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RESEARCH NOTE

Well-Defined Highly Active Heterogeneous Catalyst System for the Coupling Reactions of Carbon Dioxide and Epoxides

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The poly(4-vinylpyridine)-supported zinc halide catalysts, prepared from a reaction of ZnX_2 and poly(4-vinylpyridine), exhibit high selectivity and activity for the coupling reaction of CO_2 and ethylene oxide or propylene oxide. Solid NMR characterization of the poly(4-vinylpyridine)-supported $ZnBr_2$ catalyst and its reaction product with propylene oxide and/or CO_2 show that a pyridinium-alkoxy ion-bridged zinc bromide complex is functioning as an active species, such as in the homogeneous catalysis with L_2ZnBr_2 (L = pyridine or methyl-substituted pyridine). © 2002 Elsevier Science

Key Words: **epoxide; carbon dioxide; heterogeneous catalyst; cyclic carbonate; zinc complex.**

INTRODUCTION

As a potential pathway for the effective utilization of carbon dioxide, the synthesis of alkylene carbonates via coupling reactions of carbon dioxide and epoxides has attracted much interest, because cyclic carbonates can be used in many application areas as solvents and valuable raw materials (1–4).

Substantial literature on the catalyst development and the reaction mechanism for the coupling reactions has been reported, but most of the research is devoted to homogeneous catalyst systems (5, 6). Despite the significant progress in homogeneous catalysis, the demand for a heterogeneous catalyst system is still high for easy catalyst separation.

Recently, we have reported that the homogeneous catalyst of the formula L_2ZnX_2 (L = pyridine or substituted pyridine, X = Cl, Br, I) and its reaction product with epoxide $[ZnX_2(\mu\text{-OCHRCH}_2L)]_n$ (R = H, $n = 3$; R = CH_3, $n = 2$) are highly active for the coupling reactions of CO_2 with ethylene oxide (EO) or propylene oxide (PO) to produce corresponding alkylene carbonate, ethylene carbonate (EC), or propylene carbonate (PC) (7).

To have a better catalyst separation and an improved thermal stability of the homogeneous catalyst L_2ZnX_2, we have immobilized ZnX_2 onto poly(4-vinylpyridine) (PVP) to prepare polymer-supported catalysts, $(PVP)ZnX_2$ (X = Cl, Br, I).

In this paper, we report on the synthesis, reactivity, and characterization of the polymer-supported catalyst, $(PVP)ZnX_2$. The reaction pathway for the formation of alkylene carbonates along with the characterization of active intermediate species are also discussed on the basis of experimental and spectroscopic results from both homogeneous and heterogeneous catalysis.

METHODS

$(PVP)ZnBr_2$ complex was prepared by reacting PVP (MW = 60,000 or 25% crosslinked) (1.76 g, 16.7 mmol, pyridine base) in 70 ml methanol with $ZnBr_2$ (1.89 g, 8.6 mmol) in 20 ml methanol at a reflux temperature for 1 h. The product was filtered and dried under vacuum. Elemental analysis shows that each zinc center is coordinated by two repeating units of PVP, such as in its homogeneous analogue, L_2ZnX_2 [elemental analysis results of the $(PVP)ZnBr_2$ complex (wt%): C 38.7, H 3.52, N 5.93, Zn 13.7].

All the coupling reactions were conducted in a 100-ml stainless-steel bomb reactor equipped with a magnet bar and an electrical heater. The reactor was charged with an appropriate catalyst and an epoxide and pressurized with CO_2 (≈1.4 MPa). The bomb was then heated to 100°C with the addition of CO_2 from a reservoir tank to maintain the pressure at 3.4 MPa. After the reaction, the bomb was cooled to room temperature, and the remaining epoxide was removed. The product mixtures were analyzed by gas chromatography (GC), gas chromatography–mass spectroscopy (GC–Mass), and gel permeation

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TABLE 1

Catalytic Activities of Various Catalysts for the Coupling Reactions of CO_2 and Epoxides[a]

		Yield (%)		TOF[b] (h^{-1})	
Entry	Catalysts	EC	PC	EC	PC
1	PVP	—[c]	—[c]	—[c]	—[c]
2	$ZnBr_2$	—[c]	—[c]	—[c]	—[c]
3	$(Pyridine)_2ZnBr_2$	96.7	26.7	580	120
4	$(PVP)ZnCl_2$	8.5	2.5	51	11
5[d]	$(PVP)ZnBr_2$	53.1	8	320	36
6[e]	$(PVP^*)ZnBr_2$	32.5	6	195	27
7	$(PVP)ZnI_2$	62.0	10.5	372	68
8[f]	Dowex MSA-1	1.4	0.3	—	—
9	IRA-900	1.4	0.1	—	—

[a] Reactions were carried out at 100°C and 3.5 MPa CO_2 for 1 h. Molar ratios of epoxide to zinc were maintained at EO/Zn = 600 and PO/Zn = 400, respectively.

[b] TOF, moles of alkylene carbonate produced per mole of zinc per hour.

[c] No reaction.

[d] Weight of $(PVP)ZnBr_2$ = 0.29 g (Zn = 13.7 wt%).

[e] Weight of $(PVP^*)ZnBr_2$ = 0.41 g (Zn = 9.7 wt%). PVP*, 25% crosslinked poly(4-vinylpyridine).

[f] Weight of ion-exchange resin = weight of $(PVP)ZnX_2$.

TABLE 2

Catalyst Recycle Studies with Crosslinked PVP-Supported $ZnBr_2$ Catalyst[a]

Number of recycle	EC yield (%)	EC selectivity[b] (%)	TOF[c] (h^{-1})	Weight of Zn dissolved[d] (g)
1	33.1	99.8	201	1.5×10^{-5}
2	34.2	99.5	211	1.2×10^{-5}
3	35.4	100.0	207	1.3×10^{-5}
4	34.8	99.7	213	1.3×10^{-5}
5	35.1	99.6	199	1.4×10^{-5}
6	33.9	100.0	217	1.1×10^{-5}
7	34.7	99.8	208	1.2×10^{-5}

[a] In all cycles, reactions were carried out at 100°C, 3.5 MPa CO_2, and EO/Zn = 600 for 1 h. Weight of crosslinked PVP-supported $ZnBr_2$ (Zn = 9.7 wt%) used in the first cycle was 0.43 g.

[b] The selectivity to ethylene carbonate was obtained by GC analysis using an internal standard, propylene carbonate.

[c] TOF, moles of alkylene carbonate produced per mole of zinc per hour.

[d] Total amounts of zinc dissolved into solution after each cycle.

chromatography (GPC). The catalysts and intermediate zinc species were characterized by elemental analysis, solid-state ^1H and ^{13}C NMR, and thermogravimetric analysis/differential scanning calorimetry (TGA/DSC).

RESULTS AND DISCUSSION

The activities of various catalysts were tested for the coupling reactions of carbon dioxide with EO or PO to produce EC or PC. Table 1 shows that the polymer-supported catalysts, $(PVP)ZnX_2$, exhibit much higher activities than the conventional ion-exchange resins.

Neither $ZnBr_2$ nor PVP is able to catalyze the coupling reaction, demonstrating a drastic synergy effect between the zinc center and the PVP ligands. The linear PVP-supported $ZnBr_2$ shows higher activity than the crosslinked PVP-supported $ZnBr_2$. This is probably due to the difference in accessibility of epoxide substrates to zinc centers in the polymer matrix: the interaction of epoxides to active zinc centers in the less crowded linear PVP-supported $ZnBr_2$ would be easier than that in the crosslinked PVP-supported $ZnBr_2$.

A series of catalytic cycles were run to investigate the constancy of the catalyst activity and reusability. In each cycle, the catalyst was separated by filtration, washed with methanol, and then dried under vacuum before use for the next experiment. The results listed in Table 2 show that the

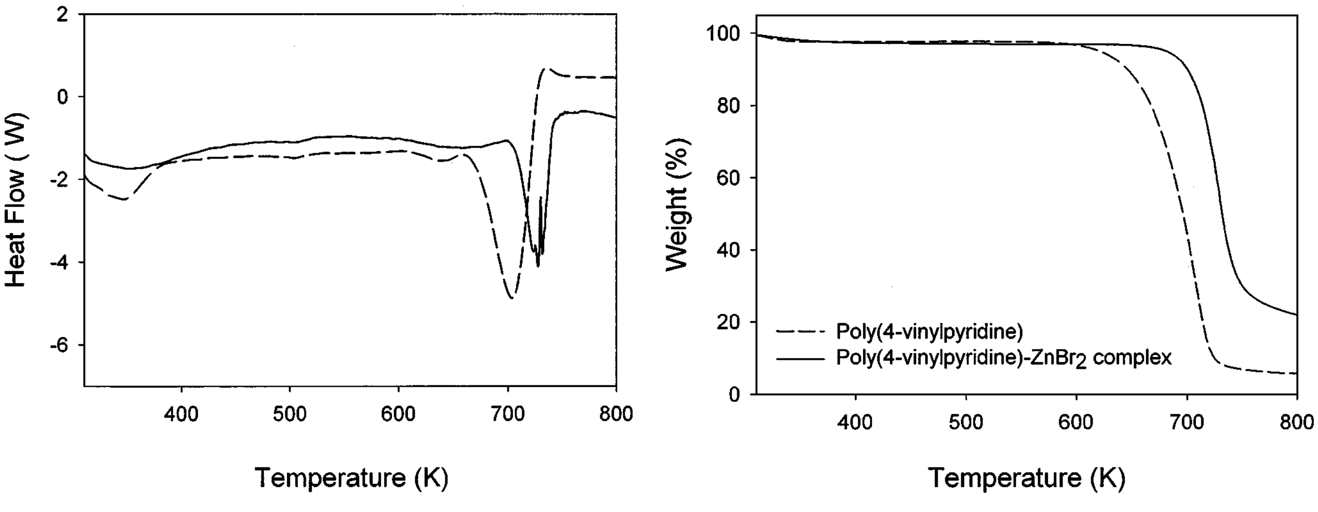


FIG. 1. TGA/DSC results for PVP* and $(PVP^*)ZnBr_2$ complexes.

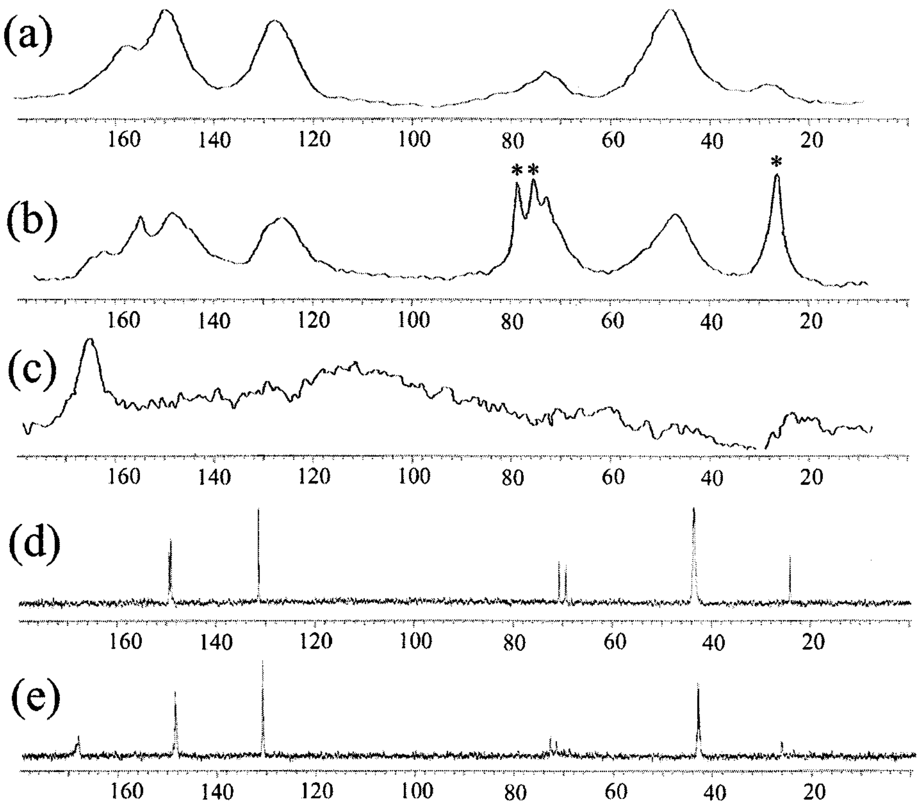
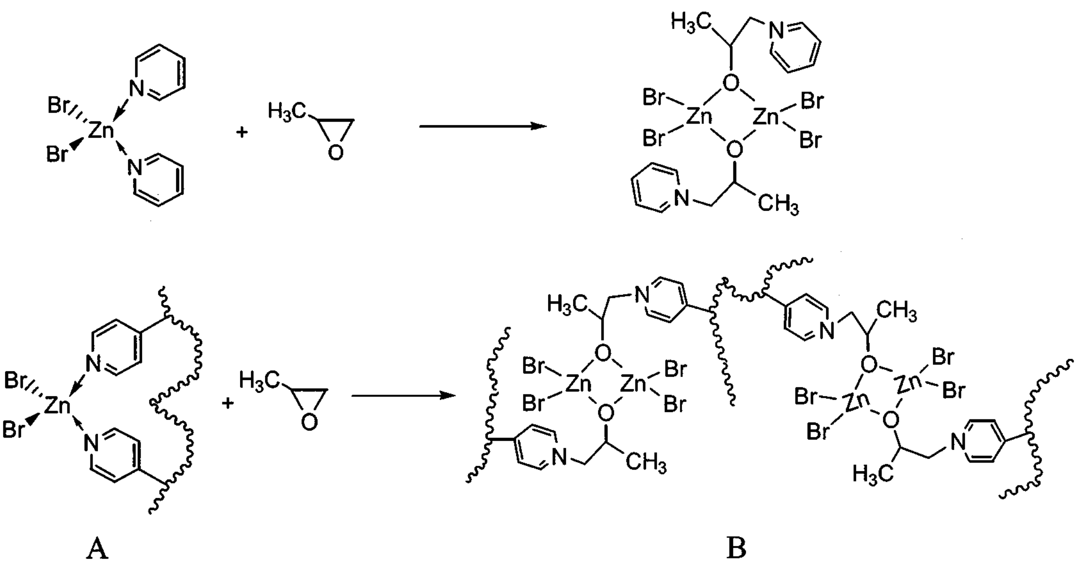
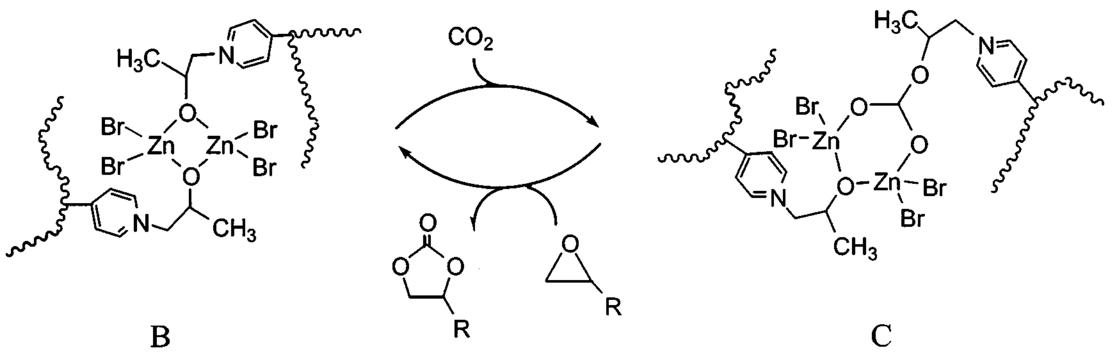


FIG. 2. CP/MAS solid-state ^{13}C NMR spectra. (a) (PVP)$ZnBr_2$ complex. (b) Reaction product of the (PVP)$ZnBr_2$ complex with propylene oxide (*, propylene oxide moiety). (c) After the reaction of (b) with $^{13}CO_2$. (d) ^{13}C solution NMR spectrum of $Zn_2Br_4(\mu\text{-}OCHCH_3CH_2NC_5H_5)_2$ in DMSO-d_6. (e) ^{13}C solution NMR spectrum of the reaction product of $Zn_2Br_4(\mu\text{-}OCHCH_3CH_2NC_5H_5)_2$ with $^{13}CO_2$ in DMSO-d_6.

crosslinked PVP-supported $ZnBr_2$ catalyst can be reusable for at least up to seven times without loss of activity and selectivity. The selectivity to ethylene carbonate was as high as 100%, but the formation of trace amounts of polymeric materials such as polyethylene oxide or polyethylene carbonate cannot be ruled out even though they were not detected by GPC. Zinc analysis of the solution by atomic absorption spectroscopy after each catalytic cycle reveals that



SCHEME 1



SCHEME 2

practically no leaching of zinc species to the solution occurs during the reaction.

As can be expected, the activities of the PVP-supported $ZnBr_2$ catalyst are lower than those of their homogeneous analogue, $(pyridine)_2ZnBr_2$.

TGA/DSC data in Fig. 1 clearly show the difference in thermal behavior between PVP and its complex with $ZnBr_2$. The crosslinked PVP-supported $ZnBr_2$ decomposes in a more complicated way at a little higher temperature than uncomplexed PVP, supporting the strong coordination of PVP to $ZnBr_2$.

To have a better insight into a mechanistic aspect of the coupling reaction in the presence of the polymer-supported catalyst, various NMR experiments were conducted with $(PVP)ZnBr_2$ [PVP = linear poly(4-vinylpyridine)], and the results were compared to those of its homogeneous analogue, $(C_5H_5N)ZnB_2$. Figure 2a is the ^{13}C CP/MAS solid NMR spectrum of $(PVP)ZnBr_2$, and Fig. 2b is the ^{13}C CP/MAS NMR spectrum of the product obtained from the reaction of $(PVP)ZnBr_2$ with propylene oxide in CH_2Cl_2 at 80°C for 2 h. The appearance of a new set of resonances at 75, 71, and 20 ppm is in good agreement with that of $Zn_2Br_4(\mu\text{-}OCHCH_3CH_2NC_5H_5)_2$ in Fig. 2d, strongly indicating the formation of a new complex containing propylene oxide moiety. From the comparison of chemical shift in Figs. 2b and 2d, the newly formed complex is believed to have the structure with two bridging pyridinium-propoxy ligands per zinc ion, similar to that of the known complex, $Zn_2Br_4(\mu\text{-}OCHCH_3CH_2NC_5H_5)_2$, as shown in Scheme 1.

The same complex has also been isolated from the coupling reaction of propylene oxide and CO_2 performed in the presence of $(PVP)ZnBr_2$ at 100°C for 1 h, suggesting that the pyridinium-propoxy ion-bridged zinc species is an active species in this catalysis.

The insertion of $^{13}CO_2$ into the metal–oxygen bond of the supported μ-alkoxy zinc species (B in Scheme 1) was also investigated by ^{13}C CP/MAS NMR spectroscopy. Complex B species was reacted with ^{13}C-enriched CO_2 in dimethyl sulfoxide at room temperature for 3 h. The solvent was removed by filtration, and the resulting solid was dried under vacuum. To obtain an improved signal-to-noise ratio (S/N) for the carbonate carbon, the data were taken with single pulse and MAS without proton decoupling. As shown in Fig. 2c, the ^{13}C CP/MAS NMR spectrum of the solid shows a characteristic carbonate resonance centered at 168 ppm, confirming the formation of zinc carbonate species (C as shown in Scheme 2). The carbonate resonance at 168 ppm has been observed in the ^{13}C solution NMR spectrum of the product obtained from the interaction of $Zn_2Br_4(\mu\text{-}OCHCH_3CH_2NC_5H_5)_2$ with $^{13}CO_2$ (Fig. 2e).

From these and previously reported homogeneous catalysis results with L_2ZnX_2, it is concluded that pyridinium-alkoxy ion-bridged zinc complexes are playing an important role as active species in both homogeneous and heterogeneous coupling reactions of epoxide with CO_2 as 1shown in Scheme 2.

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