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## A mini review on chemical fixation of CO<sub>2</sub>: absorption and catalytic conversion into cyclic carbonates

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**Abstract** In this article, we present our research results on chemical fixation of CO<sub>2</sub> using organobismuth compounds. We fabricated bismuth biphenolate complex, Zn-Mg-Al composite oxides, and SBA-15 or Al-SBA-15 immobilized hydroxyl ionic liquid for CO<sub>2</sub> cycloaddition onto epoxides. The hypervalent bismuth compounds show good ability for association and dissociation with CO<sub>2</sub>. The bismuth biphenolate complexes are catalytically effective for the cycloaddition reaction. The heterogeneous catalysts, viz. Zn-Mg-Al oxides and SBA-15 or Al-SBA-15 immobilized ionic liquid, are efficient for the synthesis of cyclic carbonate from CO<sub>2</sub> and epoxide. It is found that the presence of a trace amount of water can improve the catalytic activity of the immobilized ionic liquid.

**Keywords** Carbon dioxide, Organobismuth, Cyclic carbonate, Zn-Mg-Al oxides, Hydroxyl ionic liquid

### 1 Introduction

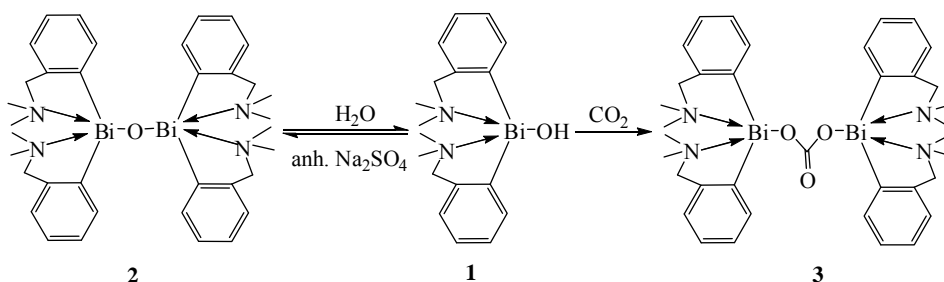
In the past decades, chemical fixation of CO<sub>2</sub> has attracted much attention [1-4]. In terms of “atom economy”, “green chemistry”, and “sustainable development”, CO<sub>2</sub> is a good C1 feedstock. The production of cyclic carbonates through the cycloaddition of CO<sub>2</sub> onto terminal epoxides (e.g., propylene oxide (PO) and ethylene oxide) has been commercialized. On the other hand, CO<sub>2</sub> is a greenhouse gas. It is worth pointing out that the transformation reactions using CO<sub>2</sub> as a raw material do not help mitigate global warming. The reasons are: (i) The energy consumed during CO<sub>2</sub> conversion produces large amount of CO<sub>2</sub>; (ii) The amount of CO<sub>2</sub> fixed by chemical reactions would be much smaller than the amount of CO<sub>2</sub> emitted in fuel combustion; and (iii) Organic chemicals in which CO<sub>2</sub> is fixed will emit CO<sub>2</sub> at the end [3]. It appears that the capture of CO<sub>2</sub> at source (e.g. at the power plants using coal as fuel) is a better strategy as far as the mitigation of greenhouse effect is concerned. Nevertheless, the fixation of CO<sub>2</sub> to a suitable substrate for the synthesis of valuable chemicals is of significance.

Bismuth is known to be nontoxic and noncarcinogenic, and bismuth compounds have been studied because of their versatile roles (such as reaction reagents, oxidizing agent, catalysts, medicine, etc.) [5-

8]. In the past decade, there has been a rapid development on bismuth chemistry [9-17]. There are various researches on novel cationic organobismuth complexes and their applications [16-23]. In this review article, representative results of organobismuth complexes as adsorbent for CO<sub>2</sub> capture and as catalysts for cycloaddition of CO<sub>2</sub> to epoxide are presented. Furthermore, the efficient syntheses of cyclic carbonates from CO<sub>2</sub> and epoxide directly over heterogeneous catalysts (e.g., Zn-Mg-Al composite oxides and SBA-15 functionalized with hydroxyl ionic liquid) are also described.

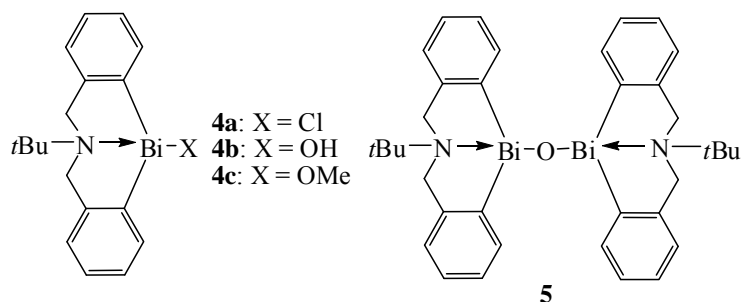
## 2 Organobismuth complexes for CO<sub>2</sub> capture

A number of metal (e.g., Ni, Rh, Ir, Fe, Cu, Re, and Co) complexes are known to react with CO<sub>2</sub> and are used to remove CO<sub>2</sub> from industrial emissions; they are also tested as catalyst for the transformation of CO<sub>2</sub> [24-27]. Further application of these materials, however, is limited because under mild conditions none of them show good ability for association as well as dissociation with CO<sub>2</sub>. Despite inorganic Bi<sub>2</sub>O<sub>3</sub> is known to react with CO<sub>2</sub> [28, 29], the use of bismuth compounds containing Bi-O bonds for CO<sub>2</sub> fixation has not been reported until very recently. Breunig et al. [30] reported that exposure of a diethyl ether or toluene solution of hypervalent diarylbismuth hydroxide [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiOH **1** as well as that of the corresponding oxide [{2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Bi]<sub>2</sub>O **2** to air could lead to CO<sub>2</sub> adsorption and the formation of carbonate [{2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Bi]<sub>2</sub>CO<sub>3</sub> **3** (Scheme 1). However, the authors did not mention whether carbonate **3** could transfer back to hydroxide **1** or oxide **2** or not.

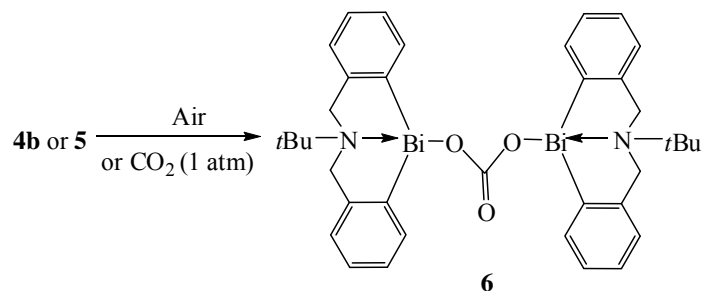


**Scheme 1** Adsorption of CO<sub>2</sub> by **1** or **2**. After Ref. [30].

The synthesis of organobismuth compounds **4a**, **4b**, **4c** and **5** (Scheme 2) of 5,6,7,12-tetrahydrodibenz [c,f]-[1,5]azabismocine framework were reported by Yin et al. [16]. The bismuth oxide **5** can be obtained by treating bismuth chloride **4a** with aqueous sodium hydroxide. Analogous to the result of Breunig et al. [30], bismuth hydroxide **4b** readily loses water to form oxide **5**. In turn, oxide **5** can be completely converted back to hydroxide **4b** by adding water to it. When a toluene solution of oxide **5** was vigorously stirred in air at room temperature for 4.5 h, **5** was quantitatively converted to bismuth carbonate **6** (Scheme 3). Also, when an anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution of **5** was exposed to CO<sub>2</sub> (1 atm), quantitative amount of **6** was obtained readily. Furthermore, carbonate **6** was obtained by using hydroxide **4b** instead of oxide **5**. It is noted that carbonate **6** is thermally rather stable, and in CH<sub>2</sub>Cl<sub>2</sub> or under vacuum at room temperature, there was no decomposition of carbonate **6**. Partial dissociation of carbonate **6** (ca. 30%) and quantitative regeneration of oxide **5** was observed when **6** was heated under vacuum at 100 °C for 10 h. For effective utilization of compounds **4b** and **5**, it is critical for them to show good association as well as good dissociation ability with CO<sub>2</sub>. Since it is possible to regenerate compounds **4b** and **5** after CO<sub>2</sub> adsorption, the two are potential candidates for CO<sub>2</sub> capture.

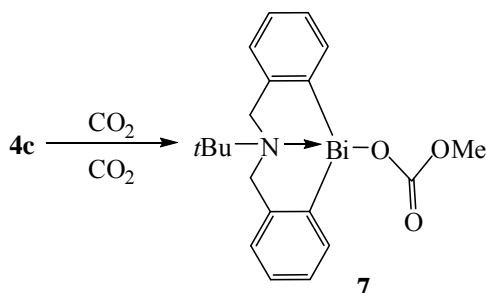


**Scheme 2** Structure of **4** and **5**. After Ref. [16].



**Scheme 3** Adsorption of CO<sub>2</sub> by **4b** or **5**. After Ref. [16].

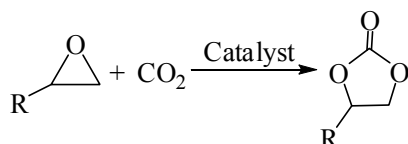
It is observed that bismuth methoxide **4c** in methanol, CH<sub>2</sub>Cl<sub>2</sub>, or toluene readily reacts with dry CO<sub>2</sub> (1 atm) to form bismuth methyl carbonate **7**, and the process is reversible (Scheme 4). Because methoxide **4c** is sensitive to water, it undergoes hydrolysis and subsequent reaction with CO<sub>2</sub> to form a mixture of **4b**, **5**, and **6** in air. In an analogous manner, diorganobismuth oxide {(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>Bi}<sub>2</sub>O [31] was also found to show association ability with CO<sub>2</sub> by Yin et al. The results suggest that the compound reacts reversibly with CO<sub>2</sub>, and the resulting carbonate is less stable than **6**. The authors regarded that the stability of compound **6** is ascribable to its hypervalent structure.



**Scheme 4** Adsorption of CO<sub>2</sub> by **4c**. After Ref. [16].

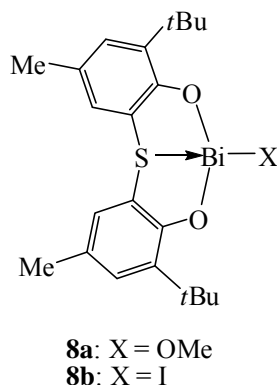
### 3 Bismuth biphenolate complexes for the cycloaddition of CO<sub>2</sub> onto propylene oxide

Cyclic carbonates (e.g., propylene carbonate (PC)), are valuable organic compounds that can be used as polar solvents, electrolytes in lithium secondary batteries, precursors for synthesizing polycarbonates and polyurethanes, and as raw materials in a wide range of chemical reactions [1-4]. The synthesis of cyclic carbonates through cycloaddition of CO<sub>2</sub> to epoxides is one of the few commercial routes that use CO<sub>2</sub> as a raw material (Scheme 5). In the past decades, a number of homogeneous and heterogeneous catalysts have been developed for the cycloaddition reaction, such as phosphines [32-34], organic bases [35-37], ionic liquids [1, 38-43], organometallic complexes [44-58], metal oxides [59-64], modified zeolites and smectites [65-69], and supported catalysts [70-77]. There are reports on organometallic complexes of Cr, Co, Ni, Al, Mn, Zn, Ru, Re, etc. of various types (salen- [44-52], porphyrin- [53-55] or others [56-58]) as homogeneous catalysts for cycloaddition, but the use of bismuth compounds for the target reaction is uncommon. There is only one paper reporting that catalytic activity over Ph<sub>3</sub>BiBr<sub>2</sub> was very low [78].



**Scheme 5** Cycloaddition of epoxide to CO<sub>2</sub>.

Based on the organobismuth compounds **4b**, **4c**, and **5**, Yin et al. synthesized two novel bismuth compounds **8a** and **8b** bearing 2,2'-thiobis(phenolato) ligands (Scheme 6) [23]. In contrast to most of the reported catalysts which require severe reaction conditions (e.g., high temperature, high CO<sub>2</sub> pressure, and high catalyst concentration), organobismuth compounds **8a** and **8b** show high catalytic activity and selectivity (100%) for the cycloaddition of CO<sub>2</sub> to PO at room temperature and 1 atm CO<sub>2</sub> pressure in the presence of a co-catalyst. From Table 1, one can see that **8b** shows slightly higher catalytic activity than **8a**, and **8b** and LiI exhibit excellent catalytic activity (PC yield = 98%). Although organobismuth compounds **4b**, **4c** and **5** show certain association ability with CO<sub>2</sub>, they show no catalytic activity for the cycloaddition reaction. The high efficiency of **8a** and **8b** may be ascribed to the hypervalent structure of the two compounds. Also, the Lewis acidity of the bismuth atom can be adjusted through the intermolecular coordination of sulfur atom to bismuth atom, consequently facilitating the exchange of product and reactant.



**Scheme 6** Structure of **8**. After Ref. [23].

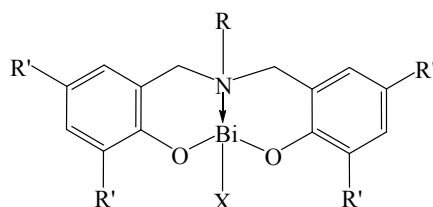
**Table 1** PC synthesis from PO and CO<sub>2</sub> catalyzed by **10** or **11**/iodide catalyst system<sup>a)</sup> [Ref. 23]

entry	catalyst	conversion (%)	PC yield (%)
1	<b>8a</b>	0	0
2	<b>8b</b>	0	0
3	Me <sub>3</sub> PhPI	0	0
4	<b>8b</b> + Me <sub>3</sub> PhPI	76	76
5	Bu <sub>4</sub> NI	0	0
6	<b>8b</b> + Bu <sub>4</sub> NI	77	77
7	NaI	14	14
8	<b>8b</b> + NaI	91	91
9	LiI	26	26
10	<b>8a</b> + LiI	92	92
11	<b>8b</b> + LiI	98	98

a) Reaction conditions: PO 23 mmol, catalyst 0.028 mmol, co-catalyst 0.112 mmol, temperature room temp., CO<sub>2</sub> pressure 1 atm, time 24 h.

Another kind of novel bismuth compounds bearing a nitrogen-bridged bis(phenolato) ligand were also synthesized and used as catalysts for the synthesis of PC from PO and CO<sub>2</sub> (Scheme 7) [21]. Under mild conditions in the presence of NaI as co-catalyst, the bismuth biphenolate complexes show high catalytic activity and selectivity (> 99%) for synthesizing PC via cycloaddition of CO<sub>2</sub> onto PO (Table 2). It is noted that **9a** shows much higher catalytic activity than chloride **10a** and **11a** in the

absence of NaI (Table 2, entries 1-3), but exhibits lower catalytic activity in the presence of NaI (Table 2, entries 4-6). When the chlorine atom is replaced by iodine, almost quantitative PC yield is obtained in 1 h over the iodide **9b**, **10b** and **11b** (Table 2, entries 7-9). The other two iodides **12a** and **12b** also show good catalytic activity in the presence of NaI (Table 2, entries 10-11). The methoxides **9c**, **10c**, **11c**, **12b** and **13b** show lower catalytic activity than the corresponding iodides (Table 2, entries 12-16). The high catalytic performance of iodides may be attributed to the high nucleophilicity of iodine atom. Furthermore, side chain group R' has higher effect on catalytic activity than group R.



- 9a:** R = Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = Cl  
**9b:** R = Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = I  
**9c:** R = Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = OMe  
**10a:** R = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = Cl  
**10b:** R = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = I  
**10c:** R = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = OMe  
**11a:** R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = Cl  
**11b:** R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = I  
**11c:** R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, R' = *t*-Bu, X = OMe  
**12a:** R = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = CH<sub>3</sub>, X = I  
**12b:** R = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = CH<sub>3</sub>, X = OMe  
**13a:** R = Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = CH<sub>3</sub>, X = I  
**13b:** R = Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, R' = CH<sub>3</sub>, X = OMe

**Scheme 7** Structure of **9-13**. After Ref. [21].

**Table 2** PC synthesis from PO and CO<sub>2</sub> catalyzed by **9-13**/sodium iodide catalyst system<sup>a)</sup> [Ref. 21]

entry	catalyst	Bi : PO : NaI <sup>b)</sup>	time/h	Yield/%
1	<b>9a</b>	1 : 100 : —	2	50.7
2	<b>10a</b>	1 : 100 : —	2	6.0
3	<b>11a</b>	1 : 100 : —	2	5.7
4	<b>9a</b>	1 : 1000 : 2	2	76.7
5	<b>10a</b>	1 : 1000 : 2	2	96.0
6	<b>11a</b>	1 : 1000 : 2	2	95.8
7	<b>9b</b>	1 : 1000 : 2	1	96.6
8	<b>10b</b>	1 : 1000 : 2	1	95.9
9	<b>11b</b>	1 : 1000 : 2	1	95.8
10	<b>12a</b>	1 : 1000 : 2	1	87.1
11	<b>13a</b>	1 : 1000 : 2	1	87.0
12	<b>9c</b>	1 : 1000 : 2	2	90.3
13	<b>10c</b>	1 : 1000 : 2	2	91.2
14	<b>11c</b>	1 : 1000 : 2	2	98.6
15	<b>12b</b>	1 : 1000 : 2	2	83.1
16	<b>13b</b>	1 : 1000 : 2	2	93.2

<sup>a)</sup> Reaction conditions: PO 28.6 mmol, temperature 120 °C, CO<sub>2</sub> pressure 2.5 MPa; <sup>b)</sup> The molar ratio of organobismuth complex : PO : NaI.

#### 4 Zn-Mg-Al composite oxides for the cycloaddition of CO<sub>2</sub> onto propylene oxide

Bhanage et al. [59] used metal oxides (e.g., MgO, CaO, ZrO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and La<sub>2</sub>O<sub>3</sub>) as catalysts for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides in the presence of *N,N*-dimethylformamide (DMF). However, the activity and selectivity over the metal oxides are

unsatisfactory. Yamaguchi et al. [62] reported that Mg-Al oxide prepared from Mg-Al hydrotalcite could be used as catalyst for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides. However, the selectivity to cyclic carbonates was not good enough. Furthermore, high catalyst concentration and large amount of co-catalyst and DMF (as solvent) were indispensable in the reaction.

It was reported that Zn-containing catalysts showed high efficiency for the cycloaddition reaction, and Zn<sup>2+</sup> was regarded essential for epoxide activation [79-81]. Yin et al. prepared alkaline earth metal (i.e. Mg, Ca, Sr, and Ba)-modified Zn-Al composite oxides via calcination of the corresponding hydrotalcite precursors, and observed good catalytic activity and selectivity for the synthesis of PC from PO and CO<sub>2</sub> in the presence of triethylamine [82]. In terms of PC yield, the Mg-modified composite oxides, Zn-Mg-Al with (Zn + Mg)/Al = 2 and Zn/Mg = 4 shows best catalytic performance. The results of CO<sub>2</sub>- and NH<sub>3</sub>-TPD characterization of the mixed oxides indicated that both acid and basic sites exist on the surface. The base strength and distribution of base sites on the catalysts were also measured by Hammett indicator method (Table 3). The results shown in Table 3 indicate that a moderate basicity of  $H_0 \approx 6.1$  is beneficial to the reaction. Despite Mg-Al oxide has more basic sites, it is lower than Zn-Mg-Al oxide ( $H_0 \approx 6.1$ ) in catalytic activity plausibly because the former has strong base sites, resulting in low selectivity to the desired product. It is noted that because of the poor solubility of triethylamine in PC, most of the triethylamine can be separated by delivery method.

**Table 3** Basicity distribution of Zn-M-Al composite oxides<sup>a)</sup> [Ref. 82]

entry	catalyst	basicity in the $H_0$ range/mmole·g <sup>-1</sup>				Total	catalytic results <sup>b)</sup>	
		4.1-5.0	5.0-6.1	6.1-7.3	≥7.3		sel. (%)	yield (%)
1	Zn-Mg-Al	0.015	0.015	0.035	0.125	0.19	99.2	88.8
2	Zn-Mg-Al <sup>c)</sup>	0.012	0.01	0.05	0	0.072	86.3	77.6
3	Zn-Ca-Al	0.01	0.08	0.01	0.07	0.17	98.1	85.0
4	Zn-Sr-Al	0.02	0.07	0.03	0.04	0.16	97.3	84.7
5	Zn-Ba-Al	0.02	0.05	0.04	0.01	0.12	97.7	84.4
6	Zn-Al	0.01	0.03	0.03	0.03	0.10	96.9	83.6
7	Mg-Al	0.01	0.03	0.05	0.22	0.31	95.7	85.8


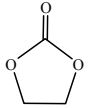

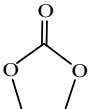
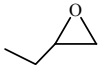
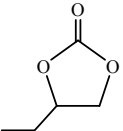
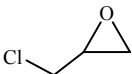
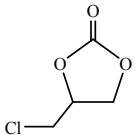
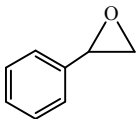
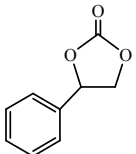
<sup>a)</sup> M = Mg, Ca, Sr, or Ba; (Zn+M)/Al=2, Zn/M=4; <sup>b)</sup> Reaction conditions: catalyst 0.5 g, propylene oxide 28.6 mmol, initial CO<sub>2</sub> pressure 2.5 MPa, triethylamine 0.5 mL, temp. 140 °C, time 12 h; <sup>c)</sup> Uncalcined.

### 5 Immobilized hydroxyl ionic liquids for the cycloaddition of CO<sub>2</sub> onto terminal oxide

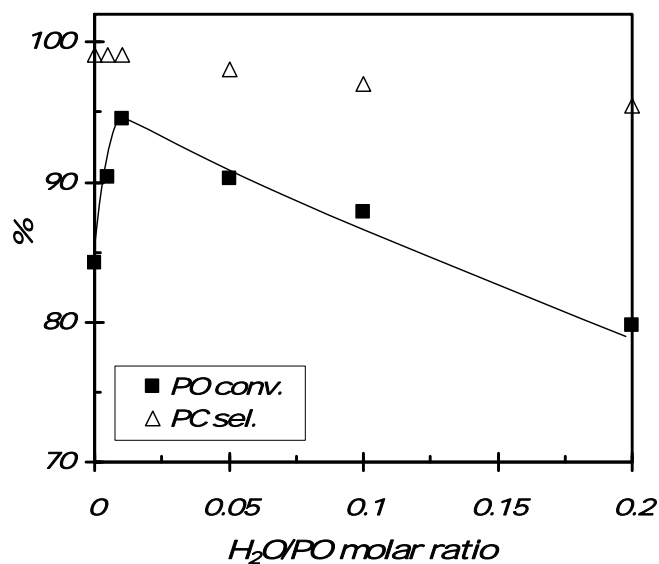
Homogeneous catalysts such as organic base [35-37], ionic liquids [1, 38-43], and organometallic complexes [44-58] are known to show high catalytic activity for the cycloaddition reaction. In recent years, ionic liquids have been extensively used as catalysts and/or alternative solvents in organic synthesis. Peng and Deng reported the first time the use of ionic liquids for the synthesis of cyclic carbonates [40]. Since then numerous ionic liquids such as quaternary ammonium, phosphonium, imidazolium and pyridinium were used for the cycloaddition of CO<sub>2</sub> to epoxides for the generation of cyclic carbonates [1, 38-43]. For better separation and reuse of catalyst, the immobilization of ionic liquids on recyclable solid materials has been studied [75-77, 83-88]. However, in most cases a co-catalyst (e.g., transition metal halide) and/or relatively rigorous reaction conditions are required. Recently, Zhang et al. reported that in the absence a co-catalyst and organic solvent, hydroxyl-functionalized ionic liquid (3-(2-hydroxyl-ethyl)-1- methylimidazolium bromide) showed catalytic activity and selectivity much higher than those of traditional ionic liquids for the cycloaddition of epoxide to CO<sub>2</sub> [89]. To facilitate catalyst separation, Yin and co-workers immobilized hydroxyl ionic liquid (3-(2-hydroxyl-ethyl)-1-propylimidazolium bromide) on SBA-15 and observed performance better than that of the unsupported ionic liquid towards the cycloaddition of CO<sub>2</sub> onto a variety of terminal epoxides (Table 4) [90]; PC yield of 99.0% can be quantitatively obtained at 120 °C and 2.5

MPa initial CO<sub>2</sub> pressure in 2 h. It is noted that the addition of a proper amount of water is beneficial to the cycloaddition reaction (Fig. 1). At a H<sub>2</sub>O/PO molar ratio of 0.01, PC yield is the highest.

**Table 4** Coupling of CO<sub>2</sub> with terminal epoxides catalyzed by SBA-15-HEPIMBr<sup>a)</sup> [Ref. 90]

entry	substrate	product	results/% <sup>b)</sup>		
			X	S	Y
1			100	99.5	99.5
2			99.3	99.7	99.0
3			97.6	99.8	97.4
5			99.6	99.6	99.2
6			99.8	99.8	99.6

<sup>a)</sup> Reaction conditions: epoxide 28.6 mmol, catalyst 0.2 g, initial CO<sub>2</sub> pressure 2.5 MPa, time 2 h, temperature 120 °C; <sup>b)</sup> X: conversion of epoxide, S: carbonate selectivity, Y: carbonate yield.



**Fig. 1** Effect of water addition on catalytic performance of SBA-15 immobilized hydroxyl ionic liquid (Reaction conditions: PO, 28.6 mmol; catalyst, 0.2 g; initial CO<sub>2</sub> pressure, 2.5 MPa; temperature, 120 °C; time 1 h.). After Ref. [90]

## 6 Conclusion



In this review article, the application of a number of novel bismuth compounds for the capture of CO<sub>2</sub> as well as the fixation of CO<sub>2</sub> to synthesize cyclic carbonates is described. Two heterogeneous catalysts, i.e. Zn-Mg-Al composite oxides and SBA-15 immobilized hydroxyl-functionalized ionic liquid that show high performance are described. The hypervalent organobismuth compounds that exhibit good thermal stability, as well as good association and dissociation ability with CO<sub>2</sub> are suitable for the removal of CO<sub>2</sub> from industrial emissions. Furthermore, the bismuth compounds with a bis(phenolato) ligand are catalytically highly active and selective for the synthesis of cyclic carbonate from CO<sub>2</sub> and epoxide. The Zn-M-Al composite oxides show higher catalytic activity, especially the selectivity (> 97%), than other metal oxide catalysts. The immobilization of hydroxyl ionic liquid (3-(2-hydroxyl-ethyl)-1-propylimidazolium bromide) on SBA-15 results in a heterogeneous catalyst that performs well. It is noted that the approach is an attractive strategy towards the fabrication of stable and reusable heterogeneous catalysts that have promising application in industry.

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