesis of various carbonate in the presence of $[C_8\text{-min}]^+[BF_4]^-$ at 100 °C for 2 h in CO_2[a]

Run	Epoxide	Carbonate	Pressure/ MPa	Yield/%	Select./%
1	 **1b**	 **2b**	14	90	99
2	 **1c**	 **2c**	14	100	100
3	 **1d**	 **2d**	14	61	97
4			7	28	98
5	 **1e**	 **2e**	14	62	98
6			7	39	99

[a] Reaction time; 2h. Carbonate yields were determined by GC using tridecane as an internal standard.

Consequently, there is a strong possibility that this reaction system composed of $scCO_2$-$[C_6$ or $C_8\text{-mim}]^+[BF_4]^-$ can be applied to the synthesis of various carbonates except for the phenyl substituted one.

In conclusion, we found that under $scCO_2$, $[C_8\text{-mim}]^+[BF_4]^-$ is the most effective IL for CO_2 fixation to carbonate. In particular, this $scCO_2$–IL reaction media not only achieves nearly 100% yield at 14 MPa and at 100 °C for the propylene carbonate production at reaction times shorter than 5 minutes, leading to a 77-fold faster rate of reaction than so far reported, but also can be applied to the synthesis of various carbonates in satisfactory yields.

Notes and references

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10 J. Peng and Y. Deng, *New J. Chem.*, 2001, **25**, 639.Reaction conditions are as follows: reactor volume 90 cm^{-3}, 110 °C, ionic liquid 2.5 mmol (0.48 mL), pressure 2.5 MPa, **1a** 100 mmol, 6 h.
11 The typical experimental procedure is as follows: ionic liquid ($[C_2\text{-mim}]^+[BF_4]^-$, 0.51 mmol, 0.1 mL) was charged into a 50 cm^3 reactor, and CO_2 was introduced using a high-pressure pump into the reactor at desired temperatures. Pressure control was achieved by a back-pressure regulator. **1a** (2.0 mL, 30 mmol) is introduced by a high-pressure liquid pump, and the reaction in CO_2 was started with stirring (about 500 rpm). After the reaction, the reactor was cooled to 0 °C and pressure was released slowly. The crude product was analyzed compared with authentic samples by GC, and the yields were determined by GC using tridecane as an internal standard. The crude product (yield: 61% by GC) was purified by distillation and **2a** was obtained in 48% (1.43 g, 14 mmol) as an isolated yield.
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