

Highly efficient synthesis of cyclic carbonate with CO₂ catalyzed by ionic liquid in a microreactor

Cite this: DOI: 10.1039/c2gc36612f

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The development of highly efficient processes for the cycloaddition of CO₂ with epoxides to produce five-membered cyclic carbonates is a very attractive topic. In this work, the cycloaddition of propylene oxide (PO) and CO₂ to give propylene carbonate (PC) is studied in a microreactor using a HETBAB ionic liquid catalyst. The microreactor performance is evaluated by studying the effects of different operating conditions, including reaction temperature, operating pressure, residence time, molar ratio of CO₂/PO, and the catalyst concentration in PO. The process characteristics of the reaction concerning the gas-liquid mass transfer and the intrinsic kinetics perspectives are discussed. The results show that the residence time can be dramatically reduced from several hours in a conventional stirred reactor to about 10 s in a microreactor. The yield of PC at 3.5 MPa can reach 99.8% at a residence time of 14 s. The turnover frequency (TOF) value varies in the range of 3000 to 14 000 h⁻¹ compared to 60 h⁻¹ in the conventional stirred reactor. The space time yield (STY) or the overall reaction rate ranges from 650 to 4500 g_{prod.} (g_{cat.} h)⁻¹, which is much larger than the value [ca. 19 g_{prod.} (g_{cat.} h)⁻¹] for the conventional stirred reactor. To some extent, the present study has also demonstrated the concept of 'Novel Process Windows'.

Received 12th October 2012,
Accepted 16th November 2012

DOI: 10.1039/c2gc36612f

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Introduction

Cyclic carbonates, *e.g.*, ethylene carbonate (EC) and propylene carbonate (PC), have been widely used as polar aprotic solvents, chemical intermediates, electrolytic elements of lithium secondary batteries, and pharmaceutical ingredients.¹ It is noteworthy that cyclic carbonate synthesis by the cycloaddition of epoxides and CO₂ has already been industrialized using halide-containing organic or inorganic salts, including tetraethylammonium bromide or KI, as homogeneous catalysts. However, there are still some disadvantages, such as long reaction times, low turnover frequency (TOF) values and space time yields (STY), low mixing performance (stirred tank reactor), and/or the need for organic solvents, which are limiting aspects of the process in terms of energy consumption and economics. The cycloaddition of epoxides and CO₂ is a typical gas-liquid multiphase catalytic process, involving the gas-liquid mixing/mass transfer in a reactor and the catalytic cycloaddition in the liquid phase feed. Therefore, a highly efficient reactor and catalyst should be required for further improving the synthesis of cyclic carbonates.

In recent years, various catalysts have been developed for the highly efficient production of cyclic carbonates, such as

metal complexes,² alkali metal halides,³ metal oxides,⁴ organic bases,⁵ and ionic liquids.^{6–11} Among these catalysts, ionic liquids (ILs) have received considerable interest because of their unique properties, such as undetectable vapor pressure, wide liquid temperature range, special solubility for many organic or inorganic compounds, and feasibility for design.¹² The mechanism of the cycloaddition can be considered as an acid-base cooperative catalytic mechanism involving the following three steps,⁶ as shown in Fig. 1. First, the epoxide is activated by the Lewis acid (metal ion, -OH, *etc.*), simultaneously, the halide anion (Lewis base, X⁻) makes a nucleophilic attack on the least-hindered carbon atom of the epoxide followed by ring-opening; then, CO₂ is coordinated to the

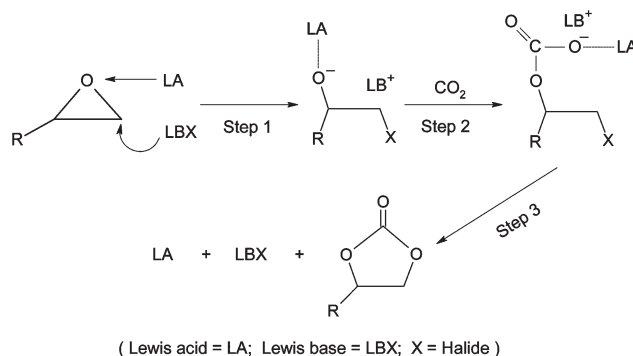


Fig. 1 Catalytic cycle for cyclic carbonate synthesis.

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ring-opened intermediate; finally, the cyclic carbonate is formed by subsequent intramolecular cyclization and the catalyst is regenerated. During the total process, the reaction performance is affected by the synergistic effects of the acid–base active sites.

Based on this mechanism, Motokura *et al.*¹³ proposed acid–base bifunctional catalyst involving acidic surface silanol and the basic 4-pyrrolidinopyridinium iodide. Zhang's group^{14–18} synthesized a series of hydroxyl-functionalized ionic liquids and systematically investigated the catalytic performance of CO₂ cycloaddition, which have both acidic and basic characteristics, and found that the hydroxyl group had a synergetic effect with the halide anion to promote the reaction. It had been demonstrated that 2-hydroxyl-ethyl-tributylammonium bromide (HETBAB) showed higher activity, selectivity, and solubility for the cycloaddition of CO₂ and epoxides without any solvent. Therefore, HETBAB was chosen as the homogeneous catalyst in this work.

The intensification of a chemical process mainly includes transport intensification, chemical intensification, and process design intensification. The capabilities of all three process intensification fields are further enhanced by the availability of reliable and highly efficient microstructured reactors.¹⁹ Microreactors are miniaturized reactor systems with channel characteristic scales in the sub-millimeter range. The extremely large surface-to-volume ratio and the short transport path in microreactors enhance heat and mass transfer dramatically, and hence provide many potential opportunities in chemical process development and intensification.^{20,21} Lots of fundamental and applied research for gas–liquid multiphase reaction systems has been carried out and reported, such as hydrogenation,^{22–24} oxidation,²⁵ Fischer–Tropsch synthesis,²⁶ carbonylation,²⁷ and CO₂ absorption,²⁸ *etc.*

Recently, based on the micro-process technology, Hessel proposed the concept of 'Novel Process Windows', which aims at speeding up the kinetics of reactions, that is, dramatically reducing the reaction time and increasing the productivity of the target products.^{29,30} Novel Process Windows is focused on enabling chemical intensification by using high temperatures, pressures, and/or concentrations to remove the limitations artificially added to chemistry. The Moffatt–Swern oxidation is

generally performed at very low temperatures (<–50 °C) in batch reactors. Kawaguchi *et al.* investigated this reaction at temperatures between –20 to 20 °C in a microreactor.³¹ The results showed that the microreactor yields were much higher than the batch yields (from 20% to 89%) at a very short residence time of 0.01 s. Trachsel *et al.* found that the reaction rate could be improved from 0.004 mol g_{cat.}^{–1} min^{–1} at ambient conditions to 0.046 mol g_{cat.}^{–1} min^{–1} at 51 bar and 71 °C for the hydrogenation of cyclohexene.³² This means that the multiphase reaction performance can be enhanced by increasing temperatures, pressures, and/or concentrations compared to operating conditions in conventional stirred reactors.

In the present work, the cycloaddition of PO and CO₂ to PC is chosen as a model reaction and was investigated in the microreactor using the HETBAB ionic liquid catalyst. The main aim is to verify the feasibility of the cycloaddition of PO and CO₂ to PC in the microreactor, decrease the reaction time from hours in batch reactors to seconds, and improve the process efficiency (TOF and STY) by process intensification.

Material and methods

Propylene oxide (PO), methanol, and *n*-butanol (analytic grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ionic liquid catalyst (HETBAB), which can be dissolved in PO, was obtained from Beijing ZhongKe Anyln Technology Co. Ltd. Carbon dioxide with a purity of 99.99% was commercially available.

The schematic of the experimental setup is shown in Fig. 2. The microreactor system used in this study includes a micromixer and a spiral capillary reactor. The micromixer is fabricated in the stainless steel plate using micromachining technology (FANUC KPC-30a) in our CNC Machining Center. The gas distributor microchannels are located at the back of the micromixer, and the liquid distributor microchannels are at the right side. They are connected by some through-holes with 500 µm diameters in the microreactor. The channels of the micromixer are rectangular with a 600 µm (width) × 300 µm (depth) cross-section. The internal channel volume of

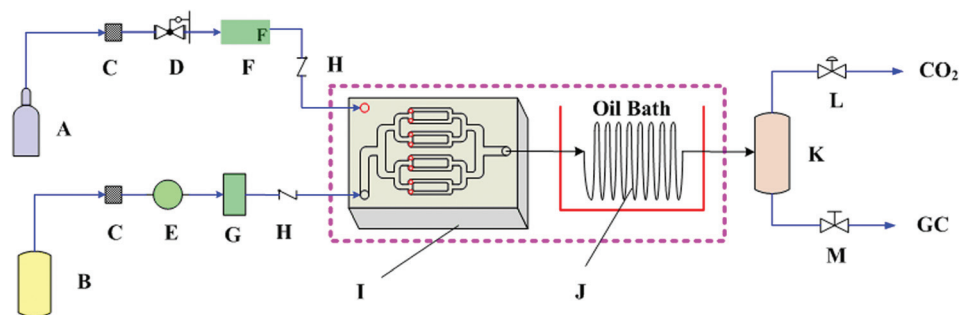


Fig. 2 Schematic of the experimental setup for the cycloaddition of PO and CO₂. A: CO₂ cylinder; B: liquid tank (including PO and HETBAB); C: filter; D: pressure regulating valve; E: series II digital pump; F: gas mass flow controller; G: liquid damper; H: one-way valve; I: micromixer; J: spiral capillary in oil bath; K: gas–liquid separator; L: back pressure regulating valve; M: needle valve.

the micromixer is about 0.31 mL. The spiral capillary reactor located in the oil bath is regarded as the residence time unit for regulating the reaction time. The internal diameter and the length of the spiral capillary reactor are 1.0 mm and 2.5 m, respectively. Thus, the volume of the spiral capillary reactor is about 1.96 mL.

The high purity CO₂ flows through the gas mass flow controller and is mixed with the liquid feed in the micromixer. The liquid feed (HETBAB in PO) is pumped into the reaction system by a high precision digital piston pump (Series II, Chrom. Tech. Inc.). After mixing of the gas–liquid phases in the micromixer, the cycloaddition of PO and CO₂ occurs in the spiral capillary reactor. Then, the gas–liquid reaction mixture is separated in the gas–liquid separator. The liquid product sample is collected in a glass vessel through the needle valve and is diluted by methanol. The yield of PC was analyzed using a gas chromatograph (GC, Agilent 7890A) equipped with a flame-ionized detector using *n*-butanol as the internal standard. Every run must be repeated at least twice to ensure the reproducibility of experimental data. During experimental processes, the operating pressure in the microreactor system is regulated by the pressure regulating valve and the back pressure regulating valve. For ensuring the pressure stability of the system, some tail gas must be continuously released through the back pressure regulating valve in all runs.

Results and discussion

Effect of the reaction temperature

Fig. 3 shows the effects of the reaction temperature on the cycloaddition reaction catalyzed by HETBAB at 3.5 MPa in the temperature range of 140–190 °C, with the residence time of 14 s and the molar ratio (CO₂/PO) of 1.19. As shown in Fig. 3, the yield of PC increases from 62.24% to 99.42%, and remains at this level within 180–190 °C. It is noteworthy the selectivity to PC is always above 99.5% in all experiments. It is plausible that side reaction, *i.e.* PC polymerization,³³ can be dramatically

inhibited due to the very short residence time. The TOF value is increased sharply from 3250 to 5796 h^{−1} with the increasing of temperature, whereas it is only about 60 h^{−1} in the conventional stirred reactor.¹⁶ These results suggest that increasing the reaction temperature has a pronounced positive effect on the TOF and gives an increase of in the activity of the catalyst. Meanwhile, the ring-opening of PO, the CO₂ addition, and the intramolecular cyclization are promoted due to the increasing of the reaction temperature. These mean that the process can be intensified by increasing of the reaction temperature in the microreactor.

The STY or the overall reaction rate only increases from 1070 to 1787 g_{prod.} (g_{cat.} h)^{−1} when the reaction temperature varies from 140 to 170 °C, which is much larger than the value [*ca.* 19 g_{prod.} (g_{cat.} h)^{−1}] of the conventional stirred reactor.¹⁶ If the cycloaddition of CO₂ and PO was controlled by the intrinsic kinetics of the reaction, there would be a more dramatic increase in the overall reaction rate with the increase in temperature. This trend indicates that even though the mass transfer performance of CO₂ and PO can be improved in the microreactor compared to conventional reactors,³⁴ the reaction is still affected by gas–liquid mass transfer.

From the above description, it can be deduced that the reaction temperature affects the reaction in three ways. Firstly, the activation of −OH and the nucleophilic attack of Br[−] increase with increasing reaction temperature. These are in favor of the ring-opening of PO, the CO₂ addition, and the intramolecular cyclization. Secondly, the gas–liquid mass transfer coefficient has a significant relation with gas diffusivity in the liquid (*D*_L) and the liquid viscosity (*μ*_L).³⁵ An increase in temperature results in the increase of *D*_L and the decrease of *μ*_L, which can improve the gas–liquid mass transfer performance. Thirdly, the increase in the reaction temperature can lead to the decrease in the solubility of CO₂ in PO, which reduces the reaction rate considering CO₂ as a reactant. The yield of PC increases as the reaction temperature rises, as shown in Fig. 3, which indicates that the former two factors dominate over the third.

Effect of the residence time

The effects of the residence time on the microreactor STY and the yield of PC are shown in Fig. 4. The experiments are performed at 140 °C and 160 °C, HETBAB concentration of 11.09 mol% in PO, pressure of 3.5 MPa, and the molar ratio of CO₂/PO of 1.41. The residence time can be defined as the total volume of the micromixer and the capillary reactor divided by the total volumetric flow rate of the gas and liquid under the operating conditions. The flow rate of the liquid and the CO₂ are varied in the range of 0.5–2.1 mL min^{−1} and 155–660 mL min^{−1} (STP), respectively. Experiments for varying the residence time are done both by changing the gas and the liquid flow rates, but the volume ratio of the gas and liquid phase is kept constant at 14 in all the runs.

The results show that the yield of PC increases and the STY decreases with the increase in the residence time, while the selectivity of PC remains almost constant (>99.5%). During

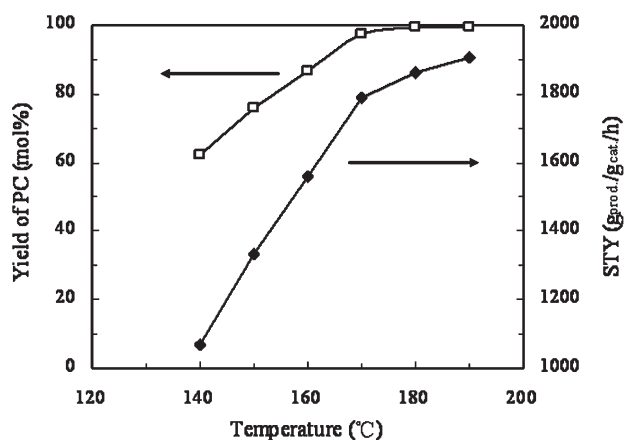


Fig. 3 Effect of the reaction temperature on the yield and STY. Reaction conditions: 4.47 mol% HETBAB in PO; CO₂/PO (mol/mol), 1.19; 3.5 MPa; 14 s.

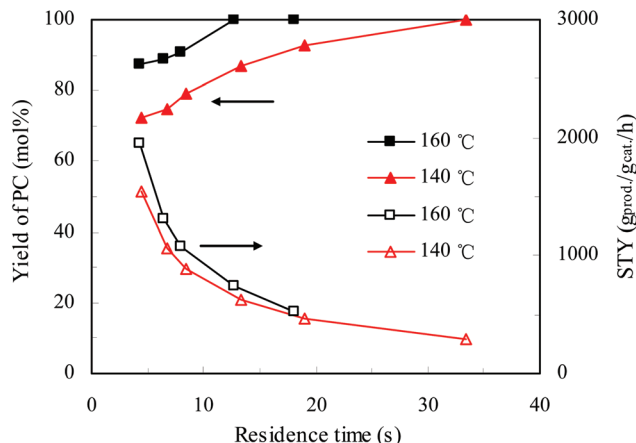


Fig. 4 Effect of the residence time on the yield and STY. Reaction conditions: 11.09 mol% HETBAB in PO; CO₂/PO (mol/mol), 1.41; 3.5 MPa.

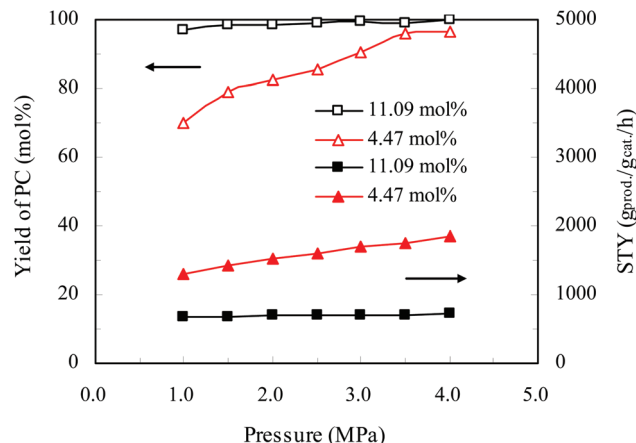


Fig. 5 Effect of the pressure on the yield and STY. Reaction conditions: CO₂/PO (mol/mol), 1.44; 170 °C; 14 s.

these experiments, the gas-liquid two-phase flow pattern is a slug flow, as investigated previously.³⁶ When the gas and liquid flow rates increase, the rate of convective mass transfer from CO₂ to PO increases. For the gas-liquid mass transfer controlled reaction, the mass transfer rate or the STY decreases with the increase in residence time (*i.e.*, with a decrease in gas and liquid flow rates).³⁴ On the other hand, for the kinetically controlled reaction, the conversion, which can be considered as the yield of PC due to high selectivity of this reaction, is expected to increase with the increase in residence time. That is, the conversion of the ring-opening of PO, the CO₂ addition, and the intramolecular cyclization catalyzed by HETBAB increase with the increase in residence time. From Fig. 4, it can be seen that the increase in the yield of PC cannot be offset by the decrease in the gas-liquid mass transfer performance with the increase in residence time. Therefore, the cycloaddition reaction catalyzed by the IL in a microreactor is controlled by both the gas-liquid mass transfer and the intrinsic kinetics under the operating conditions used for these experiments. In addition, the TOF values are varied in the range of 860–4700 h⁻¹ for 140 °C and 1600–5900 h⁻¹ for 160 °C, respectively, which are also much larger than the results of the conventional stirred reactor.¹⁶ Moreover, the residence time can be decreased from several hours to about 10 s.^{6,13,16,37}

Effect of the pressure

To study the effect of pressure on the yield and STY, experiments were carried out in the range of 1.0–4.0 MPa at 11.09 mol% and 4.47 mol% HETBAB in PO. The residence time is maintained at 14 s. The molar ratio of CO₂ and PO is kept constant by varying the gas and liquid flow rates at the same time. The actual gas/liquid volume ratios are changed from 65 to 16 for 4.47 mol% and from 52 to 13 for 11.09 mol% HETBAB in PO, respectively. Fig. 5 and 6 show the influence of CO₂ pressure on the yield and STY at 160 °C and 170 °C in the microreactor. The PC yield increases with increasing pressure from 1.0 to 3.5 MPa. The extent of the increase for 11.09 mol%

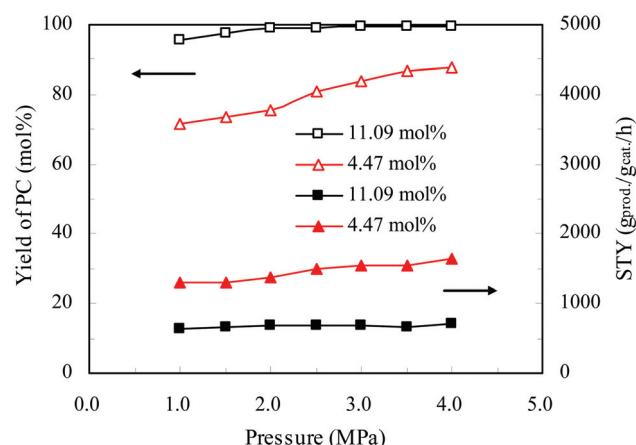


Fig. 6 Effect of the pressure on the yield and STY. Reaction conditions: CO₂/PO (mol/mol), 1.44; 160 °C; 14 s.

is smaller than that for 4.47 mol%. When the pressure is further raised up to 4.0 MPa, the PC yield is almost remains constant.

It can also be observed that the STY is increased for 4.47 mol% HETBAB in PO when the pressure is enhanced from 1.0 to 4.0 MPa. This means that the operating pressure has an effect on the cycloaddition reaction process. The cycloaddition of PO and CO₂ is a typical gas-liquid two-phase reaction process. It includes two consecutive processes, which are the gas liquid two-phase mixing or mass transfer and the cycloaddition reaction in the liquid phase. The CO₂ concentration in the liquid phase reactant is approximately proportional to the pressure, which is favorable for the increase of the overall reaction rate. As shown in Fig. 7, the variation of the STY is only about 30% at 170 °C and 21% at 160 °C when the operating pressure varies from 1.0 to 4.0 MPa, respectively. The variation of the STY is defined based on the STY of 1.0 MPa. If the cycloaddition of CO₂ and PO were controlled by the gas liquid two-phase mass transfer, there would be a more dramatic increase in the overall reaction rate with the increase

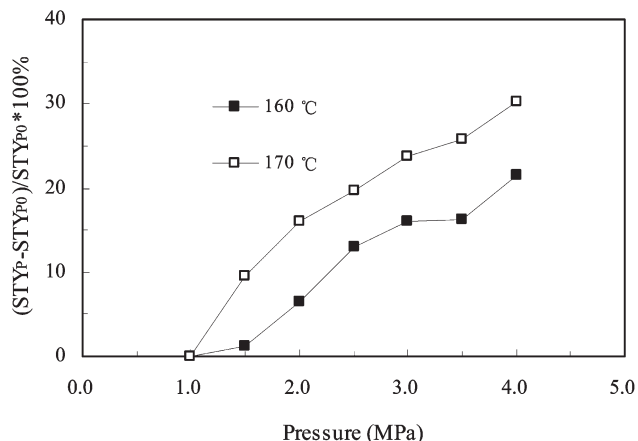


Fig. 7 Effect of pressure on the variation of the STY based on 1.0 MPa. Reaction conditions: CO_2/PO , 1.44; 4.47 mol%; 14 s.

in operating pressure. From Fig. 7, we can also see that the extent of the increase of the STY for 170 °C is larger than that for 160 °C, this means that the influence of the operating pressure increases at higher temperatures due to the increase in the intrinsic reaction rate. Therefore, we can conclude that the reaction is controlled by both mass transfer and intrinsic kinetics under the operating conditions used for these experiments.

When the concentration of HETBAB in PO increases to 11.09 mol%, the data shows that the STY is hardly affected by the operating pressure. This means that the cycloaddition reaction is controlled by the intrinsic kinetics of the reaction under these operating conditions. The cycloaddition reaction in the liquid phase is divided into the ring-opening of PO, the CO_2 addition, and the intramolecular cyclization, according to its mechanism. The intrinsic reaction rate of the ring-opening of PO increases with the increase in the concentration of HETBAB, but the CO_2 addition and the intramolecular cyclization may decrease due to the stereo-hindrance effect at extremely high ionic liquid concentration. The collision frequency of HETBAB and PO, based on the PO, increases with increasing catalyst concentration, and the ring-opening of PO is promoted. More and more PO molecules are activated by HETBAB until they are all converted to the ring-opened intermediate with a further increase in the concentration of HETBAB. In addition, the HETBAB molecules are much larger than PO and CO_2 . The ring-opened intermediate will be surrounded by the large ionic liquid molecules, which can produce the large stereo-hindrance. The STY is not influenced by the operating pressure because the CO_2 concentration is helpless to the decrease of the stereo-hindrance. Moreover, the high concentration of HETBAB can shift the intramolecular cyclization reaction equilibrium, the formation of PC and HETBAB are suppressed. As shown in Fig. 5 and 6, the STY has a slight increase when the temperature increases from 160 °C to 170 °C, this can be explained by the rise of temperature being favorable to the decrease of the stereo-hindrance by intensifying the molecule motion.

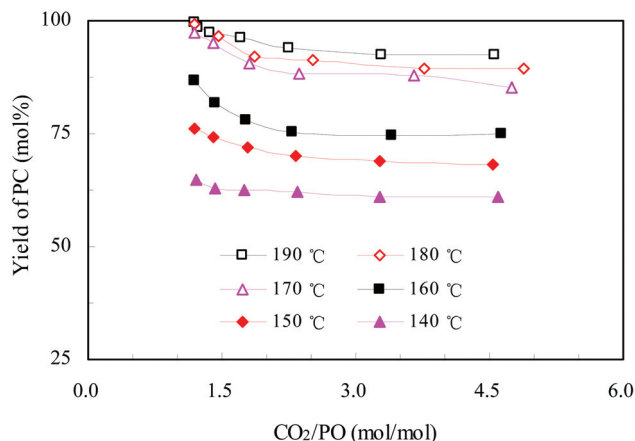


Fig. 8 Effect of the CO_2/PO (mol/mol) ratio on the yield. Reaction conditions: 3.5 MPa, 4.47 mol%, ca. 14 s.

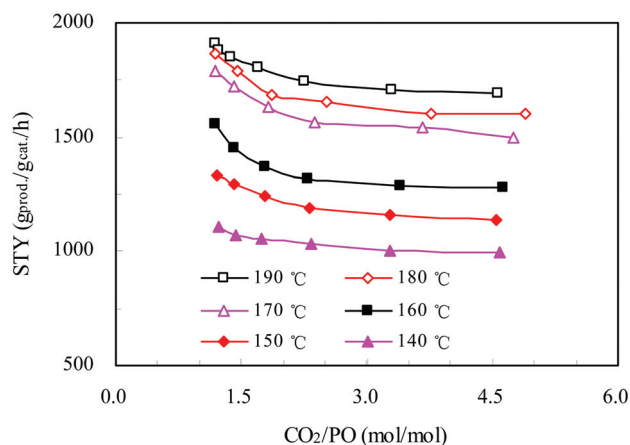


Fig. 9 Effect of the CO_2/PO (mol/mol) ratio on the STY. Reaction conditions: 3.5 MPa, 4.47 mol%, ca. 14 s.

Effect of the molar ratio of CO_2/PO

To elucidate the impact of the molar ratio of CO_2/PO , the reaction tests are conducted over a range of liquid flow rates (0.14–0.60 mL min^{-1}), whereas the gas flow rate is about 200 mL min^{-1} (STP) in this set of experiments. The reaction temperature is varied in the range of 140–190 °C. The pressure and the catalyst concentration in PO are kept constant. In these experiments, the actual gas–liquid flow rate ratio is about 15–60. So the change in liquid flow rate does not change the residence time significantly. Fig. 8 and 9 show the effect of CO_2/PO on the yield and STY. According to the gas and liquid flow rates in these runs, the flow pattern in the microchannel is a slug flow.³⁶ For a given gas flow rate, the liquid slug length increases, whereas the gas slug length decreases with the increase in liquid flow rate or the decrease in CO_2/PO .³⁸ As the rate of convective mass transfer from gas slug to liquid slug increases, the gas–liquid mass transfer is intensified in the slug flow pattern with a decrease in the CO_2/PO .^{34,39} The amount of PO in CO_2 becomes larger when the CO_2/PO ratio rises, which affects the reaction in two opposite ways. On the

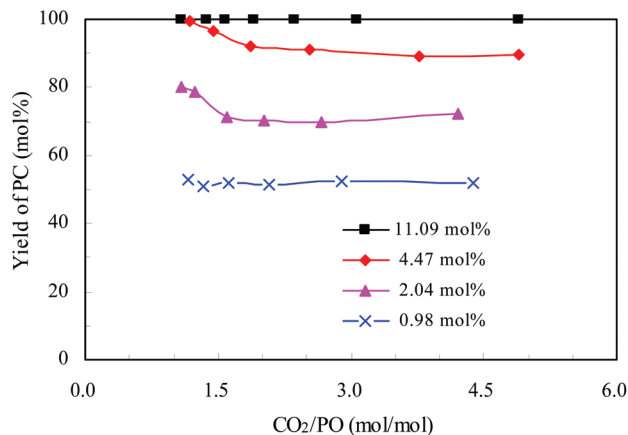


Fig. 10 Effect of the concentration of HETBAB in PO on the yield. Reaction conditions: 3.5 MPa, 14 s, 180 °C.

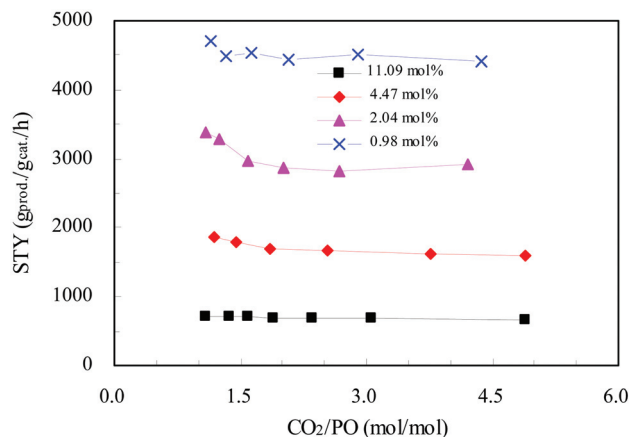


Fig. 11 Effect of the concentration of HETBAB in PO on the STY. Reaction conditions: 3.5 MPa, 14 s, 180 °C.

one hand, the concentration of PO in the liquid phase decreases with increasing CO₂/PO, which is unfavorable to the reaction considering PO as a reactant. On the other hand, the concentration of HETBAB in PO increases, which can promote the reaction rate. From the above discussion, it can be deduced that the reaction is controlled by both the mass transfer and intrinsic kinetics under these operating conditions. The three factors compensate for each other at high CO₂/PO ratios and the effect of the CO₂/PO ratio on the yield is negligible. Therefore, the PC yield and the STY decrease with the increase in CO₂/PO ratio from 1.19 to 1.85. When the CO₂/PO ratio is further increased to 4.60, the PC yield and the STY remains almost constant. In addition, the effect of the gas-liquid mass transfer on the yield and the STY decreases with the decrease in reaction temperature due to the decrease of the reaction rate. In other words, the influence of the intrinsic kinetics on the overall reaction rate is intensified.

Effect of the concentration of HETBAB in PO

Fig. 10 and 11 show the variations of the yield and the STY over different concentrations of HETBAB in PO with CO₂/PO under constant temperature, pressure, and with a constant residence time. In these experiments, the mass transfer performance is constant because the flow hydrodynamics of the gas-liquid two-phases changes a little at different IL concentrations. It is observed that an increase of the concentration of HETBAB in PO (from 0.98 to 11.09 mol%), results in an increase of the yield (from 51 to 99.8%), whereas the STY decreases from 4500 to 680 g_{prod.} (g_{cat.} h)⁻¹. This can be explained by the effect of the catalytically active sites in PO. The conversion efficiency of the substrate is mainly determined by the collision frequency between the catalytically active sites and the substrate. The number of catalytically active sites increases with the increase of catalyst concentration under a constant substrate concentration. The collision frequency based on the catalytically active sites decreases, which is unfavorable for increasing the conversion efficiency. However, the number of substrate molecules which need be

activated per unit of time by each active site, is reduced. More product is formed per unit of time due to the increase in the number of active sites. Therefore, the yield of PC increases with the increase in catalyst concentration, as shown in Fig. 10. At low catalyst concentrations, the collision frequency (based on the active sites) increases. The activation of each active site is also enhanced, indicating that more substrates are converted to products per unit of time for every active site. So the STY increases with the increase in catalyst concentration, as shown in Fig. 11.

Conclusions

The cycloaddition of propylene oxide (PO) and CO₂ was investigated in a microreactor with an IL catalyst. The microreactor performance was evaluated by studying the effects of different operating conditions, such as, the reaction temperature, the operating pressure, the residence time, the molar ratio of CO₂/PO, and the catalyst concentration in PO.

The experimental results indicate that the process can be intensified by increasing the reaction temperature, operating pressure, and catalyst concentration in the microreactor. The residence time can be dramatically reduced from several hours in a conventional stirred reactor to about 10 s in a microreactor. Even though the mass transfer performance of CO₂ and PO can be improved in the microreactor compared to conventional reactors, the reaction is still affected by gas-liquid mass transfer. The yield of PC at 3.5 MPa can reach 99.8% at a residence time of 14 s. The TOF value is varied in the range of 3000 to 14 000 h⁻¹ in these experiments, whereas the value is only ca. 60 h⁻¹ in a conventional stirred reactor. The STY or the overall reaction rate ranges from 650 to 4500 g_{prod.} (g_{cat.} h)⁻¹, which is much larger than the value [ca. 19 g_{prod.} (g_{cat.} h)⁻¹] of the conventional stirred reactor. The present study has demonstrated the concept of 'Novel Process Windows', which was proposed by Prof. Hessel. A highly efficient synthesis of PC, catalyzed by an IL, has been carried out in a microreactor.

Acknowledgements

We gratefully acknowledge the financial supports for this project from Ministry of Science and Technology of China (no. 2009CB219903), National Natural Science Foundation of China (nos. 21106141, 21225627).

Notes and references

- 1 T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
- 2 M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946.
- 3 N. Kihara, N. Hara and T. Endo, *J. Org. Chem.*, 1993, **58**, 6198.
- 4 H. Yasuda, L. N. He, T. Takahashi and T. Sakakura, *Appl. Catal., A*, 2006, **298**, 177.
- 5 A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartorio, *Tetrahedron Lett.*, 2003, **44**, 2931.
- 6 J. Sun, L. Wang, S. J. Zhang, Z. X. Li, X. P. Zhang, W. B. Dai and R. Mori, *J. Mol. Catal. A: Chem.*, 2006, **256**, 295.
- 7 J. Sun, S. J. Zhang, W. G. Cheng and J. Y. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588.
- 8 H. Kawanami, A. Sasaki, K. Matsui and Y. Ikushima, *Chem. Commun.*, 2003, 896.
- 9 F. W. Li, L. F. Xiao, C. G. Xia and B. Hu, *Tetrahedron Lett.*, 2004, **45**, 8307.
- 10 J. M. Sun, S. Fujita and M. Arai, *J. Organomet. Chem.*, 2005, **690**, 3490.
- 11 J. J. Peng and Y. Q. Deng, *New J. Chem.*, 2001, **25**, 639.
- 12 J. Dupont, R. F. de Souza and P. A. Z. Auarez, *Chem. Rev.*, 2002, **102**, 3667.
- 13 K. Motokura, S. Itagaki, Y. Iwasawa, A. Miyaji and T. Baba, *Green Chem.*, 2009, **11**, 1876.
- 14 J. Sun, J. Q. Wang, W. G. Cheng, J. X. Zhang, X. H. Li, S. J. Zhang and Y. B. She, *Green Chem.*, 2012, **14**, 654.
- 15 J. Sun, L. J. Han, W. G. Zhang, J. Q. Wang, X. P. Zhang and S. J. Zhang, *ChemSusChem*, 2011, **4**, 502.
- 16 J. Sun, S. J. Zhang, W. G. Cheng and J. Y. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588.
- 17 J. Sun, W. G. Cheng, W. Fan, Y. H. Wang, Z. Y. Meng and S. J. Zhang, *Catal. Today*, 2009, **148**, 361.
- 18 J. Sun, J. Y. Ren, S. J. Zhang and W. G. Cheng, *Tetrahedron Lett.*, 2009, **50**, 423.
- 19 V. Hessel, I. V. Gürsel, Q. Wang, T. Noël and J. Lang, *Chem. Eng. Technol.*, 2012, **35**, 1184.
- 20 K. Jähnisch, V. Hessel, H. Löwe and M. Baerns, *Angew. Chem., Int. Ed.*, 2004, **43**, 406.
- 21 G. W. Chen, Q. Yuan, H. Q. Li and S. L. Li, *Chem. Eng. J.*, 2004, **101**, 101.
- 22 R. Halder and A. Lawal, *Catal. Today*, 2007, **125**, 48.
- 23 S. Tadepalli, R. Halder and A. Lawal, *Chem. Eng. Sci.*, 2007, **62**, 2663.
- 24 K. K. Yeong, A. Gavriilidis, R. Zapf and V. Hessel, *Chem. Eng. Sci.*, 2004, **59**, 3491.
- 25 A. Leclerc, M. Alamé, D. Schweich, P. Pouteau, C. Delattre and C. de Bellefon, *Lab Chip*, 2008, **8**, 814.
- 26 S. R. Deshmukh, A. L. Y. Tonkovich, K. T. Jarosch, L. Schrader, S. P. Fitzgerald, D. R. Kilanowski, J. J. Lerou and T. J. Mazanec, *Ind. Eng. Chem. Res.*, 2010, **49**, 10883.
- 27 Y. Takebayashi, K. Sue, S. Yoda, T. Furuya and K. Mae, *Chem. Eng. J.*, 2012, **180**, 250.
- 28 C. B. Ye, G. W. Chen and Q. Yuan, *Chin. J. Chem. Eng.*, 2012, **20**, 111.
- 29 V. Hessel, *Chem. Eng. Technol.*, 2009, **32**, 1655.
- 30 V. Hessel, B. Cortese and M. H. J. M. de Croon, *Chem. Eng. Sci.*, 2011, **66**, 1426.
- 31 T. Kawaguchi, H. Miyata, K. Ataka, K. Mae and J. Yoshida, *Angew. Chem., Int. Ed.*, 2005, **44**, 2413.
- 32 F. Trachsel, C. Hutter and P. R. von Rohr, *Chem. Eng. J.*, 2008, **135**, S309.
- 33 M. Ramin, J. D. Grunwaldt and A. Baiker, *J. Catal.*, 2005, **234**, 256.
- 34 J. Yue, G. W. Chen, Q. Yuan, L. A. Luo and Y. Gonthier, *Chem. Eng. Sci.*, 2007, **62**, 2096.
- 35 A. Ferreira, C. Ferreira, J. A. Teixeira and F. Rocha, *Chem. Eng. J.*, 2010, **162**, 743.
- 36 Y. C. Zhao, G. W. Chen, C. B. Ye and Q. Yuan, *Chem. Eng. Sci.*, 2013, **87**, 122.
- 37 M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946.
- 38 N. Shao, A. Gavriilidis and P. Angeli, *Heat Transfer Eng.*, 2011, **32**, 1117.
- 39 M. T. Kreutzer, D. Du, J. J. Heiszwolf, F. Kapteijn and J. A. Moulijn, *Chem. Eng. Sci.*, 2001, **56**, 6015.