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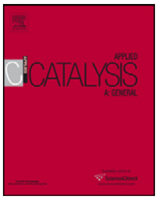

$ZnBr_2$–Ph_4PI as highly efficient catalyst for cyclic carbonates synthesis from terminal epoxides and carbon dioxide

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A B S T R A C T

The catalyst systems composed of $ZnBr_2$ and different phosphonium salts were examined for solvent-free synthesis of cyclic carbonates from CO_2 and terminal epoxides under mild conditions. Among the catalysts investigated, $ZnBr_2$–Ph_4PI was found to be the best while those of $ZnBr_2$–phosphine oxide (Bu_3PO or Ph_3PO) show no catalytic effect. It is apparent that the halide ions of phosphonium salts have an essential role to play in the reaction. The catalytic activity of $ZnBr_2$–Ph_4PI increases with a rise of Ph_4PI to $ZnBr_2$ molar ratio up to 6, above which there is little change in catalytic activity. We observed that with a rise in $ZnBr_2$ to Ph_4PI molar ratio, there is increase in epoxide conversion but decline in TOF_{PO} (estimated based on the site number of Zn^{2+}). The effect of water on the reaction was investigated for the first time. We found that the presence of even a trace amount of water would result in a marked decline in reactivity, and the observation provides a valid explanation for why reproducibility of results is poor among researchers so far. The influences of other parameters such as reaction temperature and CO_2 pressure on the catalytic performance of $ZnBr_2$–PPh_4I were also studied. It is shown that the catalyst is sensitive to reaction temperature, and a rise of reaction temperature up to 130 °C favors the formation of cyclic carbonates. We observed that activity increases with rise in CO_2 pressure and reaches a maximum at an initial CO_2 pressure of 2.5 MPa. Moreover, a plausible reaction mechanism has been proposed.

1. Introduction

Carbon dioxide is nontoxic, abundant, inexpensive, nonflammable, and highly functional, and much attention has been paid to its use as an environmentally benign chemical reagent, especially as a phosgene substitute [1]. Of the most interesting is to couple CO_2 with high-energy epoxides for the generation of cyclic carbonates. Five- and six-membered cyclic carbonates are excellent aprotic polar solvents and used extensively as intermediates in the production of fine chemicals, engineering plastics, and pharmaceuticals [1]. A wide range of catalysts have been explored for the generation of cyclic carbonates, including alkali metal salts [2,3], metal oxides [4–6], zeolites [7,8], smectites [9,10], polyoxometalate [11,12], organotin or organoantimony compounds [13,14], ionic liquids or onium salts [15–31], transition metal complexes [32–44], and so on.

There is a recent development of synthesizing cyclic carbonate by means of bi-component catalysts (e.g., onium salt and metal halide) [19,20,24–31,33,34,43,44]. It seems that the catalysts containing Zn^{2+} ions are the most attractive for CO_2 coupling with epoxides [6,11,21–30,35–41]. The catalytic performances of the Zn-containing catalysts are affected by the anion and/or ligand bonding to the Zn^{2+} centers or co-catalysts. For example, Kim et al. [21] reported that imidazolium zinc tetrahalides, $(1\text{-R-3-methylimidazolium})_2ZnX_2Y_2$ (R = CH_3, C_2H_5, n-C_4H_9, $CH_2C_6H_5$; X = Cl, Br; Y = Cl, Br) showed high activities for coupling CO_2 with ethylene oxide or propylene oxide (PO). The catalytic activity was found to be in the order of $[ZnBr_4]^{2-} > [ZnBr_2Cl_2]^{2-} \gg [ZnCl_4]^{2-}$. Li et al. [22] investigated the ZnX_2/[BMIm]Br (X = Cl, Br, OAc) system for chemical fixation of CO_2 with mono-substituted terminal epoxides or cyclohexene oxide. They observed that $ZnBr_2$ was better than $ZnCl_2$ or $Zn(OAc)_2$, and $ZnBr_2$/[BMIm]Br achieved excellent selectivity of 98% and TOF of 5580 h^{-1} using PO as substrate under mild reaction conditions of 100 °C and CO_2 pressure 1.5 MPa. They deduced that the activation of the epoxy ring was efficiently done via the formation of a zinc 1-butyl-3-methylimidazolium complex through $ZnCl_2$ coordination with the 2-H of imidazolium ring. Interestingly, Xie et al. [28] developed a hexabutylguanidi-

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nium salt/zinc bromide binary catalyst of high efficiency for the coupling of CO_2 and epoxides. Recently, Sun et al. [29] investigated an efficient Lewis acid/Lewis base catalyst composed of $ZnCl_2$ and phosphonium halides ($[PR_1R_2R_3R_4]^+X^-$; X = Cl, Br, I), and obtained PO conversion of 98.0% and high TOF value (4718.4 h^{-1}) in the presence of $ZnCl_2/PPh_3C_6H_{13}Br$ (molar ratio = 1:6) at low CO_2 pressure (1.5 MPa) and mild temperature (120 °C) without any organic solvents. Based on the survey, it is apparent that a combination of $ZnBr_2$ and a phosphonium salt is potentially a good catalyst. To the best of our knowledge, there has been no report on catalysts of this kind for the coupling of CO_2 and PO. In this study, selected combinations of $ZnBr_2$ and phosphonium salts were examined for CO_2 coupling with terminal epoxides. In order to illustrate the uniqueness of $ZnBr_2$, the catalytic performances of catalysts composed of a range of zinc salts and PPh_4I were also examined. We conducted a systematic investigation on the effects of temperature, CO_2 pressure, and water on the target reaction. Finally, a plausible reaction mechanism has been proposed.

2. Experimental

2.1. Chemicals

The reagents and chemicals (analytic grade unless otherwise stated) were purchased from Aldrich Chemical Co., and were used without further purification except that the epoxides were dried by distillation over CaH_2. The CO_2 (99.99% purity) purchased from Changsha Gas Co. were dehydrated by 4A molecular sieve in a high-pressure stainless-steel tube prior to use. All the weighing and handling procedures were conducted in a glove box under an atmosphere of dry argon.

2.2. Coupling reactions

The coupling reactions were carried out in 150 ml high-pressure stainless-steel autoclaves equipped with a magnetic bar and an electrical heater. In a typical reaction, the reactor was charged with appropriate amount of catalyst, epoxide, and biphenyl (as internal standard substance for GC analysis). After the reactor was pressurized with CO_2 to a desired pressure, the reaction mixture was heated to a designated temperature and stirred at *ca.* 800 rpm for 1 h. Then the reactor was cooled to 0 °C in an ice-water bath, and the remaining CO_2 was released using an aspirator and absorbed in a saturated solution of K_2CO_3. The resulting product mixture was defined by GC–mass spectrometry on a Hewlett Packard 6890-5973 MSD GC–MS and by ^1H NMR on a Bruck400 superconductive nuclear magnetic resonance spectrometer with TMS as internal standard. All the products were quantitatively analyzed by a Hewlett Packard 6890 gas chromatography equipped with a flame-ionized detector and Rtx-WAX capillary column (30 m × 0.25 mm × 0.25 μm).

3. Results and discussion

3.1. Catalytic performance

In order to evaluate the catalytic performance of $ZnBr_2$ and phosphonium salts, PO was first used as a model substrate to fix CO_2. One can see from Table 1 that $ZnBr_2$ by itself has no catalytic activity, and with Ph_4PI alone, propylene carbonate (PC) yield is very low. Despite the $ZnBr_2 + Ph_3PO$ and $ZnBr_2 + Bu_3PO$ catalysts show no activity, the $ZnBr_2$ + phosphonium halides show high activity. It is clear that the halide ions are essential for the coupling reaction, and one can see that catalytic activity is dependent on the kind of halide present. For catalyst system $ZnBr_2 + Ph_4PX$, PO conversion increases in the order of $Ph_4PI > Ph_4PBr \gg Ph_4PCl$, consistent with the increasing order of halide nucleophilicity. The phenomenon is similar to that of the $ZnCl_2 + PPh_3C_6H_{13}X$ (X = Cl, Br, I) system reported by Sun et al. [29]. Compared to Cl^-, Br^-, and I^- are larger in ion radius and lower in electronegativity. In other words, the Br^- and I^- ions are located further away from a nearby cation and show stronger nucleophilicity. We find that catalytic activity is also affected by the kind of phosphonium cation adopted. Taking phosphonium bromide as an example, catalytic activity decreased in the order of $Ph_4 > Ph_3C_2H_4OC_3H_5 > Ph_3C_6H_{13} > Bu_4$. We used $ZnBr_2$ + KI as a reference catalyst for the coupling reaction (entry 11), and detected very low catalytic activity. The result demonstrated that it is important to have the phosphonium cation for the reaction. These results may be explained in terms of the fact that the bulky tetrahedral phosphonium ion forces the halide ions away from the cation, and the less electrostatic interaction would render the anions more nucleophilic.

Table 1
Catalytic performance of catalysts[a]

Entry	Catalytic system	Reaction results[b]		
		X_{PO} (%)	S_{PC} (%)	TOF (h^{-1})
1	$ZnBr_2$	0	0	0
2	Ph_4PI	8.4	97.2	-
3	$ZnBr_2 + Ph_4PCl$	48.4	>99.0	3388
4	$ZnBr_2 + Ph_4PBr$	82.4	>99.0	5768
5	$ZnBr_2 + Ph_4PI$	89.6	>99.0	6272
6	$ZnBr_2 + Ph_3C_6H_{13}PBr$	77.4	>99.0	5418
7	$ZnBr_2 + Ph_3(C_2H_4OC_3H_7)PBr$	80.5	>99.0	5635
8	$ZnBr_2 + {}^nBu_4PBr$	56.6	>99.0	3962
9	$ZnBr_2 + Ph_3PO$	0	0	
10	$ZnBr_2 + Bu_3PO$	0	0	
11	$ZnBr_2$ + KI	6.5	94.0	455
12	$ZnCl_2 + Ph_4PI$	83.4	>99.0	5838
13	$ZnI_2 + Ph_4PI$	88.3	>99.0	6181
14	$ZnSO_4 + Ph_4PI$	49.7	>99.0	3479
15	$ZnO + Ph_4PI$	9.7	>99.0	679
16[c]	$ZnBr_2 + Ph_4PI + Ph_3P$	78.7	>99.0	5509
17[d]	$ZnBr_2 + Ph_4PI + Ph_3P$	72.3	>99.0	5061

[a] Reaction conditions: PO 105 mmol, $ZnBr_2$ 0.015 mmol, P salt 0.09 mmol, initial CO_2 pressure 2.5 MPa, 1 h, and 120 °C.

[b] X_{PO}: PO conversion; S_{PC}: PC selectivity; TOF: moles of PO converted per mole of Zn^{2+} per hour.

[c] PPh_3 to $ZnBr_2$ molar ratio of 1:1.

[d] PPh_3 to $ZnBr_2$ molar ratio of 2:1.

As shown in Table 1, the "PPh_4I + different zinc salts" catalysts are effective for the formation of PC, and there is variation in activity depending on the kind of Zn salts employed. The "$ZnBr_2 + PPh_4I$" (entry 5) and "$ZnI_2 + PPh_4I$" (entry 13) catalysts show similar performances which are significantly higher than those of "$ZnCl_2 + PPh_4I$" (entry 12), "$ZnSO_4 + PPh_4I$" (entry 14), and "$ZnO + PPh_4I$" (entry 15). Recently, Xiao et al. [27] investigated a binary catalyst of Zn salts and immobilized ionic liquid and observed that the activities of anions in Zn salts decreased in the order of $Br^- > Cl^- > OAc^- > SO_4^{2-}$. Kim et al. [21] found that the catalytic activity of (1-butyl-3-methylimidazolium)Cl or (1-butyl-3-methylimidazolium)Br for the coupling reaction of CO_2 and ethylene oxide or PO can be enhanced by adding $ZnBr_2$ or $ZnCl_2$, and the former is better than the latter for such a purpose. Also, Sun et al. [23] reported that $ZnBr_2$ is much better than ZnI_2 or ZnO when 1-butyl-3-methylimidazolium chloride was used for the coupling of styrene oxide and CO_2. Therefore, it seems that a proper combination of Zn salts with a co-catalyst is needed for enhancing the coupling reaction. In terms of cost and thermal stability, $ZnBr_2$ has advantages over ZnI_2. We hence consider that $ZnBr_2$–PPh_4I is