Polymer-supported Zinc Tetrahalide Catalysts for the Coupling Reactions of CO_2 and Epoxides[+]

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Homogeneous zinc tetrahalide complexes, highly active catalysts for the coupling reactions of alkylene oxide and CO_2 produce alkylene carbonates, were heterogenized due to their tendency to decompose produced alkylene carbonates during the distillation process. Heterogenization of homogeneous zinc tetrahalide complexes was achieved by polymerizing 1-alkyl-3-vinylimidazolium zinc tetrahalides. These polymerized zinc tetrahalide catalysts displayed similar activities to their corresponding monomeric analogues for the coupling reactions of carbon dioxide with ethylene oxide (EO) or propylene oxide (PO) to produce ethylene carbonate (EC) or propylene carbonate (PC). TGA studies showed that the polymer-supported zinc tetrahalide catalysts are thermally stable up to 320 °C. The catalyst recycle test showed that the supported catalysts could be reused over six times. After removal of the polymer-supported catalyst through a simple filtration, EC was able to be isolated without decomposition.

Key Words : Ionic liquids, Zinc tetrahalide, Ethylene carbonate, Propylene carbonate, Polymer-supported

Introduction

The syntheses of 5-membered cyclic carbonates by the coupling reactions of epoxides with carbon dioxide has received much attention due to the increasing demand for cyclic carbonates in a wide variety of applications including electrolytes of the secondary batteries, valuable monomers of polycarbonates and polyurethanes, aprotic polar solvents, and reactants for many chemical reactions.[1-4,23]

Accordingly, much effort has been devoted to the development of high performance catalysts and catalytic systems for the coupling reactions and, as a result, significant advances have been achieved. The catalytic systems composed of transition metal halides ($AlCl_3$, $NiCl_2$, $MoCl_5$, etc.) and Lewis bases such as amines or phosphines, and organometallic complexes have been successfully employed in the selective formation of cyclic carbonates under relatively mild condition.[5-12] Zinc(II) complexes have also been used as catalysts, owing to their high activity in the cyclization and copolymerization of CO_2 and epoxides.[13-17]

Recently, we have reported that homogeneous imidazolium zinc tetrahalide complexes, prepared from the reactions of zinc halides with imidazolium halides, exhibit surprisingly high activities in the coupling reactions of CO_2 with ethylene oxide (EO) or propylene oxide (PO) to produce ethylene carbonate (EC) or propylene carbonate (PC).[18,19]

A major obstacle in the commercial use of these homogeneous catalytic systems is that they tend to decompose EC and PC during the distillation of the product mixture in the presence of an ionic liquid-based zinc tetrahalides, as described in the previous report.[20] For this reason, homogeneous imidazolium zinc tetrahalide complexes were heterogenized by the immobilization of ZnX_4^{2-} (X = Cl, Br) on to imidazolium-based polymers. As was the case of other supported ionic liquid phase (SILP) catalysts,[21] it is hoped that the immobilized ZnX_4^{2-} could provide easy catalyst separation, thereby avoiding the decomposition alkylene carbonate.

In this paper, we describe the syntheses of polymer-supported zinc tetrahalide catalysts and their catalytic activities for the coupling reactions of CO_2 with EO or PO.

Experimental Section

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled before use according to literature procedures.[22] EO was purchased from Honam Petrochemical Co. and was used as received. CO_2 was purchased from Sin Yang Gas. Other chemicals were purchased from Aldrich Chemical Co. and were used without further purification, unless otherwise stated. 1-Ethyl-3-vinylimidazolium bromide ([EVIm]Br), 1-ethyl-3-vinylimidazolium chloride ([EVIm]Cl), 1-butyl-3-vinylimidazolium bromide ([BVIm]Br), 1,3-dimethylimidazolium zinc tetrahalide ([DMIm]_2ZnBr_2Cl_2), 1-ethyl-3-methylimidazolium zinc tetrahalide ([EMIm]_2-ZnBr_2Cl_2), and 1-butyl-3-methylimidazolium zinc tetrahalide ([BMIm]_2ZnBr_2Cl_2) were prepared according to a modified literature procedure.[19] ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer. Thermogravimetric analysis (TGA) was performed using a TGA-50 (Shimadzu) in a nitrogen atmosphere between 25 and 600 °C at a heating rate of 10 °C min^{-1}.

Synthesis of (1-ethyl-3-vinylimidazolium)$_2$ZnBr$_2$Cl$_2$ ([EVIm]$_2$ZnCl$_2$Br$_2$). A solution of [EVIm]Br (2.50 g, 12.38

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mmol) in CH_2Cl_2 (25 mL) was mixed with a solution of $ZnCl_2$ (0.84 g, 6.19 mmol) in THF (25 mL) and the resulting mixture was heated at reflux for 10 h. After cooling to room temperature, the white precipitate was collected by filtration. Yield: 91.2%; elemental analysis, calcd. (%) for $C_{14}H_{22}Br_2$-Cl_2N_4Zn: C 31.00, H 4.09, N 10.33; found: C 29.85, H 4.21, N 10.15; ^{1}H NMR (300 MHz, D_2O, 25 °C): $\delta = 1.54$ (t, 3H, -CH_3), 4.30 (q, 2H, -CH_2-), 5.43, 5.81 (dd, dd, 1H, 1H, -CH_2), 7.15 (dd, 1H, -CH), 7.60, 7.77, 9.05 (s, s, s, 1H, 1H, 1H, $C_3H_3N_2$).

Other imidazolium zinc tetrahalides were prepared in an analogous manner to [EVIm]$_2$ZnBr$_2$Cl$_2$.

Polymerization of [EVIm]₂ZnBr₂Cl₂. Poly(1-ethyl-3-vinylimidazolium zinc tetrahalide) (p([EVIm]₂ZnBr₂Cl₂)) was prepared as follows: In 100 mL one-neck flask, [EVIm]₂ZnCl₂Br₂ (2.71 g, 5 mmol) and AIBN as a radical polymerization initiator (1 wt.%) were dissolved in 20 mL benzene and then stirred at 60 °C for 1 d. After the reaction, white precipitates were collected, washed with methanol, and then dried under vacuum to give p([EVIm]₂ZnBr₂Cl₂) as a white powder (Yield: 96.7%; elemental analysis, calcd. (%) for $C_{14}H_{22}Br_2Cl_2N_4Zn$: C 31.00, H 4.09, N 10.33; found: C 30.85, H 4.17, N 10.21).

Other poly(1-R-3-vinylimidazolium zinc tetrahalide) complexes were prepared in an analogous manner to that employed in the synthesis of p([EVIm]₂ZnBr₂Cl₂): p([EVIm]₂ZnBr₄) (Yield: 97.8%; elemental analysis, calcd. (%) for $C_{14}H_{22}Br_4N_4Zn$: C 26.63, H 3.51, N 8.87; found: C 25.95, H 3.77, N 8.52); P([EVIm]₂ZnCl₄) (Yield: 95.9%; elemental analysis, calcd. (%) for $C_{14}H_{22}Cl_4N_4Zn$: C 37.07, H 4.89, N 12.35; found: C 36.82, H 5.0, N 11.99); poly(1-butyl-3-vinylimidazolium zinc tetrahalide) (p([BVIm]₂-ZnBr₂Cl₂)) (Yield: 95.2%; elemental analysis, calcd. (%) for $C_{18}H_{30}Br_2Cl_2N_4Zn$: C 36.12, H 5.05, N 9.36; found C 34.95, H 5.21, N 9.02).

Coupling reactions of epoxides and CO_2: All of the coupling reactions were conducted in a 200 mL stainless-steel bomb reactor equipped with a magnetic bar and an electric heater. The reactor was charged with desired amounts of catalyst, EO or PO, and EC or PC as the solvent. The reactor was pressurized with CO_2 (*ca.* 4.34 MPa) and then heated to a specified reaction temperature, then CO_2 was added from a reservoir tank to maintain constant pressure. After the completion of the reaction, the bomb was cooled to room temperature and the product mixture was analyzed using a GC-MS (HP 6890-5973 MSD) and a gas chromatograph (Hewlett-Packard 6890), equipped with a

flame-ionization detector and an FFAP capillary column (30 m × 0.32 mm × 0.25 mm).

Decomposition test: Decomposition tests were performed in a 100 mL stainless-steel bomb reactor equipped with a Teflon-coated magnetic bar, an electric heater, a thermocouple, and a steel condenser. The steel condenser on the lid of the reactor was attached to a digital pressure gauge, which is connected directly to a high-vacuum pump. The bomb was charged with an appropriate catalyst and EC or PC and then heated to a specified temperature. At the desired temperature, the reactor was evacuated to reduce the pressure to 0.2 mmHg by means of the vacuum pump. The degree of EC decomposition was monitored by the pressure increase during 5 min at the temperature.

Recycling experiment: The reactor was charged with p([EVIm]₂ZnBr₂Cl₂) (0.50 g, 0.92 mmol) as the catalyst, PO (20.0 g, 344.35 mmol) and EC or PC as the solvent. The reaction was carried out at 100 °C and 4.34 MPa. After the reaction, the product mixture was analyzed using GC and the catalyst was recovered by a simple filtration for further uses. The same procedure was repeated for next 5 cycles with a fresh charge of PO (20.0 g, 344.35 mmol).

Results and Discussion

Poly(1-R-3-vinylimidazolium zinc tetrahalide) complexes were initially obtained by reacting ZnX_2 (X = Cl, Br) with poly(1-R-3-vinylimidazolium)Y (R = methyl, butyl, and Y = Cl, Br, respectively) at ambient or reflux temperatures, depending on the nature of the halide groups (see Scheme 1). However, some difficulty were encountered in separating product from reactants due to the low yields of poly(1-R-3-vinylimidazolium zinc tetrahalide) complexes. As an alternative method, direct polymerization of 1-R-3-vinylimidazolium zinc tetrahalide was attempted. As shown in Scheme 2, p([EVIm]₂ZnBr₂Cl₂) was prepared in high yield

R = C_2H_5 or C_4H_9
X, Y = Cl or Br
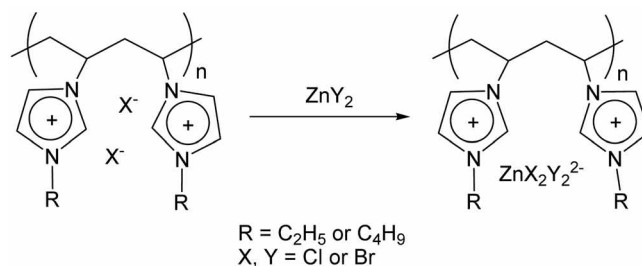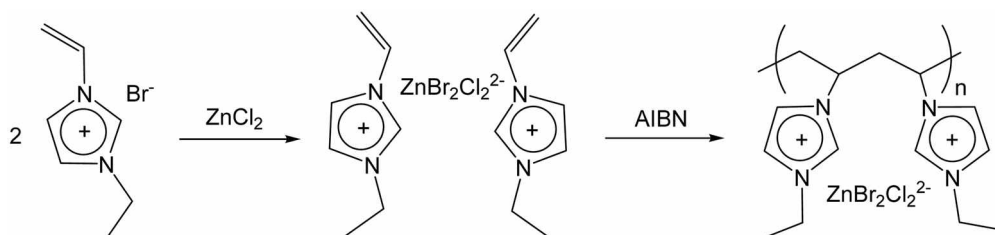
Scheme 1

Scheme 2
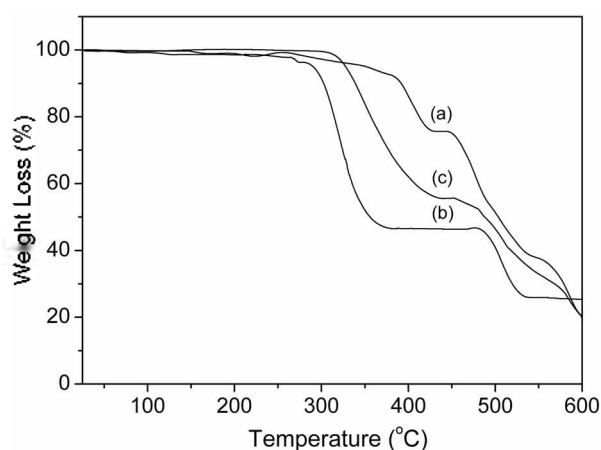
Figure 1. TGA data of (a) [EVIm]$_2$ZnBr$_2$Cl$_2$, (b) p([EVIm]Br), and (c) p([EVIm]$_2$ZnBr$_2$Cl$_2$).

over 95% by polymerizing corresponding monomer, [EVIm]$_2$ZnBr$_2$Cl$_2$ in the presence of AIBN.

To support the formation of polymeric zinc tetrahalide, thermogravimetric analysis (TGA) experiments were conducted and compared the thermal stability of p([EVIm]$_2$-ZnBr$_2$Cl$_2$) with those of [EVIm]$_2$ZnBr$_2$Cl$_2$ and p([EVIm]Br). As can be seen in Figure 1, p([EVIm]$_2$ZnX$_2$Y$_2$) exhibits completely different thermal behavior from the corresponding monomer, [EVIm]$_2$ZnBr$_2$Cl$_2$, and p([EVIm]Br), indirectly supporting the formation of polymerized zinc tetrahalide. The decomposition of p([EVIm]$_2$ZnBr$_2$Cl$_2$) starts from 320 °C, whereas p([EVIm]Br) and [EVIm]$_2$ZnBr$_2$Cl$_2$ start decomposition at lower temperature of 280 and 255 °C, respectively.

The catalytic activities of polymeric zinc tetrahalide complexes were evaluated in the coupling reactions of CO$_2$ with EO or PO to produce EC or PC. The reactions were conducted at 100 °C for 1 h and the molar ratio of EO to

Table 1. Catalytic activities of monomeric and polymeric imidazolium zinc tetrahalide for the coupling reactions of CO$_2$ and epoxides[a]

Catalyst	Weight of Catalyst (g)	EC Yield (%)	EC TOF (h^{-1})[b]	PC Yield (%)	PC TOF (h^{-1})[b]
[DMIm]$_2$ZnBr$_2$Cl$_2$	2.45	90.5	679	89.3	670
[EMIm]$_2$ZnBr$_2$Cl$_2$	2.59	92.8	696	92.1	691
[BMIm]$_2$ZnBr$_2$Cl$_2$	2.87	94.4	708	91.8	689
[EVIm]$_2$ZnBr$_2$Cl$_2$	2.71	89.2	669	89.3	670
[EVIm]$_2$ZnBr$_4$	3.16	99.2	744	98.3	737
[EVIm]$_2$ZnCl$_4$	2.27	33.2	249	25.0	188
[BVIm]$_2$ZnBr$_2$Cl$_2$	2.99	91.4	686	90.5	679
p([EVIm]Br)	2.03	2.6	20	2.2	17
p([BVIm]Cl)	1.87	2.1	16	1.8	14
p([EVIm]$_2$ZnBr$_2$Cl$_2$)	2.72	86.2	647	84.4	633
p([EVIm]$_2$ZnBr$_4$)	3.17	97.0	728	95.2	714
p([EVIm]$_2$ZnCl$_4$)	2.25	22.6	169	21.1	158
p([BVIm]$_2$ZnBr$_2$Cl$_2$)	3.01	90.3	677	89.5	671

[a]Reactions were carried out at 100 °C and 4.14 MPa of CO$_2$ for 1 h. The number of moles of Zn and epoxide were set at 5 and 3750 mmol, respectively. [b]TOF (h^{-1}): moles of alkylene carbonate/moles of catalyst/h.

catalyst was set to 750. As Table 1 indicates, all the poly(1-R-3-vinylimidazolium zinc tetrahalide) complexes showed similar activities to their corresponding monomeric analogues, implying that the catalytic activity of homogeneous monomeric zinc tetrahalide can be retained even after the polymerization.

Like monomeric imidazolium zinc tetrahalides, the catalytic activities of polymeric imidazolium zinc tetrahalides were greatly influenced by the nature of halide ligands bonded to zinc atom. The reactivity was found to be in the following order: [ZnBr$_4$]$^{2-}$ > [ZnBr$_2$Cl$_2$]$^{2-}$ >> [ZnCl$_4$]$^{2-}$, suggesting the importance of the nucleophilicity of halide ligands. The dissociation of a halide ion from the imidazolium zinc tetrahalide and the following attack of the halide ion on the carbon atom of an epoxide would take place more easily with more nucleophilic bromide ion. In contrast, the substitution on imidazolium cations was found to have a negligible effect on the catalytic activity.

As can be seen in Table 2, the effects of temperature and pressure were also investigated with p([EVIm]$_2$ZnBr$_2$Cl$_2$). The TOF (h^{-1}) increased steeply with increasing temperature from 80 to 140 °C for both ethylene oxide and propylene oxide. On the contrary, the increase in TOF (h^{-1}) was moderate when the pressure was change from 1.0 to 5.0 MPa.

To test the catalyst stability and reusability, the coupling reaction of propylene oxide and CO$_2$ was performed with p([EVIm]$_2$ZnBr$_2$Cl$_2$) for 1 h at 100 °C and 4.14 MPa. After the reaction, the liquid product mixture was separated by filtration and the recovered catalyst was reused for further reactions with a fresh charge of PO and CO$_2$. As shown in Table 3, the catalyst retained most of its initial activity even after six runs, suggesting that the polymeric zinc tetrahalide catalysts could be recyclable.

As already mentioned, EC tends to decompose into EO and CO$_2$ when the distillation of the product mixture containing EC was conducted in the presence of a homogeneous monomeric imidazolium zinc tetrahalide under a reduced pressure. Such decomposition, in principle, can be prevented by performing the coupling reaction in the presence of a heterogeneous catalyst. However, there is a

Table 2. Effect of temperature and pressure of CO$_2$ for the coupling reactions of CO$_2$ and epoxides catalyzed by p([EVIm]$_2$ZnBr$_2$Cl$_2$)[a]

Temperature (°C)	Pressure of CO$_2$ (MPa)	TOF (h^{-1})[b] EC	TOF (h^{-1})[b] PC
80	4.14	308	294
90	4.14	421	385
100	1.38	622	613
100	2.76	646	631
100	4.14	647	633
100	4.83	650	635
110	4.14	701	681
120	4.14	750	737

[a]Reactions were carried out at various temperatures and pressures of CO$_2$ for 1 h. The number of moles of Zn and epoxide were set at 5 and 3750 mmol, respectively. [b]TOF (h^{-1}): moles of alkylene carbonate/moles of catalyst/h.

Table 3. Catalyst recycling studies with p([EVIm]₂ZnBr₂Cl₂)[a]

Number of recycle	PC yield (%)	TOF (h⁻¹)[b]
1	84.4	633
2	84.1	631
3	84.3	632
4	83.6	627
5	83.5	626
6	81.4	611
7	79.7	598

[a]Reactions were carried out at 100 °C and 4.14 MPa of CO_2 for 1 h. The number of moles of Zn and epoxide were set at 5 and 3750 mmol, respectively. [b]TOF (h⁻¹): moles of alkylene carbonate/moles of catalyst/h.
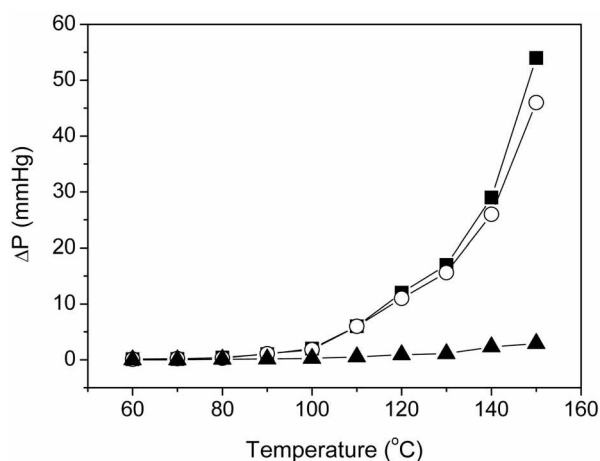

Figure 2. Effect of catalyst concentration on the EC decomposition. (■) 0.1 wt.% [EVIm]₂ZnBr₂Cl₂, (○) 0.1 wt.% p([EVIm]₂ZnBr₂Cl₂), (▲) after separation of p([EVIm]₂ZnBr₂Cl₂).

possibility that a certain amount of heterogeneous catalyst could dissolve in the organic phase even after the catalyst separation, which might cause EC decomposition during the distillation process. For this reason, ICP-Mass analysis was conducted with the remaining organic phase after the catalyst separation from the product mixture of the coupling reaction of EO and CO_2 performed at 100 °C in the presence of a polymeric zinc tetrahalide, p([EVIm]₂ZnBr₂Cl₂), but no appreciable amount of catalytic zinc species was detected in the organic phase. The absence of the catalytic zinc species in the organic phase is further supported by the decomposition test conducted under the reduced pressure of 0.2 mmHg in the temperature range 60-150 °C. Figure 2 shows the trend of EC decomposition with the temperature rise. As shown in Figure 2, almost no decomposition of EC was observed in the absence of a catalyst even at 150 °C. In contrast, a significant amount of EC decomposed into EO and CO_2 in the presence of 0.1 wt.% of [EVIm]₂ZnBr₂Cl₂ and p([EVIm]₂ZnBr₂Cl₂). These results implies that [EVIm]₂ZnBr₂Cl₂ and p([EVIm]₂ZnBr₂Cl₂) are also an effective catalyst for the EC decomposition. As expected, EC was isolated without any noticeable decomposition through a distillation from the product mixture after the separation of p([EVIm]₂ZnBr₂Cl₂).

Conclusions

Polymer-supported zinc tetrahalide complexes were obtained in high yield from the direct polymerization of 1-R-3-vinylimidazolium zinc tetrahalide. These polymerized zinc tetrahalide catalysts exhibited similar catalytic activities to their monomeric analogues in the cycloaddition of CO_2 to EO or PO to produce EC or PC. A significant EC decomposition was observed during the distillation of the product mixture containing a monomeric or polymeric zinc tetrahalide catalyst at high temperature under a reduced pressure. Such decomposition was successfully avoided by employing an easily separable polymeric zinc tetrahalide catalyst in the coupling reaction. The catalyst recycle test with p([EVIm]₂ZnBr₂Cl₂) showed that the polymer-supported catalyst, could be reused up to seven times without a significant loss of its initial activity.

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