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A Strategy to Overcome the Thermodynamic Limitation in CO_2 Conversion by Using Ionic Liquid and Urea

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Enhancing the equilibrium conversion of thermodynamically unfavorable reactions is a very interesting and challenging topic for chemists. The unique properties of ionic liquids (ILs) provide new opportunities to solve the problem. Herein a strategy is proposed to circumvent the thermodynamic limitation of chemical reactions using the designable and non-volatile natures of ILs. In this approach a reactant first reacts with a functional IL to form a high energy IL intermediate, which can further react with other reactants to yield products and the IL is regenerated. To verify the feasibility of this strategy, the syntheses of dimethyl carbonate (DMC) and methyl formate (MF) via urea, which are very important reactions to convert CO_2 but are thermodynamically unfavorable, were conducted with the aid of a diol IL. It was found that the equilibrium yields of DMC and MF obtained by this methodology could be respectively 64 times and 9 times higher than those of the conventional methods.

Introduction

Many important chemical reactions are thermodynamically unfavorable with low or very low equilibrium conversion, which limits their industrial application. Exploration of effective protocols to shift the reaction equilibrium to desired direction has been a very interesting and challenging topic in chemical community.

Carbon dioxide (CO_2) is the major greenhouse gas, and it is also an abundant, renewable, nontoxic, non-flammable, easily available carbon resource. Utilization of CO_2 as a feedstock to produce value-added chemicals and fuels benefits the sustainable development of our society, which has attracted extensively attention. CO_2 has been used as a feedstock to synthesize various chemicals,[1] such as cyclic carbonates,[2] methanol,[3] formic acid,[4] nitrogen containing chemicals,[5] and polymers.[6] However, CO_2 is the highest oxidation state of carbon, the low energy level of CO_2 blocks its conversion to chemicals and fuels. Finding a way to overcome thermodynamic limitation is crucial for extending range of CO_2 utilization.

Ionic liquids (ILs) are organic salts with low melting point (e.g. below 100 °C). ILs have some unusual properties, such as negligible vapor pressure, wide liquid-temperature range, high thermal stability, excellent solvents for both organic and inorganic substances, and their structures can be designed for desired functions.[7] Applications of ILs in different fields have been studied extensively in recent years, including chemical reactions,[8] adsorption of CO_2 and SO_2 from gas streams,[9] extraction and fractionation,[10] and so on.[11]

The unique properties of ILs provide new opportunities to solve the challenging problems in chemical reactions. In this work, we proposed a strategy to enhance the equilibrium conversion of thermodynamically unfavorable reactions using the non-volatile and designable natures of ILs. As examples, the conversion of CO_2 to dimethyl carbonate (DMC) and methyl formate (MF) via urea, which are both very important but thermodynamically unfavorable reactions, were studied to verify the feasibility of the strategy. It was demonstrated that the methodology was very successful to circumvent the thermodynamic limitation of the reactions.

Results and discussion

Principle of the strategy.

We discuss the principle using an equilibrium reaction expressed by eqn (1), in which A reacts with B to form C and D, and C is volatile. In order to overcome the thermodynamic limitation of the reaction, reactant A first reacts with a functional IL to form product C and an IL intermediate I that is a high energy substance (eqn (2)), and the reaction is also thermodynamically unfavorable. However, the thermodynamic problem can be solved by removing the C (*e.g.* ammonia in this work) produced continuously in the reaction process, which can be easily realized as C is volatile, while the IL and IL intermediate I are non-volatile. In the second step, the IL intermediate I reacts with reactant B to form product D (eqn (3)), and the IL is regenerated at the same time. Therefore, by using the designable nature and non-volatility of ILs, we can overcome the thermodynamic limitation of the reactions that meet the conditions discussed above.

$$A + B \rightleftharpoons C + D \qquad (1)$$

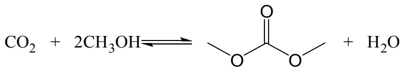
$$A + IL \rightleftharpoons C + I \qquad (2)$$

$$I + B \rightleftharpoons D + IL \qquad (3)$$

Synthesis of DMC.

DMC is a very useful and environmentally benign chemical due to its negligible toxicity and good biodegradability. It can be used as a green solvent, precursor of polycarbonate resins, methylating and carbonylating agent which can substitute for some toxic substances such as dimethyl sulphate, phosgene, and methyl chloroformate.[12] It can also be used as gasoline octane enhancer.[13] DMC can be produced by different ways, such as reaction of phosgene with methanol,[14] oxidative carbonylation of methanol,[15] oxidative reaction of carbon monoxide and methyl nitrite,[16] transesterification of methanol with cyclic carbonates which are produced from epoxides.[17] However, these routes have some inevitable shortcomings such as toxic, corrosive, explosive reactants are used. DMC can be synthesized by direct reaction of CO_2 and methanol as shown in eqn (4). This route is attractive because both reactants are very cheap. The equilibrium conversion of this reaction is very low due to thermodynamic limitation.[18] To enhance the equilibrium conversion, dehydrating agents have been used,[19] which increases the cost because of the consumption of dehydrating agents and causes separation problem.

Alcoholysis of urea can form alkyl carbonates including DMC,[20] as shown in eqn (5). Meanwhile, the ammonia liberated can be recycled and only CO_2 and alcohol are consumed in the process because urea is produced from CO_2 and ammonia in industry.[20a] The obvious advantage of this route is that simple and cheap catalyst can be used to accelerate the reaction and the reaction can be conducted at ambient pressure.[20] However, this reaction is also thermodynamically unfavorable, and the equilibrium conversion is very low even large excess of methanol is used. Removal of ammonia continuously from the reaction system can shift the reaction equilibrium to DMC side, and this can be realized by coupling of the reaction and condensing process.[20c-20e] In this route, methanol and DMC vaporized are condensed in condenser and return back to the reactor. Obviously, the evaporating-condensing of the methanol and the product occurs repeatedly in the reaction process, which leads to high energy consumption and low efficiency. The equilibrium can be shifted by neutralizing the ammonia produced,[20f] but this need post-treatment.



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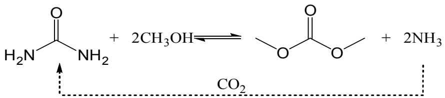
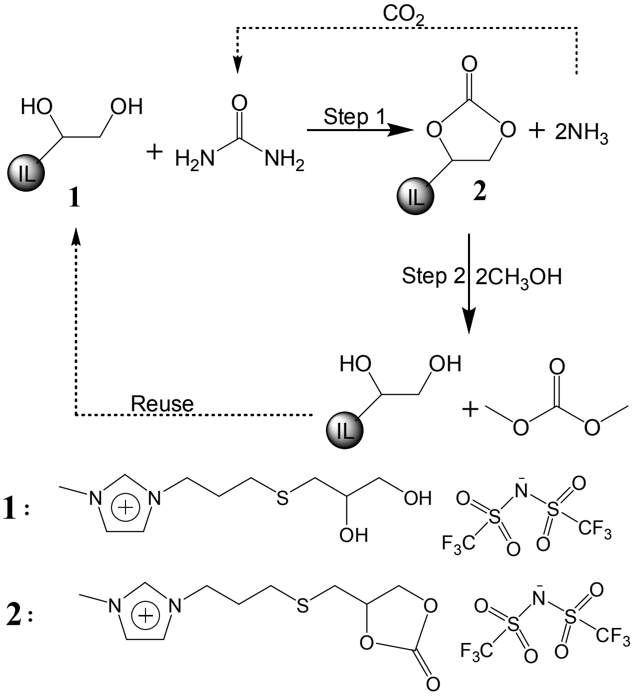


(5)

In this work, the new strategy was used to overcome the thermodynamic limitation to produce DMC from urea and methanol. Two steps are involved, as shown schematically in Scheme 1. The first step is the reaction of a diol IL (**1**), 1-(6',7'-dihydroxyl-4'-thiaheptyl)-3-methylimidazolium bis((trifluoromethyl)-sulfonyl)-imide which was synthesized according to the procedures reported in literature,[21] with urea to form the cycle carbonate IL intermediate (**2**) and ammonia. During the reaction the ammonia produced is removed continuously by blowing an inert gas (CO_2 was utilized in this work), so that the thermodynamically unfavorable reaction (Step 1 in Scheme 1) can proceed smoothly. Because the IL (**1**), the IL intermediate (**2**), urea and the catalyst are non-volatile at the experimental condition, only ammonia is carried out by the CO_2 flow. The ammonia and CO_2 can be converted into urea by the widely used process. The second step (Step 2 in Scheme 1) involves the transesterification of the high energy level IL intermediate (**2**) with methanol to yield the desired product DMC, and the diol IL (**1**) is regenerated at the same time, and the diol IL (**1**) can be reused. In this way, the nonvolatile and designable natures of ILs are used elegantly to overcome the thermodynamic limitation of the reaction shown in eqn (5).



Scheme 1 The reactions of the diol IL (**1**) with urea to form the IL intermediate (**2**) and ammonia (Step 1), and IL intermediate (**2**) reacts with methanol to produce DMC and the diol IL (**1**) is regenerated at the same time (Step 2). Structures of the diol IL (**1**) and the IL intermediate (**2**) are provided at the bottom.

To synthesize IL intermediate (**2**), some simple and commonly used catalysts[22] for the reaction of urea with hydroxyl groups to produce cycle carbonates were tested for the reaction of the diol IL (**1**) with urea (Step 1 in Scheme 1), and the results are shown in Fig. 1. Obviously, the metal oxides and metal chlorides could promote the reaction effectively, and ZnO exhibited the highest activity among them. Therefore, the reaction conditions were further optimized using ZnO as the catalyst.

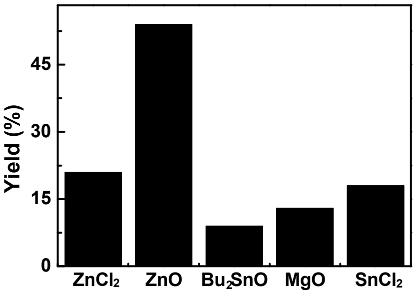


Fig. 1 The performance of various catalysts on the synthesis of IL intermediate (**2**) (step 1 in Scheme 1). Diol IL (**1**) 1.02 g, urea 0.12 g, catalysts 0.2 mmol, CO_2 flow rate 5 mL/min, 150 °C, 2 hrs.

The effects of ZnO amount and temperature on the yield of IL intermediate (2) are presented in Fig. 2a and 2b, respectively. As shown in Fig. 2a, the yield increased with increasing amount of the catalyst, and increased slowly as the amount of ZnO exceeded 1.6 wt% (IL basis). Fig. 2b demonstrates that the yield was very low at lower temperature, and increased dramatically in the range of 140 °C to 150 °C, and then decreased slightly with further increasing temperature. The main reason for this phenomenon may be that urea decomposes considerably at the higher temperature.[23]

The effect of reaction time on the yield of the IL intermediate (**2**) is illustrated in Fig. 2c. The yield increased with time at the beginning, and was independent of time after 8 hrs. The maximum yield was 87% at the urea:diol IL (**1**) molar ratio of 1:1. The maximum yield was less than the theoretical value (100%), which resulted from the decomposition and loss of urea during the reaction. For comparison, we also carried out the experiments in the reactor without removing the ammonia produced in the reaction. The maximum yield of the IL intermediate (**2**) was only 3%, as shown in Fig. 2c. When CO_2 is sealed in cell to enhance the yield of DMC,[20f] the effection is limited. This indicates that removal of the ammonia formed in the reaction process was the key to reach high yield. We also used N_2 as the blowing gas to remove the ammonia at the reaction condition of Fig. 2c, and the results were nearly the same with that when CO_2 was utilized, indicating that the only function of CO_2 was to remove the ammonia produced to shift the reaction equilibrium. However, CO_2 is preferable in practical application because CO_2 is required in the conversion of ammonia back into urea. In this way, the ammonia acts as a bridge for the reaction of CO_2 and the diol IL (**1**) to form the IL intermediate (**2**).

The effect of the urea:diol IL (**1**) molar ratio in the feed on the maximum yield of the IL intermediate (**2**) was also investigated. The yield increased as the urea:diol IL (**1**) molar ratio was increased, as can be known from Fig. 2d. At the feed molar ratio of 1.4:1, the yield of the IL intermediate (**2**) was >99%, indicating that nearly all of the diol IL (**1**) was converted into the IL intermediate (**2**) at this condition.

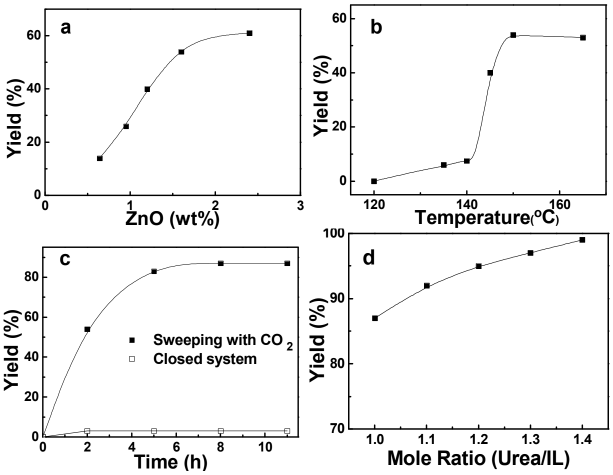


Fig. 2 Effects of reaction conditions on yield of the IL intermediate (**2**) [IL(**1**) basis]. (a) Effect of amount of ZnO (wt% in IL-ZnO mixture), IL (**1**) 1.02 g, molar ratio of urea:IL 1:1, CO_2 flow rate 5 mL/min, 150 °C, 2 hrs; (b) Effect of temperature, IL(**1**) 1.02 g, molar ratio of urea:IL 1:1, 1.6 wt% ZnO in IL-ZnO mixture, CO_2 flow rate 5 mL/min, 2 hrs; (c) Effect of reaction time, IL(**1**) 1.02 g, molar ratio of urea:IL 1:1, 1.6 wt% ZnO in IL-ZnO mixture, CO_2 flow rate 5 mL/min if used, 150 °C; (d) Effect of molar ratio of urea:IL, IL(**1**) 1.02 g, 1.6 wt% ZnO in IL-ZnO mixture, CO_2 flow rate 5 mL/min, 150 °C, 8 hrs.

Transesterification of cycle carbonates and alcohols to produce linear alkyl carbonates is a class of well established reactions, and bases can catalyze the reaction effectively.[24] Therefore, DMC can be produced by the transesterification of the IL intermediate (**2**) and methanol (Step 2 in Scheme 1), and the catalyst ZnO used in Step 1 can also catalyzed the transesterification reaction due to its basic nature. It can be known from Scheme 1 that stoichiometrically two moles of methanol react with one mole of IL intermediate (**2**) to produce one mole of DMC. In this work, the yields of DMC at the methanol:IL intermediate (**2**) feeding molar ratios of 10:1, 30:1, and 100:1 were studied, and the results are presented in Fig. 3. The yield of DMC increased with reaction time at beginning, and then became independent of time because transesterification reactions are also reversible. The maximum yields at the feeding ratios of 10:1, 30:1, and 100:1 were 73%, 82%, and 87%, respectively. For comparison, the yield of DMC by the conventional route （eqn (5)) without removing the NH_3 released was also determined at 150 °C and different feeding molar ratios of methanol and urea using ZnO as catalyst, and the results are given in Fig. 3. The equilibrium yields of DMC at the methanol:urea feed molar ratios of 10:1 and 100:1 were 1% and 2%, respectively. The yields were very low due to the thermodynamic limitation,[20c-20e] which is consistent with the results reported in the literature for this reaction.[25] It can be easily known from the results in Fig. 2 and 3 that the novel strategy proposed in this work is very efficient to overcome the thermodynamic limitation of the reaction. For example, using this strategy, one mole of urea could produce 0.87 mole of IL intermediate (**2**) at the urea:IL(**1**) feeding molar ratio of 1:1 (Fig. 2c). Therefore, one mole of urea could produce about 0.64 mole of DMC at the methanol:IL intermediate (**2**) feeding molar ratio of 10:1 because one mole of IL intermediate (**2**) could generate 0.73 mole of DMC (Fig. 3). By the direct reaction of urea with methanol without removing NH_3, one mole of urea could only produce 0.01 mole of DMC at the methanol:urea feeding molar ratio of 10:1 (Fig. 3). Therefore, the yield obtained by the present protocol can be 64 times higher than that of the conventional method.

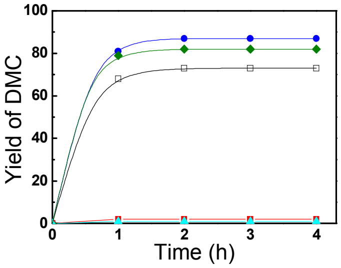


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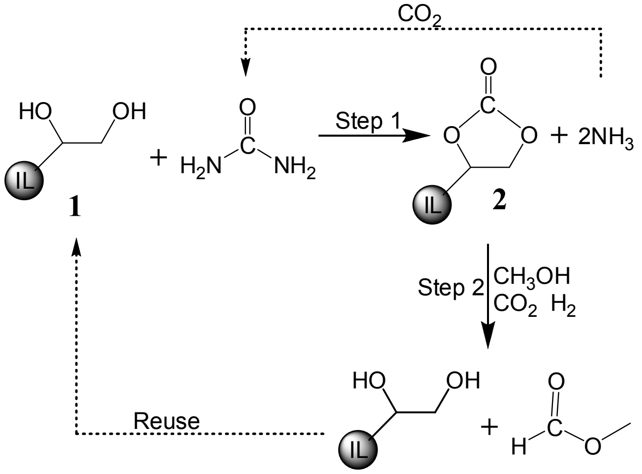
Fig. 3 The yields of DMC by the transesterification reaction of the IL intermediate (**2**) with methanol (step 2 in Scheme 1) [IL intermediate (**2**) basis] and by the alcoholysis reaction of urea and methanol shown in eq 5 （Urea basis） at the same reaction condition. IL intermediate (**2**) or urea 2.0 mmol, 150 °C, ZnO 16 mg, ☐ methanol:IL intermediate (**2**) 10:1, ◆ methanol:IL intermediate (2) 30:1, ● methanol:IL intermediate (**2**) 100:1, ▲ methanol: urea 10:1, ■ methanol:urea 100:1.

Synthesis of MF.

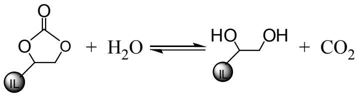
MF can be used as insecticide, solvent, and can also be used to synthesize pharmaceuticals, formamide, dimethylformamide, and formic acid.[26] In industry, MF is mainly produced by the carbonylation of methanol with CO catalyzed by strong base (such as sodium methoxide). MF can be synthesized from CO_2, H_2 and methanol as shown is eqn (6), this is an attractive reaction and has attracted considerable attention.[26,27] However, this reaction is also a thermodynamic unfavorable, and the low conversion blocks its application in industry. If water is removed from the reaction system, equilibrium will shift to the right side and yield of MF will be enhanced. The strategy proposed in this work was also used to synthesize MF from urea, H_2 and methanol, as shown schematically in Scheme 2.

Step 1 in the MF synthesis is the same as that in DMC synthesis, in which IL intermediate (**2**) is formed. Step 2 consists of two reactions. One is the reaction of CO_2, H_2 and methanol to produced MF and water as shown in eqn (6).[26,27] The other is the reaction of the IL intermediate (**2**) reacts with water to shift the reaction and it is converted to diol IL (**1**) and CO_2 as shown in eqn (7). In other words, the IL intermediate (**2**) acts as a dehydration agent, which is changed back into the diol IL in the reaction. Combining eq (6) with (7) gets the overall eqn (8).



Scheme 1 The reactions of the diol IL (1) with urea to form the IL intermediate (2) and ammonia (Step 1), and the IL intermediate (2) reacts with CO_2, H_2 and methanol to produce MF and the diol IL (1) is regenerated at the same time (Step 2).

$$CO_2 + H_2 + CH_3OH \rightleftharpoons HCOOCH_3 + H_2O \tag{6}$$



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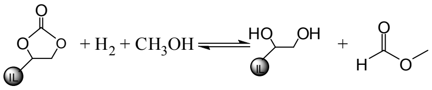

(8)

$RuCl_3$ and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) was used as catalysts for step 2. The $RuCl_3$ catalyzes the generation of formic acid and DBU promotes the reaction of formic acid and methanol to yield MF.[27d] The dependence of the yield of MF on reaction time is presented in Fig. 4. The yield of MF increased at beginning and became independent of time after 16 hrs, indicating that the equilibrium of the reactions has been reached. The maximum yield was 38% in 16 hrs under the reaction condition in this work. For comparison, the yield of MF by the conventional route eqn (6) without IL intermediate (**2**) was also determined at the same condition, and the results are also given in Fig. 4. The equilibrium yield of MF was only 4.2% due to the thermodynamic limitation.[26,27] It can be known from the results that the yield of MF by the present protocol can be 9 times higher than that of the route reported.[26,27] So the novel strategy proposed in this work is also very efficient to overcome the thermodynamic limitation in synthesis of MF.

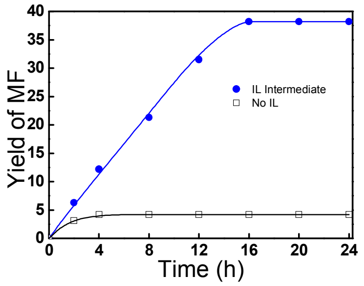

Fig. 4 The yields of MF on time for the reaction of methanol and CO_2, H_2 with and without IL intermediate (**2**). Methanol 10 mmol, $RuCl_3$•2H2O 6 mg, DBU 0.6 mmol, total pressure of H_2 and CO_2 10 MPa (H_2 5 MPa),

150 ^{o}C, methanol and carbonate IL (**2**) (if used) feeding molar ratio was 1:1.

The reusability of the diol IL(1)/ZnO.

The reusability of the diol IL(**1**)/ZnO catalytic system was studied in synthesis of DMC, and the results are given in Fig. 5. In the experiments, urea first reacted with the diol IL(**1**) to produce the carbonate IL (**2**) at the condition of Fig. 2d with a urea:diol IL(**1**) molar ratio of 1.4:1, and the yield of IL intermediate (**2**) was determined (step 1 in Scheme 1). Then IL intermediate (**2**) reacted with methanol to produce DMC by the transesterification reaction at the condition of Fig. 3 at methanol: IL intermediate (**2**) molar ratio of 100:1 with a reaction time of 2 hrs. After reaction, the reactor was cooled to 50 ^{o}C, and the DMC and methanol in the reactor were carried out by CO_2 flow and were absorbed in a cold trap with DMF as absorbent. The IL/ZnO catalytic system was reused directly for the next run at the same condition. It can be known from Fig. 5 that the yields of the IL intermediate (**2**) and DMC were almost same in the three cycles, indicating that the IL/ZnO catalytic system had excellent reusability.

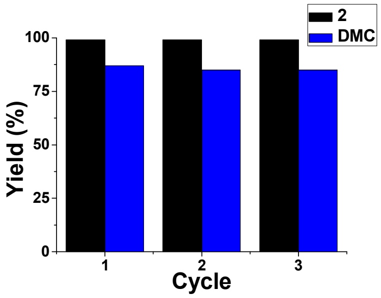

Fig. 5 Reuse of the diol IL (**1**)/ZnO. Reaction condition for producing the IL intermediate (**2**): diol IL (**1**) 1.02 g, ZnO 1.6 wt% ZnO in IL-ZnO mixture, molar ratio of diol IL (**1**):urea 1:1.4, CO_2 flow rate 5 mL/min, 150 ^{o}C, 8 hrs; reaction condition for the transesterification of the IL intermediate (**2**) and methanol to produce DMC: methanol:IL intermediate (**2**) 100:1, 150 ^{o}C, 2 hrs.

Conclusions

In summary, we have proposed a strategy to enhance the equilibrium conversion of thermodynamically unfavorable chemical reactions using the unique properties of ILs. The methodology has been successfully used for the transformation of CO_2 to DMC and MF via urea. In these reactions, urea first reacts with a diol IL to form a cycle carbonate IL that has high energy level by removing the ammonia released continuously. Then DMC is produced by the reaction of methanol with the high energy level cycle carbonate IL, and the IL is regenerated at the same time and can be reused. It is found that by using this principle, the equilibrium yield of DMC can be 64 times larger than that obtained by traditional route. Using this protocol, the equilibrium yield of MF from the reaction of CO_2, H_2 and methanol can be 9 times higher than that of the conventional methods. We believe that the highly efficient routes to produce DMC and MF have great potential of application, and the novel idea of using a functional IL as a reactive and renewable intermediate in chemical reactions opens a promising way to solve the challenging chemical problems and to explore new reactions.

Experimental section

Generals

3-Allyl-1-methylimidazolium bromide ([amim]Br) with a purity of > 99% was supplied by Centre for Green Chemistry and Catalysis, LICP, CAS. 1-Thioglycerol (>95%) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, >98%) were analytical grade and purchased from TCI Co., Ltd. ZnO, $ZnCl_2$, Bu_2SnO, MgO, and $SnCl_2$ were all analytical grade and were provided by Sinopharm Chemical Reagent Co., Ltd. CO_2 with a purity of 99.99% and H_2 with a purity of 99.999% were obtained from Beijing Analytical Instrument Factory. All reagents were used as received.

The diol IL (**1**) 1-(6',7'-dihydroxyl-4'-thiaheptyl)-3-methylimidazolium bis((trifluoromethyl)-sulfonyl)-imide was synthesized from [amim]Br and 1-thioglycero initiated by DMPA according to the procedures described in the literature1. ^{1}H NMR(400 MHz, Bruker Avance 400, CD_3CN): δ=8.43 (s, 1H); 7.38 (br s, 1H); 7.33 (br s, 1H); 4.22-4.28 (br, 2H); 3.83 (br, 3H); 3.65-3.72 (br, 1H); 3.49-3.56 (br, 1H); 3.42-3.48 (br, 1H); 3.08-3.14 (br, 1H); 2.80-2.86 (br, 1H); 2.63-2.70 (br, 1H); 2.50-2.61 (br, 3H); 2.08-2.16 (br, 2H).

Cycle carbonate IL (**2**): ^{1}H NMR (400 MHz, CD_3CN): δ=8.43 (s, 1H); 7.38 (br s, 1H); 7.33 (br s, 1H); 4.88-4.97 (br, 1H); 4.54-4.60 (br, 1H); 4.19-4.26 (br, 3H); 3.83 (br, 3H); 2.88-2.93 (br, 2H); 2.58-2.64 (br, 2H); 2.08-2.16 (br, 2H).

Typical procedures for the reactions

The procedures for the reactions are as follow. In a typical experiment to produce the IL intermediate (**2**) (Step 1 in Scheme 1), 1.02 g diol IL(**1**), desired amounts of urea, and catalyst were added into a stainless steel reactor of 10 mL with a magnetic stirrer, which was the similar to that used previously.[28] The reactor was heated to desired temperature after the air was removed, then the stirrer was started and CO_2 blowed through the reactor to remove the ammonia produced in the reaction continuously. The reactor was cooled in water to stop the reaction after a certain reaction time, and the yield of the IL intermediate (**2**) was determined by ^{1}H NMR. In synthesis of DMC (Step 2 in Scheme 1), a known amount of methanol was added into the reactor above. After reacted at 150 ^{o}C for desired time, the reactor was cooled to 50 ^{o}C quickly. The product and methanol were removed by CO_2 flow and were absorbed in a cold trap with DMF as absorbent. The amount of DMC was determined by GC (Agilent 4890 D) equipped with a flame-ionized detector using ethylbenzene as internal standard. In reuse experiments of the diol IL/ZnO system, the diol IL/ZnO catalytic system was utilized directly for the next run after the product and methanol were removed by CO_2 flow. In synthesis of methyl formate (step 2 in Scheme 2), a known amount of methanol, $RuCl_3 \bullet 2H_2O$ and DBU were added into the reactor above. The reactor was heated up to 150 ^{o}C for desired time. Hydrogen was introduced into the cell to 5 MPa, and then CO_2 was introduced into the cell up to 10 MPa. The reaction mixture was stirred and the reactor was cooled to 50 ^{o}C quickly. The quantitative determination of MF produced was the same as that of DMC analysis.

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Notes and references

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1 (a) M. Aresta, A. Dibenedetto and A. Angelini, *Chem. Rev.,* 2014, **114**, 1709-1742; (b) T. Yu, R. Cristiano and R. G. Weiss, *Chem. Soc. Rev.,* 2010, **39**, 1435-1447; (c) L. Zhang and Z. M. Hou, *Chem. Sci*., 2013, **3**, 3395-3403.

2 (a) Y. Xie, Z. F. Zhang, T. Jiang, J. L. He, B. X. Han, T. B. Wu and K. L. Ding, *Angew. Chem. Int. Ed.,* 2007, **46**, 7255-7258; (b) Q. W. Song, L. N. He, J. Q. Wang, H. Yasuda and T. Sakakura, *Green Chem.,* 2013, **15,** 110-115; (c) H. Kawanami, A. Sasaki, K. Matsuia and Y. Ikushima, *Chem. Commun.,* 2003, 896-897.

3 (a) F. Studt, I. Sharafutdinov, F. Abild-Pedersen, C. F. Elkjær, J. S. Hummelshøj, S. Dahl, I. Chorkendorff and J. K. Nørskov, *Nature Chem.,* 2014, **6**, 320-324; (b) S. Wesselbaum, T. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.,* 2012, **51**, 7499-7502.

4 (a) Z. F. Zhang, Y. Xie, W. J. Li, S. Q. Hu, J. L. Song, T. Jiang and B. X. Han, *Angew. Chem. Int. Ed.,* 2008, **47**, 1127-1129; (b) T. Schaub and R. A. Paciello, *Angew. Chem. Int. Ed*., 2011, **50**, 7278-7282.

5 (a) T. Kimura, K. Kamata and N. Mizuno, *Angew. Chem. Int. Ed*., 2012, **51**, 6700-6703; (b) X. J. Cui, X. C. Dai, Y. Zhang, Y. Q. Deng, and F. Shi, *Chem. Sci*., 2014, **5**, 649-655.

6 X. B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.,* 2012, **41**, 1462-1484.

7 (a) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis,* Wiley-VCH, Weinheim, 2003; (b) R. D. Rogers and K. R. Seddon, *Science,* 2003, **302**, 792-793; (c) V. I. Parvulescu and C. Hardacre, *Chem. Rev.,* 2007, **107***,* 2615-2665.

8 (a) P. B. Webb, M. F. Sellin, T. E. Kunene, S. Williamson, A. M. Z. Slawin and D. J. Cole-Hamilton, *J. Am. Chem. Soc*., 2003, **125**, 15577-15588; (b) N. Audic, H. Clavier, M. Mauduit and J. C. Guillemin, *J. Am. Chem. Soc*., 2003, **125***,* 9248-9249; (c) Q. H. Zhang, S. G., Zhang and Y. Q. Deng, *Green Chem.,* 2011, **13***,* 2619-2637; (d) J. P. Hallett and T. Welton, *Chem. Rev.,* 2011, **111***,* 3508-3576.

9 (a) E. D. Bates, R. D. Mayton, I. Ntai and J. H. Davis, *J. Am. Chem. Soc*., 2002, **124**, 926-927; (b) W. Z. Wu, B. X. Han, H. X. Gao, Z. M. Liu, T. Jiang and J. Huang, *Angew. Chem. Int. Ed*., 2004, **43**, 2415-2417.

10 (a) Z. G. Lei, C. N. Dai and B. H. Chen, *Chem. Rev.,* 2014, **114**, 1289-1326; (b) X. Q. Sun, H. M. Luo and S. Dai, *Chem. Rev.,* 2012, **112**, 2100-2128.

11 (a) A. Rehman and X. Q. Zeng, *Accounts Chem. Res.,* 2012, **45***,* 1667-1677; (b) S. Tang, G. A. Baker and H. Zhao, *Chem. Soc. Rev.,* 2012, **41***,* 4030-4066.

12 (a) P. Tundo and M. Selva, *Acc. Chem. Res*., 2002, **35***,* 706-716; (b) R. Juarez, P. Concepcion, A. Corma, V. Fornes and H. Garcia, *Angew. Chem. Int. Ed*., 2010, **49**, 1286-1290.

13 M. A. Pacheco and C. L. Marshall, *Energy & Fuels,* 1997, **11***,* 2-29.

14 H. Babad and A. G. Zeiler, *Chem. Rev*., 1973, **73***,* 75-91.

15 S. T. King, *Catal. Today,* 1997, **33***,* 173-182.

16 T. Matsuzaki and A. Nakamura, *Catal. Surv. Jpn*., 1997, **1***,* 77-88.

17 J. Roeser, K. Kailasam and A. Thomas, *ChemSusChem,* 2012**, 5**, 1793-1799.

18 (a) K, Tomishige, T. Sakaihori, Y. Ikeda and K. Fujimoto, *Catal. Lett*., 1999, **58***,* 225-229; (b) F. Bustamante, A. F. Orrego, S. Villegas and A. L. Villa, *Ind. Eng. Chem. Res.,* 2012, **51***,* 8945-8956; (c) T. Sakakura, Y. Saito, M. Okano, J. C. Choi and T. Sako, *J. Org. Chem*., 1998, **63***,* 7095-7096.

19 (a) T. Sakakura and K. Kohno, *Chem. Commun.,* 2009, 1312-1330; (b) Z. S. Hou, B. X. Han, Z. M., Liu, T. Jiang and G. Y. Yang, *Green Chem.,* 2002, **4***,* 467-471.

20 (a) P. Ball, H. Fullmann and W. Heitz, *Angew. Chem., Int. Ed*., 1980, **19***,* 718-720; (b) W. B. Zhao, W. C. Peng, D. F. Wang, N. Zhao, J. P. Li, F. K. Xiao, W. Wei and Y. H. Sun, *Catal. Commun*., 2009, **10***,* 655-658; (c) W. Joe, H.J. Lee, U. G. Hong, Y. S. Ahn, C. J. Song, B. J. Kwon and I. K. Song, *J. Ind. Eng. Chem*., 2012**, 18***,* 1018-1022; (d) C. Zhang, B. Lu, X. G. Wang, J. X. Zhao and Q. H. Cai, *Catal. Sci. Technol.,* 2012, **2***,* 305-309; (e) X. M. Wu, M. Kang, Y. L. Yin, F. Wang, N. Zhao, F. K. Xiao, W. Wei and Y. H. Sun, *Applied Catalysis A-General,* 2014, **473**, 13-20; (f) J. J. Sun, B. L. Yang, X. P. Wang, D. P. Wang and H. Y. Lin, *J. Mol. Catal. A: Chem*., 2005, **239**, 82-86.

21 R. A. O'Brien, A. Mirjafari, V. Jajam, E. N. Capley, A. C. Stenson, K. N. West and J. H. Davis, *Tetrahedron Lett*., 2011, **52***,* 5173-5175.

22 (a) J. H. Park, J. S. Choi, Ji Sik, S. K. Woo, S. D. Lee, M. Cheong, H. S. Kim and H. Lee, *Appl. Catal. A: Gen.,* 2012, **433***,* 35-40; (b) Q. B. Li, W. Y. Zhang, N. Zhao, W. Wei and Y. H. Sun, *Catal. Today,* 2006, **115**, 111-116; (c) S. Fujita, Y. Yamanishi and M. Arai, *J. Catal*. 2013, **297***,* 137-141; (d) D. F. Wu, Y. l. Guo, S. Geng and Y. H. Xia, *Ind. Eng. Chem. Res*., 2013, **52***,* 1216-1223.

23 D. J. Belson and A. N. Strachan, *Chem. Soc. Rev*., 1982, **11***,* 41-56.

24 (a) T. Tatsumi, Y. Watanabe and K. A. Koyano, *Chem. Commun.,* 1996, 2281-2282; (b) L. G. Wang, Y. Wang, S. M. Liu, L. J. Lu, X. Y. Ma and Y. Q. Deng, *Catal. Commun.,* 2011, **16***,* 45-49; (c) B. M. Bhanage, S. Fujita, Y. Ikushima and M. Arai, *Green Chem.,* 2003, **5***,* 429-432.

25 M. H. Wang, H. Wang, N. Zhao, W. Wei and Y. H. Sun, *Catal. Commun*., 2006, **7***,* 6-10.

26 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.,* 1995, **95***,* 259-272.

27 (a) O. Krocher, R. A. Koppel and A. Baiker, *Chem. Commun*., 1997, 453-454; (b) K. M. K. Yu, C. M. Y. Yeung and S. C. Tsang, *J. Am. Chem. Soc.,* 2007, **129**, 6360-6361; (c) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, *Angew. Chem. Int. Ed*., 2010, **49***,* 9777-9780; (d) H. Phala, K. Kudo, S. Mori and N. Sugita, *Bull. Inst. Chem. Res. Kyoto Univ.,* 1985, **63***,* 63-71.

28 H. Z. Liu, T. Jiang, B. X. Han, S. G. Liang and Y. X. Zhou, *Science,* 2009, **326***,* 1250-1252

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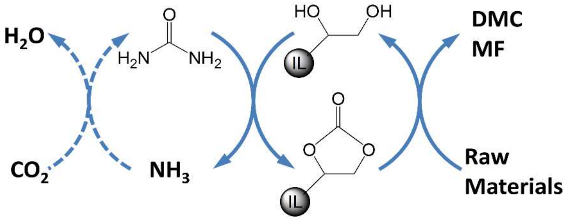

A strategy is proposed to overcome the thermodynamic limitation of chemical reactions (CO_2 conversion) using the designable and
5 non-volatile natures of ILs.