H₂O-Polyaluminium chloride-TBAB as synergistic catalysts for the synthesis of cyclic carbonate

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Abstract. An efficient catalytic system consisting of H₂O, Polyaluminium chloride (PAC) and Tetrabutylammonium bromide (TBAB) was applied to the cycloaddition of carbon dioxide (CO₂) to epoxides under mild conditions. Their catalytic cycloaddition activities were found to be well correlated with H₂O and polyaluminium chloride, which had a synergetic effect with the halide anion of TBAB. The presence of H₂O and PAC could remarkably improve the yield of propylene carbonate (PC) by which the reaction yield is about 4-5 times higher than TBAB alone. The catalytic system also exhibited excellent cycloaddition activities for various epoxide substrates.

1. Introduction
Catalytic conversion of CO₂ has been attracting more and more attention due to the growing concern about the greenhouse effect and as an inexpensive, nontoxic, nonflammable, renewable, and highly abundant single carbon-atom (C₁ resource) building block for organic synthesis [1-5]. The synthesis of the five-membered cyclic carbonates from epoxides and CO₂ is one of the most promising methods [6-9]. Not only is the reaction green for 100% atom efficiency but also the product cyclic carbonates have found wide applications as polar aprotic solvents [10-11], electrolytes [12], precursors of polymeric materials [13], and fine chemical intermediates [14]. In recent decades, a number of catalysts have been reported for this method of synthesizing cyclic carbonate, including organic bases [15], ionic liquids [16], transition metal complexes [17], metal oxides [18], and functional organic polymers [19]. Among these, Ionic liquids (ILs) have attracted much attention as a result of their unique properties, such as nonvolatility, nonflammability, and recyclability. However, the preparation of ionic liquids is high cost and time consuming and most of the ionic liquids are water or air sensitive. Therefore, how to improve the catalytic activity of simple ionic liquid has become an interesting topic. One strategy has focused on introducing a certain amount of cocatalysts (e.g., Bronsted acids [20], Lewis acids [21], water [22], alcohols [23]) into the traditional IL catalysts. Another efficient alternative strategy to improve the reactivity of ILs is to incorporate functional moieties (e.g., hydroxyl groups [24], carboxyl group [25], and even surface silanol groups [26] or metal complexes [27]) at the chain ends of ILs. Among these studies, it is accepted that there is an excellent synergistic effect between the hydrogen bond donor (the activation of epoxides) and the halide anion of ILs. Owing to functionalized IL catalysts being difficult to synthesize, numerous IL/co-catalyst binary catalytic systems have been reported up to now [28]. However, the exploration of cheap, nontoxic, highly active, easy post-processing co-catalysts is still highly desirable. In some catalyst systems, the cyclo-addition yields of CO₂ and epoxides can be significantly increased with the unsatisfactory
reaction selectivity when a small amount of water is introduced into the reaction system [24]. Though aluminum-containing complexes have high selectivity as active catalysts [29], catalyst synthesis was a complex process. Based on the above research reports, we are going to find a simpler way to improve the yield of the cyclo-addition CO$_2$ with various epoxides by using the catalytic system consisting of water, inorganic aluminium salt, and TBAB under relatively mild conditions. It was revealed that hydroxy group present on the water and bromide anion within TBAB exhibited excellent synergistic effect in promoting the reaction. More interestingly, the yield and selectivity from the cycloaddition of carbon dioxide to epoxides were dramatically increased by addition of PAC. Moreover, Polyaluminium chloride (PAC) as heterogeneous catalyst is a cheap, stable, readily available, water-tolerant, and easily recyclable cocatalyst compared to other types of additives in the coupling reactions. To the best of our knowledge, we first report PAC as catalyst for the synthesis of cyclic carbonate. Thus, the catalytic system consisting of water, PAC, and TBAB can act as a mild and highly effective catalyst system for the synthesis of cyclic carbonate.

2. Experimental:

2.1. Materials and instruments
Carbon dioxide with purity of 99.99% was purchased from Zaozhuang Meixin Industrial gases Co. Ltd. Epoxides, TBAB, Al$_2$O$_3$, Al(OH)$_3$ were purchased from Aladdin Chemical Co. Ltd. PAC (Al$_n$(OH)$_m$Cl$_{3n-m}$, pale yellow powder) was purchased from Adamas Reagent Co. Ltd and dried in vacuum at 100 $^\circ$C for 3 hours before using. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

$^1$HNMR spectra were recorded on a picoSpin 80 in CD$_3$Cl at ambient temperature. GC analyses were performed on a Varian CP-3800 equipped with a capillary column (Varian CP-Wax 52 CB), using a flame ionization detector. MS was obtained using Agilent 7000 B.

2.2. Cycloaddition of epoxides with CO$_2$
All the cycloaddition reactions were conducted in a 100 mL stainless steel reactor equipped with a magnetic stirrer and self-acting temperature control system. In the typical procedure, desired amounts of catalyst (TBAB/H$_2$O/PAC) and propylene oxide (PO) were added into the reactor. Then, CO$_2$ was charged in the reactor and the pressure was adjusted to 1.5 MPa, and the stirring was started. The reactor was heated and maintained at 120 $^\circ$C for 1 h, and the pressure was kept constant by means of a CO$_2$ cylinder connected to the reactor during the reaction. After the reaction was completed, the reactor was cooled to 0$^\circ$C in an ice-water bath, and the remaining CO$_2$ was released. The catalyst (PAC) was separated from the system by centrifugalization, then washed with ethyl acetate (2×5mL), dried under vacuum and reused for another run. The product yield was obtained by silica gel column chromatography (100-200 mesh silica gel, 12:1 petroleum ether(60-90 $^\circ$C): EtOAc) afforded target product.

3. Results and discussion

3.1. Screening of catalysts
In the investigations of synergistic effects between acidic and basic functional groups [30-31], researchers pointed out that an epoxide was activated by acid functional groups through the O atom of epoxide, The coordination of both acidic and basic functional groups promoted the reaction. Water molecules can be activated to produce acidic functional groups by inorganic aluminum salts under certain conditions [32-33], and therefore three types of aluminum compounds are used for the reaction of propylene oxide (PO) and CO$_2$ to produce propylene carbonate (PC). The results are summarized in table 1. Almost no product was detected when H$_2$O and PAC were used alone (entries 1, 10). TBAB alone could catalyze the cycloaddition, but the yield of PC was low (entry 2). Although the addition of water obviously promoted the reaction, the yield is still low (entry 3). Due to the formation of
propylene glycol, the reaction selectivity was reduced with increasing amounts of water, even if the reaction yield was improved (entries 3, 4). The addition of the aluminum compounds increased the yield of the reaction with a high selectivity (entries 5-7), and there are no polycarbonates are formed. The order of the activity of aluminum compounds was found to be PAC > Al₂O₃ > Al(OH)₃. Obviously, the reaction yield decreased when only using PAC and TBAB as catalysts without adding water (entries 8, 9). Therefore, the key to improve the yield of the reaction with a high selectivity was that H₂O and PAC were used together in the presence of TBAB (entries 1, 7, 8, and 10).

Table 1. Synthesis of PC catalyzed by different catalysts

| Entry | Catalyst | co-catalyst | Yield (%)b | Selectivity (%)c |
|-------|----------|-------------|------------|------------------|
| 1     | H₂O      | None        | 0          | -                |
| 2     | None     | TBAB        | 23         | 99               |
| 3     | H₂O      | TBAB        | 52         | 99               |
| 4d    | H₂O      | TBAB        | 78         | 95               |
| 5     | H₂O + Al₂O₃ | TBAB     | 93         | 96               |
| 6     | H₂O + Al(OH)₃ | TBAB   | 59         | 98               |
| 7     | H₂O + PAC | TBAB        | 99         | 99               |
| 8     | PAC      | TBAB        | 37         | 99               |
| 9e    | PAC      | TBAB        | 42         | 99               |
| 10    | PAC      | None        | 0          | -                |

a Reaction conditions: PO (100 mmol), H₂O (2 mmol), TBAB (0.74 mmol), Co-catalyst (0.39 g) 120 °C, 1.5 MPa, 1 h. b Isolated yield. c Determined by GC. d H₂O (0.42 g, 23 mmol). e PAC (0.78 g).

Figure 1. Effect of different proportions of H₂O/PAC. Figure 2. Effect of amount of PAC.

3.2. Effect of different proportion of H₂O and PAC

Since H₂O-PAC-TBAB as synergistic catalysts showed good catalytic activity, it was used to examine the effects of reaction parameters (catalyst amount, temperature, and CO₂ pressure) on the cycloaddition reaction of PO with CO₂. In order to further investigate the effect of the amount of water
in the synthesis rate of PC, experiments were firstly carried out in which the ratio of H₂O/PAC was increased from 0.05 to 1.27 (w/w). As shown in figure 1, only 86% of PC yield was observed at the ratio of 0.05. And the maximal PC yield (99%) obtained at the ratio of 0.09, while further increasing the ratio of H₂O/PAC from 0.09 to 1.27 caused an obvious decrease in the yield of PC though PO conversion kept at 100%. PC selectivity also decreases quickly from 99% to 86% correspondingly. It can be explained by the side reaction between water and PO to produce corresponding chemical, 1,3-propylene glycol (PG). Under the same amount of H₂O (2mmol H₂O/100mmol PO), the ratio of PAC/H₂O also could remarkably affect the synthesis rate of cyclic carbonate (figure 2). When the ratio of PAC/H₂O was 10.8, PC yield could reach 99% and no change even if increasing the ratio of PAC/H₂O.

**Figure 3.** Effect of different reaction temperature. **Figure 4.** Effect of CO₂ pressure.

3.3 Effect of reaction temperature

Figure 3 clearly shows that reaction temperature has a strong effect on PC yield. If catalytic reactions carried out at 90°C, 100°C, 110°C, and 120°C, PC yield were 21%, 41%, 75%, and 99%, respectively. The relationship between temperature and isolated yield was attributed to higher reactivity at higher temperatures. Furthermore, at reaction temperatures of 130°C and 140°C, yield variability did not change significantly.

3.4 Effect of CO₂ pressure

As seen in figure 4, the PC yield increased from 17% to 99% when the CO₂ pressure increased from 0.5 MPa to 1.5 MPa. Upon a further increase in the pressure (2.5 MPa), the PC yield also did not change significantly. During these catalytic reactions, the optimal CO₂ pressure can effectively increase the solubility of CO₂ in epoxides, enabling the reaction equilibrium to shift towards carbonate formation.

3.5 Reusability of the catalyst system

The stability of PAC was examined. There is no observable loss of catalytic activity over the PAC catalyst that even was reused for 6 times. The used PAC can be easily recovered by centrifugation, and washed with ethyl acetate. After drying, the PAC was used for the next run. The PC yield and selectivity were always above 98% across the cycles.

3.6 Cycloaddition of CO₂ with various epoxides

In order to survey the applicability of the catalyst system, we conducted cycloaddition reactions using epoxides of different kinds (table 2). It is apparent that the catalyst system exhibited high efficiency for all of the monosubstituted terminal epoxides in 1h (entries 1–4, table2). Disubstituted epoxides (entries 5–6) showed lower activity than mono-substituted terminal epoxides (entries 1–4), and required a long time (24h) to get a high yield, probably due to the high steric hindrance offered by the steric substituent.
3.7 Reaction mechanism
The catalytic activity of H$_2$O/TBAB was obviously improved by adding PAC for the cycloaddition of CO$_2$ to epoxides. However, the catalytic system PAC/TBAB showed the low catalytic activity even if the dosage of PAC was increased (table 1. entries 3, 7-9). According to the literature [34], PAC and H$_2$O can form a multimer according to a certain percentage. Therefore, water molecules can be activated to produce acidic functional groups by inorganic aluminum salts under certain conditions [32-33].

Table 2 Cycloaddition of CO$_2$ to various epoxides$^a$.

| Entry | Substrate | Product | Yield (%)$^b$ | Selectivity (%)$^c$ |
|-------|-----------|---------|---------------|---------------------|
| 1     |           |         | 99            | 99                  |
| 2     | Cl        |         | 98            | 99                  |
| 3     | Ph        |         | 99            | 99                  |
| 4     |           |         | 98            | 99                  |
| 5$^d$ |           |         | 94            | 97                  |
| 6$^d$ |           |         | 99            | 98                  |

$^a$ Reaction conditions: Epoxide (100 mmol), TBAB(0.74 mmol), H$_2$O(2 mmol), PAC(0.39g), 120°C, CO$_2$(1.5MPa), and 1h.
$^b$ Isolated yield.
$^c$ Determined by GC.
$^d$ 24h

The coordination of both acidic and basic functional groups (-OH/Br$^-$) promoted the reaction. Based on the above result, a possible mechanism for the synergetic effect of catalyst system was proposed (Scheme 1). The multimer formed by water and PAC enhanced the coordination effect of the H atom of water molecule with the O atom of epoxide through a hydrogen bond which resulted in the polarization of C–O bonds. At the same time, the halide anion made the nucleophilic attack on the less
sterically hindered β-carbon atom of the epoxide. As a result, the ring of the epoxide was opened easily (Scheme 1, step 1). Then, the interaction occurred between the oxygen anion and CO$_2$, forming a carbonate anion (Scheme 1, step 2) which would be transformed into a cyclic carbonate by the intramolecular substitution of the halide in the next step (Scheme 1, step 3). Next, the catalytic system got back into its original state for the next catalytic cycle.

**Scheme 1.** Proposed mechanism for the cycloaddition reaction of CO$_2$ to epoxides catalyzed by TBAB/H$_2$O/PAC.

4. Conclusion
In conclusion, H$_2$O-PAC-TBAB as synergistic catalysts catalyzed the conversion of different organic epoxides into a 5-membered cyclic carbonate at rather mild reaction conditions (T=120°C, p (CO$_2$) =1.5MPa, 1h). Also PAC could play a significant role in determining the selectivity in addition to the activity of the catalyst. Being cheap, recyclable, water-tolerant, and environment-benign, PAC is a promising industrial catalyst for the cycloaddition of carbon dioxide (CO$_2$) to epoxides under mild conditions.

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