

Article

Guanidine Hydrochloride/ ZnI_2 as Heterogeneous Catalyst for Conversion of CO_2 and Epoxides to Cyclic Carbonates under Mild Conditions

Bo Liu ¹, Mengshuai Liu ¹, Lin Liang ² and Jianmin Sun ^{1,3,*}

¹ The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150080, China; E-Mails: liubo1308@hotmail.com (B.L.); mshuai_liu812@163.com (M.S.L.)

² School of Life Science and Technology, Harbin Institute of Technology, Harbin 150080, China; E-Mail: lianglin@hit.edu.cn

³ State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150080, China

* Author to whom correspondence should be addressed; E-Mail: sunjm@hit.edu.cn; Tel./Fax: +86-451-8640-3715.

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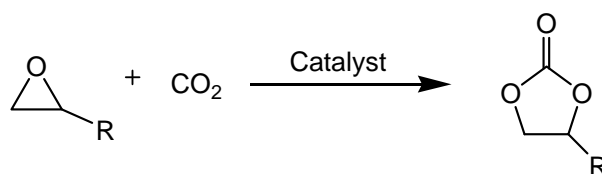
Abstract: In this article, the combination of guanidine hydrochloride with co-catalyst ZnI_2 proved to be a highly efficient heterogeneous catalyst for the environmentally benign, solvent-free synthesis of cyclic carbonates under mild reaction conditions. The effects of different co-catalysts as well as reaction parameters including catalyst loadings, CO_2 pressure, reaction temperature, and reaction time on the coupling reaction of CO_2 to propylene oxide were thoroughly investigated. With the molar ratio of guanidine hydrochloride to ZnI_2 at 5:1, excellent yield (94%) and selectivity ($\geq 99\%$) of propylene carbonate were obtained under 100 °C and at 1 MPa for 1.5 h. Additionally, ZnI_2 could be recycled, but because of the washing loss of guanidine hydrochloride, there was a slight decrease in the yield of propylene carbonate. Gratifyingly, the activity of the catalytic system could be restored by adding additional 20 mol% of fresh guanidine hydrochloride, thus exhibiting excellent recyclability of the ZnI_2 catalyst. Moreover, the binary catalysts were also versatile when using other epoxides for CO_2 cycloaddition. A possible reaction mechanism was proposed wherein guanidine hydrochloride plays a dual role in activating

CO₂ and epoxide, and ZnI₂ activated epoxide, simultaneously. The synergistic effect of guanidine hydrochloride and ZnI₂ ensure the reaction proceeds effectively.

Keywords: guanidine hydrochloride; ZnI₂; CO₂ fixation; cyclic carbonates; heterogeneous catalysis

1. Introduction

Carbon dioxide can be specially spotlighted as an abundant, inexpensive, and renewable C₁ resource, which can replace commonly used toxic C₁ building blocks such as phosgene [1]; however at the same time CO₂ is also the main greenhouse gas contributor [2]. Therefore, chemical fixation of CO₂ has been a hot topic from the viewpoint of sustainable development and green chemistry. In this regard, one of the most promising strategies is the transformation of CO₂ with epoxides to yield the corresponding cyclic carbonates (Scheme 1) [3], which is considered green because of 100% atom efficiency. Also cyclic carbonates can be widely applied in proton inert solvents, as precursors for polycarbonates and polyurethanes synthesis, as electrolytes in lithium secondary batteries, and as intermediates for production of pharmaceuticals, fine chemicals and agricultural chemicals [4,5].



Scheme 1. Cycloaddition of epoxide with CO₂.

So far, numerous homogeneous and heterogeneous catalysts for this transformation have been reported, including metal-oxides [6,7], alkali metal salts [8], organometallic complexes [9], organic bases or ammonium/phosphonium salts [10–12], *N*-heterocyclic carbenes [13], modified molecular sieves [14,15] and ionic liquids [16–18]. Nevertheless, homogeneous catalysts are undesirable in industry due to problems such as rigorous separation and purification of the products. Also the developed heterogeneous catalysts are somewhat restricted due to low activity, harsh reaction conditions, or poor stability [19]. Therefore, it is of still great importance to explore heterogeneous catalysts with excellent activity and stability under mild reaction conditions for CO₂ cycloaddition.

In order to improve the catalytic performance, the catalysts need to simultaneously possess Lewis acid and base to activate epoxides and CO₂, respectively. Additionally, it has been reported that zinc halides can coordinate with the oxygen atom to activate the epoxide by forming the zinc-epoxide adduct [20,21]. Moreover, theoretical study also indicated that the formation of a hydrogen bond between catalyst and epoxide could accelerate the ring-opening reaction of the epoxide, thus enhancing the activity significantly [22]. Guanidine hydrochloride (GndCl) is a cheap and nontoxic chemical that has two primary amino nucleophilic groups and a chlorid ion, and can serve as activator of CO₂ as well as epoxide and attacking reagent simultaneously, but still has never been used in catalytic CO₂

cycloaddition with epoxides. Herein, we developed a dual heterogeneous catalyst system composed of guanidine hydrochloride and ZnI_2 for the conversion of CO_2 and epoxides to cyclic carbonates. The effects of various Lewis acid co-catalysts as well as reaction parameters such as CO_2 pressure, catalyst loadings, reaction temperature, and reaction time on catalytic activity were investigated thoroughly. $\text{GndCl}/\text{ZnI}_2$ was the most efficient among these developed binary catalysts and showed an excellent synergetic effect in promoting the reaction under mild conditions. Moreover, the reusability of the catalytic system was investigated and a possible synergistic catalytic mechanism was proposed.

2. Results and Discussion

2.1. Screening of Catalysts and Their Reusability

The catalytic performance of GndCl with different Lewis acid co-catalysts was investigated with the coupling reaction of CO_2 to propylene oxide (PO), and the results are shown in Table 1. Almost no activity in forming the product propylene carbonate (PC) was observed with GndCl or ZnI_2 alone (Entries 1 and 2) and only 27% yield of PC was obtained when GndCl was employed under 130 °C and at 3.0 MPa CO_2 for 1.5 h (Entry 3), thus indicating the bifunctional role of GndCl to catalyze the cycloaddition reaction. Noticeably, the combination of GndCl with ZnI_2 exhibited remarkably improved catalytic activity, and PC yield approached 94% at 100 °C and 1.0 MPa CO_2 for 1.5 h (Entry 4) without any solvent. It was noted that the selectivity to PC was always above 99%, the rest was due to the trace amounts of PO polymerization in side reactions. Additionally, the performances of various Lewis acid co-catalysts for this transformation were explored. In comparison, almost no product was detected when ZnO or $\text{Zn}(\text{NO}_3)_2$ was used (Entries 7 and 8) and the reaction hardly occurred or very low conversions were obtained over GndCl with Cd^{2+} , Mn^{2+} , Co^{2+} or Fe^{3+} (Entries 9–12). The catalytic activity improved with the stronger anionic nucleophilic property of zinc halide in the order of $\text{ZnI}_2 \gg \text{ZnBr}_2 > \text{ZnCl}_2$, which was in accordance with previous works [8,23]. When ZnBr_2 and ZnCl_2 were used as the co-catalysts, 43% and 12% yield of PC were obtained, respectively (Entries 5 and 6), and ZnI_2 co-catalyst displayed a remarkable role in accelerating the reaction with 94% PC yield. GndCl combined with ZnI_2 showed higher activity than other metallic halides. Hence, GndCl coordinated with ZnI_2 was chosen for further investigation.

In the meanwhile, the GndCl dosage was a key factor to the catalytic activity. 0.5 mmol and 1.0 mmol GndCl gave 37% and 94% yields of PC (Entries 4 and 13) and further improvement of GndCl dosage at 1.5 mmol resulted in a slight increase at 95% (Entry 14). Hence, 1.0 mmol GndCl was adopted for further investigation.

For potential application in a green and economic process, the catalyst recyclability plays an important role. Experiments were carried out to test the recyclability of $\text{GndCl}/\text{ZnI}_2$ at 100 °C and 1.0 MPa CO_2 , the results are shown in Table 1. There was a slight decrease in PC yield in the second run (Entry 15) because of the washing loss of catalysts. After an additional 20 mol% of fresh guanidine hydrochloride was added together with recyclable ZnI_2 and GndCl for the third run, the PC yield again reached 90% (Entry 16).

Table 1. Screening of catalysts for the cycloaddition reaction ^a.

Entry	Catalyst system		Catalytic results ^b	
			Yield (%)	Selectivity (%)
1	GndCl	—	trace	—
2	—	ZnI ₂	trace	—
3 ^c	GndCl	—	27	≥98
4	GndCl	ZnI ₂	94	≥99
5	GndCl	ZnBr ₂	43	≥99
6	GndCl	ZnCl ₂	12	≥99
7	GndCl	ZnO	trace	≥99
8	GndCl	Zn(NO ₃) ₂	trace	—
9	GndCl	CdCl ₂	trace	—
10	GndCl	MnCl ₂	trace	—
11	GndCl	CoCl ₂	trace	—
12	GndCl	FeCl ₃	5	≥99
13 ^d	GndCl	ZnI ₂	37	≥99
14 ^e	GndCl	ZnI ₂	95	≥99
15 ^f	GndCl	ZnI ₂	80	≥99
16 ^g	GndCl	ZnI ₂	90	≥98

^a Reaction conditions: PO 34.5 mmol, GndCl 1.0 mmol, co-catalyst 0.2 mmol, 100 °C, CO₂ pressure 1.0 MPa, 1.5 h. ^b Determined by GC. ^c CO₂ pressure 3.0 MPa, 130 °C, 1.5 h. ^d GndCl 0.5 mmol. ^e GndCl 1.5 mmol. ^f The second run. ^g The third run, additional 20 mol% of GndCl was added.

2.2. Effect of Reaction Parameters

To investigate the influence of catalyst loading on the PC synthesis, a series of experiments were carried out by varying the molar ratio of ZnI₂ catalyst to propylene oxide, and the results are shown in Figure 1. With the ZnI₂/PO molar ratio increased from 0.29–0.58%, there was a sharp increase of PC yield from 46%–94%. When ZnI₂ loading was further increased to 0.87 mol%, PC yield did not apparently rise. Even at a low loading of ZnI₂ at 0.58 mol%, high PC yield (94%) and selectivity (≥99%) were obtained. Gratifyingly, the PC selectivities hardly changed on increasing the ZnI₂ catalyst loading from 0.29–0.87 mol%. Therefore, 0.58 mol% was chosen as the optimal amount of ZnI₂.

Generally, a significant drawback associated with CO₂ as reagent or reaction medium in organic synthesis, is the potential danger of operating at high pressure [24]. Hence, the effect of CO₂ pressure on the CO₂ coupling reaction was investigated. As shown in Figure 2, a dramatic increase of PC yield was detected in the low-pressure range of 0.5–1.0 MPa. Also, the yields remained nearly constant at medium CO₂ pressures of 1.0–3.0 MPa, suggesting that CO₂ was not involved in the rate-determining step in this pressure range [25]. The desired product yield was obtained even at low CO₂ pressure of 1.0 MPa over GndCl/ZnI₂ catalysts. A similar effect of CO₂ pressure on catalytic activity was observed in other catalytic systems [6,25–27], which could be explained by the fact that the introduced CO₂ was dissolved in propylene oxide or “liquefied” by the formation of a CO₂-PO complex [23]. In the low-pressure range, increasing CO₂ pressure led to an increase of CO₂-PO concentration in the liquid phase and thus enhanced the PC yield. However, on increasing CO₂ pressure, the concentration of PO

decreased in the liquid phase and increased in the vapor phase, which gave rise to the constant PC yield. Thus, 1.0 MPa was chosen as the optimal CO₂ pressure.

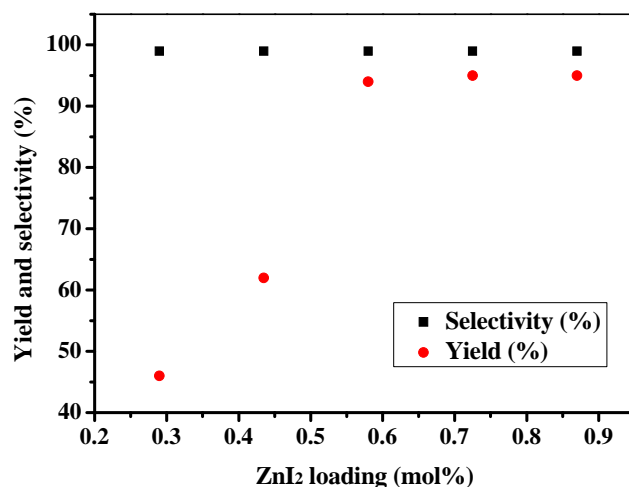


Figure 1. Influence of ZnI₂ loading on propylene carbonate (PC) yield and selectivity. Reaction conditions: propylene oxide (PO) 34.5 mmol, GndCl 1.0 mmol, CO₂ pressure 1.0 MPa, 100 °C, 1.5 h.

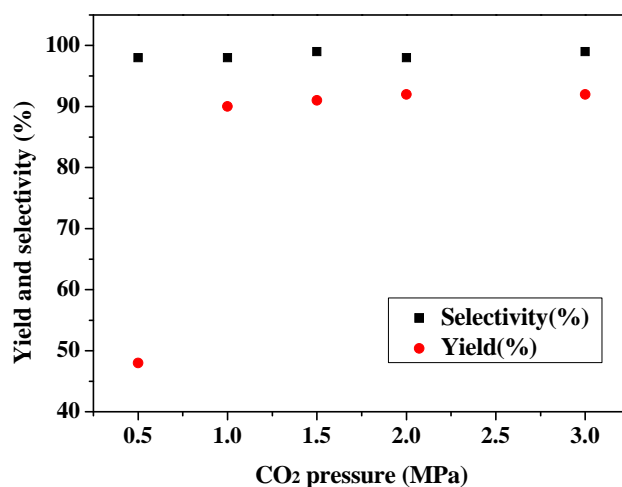


Figure 2. Influence of CO₂ pressure on the cycloaddition reaction. Reaction conditions: PO 34.5 mmol, GndCl 1.0 mmol, ZnI₂ 0.2 mmol, 100 °C, 1.5 h.

The influence of reaction temperature on PC yield and selectivity is depicted in Figure 3. It is obvious that the reaction was sensitive to reaction temperature. With the temperature increasing from 80–100 °C, PC yield rapidly increased from 41%–94% and PC selectivity stayed invariably at 99%. As the temperature was further raised to 120 °C, PC yield increased slightly to 98%. Hence, 100 °C was the optimal reaction temperature for PC synthesis in the light of energy consumption and PC yield.

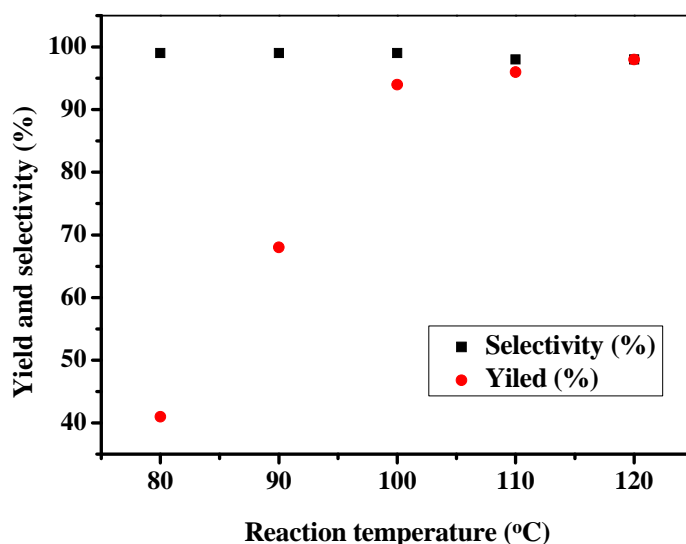


Figure 3. Influence of reaction temperature on the cycloaddition reaction. Reaction conditions: PO 34.5 mmol, GndCl 1.0 mmol, ZnI₂ 0.2 mmol, CO₂ pressure 1.0 MPa, 1.5 h.

The effect of reaction time on PC synthesis is illustrated in Figure 4. When the cycloaddition reaction proceeded for 1.5 h, PC yield rapidly achieved 94%. Afterwards, there appeared a gradual increase of PC yield. Moreover, the selectivity to PC stayed above 98% throughout.

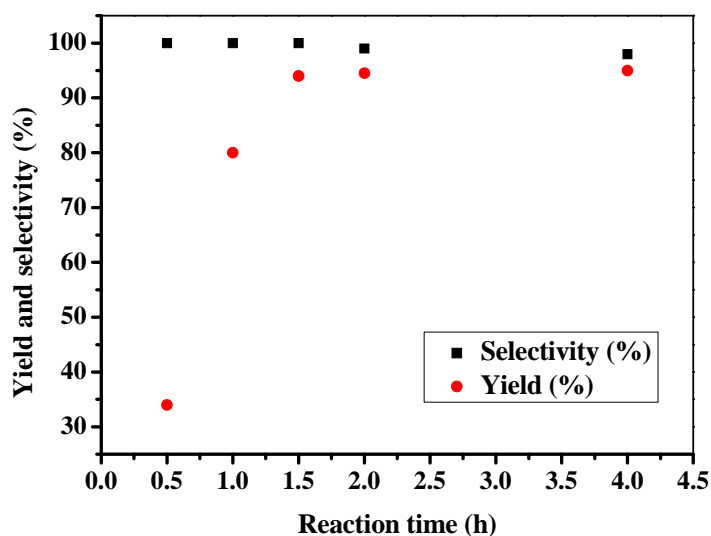


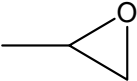
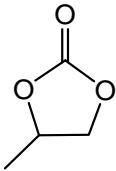
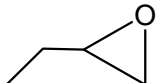
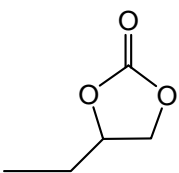
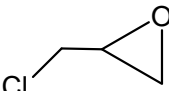
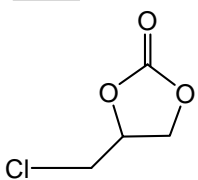
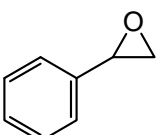
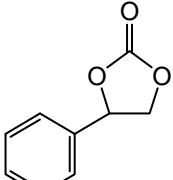
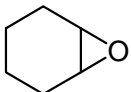
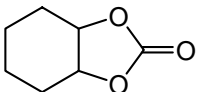
Figure 4. Influence of reaction time on the cycloaddition reaction. Reaction conditions: PO 34.5 mmol, GndCl 1.0 mmol, ZnI₂ 0.2 mmol, CO₂ pressure 1.0 MPa, 100 °C.

2.3. Catalytic Activity towards Other Epoxides

In order to study the efficiency and general applicability of the developed GndCl/ZnI₂ catalytic system, the cycloadditions of CO₂ with different substituent epoxides were conducted, and the results are exhibited in Table 2. GndCl/ZnI₂ displayed efficient activities for the conversions of a variety of epoxides to the corresponding cyclic carbonates with good to excellent yields and high selectivities. PO was the most active of the epoxides. Also, various epoxides bearing electron-donating and

electron-withdrawing groups provided the desired products in appreciably shorter time (Entries 1–3), thus reflecting the outstanding efficiency of GndCl/ZnI₂ catalysts. However, with the increase of steric hindrance from side chains of substrates, the catalytic activities of CO₂ cycloaddition to styrene oxide and cyclohexene oxide were impeded, however, satisfactory yields were also obtained at the expense of longer reaction time or higher reaction temperature compared with the terminal epoxides (Entries 4 and 5).

Table 2. Catalytic activity of CO₂ cycloaddition to various epoxides ^a.

Entry	Epoxide	Product	Time (h)	Reaction results ^b	
				Yield (%)	Selectivity (%)
1 ^c			1.5	94	99
2			1.5	92	99
3			1.5	92	99
4			3	80	98
5 ^d			11	71	98

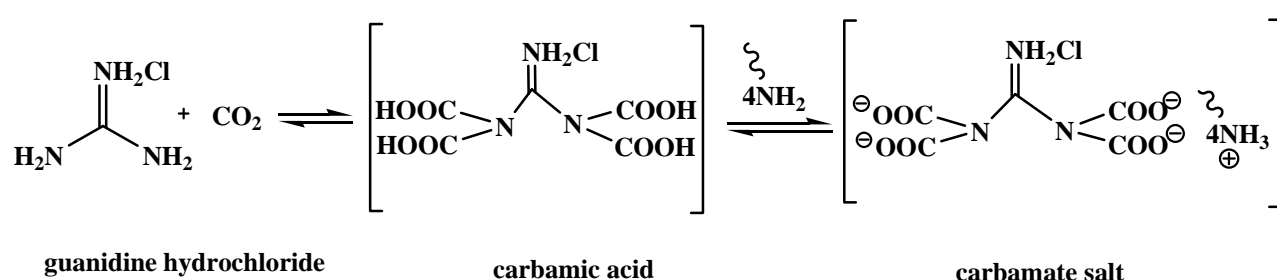
^a Reaction conditions: epoxide 13.9 mmol, GndCl 1.0 mmol, ZnI₂ 0.2 mmol, CO₂ pressure 1.0 MPa, 100 °C.

^b Determined by GC. ^c PO 34.5 mmol. ^d Reaction temperature 120 °C.

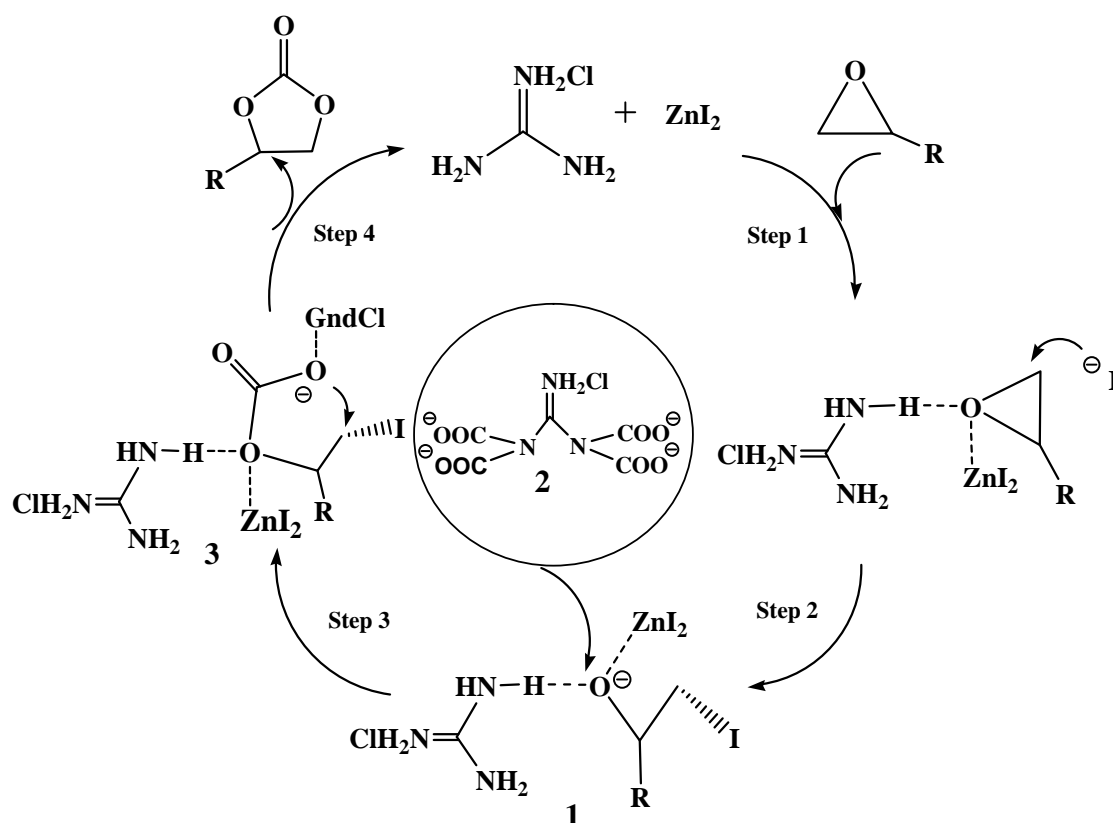
2.4. Proposed Reaction Mechanism

In previous works [6,19], it was regarded that the hydrogen bond formed between the hydrogen atom of the amine and the oxygen atom of epoxide would lead to polarization of the C–O bond, which could then facilitate the ring opening of the epoxide; and simultaneously, the primary amino group of GndCl would activate CO₂ to form a carbamate salt (Scheme 2) [19,28,29], which would facilitate the CO₂ cycloaddition reaction. Moreover, it was recognized that epoxides could be activated by zinc halides by the formation of a zinc-epoxide adduct [30], which had a positive effect on the ring opening of the epoxide. Based on this, a plausible mechanism is proposed as shown in Scheme 3. Firstly, GndCl plays the role of Lewis base to activate CO₂ to form a zwitterionic adduct (intermediate **2**). Meanwhile, the epoxide is activated by the formation of a hydrogen bond between the hydrogen atom

of the amino and oxygen atoms of the epoxide; additionally, the epoxide is further activated by the zinc atom from ZnI_2 forming a Zn-epoxide adduct. Both the integrated activations from GndCl and ZnI_2 lead to easy polarization of the C-O bond of the epoxide. Secondly, the I^- anion from ZnI_2 plays the role of Lewis base to attack the less sterically hindered β -carbon atom of the epoxide, assisting the ring-opening with the formation of the intermediate **1**. Subsequently, the GndCl simultaneously coordinates with CO_2 , affording a carbamate salt **2** as the activated species of CO_2 [29,31]. Thereafter, the carbamate salt **2** undergoes electrophilic attack on the intermediate **1** to produce the new alkyl carbonate compound **3**, simultaneously leaving one GndCl . Eventually, by the ensuing intramolecular ring-closure, the cyclic carbonate is formed and the catalysts regenerated. The synergetic roles played by GndCl and ZnI_2 ensure the reaction proceeds effectively. Also, the catalytic activity of ZnI_2 is higher than ZnBr_2 and ZnCl_2 , which can well be explained by the nucleophilic property of the anion.



Scheme 2. Structure and formation of carbamate salt **2**.



Scheme 3. Possible reaction mechanism for $\text{GndCl}/\text{ZnI}_2$ catalyzed cycloaddition reaction.

3. Experimental Section

3.1. Materials and Instruments

The reagents and chemicals (analytic grade unless otherwise stated) were purchased from Sinopharm Chemical Reagent Co., Ltd. (No. 52 Ningbo Road, Shanghai, China). Carbon dioxide with 99.99% purity was purchased from Harbin Qinghua Industrial gases Co., Ltd. (No. 46 Hongli Street, Xiangfang District, Harbin, China). Propylene oxide (99%), 1, 2-butylene oxide, epichlorhydrin, styrene oxide, cyclohexene oxide were purchased from Beijing InnoChem Science & Technology Co., Ltd. (No. 170 Beiyuan Road, Chaoyang District, Beijing, China) Guanidine hydrochloride (99%), ZnI₂ ($\geq 98\%$) were purchased from Adamas Reagent Co., Ltd. (No. 245 Jiachuan Road, Xuhui District, Shanghai, China).

GC analyses were performed on an Agilent GC-7890A equipped with a capillary column (Agilent 19091J-413).

3.2. Typical Procedure for the CO₂ Cycloaddition Reaction to Propylene Oxide

The cycloaddition reaction of propylene oxide (PO) and CO₂ was conducted in a 50 mL high pressure stainless-steel autoclave equipped with a magnetic stirring bar. In a typical run, a certain amount of GndCl/ZnI₂ catalyst and PO (34.5 mmol) were added into the reactor successively, then the reactor was heated using an oil bath. At a fixed reaction temperature, CO₂ was introduced into the reactor to a fixed pressure, and then the autoclave was heated at that temperature for a desired time. After the reaction was completed, the reactor was cooled to 0 °C in ice-water bath, and the remaining CO₂ was released slowly to avoid the rest of the PO escaping with the gas. The catalysts were separated from the system by centrifugation, then washed with toluene (3 × 5 mL), dried and reused for the next run. The products were analyzed by GC with a flame ionization detector.

4. Conclusions

In summary, we developed a cheap, readily available and highly active GndCl/ZnI₂ catalytic system for the synthesis of cyclic carbonates under mild, solvent-free conditions. GndCl/ZnI₂ catalysts proceeded efficiently for the CO₂ cycloaddition with different substituted epoxides, even with the less active epoxides such as styrene oxide and cyclohexene oxide, due to the synergetic effects of guanidine hydrochloride and ZnI₂. The catalysts could be reused at least three times, however at the expense of an additional 20 mol% fresh guanidine hydrochloride to compensate for the partial loss on washing during recycles. Compared with previous heterogeneous catalysts, the catalytic system developed in this study was cheap, easily available, solvent-free for CO₂ cycloaddition and under mild reaction conditions, which is of benefit for practical applications of CO₂ conversion.

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Author Contributions

Bo Liu and Jianmin Sun contributed to the experiment design, the article writing and revising. Bo Liu also contributed to all the experimental data collection, and Mengshuai Liu and Lin Liang contributed to product analyses as well as helpful discussion.

Conflicts of Interest

The authors declare no conflict of interest.

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