Review

Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids

Jianmin Sun, Shin-ichiro Fujita, Masahiko Arai *

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Abstract

This brief review presents the recent development in the synthesis of cyclic carbonate from carbon dioxide (CO_2) using ionic liquids as catalyst and/or reaction medium. The synthesis of cyclic carbonate includes three aspects: catalytic reaction of CO_2 and epoxide, electrochemical reaction of CO_2 and epoxide, and oxidative carboxylation of olefin. Some ionic liquids are suitable catalysts and/or solvents to the CO_2 fixation to produce cyclic carbonate. The activity of ionic liquid is greatly enhanced by the addition of Lewis acidic compounds of metal halides or metal complexes that have no or low activity by themselves. Using ionic liquids for the electrochemical synthesis of the cyclic carbonate can avoid harmful organic solvents, supporting electrolytes and catalysts, which are necessary for conventional electrochemical reaction systems. Although the ionic liquid is better for the oxidative carboxylation of olefin than the ordinary catalysts reported previously, this reaction system is at a preliminary stage. Using the ionic liquids, the synthesis process will become greener and simpler because of easy product separation and catalyst recycling and unnecessary use of volatile and harmful organic solvents.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Carbon dioxide; Cyclic carbonate; Cycloaddition; Oxidative carboxylation; Ionic liquid

Contents

* Corresponding author. Tel./fax: +81 11 706 6594.
 *E-mail address:* marai@eng.hokudai.ac.jp (M. Arai).

1. Introduction

Carbon dioxide (CO_2) is the most abundant waste produced by human activities and one of the greenhouse gases. In order to prevent the risky reinforcement of the greenhouse effect, the accumulation of CO_2 in the atmosphere should be controlled by removing it from industrial emissions. On the other hand, CO_2 is recognized to be a naturally abundant, cheap, recyclable and non-toxic carbon source that can sometimes replace toxic chemicals such as phosgene, isocyanates or carbon monoxide [1–4]. Under these circumstances, chemical fixation of CO_2 becomes more and more important from the ecological and economic points of view. The synthesis of cyclic carbonate via cycloaddition of CO_2 to epoxide (Scheme 1) is one of effective routes of CO_2 chemical fixation. Cyclic carbonates have found extensive use as excellent aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of pharmaceuticals and fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc. [5,6]. Some reactions using cyclic carbonates are illustrated in Scheme 2 as its major applications [2]. Various catalysts such as alkali metal halides [7–10], organic bases [11–13], metal oxides [14–17], zeolite [18,19], tita-

nosilicates [20], smectites [21,22], and metal complexes [23–32] have been investigated. The synthesis of cyclic carbonates from CO_2 and epoxides has been applied in industrial scales and a number of works as above-cited on the catalyst development and the reaction mechanisms were reported in the literature. However, activity, stability and recovery of catalysts still remain to be improved. Besides the catalytic reaction of CO_2 and epoxide, electrochemical synthesis of cyclic carbonate from them is also possible, although there are only a few papers on this reaction [33,34].

Another way to synthesize cyclic carbonate from CO_2 is oxidative carboxylation of olefin (Scheme 3), which couples two sequential reactions of epoxidation of olefin and CO_2 cycloaddition to epoxide formed. If the reaction effectively proceeds in one-pot, it is of practical importance in that easily available, low-priced chemicals of olefins may be used to produce valuable chemicals. Despite usefulness of this reaction, little effort has been given to it so far, in contrast to extensive study on the reaction of CO_2 and epoxide.

In recent years, significant progress has been made in the application of ionic liquids as catalysts and alternative solvents in organic synthesis because they possess unique advantages of negligible vapour pressure, a broad range of room temperature liquid compositions,
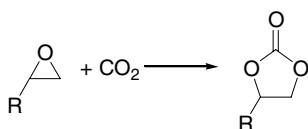
Scheme 1. Cycloaddition of CO_2 to epoxide.
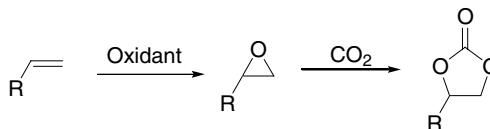
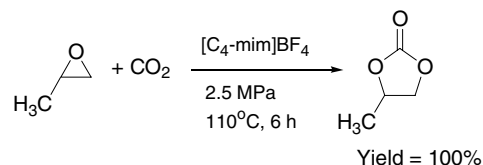
Scheme 3. Oxidative carboxylation of olefin.
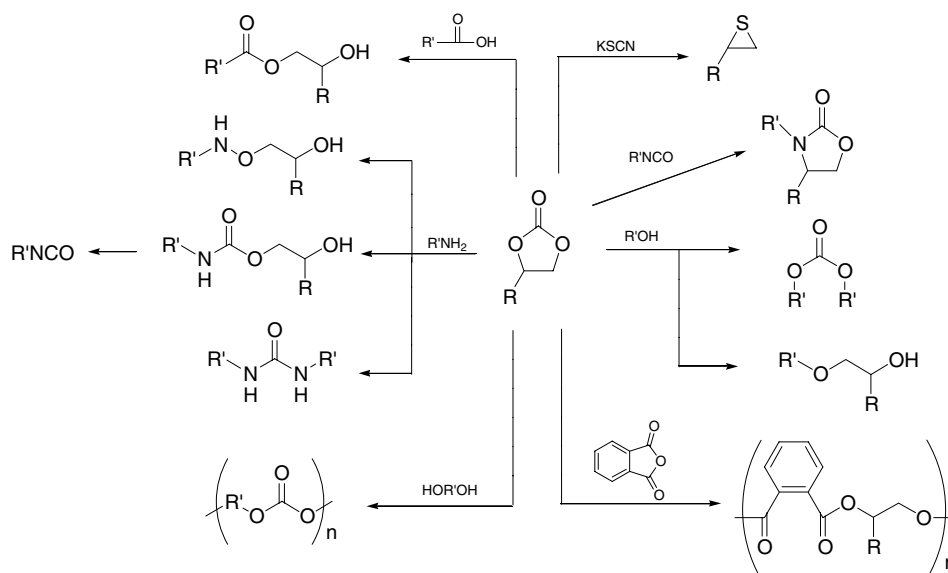
Scheme 2. Some applications of cyclic carbonate.
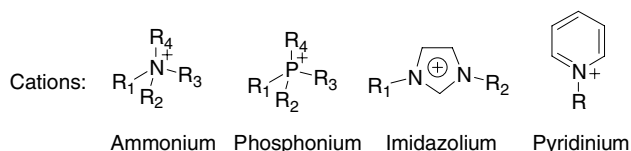
Scheme 4. Ionic liquids used in the synthesis of cyclic carbonate.

Scheme 5.

excellent thermal and chemical stabilities, interesting tunable physicochemical characteristics, and selective dissolvability to many organic and inorganic materials. The use of ionic liquid as reaction media and/or catalysts for clean catalytic transformations would indicate profound effects on the reaction rate and product selectivity. The majority of ionic liquids used in the literature are salts of quaternary ammonium, phosphonium, imidazolium and pyridinium cations with inorganic counter anions (Scheme 4). It has been extensively reviewed that catalytic activity and product selectivity are accelerated when they are used for hydrogenation, oxidation, alkylation, hydroformylation, and Heck and Suzuki coupling reactions [35–39]. Additionally, if the synthesis is carried out with an ionic liquid as the catalyst and the product is immiscible to it, the separation and recycling of the catalyst is easy. It has been also reported that CO_2 can significantly dissolve into the ionic liquid phase, which, therefore, makes the reactions of CO_2 in it possible and suitable [40,41]. Under these circumstances, the use of ionic liquids would be attractive for synthesis of cyclic carbonate from CO_2 and epoxide. The present article focusses on this reaction in the presence of ionic liquids as catalysts and/or solvents. The oxidative carboxylation of olefin using ionic liquids has also been described.

Very recently a comprehensive review on the copolymerization of CO_2 and epoxides has been published by Coates and Moore [42], which is focused on polymerization with single-site homogeneous catalysts but a part is also given to the production of cyclic carbonates.

2. Synthesis of cyclic carbonate via CO_2 cycloaddition to epoxide

2.1. Synthesis of cyclic carbonate in the presence of imidazolium salt

The first successful synthesis of cyclic carbonate using ionic liquids was reported by Peng and Deng in [43]. It has been shown that cycloaddition of CO_2 to propylene oxide (Scheme 5) is effectively catalyzed by 1-butyl-3-imidazolium tetrafluoroborate ([C_4-mim]BF_4). When propylene oxide was allowed to react with CO_2 (2.5

MPa) at 110 °C for 6 h in the presence of 2.5 mol% [C_4-mim]BF_4, propylene carbonate was obtained quantitatively. After the reaction, the propylene carbonate was distilled from the reaction mixture and the ionic liquid catalyst was recycled up to four times with only a minor loss in activity. The ionic liquid catalyst is recyclable for the cycloaddition of CO_2 to propylene oxide. They also show that the type of either cation or anion affects the activity of the ionic liquid. The activity decreases in the order of imidazolium > pyridinium and of $BF_4^- > Cl^- > PF_6^-$.

The mixture of ionic liquids and supercritical carbon dioxide (scCO_2) may offer new opportunities for the development of the reaction due to the complete miscibility of CO_2 in the ionic liquids under high pressure conditions [41,44]. As a first application of this interesting system, Kawanami and coworkers [45] investigated the cyclic carbonate synthesis using various 1-alkyl-3-methylimidazolium salts ([C_n-mim]X) under scCO_2. The experimental results showed that both the type of anion and the length of alkyl chain in the cation have decisive effects on the conversion and selectivity. The performance of different ionic liquids of C_2-mim$^+$ with NO_3^-, $CF_3SO_3^-$, BF_4^- and PF_6^- was investigated, and BF_4^- was found to be the most effective. In addition, the carbonate yield increased markedly with an increase of the alkyl chain length (from C_2 to C_8). In the presence of [C_8-mim]BF_4 98% yield and 100% selectivity for the production of propylene carbonate from CO_2 and propylene oxide were achieved at 100 °C and 14 MPa of CO_2 in a short reaction time of 5 min. On the other hand, the yield and the selectivity obtained with [C_2-mim]BF_4 were 61% and 87%, respectively, under the same conditions except for the reaction time of 2 h. This enhancement was attributed to higher solubility of both the epoxide and CO_2 in the ionic liquid having longer alkyl chain under the same pressure and temperature. Interestingly, because of the difference in the solubility, influence of CO_2 pressure on the yield also depends on the alkyl chain length. In the case of [C_8-mim]BF_4, when the CO_2 pressure was reduced from 14 MPa to a subcritical pressure of 6 MPa, a remarkable decrease in the yield was observed. In contrast to this [C_2-mim]BF_4 gave a higher yield at 6 MPa than 14 MPa. It was also reported that the [C_8-mim]BF_4–scCO_2 reaction media gave satisfactory yields for the synthesis of other carbonates.

The presence of Lewis acidic compounds as co-catalysts greatly enhances the activity of ionic liquid for the cyclic carbonate synthesis. Kim et al. [46] showed that the catalytic activities of ionic liquid such as [C_4-mimi]Cl and [C_4-mim]Br for the reactions of CO_2 with ethylene oxide and propylene oxide can surprisingly be improved by the combination of them with zinc bromide ($ZnBr_2$), although zinc bromide has no activity for the reactions. They concluded that the high activities are attributed to the in situ formation of bis(1-butyl-3-methylimidazolium) zinc tetrahalides from $ZnBr_2$ with [C_4-mim]Cl and [C_4-mim]Br, since the imidazolium zinc tetrahalides separately prepared show similar activities to the corresponding catalyst systems of [C_4-mim]Cl and $ZnBr_2$ and of [C_4-mim]Br and $ZnBr_2$. The catalytic activity of imidazolium zinc tetrahalide was greatly influenced by the nature of halide groups bonded to the zinc center. The activity was found in an order of $[ZnBr_4]^{2-} > [ZnBr_2Cl_2]^{2-} \gg [ZnCl_4]^{2-}$, suggesting the importance of the nucleophilicity of halide ligands. They propose that a halide ion is dissociated from the zinc tetrahalide and subsequently attacks the carbon atom of epoxide. On the contrary, the alkyl group attached on the imidazolium cation was found to have a negligible effect on the activity. It is also shown that the imidazolium zinc tetrahalide is stable and reusable.

The conversion of styrene oxide to styrene carbonate is more difficult due to its less reactivity of β-carbon atom as compared with propylene oxide and ethylene oxide [13,16,20,29,45]. So, high reaction temperature, long reaction time, high CO_2 pressure, and/or toxic organic solvent are required to obtain high yield of styrene carbonate. Recently, we found that the catalyst system comprised of zinc bromide ($ZnBr_2$) and an ionic liquid [C_4-mim]Cl, can afford 93% yield with 100% selectivity for styrene carbonate at a low reaction temperature of 80 °C for 1 h (Scheme 6) [47]. No activity was observed with $ZnBr_2$ alone and [C_4-mim]Cl itself gave a very low yield (6%) of styrene carbonate. However, the combination of $ZnBr_2$ and [C_4-mim]Cl can exhibit an appreciably high activity for the carbonate synthesis. Several metal halides as a co-catalyst with [C_4-mim]Cl were screened for the coupling reaction of styrene oxide and CO_2. The type of metal cations had strong effect on the carbonate yield, the order of activity being $Zn^{2+} > Fe^{3+} > Fe^{2+} > Mg^{2+} > Li^+ > Na^+$. Ionization potential is in the order of $Fe^{3+} > Zn^{2+} > Fe^{2+} > Mg^{2+} > Li^+ >$

Na^+, while ionic radius is in the order of $Fe^{3+} < Mg^{2+} < Li^+ < Zn^{2+} < Fe^{2+} < Na^+$. Probably, these two factors should determine the Lewis acidity of the metal cations, resulting in the order of activity observed. When ZnI_2, $ZnCl_2$ or ZnO was used instead of $ZnBr_2$, the styrene carbonate yield was lowered. The influence of ionic liquids showed that both the type of anion and the length of alkyl chain on the imidazolium cation had strong effects on the conversion and selectivity. Due to non-nucleophilic nature of BF_4^- and PF_6^- ions, when the [C_4-mim]BF_4 and [C_4-mim]PF_6 were used instead of [C_4-mim]Cl, low epoxide conversions were obtained. With these catalysts, selectivity for the styrene carbonate was also low because of the formation of oligomer of styrene oxide and/or styrene carbonate. When the ionic liquid having a longer alkyl chain [C_8-mim]Cl, was used instead of [C_4-mim]Cl, the conversion was increased. Such enhancement of the activity by lengthening the alkyl chain was also observed in the system of [C_n-mim]-BF_4 and scCO_2, as described above. Interestingly, besides the influence of the types of metal halides and the ionic liquids, the [C_4-mim]Cl/$ZnBr_2$ ratio also affected the carbonate yield, a ratio of 2 being optimum. The optimum CO_2 pressure was 4 MPa and elevated pressures had no positive effect on this styrene carbonate synthesis. After the reaction, the catalyst phase of [C_4-mim]Cl and $ZnBr_2$ can be separated by an extraction with ethyl acetate and reused for another run without significant loss in activity.

With respect to the reaction mechanisms for the synthesis of cyclic carbonate from epoxide and CO_2, several groups proposed the parallel requirement of both Lewis base for the activation of CO_2 and Lewis acid for the activation of epoxide in the reaction, although the catalysts employed were different [14,15,27,29,32,48,49]. We proposed the reaction mechanisms as illustrated in Scheme 7 for the styrene carbonate synthesis with the catalyst system of [C_4-mim]Cl and $ZnBr_2$ [47]. The notable catalytic activity may originate from the cooperative actions of both the acidic site (Zn) for epoxide activation and basic site (Cl$^-$ in [C_4-mim]Cl and/or Br$^-$ in $ZnBr_2$) for CO_2 activation. The influence of the types of metal halides and ionic liquids and the appearance of the optimum [C_4-mim]Cl/$ZnBr_2$ ratio of 2 may be explained by these proposed mechanisms.

Ionic liquids can be convenient solvents, which make the separation, recovery, and recycling of catalysts easy. Garcia et al. [50] have reported that [C_4-mim]PF_6 is a suitable reaction media for the CO_2 cycloaddition to epoxide catalyzed by chromium salen complex. When the catalyst is dissolved in [C_4-mim]PF_6 ionic liquid and used for the reaction of CO_2 with styrene oxide, it can be recovered and reused by liquid–liquid extraction of the substrate and the products after the reaction. Interestingly, the conversion was found to increase by the catalyst recycling, although the reason was not clear.
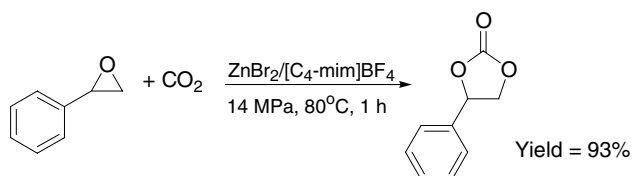
Scheme 6.
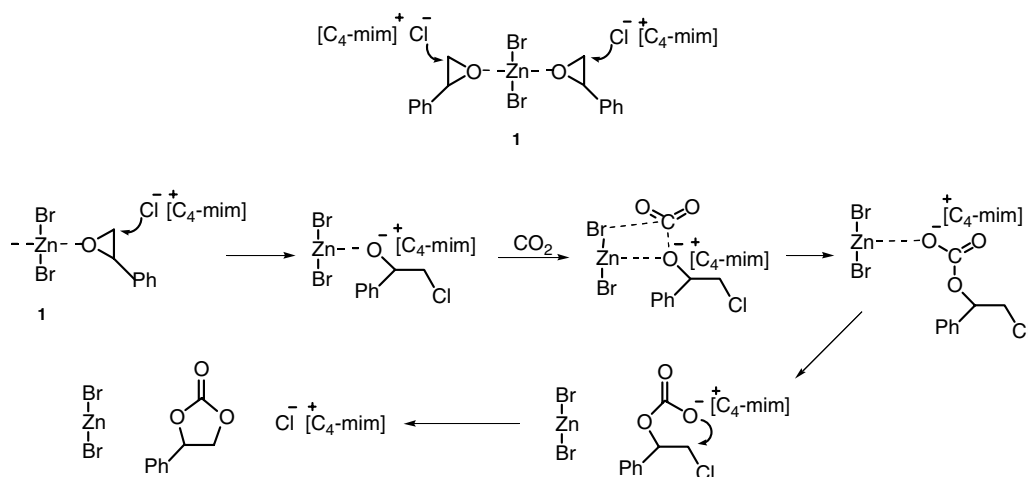
Scheme 7. A mechanism proposed for the synthesis of styrene carbonate from styrene oxide and CO_2 with $ZnBr_2$/[C_4-mim]Cl catalyst. The successive steps are illustrated only for one of the two styrene oxide molecules coordinated with a $ZnBr_2$ molecule.

Although they did not stated, a bifunctional catalyst system might be composed from [C_4-mim]PF_6 and chromium salen complex, since the metal complex can act as a Lewis acid.

2.2. Synthesis of cyclic carbonate in the presence of ammonium salt

Quaternary ammonium salts may also catalyze CO_2 fixation into cyclic carbonate. Caló et al. [51] reported that this reaction was effectively promoted by molten tert-butylammonium bromide (TBAB) and/or tetrabutylammonium iodide (TBAI) under atmospheric pressure of CO_2. Using these salts as solvent and catalyst, inactive substrate (styrene oxide) and polymerization-sensitive oxirane (glycidyl methacrylate oxirane) were converted to the corresponding cyclic carbonates in satisfactory yields. TBAI showed higher activity than TBAB because of the difference in the nucleophilicity of the halide ions. The reaction rate depended greatly on the structure of the cation as well as the nucleophilicity of anion. They showed significant difference in reactivity among imidazolium, thiazole, pyridinium and tetraalkyl ammonium salts. The first three salts indicated inefficient catalytic performance for the cyclic carbonate synthesis. They suggested that the effective activity of the tetraalkylammonium salt comes from the bulkiness of the tetrahedral ammonium ion, which forces the halide ion away from the cation easier, resulting in less electrostatic interaction between anion and cation and consequently in more nucleophilicity of the anion. It was also shown that the ammonium salt was easily recyclable by vacuum distillation or extraction with ethyl acetate, in which the salt is insoluble.
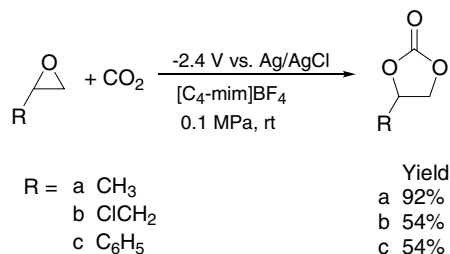
Similar to the cases of the imidazolium salts, Lewis acid enhances the activity of ammonium salt. Kossev et al. [52] observed that calcium chloride promoted the synthesis of cyclic carbonates from the reaction between CO_2 and epoxides catalyzed by tetraalkylammonium or phosphonium halides. It was shown again that 2 is the most optimum ratio of onium salt and calcium chloride, i.e., Lewis base/Lewis acid. Recently, we have also found that a catalyst system consisting of $ZnBr_2$/TBAB is active for the CO_2 cycloaddition [53], which quantitatively produces styrene carbonate from styrene oxide at 80 °C for 1 h.

Such synergistic effect also occurs by the combination of metal complex and onium salt. Refs. [54–57] showed that a coupled catalyst system of the tetradentate Schiff-base aluminium complex (SalenAlCl) and tetraalkylammonium halide is highly active for the reaction of CO_2 and epoxide. It was reported that various cyclic carbonates are produced from corresponding epoxides even at room temperature with good yields, although the reaction time required is slightly long [55]. They proposed the reaction mechanism in which ring-opening insertion of epoxide into Al–Cl bond and subsequent insertion of CO_2 into Al–O bond of the resulting alkoxy complex are involved. The ammonium halide is supposed to contribute to the activation of epoxide.

3. Electrochemical cycloaddition of CO_2 to epoxides

Electrochemical synthesis of cyclic carbonates from CO_2 with epoxides, alcohols and glycols is also known [33,34,58–60]. In these methods, harmful organic solvents, supporting electrolytes and/or catalysts were necessarily used. This makes the reaction system complicated. There is only one report on the use of ionic liquid for this reaction. Yang et al. [61] reported that the use of pure room temperature ionic liquids as reaction media in the electrochemical activation of CO_2 for synthesis of cyclic carbonate from epoxide under mild
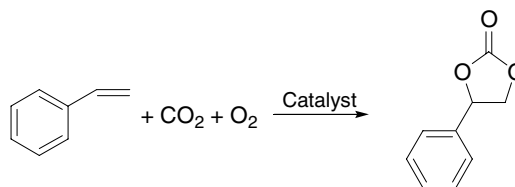
Scheme 8. Electrochemical cycloaddition of CO_2 to epoxide in the presence of [C_4-mim]BF_4.

Scheme 9. Oxidative carboxylation of styrene to styrene carbonate.

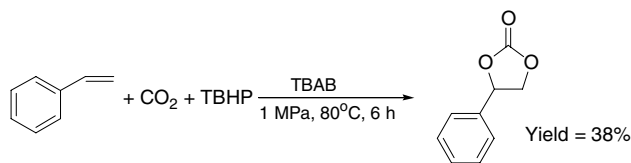Scheme 10. One-pot synthesis of styrene carbonate from styrene and CO_2.

conditions (Scheme 8). This reaction system can avoid a harmful organic solvent, supporting electrolyte and catalyst. For the reactions of CO_2 with propylene oxide, epichlorohydrin and styrene oxide [C_4-mim]BF_4 gave the conversions of 54–92% with 69–100% selectivities and the best current efficiency was 87%. If [C_4-mim]BF_4 was replaced with [C_2-mim]BF_4 or [BPy]BF_4 (Bpy: butyl-pyridinium), the conversions were decreased slightly and remarkably, respectively, while the selectivities were almost not changed. However, poor conversion was obtained when [C_4-mim]PF_6 was used. These results indicate that both cation and anion in the ionic liquid greatly affect the addition reaction. As described in the foregoing section, similar influence of cation and anion was observed in the thermal reaction catalyzed by the ionic liquid. The conversion of epoxide and the selectivity for cyclic carbonate also depend on the structure of the epoxide. It was found that the highest conversion, selectivity and current efficiency were achieved when using propylene oxide as the substrate among the epoxides investigated. For epichlorohydrin, the conversion to cyclic carbonate was decreased remarkably but no other byproducts were detected. For styrene oxide, though the conversion was better than that of epichlorohydrin, the selectivity was relatively low and benzaldehyde was found to form. The application of ionic liquids in the electrochemistry has just opened a new research field and it should be employed for the synthesis of cyclic carbonate and other various reactions.

4. Synthesis of cyclic carbonate via oxidative carboxylation of olefin

Oxidative carboxylation of olefin is a direct method to synthesize cyclic carbonate from olefin, which is one of cheap chemicals. Aresta et al. [62,63] first reported the one-pot synthesis of styrene carbonate from styrene, CO_2 and molecular oxygen as an oxidant (Scheme 9) with homogeneous rhodium complex catalysts, which, however, suffer from short lifetime and low yields of the desired carbonates. They also used various metal oxide catalysts [63,64]. The carbonate yield depended on the catalyst used and the highest yield was obtained

with niobium oxide. However, its value was still low because of low carbonate selectivity due to the formation of byproducts such as benzaldehyde and benzoic acid. Srivastava et al. [20] used titanosilicate catalysts for the synthesis of cyclic carbonate in a single reactor from olefins in a sequential manner. Initially, they carried out the epoxidation of olefin with H_2O_2 or *tert*-butyl hydroperoxide (TBHP) and then the resulting reaction mixture was further subjected to the CO_2 addition reaction after adding CO_2 and a co-catalyst of organic base. Although the reaction conditions were optimized for both the reactions, the yield was not high. Furthermore, their catalyst needed toxic organic solvents such as CH_2Cl_2 and long reaction time. So, stable and effective catalysts with high selectivity to carbonates are being sought for direct carbonate synthesis from olefin.

Recently, we have found that the direct oxidative carboxylation of styrene to styrene carbonate is feasible in the presence of ionic liquids (Scheme 10) [65,66]. We conducted the reaction using TBHP as an oxidant in the presence of quarternary ammonium halides or imidazolium salts. Among the catalysts tested, molten TBAB was proved to be a particularly effective catalyst [65]. Various reaction parameters such as CO_2 pressure, reaction time, temperature, TBAB concentration, molar ratio of TBHP to styrene and oxidant type were investigated in detail. CO_2 pressure was found to play a crucial role in obtaining the high yield of styrene carbonate [66]. When the CO_2 pressure was varied in a wide range, the yield appeared to be maximal at 1, 8 and 15 MPa. The reason for this was discussed on the basis of the phase behavior. Under optimum reaction conditions, the yield of styrene carbonate can reach to 38%. Scheme 11 illustrates a proposed reaction mechanism in which hypobromite (OBr$^-$) and bromide ion (Br$^-$) catalyze the epoxidation and the CO_2 cycloaddition, respectively. The formation of styrene oxide (an intermediate) was observed on the one-pot synthesis of styrene carbonate
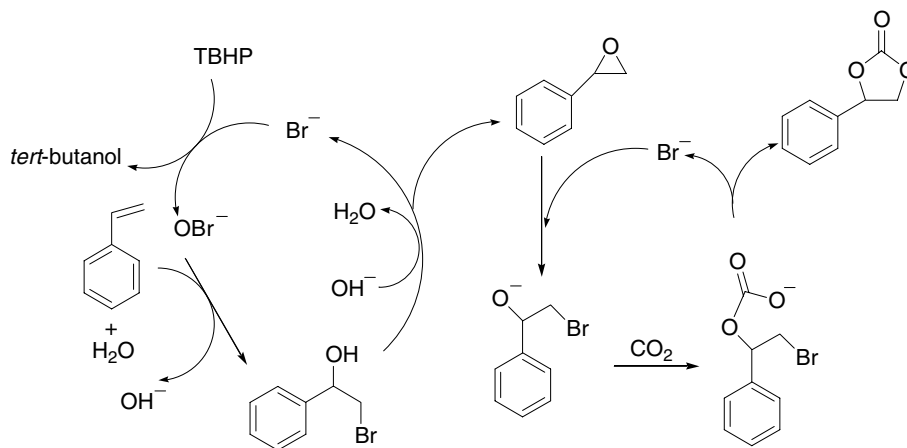
Scheme 11. A proposed mechanism for the one-pot synthesis of styrene carbonate from styrene and CO_2 with TBHP in the presence of TBAB.

from styrene. Although the styrene carbonate yields obtained are not satisfactory in view of industrial application, enhancement in the carbonate yield has been achieved compared with the previous works of other groups. This is an important advancement toward the development of simple, green and more economic synthesis process for cyclic carbonate.

5. Conclusion

The recent development in the synthesis of cyclic carbonate using ionic liquids as catalysts or reaction media was described in this review. It has been shown that some ionic liquids are suitable catalysts and/or solvents to the CO_2 fixation to produce cyclic carbonate. In some cases the ionic liquid appears to be a stable and easily recyclable catalyst. Furthermore, the activity of the ionic liquid is greatly enhanced by the presence of Lewis acidic compounds of metal halides or metal complexes. The electrochemical synthesis of the cyclic carbonate using ionic liquids may open a new field in organic synthesis. This reaction system can avoid the use of harmful organic solvents, supporting electrolytes and catalysts, which are necessary for conventional electrochemical systems. Although the ionic liquid is better for the oxidative carboxylation of olefin than the ordinary catalysts reported previously, this reaction system is at a preliminary stage. Although the present article describes the use of ionic liquids only for the cyclic carbonate synthesis from CO_2, they would contribute to green chemistry because of their unique advantageous properties.

Acknowledgements

References

[1] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.
[2] X.D. Xu, J.A. Moulijin, Energy Fuels 10 (1996) 305, and references therein.
[3] D.H. Gibson, Coord. Chem. Rev. 185–186 (1999) 335.
[4] M. Shi, Y.-M. Shen, Curr. Org. Chem. 7 (2003) 737.
[5] A.-A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
[6] K. Weissermel, H. Arpe (Eds.), Industrial Organic Chemistry, third ed., Wiley-VCH, Weinheim, NY, 1997, pp. 162–163.
[7] N. Kihara, N. Hara, T. Endo, J. Org. Chem. 58 (1993) 6198.
[8] H. Zhu, L.B. Chen, Y.-Y. Jiang, Polym. Adv. Techn. 7 (1996) 701.
[9] T. Zhao, Y. Han, Y. Sun, Phys. Chem. Chem. Phys. 1 (1999) 3047.
[10] T. Iwasaki, N. Kihara, T. Endo, Bull. Chem. Soc. Jpn. 73 (2000) 713.
[11] H. Kawanami, Y. Ikushima, Chem. Commun. (2000) 2089.
[12] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartrio, Tetrahedron Lett. 44 (2003) 2931.
[13] Y.M. Shen, W.L. Duah, M. Shi, Adv. Synth. Catal. 345 (2003) 337.
[14] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, Chem. Commun. (1997) 1129.
[15] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
[16] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, Appl. Catal. A: Gen. 219 (2001) 259.
[17] H. Yasuda, L.N. He, T. Sakakura, J. Catal. 209 (2002) 547.
[18] E.J. Doskocil, S.V. Bordawekar, B.C. Kaye, R.J. Davis, J. Phys. Chem. B 103 (1999) 6277.
[19] M. Tu, R.J. Davis, J. Catal. 199 (2001) 85.
[20] R. Srivastava, D. Srinivas, P. Ratnasamy, Catal. Lett. 91 (2003) 133.
[21] S. Fujita, B.M. Bhanage, Y. Ikushima, M. Arai, Catal. Lett. 79 (2002) 95.
[22] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, Green Chem. 5 (2003) 71.
[23] R. Nomura, A. Ninagawa, H. Matsuda, J. Org. Chem. 45 (1980) 3735.
[24] A. Baba, T. Nozaki, H. Matsuda, Bull. Chem. Soc. Jpn. 60 (1987) 1552.
[25] D. Ji, X. Lu, R. He, Appl. Catal. A: Gen. 203 (2000) 329.
[26] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, Angew. Chem. Int. Ed. Engl. 39 (2000) 4096.

[27] R.L. Paddock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498.
[28] H.S. Kim, J.J. Kim, H.N. Kwon, M.J. Chung, B.G. Lee, H.G. Jang, J. Catal. 205 (2002) 226.
[29] Y.-M. Shen, W.-L. Duan, M. Shi, J. Org. Chem. 68 (2003) 1559.
[30] F.W. Li, C.G. Xia, L.W. Xu, W. Sun, G.X. Chen, Chem. Commun. (2003) 2042.
[31] R. Srivastava, D. Srinivas, R. Ratnasamy, Catal. Lett. 89 (2003) 81.
[32] R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, Tetrahedron Lett. 45 (2004) 2023.
[33] P. Tascedda, E. Dunach, J. Chem. Soc. Chem. Commun. (1995) 43.
[34] P. Tascedda, M. Weidmann, E. Dinjus, E. Dunach, Appl. Organometal. Chem. 15 (2001) 141.
[35] R. Sheldon, Chem. Commun. (2001) 2399.
[36] D.B. Zhao, M. Wu, Y. Kou, E.Z. Min, Catal. Today 74 (2002) 157.
[37] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
[38] D. Jairton, F.D.S. Roberto, A.Z.S. Paulo, Chem. Rev. 102 (2002) 3667.
[39] J.D. Holbrey, K.R. Seddon, Clean Prod. Process. 1 (1999) 223.
[40] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Nature 399 (1999) 28.
[41] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315.
[42] G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6618.
[43] J.J Peng, Y.Q. Deng, New. J. Chem. 25 (2001) 639.
[44] A. Corma, H. Garcia, Chem. Rev. 103 (2003) 4307.
[45] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, Chem. Commun. (2003) 896.
[46] H.S. Kim, J.J. Kim, H. Kim, H.G. Jang, J. Catal. 220 (2003) 44.
[47] J.M. Sun, S. Fujita, F.Y. Zhao, M. Arai, Green Chem. 6 (2004) 613.
[48] H. Kisch, R. Millini, I.-J. Wang, Chem. Ber. 119 (1986) 1090.
[49] Y.-M. Shen, W.-L. Duan, M. Shi, J. Org. Chem. 68 (2003) 1559.
[50] M. Alvaro, C. Baleizao, D. Das, E. Carbonell, H. Garcia, J. Catal. 228 (2004) 254.
[51] V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561.
[52] K. Kossev, N. Koseva, K. Troev, J. Mol. Catal. A: Chem. 194 (2003) 29.
[53] J.M. Sun, S. Fujita, F.Y. Zhao, M. Hasegawa, M. Arai, J. Catal. 230 (2005) 43.
[54] X.-B. Lu, R. He, C.X. Bai, J. Mol. Catal. A: Chem. 186 (2002) 1.
[55] X.-B. Lu, X.J. Feng, R. He, Appl. Catal. A: Gen. 234 (2002) 25.
[56] X.-B. Lu, Y.J. Zhang, B. Liang, X. Li, H. Wang, J. Mol. Catal. A: Chem. 210 (2004) 31.
[57] F. Li, C. Xu, L. Xu, W. Sun, G. Chen, Chem. Commun. (2003) 2042.
[58] M.A. Casadei, A. Inesi, L. Rossi, Tetrahedron Lett. 38 (1997) 3563.
[59] M.A. Casadei, S. Cesa, M. Feroci, A. Inesi, New J. Chem. 23 (1999) 433.
[60] M.A. Casadei, S. Cesa, L. Rossi, Eur. J. Org. Chem. 2000 (2000) 2445.
[61] H.Z Yang, Y.L. Gu, Y.Q. Deng, F. Shi, Chem. Commun. (2002) 274.
[62] M. Aresta, E. Quaranta, J. Mol. Catal. A: Chem. 41 (1987) 355.
[63] M. Aresta, A. Dibenedetto, J. Mol. Catal. A: Chem. 182–183 (2002) 399.
[64] M. Aresta, A. Dibenedetto, I. Tommasi, Appl. Organomet. Chem. 14 (2000) 799.
[65] J.M. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Commun. 5 (2004) 83.
[66] J.M. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Today 93-95 (2004) 383.