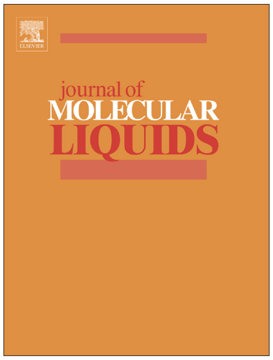


Highly synergistic effect of ionic liquids and Zn-based catalysts for synthesis of cyclic carbonates from urea and diols

Lili Deng, Wenzhong Sun, Zijie Shi, Wei Qian, Qian Su, Li Dong,
Hongyan He, Zengxi Li, Weiguo Cheng

PII: S0167-7322(20)31525-7

DOI: https://doi.org/10.1016/j.molliq.2020.113883

Reference: MOLLIQ 113883

To appear in: *Journal of Molecular Liquids*

Received date: 12 March 2020

Revised date: 23 May 2020

Accepted date: 19 July 2020

Please cite this article as: L. Deng, W. Sun, Z. Shi, et al., Highly synergistic effect of ionic liquids and Zn-based catalysts for synthesis of cyclic carbonates from urea and diols, *Journal of Molecular Liquids* (2020), https://doi.org/10.1016/j.molliq.2020.113883

Highly synergistic effect of ionic liquids and Zn-based catalysts for synthesis of cyclic carbonates from urea and diols

Lili Deng, [a,b] Wenzhong Sun, [b,c] Zijie Shi, [a,b] Wei Qian, [a,b] Qian Su, [b,d] Li Dong [b,d],
Hongyan He [b], Zengxi Li*[a,b] and Weiguo Cheng* [b,d]

[a] University of Chinese Academy of Sciences, School of Chemical Sciences, Beijing 100049, China
[b] CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.
[c] Dalian Polytechnic University, School of Light Industry Chemical Engineering, Dalian 116034, China.
[d] Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing 100190, China.
E-mail: lizengxi@ucas.edu.cn
wgcheng@ipe.ac.cn

Abstract

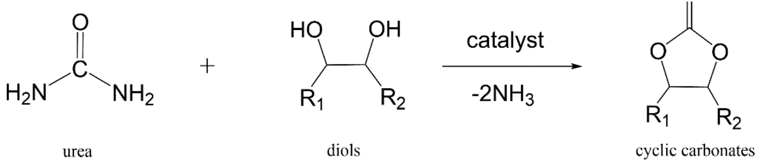
The development of stable and efficient catalysts is an attractive topic for green chemistry reactions under mild reaction conditions. In order to improve solvent-free synthesis of cyclic carbonates from urea and diols, a binary catalyst systems of Zn-based and different ionic liquids (ILs) were developed and examined in this study. The yield of ethylene carbonate (EC) could reach to 92.2% in the presence of $C_{16}mimCl/ZnCl_2$ catalyst. Through exploring the structure-activity relationships of cation and anion, it was confirmed that a synergistic effect of cation and anion of catalyst had important influences on urea alcoholysis. Additionally, the controlling step of EC synthesis reaction involving the elimination of an ammonia molecule from intermediates had been revealed by *in situ* FT-IR. This could afford a guided insight for synthesizing cyclic carbonates with high yield. Furthermore, a possible mechanism for the catalytic process was proposed based on DFT and the experimental results *via* FT-IR, ^{1}H-NMRand ^{13}C-NMR analysis, which revealed that not only a probable synergistic effects of cation-anion matters, but also C(2)-H of ILs and Zn^{2+} played a key role in accelerating the reaction of urea alcoholysis. This catalytic mechanism study is to provide a preliminary basis to develop novel catalysts for cyclic carbonates from urea and diols through a green synthetic pathway.

Keywords

Ionic liquids; Catalysts; Synergistic effect; Urea; Cyclic carbonates

1. Introduction

Organic carbonates are crucial commercial chemicals and can be widely used as intermediates in various synthetic, industrial applications and also as solvents [1-3]. Cyclic carbonates, as a kind of organic carbonates, can be considered as reactants and intermediates in chemical reaction for alkoxylation [4, 5], carbamate synthesis [5], diols formation [6] and preparation of dimethyl carbonate (DMC) [7-9]. They are not only vital organic chemicals, but also as solvents with high polarity and boiling point, attracting extensive attention in organic synthesis, electrochemistry, gas separation and other fields [2, 5, 10-12]. The routes for the synthesis of cyclic carbonates include reaction of phosgene method [2], carbon dioxide (CO_2) with diols [13, 14], cycloaddition of epoxides with CO_2 [15-18] and urea alcoholysis (Scheme 1) [4, 19, 20]. Among all these routes, the reaction of urea alcoholysis shows a great deal of superiorities, i.e., mild reaction conditions, inexpensive and accessible raw materials, low production cost and safe reaction process [4, 19-23]. In addition, it is of great significance that by-product diols (PG and EG) in the preparation of DMC by transesterification, can be as the reactant to synthesize cyclic carbonates successfully in this reaction [7-9]. Besides that, the released ammonia in the reaction of urea and diols can further react with CO_2 to produce urea to realize recycling economy, which should be regarded as an effective and indirect way for CO_2 utilization [19-23]. Furthermore, this will improve the utilization ratio of the raw materials for downstream DMC synthesis by transesterification reaction. Among them, the first step is the key for this route and the development of catalysts is the most important.

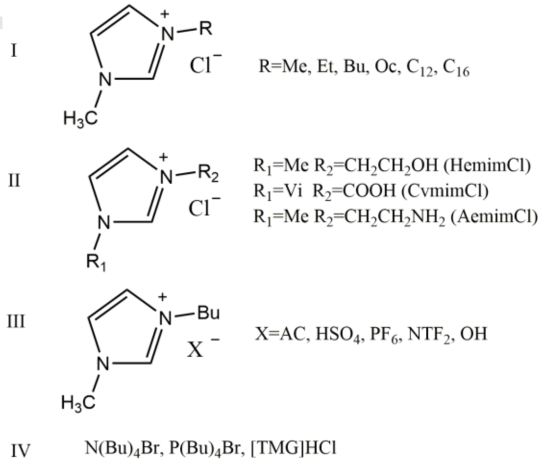


Scheme 1 The synthesis of cyclic carbonates from urea and diols

In recent years, numerous catalysts including tin-based [5], metal salts [24, 25] and (mixed) metal oxides [19-23, 26-28] etc. have been reported in the reaction of diols with urea to cyclic carbonates. However, these metal based catalysts are generally faced with the problems of environment unfriendly, low activity and loss of active components [25, 26]. Nowadays, ionic liquids (ILs) are receiving tremendous attention in various chemical engineering and scientific fields because of their special properties such as green, adjustable structure and higher thermal stability [29-33]. Kuznetsov et al. [34] proposed a new method by forming homogeneous catalytic system of $ZnCl_2$-urea-glycol in organic solvent-IL under mild conditions, but it still required a long reaction time (24 h) and additional solvents. In this study, these ILs did not be used as catalyst to realize the catalytic effect because of the structure of these used ILs were not be designed with active sites to catalyze reactive molecules. Consequently, it is important to understand the reaction process and design the structure of ILs for the development of highly active catalytic systems.

It was found that metal-based catalysts mainly activated the urea molecule by combining the metal empty orbit with the carbonyl oxygen atom or nitrogen atom in the reaction of urea alcoholysis from previous studies and the main function of metal salt anion was to stabilize metal salt [22-25]. And these reported catalysts for this reaction were mainly zinc-based catalysts, as reported by Arai et al. [35] who firstly established suitable zinc oxide catalyst for the reaction of urea and EG, which had been found ZnO with weak basicity showed highly catalytic performance, the formation of these products under different reaction conditions were illustrated and most plausible reaction pathways were also proposed. This first study on weakly basic catalyst not only provided a good research idea for the development and design of weakly basic and amphoteric zinc-based catalyst by adjusting the charge density of metal active center for urea alcoholysis reaction, but also made an important foundation about synergetic catalytic mechanism of metal anions and cations. Based on other catalytic reaction system, it was also verified the catalytic activity may be improved by controlling the charge density of the metal holes [36]. In addition, considering the weak compatibility between inorganic salts and organic reaction molecules, the ILs with excellent solubility can be used as the connection bridge which is supposed to achieve effective contact between reaction molecules and active sites. At the same time, the chain length of ILs have an important influence on the construction of reaction space to regulate molecular diffusion, for example, imidazolium ILs with lengths of alkyl side chains for the cycloaddition of CO_2 and epoxides showed higher catalytic activity [37-39] and the effective absorption properties of CO_2 was realized by governing the amino-alkyl chain length of IL through DFT caculation [40]. Therefore, it is expected to realize the construction of binary catalysts system with high catalysis activity by effectively adjusting the structure of ILs to control the charge density of metal active center and improving the mass transfer of reaction molecules.

In this work, the binary catalyst systems of Zn-based and other metal salts ($ZnCl_2$, $ZnBr_2$, $FeCl_3$, etc.) with different ILs were examined for solvent-free to synthesize EC from urea and EG. Among the catalysts investigated, ILs featuring different lengths of alkyl side chains, different functional groups and different counter anions such as AC^-, HSO_4^-, PF_6^-, NTF_2^- and OH^- were tested (Scheme 2). The effects of reaction parameters such as temperature, pressure, reaction time, amount of catalysts and molar ratio of urea/EG had been investigated. Additionally, the catalyst was also proved to be applicable to other dihydric alcohols and the catalyst could be reused for five times. Moreover, *in situ* FT-IR was used for detection of the reaction process and gained the controlling step of EC synthesis reaction involving the elimination of ammonia from intermediates. A possible mechanism of this catalytic process was proposed based on DFT and the experimental results of FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy.



Scheme 2. Structures of the ILs used in this work

2 Experimental

2.1 Reagents

Zinc chloride ($ZnCl_2$, 98.0%), zinc oxide(ZnO, 98.0%), zinc nitrate ($Zn(NO_3)_2$, 98.0%), zinc acetate ($Zn(AC)_2$, 98.0%)，zinc bromide($ZnBr_2$, 98.0%)，copper chloride ($CuCl_2$, 98.0%)，ferric chloride ($FeCl_3$, 98.0%)，urea (99.0%), EG (99.5%) and PG (99.5%) were received from Sinopharm Chemical Reagent Co., Ltd. (China). In this work, all ILs were purchased from Shanghai Chengjie Chemical Reagent Co., Ltd. (China). Other diols were obtained from Aladdin Reagent Co., Ltd. All materials were used without further purification.

2.2 Catalysts characterization

The fresh and used IL (C_{16}mimCl) were characterized by fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet 380) and anhydrous KBr was used as the standard. Thermogravimetric analysis was analyzed with a DTG-60H thermal analyzer (TGA, Shimadzu, Japan) under the nitrogen atmosphere at a heating rate of 10 °C/min and an empty crucible was used as the reference. *In situ* IR spectra were measured by the ReactIR 10 with a MCT Detector using HappGenzel apodization, DiComp (Diamond) probe connected via K6 Conduit (16 mm probe) and sampling 1900 to 1400 at 16 wavenumber resolution. ^{1}H-NMR spectra were recorded by Bruker AVANCE III 600 MHz nuclear magnetic resonance spectrometer with deuterated dimethyl sulfoxide (DMSO-d_6). High resolution mass spectra (HRMS (ESI-MS)) were collected on a Brucker high resolution mass spectrometer (micrOTOF-QII). Then the purity of EC was determined by 6820GC-TCD gas chromatography of Agilent Technologies.

2.3 Typical procedure for the synthesis of EC from EG and urea

The urea alcoholysis reaction was operated in a 50 mL three-necked flask with a reflux condenser, magnetic stirrer and an absorption device. A series of ILs (Scheme 2) were tested for comparisons. In a typical procedure, urea (1.8 g), EG (5 mL), C_{16}mimCl (0.41 g) and $ZnCl_2$ (0.33 g) were added into the three-necked flask. Then it was heated to 160 ^{o}C reaction temperature gradually and adjusted to the initial value under reduced pressure at the same time, because a great deal of ammonia could be produced in this reaction and it must be released through an absorption device from the reaction system. At the end of this reaction, the mixtures were cooled at room temperature, and they were analyzed on a gas chromatograph equipped with 6820GC-TCD gas chromatography of Agilent Technologies. The alike procedure was also carried out for the urea with other diols. The tests of catalyst recycling were performed in a 200 mL three-necked-flask with a scale-up experiment of 10 times amount of urea, EG and catalyst. Since IL has high boiling points compared with organic compounds (EG and EC), IL and $ZnCl_2$ could be separated from products by distillation under vacuum and can be reused for the next run directly.

3 Results and discussion

3.1 Catalytic activity of ILs

The development of an appropriate catalyst was an efficient and simple way to attain high yield of EC. In this representative reaction, ILs with different lengths of alkyl side chains were further characterized by TGA and found that they thermally stable up to 200 ^{o}C (Figure S1), which could avoid the degradation of ILs to bring out the contamination of products. After that, a series of ILs (Scheme 2) based on imidazolium cations countered with different lengths of alkyl side chains, different functional groups and different anions were examined for the synthesis of EC from urea and EG under identical reaction conditions. The results were summarized in Table 1, and revealed the synergistic effect of anion and cation on catalytic activities (entries 2-17).

In the case of the Cl^- anion, the yield and selectivity of EC increased with the lengths of alkyl chains in the cation and obeyed the order of $C_{16}mim^+ > C_{12}mim^+ > Omim^+ > Bmim^+ > Emim^+$ (Table 1, entries 2-6). The results indicated long-chain cation was beneficial for improving the catalytic activity, in accordance with the result in previous work [38, 39]. The main reason was that with the increase of side-chain length, the longer carbon chain prolonged the distance between cation and anion, which could weaken the electrostatic interaction between them [38, 39]. Then cation C(2)-H had stronger activation ability and was easier to react with urea. Under the same scenario of anion, the effects of ILs with different functional groups on the reaction were investigated (entries 7-9), but these catalytic performances were not significantly improved. The main reason was not only anions of ILs could form hydrogen bonds with the hydroxyl group of EG but also imidazole cations of ILs also formed hydrogen bonds with EG [41], and the former one was not quite conducive to the formation of hydrogen bonds between cations and urea.

The effects of different anions (AC^-, HSO_4^-, PF_6^-, NTF_2^-, OH^-) on the reaction were interrogated by the same imidazole cation (entries 10-14). The experimental results showed the catalytic effect of NTF_2^- was the best. The experimental results were similar to those in the literature [42]. The main reason was that NTF_2^- was easier to form hydrogen bonds with ethylene glycol, which weakened the interaction between anions and cations in IL and promoted the interaction of cations with urea, thus increasing the yield and selectivity of EC. The other three ILs had no obvious catalytic effect on the reaction (entries 15-17). Besides, white precipitate, which reduced the yield of reaction, was formed in the reaction of protonic IL and urea (entries 8 and 11). Although single IL catalysts had no excellent catalytic activity, the binary catalysts showed superior activity, confirming that a synergistic effect between cation and anion had indispensable results on urea alcoholysis with diols obviously.

Table 1. Effects of different IL catalyst on the reaction of urea and EG

Entry	Catalyst	EC Y. %	EC Sel. %
1	None	1.9	4.7
2	EmimCl	10.5	18.9
3	BmimCl	15.5	20.1
4	OmimCl	21.8	29.3
5	C_{12}mimCl	23.0	31.4
6	C_{16}mimCl	26.2	33.1
7	HemimCl	12.3	24.3
8	CvmimCl	7.3	14.5
9	AemimCl	11.5	22.9
10	BmimAC	11.9	16.1
11	$BmimHSO_4$	10.3	19.6
12	$BmimPF_6$	15.6	27.2
13	$BmimNTF_2$	30.4	41.0
14	BmimOH	22.2	33.6

15	$N(Bu)_4Br$	15.3	29.0
16	$P(Bu)_4Br$	15.0	21.4
17	[TMG]HCl	15.6	22.7

Reaction conditions: temperature, 140 °C; pressure, 15KPa; reaction time, 3 h; urea:EG (mol:mol)=1:3; IL, 4%mol(urea)

3.2 Catalytic activity of binary catalysts

3.2.1 Catalytic activity of ILs and metal salts catalysts

To investigate the effects of different ILs and metal salts on the formation of EC, first of all, we need to ensure the structure of ILs with different lengths of alkyl side chains would not be changed after metal salt was added through FT-IR (Figure S2). Then Zn-based and other metal salts ($ZnCl_2$, $ZnBr_2$, $FeCl_3$, etc.) with ILs (Scheme 2) were selected and explored, and the corresponding results were summarized in Table 2. According to Table 1, it could be concluded that the catalytic effect of single IL was not good and $ZnCl_2$ exhibited a 31.6% EC yield (entry 1, Table 2). However, the binary catalysts of ILs and $ZnCl_2$ realized a further enhancement in catalytic activity compared to that achieved by every single one, indicating the necessary synergistic effect of ILs and $ZnCl_2$ on accelerating the reaction by which the EC yield approached 75.8% with a 88.5% selectivity (entry 6). This could also be proved by the FT-IR (Figure 6) and DFT calculations below. Interestingly, the catalytic performance of binary IL catalysts with different lengths of alkyl side chains (entries 2-6) and different functional groups (entries 7-9) was similar to Table 1. However, the anion with NTF_2^- did not exhibit excellent catalytic effect in the study of binary IL catalysts (entry 13). That possibly because adding $ZnCl_2$ decreased the H-bond between the anion (NTF_2^-) of IL and EG. Thus, the strengthened H-bonding role between anion and cation of IL was able to be counterbalanced by the weakened interaction of imidazole cation and urea simultaneously. Therefore, the catalytic performance of the catalytic system was not greatly enhanced.

In order to investigate the effect of the different metal salts ($ZnCl_2$, $ZnBr_2$, $FeCl_3$, etc.) on the catalytic activity, the other catalysts including C_{16}mimCl/$Zn(NO_3)_2$, C_{16}mimCl/$Zn(AC)_2$, C_{16}mimCl/$ZnBr_2$, C_{16}mimCl/$CuCl_2$ and C_{16}mimCl/$FeCl_3$ were also studied and the results were presented in Table 2 (entries 18-23). It was obvious that C_{16}mimCl/$ZnBr_2$ catalyst could also show high catalytic activity under the mild conditions, while the others did not. Among the catalysts employed, $C_{16}mimCl/ZnCl_2$ exhibited the highest activity (yield=75.8% and selectivity=88.5%) under the conditions of 140 °C, 15 KPa, 3 h, urea:EG (mol:mol)=1:3, IL, 4%mol(urea), $ZnCl_2$, 8%mol(urea) (entry 6). Due to its stable and high catalytic activity, $C_{16}mimCl/ZnCl_2$ was chosen for further investigation.

Table 2. Effects of different binary catalytic systems on the reaction of urea and EG

Entry	Catalyst	EC Y. %	EC Sel. %
1	$ZnCl_2$	31.6	58.9
2	$EmimCl/ZnCl_2$	39.2	76.7
3	$BmimCl/ZnCl_2$	58.6	86.5
4	$OmimCl/ZnCl_2$	67.3	88.3
5	$C_{12}mimCl/ZnCl_2$	73.4	87.6
6	$C_{16}mimCl/ZnCl_2$	75.8	88.5
7	$HemimCl//ZnCl_2$	36.2	55.6
8	$CvmimCl/ZnCl_2$	32.0	51.4
9	$AemimCl/ZnCl_2$	43.1	83.6
10	$BmimAC/ZnCl_2$	40.9	69.9
11	$BmimHSO_4/ZnCl_2$	37.7	49.3
12	$BmimPF_6/ZnCl_2$	34.3	64.7
13	$BmimNTF_2/ZnCl_2$	42.4	64.4
14	$BmimOH//ZnCl_2$	45.4	77.1
15	$N(Bu)_4Br/ZnCl_2$	37.3	60.8
16	$P(Bu)_4Br/ZnCl_2$	35.3	73.4
17	$[TMG]HCl/ZnCl_2$	33.5	57.9
18	$C_{16}mimCl/ZnO$	39.3	53.1
19	$C_{16}mimCl/Zn(NO_3)_2$	36.3	72.6
20	$C_{16}mimCl/Zn(AC)_2$	35.8	70.1
21	$C_{16}mimCl/ZnBr_2$	74.3	87.3
22	$C_{16}mimCl/CuCl_2$	61.7	80.1
23	$C_{16}mimCl/FeCl_3$	67.3	84.3

Reaction conditions: temperature, 140 °C; pressure, 15KPa; reaction time, 3 h; urea:EG (mol:mol)=1:3; IL, 4%mol(urea); metal salts, 8%mol(urea)

3.2.2 Effect of ILs and Zn-based catalysts

The influence of the binary catalytic systems on the urea alcoholysis reaction was demonstrated and the result was shown in Table 3. From the result, it could be concluded that the catalytic activity strongly depended on the ratio of C_{16}mimCl/$ZnCl_2$. When the molar amount of $ZnCl_2$ was fixed at 8 mol% of urea, the catalyst activity increased apparently with the mounting molar ratio of C_{16}mimCl to $ZnCl_2$ from 0.1:1-0.5:1, and the EC yield increased from 31.6% to 75.8% (entries 1-4), whereas further improvement of molar ratio to 6:1 resulted in an obvious drop for the yield of EC (entries 5-8). This may be due to the fact that with the increase of C_{16}mimCl concentration, the IL was hard to flow smoothly, which caused the elevated resistance of mass transfer between active sites and reagents and the low dispersion of excess C_{16}mimCl in this homogeneous catalytic process [43-45]. Thus, the optimum C_{16}mimCl/$ZnCl_2$ molar ratio was 1:2 and the $ZnCl_2$ was fixed at 8 mol% of urea.

Table 3. Effects of the molar ratio of C_{16}mimCl/$ZnCl_2$ on the reaction of urea and EG

Entry	C_{16}mimCl:$ZnCl_2$ (mol:mol)	EC Y. %	EC Sel. %
1	0:1	31.6	58.9
2	0.1:1	43.3	64.7
3	0.2:1	54.2	76.0
4	0.5:1	75.8	88.5
5	1:1	74.8	87.1
6	2:1	63.2	81.6
7	4:1	56.6	77.3
8	6:1	41.7	69.8

Reaction conditions: temperature, 140 ^{o}C; pressure, 15KPa; reaction time, 3 h；urea:EG (mol:mol)=1:3; $ZnCl_2$, 8%mol(urea)

3.3 Effect of reaction conditions

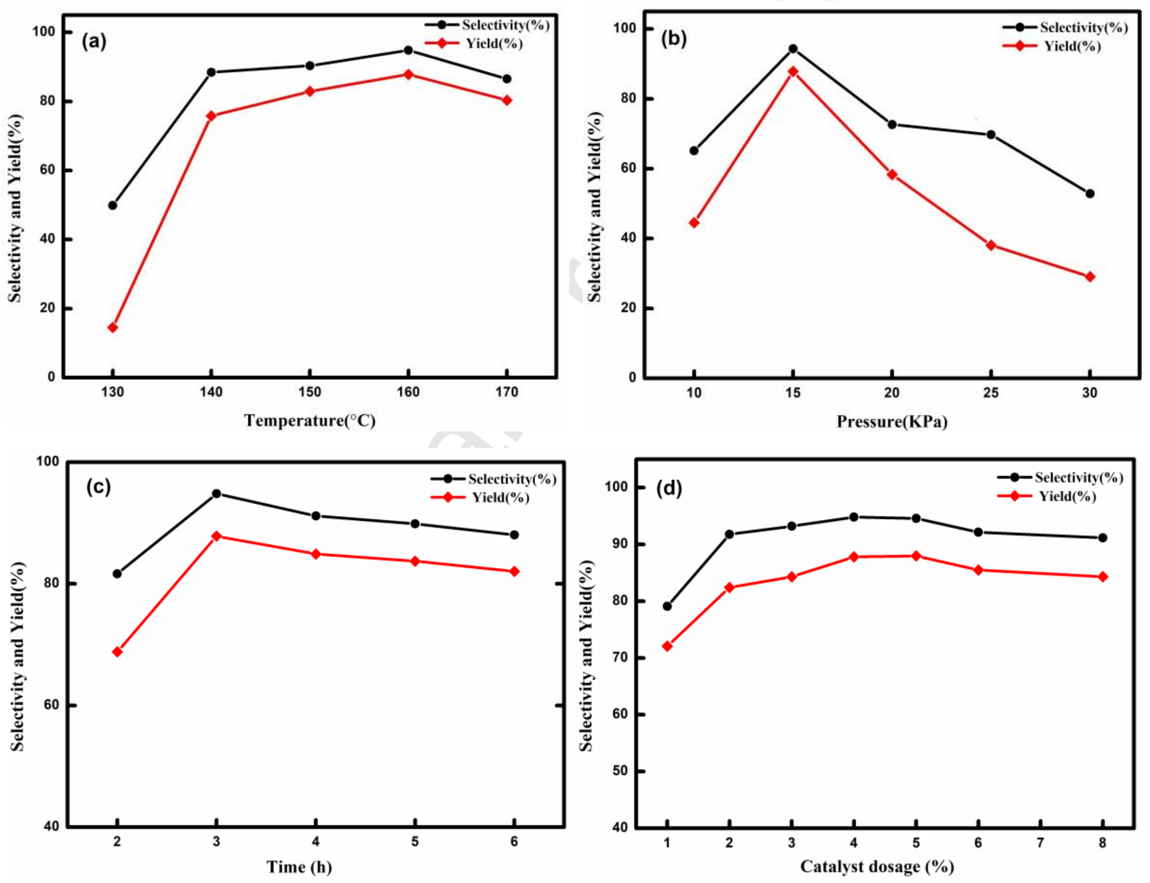
To find the optimum reaction conditions in this binary catalytic system, the reaction parameters of temperature, pressure, reaction time, amount of catalysts and molar ratio of urea/EG were investigated. And yield and selectivity on different parameters catalyzed by C_{16}mimCl/$ZnCl_2$ were shown in Figure 1. In Figure 1(a), the yield and selectivity of EC enhanced firstly along with increasing temperature from 130 ^{o}C to 170 ^{o}C, and the yield and selectivity of EC would reach the highest value of 87.8% and 94.8% when reaction temperature rose to 160 ^{o}C, but the yield and selectivity would decrease at higher reaction temperature of 170 ^{o}C. The thermodynamic calculation results indicated the elevation of reaction temperature was advantageous for EC synthesis because it was an endothermal reaction [46]. However, the reason that EC yield and selectivity reduced with a further increasing temperature was thought to be the acceleration of side reactions and the decomposition of urea [24, 47]. Therefore, the optimized reaction temperature for EC synthesis was 160 °C.

As is well known, a great deal of ammonia was released from the reaction during the experiment and that would be an obvious negative impact on the reaction equilibrium with the pressure increased. Therefore, it was very essential to explore the effect of pressure on the reaction. The result (Figure 1(b)) showed as the pressure of the reaction system increased, the yield and selectivity of EC decreased in the range of 15 KPa-30 KPa. When the pressure of the system was higher, the ammonia produced by the reaction was not easily brought out of the reaction system in time, which made the equilibrium conversion of EC decrease, therefore, 15 KPa was selected as the appropriate pressure on this reaction.

Figure 1(c) showed the yield and selectivity of EC could increase remarkably with the added reaction time, and then the EC yield and selectivity decreased with the extension of the reaction time. That might be caused by the side reactions that would occur in accordance with the major reaction such as the polymerization of EC when the concentration of EC was high after 3 h [4, 24, 47]. The optimum reaction time was determined to be 3 h for the EC synthesis.

To illuminate the effect of catalyst amount on the properties of EC, EC was synthesized by C_{16}mimCl/ZnCl_2 in different amounts. As shown in Figure 1(d), the catalyst amount also had obvious effection EC yield and selectivity. When the amount of the catalyst was increased from 1-4 mol% (the molar ration of C_{16}mimCl to urea), the yield and selectivity of EC increased drastically. However, the yield and selectivity of EC decreased with an increased catalyst amount, while the same phenomenon had also been reported in other literature [4, 24, 47]. Thus, the good yield could be obtained at a catalyst amount of 4 mol% (C_{16}mimCl) of urea.

Figure 1(e) presented the effect of urea/EG molar ratio on the reaction of EC synthesis, the yield and selectivity of EC increased at first and then decreased with the rising molar ratio of urea/EG, and when the molar ratio reached at 1:4, the highest yield and selectivity of EC could be obtained, which were 92.2% and 97.9%, respectively. EG was not only as a reactant but also a solvent for this reaction process. The decrease of EC yield and selectivity as urea/EG molar ratio continued to rise at 1:5, which might be due to low concentration of urea reactant and low reaction rate [4, 24]. Therefore, the appropriate molar ratio of urea/EG was 1:4.



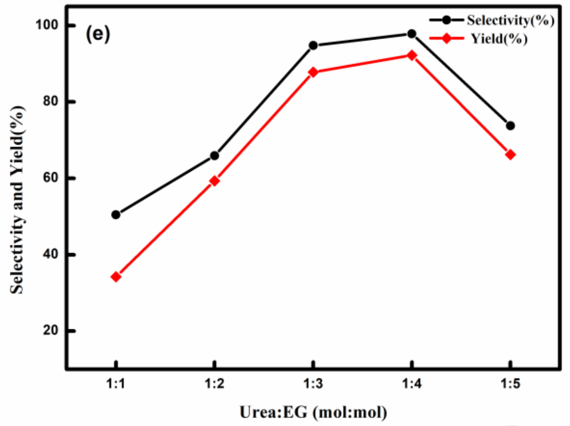


Figure 1 Effect of reaction conditions on EC synthesis

Reaction conditions: (a) 15 Kpa, 3 h, urea:EG (mol:mol)=1:3; IL, 4%mol(urea); $ZnCl_2$, 8%mol(urea); (b) 15Kpa, 3 h, urea:EG (mol:mol)=1:3; IL, 4%mol(urea); $ZnCl_2$, 8% mol(urea); (c) 160 ^oC, 15 Kpa, urea:EG (mol:mol)=1:3; IL, 4%mol(urea); $ZnCl_2$, 8%mol(urea); (d) 160 ^oC, 15Kpa, 3 h, urea:EG (mol:mol)=1:3, IL:$ZnCl_2$ (mol:mol)=1:2; (e) 160 ^oC, 15Kpa, 3 h, IL, 4%mol(urea); $ZnCl_2$, 8%mol(urea)

3.4 Catalyst recycling and catalytic activity towards other diols

In order to test the catalyst recycling with the dependence of the yield and selectivity of EC to confirm the stability of catalyst, the C_{16}mimCl/$ZnCl_2$ catalyst was chosen for recycling reaction. After every cycle, the separation between products and C_{16}mimCl/$ZnCl_2$ catalyst was achieved by vacuum distillation, and the obtained catalyst was reused directly for the next run. The relevant result was shown in Figure 2. The decline in yield and selectivity of EC was minimal after 5 cycles, showing the catalyst was stable and suitable for reuse.

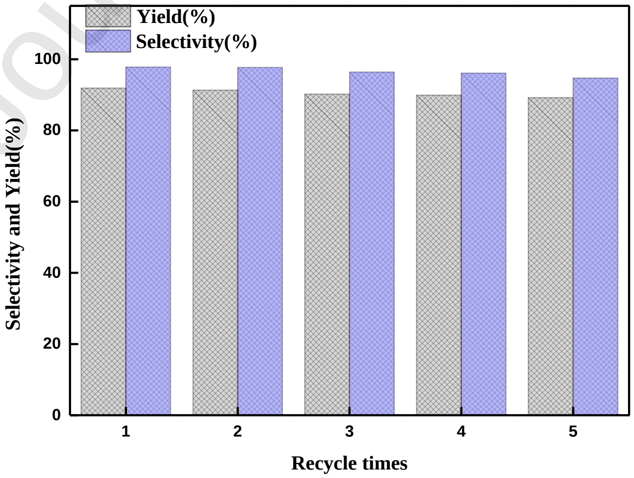


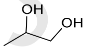
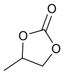
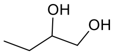
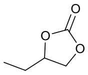
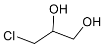
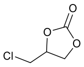
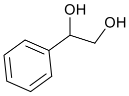
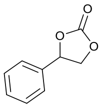
Figure 2 The performance for recycling of catalyst

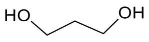
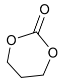
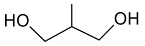
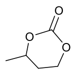
Reaction conditions: temperature, 160 ^oC; pressure, 15KPa; reaction time, 3 h; urea:EG (mol:mol)=1:4; IL, 4%mol(urea); $ZnCl_2$, 8%mol(urea)

To further survey the scope of substrates, we investigated the synthesis of cyclic carbonates from urea and various diols (1,2-propylene glycol, 1,2-butylene glycol, 3-chloro-1,2-diol, 1-phenylethane-1,2-diol, 1,3-Propanediol, 1,3-Butanediol) over $C_{16}mimCl/ZnCl_2$ (Table 4). All the diols could convert, and the high yield of five-membered cyclic carbonates could be obtained from urea. Without a doubt, the yield of cyclic carbonate was affected by the polarity of vicinal glycols, and the greater polarity of the vicinal glycol had an adverse effect on the yield of cyclic carbonate [20]. Although 1-phenylethane-1,2-diol can turn into cyclic carbonates successfully, only 81.2% of product yielded because of steric hindrance [37]. Nonetheless, the yield of six-membered cyclic carbonates were lower than that of five-membered cyclic carbonates, which was due to the reaction influenced by the difference of three-dimensional structure between 1,2-diols and 1,3-diols [20]. Therefore, the $C_{16}mimCl/ZnCl_2$ had good suitability for urea with various diols to transform into corresponding products.

Through the above results analysis, it was found that the catalytic activity of binary catalyst in the reaction of urea and EG was lower than the ZnO catalyst reported by Arai et al. [35], but that was better than other explored metal-based catalysts [4, 20, 21, 25]. And it displayed good recycling and universality. Based on the study of binary catalyst and ZnO catalyst [35] the reaction pathway for EC synthesis, and the synergistic mechanism of ionic liquid and zinc-based catalyst were further studied.

Table 4 Synthesis of cyclic carbonates from urea and various diols

Entry	Diols	Product	Y. %
1			94.1
2			94.3
3			87.7
4			81.2

5			72.3
6			75.6

Reaction conditions: temperature, 160 °C; pressure, 15KPa; reaction time, 3 h; urea:EG (mol:mol)=1:4; IL, 4%mol(urea); $ZnCl_2$, 8%mol(urea)

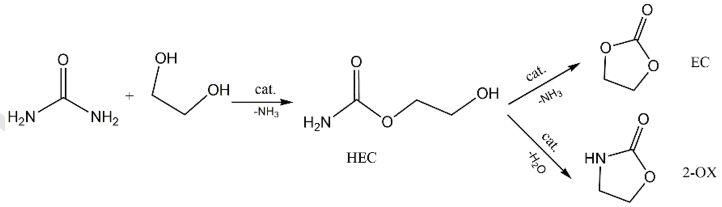
3.5 Study on catalytic mechanism

3.5.1 Reaction pathway for EC synthesis

To gain more insight for the urea alcoholysis process, the reaction between urea and EG catalyzed by $C_{16}mimCl/ZnCl_2$ was investigated using *in situ* IR monitoring under certain conditions (Figure 3(a) and 3(b)). In the first stage, the characteristic peaks of urea decrease rapidly while the characteristic peak of hydroxyethyl carbamate (HEC) rose quickly. This indicated the synthesis of HEC from EG and urea was a fast reaction. Then the characteristic peak of HEC lessened and the characteristic peaks of EC ascended gradually in the second stage. However, when the reaction of EC synthesis was near equilibrium, the characteristic peaks of HEC were also evident. It suggested the controlling step of EC synthesis was the reaction involving the elimination of ammonia from HEC to give EC [4]. Therefore, it was significant for the catalyst to activate HEC to form cyclic carbonates. *In situ* IR spectra of EC synthesis at different reaction times were shown in Figure 3(c). The two bands centered at 1679 and 1620 cm^{-1} were attributed to the C=O and N-H absorption peak of urea [4, 20, 21, 48] and the band at 1714 cm^{-1} corresponded to the C=O absorption peak of HEC [4, 5]. In addition, the bands at 1804 cm^{-1} and 1775 cm^{-1} corresponded to the C=O absorption peak of EC and 2-oxazolidone (2-OX), respectively [5]. The curve represented the urea which dissolved totally in EG at 5 min and the spectrum showed HEC, EC and 2-OX had existed in this reaction at 65 min. At this point, the characteristic peaks of urea decreased obviously and a certain amount of EC was formed while there was still some HEC left in the reaction system at 155 min, but the characteristic peak of HEC almost disappeared at 265 min, which suggested that the reaction of EC synthesis was completed essentially.

Arai et al.[35] revealed the side products of this reaction could increase with increasing the pressure and proposed the plausible reaction pathways (Figure S3). In order to verify whether side products were produced at higher pressure with

C_{16}mimCl/$ZnCl_2$, the ESI-MS analysis was also implemented. These substances of products reported in the literature [35] all existed when the catalyst of ZnO was used at 100 KPa (Figure S4 (a)). Based on the results of ZnO (Figure S4 (a)), the products gained from binary catalyst (C_{16}mimCl/$ZnCl_2$) were also analyzed by ESI-MS under different pressures (15 KPa, 50 KPa and 100 KPa). The result showed there were only three of six substances in products including 1 (EC), 2 (HEC) and 3 (2-OX) at 15 KPa (Figure S4 (b)) which was consistent with the results of *in situ* IR (Figure 3) and some reported literatures [4, 5]. Therefore, the main product was EC under lower pressure and the selectivity calculated in literatures was mainly based on these three substances [20, 35]. According to the above analysis, it could be found that there were two steps for the synthesis of EC process. The first step was the forming of HEC by urea and EG, and then EC was produced by elimination of ammonia from HEC molecule. Thus, the reaction pathway for EC synthesis was proposed as follows (Scheme 3). When the reaction pressure was increased to 50 KPa, there were other substances 4 (N-(2-hydroxyethyl)-2-oxazolidone) and 5 (ethyleneurea) apart from the previous three substances 1, 2 and 3 (Figure S4 (c)), and all substances were also detected at 100 KPa (Figure S4 (d)). More side products would be generated if ammonia was not driven out properly quite for this reaction, therefore, the removal of ammonia is essential to enhance the yield and selectivity of EC.



Scheme 3 Possible reaction pathway for EC synthesis

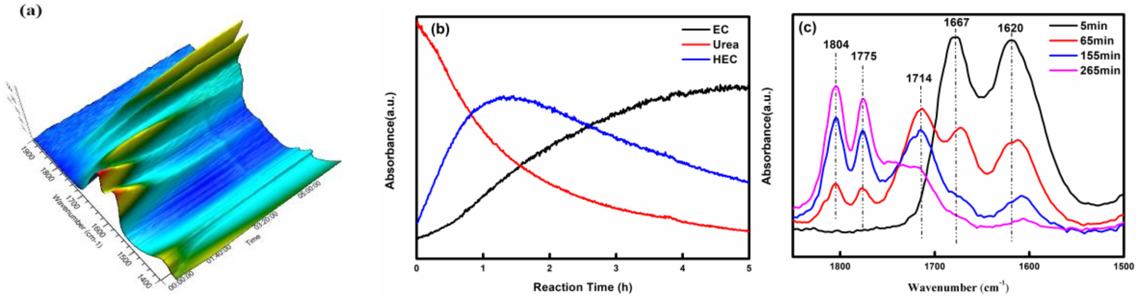


Figure 3 *In situ* IR monitoring of urea alcoholysis with EG and subsequent analysis
Reaction conditions: temperature, 140 °C; pressure, 15KPa; reaction time, 5 h; urea:EG (mol:mol)=1:4; IL, 4% mol(urea); $ZnCl_2$, 8% mol(urea)

3.5.2 Determination of action sites of ILs C(2)-H

For further investigation of the interaction between C(2)-H of ILs and urea (HEC), the ^{1}H-NMR and ^{13}C-NMR analyses were also implemented. The proton signal of C(2)-H (C_{16}mimCl) shifted from 9.19 ppm to 9.13 ppm, and other proton signals of C_{16}mimCl almost unchanged (Figure 4). As expected, the chemical shifts of the cation atom of imidazole IL(C_{16}mimCl) were all downfield shifts [32, 37]. This was explained by that urea and HEC formed H-bond with the C_{16}mimCl and caused a substantial change in the proton signal of C(2)-H (C_{16}mimCl). Upon introduction of the IL, the C signal of the C(2)-H (C_{16}mimCl) shifted from 137.08 ppm to 137.01 and 137.03 ppm (Figure 5), implying that the C(2)-H of the C_{16}mimCl was activated by forming an H-bond with urea and HEC. These results were in agreement with the description of the experiment results. Furthermore, urea and HEC were activated by IL, which could be deduced from the ^{1}H-NMR and ^{13}C-NMR spectroscopy of the mixture of IL-urea and IL-HEC (Figure S5 and S6 in the supporting information).

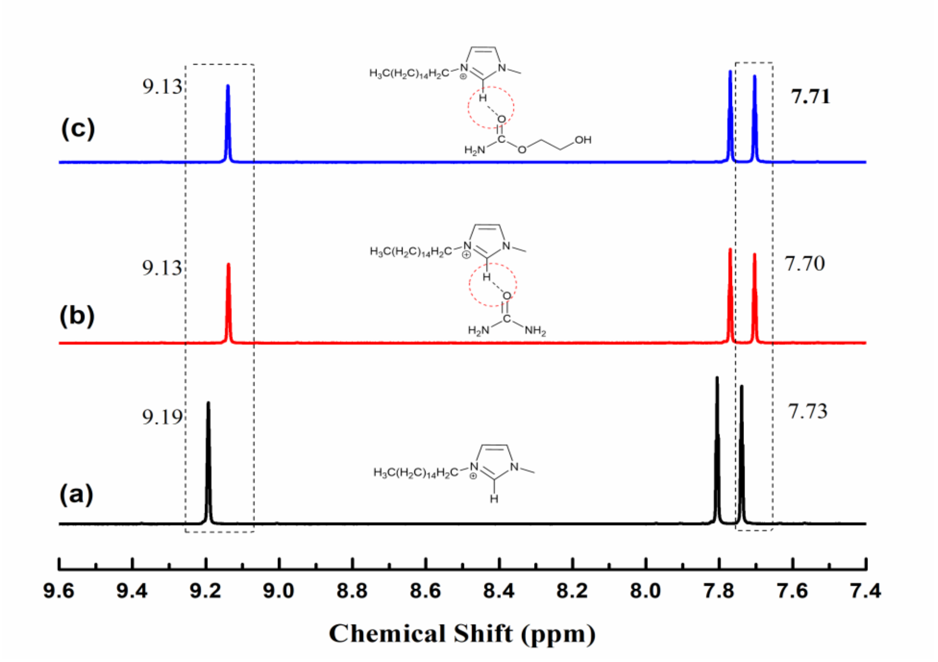


Figure 4 ^{1}H-NMR of C_{16}mimCl (a), C_{16}mimCl-Urea(b), C_{16}mimCl-HEC (c)

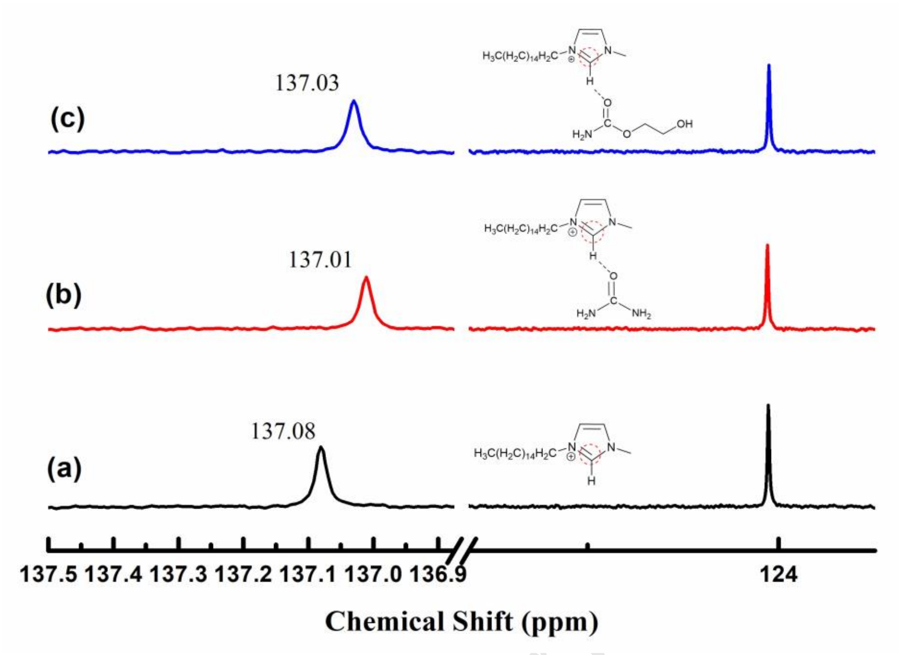


Figure 5 ^{13}C-NMR of C_{16}mimCl (a), C_{16}mimCl-Urea(b), C_{16}mimCl-HEC (c)

3.5.3 Study on synergistic effect of ILs and Zn-based catalysts

This deduction was verified by the FT-IR spectroscopy (130 ^{o}C, 30min) of the mixture of catalyst-urea and catalyst-HEC. The interaction between urea and catalysts ($ZnCl_2$, C_{16}mimCl and C_{16}mimCl/$ZnCl_2$) was shown in Figure 6 (a). Also, it was showed the absorption peak of the C=O bond of urea moved from 1679 cm^{-1} to 1633, 1675 and 1628 cm^{-1} obviously and the N-H bond of urea shifted from 1618 cm^{-1} to 1572, 1613 and 1563 cm^{-1}, respectively. The main reason was that the -NH_2 of urea became active in order to produce isonitrile acid under high temperature and the N-H band shifted clearly (Figure S5 (a) in the supporting information) [43, 48]. However, the C-N bond hardly shifted. These results could show these catalysts interacted with O atom instead of N atom of urea. Similarly, the catalysts of $ZnCl_2$, C_{16}mimCl and C_{16}mimCl/$ZnCl_2$ had interacted with HEC shown in Figure 6(b), and the absorption peak of the C=O bond of HEC moved from 1726 cm^{-1} to 1711, 1719 and 1709 cm^{-1}. Although the N-H bond shifted obviously from the result; the C-N bond did not move evidently. Thus, the C=O bond of urea and HEC shifted more when $ZnCl_2$ interacted with the C=O bond than that when IL interacted with the C=O bond (Figure 6 (a) and Figure 6 (b)) [22, 25]. This was the reason why the catalyst activity increased with $ZnCl_2$ in IL catalyst system. The FT-IR spectroscopy results were in consistent with the experiment results (Figure S7 in the supporting information).

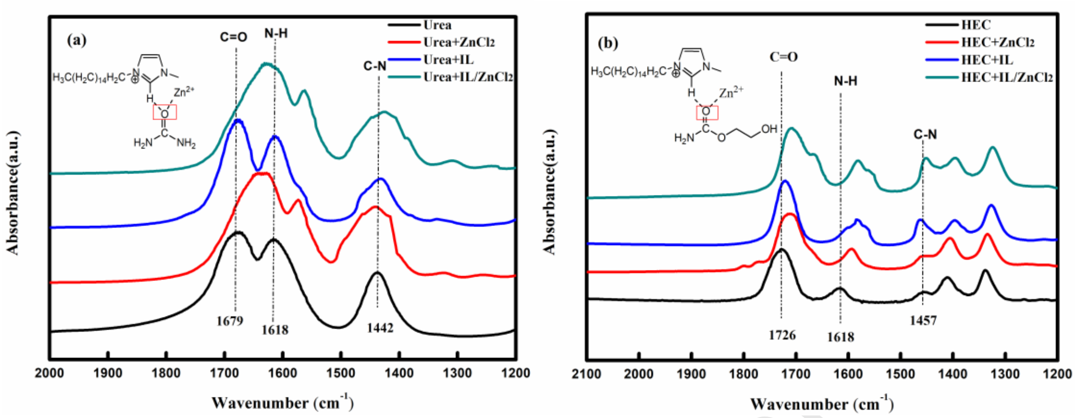
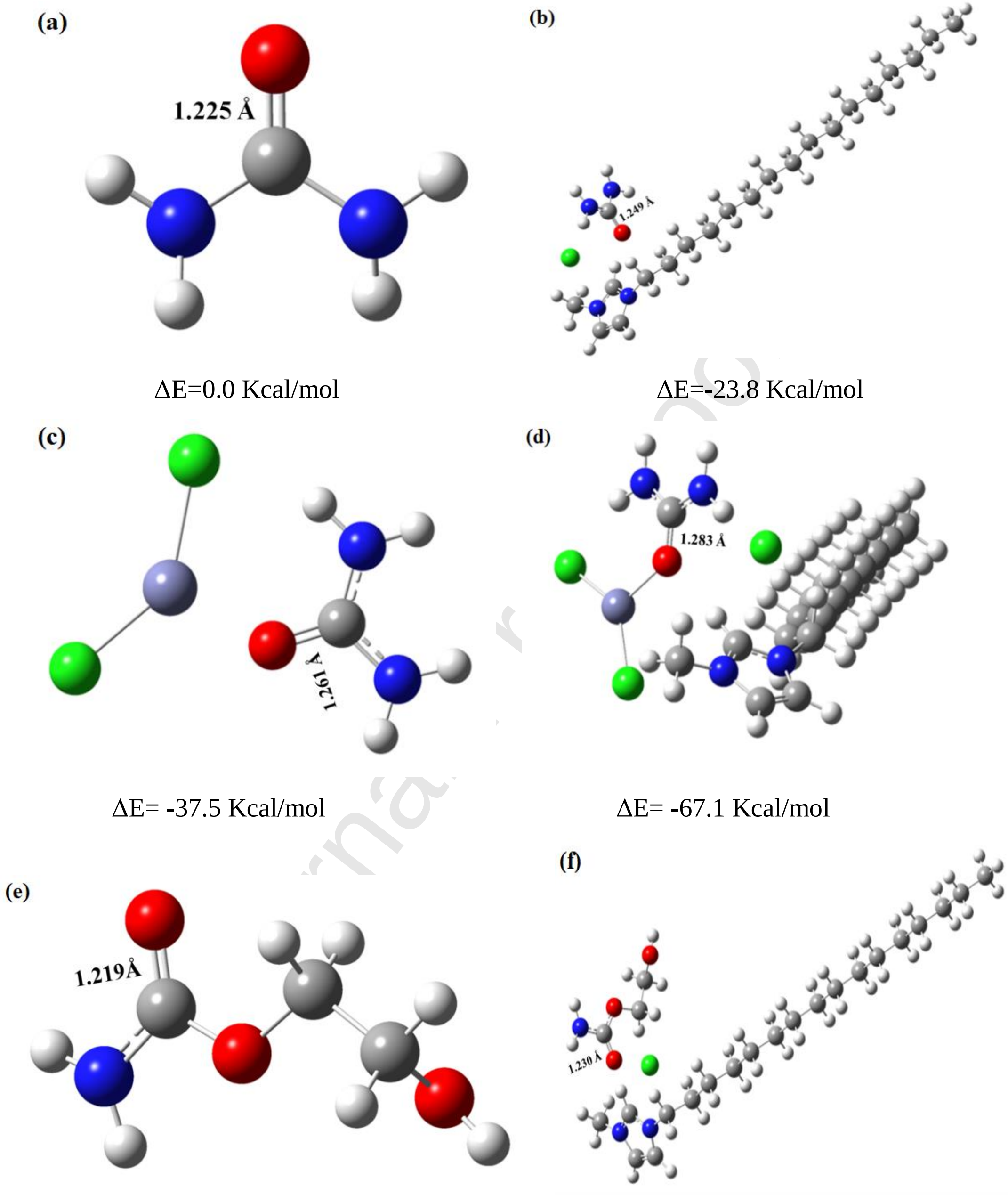


Figure 6 FT-IR spectra of urea and HEC interacted with different catalysts at 130℃

To verify this deduction of the detailed interactions between catalysts (C_{16}mimCl, $ZnCl_{2,}$ and C_{16}mimCl/$ZnCl_2$) and urea (HEC), DFT calculations were also performed by Gaussian 09 program. According to the crystal structure data of urea and HEC, we calculated the geometry and energy optimizations at the B3LYP/6-31+G(d,p) level. The energetic minimum of urea and HEC was shown in Figure 7(a) and Figure 7(e), respectively.

As shown in Figure 7, the complex energy of the C=O group of urea interacted with the cation C(2)-H of C_{16}mimCl and Zn^{2+} of $ZnCl_2$ were higher than C(2)-H and Zn^{2+} of C_{16}mimCl/$ZnCl_2$ from the original 0.0 Kcal/mol to -23.8, -37.5 and -67.1 Kcal/mol. And the complex energy of the C=O (HEC) group interaction showed the same rule from the original 0.0 Kcal/mol to -15.7, -34.2 and -53.0 Kcal/mol. That was to say, the cooperative C(2)-H of ILs and Zn^{2+} played a key role in accelerating the reaction of urea alcoholysis. Additionally, the C=O bond lengths of the C=O group of urea/HEC after interacting with C(2)-H, Zn^{2+} and C(2)-H/Zn^{2+} became longer than before the interaction (original 1.225 Å to 1.249 Å, 1.261 Å and 1.263 Å/ original 1.219 Å to 1.230 Å, 1.253 Å and 1.255 Å), which illustrated C(2)-H/Zn^{2+} had stronger complex role. These consisted with the abovementioned experimental results. The complex interaction between urea/HEC and catalyst (C(2)-H, Zn^{2+} and C(2)-H/Zn^{2+}) could change the charge of the C=O in urea /HEC, and the electrophilicity of the C of C=O group in urea/HEC was further changed from the original 0.787/0.914 to 0.795/0.933, 0.828/0.970 and 0.928/0.999, respectively. It made the electrophilicity of the C of C=O in urea/HEC stronger, causing the carbon atom of C=O to be attacked more easily (See Table 5 and S8 in Supporting information) [31, 32].



ΔE=0.0 Kcal/mol

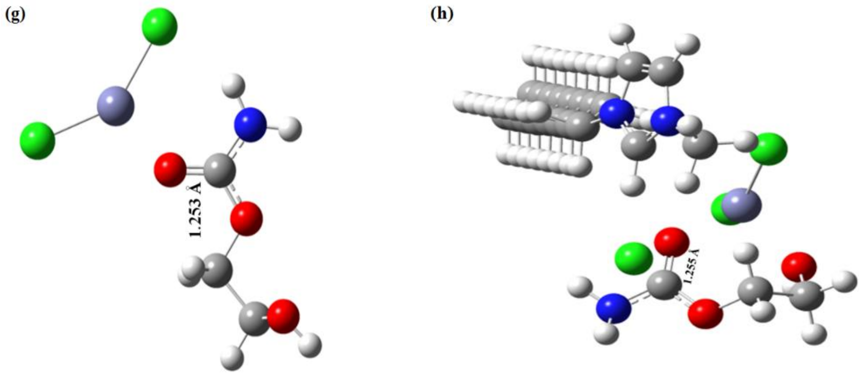
ΔE=-23.8 Kcal/mol

ΔE= -37.5 Kcal/mol

ΔE= -67.1 Kcal/mol

ΔE= 0.0 Kcal/mol

ΔE= -15.7 Kcal/mol



ΔE= -34.2 Kcal/mol ΔE= -53.0 Kcal/mol

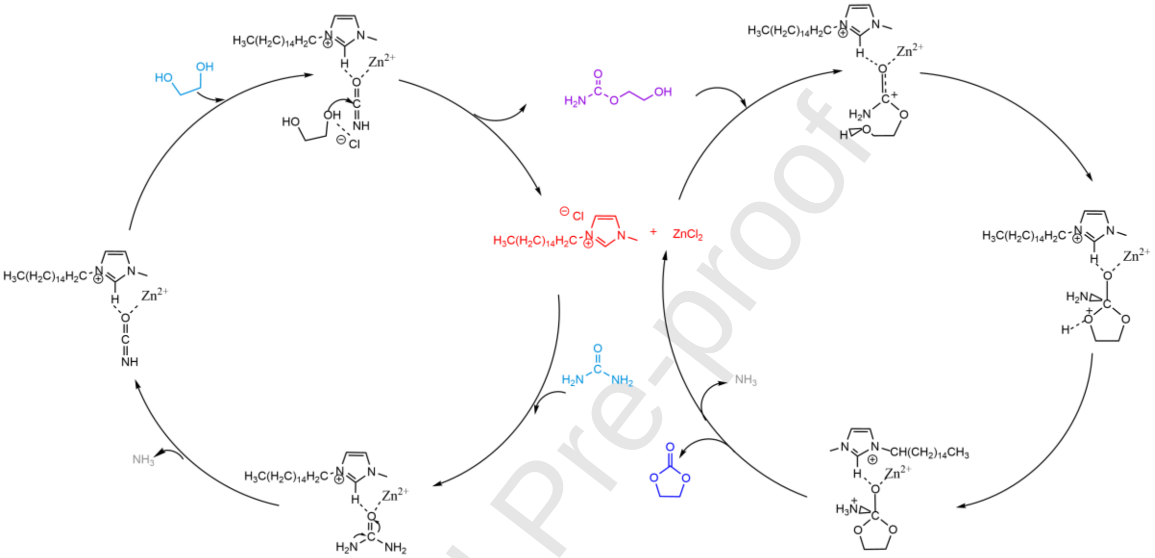
Figure 7 Optimized structure of (a) urea; (b) urea C=O interaction with C_{16}mimCl; (c) urea C=O interaction with $ZnCl_2$ (d) urea C=O interaction with C_{16}mimCl/$ZnCl_2$; (e) urea; (f) HEC C=O interaction with C_{16}mimCl; (g) HEC C=O interaction with $ZnCl_2$ (h) HEC C=O interaction with C_{16}mimCl/$ZnCl_2$. C atoms (dark grey), H atoms (light grey), O atoms (red), N atoms (blue), chlorine atoms (green)

Table 5 Charges in the calculated NPA (natural population analysis) atomic charge of C=O in Urea and HEC in catalysts

Entry	Charge of C of C=O in Urea	Charge of C of C=O in HEC
None catalyst	0.787	0.914
C_{16}mimCl	0.795	0.933
$ZnCl_2$	0.828	0.970
C_{16}mimCl/$ZnCl_2$	0.982	0.999

3.5.4 Possible reaction mechanism

From the experimental results, theoretical calculation results and published reports [22, 25, 43, 48], a possible mechanism was proposed (Scheme 4). The cation C(2)-H of imidazole IL formed hydrogen bond with urea (C=O) and cooperated with the cation of metal salts (Zn^{2+}) to react with C=O of urea, thus C=O of urea was activated, then one molecule ammonia was released and the formation of isonitrile acid was promoted. The anions of imidazole IL and metal salt formed hydrogen bond with one hydroxyl hydrogen of EG, and the oxygen atom of EG attacked the electrophilic carbonyl carbon on isonitrile acid to promote the formation of intermediate product (HEC). Similarly, the cation C(2)-H of imidazole IL formed hydrogen bond with HEC (C=O) and cooperated with the cation of metal salts (Zn^{2+}) to react with C=O of HEC, thus C=O of HEC was active, and another hydroxyl atom of EG attacked the carbonyl carbon of intermediate product, which promoted the formation of cyclic carbonate after intramolecular addition. The composite catalyst of metal salts and imidazole ILs had high selectivity catalytic performance for the synthesis of cyclic carbonates, since the composite catalysts could activate not only urea carbonyl but also one hydroxyl hydrogen of EG to accelerate the formation of intermediate in this catalytic system which was more inclined to form stable cyclic carbonate through amide alcoholysis reaction.



Scheme 4 A possible reaction mechanism

4. Conclusion

In this study, we demonstrated the successful binary catalyst systems of Zn-based and different ionic liquids (ILs) for synthesis of ethylene carbonate (EC) from urea and ethylene glycol (EG). The lengths of alkyl side chains of imidazolium ILs could improve catalytic performance in the reaction, and the yield and selectivity of EC could reach 92.2% and 97.9%, respectively. Furthermore, according to the DFT and experimental results, a possible mechanism for this kind of catalytic process was proposed, which confirmed that a probable synergy cation-anion of catalyst, C(2)-H of ILs and Zn^{2+} playing key role in accelerating the reaction, thereby conveniently providing a useful catalyst for urea alcoholysis to produce cyclic carbonates through a green synthetic pathway. Besides, this study concerning catalytic mechanism can provide a preliminary basis for the development of catalysts for cyclic carbonates from urea and diols.

Acknowledgements

We sincerely appreciate Prof. Suojiang Zhang (IPE, CAS) for his careful academic guidance and great support. This work is financially supported by the Innovation Academy for Green Manufacture, Chinese Academy of Sciences (No. IAGM-2019-A01); "Transformational Technologies for Clean Energy and Demonstration", Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDA 21030500; National Natural Science Foundation of China (No. 21890763, No. 21908226);.

References

[1] Y. X. Liu, H. H. Wang, T. J. Zhao, B. Zhang, H. Su, Z. H. Xue, X. H. Li, J. S. Chen, Schottky barrier induced coupled interface of electron-rich N-doped carbon and electron-deficient Cu: In-built lewis acid-base pairs for highly efficient CO_2 fixation, J. Am. Chem. Soc. 141 (2019) 38-41.

[2] Z. Zhou, C. He, J. Xiu, L. Yang, C. Duan, Metal-organic polymers containing discrete single-walled nanotube as a heterogeneous catalyst for the cycloaddition of carbon dioxide to epoxides, J. Am. Chem. Soc. 137 (2015) 15066-15069.

[3] F. Sarria, D. Tatini, M. Ambrosi, E. Carrettia, B. W. Ninham, L. Dei, P. L. Nostro, The curious effect of potassium fluoride on glycerol carbonate. How salts can influence the structuredness of organic solvents, J. Mol. Liq. 255 (2018) 397-405.

[4] X. Zhao, H. An, S. Wang, F. Li, Y. Wang, Synthesis of ethylene carbonate from urea and ethylene glycol over zinc/iron oxide catalyst, J. Chem. Technol. Biot. 83 (2008) 750-755.

[5] D. Fakhrnasova, R. J. Chimentão, F. Medina, A. Urakawa, Rational and statistical approaches in enhancing the yield of ethylene carbonate in urea transesterification with ethylene glycol over metal oxides, ACS Catal. 5 (2015) 6284-6295.

[6] V. Zubar, Y. Lebedev, L. M. Azofra, L. Cavallo, O. El-Sepelgy, M. Rueping, Hydrogenation of CO_2-derived carbonates and polycarbonates to methanol and diols by metal-ligand cooperative manganese catalysis, Angew. Chem. Int. Edit. 57 (2018) 13439-13443.

[7] M. Selva, A. Perosa, D. Rodríguez-Padrón and R. Luque, ACS Sustain. Chem. Eng. 7 (2019) 6471-6479.

[8] P. Tundo, M. Musolino, F. Aricò, The reactions of dimethyl carbonate and its derivatives, Green Chem. 20 (2018) 28-85.

[9] Z. Song, X. Jin, Y. Hu, B. Subramaniam and R. V. Chaudhari, ACS Sustain. Chem.

Eng. 5 (2017) 4718-4729.

[10] A. Decortes, A. M. Castilla, A. W. Kleij, Salen-complex-mediated formation of cyclic carbonates by cycloaddition of CO_2 to epoxides, Angew. Chem. Int. Edit. 49 (2010) 9822-9837.

[11] L. T. M. Le, T. D.Vo, K. H. P. Ngo, S. Okada, F.Alloin, A. Garge, P. M. L. Le, Mixing ionic liquids and ethylene carbonate as safe electrolytes for lithium-ion batteries, J. Mol. Liq. 271 (2018) 769-777.

[12] M. North, R. Pasquale, C. Young, Synthesis of cyclic carbonates from epoxides and CO_2, Green Chem. 12 (2010) 1514-1539.

[13] T. Kitamura, Y. Inoue, T. Maeda, J. Oyamada, Convenient synthesis of ethylene carbonates from carbon dioxide and 1,2-diols at atmospheric pressure of carbon dioxide, Synth. Commun. 46 (2016) 39-45.

[14] M. Tamura, M. Honda, Y. Nakagawa, K. J. Tomishige, Direct conversion of CO_2 with diols, aminoalcohols and diamines to cyclic carbonates, cyclic carbamates and cyclic ureas using heterogeneous catalysts, Chem. Technol. Biotechnol. 89 (2014) 19-33.

[15] T. D. Hu, Y. W. Sun, Y. H. Ding, A quantum-chemical insight on chemical fixation carbon dioxide with epoxides co-catalyzed by MIL-101 and tetrabutylammonium bromide, J. CO_2 Util. 28 (2018) 200-206.

[16] Q. Su, Y. Q. Qi, X. Q. Yao, W. G. Cheng, L. Dong, S. S. Chen, S. J. Zhang, Ionic liquids tailored and confined by one-step assembly with mesoporous silica for boosting the catalytic conversion of CO_2 into cyclic carbonates, Green Chem. 20 (2018) 3232-3241.

[17] T. F. Wang, X. R. Zhu, L. Mao, Y. Liu, T. G. Ren, L. Wang, J. L. Zhang, Synergistic cooperation of bi-active hydrogen atoms in protic carboxyl imidazolium ionic liquids to push cycloaddition of CO_2 under benign conditions, J. Mol. Liq. 296 (2019) 111936.

[18] B. Zhang, L. Zhang, Q. H. Wu, Q. X. Wang, B. A. Song, W. J. Wu, B. Lu, T. R. Ren, Efficient heterogeneous functionalized polymer ionic liquid catalyst for the synthesis of ethylene carbonate via the coupling of carbon dioxide with ethylene oxide, RSC Adv. 4 (2014) 20506-20515.

[19] P. Wang, S. Liu, F. Zhou, B. Yang, A. S. Alshammari, L. Lu, Y. Deng, Two-step synthesis of dimethyl carbonate from urea, ethylene glycol and methanol using acid–base

bifunctional zinc-yttrium oxides, Fuel Process. Technol. 126 (2014) 359-365.

[20] Q. Li, W. Zhang, N. Zhao, W. Wei, Y Sun, Synthesis of cyclic carbonates from urea and diols over metal oxides, Catal. Today 115 (2006) 111-116.

[21] H. An, Y. Ma, X. Zhao, Y. Wang, Preparation of Zn-Al oxide catalyst and its catalytic performance in propylene carbonate synthesis from urea and propylene glycol on a fixed-bed reactor, Catal. Today 264 (2016) 136-143.

[22] Q. Li, N. Zhao, W. Wei, Y. Sun, Catalytic performance of metal oxides for the synthesis of propylene carbonate from urea and 1,2-propanediol, J. Mol. Catal. A: Chem. 270 (2007) 44-49.

[23] X. Q. Zhao, Y. Zhang, Y. J. Wang, Synthesis of propylene carbonate from urea and 1,2-propylene glycol over a zinc acetate catalyst, Ind. Eng. Chem. Res. 43 (2004) 4038-4042.

[24] Z. W. Gao, S. F. Wang, C. G Xia, Synthesis of propylene carbonate from urea and 1,2-propanediol, Chin. Chem. Lett. 2 (2009) 131-135.

[25] M. Pena-Lopez, H. Neumann, M. Beller, Iron-catalyzed synthesis of five-membered cyclic carbonates from vicinal diols: Urea as sustainable carbonylation agent, Eur. J. Org. Chem. 22 (2016) 3721-3727.

[26] Z. Du, F. Chen, Z. Lin, X. Li, H. Yuan, Y. Wu, Effect of MgO on the catalytic performance of $MgTiO_3$ in urea alcoholysis to propylene carbonate, Chem. Eng. J. 278 (2015) 79-84.

[27] Z. Du, L. Liu, H. Yuan, J. Xiong, B. Zhou, Y. Wu, Synthesis of propylene carbonate from alcoholysis of urea catalyzed by modified hydroxyapatites, Chin. J. Catal. 31 (2010) 371-373.

[28] L. Hao, J. Wang, W. Shen, Z. Zhu, Y. Fang, Carbonylation of 1,2-propylene glycol with urea to propylene carbonate under the catalysis of Zn-Al oxide from the view of homgeneous catalysis, Mol. Catal. 452 (2018) 54-59.

[29] H. Wang, X. Meng, G. Zhao, S. Zhang, Isobutane/butene alkylation catalyzed by ionic liquids: a more sustainable process for clean oil production, Green Chem. 19 (2017) 1462-1489.

[30] S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao, J. Wang, Ionic liquid-based green processes for energy production, Chem. Soc. Rev. 43 (2014) 7838-7869.

[31] Z. Zhang, F. Xu, H. He, W. Ding, W. Fang, W. Sun, Z. Li, S. Zhang, Synthesis of high-molecular weight isosorbide-based polycarbonates through efficient activation of endo-hydroxyl groups by an ionic liquid, Green Chem. 2 (2019) 3891-3901.

[32] W. Qian, X. Tan, Q. Su, W. Cheng, F. Xu, L. Dong, S. Zhang, Transesterification of isosorbide with dimethyl carbonate catalyzed by task-specific ionic liquids, ChemSusChem 12 (2019) 1169-1178.

[33] T. Itoh, M. Watanabe, L. He, Ionic liquids in energy and environment, Green Energy Environ. 4 (2019) 93-94.

[34] V. A. Kuznetsov, M. G. Pervova, A. V. Pestov, Synthesis of alkylene carbonates in ionic liquid, Russ. J. Org. Chem. 49 (2013) 1859-1860.

[35] B. M. Bhanage, S. Fujita, Y. Ikushim, M. Arai, Transesterification of urea and ethylene glycol to ethylene carbonate as an important step for urea based dimethyl carbonate synthesis, Green Chem. 5 (2003) 429-432.

[36] Z. Li, L. Zhang, Y. Liu, C. Y. Shao, Y. Y. Gao, F. T. Fan, J. X. Wang, J. M. Li, J. C. Yan, R. G. Li, C. Li, Surface- polarity- induced spatial charge separation boosts photocatalytic overall water splitting on GaN nanorod arrays, Angew. Chem. Int. Edit. 59 (2020) 935-942.

[37] H. Sun, D. Zhang, Density functional theory study on the cycloaddition of carbon dioxide with propylene oxide catalyzed by alkylmethylimidazolium chlorine ionic liquids, J. Phys. Chem. A 32 (2007) 8036-8043.

[38] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, A rapid and effective synthesis of propylene carbonate using a supercritical CO_2-ionic liquid system, Chem. Commun. 7 (2003) 896-897.

[39] E. H.Lee, J. Y. Ahn, M. M. Dharman, D. W. Park, S. W. Park, I. Kim, Synthesis of cyclic carbonate from vinyl cyclohexene oxide and CO_2 using ionic liquids as catalysts, Catal. Today 131 (2008) 130-134.

[40] J. J. Chen, W. W. Li, X. L. Li, H. Yu, Carbon dioxide capture by aminoalkyl imidazole-based ionic liquid: a computational investigation, Phys. Chem. Chem. Phys. 14 (2012) 4589-4596.

[41] L. J. Bellamy, R. J. Pace, Hydrogen bonding by alcohols and phenols .I. nature of Hydrogen bond in alcohols dimers and polymers, Spectrochim. Acta 22 (1966) 525-&.

[42] J. J. Chen, C. Wang, B. Dong, W. G. Leng, J. Huang, R. L. Ge, Y. N. Gao, Ionic liquids as eco-friendly catalysts for converting glycerol and urea into high value-added glycerol carbonate, Chin. J. Catal. 36 (2015), 336-343.

[43] M. Liu, L. Liang, T. Liang, X. Lin, L. Shi, F. Wang, J. Sun, Cycloaddition of CO_2 and epoxides catalyzed by dicationic ionic liquids mediated metal halide: Influence of the dication on catalytic activity, J. Mol. Catal. A: Chem. 408 (2015) 242-249.

[44] S. Zhong, L. Liang, B. Liu, J. Sun, $ZnBr_2$/DMF as simple and highly active lewis acid-base catalysts for the cycloaddition of CO_2 to propylene oxide, J. CO_2 Util. 6 (2014) 75-79.

[45] H. Wang, B. Lu, X. Wang, J. Zhang, Q. Cai, Highly selective synthesis of dimethyl carbonate from urea and methanol catalyzed by ionic liquids, Fuel Proce. Technol. 90 (2009) 1198-1201.

[46] X. Wu, T. Ding, C. He, H. Tian, Synthesis of ethylene carbonate by urea alcoholysis, Chem. Ind. Eng. Prog. 35 (2016) 3263-3266.

[47] Q. Li, N. Zhao, W. Wei, Y. Sun, Synthesis of propylene carbonate from urea and propylene glycol, Stud. Surf. Sci. Catal. 153 (2004) 573-576.

[48] S. I. Fujita, Y. Yamanishi, M. Arai, Synthesis of glycerol carbonate from glycerol and urea using zinc-containing solid catalysts: A homogeneous reaction, J. Catal. 297 (2013) 137-141.

Author Statement

Lili Deng: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization

Wenzhong Sun: Software

Zijie Shi: Formal analysis, Writing - Review & Editing

Wei Qian: Formal analysis, Writing- Reviewing & Editing

Qian Su: Writing- Reviewing & Editing, Funding acquisition

Li Dong: Funding acquisition, Project administration

Hongyan He: Software

Zengxi Li: Conceptualization, Methodology, Resources

Weiguo Cheng: Conceptualization, Methodology, Resources, Funding acquisition

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract

Highlights

- An efficient ionic liquid and zinc-based catalyst system is developed for urea alcoholysis.
- The reaction system is analyzed with *in situ* FT-IR spectroscopy.
- Investigate the synergistic effects of ionic liquid and zinc-based catalysts.
- A possible mechanism is proposed.