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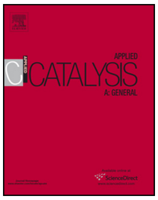

Catalytic fixation of CO_2 to cyclic carbonates over biopolymer chitosan-grafted quarternary phosphonium ionic liquid as a recylable catalyst

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ABSTRACT

We prepared chitosan-grafted quarternary phosphonium ionic liquid (1-butyl-triphenylphosphonium bromide) by a simple method and used it as catalyst for the synthesis of cyclic carbonates through CO_2 cycloaddition to epoxides in the absence of co-catalyst and solvent. High yield of propylene carbonate (96.3%) is obtained at 120 °C and 2.5 MPa in 4 h. We studied the roles of chitosan hydroxyl groups and ionic liquid counter anions on catalytic activity. It is proposed that the facilitation of ring opening of epoxides is a combined result of polarization (by hydrogen bonding due to hydroxyl groups), electronic interaction (by $[BuPh_3P]^+$), and nucleophilic attack (by bromide anion). The catalyst can be easily recovered and reused as demonstrated in a test of five runs without showing any significant loss of activity. From the view point of commercial application, the catalyst is attractive because it is low-cost, ecology-safe, stable and efficient. Furthermore, it is potentially applicable for fixed-bed continuous flow reactors.

1. Introduction

Despite classified as a greenhouse gas, carbon dioxide is an ideal C1 feedstock that is renewable, non-toxic, and low-cost [1–4]. With the fast consumption of fossil fuels and the foreseeable “C1 crisis”, the transformation of CO_2 into valuable chemicals has received much attention. One of the most attractive and feasible strategies for CO_2 utilization is the cycloaddition of CO_2 into epoxides. The desired products are cyclic carbonates that are used as polar aprotic solvents, electrolytes in lithium secondary batteries, as well as precursors for the formation of polycarbonates and numerous fine chemicals [2,4].

A wide range of homogeneous and heterogeneous catalysts were developed, including alkali metal salts [5], organic bases [6–8], metal oxides [9,10], modified molecular sieves [11,12], organometallic complexes [13,14], and ionic liquids (ILs) [15–22]. The use of ILs for the reaction is studied extensively and intensely. Besides being low-cost and simple to synthesize, ILs are used because of their polarity, structure adjustability, and acid-basic property. Frequently they were immobilized on suitable materials (*e.g.*, SiO_2 [23], SBA-15 [24], MCM-41 [25], and polymers [20,26–29]) for efficient catalyst separation and product purification. However, the immobilization of ILs onto inorganic supports always results in catalysts that are poor in reusability. On the other hand, the use of polymers for the grafting of ILs is found promising. For example, the grafting of imidazolium or quaternary phosphonium ILs on polymer nanoparticles [27], porous polymer beads [20,26,28] and tubular polymer [29], as well as polymerizing imidazolium ILs themselves [17] or with cross-linker [22,30] generated catalysts that were reported to be good in catalytic activity and reusability. Nevertheless, the preparation procedures of catalysts and/or supports are complicated, high-cost, and not environment-benign. Hence, the development of an efficient, highly selective, stable and reusable catalyst that can be fabricated cheaply and simply for the cycloaddition reaction is still a challenge.

Chitosan (CS) which is a deacetylated derivative of chitin is a natural, abundant, and low-cost biopolymer. The material exhibits interesting properties such as nontoxicity, biocompatibility, and controllable biodegradability [31–33]. Besides, CS can be easily modified chemically or physically, making it a versatile support material [31–33]. However, there are few reports of CS being

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used as catalyst support for the synthesis of cyclic carbonates from CO_2 and epoxides [34–37]. Xiao et al. [34] reported that CS-$ZnCl_2$ together with 1-butyl-3-methyl imidazolium IL showed good catalytic activity for the cycloaddition reaction. However, the co-catalyst 1-butyl-3-methyl imidazolium IL is hard to separate from products, and there is the need of adding fresh 1-butyl-3-methyl imidazolium IL in each reaction. Zhao et al. [35] and Tharun et al. [36,37] developed CS-supported quarternary ammonium ILs which showed certain catalytic activity in the cycloaddition reaction but the harsh reaction conditions and poor reusability of catalysts limit their application.

Recently, it was reported that task-specific ILs such as hydroxyl- or carboxyl-functionalized imidazolium [18,20,24], guanidinium [15], quarternary ammonium [18] and quarternary phosphonium ILs [16] showed good activity for the cycloaddition reaction due to hydrogen bonding between the functional groups and epoxides. The CS active sites for bonding with ILs and to facilitate hydrogen bonding are, respectively, the amino and hydroxyl groups in hexosaminide. Recently, we reported the synthesis of hydroxyl-functionalized quarternary phosphonium IL ($[HOC_2H_4Ph_3P]Br$) that is much superior to the corresponding traditional IL ($[C_2H_5Ph_3P]Br$) in terms of catalytic activity [16]. In this paper, we reported for the first time the fabrication of a CS-grafted quarternary phosphonium IL and its application in the synthesis of cyclic carbonates. Similar to the case of $[HOC_2H_4Ph_3P]Br$ [16], the hydroxyl groups of CS show synergetic effect that promotes the reaction. The catalyst exhibits good catalytic activity and selectivity, even in the absence of co-catalyst and solvent. Furthermore, the catalyst can be easily recovered by filtration and reused for up to 5 times without showing any significant loss of activity. It is envisaged that the catalyst is suitable for large-scale production of cyclic carbonates.

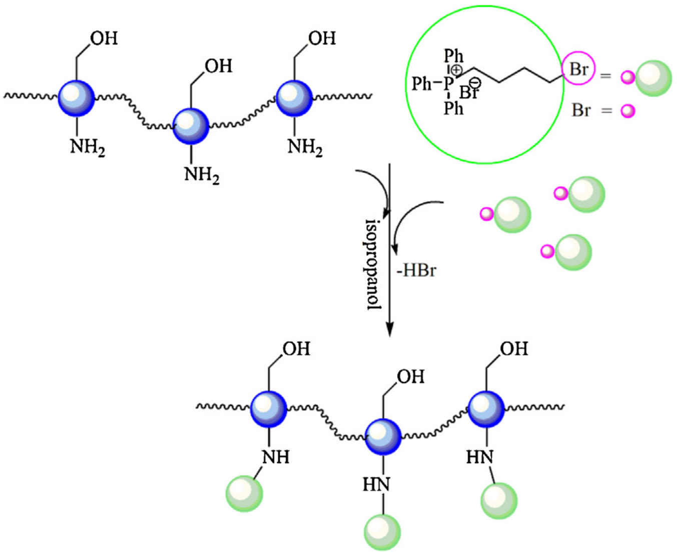
2. Experimental

2.1. Chemicals

Chitosan was purchased from Sinopharm Chemical Reagent Co., Ltd. The degree of deacetylation was 90% and the average molecular weight was 5×10^4. Propylene oxide, triphenylphosphine, 1-bromobutane, 1,4-dibromobutane were purchased from Shanghai Jingchun Industry Co., Ltd. The other epoxides were purchased from Alfa Aesar China Co., Ltd. All chemicals were used as received. The CO_2 (99.9% purity) purchased from Nanchang Guoteng Gas Co. was used without any purification treatment.

2.2. Catalysts preparation

The preparation procedure of CS-grafted 1-butyl-triphenyl phosphonium bromide (denoted hereinafter as CS-$[BuPh_3P]Br$) is illustrated in Scheme 1. First, a solution of triphenylphosphine (10 mmol) in 10 mL toluene was dropped slowly into 10 mL toluene solution containing 1,4-dibromobutane (10 mmol). The mixture was stirred at 110 °C for 24 h under a nitrogen atmosphere. After the reaction, the mixture was cooled down to room temperature (RT), and the resultant crude solid was filtered out and washed three times with diethyl ether, then dried under vacuum at 60 °C for 12 h to give 4-bromobutyl-triphenyl phosphonium bromide ($[BrBuPh_3P]Br$) as a white solid. Second, CS (2 g), 20 wt% NaOH aqueous solution (2 g), $[BrBuPh_3P]Br$ (6 g) and isopropanol (20 mL) were added into a 100 mL two-necked flask and the mixture was stirred at 80 °C for 24 h under nitrogen. When the reaction was completed, the mixture was neutralized by diluted hydrochloric acid. With the addition of ethanol into the reaction solution, there was the precipitation of product which was filtered out, washed with ethanol for three times, and dried under vacuum at 80 °C for 12 h to give the CS-$[BuPh_3P]Br$ catalyst.



Scheme 1. Synthesis procedure of CS-$[BuPh_3P]Br$.

$[BrBuPh_3P]Br$. ^1H NMR (400 MHz, DMSO-d_6): δ = 7.90-7.73 (m, 15H), 3.63–3.32 (m, 4H), 2.49–2.47 (m, 2H), 1.99–1.64 (m, 2H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 135.4, 130.8, 119.3, 34.2, 33.2, 20.8, 19.6. IR (neat): n = 3074, 3057, 2931, 2885, 2862, 1585, 1485, 1436, 750, 690 cm^{-1}. HR-MS (QTOF): m/z = 399.0864, calcd. for $C_{22}H_{25}PBr$ (M+H): 399.0877.

2.3. Characterization

Scanning electron microscopic (SEM) observations were carried out over a Nova NanoSEM 450 microscope. Energy dispersive X-ray spectroscopy (EDS) was performed using accessory (INCA 250) of the Nova NanoSEM 450 instrument. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max 2200PC operating at 40 kV and 40 mA using Ni-filtered Cu Kα radiation (λ = 1.542 Å). The XRD patterns were recorded in the 2θ range of 10° to 80°. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer using DMSO-d_6 as solvent. High-resolution mass spectra (MS-ESI) were recorded on a Waters Xevo G2-S QTof whereas the FT-IR spectra were collected using a Bruker vertex 70 FT-IR spectrophotometer. TG analysis was performed on a SDT Q600 (TA Instruments-Waters LLC) at a heating rate of 15 °C/min in N_2 flow.

2.4. Cycloaddition reaction

The cycloaddition reactions were conducted in a 50 mL high-pressure stainless-steel autoclave equipped with a magnetic stirring bar. In a typical run, the reactor was charged with epoxide (35.7 mmol), catalyst (1.5 mol%, calculated according to the amount of IL), and an appropriate amount of biphenyl (as internal standard for GC analysis). After the reactor was fed with CO_2 to a desired pressure, the autoclave with its contents was heated to a selected temperature and stirred for a designated period of time. Then the reactor was cooled to 0 °C in an ice-water bath, and the residual CO_2 was released. The resulting mixture was analyzed using a GC-mass spectrometer. The products were quantitatively analyzed on a gas chromatograph (Agilent 7890A) that was equipped with a FID and a DB-wax capillary column (30 m × 0.53 mm × 1.0 μm).

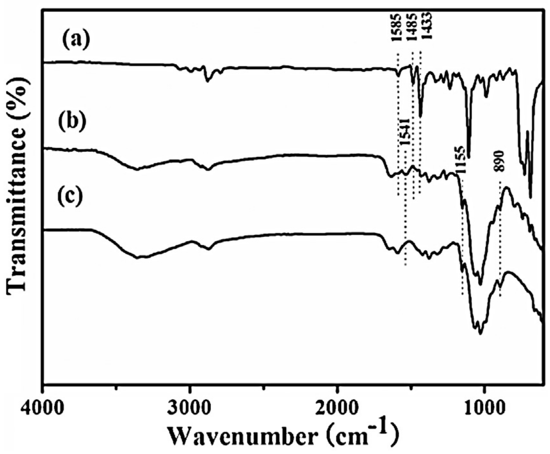


Fig. 1. FT-IR spectra of (a) $[BuPPh_3]Br$, (b) CS-$[BuPh_3P]Br$, and (c) CS.

3. Results and discussion

3.1. Catalyst characterization

To confirm the successful grafting of quaternary phosphonium IL on CS, the FT-IR spectra of $[BuPh_3P]Br$, CS-$[BuPh_3P]Br$, and CS were collected (Fig. 1). The spectra of both $[BuPh_3P]Br$ (Fig. 1a) and CS-$[BuPh_3P]Br$ (Fig. 1b) exhibit bands at 1585, 1485 and 1433 cm^{-1}, characteristic of the stretching vibrations of benzene skeleton. The peaks at 890 and 1155 cm^{-1} that appear in the spectra of both CS-$[BuPh_3P]Br$ (Fig. 1b) and CS (Fig. 1c) are characteristic of saccharine structure [36,38]. The broad band in the region of 3200–3500 cm^{-1} observed in Fig. 1b and c is attributed to stretching vibrations of –NH and –OH with inter- as well as intra-molecular hydrogen bonding [39,40]. It is noted that the 3200–3500 cm^{-1} band of CS-$[BuPh_3P]Br$ is weaker than that of CS, plausibly due to the destruction of hydrogen bonding during the grafting process. Compared with the spectrum of CS, there is the detection of the 1541 cm^{-1} band that is characteristic of C–N stretching vibration in the spectrum of CS-$[BuPh_3P]Br$. All the results indicate that there is successful grafting of $[BuPh_3P]Br$ on the CS.

The XRD patterns of CS and CS-$[BuPh_3P]Br$ are shown in Fig. 2. In the case of CS, there are CS peaks at $2\theta = 13^\circ$ and 20° that can be ascribed to the chitosan structure [41]. As for CS-$[BuPh_3P]Br$, there is only one broad peak centered at $2\theta = 22^\circ$, indicating amorphous structure. With CS, crystallinity is enhanced due to intramolecular hydrogen bonding between the NH_2 and OH groups within the repeating hexosaminide residues [42]. When CS is used for grafting $[BuPh_3P]Br$, there is the involvement of the NH_2 sites at the C2 position of pyranoid rings. The consequence is destruction of hydrogen bonding and hence lowering of symmetry and regularity of the CS chains.

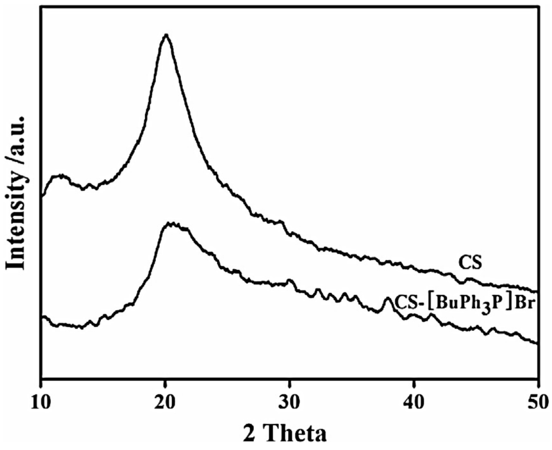


Fig. 2. XRD patterns of CS and CS-$[BuPh_3P]Br$.

Table 1
Catalytic performance of various catalysts [a]

Entry	Catalyst	Catalytic results	
		Yield (%)	Sel. (%)
1	None	0	0
2	CS[b]	2.9	97.0
3	Ph_3P	15.0	98.1
4	CS/Ph_3P/BuBr[c]	16.3	98.5
5	CS-$[BuPh_3P]Br$	96.3	98.7
6	$[BuPh_3P]Br$	85.2	98.5
7	$[BrBuPh_3P]Br$	84.2	98.6
8	$[HOBuPh_3P]Br$	98.0	98.4
9	CS/$[BuPh_3P]Br$[d]	92.3	99.0
10	CS-$[BuPh_3P]Br$[e]	83.9	98.6
11	CS-$[BuPh_3P]Br/H_2O$[e]	90.1	98.5
12	KBr	0.51	87.2
13	$[BuPh_3P]Br$/KBr[f]	96.6	99.7
14	Ph_3P/KBr[f]	21.2	99.6

[a] Reaction conditions: PO 35.7 mmol, catalyst 1.5 mol%, CO_2 pressure 2.5 MPa, temp. 120 °C, time 4 h.
[b] CS 0.24 g.
[c] CS 0.24 g, Ph_3P 0.54 mmol, BuBr 0.54 mmol.
[d] CS 0.24 g, $[BuPh_3P]Br$ 0.54 mmol.
[e] CS-$[BuPh_3P]Br$ 0.9 mol%, H_2O 0.32 mmol.
[f] Equal catalyst amount (0.54 mmol).

The morphology of CS and CS-$[BuPh_3P]Br$ were studied by SEM. As shown in Fig. 3, the smooth surface of CS is roughened with the grafting of $[BuPh_3P]Br$, which is ascribed to the loss of crystallinity, in consistent with the results of XRD analysis. The EDS spectrum of CS-$[BuPPh_3]Br$ (Fig. S1, Electronic Supplementary Material) shows the presence of bromine and phosphine, and can be considered as additional evidence for the successful grafting of quaternary phosphonium ILs on CS. Based on the EDS results, the ILs loading on CS is estimated to be 2.28 mmol/g.

The thermal stability of CS and CS-$[BuPh_3P]Br$ as investigated by TG analysis. Weight loss attributable to the decomposition of polysaccharide chain [36,43] is observed at *ca.* 250 °C over CS and at *ca.* 210 °C over CS-$[BuPh_3P]Br$ (Fig. S2, Electronic Supplementary Material). The poorer thermal stability of CS-$[BuPh_3P]Br$ is due the breakdown of CS crystallinity upon $[BuPh_3P]Br$ grafting. It should be noted that the reaction temperature for the cycloaddition reaction is within the 90–140 °C range, far below the destruction temperature of the catalyst. Furthermore, the thermal stability results of CS and CS-$[BuPh_3P]Br$ are in good agreement with those obtained in XRD and SEM analysis.

3.2. Catalytic performance

The catalytic activity of CS-$[BuPh_3P]Br$ for the cycloaddition of CO_2 to epoxides is compared with those of the other catalysts. In this study, the reaction of PO with CO_2 to produce propylene carbonate (PC) was chosen as model reaction, and the results are summarized in Table 1. In the absence of a catalyst, there is no reaction whatsoever (entry 1). In the presence of CS, Ph_3P, and CS/Ph_3P/BuBr (entries 2–4), PC yield is poor (<16.3%). It is only over CS-$[BuPh_3P]Br$ that excellent performance can be achieved (PC yield = 96.3%) (entry 5). It is noted that CS-$[BuPh_3P]Br$ is also superior to the homogeneous catalysts $[BuPh_3P]Br$ and $[BrBuPh_3P]Br$ (entry 5 *vs* 6 and 7) in performance. We deduce that there is synergism between phosphonium IL and the hydroxyl groups of CS, leading to the performance of CS-$[BuPh_3P]Br$ superior to that of $[BuPh_3P]Br$ and $[BrBuPh_3P]Br$. It is reminded that $[BuPh_3P]Br$ is

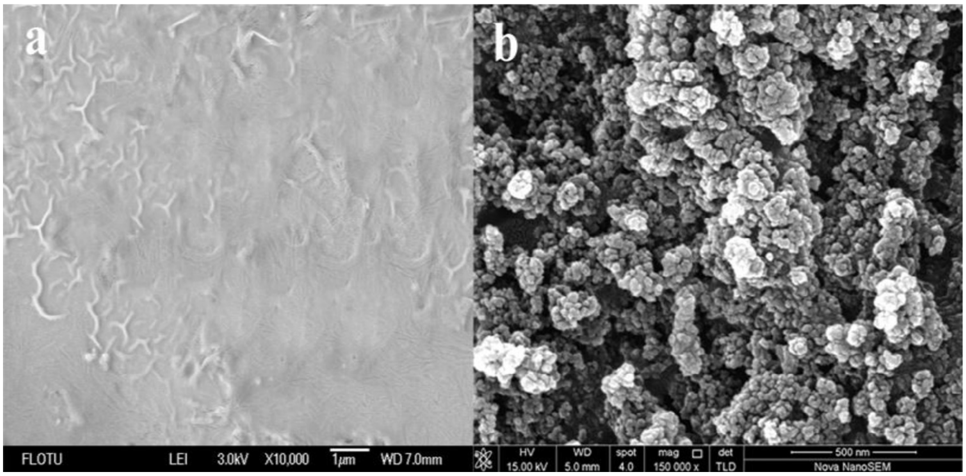


Fig. 3. SEM images of (a) CS and (b) CS-[BuPh$_3$P]Br.

catalytically active itself while [BrBuPh$_3$P]Br is the intermediate adopted for the formation of CS-[BuPh$_3$P]Br.

In order to study the synergism between phosphonium IL and CS hydroxyl groups as well as to confirm the synergistic effect on the cycloaddition reaction, catalysts with or without hydroxyl groups were prepared and investigated. From Table 1, one can see that over [BuPh$_3$P]Br with no hydroxyl groups, PC yield is only 85.2%. While over the corresponding hydroxyl-functionalized catalyst ([HOBuPh$_3$P]Br), PC yield is 98.0%, much higher than that over [BuPh$_3$P]Br (entry 8 *vs* 7). It is noted that CS-[BuPh$_3$P]Br is slightly lower than [HOBuPh$_3$P]Br (entry 5 *vs* 8), but much higher than [BuPh$_3$P]Br (entry 5 *vs* 6) in catalytic activity. Furthermore, the mixing of CS with [BuPh$_3$P]Br can also promote the catalytic activity of [BuPh$_3$P]Br (entry 6 *vs* 9). The above results illustrate that the superior activity of CS-[BuPh$_3$P]Br is likely to be due to the CS hydroxyl groups that are present in abundance. In other words, the hydroxyl groups of CS promote the ring opening of epoxide through efficient synergistic interaction involving the step of hydrogen bonding [18,21,24,30,44]. We purposely added certain amount of water into the reaction system and observed significant enhancement of activity over CS-[BuPh$_3$P]Br (entry 10 *vs* 11). The result further proves that hydroxyl groups have a critical role in the cycloaddition reaction.

It is well known that the nucleophilic attack of epoxides by halide anions is also crucial for the opening of epoxy ring [18,21,24,30,44]. Compared to [BuPh$_3$P]Br, [BrBuPh$_3$P]Br that has one more bromine atom as substituent group shows activity similar to that of [BuPh$_3$P]Br (entry 6 *vs* 7). Nevertheless, despite KBr by itself is almost inactive (entry 12), the addition of KBr results in activity enhancement of [BuPh$_3$P]Br (entry 6 *vs* 13) and Ph$_3$P (entry 3 *vs* 14). The results clearly confirm the important role of bromide anions in the cycloaddition reaction.

3.3. *Effect of reaction parameters*

Fig. 4 shows the effect of CS-[BuPh$_3$P]Br loading on PC yield and selectivity. It is observed that PC selectivity stays at *ca.* 99% in the catalyst loading range of 0.3–2.1 mol%. With increase of catalyst loading from 0.3 to 1.5 mol%, there is sharp rise of PC yield from 63.8 to 96.3%. The increase of PC yield is not significant above catalyst loading of 1.5 mol%, plausibly due to the poor dispersion of the excess catalyst that hinders the mass transfer of reagents towards the active sites [45].

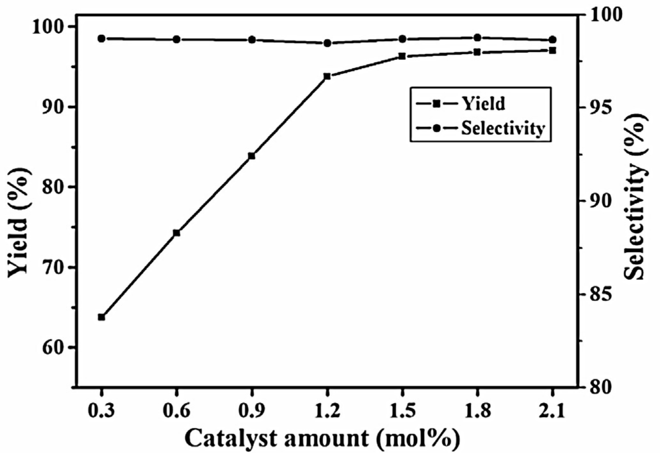


Fig. 4. Effect of catalyst loading on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, CO$_2$ pressure 2.5 MPa, 120 °C, 4 h.)

The influence of reaction temperature on the activity of CS-[BuPh$_3$P]Br is shown in Fig. 5. It is found that PC selectivity is insensitive to the change of temperature from 90 to 140 °C, staying roughly at *ca.* 99%. With the change of reaction temperature from 90 to 120 °C, there is a rise of PC yield from *ca.* 63 to 95%. Above 120 °C, there is a slight decrease of PC yield and selectivity. An increase of reaction temperature results in increase of reactivity but decrease in solubility of gas-phase CO$_2$ in the reaction system. At temperature higher than 120 °C, there is decrease of propylene

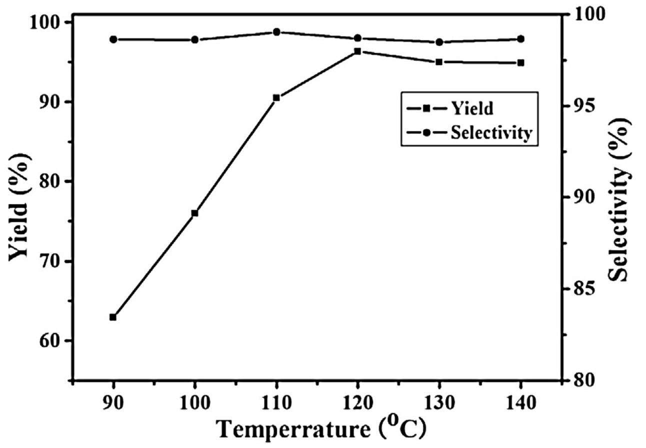


Fig. 5. Effect of reaction temperature on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, catalyst 1.5 mol%, CO$_2$ pressure 2.5 MPa, 4 h.)

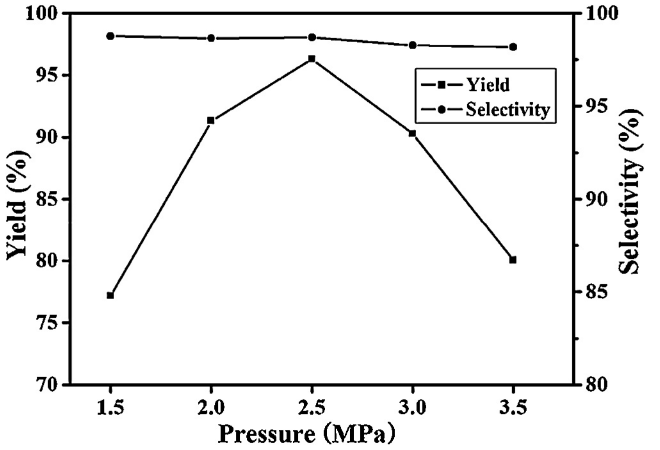


Fig. 6. Effect of CO_2 pressure on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, catalyst 1.5 mol%, 120 °C, 4 h.)

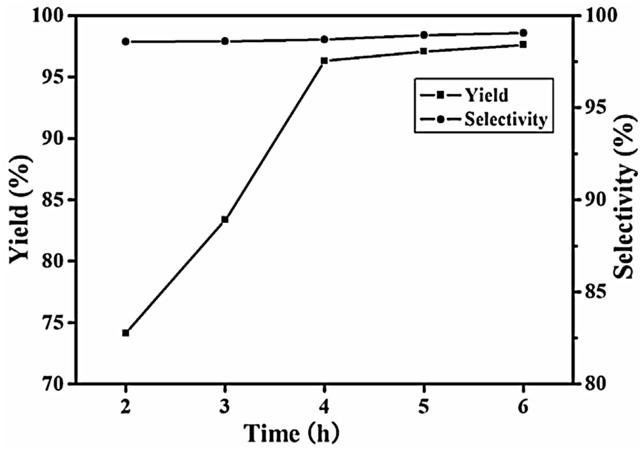


Fig. 7. Effect of reaction time on PC yield and selectivity. (Reaction conditions: PO 35.7 mmol, catalyst 1.5 mol%, CO_2 pressure 2.5 MPa, 120 °C.)

oxide (PO) conversion due to the poor CO_2 solubility [19]. Furthermore, a higher reaction temperature accelerates side reactions such as isomerization to acetone, as well as hydrolysis to diol, causing decline of selectivity to propylene carbonate (PC) as a result [30,44]. The results indicate that the temperature has a pronounce effect on the reaction, and 120 °C is the most suitable for cycloaddtion.

We also studied the influence of CO_2 pressure on the cycloaddition reaction. As shown in Fig. 6, an increase of CO_2 pressure from 1.5 to 2.5 MPa results in a rapid rise of PC yield, but there is decline of PC yield in the high-pressure region (2.5–3.5 MPa). It can be seen that a moderate CO_2 pressure of 2.5 MPa is the most suitable for the reaction. Similar effects of CO_2 pressure on catalytic activity were observed in other catalytic systems [15,26,30,35,36,45–47]. The phenomenon can be explained based on the concepts of reaction equilibrium and mass transfer of reactants. For the cycloaddition reaction, PC is in its liquid form under the adopted reaction conditions, and the increased of CO_2 pressure should be a positive factor for PO conversion. It is regarded that there are two phases in the reaction system. In the low-pressure region (1.5–2.5 MPa), a rise of CO_2 pressure leads to an increase of CO_2 concentration in the liquid phase, which is a favorable factor for the reaction. However, in the high-pressure region (2.5–3.5 MPa), it is envisaged that too high a CO_2 pressure could decrease the concentration of PO as a result of dilution by excessive amount of CO_2, which was not favorable for the reaction. In addition, it is known that acidic CO_2 dissolves in basic epoxide, forming CO_2-epoxide complexes as a result [23,48]. Too high a CO_2 pressure could retard the separation of CO_2 from PO in the duration of cycloaddition reaction, decreasing the PC yield as a result [10,15,16,47]. Therefore, a higher CO_2 pressure does not benefit the cycloaddition reaction catalyzed by chitosan-grafted phosphonium IL. It is noted that the PC selectivity (*ca.* 99%) is almost independent of the rise of CO_2 pressure.

The influence of reaction time on PC yield and selectivity was investigated and the results are depicted in Fig. 7. It can be seen that the yield of PC increases rapidly to reach *ca.* 96% within the first 4 h while PC selectivity remains at *ca.* 99% throughout. Thus, a reaction time of 4 h is appropriate for the cycloaddition reaction under the adopted conditions.

3.4. Catalyst recovery

The stability and recyclability of the CS-[$BuPh_3P$]Br catalyst was tested in an experiment of five runs (Fig. 8). The catalyst was recovered by simple filtration, drying in vacuum, and then reused for the next cycle. It was found that the catalyst CS-[$BuPh_3P$]Br performs well without showing any significant loss of PC yield and selectivity across the five consecutive runs. To further investigate the stability of CS-[$BuPh_3P$]Br, we characterized the recovered catalyst (after five runs) by TG and FT-IR. It was found that similar to the fresh catalyst, the used catalyst is stable at *ca.* 210 °C (Fig. S3, Electronic Supplementary Material). Furthermore, the FT-IR spectra of fresh and recycled (5 times) CS-[$BuPh_3P$]Br are alike (Fig. S4, Electronic Supplementary Material). The results show that the CS-[$BuPh_3P$]Br catalyst is thermally as well as chemically stable, indicating that the catalyst has high potential for commercial application.

3.5. Catalytic activity towards different epoxides

We find that the CS-[$BuPh_3P$]Br catalyst can be applied to other epoxide substrates for the synthesis of cyclic carbonates (Table 2). A variety of monosubstituted terminal epoxides (entries 1–5) can be converted to the corresponding cyclic catbonates in high yield and selectivity. It is well known that the epoxides with an electron-withdrawing group are able to stabilize the intermediate structure formed after ring-opening of epoxides, thus enhancing the reactivity [49]. Hence, the epichlorohydrin (entry 2) shows the best reactivity, and the corresponding carbonates are obtained almost quantitatively in 4 h. On the other hand, the conversions of other epoxides (*i.e.* 1,2-hexene oxide, styrene oxide, glycidyl phenyl ether) were lower than those of other monosubstituted terminal epoxides, probably because of the low reactivity of the β-carbon

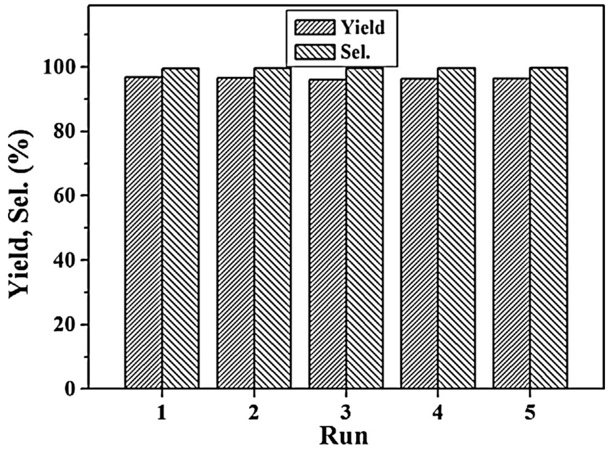
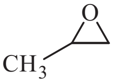
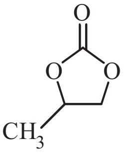
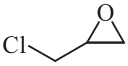
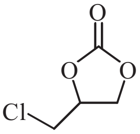
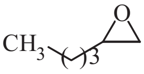
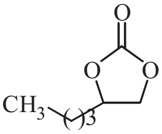
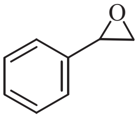
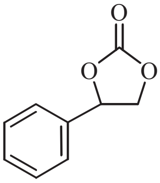
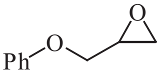
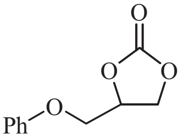
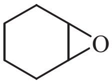
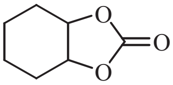


Fig. 8. Recycle of catalyst for cycloaddition reaction. (Reaction conditions: PO 35.7 mmol, catalyst 1.5 mol%, CO_2 pressure 2.5 MPa, 120 °C, 4 h.)

Table 2
Cycloaddition of CO_2 to various epoxides.[a]

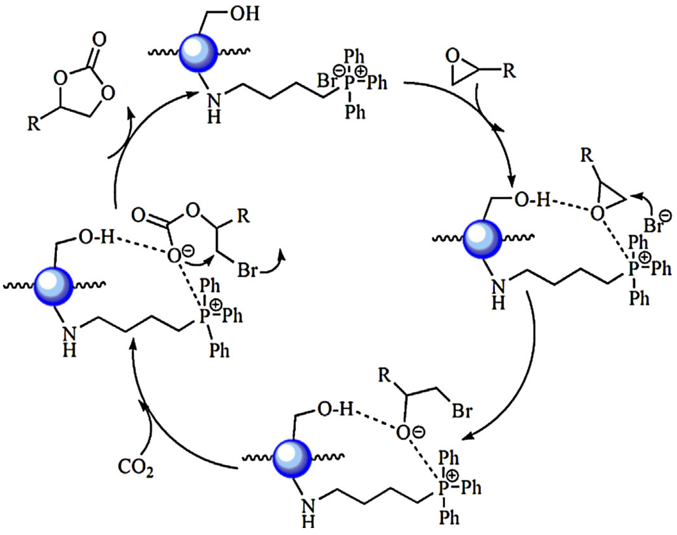
Entry	Epoxide	Product	Time (h)	Catalytic results	
				Yield (%)	Sel. (%)
1			4	96.3	98.7
2			4	97.3	98.6
3			6	97.1	97.6
4			6	96.9	97.4
5			6	95.0	96.4
6			24	74.3	98.9

[a] Reaction conditions: PO 35.7 mmol, CS-[$BuPh_3P$]Br 1.5 mol%, CO_2 pressure 2.5 MPa, temp. 120 °C.

atom of those epoxides (entries 3–5) [36]. The disubstituted epoxide, cyclohexene oxide (entry 6), exhibits the lowest activity for the production of the corresponding cyclic carbonate, probably due to the high steric hindrance as a result of the rings.

3.6. Possible mechanism

From the results displayed so far, one can see that both the hydroxyl groups and bromide anions are essential for the excellent performance of the CS-[$BuPh_3P$]Br catalyst. It was reported that when carboxyl- or hydroxyl-functionalized IL are used as catalysts, there is polarization of C–O bond as a result of hydrogen bonding between the hydrogen atom of carboxyl (or hydroxyl) and the oxygen atom of epoxide, facilitating the opening of epoxide ring [15,18,21,26,30,44,47]. In the use of imidazolium [19] or guanidinium [50] IL as catalysts, it is regarded that the opening of epoxy rings can be attributed to the cooperation of nucleophilic attack by an anion and the activation by an onium cation through electronic interaction. On the basis of these findings, we consider that the synergism of polarization (due to hydrogen bonding) and electronic interaction (due to phosphonium cation) as well as the nucleophilic attack by a bromide anion account for the excellent activity of the catalyst. A mechanism is proposed for the catalytic process as shown in Scheme 2. The bromide anion of the catalyst opens the epoxy ring, which was activated by the hydroxyl groups and phosphonium cation through hydrogen bonding as well as electronic interaction. Then the haloalkoxy intermediate further reacts with CO_2 to form a linear halocarbonate that transforms



Scheme 2. Proposed mechanism for the cycloaddition reaction.

into cyclic carbonate through the intramolecular substitution of the bromide anion.

4. Conclusion

By grafting quarternary phosphonium IL onto chitosan surface, we synthesize the CS-[BuPh$_3$P]Br catalyst that is efficient in the synthesis of cyclic carbonates from CO$_2$ and epoxides in the absence of co-catalyst and solvent. We find that the vicinal hydroxyl groups in CS play a key role in promoting the cycloaddition reaction. The superior performance of the catalyst can be attributed to the opening of epoxy ring as an outcome of the combined effect of C–O polarization, electronic interaction as well as nucleophilic attack. The catalyst can be separated easily by filtration and used effectively in a test of 5 cycles without significant loss of activity. In terms of efficiency, stability, simplicity, recyclability, environment-friendliness, and cost effectiveness, the CS-[BuPh$_3$P]Br catalyst is potentially an industrial catalyst for large-scale production of cyclic carbonates.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.07.008.

References

[1] T. Sakakura, J.C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365–2387.
[2] W.L. Dai, S.L. Luo, S.F. Yin, C.T. Au, Appl. Catal. A: Gen. 366 (2009) 2–12.
[3] T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312–1330.
[4] M. North, R. Pasquale, C. Young, Green Chem. 12 (2010) 1514–1539.
[5] T. Sako, T. Fukai, R. Sahashi, Ind. Eng. Chem. Res. 41 (2002) 5353–5358.
[6] H. Kawanami, Y. Kushima, Chem. Commun. (2000) 2089–2090.
[7] A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, Tetrahedron Lett. 44 (2003) 2931–2934.
[8] J.L. Jiang, R.M. Hua, Synth. Commun. 36 (2006) 3141–3148.
[9] B.M. Bhanage, S.I. Fujita, Y. Ikushima, M. Arai, Appl. Catal. A: Gen. 219 (2001) 259–266.
[10] W.L. Dai, S.F. Yin, R. Guo, S.L. Luo, X. Du, C.T. Au, Catal. Lett. 136 (2010) 35–44.
[11] E.J. Doskocil, J. Phys. Chem. B 109 (2005) 2315–2320.
[12] R. Srivastava, D. Srinivas, P. Ratnasamy, Catal. Lett. 91 (2003) 133–139.
[13] F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, A.R. Khosropour, Polyhedron 32 (2012) 68–72.
[14] C.J. Whiteoak, N. Kielland, V. Laserna, E.C. Escudero-Adán, E. Martin, A.W. Kleij, J. Am. Chem. Soc. 135 (2013) 1228–1231.
[15] W.L. Dai, B. Jin, S.L. Luo, X.B. Luo, X.M. Tu, C.T. Au, J. Mol. Catal. A: Chem. 378 (2013) 326–332.
[16] W.L. Dai, B. Jin, S.L. Luo, X.B. Luo, X.M. Tu, C.T. Au, Appl. Catal. A: Gen. 470 (2014) 183–188.
[17] S. Ghazali-Esfahani, H.B. Song, E. Păunescu, F.D. Bobbink, H.Z. Liu, Z.F. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan, P.J. Dyson, Green Chem. 15 (2013) 1584–1589.
[18] J. Sun, S.J. Zhang, W.G. Cheng, J.Y. Ren, Tetrahedron Lett. 49 (2008) 3588–3591.
[19] L. Han, H.J. Choi, S.J. Choi, B. Liu, D.W. Park, Green Chem. 13 (2011) 1023–1028.
[20] Y.Y. Zhang, S.F. Yin, S.L. Luo, C.T. Au, Ind. Eng. Chem. Res. 51 (2012) 3951–3957.
[21] R.A. Watile, K.M. Deshmukh, K.P. Dhake, B.M. Bhanage, Catal. Sci. Technol. 2 (2012) 1051–1055.
[22] Y. Xie, Z.F. Zhang, T. Jiang, J.L. He, B.X. Han, T.B. Wu, K.L. Ding, Angew. Chem. Int. Ed. 46 (2007) 7255–7258.
[23] L.F. Xiao, F.W. Li, J.J. Peng, C.G. Xia, J. Mol. Catal. A: Chem. 253 (2006) 265–269.
[24] W.L. Dai, L. Chen, S.F. Yin, S.L. Luo, C.T. Au, Catal. Lett. 135 (2010) 295–304.
[25] S. Udayakumar, Y.S. Son, M.K. Lee, S.W. Park, D.W. Park, Appl. Catal. A: Gen. 347 (2008) 192–199.
[26] W.L. Dai, L. Chen, S.F. Yin, W.H. Li, Y.Y. Zhang, S.L. Luo, C.T. Au, Catal. Lett. 137 (2010) 74–80.
[27] Y.B. Xiong, H. Wang, R.M. Wang, Y.F. Yan, B. Zheng, Y.P. Wang, Chem. Commun. 46 (2010) 3399–3401.
[28] L.N. Han, H.J. Choi, D.K. Kim, S.W. Park, B.Y. Liu, D.W. Park, J. Mol. Catal. A: Chem. 338 (2011) 58–64.
[29] H.C. Cho, H.S. Lee, J. Chun, S.M. Lee, H.J. Kim, S.U. Son, Chem. Commun. 47 (2011) 917–919.
[30] T.Y. Shi, J.Q. Wang, J. Sun, M.H. Wang, W.G. Cheng, S.J. Zhang, RSC Adv. 3 (2013) 3726–3732.
[31] J.H. Zhou, Z.P. Dong, H.L. Yang, Z.Q. Shi, X.C. Zhou, R. Li, Appl. Surf. Sci. 279 (2013) 360–366.
[32] Z.D. Wang, L.C. Zheng, C.C. Li, D. Zhang, Y.N. Xiao, G.H. Guan, W.X. Zhu, Carbohydr. Polym. 94 (2013) 505–510.
[33] C.S. Catano, M. Caiado, J. Farinha, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, Chem. Eng. J. 230 (2013) 567–572.
[34] L.F. Xiao, F.W. Li, C.G. Xia, Appl. Catal. A: Gen. 279 (2005) 125–129.
[35] Y. Zhao, J.S. Tian, X.H. Qi, Z.N. Han, Y.Y. Zhuang, L.N. He, J. Mol. Catal. A: Chem. 271 (2007) 284–289.
[36] J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A.C. Kathalikkattil, D.W. Park, Catal. Sci. Technol. 2 (2012) 1674–1680.
[37] J. Tharun, D.W. Kim, R. Roshan, Y. Hwang, D.W. Park, Catal. Commun. 31 (2013) 62–65.
[38] Z. Guo, R. Xing, S. Liu, Z. Zhong, P. Li, Carbohydr. Polym. 73 (2008) 173–177.
[39] E.A. Stepnova, V.E. Tikhonov, T.A. Babushkina, T.P. Klimova, E.V. Vorontsov, V.G. Babak, S.A. Lopatin, I.A. Yamskov, Eur. Polym. J. 43 (2007) 2414–2421.
[40] M. Ghiaci, N. Dorostkar, M.V. Martínez-Huerta, J.L.G. Fierro, P. Moshiri, J. Mol. Catal. A: Chem. 379 (2013) 340–349.
[41] S. Lu, X. Song, D. Cao, Y. Chen, K. Yao, J. Polym. Sci. 91 (2004) 3497–3503.
[42] I. Aranaz, M. Mengíbar, R. Harris, I. Panos, B. Miralles, N. Acosta, G. Galed, Á. Heras, Curr. Chem. Biol. 3 (2009) 203–230.
[43] H. Xie, S. Zhang, S. Li, Green Chem. 8 (2006) 630–633.
[44] J. Sun, J.Q. Wang, W.G. Cheng, J.X. Zhang, X.H. Li, S.J. Zhang, Y.B. She, Green Chem. 14 (2012) 654–660.
[45] J. Sun, W.G. Cheng, W. Fan, Y.H. Wang, Z.Y. Meng, S.J. Zhang, Catal. Today 148 (2009) 361–367.
[46] C.W. Tsang, B. Baharloo, D. Riendl, M. Yam, D.P. Gates, Angew. Chem. Int. Ed. 43 (2004) 5682–5685.
[47] W.L. Dai, B. Jin, S.L. Luo, X.B. Luo, X.M. Tu, C.T. Au, Catal. Sci. Technol. 4 (2014) 556–562.
[48] R. Nomura, M. Kimura, S. Teshima, A. Ninagawa, H. Matsuda, Bull. Chem. Soc. Jpn. 55 (1982) 3200–3203.
[49] B. Ochiai, T. Iwamoto, T. Endo, Green Chem. 8 (2006) 138–140.
[50] H.B. Xie, H.F. Duan, S.H. Li, S.B. Zhang, New J. Chem. 29 (2005) 1199–1203.