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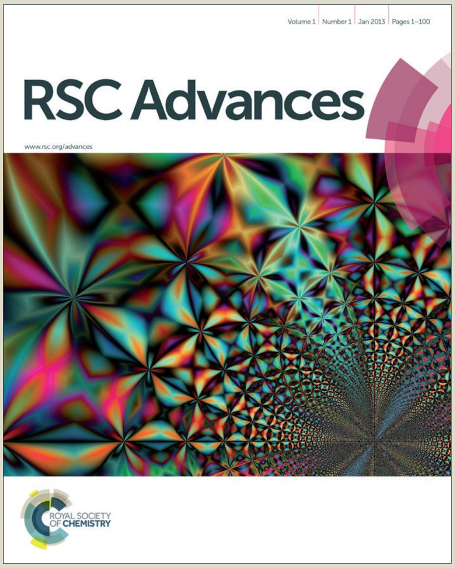

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Bis-ammonium immobilized polystyrenes with co-catalyzing functional end groups as efficient and reusable heterogeneous catalysts for synthesis of cyclic carbonate from CO_2 and epoxides

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A series of novel bis-ammonium ionic liquid immobilized polystyrene (BisAm-i-PS) heterogeneous catalysts with co-catalyzing functional end groups of $–CH_2COOH$, $–CH_2CH_2OH$, and $–CH_2CH_2NH_2$ were synthesized for the cycloaddition reaction of CO_2 and epoxides without any additional co-catalyst and organic solvent. All the ammonium immobilized catalysts showed high selectivity. Bis-ammonium immobilized catalysts were more efficient than single-ammonium ones did. The yield was further increased by introducing the functional end groups. Both $–CH_2COOH$ and $–CH_2CH_2OH$ ended BisAm-i-PS catalysts achieved high activities (yield: >99%), while $–NH_2$ ended one had slightly lower activity (yield: 97.3%) under the same reaction condition. The effects of parameters, such as halide anions of the catalysts, reaction temperature, initial pressure and reaction time were also investigated with $–CH_2CH_2OH$ ended BisAm-i-PS (BisAm-OH-i-PS) as the catalyst. Under an optimal reaction condition (1.2 MPa, 130 °C and 2.5 h), BisAm-OH-i-PSs with $2Br^-$ and $2I^-$ showed very high efficiencies. For each of them, propylene carbonate selectivity and yield were more than 99% and 99%, respectively. In addition, the catalyst possessed good stability, and both catalytic activity and selectivity were always more than 99% for 5 times recycle tests.

Introduction

Carbon dioxide has been considered as a renewable carbon resource, which has the advantages of abundant reserves, nontoxicity and low cost.[1] One of the most promising ways to utilize CO_2 is the fixation of it to generate commodity chemicals such as cyclic carbonates, which is significant for a good example of 100% atom economy.[2] At present, cyclic carbonates play an increasingly important role in our society. They are widely used as electrolytes of batteries, as precursors for polycarbonate, as chemical intermediates, as engineering plastics and excellent aprotic polar solvents.[3]

Over the past few decades, a wide range of homogeneous and heterogeneous catalysts including alkali metal salts,[4] organometallic complexes,[5–12] organic bases,[13,14] ionic liquids(ILs),[15–18] metal oxides,[19–21] modified molecular sieves,[22,23] supported ILs,[24–30] ion-exchange resins[31] and calcined hydrotalcite[32] have been developed for the coupling epoxides and carbon dioxide. The catalytic activity is usually efficient with homogeneous catalysts system, however, the separation of the catalysts from products would be a difficult work, and what's more, co-solvents or co-catalyst were usually required. Apparently, the application of heterogeneous catalysts make the separation easier, but the stability and reusability, especially the poor catalytic activity is urgently need to be improved. Therefore, to develop a kind of catalyst with high activity, low-cost, well reusability, and easy separation is still a challenge.

Recently, ionic liquids including quaternary ammonium salts[33–38], quaternary phosphonium salts[39–41], imidazolium salts[25,42–44], pyridinium salts,[45] guanidinium salts[46–48] and other types of ILs[47,49] attract researchers' much interest because of their high catalytic activities, especially the functionalized ionic liquids, which is fabricated with hydroxyl, amidogen, carboxyl and so on. Sun et al. reported that hydroxyl-functionalized quaternary ammonium salts and imidazolium salts shown high activity for the synthesis of cyclic carbonate.[50] And then they made immobilization of it with polystyrene resin to get a reusable and efficient catalyst. Furthermore, a series of functionalized ILs were got and supported with different carriers.[25, 38, 39]

Compared to single cation ILs, dication ILs exert better activities in physical and chemical.[35,53] They are widely used in high temperature solvents, lubricants, and catalysts in transesterification and esterification.[54,55] However, to the best of our knowledge, there are few reports about bis-functionalized heterogeneous catalysts for cyclic carbonate synthesis from carbon dioxide and epoxides.[33,55] Here, a series of bis-ammonium immobilized polystyrene resins with the co-catalyzing end groups of hydroxyl, carboxyl and amino groups were synthesized (Scheme 1). Then, these novel dication functionalized catalysts were used for the synthesis of propylene carbonate from CO_2 and epoxide without any solvent and co-catalyst (Scheme 2). The influence of catalyst structure, the types and amount of nucleophilicity anions, and the reaction conditions of temperature, initial pressure and reaction time were also studied in

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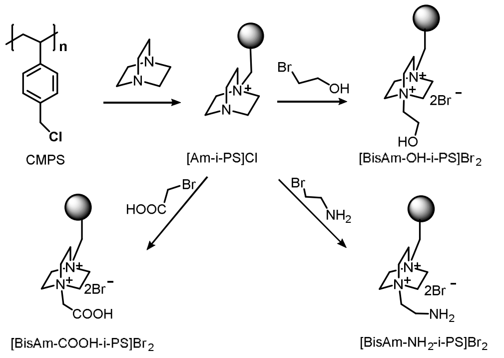
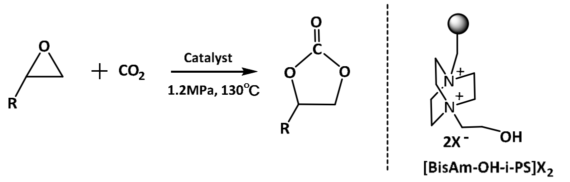


Scheme 1 The synthesis of bis-ammonium immobilized polystyrene heterogeneous catalysts.



Scheme 2 Synthesis of cyclic carbonates from epoxides and carbon dioxide.

Experimental

General information

The products were analyzed by gas chromatograph (Techcomp 7900) that equipped with a FID detector and a DB-wax capillary column (30 m × 0.25 mm × 0.25 μm). Nuclear magnetic resonance (NMR) spectra were performed on Bruker 500 AVANCE Ⅱ, using $CDCl_3$ as a solvent. Fourier transformation infrared (FT-IR) spectra were obtained on a Nicolet iN10 of Thermo Fisher. 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 XRD-7000S 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 5^o to 80^o. Thermal gravimetric analysis (TGA) was performed on a TGA/DSC1 of Mettler Toledo. The content of active components was determined by Elementar Vario EL III element analysis.

Chemicals

Spherical Chloromethtlated polystyrene resin (CMPS, 1 mm) with 17% Cl content and 7% cross-linked with divinylbenzene was purchased from the Chemical Plant of NanKai University (China). CO_2 was commercially available with a purity of 99.99% and be further purified by a filter. Propylene oxide was purchased from Sinopharm Chemical Reagent Co., Ltd and purified by distillation before the reaction. Other epoxides were purchased from J&K Chemical. 2-bromine ethanol, 2-bromoethylamine hydrobromide, 2-Bromoacetic acid and 1, 4-diazobicyclo [2.2.2] octane (DABCO) were purchased from Aladdin Industrial Corporation. The other chemical solvents were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. without any further treatment.

Catalysts preparation

First, CMPS (1 g) was swelled in 30mL acetonitrile for 12h, and then a solution of DABCO (10 mmol) in 20mL acetonitrile was added to the reaction system and reacted for 24h at 30 ^oC, after that, the product was filtered and washed three times with diethyl ether and ethyl acetate, then dried at 65 ^oC under vacuum for 12h to get the product [Am-i-PS]Cl. As for this reaction, the product is almost [Am-i-PS]Cl because that the reaction sites are nearly on the surface of the carrier and DABCO is also far excess, besides, the further reaction can be hard when one end of DABCO is reacted. After the [Am-i-PS]Cl was again swelled for 12 h, 2-bromine ethanol (10 mmol) was added into the system and the reaction solution was refluxed for 24h. The obtained product was [BisAm-OH-i-PS]ClBr, then the catalyst was immersed into saturated NaBr solution at room temperature for 12h to perform ion-exchange. After that, the product was filtered and washed three times with deionized water, diethyl ether and ethyl acetate, then dried at 65 ^oC under vacuum for 12h to get the product of [BisAm-OH-i-PS]Br_2. And the catalysts of [BisAm-COOH-i-PS]Br_2 and [BisAm-NH_2-i-PS]Br_2 were prepared in the same procedure. For the synthesis of catalyst [BisAm-OH-i-PS]I_2, [BisAm-OH-i-PS]ClBr was immersed into saturated NaI solution to perform ion-exchange at nitrogen atmosphere. And for the synthesis of catalyst [BisAm-i-PS]Cl_2, when the catalyst [Am-i-PS]Cl was swelled for 12h, methyl iodide (10 mmol) was added into the system at 40 ^oC to react for 12h, the obtained product was [BisAm-i-PS]ClI, then the catalyst was immersed into saturated NaCl solution to perform ion-exchange to get the product [BisAm-i-PS]Cl_2. Besides, the catalysts [BisAm-i-PS]Br_2 and [BisAm-i-PS]I_2 were prepared in the same way.

The synthesis process and chemical structure of bis-ammonium immobilized polystyrene heterogeneous catalysts are shown in Scheme 1. FT-IR, SEM, XRD and elemental analysis were used to confirm the synthesis of bis-ammonium immobilized polystyrene. The thermal stability of the catalyst was measured by thermo gravimetric analysis (TGA) at a heating rate of 10 ^oC min^{-1} with temperature ranging from 25 ^oC to 600 ^oC under a nitrogen atmosphere.

General procedure for the cycloaddition reaction

The cycloaddition reactions were conducted in a 100 mL high-pressure stainless-steel with magnetic stirring. In the typical reaction procedure, 0.75 mol% (calculated according to the amount of ionic liquid) of the catalyst was added into the reactor, then pressurized to 5 MPa of CO_2 pressure and then released it, after repeating the above steps three times, epoxide (21.5 mmol) was injected in the reactor and we finally pressurized it to the desired pressure at a specified temperature. After reaction, the reactor was chilled to -10 ^oC in low-temperature pump and CO_2 was liberated slowly. The product was segregated from the mixture by paper-filter and analyzed by GC. The products were identified by ^1H NMR with the internal standard of TMS.

^1H NMR data of the cyclic carbonates in Table 2 are as follows:

4-Methyl-1, 3-dioxolan-2-one (Table 2 entry 1). ^1H NMR (500 MHz,

TMS $CDCl_3$): δ= 1.50 (d, CH_3, 3H), 4.05 (t, CH, 1H), 4.57 (t, CH_2, H), 4.88 (m, CH_2, H);
4-Ethyl-1, 3-dioxolan-2-one (Table 2 entry 2). ^{1}H NMR (500 MHz, TMS $CDCl_3$): δ = 0.99 (t, CH_3, 3H), 1.47 (m, CH_2, 2H), 4.10 (dd, CH, 1H), 4.48 (dd, CH_2, H), 4.65(m, CH_2, H);
4-Chloromethyl-1, 3-dioxolan-2-one (Table 2, entry 3). ^{1}H NMR (500 MHz, TMS $CDCl_3$): δ =3.73–3.82 (dd, CH_2, 2H), 4.26 (dd, CH, 1H), 4.63 (dd, CH_2, 1H), 4.95 (m, CH_2, 1H);
4-Phenyl-1, 3-dioxolan-2-one (Table 2, entry 4). ^{1}H NMR (500 MHz, TMS $CDCl_3$): δ = 4.37 (t, CH, 1H), 4.72 (t, CH_2, 1H), 5.83 (t, CH_2, 1H), 7.36–7.48(m, Ar–H, 5H);
4, 5-Tetramethylene-1, 3-dioxolan-2-one (Table 2 entry 5). ^{1}H NMR (500 MHz, TMS CDCl3): δ =1.65–1.72 (m, CH_2, 2H); 1.99–2.08 (m, CH_2, 2H); 2.21-2.27 (m, CH_2, 4H); 4.96 (m, CH, 2H);

Results and discussion

Catalyst characterization

FT-IR spectra of [BisAm-OH-i-PS]Br_2, [BisAm-COOH-i-PS]Br_2, [BisAm-NH_2-i-PS]Br_2 and CMPS are shown in Fig. 1. As seen in Fig. 1(a), a typical peak at 1265 cm^{-1} is the stretching frequency of the functional group –CH_2Cl. It disappears in the spectra of [BisAm-COOH-i-PS]Br_2 (Fig. 1(b)), [BisAm-OH-i-PS]Br_2 (Fig. 1(c)) and [BisAm-NH_2-i-PS]Br_2, that indicates the introduction of functional group DABCO. And in comparison with chloromethylated polystyrene resin, the newly appeared peaks centered at 1460 cm^{-1}, 2920 cm^{-1} are the typical peaks of C-H bonds of DACBO. These results suggest the complete conversion from chloromethyl groups to ammonium groups. In addition, as shown in Fig. 1(b), [BisAm-COOH-i-PS]Br_2 exhibits the characteristic bands of C=O at 1700cm^{-1} and C-O-C at 1220cm^{-1}, and the [BisAm-OH-i-PS]Br_2 displays a typical strong peak corresponding to O-H stretching frequency centered at about 3401 cm^{-1} and C-OH stretching frequency centered at 1052 cm^{-1} in Fig. 1(c). The peak centered at 3441 cm^{-1} corresponds to the antisymmetric amino, which indicated the successfully modified of –NH_2 functional group of the catalyst.[56] Based on these, it is indicated that [BisAm-COOH-i-PS]Br_2 , [BisAm-OH-i-PS]Br_2 and [BisAm-NH_2-i-PS]Br_2 were successfully synthesized.

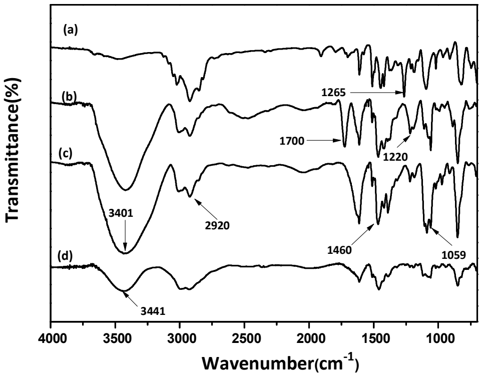


Fig. 1 FT-IR spectra of (a) CMPS, (b) [BisAm-COOH-i-PS]Br_2, (c) [BisAm-OH-i-PS]Br_2 and (d) [BisAm-NH_2-i-PS]Br_2.

The elemental analysis (C, H, and N) as shown in Table 1 was also employed to confirm the introduction of functional groups. The nitrogen contents of the [BisAm-OH-i-PS]Br_2, [BisAm-COOH-i-PS]Br_2 and [BisAm-NH_2-i-PS]Br_2 are lower than [Am-i-PS]Br, but the [BisAm-NH_2-i-PS]Br_2's is higher than [BisAm-OH-i-PS]Br_2 and [BisAm-COOH-i-PS]Br_2, which suggests the successfully modified of functional groups.

The SEM images of the [BisAm-OH-i-PS]Br_2 and CMPS were shown in Fig. 2. The surface of resin is roughened with the grafting of [BisAm-OH]Br_2, which is ascribed to the loss of crystallinity. Fig. S1 (ESI) shows the XRD curves of CMPS and [BisAm-OH-i-PS]Br_2. CMPS exhibits a peak at 2θ = 20.1° ascribed to diffraction at the crystalline region of the polymer structure. With the grafting of functional group, the catalyst [BisAm-OH-i-PS]Br_2 shows a broadened peak centered at 2θ = 22.0°, suggesting an amorphous structure.[55] This phenomenon may be caused by the collapse of regular carrier and also can be an evidence for the successful synthesis of the catalyst. The EDS spectra of [BisAm-OH-i-PS]Cl_2, [BisAm-OH-i-PS]Br_2 and [BisAm-OH-i-PS]I_2 were observed to confirm the successfully progress of ion-exchange.[57] To make sure the accuracy of the test, the measurement area of the catalysts are more than 200*200 μm^2. As shown in Fig. S3 (ESI) The percentage of Cl/Br, Br/Cl and I/Cl are all above 99%.

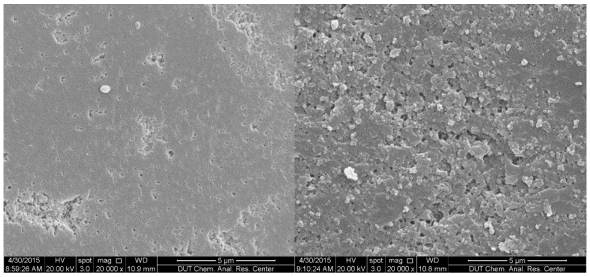


Fig. 2 SEM images of CMPS and [BisAm-OH-i-PS]Br_2.

TGA and DTG curves of [BisAm-OH-i-PS]Br_2 are shown in Fig. 3. [BisAm-OH-i-PS]Br_2 has two weight loss steps characterized by the onset decomposition temperature, T_{OD}, and the fastest decomposition temperature, T_{FD}. The first step (T_{OD}: 215 °C, T_{FD1}: 251 °C) is ascribed to the degradation of the side chain ammonium groups. The second one (T_{FD2}: 307 °C) is attributed to the decomposition of the polystyrene resin. The thermal stability of bis-ammonium immobilized polystyrene heterogeneous catalyst is high enough for the application in the cycloaddition reaction.

Table 1 Elemental analysis (CHN) of catalysts

Entry	Catalyst	C (wt%)	H (wt%)	N (wt%)
1	CMPS	74.06	6.46	0.067
2	[Am-i-PS]Br	70.22	7.90	8.69
3	[BisAm-OH-i-PS]Br_2	51.26	6.66	5.54
4	[BisAm-COOH-i-PS]Br_2	52.9	6.71	5.73
5	[BisAm-NH_2-i-PS]Br_2	59.60	7.27	8.49

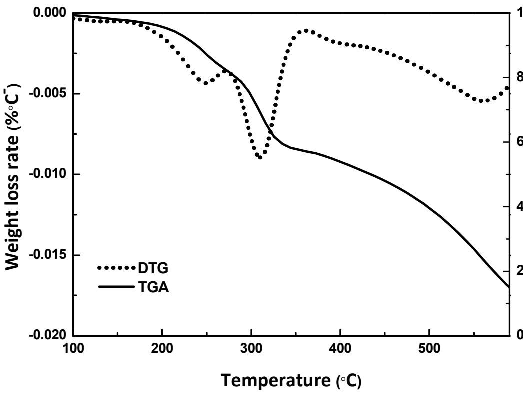


Fig. 3 TGA and DTG curve of [BisAm-OH-i-PS]Br_2.

Catalytic performance

The synthesis of propylene carbonate (PC) from CO_2 and propylene epoxide (PO) according to cycloaddition reaction was chosen as the model to text the catalytic activity of different catalyst systems. All of the reactions were taken under 130 °C, 1.2MPa and 2.5h, and corresponding results were listed in Table 2. As shown in Table 2, CMPS, 2-bromopropane-ethanol and DABCO have poor activities and selectivities for the reaction. All the ammonium immobilized heterogeneous catalysts have high selectivity of above 99%. The two single-ammonium immobilized PS heterogeneous catalysts of [Am-i-PS]Cl and [Am-i-PS]Br show the yields of 40.5% and 60.3%, respectively. It indicates that DABCO-based ammonium could activate CO_2 in the reaction as a kind of organic base and the halide ion can promote the ring-opening reaction of PO. Besides, the catalyst [Am-i-PS]Br which contains bromide ion behaves better than that of [Am-i-PS]Cl, indicating the importance of nucleophilic attack ability of anion. [BisAm-i-PS]Br_2 shows higher yield than [Am-i-PS]Br does. It is because that the ammonium content is two times for [BisAm-i-PS]Br_2 than [Am-i-PS]Br. By using [BisAm-OH-i-PS]Br_2 as the catalyst, the PC yield comes up to 98.7%, which is ascribed to a great promotion of the hydroxyl functional group of [BisAm-OH-i-PS]Br_2 to the ring-opening of epoxide[58]. [BisAm-COOH-i-PS]Br_2 and [BisAm-NH_2-i-PS]Br_2 also exhibit high catalytic activities. It might be because of the hydrogen bonding between these three functioned groups and epoxides. [BisAm-OH-i-PS]Br_2 and [BisAm-COOH-i-PS]Br_2 show similarly high activities. The yield for each of them is above 97%. With different halide anions, the activity order of the catalysts is I+I > Br+Br > Br+Cl > Cl+Cl, which is accordance with the nucleophilicity order of halides. It indicates that the stronger the nucleophilicity is, the easier the attack at the β-carbon atom of epoxide is. All these results suggest that the synergistic effect of polarization caused by hydrogen bonding and the more nucleophilic attacks by the double halide anions accounts for the excellent activity.

Table 2 Catalytic performance of various catalysts[a]

Entry	Catalyst	Catalytic results	
		Yield (%)	Selectivity (%)
1	CMPS[b]	1.7	98.2
2	BrC_2H_4OH[c]	5.3	97.5
3	DABCO[c]	6.1	95.7
4	[Am-i-PS]Cl	40.5	99.5
5	[Am-i-PS]Br	60.3	99.5
6	[BisAm-i-PS]Br_2	71.4	99.2
7	[BisAm-i-PS]I_2	83.8	99.2
8	[BisAm-OH-i-PS]Cl_2	81.6	99.3
9	[BisAm-OH-i-PS]ClBr	92.5	99.2
10	[BisAm-OH-i-PS]Br_2	99.1	99.2
11	[BisAm-OH-i-PS]I_2	99.3	99.3
12	[BisAm-COOH-i-PS]Br_2	99.3	99.3
13	[BisAm-NH_2-i-PS]Br_2	97.3	99.4

[a] Reaction conditions: PO 21.5 mmol, catalyst 0.75 mol%, initial CO_2 pressure 1.2 MPa, Temp. 130 °C, time 2.5 h.

[b] CMPS 0.1 g

[c] Equal catalyst amount (0.75 mol%)

Effect of reaction parameters

Fig. 4 shows the catalytic activity of [BisAm-OH-i-PS]Br_2 as a function of temperature. Apparently, the performance of [BisAm-OH-i-PS]Br_2 is closely bound with temperature. The yield of PC sharply increases from 21.0 to 96.9% when the temperature rises from 90 to 120 °C, and with further rising to 140 °C , there is a slight increase in the yield of PC. However, the selectivity of PC is not correlated with temperature. The selectivity is always above 99% at 90-140 °C. It indicates that this type of ammonium salt has a good selectivity of the cycloaddition reaction.

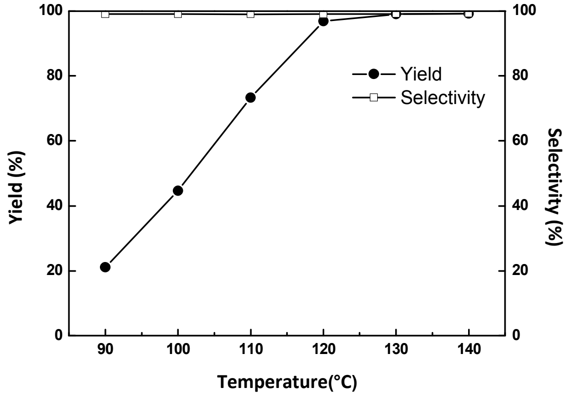


Fig. 4 PC yield and selectivity as a function of reaction temperature. (Reaction conditions: PO 21.5 mmol, [BisAm-OH-i-PS]Br_2 0.75mol%, initial CO_2 pressure 1.2MPa, 2.5 h).

Generally, the CO_2 pressure is one of the significant factors impacting on the cycloaddition reaction[30,41,57,59]. The influence of initial CO_2 pressure was studied under the condition of 130 °C with [BisAm-OH-i-PS]Br_2 as the catalyst and the reaction time of 2.5 h. Fig. 5 shows the PC yield and selectivity as a function of initial pressure. The yield increases from 92.6 to 99% with increasing initial pressure from 0.3 to 1.2 MPa. However, when the initial pressure was further improved from 1.2 MPa to 3.0 MPa, the yield of PC decreases. A possible explanation for this phenomenon is: in the liquid phase of the reaction system, the CO_2 concentration increases with adding initial system pressure, however, too high pressure would reduce the PO concentration around the catalyst, causing a decline of catalytic activity. The selectivity is almost irrelevant to the initial pressure of CO_2.

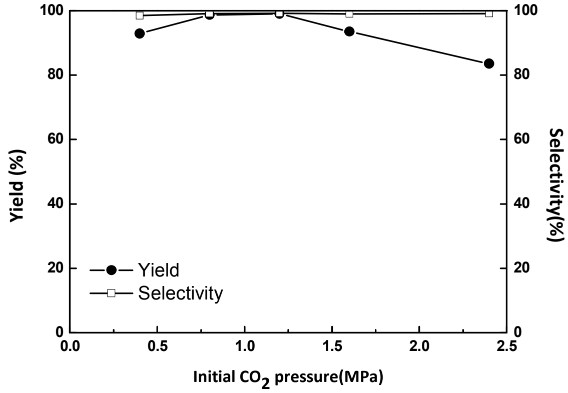


Fig. 5 PC yield and selectivity as a function of reaction pressure.(Reaction conditions: PO 21.5 mmol, [BisAm-OH-i-PS]Br_2 0.75 mol%, 130 °C, 2.5 h).

Fig. 6 represents the influence of reaction time on PC yield and selectivity at 130 °C and initial CO_2 pressure of 1.2 MPa. It is found that the yield increases with reaction time from 0 to 2.5 h, and then there is almost no change in the yield after 2.5 h. It indicates that a reaction time of 2.5 h is required for the complete conversion from PO to PC. The selectivity is always above 99%.

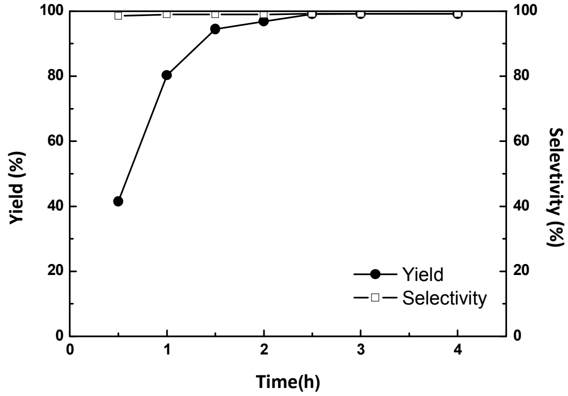


Fig. 6 PC yield and selectivity as a function of reaction time. (Reaction conditions: PO 21.5 mmol, [BisAm-OH-i-PS]Br_2 0.75 mol%, 130 °C, initial CO_2 pressure 1.2 MPa).

Fig. 7 shows the influence of catalyst dosage on the catalytic activity. It was found that the PC yield increased with catalyst dosage from 0.3 mol% to 0.75 mol%, however, there is a slight increase in the yield of PC when the dosage of catalyst is further improved. It is indicated that the catalyst dosage of 0.75 mol% is suitable for the reaction in this condition. Besides, the selectivity of PC is always more than 99%.

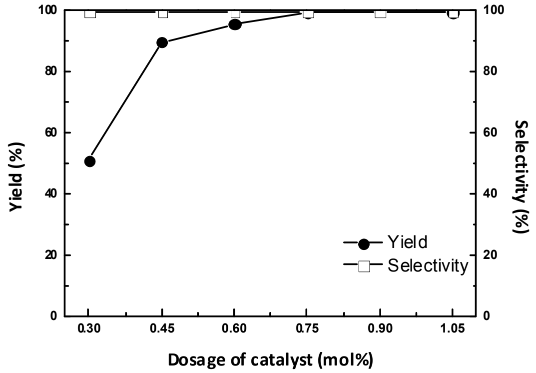


Fig. 7 PC yield and selectivity as a function of reaction dosage of catalyst(Reaction conditions: PO 21.5 mmol, [BisAm-OH-i-PS]Br_2, 130 °C, 2.5 h, and initial CO_2 pressure 1.2 MPa).

Catalyst recovery

With PO as the substrate, the recyclability of [BisAm-OH-i-PS]Br_2 were carried out at 130 °C, initial CO_2 pressure 1.2 MPa for 2.5 h. In each run, the catalyst was recovered by filtration. As shown in Fig. 8, the [BisAm-OH-i-PS]Br_2 catalyst exhibited excellent efficiency for 5 consecutive cycles. Both the yield and selectivity are always above 99%. The results show that the [BisAm-OH-i-PS]Br_2 catalyst is highly stable and very promising for commercial application. Besides, the characterization of FT-IR and TGA were employed as shown in Fig. S4 and Fig. S5 (ESI) to test the [BisAm-OH-i-PS]Br_2 after five times recycle. The recovered catalyst showed the similar character to the fresh one, which also suggests a good reusability of the catalyst [BisAm-OH-i-PS]Br_2.

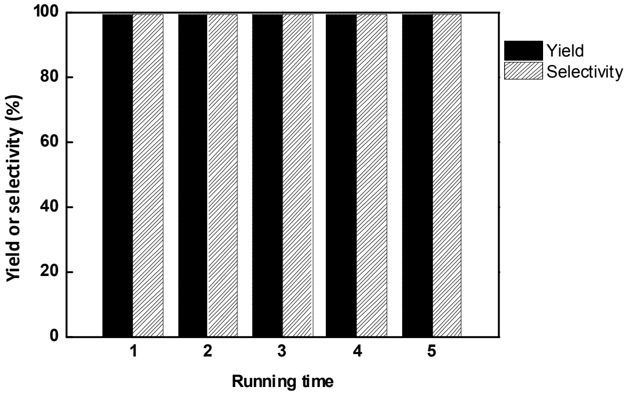
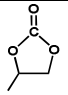
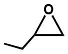
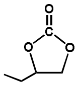
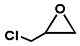
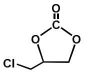
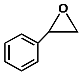
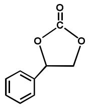
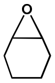
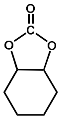


Fig. 8 Recyclability of [BisAm-OH-i-PS]Br_2 catalyst. (Reaction conditions: PO 21.5 mmol, [BisAm-OH-i-PS]Br_2 0.75 mol%, 130 °C, 2.5 h, and initial CO_2 pressure 1.2 MPa).

Catalytic activity towards different epoxides

The catalytic performance of the catalyst [BisAm-OH-i-PS]Br_2 on the cycloaddition of CO_2 with varieties of epoxides were studied, and the results were listed in Table 3. It is found that the catalyst works on diversified terminal epoxides. And the propylene epoxide shows the best reactivity and selectivity. The selectivity order is propylene epoxide = epoxybutane > epichlorohydrin > styrene oxide > cyclohexene. The reactivity order is propylene epoxide > epoxybutane > epichlorohydrin > styrene oxide > cyclohexene. The lower reactivity of styrene oxide and cyclohexene is possibly due to the larger sterically hindered of β-C.

Table 3 Cycloaddition of CO_2 with different epoxides catalyzed by [BisAm-OH-i-PS]Br_2[a]

Entry	Epoxide	Products	t/h	Selectivity (%)	Yield (%)
1			2.5	99.2	99.1
2			2.5	99.2	98.6
3			5	98.8	98.3
4			5	96.1	94.4
5			5	95.2	64.7

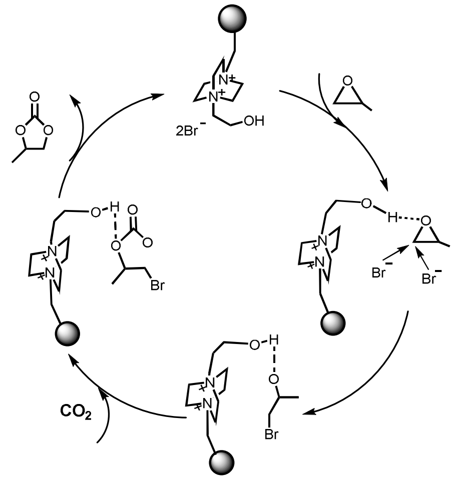
[a] Reaction conditions: PO 21.5 mmol, [BisAm-OH-i-PS]Br_2 0.75 mol%, 130 °C, 2.5 h and initial CO_2 pressure 1.2 MPa

Possible reaction mechanism

As shown in Table 2, the nucleophilic attack of halogen anion on epoxide is essential for the cycloaddition reaction, and the stronger the nucleophilicity is, the easier the attack at the β-carbon atom of epoxide is. On the other hand, the BisAm-i-PS heterogeneous catalysts with functional end groups of $–CH_2COOH$, $–CH_2CH_2OH$, and $–CH_2CH_2NH_2$ show better catalytic activities compared with those without functional groups, which is accordant with the results of other researchers reported[41,55,57,60]. It indicates that these functional groups play an important role in the cycloaddition reaction. According to the present work and the previous literatures[26,30,41,51], a possible mechanism was put forwarded as shown in Scheme 3. The hydrogen bonds between O atom in propylene epoxide and H atom in OH group of the catalyst would give rise to the polarization of C-O bonds. As a result, the PO can be activated to ring-opening. At the same time, halide ions make the nucleophilic attack on β-C of PO which has the minimal steric hindrance. Bis-ammonium immobilized catalysts prepared here have two halide anions, which makes the attack more efficient compared to those with one halide anion. It further promotes the ring-opening reaction of PO. After that, the anion shifts to O atom of PO to attack the C atom of CO_2 to form C-O bond because of the acidity of CO_2. At last, the intermediate is converted into propylene carbonate by the intramolecular substitution of halide anion.

Conclusions

A series of novel BisAm-i-PS heterogeneous catalysts with the functional end groups of –COOH, –OH, and $–NH_2$ were synthesized in the present work for the cycloaddition reaction of CO_2 with epoxides without any additional co-catalyst and organic solvent. The series of functionalized catalysts showed excellent performance under relatively mild conditions, which is ascribed to the nucleophilic attack of halide anion to the epoxide and the synergetic effect of hydrogen bonding formed between functional group and epoxide. Bis-ammonium immobilized catalysts were more efficient than single-ammonium one did because of the doubled nucleophilic anion concentration in one unit function group. The effects of parameters, such as halide anions of the catalysts, reaction temperature, initial pressure, reaction time and dosage of catalyst were also investigated with –OH ended BisAm-i-PS as the catalyst. BisAm-i-PS with Br^- anion I^- anion showed higher efficiency than those with Cl^-. Under an optimal reaction condition (1.2 MPa, 130 °C and 2.5 h), propylene carbonate selectivity and yield were above 99% and 99%, respectively. In addition, the catalyst possessed good stability for 5 times recycle tests, which is in conformity with the development of green chemistry and can be used as a potential catalyst for large-scale production of cyclic carbonates.



Scheme 3 Proposed mechanism for the cycloaddition reaction.

Acknowledgements

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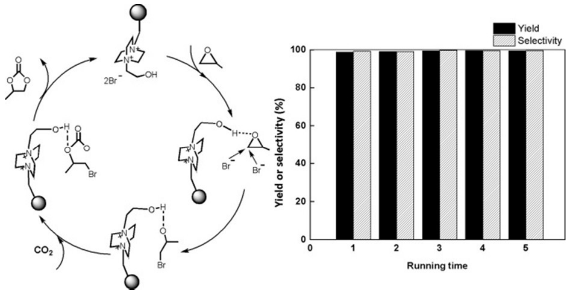

Novel bis-ammonium immobilized polystyrenes with co-catalyzing functional groups were prepared for efficient synthesis of cyclic carbonate from CO_2 and epoxides.