Environmental Chemistry Letters (2019) 17:501–508
https://doi.org/10.1007/s10311-018-0793-9

ORIGINAL PAPER

Quaternary phosphonium cationic ionic liquid/porous metal–organic framework as an efficient catalytic system for cycloaddition of carbon dioxide into cyclic carbonates

Yu Lin Hu[1] · **Rui Li Zhang**[1] · **Dong Fang**[2]

Received: 10 April 2018 / Accepted: 17 August 2018 / Published online: 5 September 2018

Abstract

Global warming and climate change concerns are triggering worldwide interest for sustainable transformation of CO_2 into useful chemicals. Here, a new and efficient multifunctional catalytic system for the cycloaddition of carbon dioxide with epoxides to synthesize cyclic carbonates under mild and solvent-free reaction conditions has been developed. The catalytic tests revealed that $[P_{12,4,4,4}]$Br/MIL-53(Cr) (MIL: Materials of Institut Lavoisier) was the best and powerful catalytic system in the cycloaddition with excellent yields (96–99%) under solvent-free condition and 100 °C, 1.0 MPa for 2–3 h. The synergistic effect of anion and cation of ionic liquid $[P_{12,4,4,4}]$Br as well as the chromium site of cocatalyst MIL-53(Cr) contributed to the excellent catalytic activity. The present catalytic system has several unique features such as simple operation, good to excellent yields, high catalytic activity, environmentally benign and safe. This study provides a sustainable and efficient synergistic strategy for chemical carbon dioxide fixation via the combination of ionic liquids and metal–organic frameworks.

Keywords Ionic liquid · Metal–organic framework · Cycloaddition · Epoxides · Carbon dioxide · Cooperative catalysis

Introduction

Carbon dioxide (CO_2) is the main greenhouse gas which caused the global warming and climate change. The keeping increase of CO_2 emission aggravates global warming, and controlling its emission is the only way to stop the climatic deterioration. Hence, a number of strategies have been proposed to reduce the CO_2 emission such as CO_2 capture, storage and chemical utilization (Carena and Vione 2016; Chaterjee and Krupadam 2018; Kumar et al. 2018; Lais et al. 2018; Liu et al. 2018; Nandigama et al. 2018; Zhang et al. 2016). Among them, CO_2 chemical utilization is regarded as the most attractive one because CO_2 has been sorted as a cheap, nontoxic and abundant C1 building block for the preparation of a wide range of valuable chemicals (Sołtys-Brzostek et al. 2017). Currently, numerous strategies have been developed for CO_2 chemical utilization, and the cycloaddition of CO_2 and epoxides is one of the most attractive and sustainable crafts due to a wide range of applications of the target products cyclic carbonates in fine chemistry (Arshadi et al. 2017). However, the activation of CO_2 is difficult due to its inert nature resulting from its high thermodynamic and kinetic stability. The development of efficient catalytic systems for conversion of CO_2 into the desired cyclic carbonates is a crucial role for CO_2 utilization. In general, the cycloaddition of CO_2 to epoxides can proceed under alkali metal or quaternary ammonium salts catalysts (Ju et al. 2008; Zhou et al. 2010; Martín et al. 2015). However, these traditional catalysts are not entirely satisfactory owning to the limitations of corrosive wastes, tedious work-up and harsh reaction conditions. To overcome these restrictions, some representative catalytic systems used for the cycloaddition have been developed, including zinc(II) complexes of arylhydrazones of β-diketones/tetrabutylammonium bromide (Montoya et al. 2016), KI-tetraethylene

---

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10311-018-0793-9) contains supplementary material, which is available to authorized users.

✉ Yu Lin Hu
huyulin1982@163.com

[1] College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, People's Republic of China

[2] College of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng 224002, People's Republic of China

glycol (Kaneko and Shirakawa 2017), organocatalysts (Alves et al. 2017; Sopeña et al. 2017; Fiorani et al. 2015; Whiteoak et al. 2012; Gennen et al. 2015; Wang and Zhang 2016), organometallic complexes (Tian et al. 2012; Chen et al. 2017), ascorbic acid/tetrabutylammonium iodide (Arayachukiat et al. 2017), poly(4-vinylimidazolium)s/diazabicyclo[5.4.0]undec-7-ene/$ZnBr_2$ (Seo and Chung 2014) and others (Kelly et al. 2017; Khatun et al. 2017; Lan et al. 2014, 2015, 2016a, b). Most of these catalytic methodologies, however, still suffer from several shortcomings such as the use of expensive reagents, high reaction temperature and pressure, unsatisfactory activity without co-catalysts, difficulties in work-up and environmental hazards. Consequently, there is an enormous demand for the development of efficient and eco-friendly catalytic systems for conversion of CO_2 to cyclic carbonates.

Ionic liquids, completely composed of ions, could be designed to possess a definite set of properties, and thus have wide applications as reaction medium or catalyst in chemical reactions. Further, due to their low vapor pressure and nonflammable, ionic liquids were assigned as a class of environmental materials (Sharifi et al. 2014; Tomé and Marrucho 2016; Costa et al. 2017). Nowadays, examples of their applications as catalysts in cycloaddition of CO_2 to epoxides were reported and demonstrated good catalytic activities (Qiu et al. 2017; Rojas et al. 2014; Lan et al. 2018). However, because of the difficulties associated with unsatisfactory catalytic performance and harsh reaction conditions, the development of novel and efficient ionic liquid-based catalytic systems is still in great demand. Phosphonium cation-based ionic liquids as a family of ionic liquids that in catalytic cycloaddition of CO_2 applications offer superior properties of thermal stability, solubility and high efficiency compared to the corresponding ammonium cation-based ionic liquids. Therefore, phosphonium ionic liquids have been utilized as nontoxic, environmentally benign and recyclable catalysts and widely adopted in foregoing researches (Bellina et al. 2012; Dai et al. 2016). Metal–organic frameworks (MOFs) are a class of fascinating materials that consist of coordination bonds between transition-metal cations and multidentate organic linkers, and they have been received considerable attentions as nontoxic and environmentally friendly heterogeneous catalysts in cycloaddition of CO_2 due to their attractive physical structure properties (Rubio-Martinez et al. 2017; Kaneti et al. 2017; He et al. 2016; Zhu et al. 2018). However, their weak activity and hydrothermal stability limited their catalytic applications. It is obvious that ionic liquids and metal–organic frameworks based dual catalytic system would exhibit more outstanding catalytic performances by combining the advantages of two materials, based on a synergetic effect of transition-metal center of metal–organic framework and the basic sites (anion and cation) of ionic liquid (Ding et al. 2017). In light of the above-mentioned advantages of phosphonium ionic liquids and metal–organic frameworks, it is envisaged that phosphonium ionic liquid/metal–organic framework dual catalytic systems would have excellent synergetic effect and exhibit more highly efficient catalytic activity toward the cycloaddition of CO_2 to epoxides.

On the basis of the aforementioned considerations, herein, we report a simple, novel and efficient dual catalytic system containing porous metal–organic framework for the cycloaddition of CO_2 to epoxides in the presence of phosphonium ionic liquid tributyldodecylphosphonium bromide ($[P_{12,4,4,4}]Br$). To our pleasure, the newly developed multifunctional synergistic system was endowed with excellent catalytic activity and reusability in good yields and selectivity for the cycloaddition under mild conditions.

Experimental

Materials and methods

The reagents were of analytical grade, and the ionic liquids were purchased from Aladdin and Lanzhou Greenchem ionic liquids, Chinese Academy Science. The chemical structures of catalysts were characterized by Fourier transform infrared spectroscopy (FT-IR) spectra using a Nicolet Nexus 470 spectrometer. The powder X-ray diffraction (XRD) analysis was carried out on a Rigaku Ultima IV diffractometer. N_2 adsorption–desorption measurements were measured on a Micromeritics-2010 apparatus. Thermal gravimetric (TG) analysis was performed using a Netzsch Thermoanalyzer STA 449 analyzer under nitrogen atmosphere. The element analysis of catalysts was determined by an Arcos EOP ICP-OES (Kleve, Germany). Scanning electron microscopy (SEM) was recorded on a JSM-7500F instrument. Gas chromatography (GC) analysis was carried out on a Agilent GC-7890A instrument. ^1H NMR (nuclear magnetic resonance) spectra were recorded on a Bruker 400 MHz spectrometer. Elemental analysis was performed on a Vario Micro cube elemental analyzer.

Preparation of metal–organic frameworks

Metal–organic frameworks were prepared following the procedures (Rubio-Martinez et al. 2017; Kaneti et al. 2017), and their characterization results (Fig. 1a, Fig. S1–S5, ESI) match well with those in the studies.

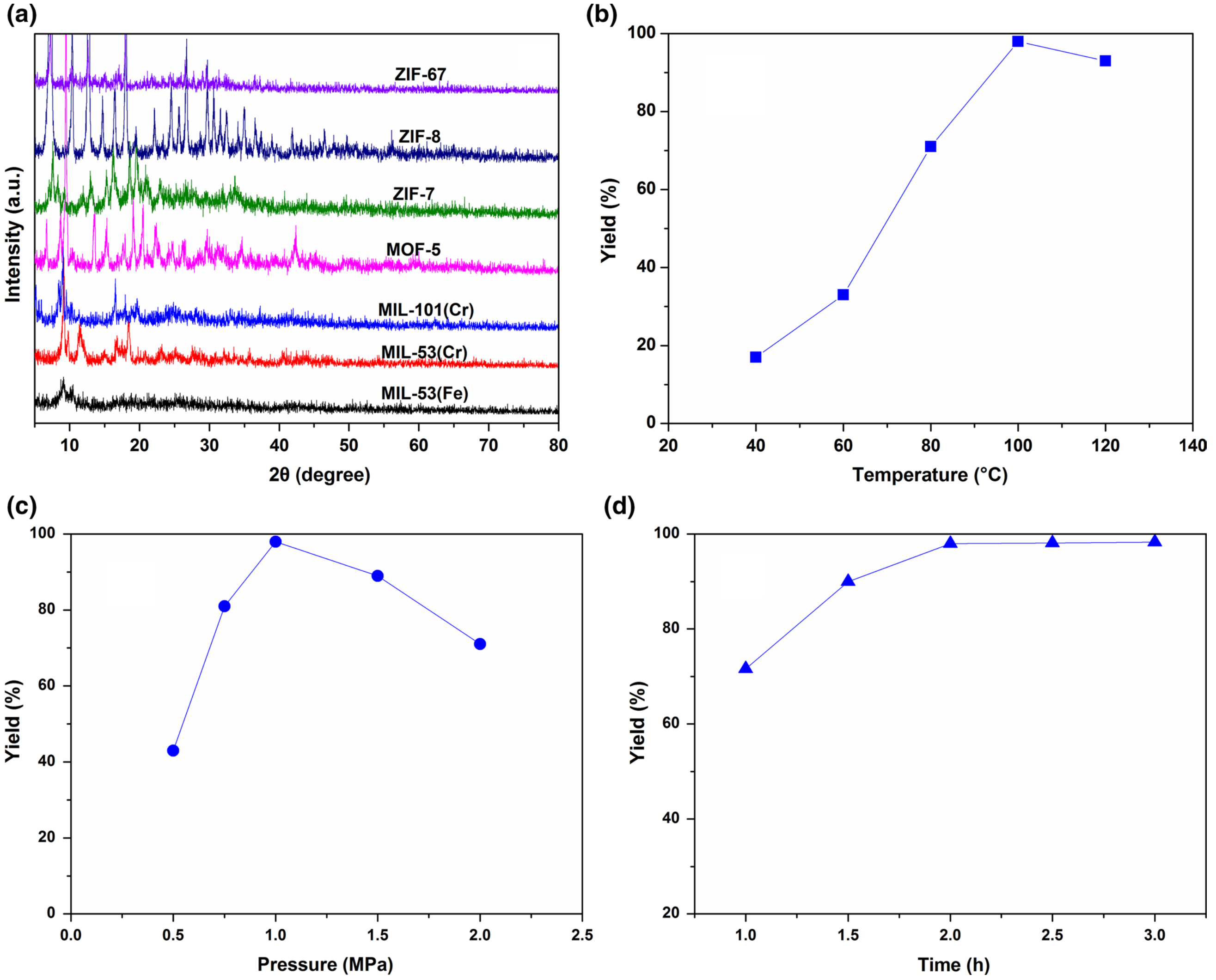


Fig. 1 XRD patterns of metal–organic frameworks (**a**) and influences of reaction conditions on the cycloaddition of CO_2 to propylene oxide over $[P_{12,4,4,4}]Br$/MIL-53(Cr) (**b**, **c**, **d**)

General procedure for catalytic cycloaddition of CO_2 to epoxides

In a typical process, epoxide (20 mmol) and ionic liquid (1.2 mmol), metal–organic framework cocatalyst (15 mg) were introduced into a stainless steel high pressure reactor. The reactor was sealed and flushed three times with CO_2 at room temperature. The pressure was then adjusted to 1.0 MPa, and the reaction mixture was stirred at 100 °C for the desired time. After the completion of the reaction, monitored by GC, the pressure of reactor falls down to a presetting value; then, the excess of CO_2 was vented. The catalytic system was collected by centrifugation and the products were analyzed by GC. For the recycling experiments, collection of the catalytic system was separated by centrifugation, and then fresh substrates were then recharged to the recovered catalytic system and then recycled under identical reaction conditions. The products were identified by comparing their physical and GC spectra with those of commercial materials.

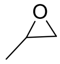
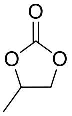
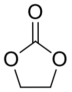
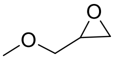
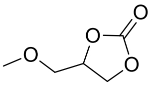
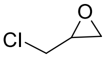
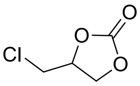
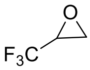
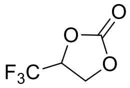
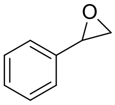
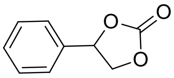
Spectral data

4-Methyl-1,3-dioxolan-2-one (Table 1, entry 1): ^{1}H NMR: $\delta = 1.41$ (dd, $J = 7.2$ Hz, CH_3, 3H), 3.97 (t, $J = 5.2$ Hz, CH, 1H), 4.56 (t, $J = 5.0$ Hz, CH, 1H), 4.93 (t, $J = 7.0$ Hz, CH, 1H). Anal. Calcd. for $C_4H_6O_3$: C, 47.02; H, 5.89; O, 46.97. Found: C, 47.06; H, 5.92; O, 47.02.

1,3-Dioxolan-2-one (Table 1, entry 2): ^{1}H NMR: $\delta = 4.54$ (s, CH_2CH_2, 4H). Anal. Calcd. for $C_3H_4O_3$: C, 40.89; H, 4.55; O, 54.48. Found: C, 40.92; H, 4.58; O, 54.50.

4-(Methoxymethyl)-1,3-dioxolan-2-one (Table 1, entry 3): ^{1}H NMR: $\delta = 3.33$ (s, OCH_3, 3H), 3.72 (dd, $J = 7.0$ Hz, OCH_2, 2H), 4.08 (dd, $J = 7.0$ Hz, CH_2, 2H), 4.96 (m, CH,

Table 1 Catalytic cycloaddition of various epoxides with CO_2

Entry[a]	Epoxide	Product	Time (h)	Conversion (%)[b]	Yield (%)[c]
1			2	99	98
2			2	99	99
3			2	100	99
4			3	98	97
5			3	97	96
6			3	98	96

[a] Reaction conditions: epoxide (20 mmol), $[P_{12,4,4,4}]$Br (1.2 mmol), MIL-53(Cr) (15 mg), CO_2 (1.0 MPa), were stirred at 100 °C

[b] Isolated conversion

[c] Isolated yield

1H). Anal. Calcd. for $C_5H_8O_4$: C, 45.42; H, 6.05; O, 48.42. Found: C, 45.46; H, 6.10; O, 48.44.

4-(Chloromethyl)-1,3-dioxolan-2-one (Table 1, entry 4): ^{1}H NMR: $\delta = 3.76$ (dd, $J = 6.8$ Hz, CH_2, 2H), 4.35 (dd, $J = 7.0$ Hz, CH_2, 1H), 4.63 (dd, $J = 7.0$ Hz, CH_2, 1H), 4.91 (m, CH_2, 1H). Anal. Calcd. for $C_4H_5ClO_3$: C, 35.15; H, 3.63; Cl, 25.95; O, 35.13. Found: C, 35.19; H, 3.69; Cl, 25.97; O, 35.15.

4-(Trifluoromethyl)-1,3-dioxolan-2-one (Table 1, entry 5): ^{1}H NMR: $\delta = 4.06$–4.15 (dd, $J = 7.4$ Hz, CH_2, 2H), 5.09 (t, $J = 6.9$ Hz, CH, 1H). Anal. Calcd. for $C_4H_3F_3O_3$: C, 30.76; H, 1.90; F, 36.48; O, 30.74. Found: C, 30.78; H, 1.94; F, 36.52; O, 30.76.

4-Phenyl-1,3-dioxolan-2-one (Table 1, entry 6): ^{1}H NMR: $\delta = 4.36$ (t, $J = 8.2$ Hz, CH_2, 1H), 4.75 (t, $J = 8.2$ Hz, CH_2, 1H), 5.66 (t, $J = 8.0$ Hz, CH_2, 1H), 7.29–7.46 (m, Ar–H, 5H). Anal. Calcd. for $C_9H_8O_3$: C, 65.82; H, 4.89; O, 29.21. Found: C, 65.85; H, 4.91; O, 29.24.

Results and discussion

Initial experiments were using the cycloaddition of CO_2 and propylene oxide to screen of catalysts. The catalytic activities of different ionic liquids, such as tetrabutylphosphonium bromide ($[P_{4,4,4,4}]$Br), tetrabutylphosphonium bis(trifluoromethyl)sulfonylimide ($[P_{4,4,4,4}]NTf_2$), tetrabutylphosphonium tetrafluoroborate ($[P_{4,4,4,4}]BF_4$), tetrabutylphosphonium hexafluorophosphate ($[P_{4,4,4,4}]PF_6$), tetrabutylphosphonium chloride ($[P_{4,4,4,4}]$Cl), tributyloctylphosphonium bromide ($[P_{8,4,4,4}]$Br), tributyldodecylphosphonium bromide ($[P_{12,4,4,4}]$Br), tetrabutylammonium bromide ([*n*-Bu_4N]Br), 1-butyl-1-methylpyrrolidinium bromide ($[P_{1,4}]$Br), were tested with MIL-53(Cr) as cocatalyst in the reaction (Table 2, entries 1–9). The results demonstrated that the types of ionic liquids had great effects on the catalytic activity. Results showed that $[P_{12,4,4,4}]$Br exhibited the highest reactivity (Table 2, entry 7). Besides MIL-53(Cr), the effects of other metal–organic frameworks co-catalysts including MIL-53(Fe), MIL-101(Cr), ZIF-67 (ZIF: zeolitic imidazolate framework), ZIF-7, ZIF-8 and MOF-5 were studied (Table 2, entries 15–20). The results showed MIL-53(Cr) and MIL-101(Cr) present more catalytic activity than MIL-53(Fe), ZIF-67, ZIF-7, ZIF-8 and MOF-5, and the activity of MIL-53(Cr) is slightly higher than that of MIL-101(Cr). The results indicated that the highly active chromium sites of metal–organic frameworks are crucial for the reaction, possibly facilitating the activation of epoxide and CO_2. For more investigation, a decrease in the catalytic activity was observed when common MIL-53(Cr) or

Table 2 Catalyst effect in the cycloaddition of CO_2 to propylene oxide

Entry[a]	Ionic liquid	Cocatalyst	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	$[P_{4,4,4,4}]Br$	MIL-53(Cr)	3	91	89
2	$[P_{4,4,4,4}]NTf_2$	MIL-53(Cr)	6	75	69
3	$[P_{4,4,4,4}]BF_4$	MIL-53(Cr)	6	62	57
4	$[P_{4,4,4,4}]PF_6$	MIL-53(Cr)	6	67	63
5	$[P_{4,4,4,4}]Cl$	MIL-53(Cr)	4	80	75
6	$[P_{8,4,4,4}]Br$	MIL-53(Cr)	2	95	93
7	$[P_{12,4,4,4}]Br$	MIL-53(Cr)	2	99	98
8	$[n\text{-}Bu_4N]Br$	MIL-53(Cr)	3	85	80
9	$[P_{1,4}]Br$	MIL-53(Cr)	3	82	77
10	–	MIL-53(Cr)	6	55	51
11	$[P_{12,4,4,4}]Br$	–	6	83	82
12	$[P_{12,4,4,4}]Br$	MIL-53(Cr)	2	98	97[d]
13	$[P_{12,4,4,4}]Br$	MIL-53(Cr)	2	98	97[e]
14	$[P_{12,4,4,4}]Br$	MIL-53(Cr)	2	96	95[f]
15	$[P_{12,4,4,4}]Br$	MIL-53(Fe)	2	90	87
16	$[P_{12,4,4,4}]Br$	MIL-101(Cr)	2	94	92
17	$[P_{12,4,4,4}]Br$	ZIF-67	3	89	86
18	$[P_{12,4,4,4}]Br$	ZIF-7	3	85	83
19	$[P_{12,4,4,4}]Br$	ZIF-8	3	88	85
20	$[P_{12,4,4,4}]Br$	MOF-5	3	87	86

[a] The reactions were carried out with propylene oxide (20 mmol), ionic liquid (1.2 mmol), cocatalyst (15 mg) and CO_2 (1.0 MPa) at 100 °C

[b] Isolated conversion

[c] Isolated yield

[d] The first run

[e] The second run

[f] The third run

$[P_{12,4,4,4}]Br$ as the catalyst was used (Table 2, entries 10 and 11). The results mean that ionic liquid or metal–organic framework alone does not work effectively in the reaction, and $[P_{12,4,4,4}]Br$/MIL-53(Cr) was the most suitable catalytic system for the cycloaddition. The active sites of this catalytic system were sufficient for the reaction, which may be attributed to the synergistic effects of MIL-53(Cr) active site and the basic sites of ionic liquid. Furthermore, the catalytic system $[P_{12,4,4,4}]Br$/MIL-53(Cr) could be typically recovered and reused with no obvious decrease in catalytic activity (Table 2, entries 12–14). The TGA spectra confirmed the good thermal stability up to 500 °C of MIL-53(Cr) (Fig. S5, ESI) and 200 °C of $[P_{12,4,4,4}]Br$ (Fig. S8, ESI), providing beneficial information for the reusability of the catalytic system. The morphology of cocatalyst displayed obviously unchangeable after recycling has been confirmed by SEM image (Fig. S3 h, ESI). FT-IR and XRD analysis of the reused cocatalyst after three runs was very similar to that of the fresh catalyst, indicating that no obvious change in the characteristic structure of the catalyst happened exhibits during the reaction (Fig. S6 and S7, ESI). Moreover, elemental analysis of the reused catalytic system illustrated that the content of active species in $[P_{12,4,4,4}]Br$ and MIL-53(Cr) did not change obviously (Tables S1 and S2, ESI). On the basis of these results, we concluded that $[P_{12,4,4,4}]Br$/MIL-53(Cr) shows excellent stability and reusability during the reaction.

The reaction parameters such as reaction temperature, CO_2 pressure and reaction time have significant effects on the cycloaddition (Fig. 1). It can be seen that an increase in reaction temperature up to 100 °C led to a remarkable increase of the propylene oxide conversion (~99%) and yield of 4-methyl-1,3-dioxolan-2-one (~98%). However, when the reaction temperature is further increased to 120 °C, the product yield will decline to 93% (Fig. 1b). During the catalytic process at overly high temperatures, a small amount of by-products of acetone and propylene glycol were formed, which were detected by GC analysis, mostly due to the side reactions including the propylene oxide isomerization and hydrolysis of propylene oxide. Effect of CO_2 pressure on the cycloaddition was studied, and the results are shown in Fig. 1c. It was found that propylene oxide conversion and product yield could be enhanced when the CO_2 pressure increases from 0.5 to 1.0 MPa, with 57% increase in conversion and 55% increase in yield being probed. The increased pressure can enhance the concentration of CO_2 and the interaction between propylene oxide and CO_2, which favors the cyclic carbonate formation (Alves et al. 2015). However, the yield and conversion were obviously decreased with further increasing CO_2 pressure beyond 1.0 MPa. Increasing the pressure to 2.0 MPa exhibited a severely negative effect on the cycloaddition, and only 71% yield and 74% conversion were obtained. A possible explanation was that the exceedingly high CO_2 pressure may block the interaction between propylene epoxide and the catalyst, and would reduce the concentration of propylene epoxide in the bottom catalyst phase. More propylene epoxide was extracted into CO_2 phase leading to the decreased conversion and yield. The effect of the reaction time (Fig. 1d) on the cycloaddition was also investigated; the propylene oxide conversion and product yield increased when the reaction duration was extended from 1.0 to 2.0 h, with 27 % increase in conversion and 26% increase in yield being probed. Further increases in reaction time did not significantly improve the conversion and yield.

To survey the efficiency and generality of the catalytic system $[P_{12,4,4,4}]Br$/MIL-53(Cr), the cycloaddition of CO_2 to different terminal epoxides was examined, and the results are presented in Table 1. All terminal epoxides including electron-deficient and electron-rich groups were smoothly and successfully converted and gave their corresponding cyclic carbonates with excellent yields and selectivities (Table 1, entries 1–6). It is worth noting that this novel catalytic

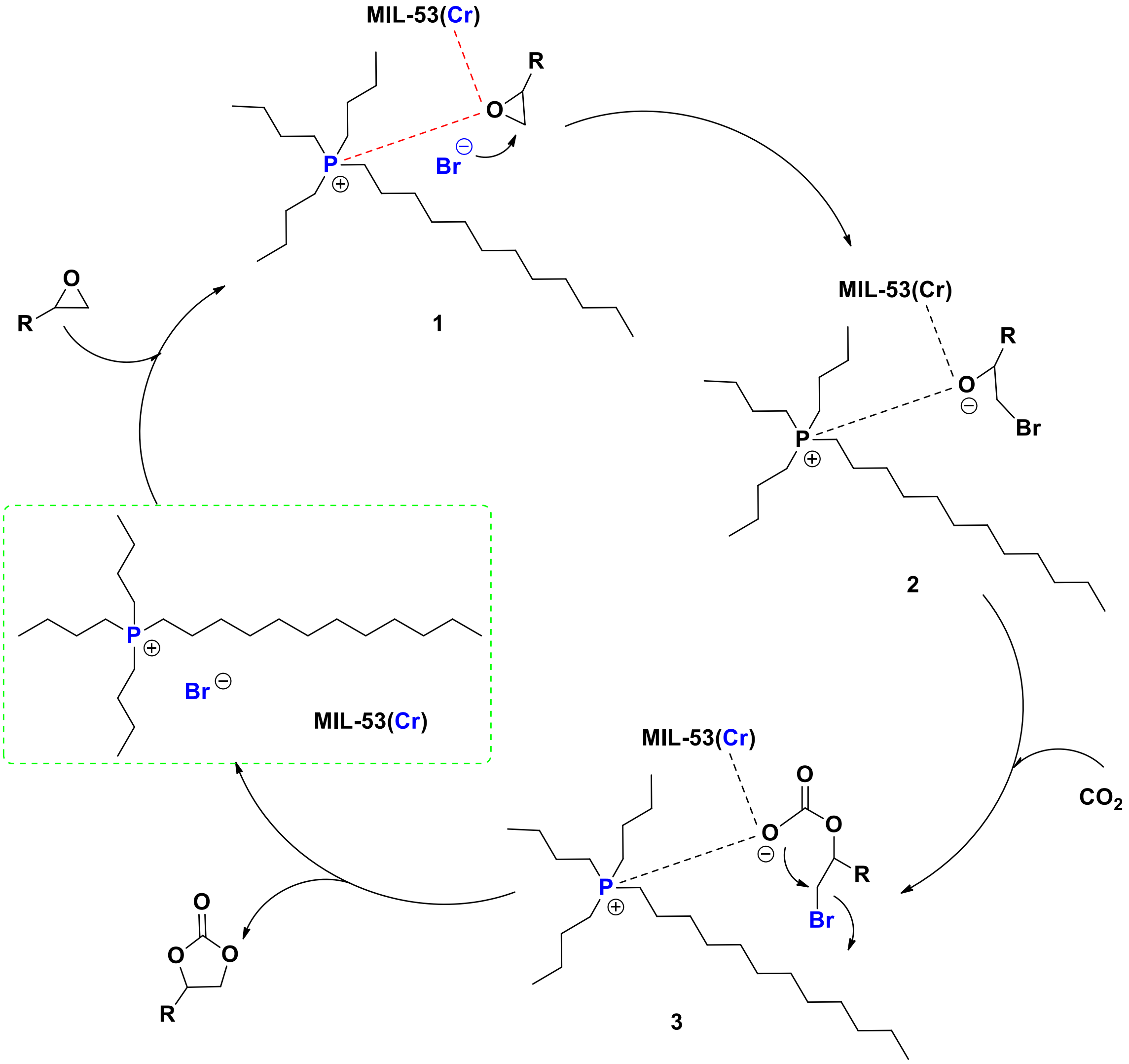


Fig. 2 Possible mechanism for cycloaddition of CO_2 to epoxides

system could tolerate a broad range of groups. However, epoxides with electron-withdrawing groups decreased the reaction rate, and slightly longer reaction times were needed to obtain excellent yields (Table 1, entries 4–6).

On the basis of the above results and previously reported works (Montoya et al. 2016; Arayachukiat et al. 2017; Seo and Chung 2014), a possible mechanism for the cycloaddition is proposed in Fig. 2. Epoxide is firstly activated by the cooperative catalytic system $[P_{12,4,4,4}]$Br/MIL-53(Cr) to form intermediate 1 through the coordination of MIL-53(Cr) and the cationic site of ionic liquid (P) with O atom, followed by nucleophilic attack of the anionic site of ionic liquid (Br) on the less sterically hindered carbon atom of epoxide to form intermediate 2. Then, the interaction occurred between the intermediate 2 and CO_2 to afford intermediate 3 undergoes the nucleophilic attack and coordination. Finally, the cyclic carbonate was generated through an intramolecular substitution cyclic step, together with liberation of the $[P_{12,4,4,4}]$Br/MIL-53(Cr) cooperative catalytic system.

Conclusion

In summary, we have developed a new and highly efficient multifunctional catalytic system with applications to the cycloaddition CO_2 to different epoxides under mild and solvent-free reaction conditions. The catalytic tests revealed that the dual catalytic system of $[P_{12,4,4,4}]$Br coupled with MIL-53(Cr) displayed the best catalytic property due to the synergetic effects involving basic sites phosphonium cation and bromide anion of ionic liquid as well as the active site chromium of MIL-53(Cr). Compared with the previous catalytic systems, the present catalytic system has several attractive features such as simple operation, good to excellent yields, high catalytic activity, low loading of catalyst, environmentally benign and safe. This study provides a new insight into design of sustainable and efficient catalytic systems via the combination of metal–organic frameworks and ionic liquids for chemical carbon dioxide fixation.

Acknowledgements The authors are grateful to the National Natural Science Foundation of China (No. 21506115) for financial support of this research.

References

Alves M, Grignard B, Gennen S, Detrembleur C, Jerome C, Tassaing T (2015) Organocatalytic synthesis of bio-based cyclic carbonates from CO_2 and vegetable oils. RSC Adv 5:53629–53636. https://doi.org/10.1039/c5ra10190e

Alves M, Grignard B, Mereau R, Jerome C, Tassaing T, Detrembleur C (2017) Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies. Catal Sci Technol 7:2651–2684. https://doi.org/10.1039/c7cy00438a

Arayachukiat S, Kongtes C, Barthel A, Vummaleti SVC, Poater A, Wannakao S, Cavallo L, D'Elia V (2017) Ascorbic acid as a bifunctional hydrogen bond donor for the synthesis of cyclic carbonates from CO_2 under ambient conditions. ACS Sustain Chem Eng 5:6392–6397. https://doi.org/10.1021/acssuschemeng.7b01650

Arshadi S, Vessally E, Hosseinian A, Soleimani-amiri S, Edjlali L (2017) Three-component coupling of CO_2, propargyl alcohols, and amines: an environmentally benign access to cyclic and acyclic carbamates (a review). J CO2 Util 21:108–118. https://doi.org/10.1016/j.jcou.2017.07.008

Bellina F, Chiappe C, Lessi M (2012) Synthesis and properties of trialkyl(2,3-dihydroxypropyl) phosphonium salts, a new class of hydrophilic and hydrophobic glyceryl-functionalized ILs. Green Chem 14:148–155. https://doi.org/10.1039/c1gc16035d

Carena L, Vione D (2016) Photochemical reaction of peroxynitrite and carbon dioxide could account for up to 15% of carbonate radicals generation in surface waters. Environ Chem Lett 14:183–187. https://doi.org/10.1007/s10311-016-0549-3

Chaterjee S, Krupadam RJ (2018) Amino acid-imprinted polymers as highly selective CO_2 capture materials. Environ Chem Lett. https://doi.org/10.1007/s10311-018-0774-z

Chen Y, Luo R, Xu Q, Zhang W, Zhou X, Ji H (2017) State of the art aluminum porphyrin-based heterogeneous catalysts for the chemical fixation of CO_2 into cyclic carbonates at ambient conditions. Chem Cat Chem 9:767–773. https://doi.org/10.1002/cctc.201601578

Costa SPF, Azevedo AMO, Pinto PCAG, Saraiva MLMFS (2017) Environmental impact of ionic liquids: recent advances in (eco) toxicology and (bio)degradability. ChemSusChem 10:2321–2347. https://doi.org/10.1002/cssc.201700261

Dai W, Zhang Y, Tan Y, Luo X, Tu X (2016) Reusable and efficient polymer nanoparticles grafted with hydroxyl-functionalized phosphonium-based ionic liquid catalyst for cycloaddition of CO_2 with epoxides. Appl Catal A Gen 514:43–50. https://doi.org/10.1016/j.apcata.2016.01.004

Ding LG, Yao B, Jiang WL, Li JT, Fu QJ, Li YA, Liu ZH, Ma JP, Dong YB (2017) Bifunctional imidazolium-based ionic liquid decorated UiO-67 type MOF for selective CO_2 adsorption and catalytic property for CO_2 cycloaddition with epoxides. Inorg Chem 56:2337–2344. https://doi.org/10.1021/acs.inorgchem.6b03169

Fiorani G, Guo W, Kleij AW (2015) Sustainable conversion of carbon dioxide: the advent of organocatalysis. Green Chem 17:1375–1389. https://doi.org/10.1039/c4gc01959h

Gennen S, Alves M, Méreau R, Tassaing T, Gilbert B, Detrembleur C, Jerome C, Grignard B (2015) Fluorinated alcohols as activators for the solvent-free chemical fixation of carbon dioxide into epoxides. Chemsuschem 8:1845–1849. https://doi.org/10.1002/cssc.201500103

He H, Perman JA, Zhu G, Ma S (2016) Metal-organic frameworks for CO_2 chemical transformations. Small 12:6309–6324. https://doi.org/10.1002/smll.201602711

Ju HY, Manju MD, Kim KH, Park SW, Park DW (2008) Catalytic performance of quaternary ammonium salts in the reaction of butyl glycidyl ether and carbon dioxide. J Ind Eng Chem 14:157–160. https://doi.org/10.1016/j.jiec.2007.12.001

Kaneko S, Shirakawa S (2017) Potassium iodide–tetraethylene glycol complex as a practical catalyst for CO_2 fixation reactions with epoxides under mild conditions. ACS Sustain Chem Eng 5:2836–2840. https://doi.org/10.1021/acssuschemeng.7b00324

Kaneti YV, Tang J, Salunkhe RR, Jiang X, Yu A, Wu KCW, Yamauchi Y (2017) Nanoarchitectured design of porous materials and nanocomposites from metal–organic frameworks. Adv Mater 29:1604898. https://doi.org/10.1002/adma.201604898

Kelly MJ, Barthel A, Maheu C, Sodpiban O, Dega FB, Vummaleti SVC, Abou-Hamad E, Pelletier JDA, Cavallo L, D'Elia V, Basset JM (2017) Conversion of actual flue gas CO_2 via cycloaddition to propylene oxide catalyzed by a single-site, recyclable zirconium catalyst. J CO2 Util 20:243–252. https://doi.org/10.1016/j.jcou.2017.05.020

Khatun R, Bhanja P, Mondal P, Bhaumik A, Das D, Islam SM (2017) Palladium nanoparticles embedded over mesoporous TiO_2 for chemical fixation of CO_2 under atmospheric pressure and solvent-free conditions. New J Chem 41:12937–12946. https://doi.org/10.1039/c7nj02459b

Kumar P, Faujdar E, Singh RK, Paul S, Kukrety A, Chhibber VK, Ray SS (2018) High CO_2 absorption of *O*-carboxymethylchitosan synthesised from chitosan. Environ Chem Lett. https://doi.org/10.1007/s10311-018-0713-z

Lais A, Gondal MA, Dastageer MA (2018) Semiconducting oxide photocatalysts for reduction of CO_2 to methanol. Environ Chem Lett 16:183–210. https://doi.org/10.1007/s10311-017-0673-8

Lan DH, Yang FM, Luo SL, Au CT, Yin SF (2014) Water-tolerant graphene oxide as a high-efficiency catalyst for the synthesis of propylene carbonate from propylene oxide and carbon dioxide. Carbon 73:351–360. https://doi.org/10.1016/j.carbon.2014.02.075

Lan DH, Chen L, Au CT, Yin SF (2015) One-pot synthesized multifunctional grapheme oxide as a water-tolerant and efficient metal-free heterogeneous catalyst for cycloaddition reaction. Carbon 93:22–31. https://doi.org/10.1016/j.carbon.2015.05.023

Lan DH, Fan N, Wang Y, Gao X, Zhang P, Chen L, Au CT, Yin SF (2016a) Recent advances in metal-free catalysts for the synthesis of cyclic carbonates from CO2 and epoxides. Chin J Catal 37:826–845. https://doi.org/10.1016/s1872-2067(15)61085-3

Lan DH, Wang HT, Chen L, Au CT, Yin SF (2016b) Phosphorous-modified bulk graphitic carbon nitride: facile preparation and application as an acid-base bifunctional and efficient catalyst for CO_2 cycloaddition with epoxides. Carbon 100:81–89. https://doi.org/10.1016/j.carbon.2015.12.098

Lan DH, Gong YX, Tan NY, Wu SS, Shen J, Yao KC, Yi B, Au CT, Yin SF (2018) Multi-functionalization of GO with multi-cationic ILs as high efficient metal-free catalyst for CO_2 cycloaddition under mild conditions. Carbon 127:245–254. https://doi.org/10.1016/j.carbon.2017.11.007

Liu S, Zhang Y, Jiang H, Wang X, Zhang T, Yao Y (2018) High CO_2 adsorption by amino-modified bio-spherical cellulose nanofibres aerogels. Environ Chem Lett 16:605–614. https://doi.org/10.1007/s10311-017-0701-8

Martín C, Fiorani G, Kleij AW (2015) Recent advances in the catalytic preparation of cyclic organic carbonates. ACS Catal 5:1353–1370. https://doi.org/10.1021/cs5018997

Montoya CA, Gómez CF, Paninho AB, Nunes AVM, Mahmudov KT, Najdanovic-Visak V, Martins LMDRS, da Silva MFCG, Pombeiro AJL, da Ponte MN (2016) Cyclic carbonate synthesis from CO_2 and epoxides using zinc(II) complexes of arylhydrazones of β-diketones. J Catal 335:135–140. https://doi.org/10.1016/j.jcat.2015.12.027

Nandigama SK, Bheeram VR, Mukkamala SB (2018) Rapid synthesis of mono/bimetallic (Zn/Co/Zn–Co) zeolitic imidazolate frameworks at room temperature and evolution of their CO_2 uptake capacity. Environ Chem Lett. https://doi.org/10.1007/s10311-018-0775-y

Qiu J, Zhao Y, Li Z, Wang H, Fan M, Wang J (2017) Efficient ionic liquid promoted chemical fixation of CO_2 into α-alkylidene cyclic carbonates. Chemsuschem 10:1120–1127. https://doi.org/10.1002/cssc.201601129

Rojas MF, Bernard FL, Aquino A, Borges J, Vecchia FD, Menezes S, Ligabue R, Einloft S (2014) Poly(ionic liquid)s as efficient catalyst in transformation of CO_2 to cyclic carbonate. J Mol Catal A Chem 392:83–88. https://doi.org/10.1016/j.molcata.2014.05.007

Rubio-Martinez M, Avci-Camur C, Thornton AW, Imaz I, Maspoch D, Hill MR (2017) New synthetic routes towards MOF production at scale. Chem Soc Rev 46:3453–3480. https://doi.org/10.1039/c7cs00109f

Seo UR, Chung YK (2014) Poly(4-vinylimidazolium)s/diazabicyclo[5.4.0]undec-7-ene/Zinc(II) bromide catalyzed cycloaddition of carbon dioxide to epoxides. Adv Synth Catal 356:1955–1961. https://doi.org/10.1002/adsc.201400047

Sharifi A, Abaee MS, Mokhtare Z, Mirzaei M (2014) Room temperature synthesis of 2H-1,4-benzoxazine derivatives using a recoverable ionic liquid medium. Environ Chem Lett 12:365–370. https://doi.org/10.1007/s10311-014-0456-4

Sołtys-Brzostek K, Terlecki M, Sokołowski K, Lewiński J (2017) Chemical fixation and conversion of CO_2 into cyclic and cage-type metal carbonates. Coord Chem Rev 334:199–231. https://doi.org/10.1016/j.ccr.2016.10.008

Sopeña S, Martin E, Escudero-Adán EC, Kleij AW (2017) Pushing the limits with squaramide-based organocatalysts in cyclic carbonate synthesis. ACS Catal 7:3532–3539. https://doi.org/10.1021/acscatal.7b00475

Tian D, Liu B, Gan Q, Li H, Darensbourg DJ (2012) Formation of cyclic carbonates from carbon dioxide and epoxides coupling reactions efficiently catalyzed by robust, recyclable one-component aluminum-salen complexes. ACS Catal 2:2029–2035. https://doi.org/10.1021/cs300462r

Tomé LC, Marrucho IM (2016) Ionic liquid-based materials: a platform to design engineered CO_2 separation membranes. Chem Soc Rev 45:2785–2824. https://doi.org/10.1039/c5cs00510h

Wang J, Zhang Y (2016) Boronic acids as hydrogen bond donor catalysts for efficient conversion of CO_2 into organic carbonate in water. ACS Catal 6:4871–4876. https://doi.org/10.1021/acscatal.6b01422

Whiteoak CJ, Nova A, Maseras F, Kleij AW (2012) Merging sustainability with organocatalysis in the formation of organic carbonates by using CO_2 as a feedstock. Chemsuschem 5:2032–2038. https://doi.org/10.1002/cssc.201200255

Zhang H, Liu R, Lal R (2016) Optimal sequestration of carbon dioxide and phosphorus in soils by gypsum amendment. Environ Chem Lett 14:443–448. https://doi.org/10.1007/s10311-016-0564-4

Zhou X, Zhang Y, Yang X, Yao J, Wang G (2010) Hydrated alkali metal halides as efficient catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides. Chin J Catal 31:765–768. https://doi.org/10.1016/s1872-2067(09)60086-3

Zhu J, Usov PM, Xu W, Celis-Salazar PJ, Lin S, Kessinger MC, Landaverde-Alvarado C, Cai M, May AM, Slebodnick C, Zhu D, Senanayake SD, Morris AJ (2018) A new class of metal-cyclam-based zirconium metal–organic frameworks for CO_2 adsorption and chemical fixation. J Am Chem Soc 140:993–1003. https://doi.org/10.1021/jacs.7b10643