

Article

Solvent-Free Coupling Reaction of Carbon Dioxide and Epoxides Catalyzed by Quaternary Ammonium Functionalized Schiff Base Metal Complexes under Mild Conditions

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Abstract: A series of bifunctional Schiff base metal catalysts (Zn-NPCIR, Zn-NPXH, and M-NPCIH) with two quaternary ammonium groups were prepared for carbon dioxide (CO₂) and epoxide coupling reactions. The effects of the reaction variables on the catalytic activity were systematically investigated, and the optimal reaction conditions (120 °C, 1 MPa CO₂, 3 h) were screened. The performances of different metal-centered catalysts were evaluated, and Co-NPCIH showed excellent activity. This kind of bifunctional catalyst has a wide range of substrate applicability, excellent stability, and can be reused for more than five runs. A relatively high TOF could reach up to 1416 h⁻¹ with Zn-NPCIH as catalyst by adjusting reaction factors. In addition, the kinetic study of the coupling reaction catalyzed by three catalysts (Zn, Co, and Ni) was carried out to obtain the activation energy (*E_a*) for the formation of cyclic carbonates. Finally, a possible mechanism for this cyclization reaction was proposed.

Keywords: carbon dioxide; bifunctional metal complexes; cyclic carbonate; atmospheric pressure; activation energy



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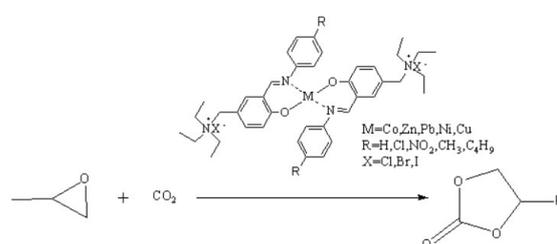
1. Introduction

Since the industrial revolution, large amounts of CO₂ emissions are causing its concentration in the air to increase every year; it is now about 400 ppm (mg/L), leading to a series of environmental and social problems [1,2]. However, CO₂ can be used as a non-toxic, cheap, easily available, and abundant C1 resource for constructing C-C, C-N, and C-O bonds to produce high-value chemicals such as carboxylic acids, oxazolidinones, urea, isocyanates, cyclic carbonates, etc. [3–9]. The synthesis of cyclic carbonates using carbon dioxide has been extensively studied. One is due to the 100% atomic utilization of the reaction, and the other is that the products have favorable physicochemical properties such as environmental friendliness, high boiling point, low odor, and low toxicity, and can be used as an alternative solvent to the high boiling point polar solvents DMF and DMSO [6]. In addition, cyclic carbonate can be applied to fuel additives, electrolytes for lithium-ion batteries [10,11], and polycyclic carbonate synthesis [12,13].

The thermodynamic and kinetic inertness of CO₂ make its conversion require a large energy input (e.g., high temperature and pressure), and the search for suitable catalysts is a focus of research on whether CO₂ can be used efficiently [6]. From a mechanistic point of view, in the synthesis of cyclic carbonates using CO₂ and epoxides, catalysts have an important role in the ring opening of epoxides: (1) acting on the oxygen atom of the ring via Lewis acid or the formation of hydrogen bonds, and (2) nucleophilic reagents attacking the carbon atom of the epoxide to promote its ring opening [14]. Based on these presumptions,

many catalytic systems have been developed for applications in the cycloaddition reactions of epoxides with carbon dioxide, such as ionic liquids [15–18], N-heterocyclic carbenes (NHCs) [19], porphyrins [20], organometallic framework materials (MOF) [21], inorganic catalysts [22], metal complex catalysts [23,24], carboxylic acid compounds [25–27], and quaternary ammonium salt-based catalysts [28,29].

Based on the need for catalytic systems to have both electrophilic and nucleophilic centers, various “bifunctional catalysts” have been developed [30–32]. In this paper, a variety of quaternary ammonium salt-based bifunctional metal catalysts were designed and synthesized for the cycloaddition reaction of epoxides with carbon dioxide (Scheme 1). The results show that such bifunctional catalysts can effectively promote the formation of cyclic carbonate from epoxide and CO₂ at low catalyst loadings (1 mol%) and relatively mild conditions (atmospheric pressure). In addition, since the reaction is heterogeneously catalyzed, catalyst recycling is simple and convenient. The catalyst recycling experiments and IR analysis of the catalysts showed that the prepared bifunctional catalysts can be effectively recycled five times without deactivation.



Scheme 1. Cycloaddition of CO₂ to epoxides with bifunctional quaternary ammonium metal complexes as catalysts.

2. Materials and Methods

2.1. Chemicals and Analytical Methods

The information on materials is listed in Table S1: Provenance and mass fraction purity of the materials. All the chemicals were used as received except for the epoxides, which were purified by distillation from CaH₂ before utilization. The general procedure for the cycloaddition of CO₂ to epoxides and spectra copies of all synthesized complexes and carbonate products are provided in the Supporting Information (SI). The yield and selectivity are determined by ¹H NMR characterization.

2.2. Synthesis of Quaternary Ammonium Modified Metal Complexes Zn-NPClR, Zn-NPXH, M-NPCH

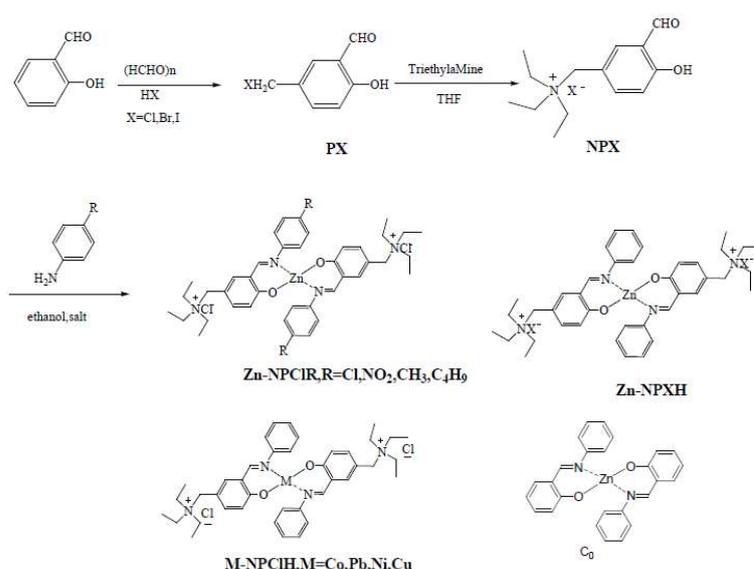
The synthetic route for catalysts is shown in Scheme 2.

2.2.1. Synthesis of 5-Chloromethyl Salicylaldehyde (PX, NPX)

The ligand precursors PX and NPX (X = Cl, Br, I) were prepared and characterized according to the method reported by Ji et al. (Scheme 2) [33,34]. For comparison, a complex C₀ was synthesized as a non-bifunctional catalyst.

2.2.2. General Procedure for Synthesis of Quaternary Ammonium Modified Metal Complexes Zn-NPClR, Zn-NPXH

To a 100 mL dry round-bottom flask equipped with a magnetic stir bar, an ethanol solution (20 mL) of quaternary ammonium modified salicylaldehyde NPX (0.01186 mol) and an ethanol solution (10 mL) of 0.01533 mol amine C₆H₆R (R = H, Cl, NO₃, CH₃, C₄H₉) were added sequentially. The obtained mixture was heated and refluxed for 4 h. Then zinc acetate anhydrous (7.74 mmol) was added to the mixture. After another 6 h reflux, a large amount of precipitates were obtained. These precipitates were filtered and washed with ethanol several times, then dried in vacuum to obtain quaternary ammonium-modified salicylaldehyde-zinc catalysts. Details of these complexes are shown in SI.



Scheme 2. Synthesis of the quaternary ammonium catalysts.

2.2.3. Synthesis of Other Metal Center (Cobalt, Plumbum, Nickel, Copper) Complexes M-NPClH

Following the procedure of Zn-NPClH, we have also prepared different metal-centered quaternary ammonium salt complexes using other metal salts (cobalt chloride hexahydrate, lead acetate, nickel chloride hexahydrate, copper chloride dihydrate). The physicochemical information of these complexes is shown in Supporting Information.

2.3. Catalytic Performance for CO₂/Epoxide Cycloaddition Reaction

The cycloaddition reaction of CO₂ and epoxide was conducted in a 50 mL stainless steel autoclave. The required catalyst and epoxide were added, and then CO₂ was pressurized into the reactor at a certain pressure. The autoclave was immersed in an oil bath at a preset temperature, with stirring. After a proper time, the autoclave was cooled down to room temperature and then vented slowly. The resulting mixture was analyzed by ¹H NMR to give the yield and the selectivity.

3. Results and Discussion

3.1. The Effect of Time on Cycloaddition of Propylene Oxide (PO) and CO₂

To optimize the reaction conditions for the cyclization reaction of epoxide and carbon dioxide, Zn-NPClH was used as a catalyst and PO as a substrate. The effect of time on the reaction was investigated at 120 °C and 1 MPa CO₂, as shown in Figure 1A. The propylene carbonate (PC) content increased steeply with time, reaching 3 h. It is obvious that within the initial 3 h, both the reaction rate and the PC yield increased rapidly. After 3 h, the PC yield still increased, but not as dramatically as before. The possible reason is that as the reaction proceeds, the PC concentration increases and the PO concentration decreases; in addition, the generated PC increases the viscosity of the system, which leads to a reduced opportunity for contact between the catalytically active site and the reaction substrate [35]. Therefore, 3 h was chosen as the optimal reaction time.

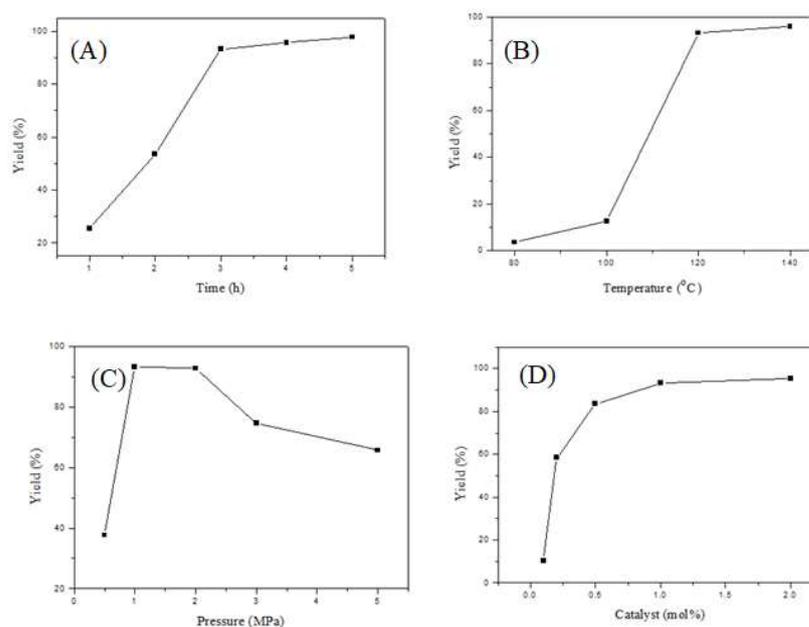


Figure 1. Effects of different reaction parameters on PC yield. (A) Reaction time effect on PC yield: PO (10 mL, 0.143 mol), catalyst Zn-NPCIH (1.43 mmol, 1 mol%), $T = 120\text{ }^{\circ}\text{C}$, $P = 1\text{ MPa}$; (B) Reaction temperature effect on PC yield: PO (10 mL, 0.143 mol), catalyst Zn-NPCIH (1.43 mmol, 1 mol%), $t = 3\text{ h}$, $P = 1\text{ MPa}$; (C) CO_2 pressure effect on PC yield: PO (10 mL, 0.143 mol), catalyst Zn-NPCIH (1.43 mmol, 1 mol%), $t = 3\text{ h}$, $T = 120\text{ }^{\circ}\text{C}$; (D) The mole ratio of PO to catalyst effect on PC yield: PO (10 mL, 0.143 mol), catalyst Zn-NPCIH (1.43 mmol), $t = 3\text{ h}$, $T = 120\text{ }^{\circ}\text{C}$, $P = 1\text{ MPa}$. The selectivity of PC was $>99\%$.

3.2. The Effect of Temperature on Cycloaddition of PO and CO_2

The PC yield was low at $100\text{ }^{\circ}\text{C}$ (Figure 1B), while increasing the temperature greatly improved the catalytic activity, which confirms the fact that the temperature has a significant effect on the reaction activity, and the fact that a high temperature can promote the PO conversion also indicates that this cycloaddition reaction is thermodynamically favorable [36–38]. When the temperature was increased from $100\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$, the PC yield increased steeply from 16% to 93%, but there was no significant change in the PC yield when the temperature was continued to increase to $140\text{ }^{\circ}\text{C}$ (Figure 1B). This is because the cycloaddition reaction of CO_2 and PO is exothermic, so too high a temperature will hinder the formation of cyclic carbonate. In addition, high temperatures will also lead to the polymerization of cyclic carbonate [39,40]. Based on the above study, $120\text{ }^{\circ}\text{C}$ was chosen as the optimal reaction temperature.

3.3. The Effect of CO_2 Pressure on Cycloaddition of PO and CO_2

CO_2 pressure affects the mass transfer kinetics of this cycloaddition reaction as well as the yield and selectivity of PC [41], so the relationship between pressure and yield was explored in the range of 0.5–5 MPa (Figure 1C). The yield of PC increased from 35% to 96% when the pressure was increased from 0.5 MPa to 1 MPa and decreased slightly to 94% when the pressure was continually increased to 2 MPa. Further raising the reaction pressure to 3 MPa and 5 MPa, the PC yield lowered to 73% and 66%, respectively. The increase in pressure makes the concentration of CO_2 in PO higher, which promotes the reaction. However, too high pressure will reduce the concentration of PO in the vicinity of the catalyst, which will bring down the catalytic activity and thus reduce the reaction rate and the PC yield [42,43]. Experimental results show that the optimal CO_2 pressure for this reaction is 1 MPa.

3.4. The Effect of the Ratio of PO to Catalyst on Cycloaddition of PO and CO₂

Figure 1D shows the effect of catalyst loadings on PC yield at 120 °C and 1 MPa CO₂. When the amount of catalyst was varied from 0.1 to 1 mol%, the PC yield dramatically improved from 10.2% to 93.2%. As the catalyst dosage increases, more catalytic active centers can be supplied to the catalytic system, so the PC yield is significantly increased [44]. However, further increasing the amount of the catalyst cannot lead to a big increase in the yield of carbonate; this may be due to the fact that the presence of excess catalyst makes its dispersion low in the system, thus hindering mass transfer between the catalyst active center and the reactants [45,46]. Therefore, the optimal ratio of catalyst to PO is 1:100.

3.5. Cycloaddition of CO₂ to PO by Various Bifunctional Catalysts

The catalytic performances of various bifunctional catalysts were investigated for the cycloaddition reaction of PO and CO₂ under optimal conditions (120 °C, 1 MPa, 3 h, 1:100). The corresponding results were summarized in Table 1. With the non-bifunctional complex C₀ or Et₃N as the sole catalyst, very low activity was observed (Table 1, entries 1,2). Using TBAC/Et₃N or C₀/Et₃N as two-component catalysts, the catalytic activity was clearly improved (Table 1, entries 4,5). However, under the same conditions, a high yield of 93.2% was obtained using a quaternary ammonium salt bifunctional complex of Zn-NPClH as the catalyst (Table 1, entry 6). The electron effect of different substituents on ligands can affect the catalytic activity, so the effect of different ligands with electron-donating or electron-withdrawing substituents on the catalytic results was investigated. Under the same condition, the catalytic activity of the catalyst differs as follows: Zn-NPClNO₂ > Zn-NPClCl > Zn-NPClH > Zn-NPClCH₃ > Zn-NPClC₄H₉ (-NO₂ > -Cl > -H > -CH₃ > -C₄H₉) (Table 1, entries 6–10). This result demonstrates that the catalytic effect was related to the electronegativity of the substituents on the catalyst, and catalysts with a strong electron-withdrawing substituent showed better catalytic activity. It could be attributed to the ability of the strong withdrawing substituent, which can reduce the electron cloud density of the metal complexes and enhance their Lewis acidity. We also studied the effect of different metal centers in coordination compounds on catalytic activity (Table 1, entries 6,11–14). The results showed that cobalt, zinc, lead, and nickel metal center complexes have relatively good catalytic activity but poor activity for the copper center; the activity order is Co-NPClH > Zn-NPClH > Pb-NPClH > Ni-NPClH > Cu-NPClH (Co > Zn > Pb > Ni > Cu). The catalytic activity of different metal centers is highly dependent on the metal center type, which may be related to the different coordination abilities of metal centers with PO, while the low activity of bifunctional complexes with Cu metal centers may be attributed to the low acidity of Cu centers [47,48]. The anion plays an important role in the reaction of the epoxide with CO₂ by nucleophilically attacking the epoxide to form a C-X bond to open its ring, so the anion species are screened. Accordingly, the more easily departed anion exhibits the best catalytic effect, which is consistent with the experimental results: I⁻ > Br⁻ > Cl⁻ (Table 1, entries 6, 15, 16). To our delight, by adjusting reaction factors (0.1 mol% Zn-NPClH, 150 °C, 0.5 h), a relatively high TOF could reach up to 1416 h⁻¹ with Zn-NPClH as catalyst (Table 1, entry 17).

3.6. Study of Catalytic Performance at Atmospheric Pressure

The catalytic activity of these bifunctional catalysts at atmospheric pressure has also been studied to meet the needs of sustainable development and green industrialization. The cycloaddition reaction of CO₂ with isopropyl glycidyl ether was used as a model reaction to study the catalytic activity of the bifunctional metal catalysts M-NPClH at 0.1 MPa (Figure 2). All catalysts showed good to excellent activity. Overall, the order of catalytic activity of different metals at atmospheric pressure was consistent with that at high pressure: Co-NPClH > Zn-NPClH > Pb-NPClH > Ni-NPClH > Cu-NPClH. Zn-NPClH, Co-NPClH, Pb-NPClH, and Ni-NPClH all catalyzed glycidyl isopropyl ether better, with the catalyst Co-NPClH reaching 96.4% yield after 14 h of continuous reaction.

Table 1. Effect of different kinds of catalyst systems on the coupling of CO₂ with PO^a.

| Entry | Catalyst | Yield (%) ^b | TON ^c | TOF (h ⁻¹) ^d | Selectivity (%) ^b |
|-----------------|--------------------------------------|------------------------|------------------|-------------------------------------|------------------------------|
| 1 | C ₀ | 2.5 | 2.5 | 0.8 | >99 |
| 2 | Et ₃ N | 0.6 | 0.6 | 0.2 | >99 |
| 3 | TBAC | 20.3 | 20.3 | 6.8 | >99 |
| 4 | TBAC/Et ₃ N | 40.4 | 40.4 | 13.5 | >99 |
| 5 | C ₀ /Et ₃ N | 68.8 | 68.8 | 22.9 | >99 |
| 6 | Zn-NPClH | 93.2 | 93.2 | 31.1 | >99 |
| 7 | Zn-NPClCl | 95.4 | 95.4 | 31.8 | >99 |
| 8 | Zn-NPClNO ₂ | 96.9 | 96.9 | 32.3 | >99 |
| 9 | Zn-NPClCH ₃ | 90.8 | 90.8 | 30.3 | >99 |
| 10 | Zn-NPClC ₄ H ₉ | 89.5 | 89.5 | 29.8 | >99 |
| 11 | Co-NPClH | 98.6 | 98.6 | 32.9 | >99 |
| 12 | Pb-NPClH | 89.0 | 89.0 | 29.7 | >99 |
| 13 | Ni-NPClH | 83.3 | 83.3 | 27.8 | >99 |
| 14 | Cu-NPClH | 61.2 | 61.2 | 20.4 | >99 |
| 15 | Zn-NPBrH | 95.6 | 95.6 | 31.9 | >99 |
| 16 | Zn-NPIH | 96.3 | 96.3 | 32.1 | >99 |
| 17 ^e | Zn-NPClH | 70.8 | 708 | 1416 | 98 |

^a Reaction conditions: PO (10 mL, 0.143 mol), Catalyst loading = 1 mol%, $t = 3$ h, $T = 120$ °C, $P = 1$ MPa. ^b Results determined by ¹H NMR. ^c TON = n (product)/ n (catalyst). ^d TOF = TON/reaction time. ^e Reaction conditions: PO (10 mL, 0.143 mol), Catalyst loading = 0.1 mol%, $t = 0.5$ h, $T = 150$ °C, $P = 1$ MPa.

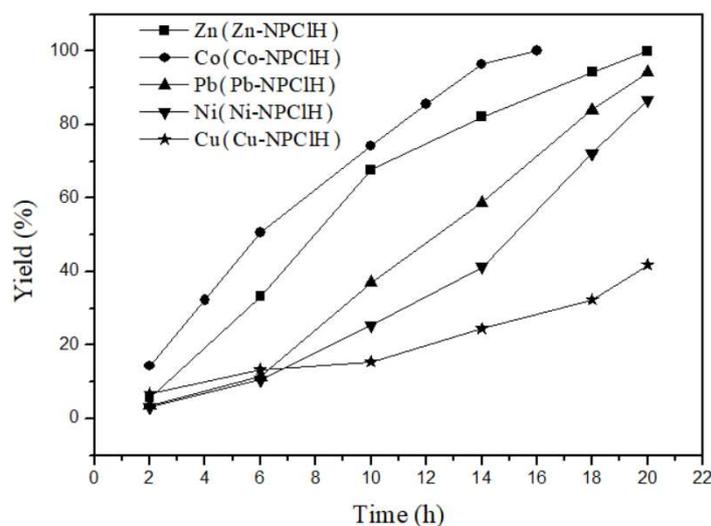


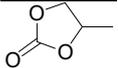
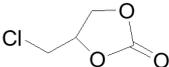
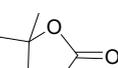
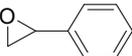
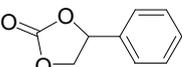
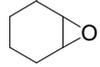
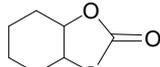
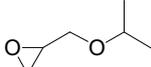
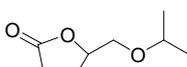
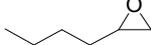
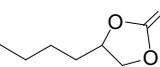
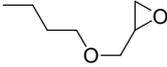
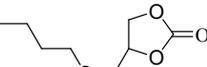
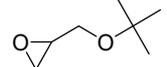
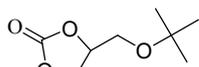
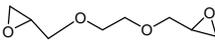
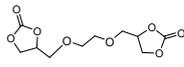
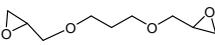
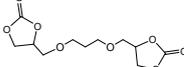
Figure 2. The quaternary ammonium catalyst system reaction of carbon dioxide and glycidyl isopropyl ether at atmospheric pressure. Reaction conditions: glycidyl isopropyl ether (5 mL, 0.071 mol), catalyst Zn-NPClH (0.71 mmol, 1 mol%), $T = 120$ °C, $P = 0.1$ MPa. The selectivity of PC was >99%.

3.7. Substrate Scope of CO₂/Epoxide Coupling

In order to investigate the generalizability of the bifunctional catalyst to other cycloaddition reactions of epoxides with CO₂, we examined the adaptation of the bifunctional catalyst Zn-NPClH to a variety of epoxyalkane substrates under the above-mentioned optimized conditions, and the results are shown in Table 2 (Condition A). The results show that the catalyst system is effective in converting the studied common epoxides to their corresponding cyclic carbonates. For terminal epoxides, better yields of substrates with either electron-absorbing or electron-donating groups attached were obtained with the activation of the catalyst (Table 2, entries 1–2, 7–9). The nucleophilic attack of the epoxide by chloride ions is hindered by the high spatial site resistance of the epoxide environment, resulting in very low yields of dimethyloxirane, cyclohexene oxide, and 1,2-epoxyphenylethane (Table 2, entries 3–6), as previously reported in the literature [49–51]. In addition, the epoxide substrates of the glycidyl ether series can also be coupled with carbon dioxide,

as in the case of dicyclic oxides, which can also be well formed as cyclic carbonates of the corresponding dicyclic ring. It is worth pointing out that bicyclic carbonates can be used as raw materials to produce non-isocyanate polyurethanes (NIPUs) by reacting with polyfunctional primary amines, which have important applications in industry [52,53].

Table 2. Cycloaddition between CO₂ and various epoxides catalyzed by Zn-NPClH.

| Entry | Epoxide | Product | Condition A ^a | | Condition B ^b | |
|-------|---|--|--------------------------|-----------|--------------------------|-----------------|
| | | | <i>t</i> (h) | Yield (%) | <i>t</i> (h) | Yield (%) |
| 1 |  |  | 3 | 96 | - | - |
| 2 |  |  | 3 | 97 | - | - |
| 3 |  |  | 10 | 32 | - | - |
| 4 |  |  | 10 | 91 | 24 | 99 |
| 5 |  |  | 10 | 22 | 24 | 21 |
| 6 |  |  | 10 | 96 | 24 | 88 |
| 7 |  |  | 3 | 94 | 24 | 72 |
| 8 |  |  | 3 | 90 | 24 | 90 |
| 9 |  |  | 3 | 88 | 24 | 88 |
| 10 |  |  | 3 | 61 | 24 | 68 ^c |
| 11 |  |  | 3 | 52 | 24 | 62 |

^a Reaction conditions: 1 mol% Zn-NPClH, 0.143 mol epoxide; CO₂ pressure 1 MPa; temperature 120 °C, the selectivity was determined by ¹H NMR to be >99%. ^b Reaction conditions: 1 mol% Zn-NPClH, 0.143 mol epoxide; CO₂ pressure 0.1 MPa; temperature 120 °C; the selectivity was determined by ¹H NMR to be >99%. ^c Reaction temperature 110 °C.

The application of various epoxides with a higher boiling point (>110 °C) to couple with CO₂ was also tested at atmospheric pressure. Although a longer time was necessary for the challenging epoxides (Table 2, Condition B), these bifunctional catalysts are generally still workable for a wide scope of epoxides, even under 0.1 MPa.

3.8. Catalyst Recycling

The reuse of catalysts in industry will not only reduce costs, but their reusability also reflects the stability of the catalyst under reaction conditions. Using Zn-PPBCl as a catalyst to catalyze the formation of PC from CO₂ and PO as a model reaction, its reusability performance under optimal conditions was investigated. The synthesized Zn-PPBCl could be reused at least five times without significant loss of catalytic activity and selectivity (Figure 3). In addition, to further investigate the stability of this catalyst, the structures of

both the 5-cycle and fresh catalysts were also characterized by IR. As shown in Figure 4, the structure of the catalyst was maintained after five times of reuse, which proves that the synthesized catalyst is not only efficient but also stable and reusable.

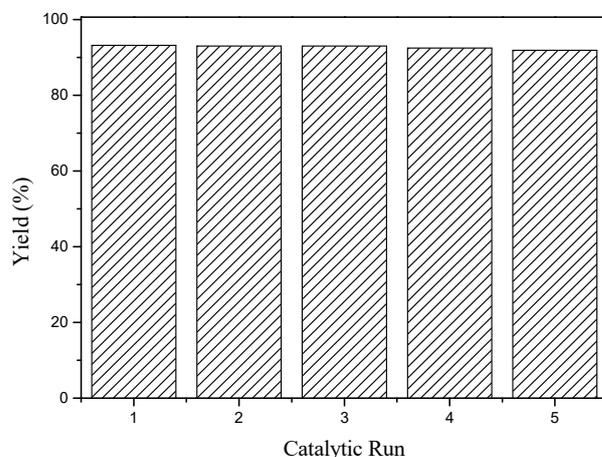


Figure 3. Reutilization of the Zn-NPClH catalyst. PO (10 mL, 0.143 mol), catalyst Zn-NPClH (1.43 mmol, 1 mol%), $t = 3$ h, $T = 120$ °C, $P = 1$ MPa. The selectivity of PC was >99%.

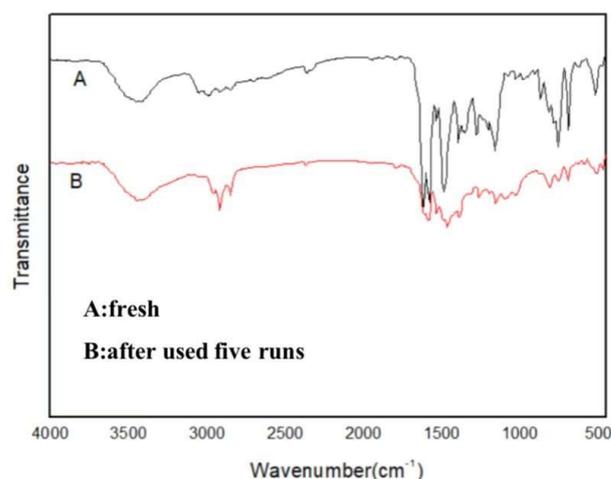


Figure 4. The FT-IR spectra of fresh catalyst and that used after five runs.

3.9. Kinetic Studies

Kinetics study of the cycloaddition reaction using glycidyl isopropyl ether (GIE) as substrate using three bifunctional quaternary ammonium metal catalysts M-NPClH (M = Zn, Co, Ni) at 1 atm CO₂ pressure (see the ESI, Table S2: Structure of ligands-S15: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Ni-NPClH at 393 K). The activation energies (E_a) for the three catalysts were 30.8 kJ/mol (Zn), 26.1 kJ/mol (Co), and 32.9 kJ/mol (Ni), respectively, which were consistent with the order of catalytic activity (Figures 4–6). The higher conversion obtained with Co-NPClH could likely be attributed to the higher Lewis acidity of the Co center compared with other metal centers [54].

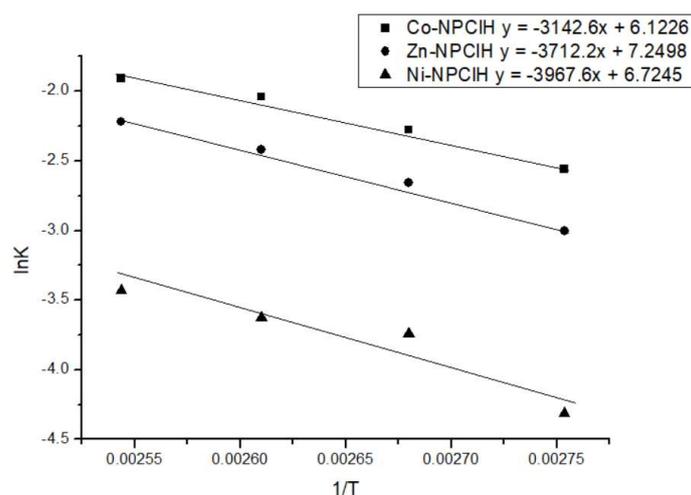


Figure 5. Arrhenius plots for the formation of cyclic carbonate from the cycloaddition of CO₂ and GIE using catalysts M–NPClH.

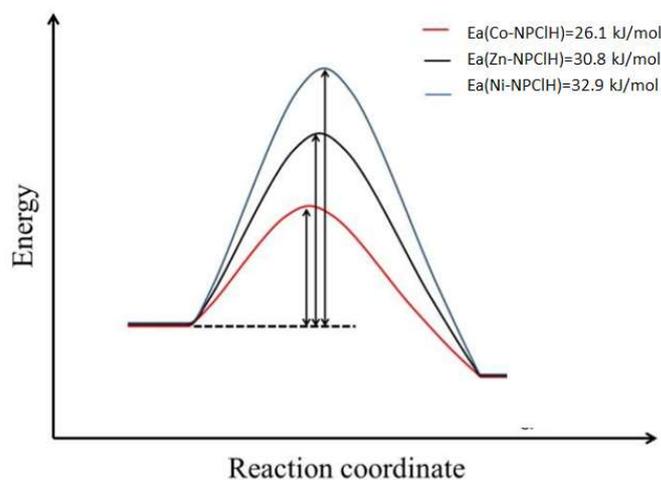
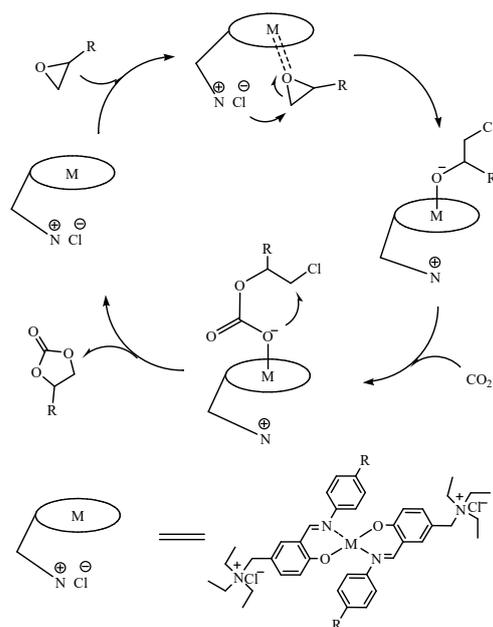


Figure 6. The activation energies (E_a) for the cycloaddition of CO₂ and GIE catalyzed by M-NPClH.

4. Proposed Reaction Mechanism

Based on the experimental results, kinetic study analysis, and previously reported literature [53,54], we proposed a possible mechanism for the cycloaddition reaction of CO₂ with epoxide (Scheme 3). The metal center of the catalyst activates the oxygen on the epoxide, and the halogen ion on the functional group of the bifunctional metal complex catalyst nucleophilically attacks the less site-resistant carbon on the epoxide, causing the epoxide to undergo a ring-opening step to form a metal alcohol salt intermediate. At the same time, CO₂ is inserted into this intermediate to form a metal carboxylate. Finally, the oxygen anion of the intermediate attacks the C-X bond, closing the loop to form propylene carbonate while completing the catalytic cycle to release the catalyst.



Scheme 3. Proposed mechanism for the coupling reaction of CO₂ with epoxide.

5. Conclusions

The coupling reactions of various epoxides with CO₂ were successfully achieved by using halogenated quaternary ammonium salt metal complex catalysts without the addition of co-catalysts and solvents. When using Co-NPClH as a catalyst to promote the reaction with PO, the conversion was 98.6% and the PC selectivity was 99% under the optimal conditions (120 °C, 1 MPa CO₂, and 1.0 mol% Co-NPClH). In addition, the synthesized bifunctional catalysts can be reused by simple operations and reused at least five times with essentially no decrease in activity or selectivity. The kinetic studies using catalysts M-NPClH (M = Co, Zn, Ni) are documented for the cycloaddition of GIE and CO₂, in which the apparent activation energies (E_a) are 26.1, 30.8, and 32.9 kJ/mol, respectively. The series of bifunctional metal catalysts synthesized in this study exhibited excellent catalytic performance, high TOF values, and strong stability, which proved the potential of these catalysts for industrial applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma16041646/s1>, Table S1: Provenance and mass fraction purity of the materials. Table S2: Structure of ligands. Table S3: Structure of catalysts. Figure S1: ¹H NMR and ¹³C NMR spectra for NPCl in DMSO-d₆. Figure S2: ¹H NMR and ¹³C NMR spectra for Zn-NPClH in DMSO-d₆. Figure S3: ¹H NMR spectrum for Zn-NPClCH₃ in DMSO-d₆. Figure S4: ¹H NMR and ¹³C NMR spectra for Zn-NPClCl in DMSO-d₆. Figure S5: ¹H NMR spectrum for Zn-NPClNO₂ in DMSO-d₆. Figure S6: ¹H NMR and ¹³C NMR spectra for Zn-NPClC₄H₉ in DMSO-d₆. Table S4. Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Zn-NPClH at 363 K. Table S5: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Zn-NPClH at 373 K. Table S6: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Zn-NPClH at 383 K. Table S7: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Zn-NPClH at 393 K. Figure S7: Logarithmic plots of (1 - x) versus time by Zn-NPClH at 363–393 K. Table S8: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Co-NPClH at 363 K. Table S9: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Co-NPClH at 373 K. Table S10: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Co-NPClH at 383 K. Table S11: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Co-NPClH at 393 K. Figure S8: Logarithmic plots of (1 - x) versus time by Co-NPClH at 363–393 K. Table S12: Effects

of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Ni-NPCIH at 363 K. Table S13: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Ni-NPCIH at 373 K. Table S14: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Ni-NPCIH at 383 K. Table S15: Effects of the reaction time on cycloaddition of CO₂ and glycidyl isopropyl ether at atmospheric pressure by Ni-NPCIH at 393 K. Figure S9. Logarithmic plots of (1 - x) versus time by Ni-NPCIH at 363–393 K.

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