



Qin Wen¹, Xuexin Yuan¹, Qiqi Zhou¹, Hai-Jian Yang^{1,*}, Qingqing Jiang¹, Juncheng Hu¹ and Cun-Yue Guo^{2,*}

- ¹ College of Chemistry and Materials Science, South-Central Minzu University, Wuhan 430074, China
- ² School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

* Correspondence: yanghaijian@vip.sina.com (H.-J.Y.); cyguo@ucas.ac.cn (C.-Y.G.)

Abstract: Ammonium, imidazole, or pyridinium functionalized β -cyclodextrins (β -CDs) were used as efficient one-component bifunctional catalysts for the coupling reaction of carbon dioxide (CO₂) and epoxide without the addition of solvent and metal. The influence of different catalysts and reaction parameters on the catalytic performance were examined in detail. Under optimal conditions, Im-CD1-I catalysts functionalized with imidazole groups were able to convert various epoxides into target products with high selectivity and good conversion rates. The one-component bifunctional catalysts can also be recovered easily by filtration and reused at least for five times with only slight decrease in catalytic performance. Finally, a possible process for hydroxyl group-assisted ring-opening of epoxide and functionalized group- induced activation of CO₂ was presented.

Keywords: carbon dioxide fixation; functionalized β -cyclodextrins; solvent- and metal-free catalysis; environment-friendliness; cyclic carbonate

1. Introduction

 CO_2 has been attracting much attention because of its unique properties, such as nontoxicity, low cost, bio-renewability and C1 building block for organic synthesis, and so on [1–4]. During past decades, a great deal of efforts has been devoted to investigating efficient procedures for CO_2 fixation to produce valuable products. The formation of cyclic carbonates via cycloaddition of CO_2 with epoxides is among the most potential ways, and the obtained cyclic carbonates are used widely as aprotic polar solvents, precursors for polymerization reactions, electrolytes for lithium-ion batteries, and fine chemical intermediates [5–9]. Mechanistically, the Lewis acid center (e.g., metal center or H) ligates with the O of the epoxide to activate the epoxide substrate, while the Lweis base (e.g., halogen anion) acts as a nucleophilic reagent to open the ring of the epoxide so that the next steps such as CO_2 insertion and intramolecular cyclization occur [10–12]. Therefore, various catalytic systems such as metal complexes [13–19], metal oxides [20–23], metalloporphyrins [24–30], ionic liquids [31–35], functional polymers [36–40], organocatalysts [41–48], metal-organic frameworks (MOFs) [49–59], mesoporous materials [60–65] and biomass [66–86] have been developed to promote such reaction up to now.

Though significant improvements in catalyst species have been achieved, some drawbacks such as scarce active sites and low carrier still remain to be overcome for effective chemical conversion of CO_2 via its coupling reaction with epoxides [87,88]. Moreover, in many cases harsh reaction conditions (e.g., high pressure and/or high temperature) and participation of co-solvent/additive are generally required. Furthermore, accompanying issues of inherent corrosion, toxicity and environmental concerns associated with the use of metallic cations remain challenging. Therefore, it is very demanding to put forward efficient environment-friendly catalysts for the coupling reaction of carbon dioxide and epoxide.

Regarding catalysts reported so far, biomass-based environment-friendly catalysts have drawn great attention such as betaine [68], lecithin [70], sugarcane bagasse [77],



 $\label{eq:citation: Wen, Q.; Yuan, X.; Zhou, Q.; } \\ Yang, H.-J.; Jiang, Q.; Hu, J.; Guo, C.-Y. \\ Functionalized β-Cyclodextrins \\ Catalyzed Environment-Friendly \\ Cycloaddition of Carbon Dioxide and \\ Epoxides.$ *Materials***2023**,*16* $, 53. \\ https://doi.org/10.3390/ma16010053 \\ \end{cases}$

Academic Editor: Haris Ishaq

Received: 27 November 2022 Revised: 17 December 2022 Accepted: 19 December 2022 Published: 21 December 2022



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). chitosan-based [66,67,71,73,76], cellulose-based [69,72,74,75,78], chitin-supported [83] compounds, Xylan [89] and β -CD [90,91]. β -CD, a well-known inexpensive, stable, and readily available natural hydrogen bond donor, is of abundant hydroxyl groups. In 2008, Han et al. firstly reported an efficient catalytic system of β -CD/KI for CO₂ cycloaddition with epoxides [90]. This work broadened the application of β -CD in CO₂ fixation and more β -CD-based catalytic systems are highly expected. Unfortunately, there has been no substantial advance in this field until 2017 when an efficient [DBUH][PFPhO]/ β -CD system was developed in Hou's group [91]. However, functionalized β -CDs as efficient catalytic systems compared to other biological materials are still rarely reported. Therefore, ammonium functionalized bis- β -CDs as effective catalysts were synthesized in our group to catalyze the coupling reaction of CO₂ and epoxides [84].

Although the catalytic results are positive and encouraging, the synthesis and yield of modified bis- β -CDs are difficult. Young and Ng et al. synthesized a series of functionalized β -CDs by displacing 6-tosyl- β -CD with alkylamines, pyridinium or alkylimidazoles via easy ways [92]. Inspired by their work, we herein designed and synthesized a series of functionalized β -CDs to be as one-component catalysts, in which hydroxyl groups were functionalized as Lewis acid to activate the epoxide and halide ions were functionalized as Lewis base to promote the ring-opening step. The catalytic performance of newly synthesized, functionalized β -CD for the coupling reaction of CO₂ and epoxides were systematically investigated without adding co-catalyst and solvent. Moreover, these β -CD based catalysts can be reused conveniently, which is important for developing practical processes. Furthermore, a synergistic mechanism involved hydroxyl group and halide ion was discussed based on the literatures and experimental results. This ecologically safe, simple, inexpensive catalytic system has potential of CO₂ conversion at the industrial level in the future.

2. Materials and Methods

2.1. Chemicals and Analytical Methods

All the chemicals were purchased from Acros and used as received except for epoxides which were purified by distillation from CaH₂ before use. A Bruker Al-400 MHz instrument manufactured by Bruker Technologies Switzerland Ltd., Fällanden, Switzerland, was used for recording NMR spectra using TMS as an internal standard.

2.2. Synthesis of Functionalized β -CDs

The ammonium, imidazole, and pyridinium functionalized β -CDs (Scheme 1) were exactly synthesized and characterized according to previously reported methods [92]. After synthesis and purification following the reported procedures, these functionalized β -CDs were directly employed to initiate CO₂ coupling reaction with epoxides.



Scheme 1. Structures of β -CD and various functionalized β -CDs.

2.3. General Procedure for Cyclic Carbonates Synthesis from Epoxides and CO₂

Cycloaddition reaction of CO_2 and epoxide was conducted in a 250 mL stainless steel autoclave. In a typical reaction, predetermined amounts of catalyst and epoxide were fed into the reactor, CO_2 was then added into the reactor at certain pressure. The autoclave was sealed and then immersed into an oil bath at preset temperature with stirring. The reactor was cooled down in an ice-water bath after predesigned time and the unreacted CO_2 was released slowly. The yield and selectivity are determined by ¹H NMR characterization.

3. Results and Discussion

3.1. Effect of Reaction Parameters with Am-CD1-I

Reaction conditions were screened for optimizing the catalytic activity based on the ammonium functionalized β -CD Am-CD1-I and the coupling reaction of CO₂ and propylene oxide (PO). The reaction conditions as collected in Figure 1 were standardized by observing the effect of reaction temperature, pressure, time, and catalyst loading on the yield of propylene carbonate (PC).



Figure 1. Effects of different reaction parameters on PC yield over Am-CD1-I: (**a**) Effects of reaction temperature, conditions: PO (5 mL, 71.5 mmol), Am-CD1-I (0.2 mol%), CO₂ pressure 3 MPa, time 5 h; (**b**) Effects of CO₂ pressure, conditions: PO (5 mL, 71.5 mmol), Am-CD1-I (0.2 mol%), reaction temperature 130 °C, time 5 h. (**c**) Effects of reaction time, conditions: PO (5 mL, 71.5 mmol), Am-CD1-I (0.2 mol%), reaction time 130 °C, CO₂ pressure 3 MPa. (**d**) Effects of catalyst loading, conditions: PO (5 mL, 71.5 mmol), reaction time 130 °C, CO₂ pressure 3 MPa. (**d**) Effects of the function time 5 h.

The reaction temperature was first investigated to test its effect on the PC yield. Figure 1a displays a strong effect of temperature on the PO conversion. A high reaction temperature is favorable for the synthesis of PC, indicating that the cycloaddition reaction was thermodynamically favorable [93,94]. To our satisfaction, low temperature appears insensitive to the PC selectivity in view of the fact that low temperature would be favorable for producing polycarbonate. Considering that polymerization of cyclic carbonates occurs at higher temperatures [95] and has adverse effect on the equipment, an optimal reaction temperature of 130 °C was selected for following studies.

Figure 1b reflects the influence of the CO₂ pressure on the PC yield. Low pressures ranging from 0.5 to 1.0 MPa gave rise to increase in the PC yield. The PC yield decreased in high-pressure range (3.0–5.0 MPa) after a plateau from 1.0 to 3.0 MPa of CO₂ pressure. Such phenomenon is observed as well in other catalytic systems [96–98]. It could be explained

that in the low-pressure region, the increase in CO_2 pressure enhanced PC yield due to higher CO_2 concentration in the liquid phase. However, much higher CO_2 pressure would lower the PC yield due to decreased PO concentration around the catalyst, this is not favorable for the cycloaddition because PO is another reactant [99,100]. As a result, a maximal PC yield was obtained.

The PC yield increased steadily with reaction time until 7 h and the coupling reaction proceeded rapidly within the first 5 h, and no appreciable increment in PC yield was observed thereafter (Figure 1c). This might originate from a hampered interaction between the catalyst and reactant due to the formation of PC [101]. A more viscous reaction system after prolonged reaction time was another negative factor disfavoring the activation of CO₂. Thus, the reaction time of 5 h was chosen to be optimal. Increasing of the catalyst loading from 0.14 mol% to 1 mol% led to rising catalytic activity (Figure 1d). However, there was a decrease in the PC yield for the reaction conducted with 2 mol% catalyst, which may be from a hindered mass transfer due to excess catalyst. Thus, 1 mol% **Am-CD1-I** is optimum for this work and selected for subsequent research.

3.2. Effect of Reaction Parameters over Im-CD1-I

Inspired by the high performance of ammonium functionalized β -CD Am-CD1-I, the imidazole functionalized β -CD Im-CD1-I was also attempted to catalyze the cycloaddition of CO₂ and PO. PC yields catalyzed by Im-CD1-I trended similarly to those in the case of using Am-CD1-I (Figure 2). The reaction temperature also affected the PC yield and 110 °C is chosen to be optimal (Figure 2a). The PC formation with Im-CD1-I correlated with CO₂ pressure (Figure 2b). The peak PC yield appeared at 3 MPa and much higher CO₂ pressure resulted in decreased yield. Moreover, prolonged reaction time exceeding 3 h failed in further increasing PC yield (Figure 2c). The PC yield at the low catalyst loading (0.14–0.33 mol%) rose with increasing catalyst loading, realizing a drastic elevation in PC yield. However, a further increase in catalyst loading contributed little to PC yield (Figure 2d). To sum up, the optimal condition of the cycloaddition over Im-CD1-I is 110 °C, 3 MPa, 3 h and 0.33 mol%.



Figure 2. Effects of different reaction parameters on PC yield over Im-CD1-I: (**a**) Effects of reaction temperature, conditions: PO (5 mL, 71.5 mmol), Im-CD1-I (0.33 mol%), CO₂ pressure 2 MPa, time 3 h; (**b**) Effects of CO₂ pressure, conditions: PO (5 mL, 71.5 mmol), Im-CD1-I (0.33 mol%), reaction temperature 110 °C, time 3 h; (**c**) Effects of reaction time, conditions: PO (5 mL, 71.5 mmol), Im-CD1-I (0.33 mol%), reaction time 110 °C, CO₂ pressure 3 MPa; (**d**) Effects of catalyst loading, conditions: PO (5 mL, 71.5 mmol), reaction time 110 °C, CO₂ pressure 3 MPa, reaction time 3 h.

Comparison of the optimal conditions for Am-CD1-I and Im-CD1-I (130 °C, 1 MPa, 5 h, 1 mol% Am-CD1-I vs. 110 °C, 3 MPa, 3 h, 0.33 mol% Im-CD1-I) found that ammonium functionalized β -CD Am-CD1-I required higher reaction temperature and more time, along with higher catalyst loading, while the imidazole functionalized β -CD Im-CD1-I only required relatively higher CO₂ pressure, which may be due to the different solubility of the two functional β -CDs in the reaction system. In general, the optimal condition for Im-CD1-I is milder than that forAm-CD1-I, reflecting the superiority of imidazole functionalized β -CDs catalysts although Im-CD1-I and Am-CD1-I are both metal-, solvent-and cocatalyst-free.

3.3. Catalytic Performances of Various Catalysts

Under optimal conditions, solvent-free synthesis of PC from CO_2 and PO catalyzed by ammonium, imidazole, and pyridinium functionalized β -CDs was investigated. As listed in Table 1, most of functionalized β -CDs afforded excellent selectivity for PC. The reason for such a high selectivity of this reaction is due to the tendency of the X^{-} ion to attack the C with small site resistance during the nucleophilic attack on the epoxide to open its ring. The details will be shown in the description of the mechanism section. For various catalysts, the catalytic activities correlated with their structures. The mono-6-halide- β -CDs can convert PO in quantitative yields (Table 1, entries 1–3), suggesting synergetic effect of rich hydroxyl groups and halide ions in the modified β -CDs. The synergetic effect of these two functional groups has been reported and testified using a DFT calculation by Zhang et al. [102]. Moreover, when β -CD was modified by ammonium, imidazole, and pyridinium, the catalyst performance was improved visibly. For the ammonium functionalized β -CDs (Table 1, entries 4–9), higher catalytic activities of Am-CD1-I and Am-CD2-I are attributed to bulky alkyl on the butyl amine group. The more-bulky butyl on the amine group might form a more flexible ion pair with I-, thus increasing its nucleophilicity and making it the most viable catalyst [103,104]. For both mono-6-halide- β -CDs and functionalized β -CDs, the activity for various halogen anions decreases in the order of $I^- > Br^- > Cl^-$ (Table 1, entries 1–3,5–7,13–15) probably owing to the leaving ability and nucleophilicity of the anion [105,106]. To study the effect of imidazole functionalized β -CD structure on the catalytic activity, a milder reaction condition was conducted afterwards. A longer alkyl chain endowed imidazole functionalized β -CD with higher catalytic performance (Table 1, entries 16–18) because a long alkyl chain may weaken electrostatic interaction, thus enhancing the nucleophilicity of anion [107]. The ammonium, imidazole, and pyridinium functionalized β -CDs played quite well in coupling reaction between CO_2 and epoxides with much better performance compared with binary catalytic system β -CD/KI [90] or β -CD/TBAI [108], because our catalyst only required lower CO₂ pressure and catalyst loading without adding metal and additive.

3.4. Recycling Test

A series of reaction recycles using Am-CD1-I and Im-CD1-I as catalysts were performed to investigate the stability of the catalyst for the cycloaddition reaction of PO with CO₂ under each optimal condition. In each cycle, Am-CD1-I and Im-CD1-I were recovered via simple filtration, washed with acetone, dried in vacuo and directly reused for the next cycle. As Figure 3 presents, both Am-CD1-I and Im-CD1-I can be reused for at least 5 times without obvious loss in catalytic activity. In order to confirm the stability of Im-CD1-I (showing slight decrease after 5 times of recycling, Figure 3), the reused Im-CD1-I was characterized by FT-IR analysis. Strong characteristic bands assigned to the in-plane C-H deformation vibration and in-plane C-C and C-N stretching vibration of the imidazole ring (1629 and 1318 cm⁻¹), along with the characteristic band of C-I bond at 604 cm⁻¹ remain after reuse (Figure 4), indicating a very stable Im-CD1-I for this reaction. As shown in Figure 4, the structure of the catalyst was maintained after five times of reuse, which proved the stability and reusability of the synthesized catalyst, and the slight decrease in the catalytic effect after five times of use might be due to the partial loss of catalyst during the recycling process.

Entry	Catalyst	Yield (%) ^b	Selectivity (%) ^b	TON ^c	TOF (h ⁻¹) ^d
1	β-CD-I	78	99	78	16
2	β-CD-Br	65	99	65	13
3	β-CD-Cl	60	99	60	12
4	Am-CD1-I	97	99	97	19
5	Am-CD2-I	96	99	96	19
6	Am-CD2-Br	89	99	89	18
7	Am-CD2-Cl	79	99	79	16
8	Am-CD3-I	90	99	90	18
9	Am-CD4-I	84	99	84	17
10 ^e	β-CD-I	26	98	80	27
11 ^e	β-CD-Br	20	99	61	20
12 ^e	β-CD-Cl	3	99	9	3
13 ^e	Im-CD1-I	98	99	297	99
14 ^e	Im-CD1-Br	91	98	276	92
15 ^e	Im-CD1-Cl	3	99	10	3
16 ^f	Im-CD1-I	80	99	320	107
17 ^f	Im-CD2-I	90	98	360	120
18 ^f	Im-CD3-I	92	99	367	122
19 ^e	Py-CD-I	89	99	271	90
20 ^g	β-CD/KI	98	99	223	56

Table 1. Results of coupling reaction of CO₂ and PO catalyzed by various catalysts ^a.

^a Reaction conditions: PO (5 mL, 71.5 mmol), catalyst 1 mol%, CO₂ pressure 1 MPa, reaction temperature 130 °C, reaction time 5 h. ^b Determined by ¹H NMR spectra analysis using TMS as an internal standard. ^c Turnover number for PC calculated as mole of PC produced per mole of catalyst. ^d Turnover frequency for PC calculated as mole of PC produced per hour. ^e Reaction conditions: PO (5 mL, 71.5 mmol), catalyst 0.33 mol%, CO₂ pressure 3 MPa, reaction temperature 110 °C, reaction time 3 h. ^f Reaction conditions: Catalyst 0.25 mol%. ^g Reaction conditions: PO (22 mmol), β-CD 0.1 g, KI 2.5 mol%, CO₂ pressure 6 MPa, reaction temperature 120 °C, reaction time 4 h.



Figure 3. Catalyst recycling for coupling reaction catalyzed by Am-CD2-I and Im-CD1-I. Reaction condition for Am-CD2-I: PO (5 mL, 71.5 mmol), Am-CD2-I (1 mol%), CO₂ pressure 1 MPa, reaction temperature 130 °C, time 5 h. Reaction condition for Im-CD1-I: PO (5 mL, 71.5 mmol), Im-CD1-I (0.33 mol%), CO₂ pressure 3 MPa, reaction temperature 110 °C, time 3 h. The selectivity for target products are all > 99%.

3.5. Cycloaddition of Various Epoxides and CO₂

To probe the prospect and versatility of as-synthesized functionalized β -CD catalyst, the cycloaddition reaction of CO₂ with various epoxides with Im-CD1-Iwas studied (Table 2). Im-CD1-I worked well towards various epoxides possessing both electron-withdrawing and electron-donating substituents, forming respective cyclic carbonates with excellent selectivity and good yields. For isobutyl oxide (Table 2, entry 7) and cyclohexene oxide (Table 2, entry 8), identical reaction conditions gave rise to relatively low yield possibly due to that a steric hindrance obstructed the nucleophilic attack of the epoxide while its coordination to the Lewis acid metal center benefited the yield [108–111]. The aliphatic substituted epoxides (including PO in Table 1) were transformed with CO₂ to desired products in good yields. Especially, the activated epoxide epichlorohydrin was

converted by as-designed catalysts and transformed into respective cyclic carbonate in good yield in 3 h (Table 2, entry 1). Surprisingly, aromatic substituted epoxide styrene oxide reacted with CO₂ in a yield of 100% (Table 2, entry 3). Furthermore, the glycidyl ethers were turned into corresponding carbonates in good yields from 75 to 98% (Table 2, entries 4–6). It is also noteworthy that the Im-CD1-I catalyzed the diepoxides to produce respective bicyclic carbonates as well (Table 2, entries 10,11), raw materials for synthesizing non-isocyanate polyurethanes (NIPUs) without using toxic phosgene or isocyanates via the reaction with polyfunctional primary amines [112–114]. With increasing aliphatic chain length, the addition of CO₂ was hindered because of chain folding or the fluidity of chains and the hindrance of methylene groups. Such phenomenon was also observed by Qin et al. [115–117].



Figure 4. FT–IR spectra of Im-CD1-I and Im-CD1-I after five catalytic runs. Reaction condition: PO (5 mL, 71.5 mmol), Im-CD1-I (0.33 mol%), CO₂ pressure 3 MPa, reaction temperature 110 °C, time 3 h.

Table 2. Cycloaddition between CO₂ and various epoxides catalyzed by Im-CD1-I^a.

Entry	Epoxide	Product	Yield (%) ^b	Selectivity (%) ^b	TON ^c	TOF (h ⁻¹) ^d
1 ^e	cı	CI CI	86	99	259	86
2	∽,∽,⊂		80	98	240	10
3			100	99	300	13
4	ot		75	98	226	9
5	0-0-		88	99	265	11
6			98	99	294	12
7	-		38	98	115	5
8	$\bigcirc \circ$	⊂o>=o	6	99	17	1
10	2 jo	je je	86	99	259	11
11	Å_o		98	98	294	12

^a Reaction conditions: Im-CD1-I (0.33 mol%), epoxide (71.5 mmol), reaction temperature 110 °C, pressure 3 MPa, reaction time 24 h. ^b Determined by ¹H NMR spectra analysis using TMS as an internal standard. ^c TON for cyclic carbonate calculated as mole of cyclic carbonate produced per mole of catalyst. ^d TOF for cyclic carbonate calculated as mole of cyclic carbonate produced per mole of catalyst per hour. ^e Reaction time 3 h.

3.6. Proposed Mechanism

A mechanism is proposed for the functionalized β -CD catalyzed reaction as shown in Scheme 2 based on experimental results and literatures [118]. Firstly, the interaction between the epoxide oxygen and hydroxyl groups of Im-CD1-I promoted the polarization of the C-O bond in epoxide as reported in literature [119–123]. Simultaneously, CO₂ was activated by functionalized group, such as imidazole herein. Moreover, the imidazolium cations could also stabilize the metal-alkoxide bond through charge interactions, which would help explain the superior performance of imidazole, ammonium, or pyridinium functionalized β -CDs than mono-6-halide- β -CDs. Subsequently, the nucleophilic halide anion attacked the less hindered carbon atom of epoxide followed by ring opening step to form an intermediate of oxygen anion. The oxygen anion intermediate then reacted with activated CO₂ to form a carbonate anion, followed by an intramolecular ring-closure step to produce cyclic carbonate and regenerate the catalyst. According to this mechanism, the cooperative effect between the electrophile (hydrogen bond) and nucleophile (flexible halide anion) in the same catalyst molecules could effectively promote the coupling reaction in an eco-friendly mode without the introduction of metal, additive, and solvent [124,125].

3.7. Comparison of Different Biological Catalytic Systems

Catalytic activities of as-synthesized functionalized β -CDs in the coupling reaction of CO₂ and PO are compared with those of other biological catalyst systems reported in literature [66–78,83,89–91]. Though the reaction conditions differ from each other to some extent (reaction temperature: 100–140 °C; CO₂ pressure: 1.17–8 MPa; reaction time: 1–10 h; yield: 85–100%; TOF: 5–81 h⁻¹), approximate comparison is reasonable. Compared with either β -CD-based catalytic systems [90,91], or other biological catalytic systems [66–78,83], the as-synthesized functionalized β -CDs Am-CD2-I, Im-CD1-I and Py-CD-I demonstrated better performance as indicated by significantly higher yield values (96% for Am-CD2-I and 98% for Im-CD1-I) than the yield of 85% for the Xylan/DBU catalytic system [89] in addition to metal- and cocatalyst-free conditions adopted in this work. The comprehensive catalytic performance of the present catalysts is also better than that of MOFs and metal oxides [22,49,54]. Overall, the functionalized β -CDs utilized in this work are among excellent catalysts in comparison to most of efficient biological catalyst systems reported so far.



Scheme 2. Proposed mechanism.

4. Conclusions

A series of imidazole, ammonium, and pyridinium functionalized β -CDs were first employed as a one-component and recyclable catalyst for the coupling reaction between various epoxides and CO₂ without the addition of metal, cocatalyst, and solvent. Excellent selectivity and high cyclic carbonate yields are realized under mild conditions. As disclosed by the mechanism, the reaction proceeded smoothly owing to a synergistic effect from abundant hydroxyl groups of β -CD and the halide anion of functional groups. These green, biocompatible, and non-toxic catalysts derived from inexpensive environment-friendly starting material β -CD have great potential in industrial application for the conversion of CO₂.

Author Contributions: Q.W., validation, formal analysis, resources, writing—original draft preparation. X.Y., methodology. Q.Z., data curation. H.-J.Y., conceptualization, validation, writing—review and editing, project administration, funding acquisition. Q.J., software, visualization. J.H., investigation. C.-Y.G., conceptualization, validation, supervision, project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China, grant number 51073175.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are openly available in MDPI.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Song, Q.-W.; Zhou, Z.-H.; He, L.-N. Efficient, selective and sustainable catalysis of carbon dioxide. *Green Chem.* 2017, 19, 3707–3728. [CrossRef]
- Arshadi, S.; Vessally, E.; Sobati, M.; Hosseinian, A.; Bekhradnia, A. Chemical fixation of CO₂ to N-propargylamines: A straightforward route to 2-oxazolidinones. *J. CO₂ Util.* 2017, 19, 120–129. [CrossRef]
- Rahman, F.A.; Aziz, M.M.A.; Saidur, R.; Bakar, W.A.W.A.; Hainin, M.R.; Putrajaya, R.; Hassan, N.A. Pollution to solution: Capture and sequestration of carbon dioxide (CO₂) and its utilization as a renewable energy source for a sustainable future. *Renew. Sustain. Energy Rev.* 2017, 71, 112–126. [CrossRef]
- 4. Qiu, L.-Q.; Chen, K.-H.; Yang, Z.-W.; He, L.-N. A rhenium catalyst with bifunctional pyrene groups boosts natural light-driven CO₂ reduction. *Green Chem.* **2020**, *22*, 8614–8622. [CrossRef]
- 5. Sankar, M.; Ajithkumar, T.G.; Sankar, G.; Manikandan, P. Supported imidazole as heterogeneous catalyst for the synthesis of cyclic carbonates from epoxides and CO₂. *Catal. Commun.* **2015**, *59*, 201–205. [CrossRef]
- Cokoja, M.; Wilhelm, M.E.; Anthofer, M.H.; Herrmann, W.A.; Kühn, F.E. Synthesis of cyclic carbonates from epoxides and carbon dioxide by using organocatalysts. *ChemSusChem* 2015, *8*, 2436–2454. [CrossRef] [PubMed]
- Yuan, G.-Q.; Qi, C.-R.; Wu, W.-Q.; Jiang, H.-F. Recent advances in organic synthesis with CO₂ as C1 synthon. *Curr. Opin. Green* Sustain. Chem. 2017, 3, 22–27. [CrossRef]
- 8. Lawrenson, S.B.; Arav, R.; North, M. The greening of peptide synthesis. Green Chem. 2017, 19, 1685–1691. [CrossRef]
- Gómez, J.E.; Kleij, A.W. Recent progress in stereoselective synthesis of cyclic organic carbonates and beyond. *Curr. Opin. Green* Sust. Chem. 2017, 3, 55–60. [CrossRef]
- Santos, R.B.; Rivelino, R.; Mota, F.B.; Kakanakova-Georgievab, A.; Gueorguiev, G.K. Feasibility of novel (H₃C)nX(SiH₃)3-n compounds (X = B, Al, Ga, In): Structure, stability, reactivity, and Raman characterization from ab initio calculations. *Dalton Trans.* 2015, 44, 3356–3366. [CrossRef]
- Guo, Z.-J.; Cai, X.-C.; Xie, J.-Y.; Wang, X.-C.; Zhou, Y.; Wang, J. Hydroxyl-exchanged nanoporousionic copolymer toward low-temperature cycloaddition of atmospheric carbon dioxide into carbonates. ACS Appl. Mater. Interfaces 2016, 8, 12812–12821. [CrossRef]
- Butera, V.; Detz, H. Cyclic carbonate formation from epoxides and CO₂catalyzed by sustainable alkali halide-glycol complexes: A DFT study to elucidate reaction mechanism and catalytic activity. ACS Omega 2020, 5, 18064–18072. [CrossRef]
- 13. Comerford, J.W.; Ingram, D.V.I.; North, M.; Wu, X. Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings. *Green Chem.* **2015**, *17*, 1966–1987. [CrossRef]
- 14. Peng, J.; Yang, H.-J.; Wei, Z.-D.; Guo, C.-Y. Metal complexes bearing 2-(imidazol-2-yl)phenol ligands: Synthesis, characterization and catalytic performance in the fixation of carbon dioxide with epoxides. *RSC Adv.* **2015**, *5*, 53063–53072. [CrossRef]
- Peng, J.; Yang, H.-J.; Geng, Y.-C.; Wei, Z.-D.; Wang, L.-H.; Guo, C.-Y. Novel, recyclable supramolecular metal complexes for the synthesis of cyclic carbonates from epoxides and CO₂ under solvent-free conditions. J. CO₂ Util. 2017, 17, 243–255. [CrossRef]

- Li, C.-Y.; Su, Y.-C.; Lin, C.-H.; Huang, H.-Y.; Tsai, C.Y.; Lee, T.-Y.; Ko, B.-T. Synthesis and characterization of trimetallic cobalt, zinc and nickel complexes containing amine-bis(benzotriazole phenolate) ligands: Efficient catalysts for coupling of carbon dioxide with epoxides. *Dalton Trans.* 2017, 46, 15399–15406. [CrossRef]
- 17. Xu, C.; Liu, Y.; Wang, L.; Ma, J.-X.; Yang, L.-Z.; Pan, F.-X.; Kirillovc, A.M.; Liu, W.-S. New lanthanide(iii) coordination polymers: Synthesis, structural features, and catalytic activity in CO₂ fixation. *Dalton Trans.* **2017**, *46*, 16426–16431. [CrossRef]
- Cruz-Martínez, F.D.L.; Buchaca, M.M.D.S.; Martínez, J.; Fernández-Baeza, J.; Sánchez-Barba, L.F.; Rodríguez-Diéguez, A.; Castro-Osma, J.A.; Lara-Sánchez, A. Synthesis of bio-derived cyclic carbonates from renewable resources. ACS Sustain. Chem. Eng. 2019, 7, 20126–20138. [CrossRef]
- Navarro, M.; Sánchez-Barba, L.F.; Garcés, A.; Fernández-Baeza, J.; Fernández, I.; Lara-Sánchez, A.; Rodríguez, A.M. Bimetallic scorpionate-based helical organoaluminum complexes for efficient carbon dioxide fixation into a variety of cyclic carbonates. *Catal. Sci. Technol.* 2020, 10, 3265–3278. [CrossRef]
- 20. Xie, Z.-Z.; Zhu, M.-Q.; Nambo, A.; Jasinski, J.B.; Carreon, M.A. Microwave-assisted synthesized SAPO-56 as a catalyst in the conversion of CO₂ to cyclic carbonates. *Dalton Trans.* **2013**, *42*, 6732–6735. [CrossRef]
- Yoshikawa, K.; Sato, H.; Kaneeda, M.; Kondo, J.N. Synthesis and analysis of CO₂ adsorbents based on cerium oxide. *J. CO₂ Util.* 2014, *8*, 34–38. [CrossRef]
- Song, B.; Guo, L.; Zhang, R.; Zhao, X.-G.; Gan, H.-M.; Chen, C.; Chen, J.-Z.; Zhu, W.-W.; Hou, Z.-S. The polymeric quaternary ammonium salt supported on silica gel as catalyst for the efficient synthesis of cyclic carbonate. *J. CO*₂ *Util.* 2014, *6*, 62–68. [CrossRef]
- Wang, M.-Y.; Ma, R.; He, L.-N. Polyoxometalate-based ionic liquids-promoted CO₂ conversion. *Sci. China Chem.* 2016, 59, 507–516. [CrossRef]
- Maeda, C.; Taniguchi, T.; Ogawa, K.; Ema, T. Bifunctional catalysts based on m-phenylene-bridged porphyrin dimer and trimer platforms: Synthesis of cyclic carbonates from carbon dioxide and epoxides. *Angew. Chem. Int. Ed.* 2015, 54, 134–138. [CrossRef]
- Jiang, X.; Gou, F.-L.; Fu, X.-Y.; Jing, H.-W. Ionic liquids-functionalized porphyrins as bifunctional catalysts for cycloaddition of carbon dioxide to epoxides. J. CO₂ Util. 2016, 16, 264–271. [CrossRef]
- Kumar, S.; Silva, J.A.; Wani, M.Y.; Gil, J.M.; Sobral, A.J.F.N. Carbon dioxide capture and conversion by an environmentally friendly chitosan based meso-tetrakis(4-sulfonatophenyl) porphyrin. *Carbohyd. Polym.* 2017, 175, 575–583. [CrossRef]
- Kim, M.H.; Song, T.; Seo, U.R.; Park, J.E.; Cho, K.; Lee, S.M.; Kim, H.J.; Ko, Y.J.; Chung, Y.K.; Son, S.U. Hollow and microporous catalysts bearing Cr(III)-F porphyrins for room temperature CO₂ fixation to cyclic carbonates. *J. Mater. Chem. A* 2017, *5*, 23612–23619. [CrossRef]
- Peng, J.; Geng, Y.-C.; Yang, H.-J.; He, W.; Wei, Z.-D.; Yang, J.-K.; Guo, C.-Y. Efficient solvent-free fixation of CO₂ into cyclic carbonates catalyzed by Bi(III) porphyrin/TBAI at atmospheric pressure. *Mol. Catal.* 2017, 432, 37–46. [CrossRef]
- Bai, X.-L.; Su, Z.-P.; Wei, J.-J.; Ma, L.-J.; Duan, S.-J.; Wang, N.; Zhang, X.-F.; Li, J. Zinc(II)porphyrin-based porous ionic polymers (PIPs) as multifunctional heterogeneous catalysts for the conversion of CO₂ to cyclic carbonates. *Ind. Eng. Chem. Res.* 2022, *61*, 5093–5102. [CrossRef]
- Lia, G.; Zhou, X.; Wang, Z.-G. CO₂ capture and conversion to difunctional cyclic carbonates in metalloporphyrin-based porous polyaminals with large surface area. *Microporous Mesoporous Mater.* 2022, 343, 112–119.
- Zhang, J.-M.; Sun, J.; Zhang, X.-C.; Zhao, Y.-S.; Zhang, S.-J. The recent development of CO₂ fixation and conversion by ionic liquid. *Greenh. Gas Sci. Technol.* 2011, 1, 142–159. [CrossRef]
- Yang, H.; Nie, H.; Wen, Q.; Yu, P.; Peng, J.; Hu, J. Cycloaddition reaction of azridinane and CO₂ catalyzed by bifunctional zinc catalyst. J. Xuzhou Inst. Technol. (Nat. Sci. Ed.) 2022, 2, 28–35.
- 33. Bobbink, F.D.; Dyson, P.J. Synthesis of carbonates and related compounds incorporating CO₂ using ionic liquid-type catalysts: State-of-the-art and beyond. *J. Catal.* **2016**, *343*, 52–61. [CrossRef]
- Saptal, V.B.; Bhanage, B.M. Bifunctional ionic liquids for the multitask fixation of carbon dioxide into valuable chemicals. ChemCatChem 2016, 8, 244–250. [CrossRef]
- Yang, X.-Q.; Zou, Q.-Z.; Zhao, T.-X.; Chen, P.; Liu, Z.-M.; Liu, F.; Lin, Q. Deep eutectic solvents as efficient catalysts for fixation of CO₂ to cyclic carbonates at ambient temperature and pressure through synergetic catalysis. ACS Sustain. Chem. Eng. 2021, 9, 10437–10443. [CrossRef]
- 36. Xu, B.-H.; Wang, J.-Q.; Sun, J.; Huang, Y.; Zhang, J.-P.; Zhang, X.-P.; Zhang, S.-J. Fixation of CO₂ into cyclic carbonates catalyzed by ionic liquids: A multi-scale approach. *Green Chem.* **2015**, *17*, 108–122. [CrossRef]
- Peng, J.; Wang, S.; Yang, H.-J.; Ban, B.; Wei, Z.; Wang, L.; Lei, B. Highly efficient fixation of carbon dioxide to cyclic carbonates with new multi-hydroxyl bis-(quaternary ammonium) ionic liquids as metal-free catalysts under mild conditions. *Fuel* 2018, 224, 481–488. [CrossRef]
- 38. Dai, W.-L.; Yang, W.-Y.; Zhang, Y.; Wang, D.; Luo, X.-B.; Tu, X.-M. Novel isothiouronium ionic liquid as efficient catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides. *J. CO₂ Util.* **2017**, *17*, 256–262. [CrossRef]
- 39. Yue, S.; Wang, P.-P.; Hao, X.-J.; Zang, S.-L. Dual amino-functionalized ionic liquids as efficient catalysts for carbonate synthesis from carbon dioxide and epoxide under solvent and cocatalyst-free conditions. *J.* CO₂ Util. **2017**, 21, 238–246. [CrossRef]
- Alves, M.; Grignard, B.; Mereau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C. Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: Catalyst design and mechanistic studies. *Catal. Sci. Technol.* 2017, 7, 2651–2684. [CrossRef]

- 41. Fiorani, G.; Guo, W.-S.; Kleij, A.W. Sustainable conversion of carbon dioxide: The advent of organocatalysis. *Green Chem.* **2015**, *17*, 1375–1389. [CrossRef]
- 42. Cho, W.; Shin, M.-S.; Hwang, S.; Kim, H.; Kim, M.; Kim, J.G.; Kim, Y. Tertiary amines: A new class of highly efficient organocatalysts for CO₂ fixations. *Ind. Eng. Chem.* **2016**, *44*, 210–215. [CrossRef]
- Büttner, H.; Longwitz, L.; Steinbauer, J.; Wulf, C.; Werner, T. Recent developments in the synthesis of cyclic carbonates from epoxides and CO₂. *Top. Curr. Chem.* 2017, 375, 50–56. [CrossRef] [PubMed]
- 44. Zhou, H.; Lu, X.-B. Lewis base-CO₂ adducts as organocatalysts for CO₂ transformation. *Sci. China Chem.* **2017**, *60*, 904–911. [CrossRef]
- 45. Kim, H.G.; Lim, C.S.; Kim, D.W.; Cho, D.H.; Lee, D.K.; Chung, J.S. Multifunctional alkanolamine as a catalyst for CO₂ and propylene oxide cycloaddition. *Mol. Catal.* **2017**, *438*, 121–129. [CrossRef]
- Ma, R.; He, L.-N.; Liu, X.-F.; Liu, X.; Wang, M.-Y. DBU as activator for the N-iodosuccinimide promoted chemical fixation of carbon dioxide with epoxides. J. CO₂ Util. 2017, 19, 28–32. [CrossRef]
- Zhang, Y.; Yang, G.; Xie, R.; Yang, L.; Li, B.; Wu, G. Scalable, durable, and recyclable metal-free catalysts for highly efficient conversion of CO₂ to cyclic carbonates. *Angew. Chem. Int. Ed.* 2020, 59, 23291–23298. [CrossRef]
- Xu, J.-X.; Xian, A.-M.; Li, Z.-J.; Liu, J.-J.; Zhang, Z.-H.; Yan, R.; Gao, L.-Y.; Liu, B.; Zhao, L.-L.; Guo, K. A strained ion pair permits carbon dioxide fixation at atmospheric pressure by C-H H-bonding organocatalysis. J. Org. Chem. 2021, 86, 3422–3432. [CrossRef]
- Kuruppathparambil, R.R.; Jose, T.; Babu, R.; Hwang, G.Y.; Kathalikkattil, A.C.; Kim, D.W.; Park, D.W. A room temperature synthesizable and environmental friendly heterogeneous ZIF-67 catalyst for the solvent less and co-catalyst free synthesis of cyclic carbonates. *Appl. Catal. B* 2016, 182, 562–569. [CrossRef]
- 50. Das, S.K.; Chatterjee, S.; Bhunia, S.; Mondal, A.; Mitra, P.; Kumari, V.; Pradhan, A.; Bhaumik, A. A new strongly paramagnetic cerium-containing microporous MOF for CO₂ fixation under ambient conditions. *Dalton Trans.* **2017**, *46*, 13783–13792. [CrossRef]
- 51. Cota, I.; Martinez, F.F. Recent advances in the synthesis and applications of metal organic frameworks doped with ionic liquids for CO₂ adsorption. *Coordin. Chem. Rev.* 2017, 351, 189–204. [CrossRef]
- 52. Saptal, V.B.; Bhanage, B.M. Current advances in heterogeneous catalysts for the synthesis of cyclic carbonates from carbon dioxide. *Curr. Opin. Green Sustain. Chem.* **2017**, *3*, 1–10. [CrossRef]
- Maina, J.W.; Pozo-Gonzalo, C.; Kong, L.-X.; Schütz, J.; Hillc, M.; Dumée, L.F. Metal organic framework based catalysts for CO₂ conversion. *Mater. Horiz.* 2017, 4, 345–361. [CrossRef]
- 54. Li, X.-Y.; Li, Y.-Z.; Yang, Y.; Hou, L.; Wang, Y.-Y.; Zhu, Z. Efficient light hydrocarbon separation and CO₂ capture and conversion in a stable MOF with oxalamide-decorated polar tubes. *Chem. Commun.* **2017**, *53*, 12970–12973. [CrossRef] [PubMed]
- 55. Wu, Y.; Song, X.; Li, S.; Zhang, J.; Yang, X.; Shen, P.; Gao, L.; Wei, R.; Zhang, J.; Xiao, G.-M. 3D-monoclinic M-BTC MOF (M = Mn, Co, Ni) as highly efficient catalysts for chemical fixation of CO₂ into cyclic carbonates. *Ind. Eng. Chem.* **2018**, *58*, 296–303. [CrossRef]
- Liang, J.; Xie, Y.-Q.; Wang, X.-S.; Wang, Q.; Liu, T.-T.; Huang, Y.-B.; Cao, R. An imidazolium-functionalized mesoporous cationic metal-organic framework for cooperative CO₂ fixation into cyclic carbonate. *Chem. Commun.* 2018, 54, 342–345. [CrossRef]
- Zhang, T.; Chen, H.-T.; Liu, S.-R.; Lv, H.-X.; Zhang, X.-T.; Li, Q.-L. Highly robust {Ln4}-organic frameworks (Ln = Ho, Yb) for excellent catalytic performance on cycloaddition reaction of epoxides with CO₂ and knoevenagel condensation. ACS Catal. 2021, 11, 14916–14925. [CrossRef]
- Chen, H.-T.; Liu, S.-R.; Lv, H.-X.; Qin, Q.-P.; Zhang, X.-T. Nanoporous {Y2}-organic frameworks for excellent catalytic performance on the cycloaddition reaction of epoxides with CO₂ and deacetalization-knoevenagel condensation. ACS Appl. Mater. Interfaces 2022, 14, 18589–18599. [CrossRef]
- 59. Das, R.; Ezhil, T.; Nagaraja, C.M. Design of bifunctional Zinc(II)-organic framework for efficient coupling of CO₂ with terminal/internal epoxides under mild conditions. *Cryst. Growth Des.* **2022**, *22*, 598–607. [CrossRef]
- 60. Liu, H.-L.; Huang, Z.-W.; Han, Z.-B.; Ding, K.-L.; Liu, H.-C.; Xia, C.-G.; Chen, J. Efficient production of methanol and diols via the hydrogenation of cyclic carbonates using copper-silica nanocomposite catalysts. *Green Chem.* **2015**, *17*, 4281–4290. [CrossRef]
- Vessally, E.; Babazadeh, M.; Hosseinian, A.; Arshadi, S.; Edjlali, L. Nanocatalysts for chemical transformation of carbon dioxide. J. CO₂ Util. 2017, 21, 491–502. [CrossRef]
- 62. Yang, Z.-Z.; Wang, H.; Ji, G.-P.; Yu, X.-X.; Chen, Y.; Liu, X.-W.; Wu, C.-L.; Liu, Z.-M. Pyridine-functionalized organic porous polymers: Applications in efficient CO₂ adsorption and conversion. *New J. Chem.* **2017**, *41*, 2869–2872. [CrossRef]
- 63. Poland, S.J.; Darensbourg, D.J. A quest for polycarbonates provided via sustainable epoxide/CO₂ copolymerization processes. *Green Chem.* **2017**, *19*, 4990–5011. [CrossRef]
- 64. Ghosh, S.; Bhanja, P.; Salam, N.; Khatun, R.; Bhaumik, A.; Islam, S.M. Porous iron-phosphonate nanomaterial as an efficient catalyst for the CO₂ fixation at atmospheric pressure and esterification of biomass-derived levulinic acid. *Catal. Today* **2018**, *309*, 253–262. [CrossRef]
- 65. Liu, D.; Li, G.; Guo, H.-C.; Liu, J.-X. Facile preparation of bi-functional iron doped mesoporous materials and their application in the cycloaddition of CO₂. *J. Energy Chem.* **2020**, *41*, 52–59. [CrossRef]
- Xiao, L.-F.; Li, F.-W.; Xia, C.-G. An easily recoverable and efficient natural biopolymer-supported zinc chloride catalyst system for the chemical fixation of carbon dioxide to cyclic carbonate. *Appl. Catal. A* 2005, 279, 125–129. [CrossRef]
- Zhao, Y.; Tian, J.-S.; Qi, X.-H.; Han, Z.-N.; Zhuang, Y.-Y.; He, L.-N. Quaternary ammonium salt-functionalized chitosan: An easily recyclable catalyst for efficient synthesis of cyclic carbonates from epoxides and carbon dioxide. *J. Mol. Catal.* 2007, 271, 284–289. [CrossRef]

- 68. Zhou, Y.-X.; Hu, S.-Q.; Ma, X.-M.; Liang, S.-G.; Jiang, T.; Han, B.-X. Synthesis of cyclic carbonates from carbon dioxide and epoxides over betaine-based catalysts. *J. Mol. Catal.* **2008**, *284*, 52–57. [CrossRef]
- 69. Liang, S.-G.; Liu, H.-Z.; Jiang, T.; Song, J.-L.; Yang, G.-Y.; Han, B.-X. Highly efficient synthesis of cyclic carbonates from CO₂ and epoxides over cellulose/KI. *Chem. Commun.* **2011**, *47*, 2131–2133. [CrossRef]
- Song, J.-L.; Zhang, B.-B.; Zhang, P.; Ma, J.; Liu, J.-L.; Fan, H.-L.; Jiang, T.; Han, B.-X. Highly efficient synthesis of cyclic carbonates from CO₂ and epoxides catalyzed by KI/lecithin. *Catal. Today* 2012, 183, 130–135. [CrossRef]
- Sun, J.; Wang, J.-Q.; Cheng, W.-G.; Zhang, J.-X.; Li, X.-H.; Zhang, S.-J.; She, Y.-B. Chitosan functionalized ionic liquid as a recyclable biopolymer-supported catalyst for cycloaddition of CO₂. *Green Chem.* 2012, 14, 654–660. [CrossRef]
- 72. Roshan, K.R.; Mathai, G.; Kim, J.; Tharun, J.; Park, G.-A.; Park, D.-W. A biopolymer mediated efficient synthesis of cyclic carbonates from epoxides and carbon dioxide. *Green Chem.* **2012**, *14*, 2933–2940. [CrossRef]
- 73. Tharun, J.; Kim, D.W.; Roshan, R.; Hwang, Y.; Park, D.W. Microwave assisted preparation of quaternized chitosan catalyst for the cycloaddition of CO₂ and epoxides. *Catal. Commun.* **2013**, *31*, 62–65. [CrossRef]
- 74. Roshan, K.R.; Jose, T.; Kathalikkattil, A.C.; Kim, D.W.; Kim, B.; Park, D.W. Microwave synthesized quaternized celluloses for cyclic carbonate synthesis from carbon dioxide and epoxides. *Appl. Catal. A* 2013, 467, 17–25. [CrossRef]
- 75. Sun, J.; Cheng, W.-G.; Yang, Z.-F.; Wang, J.-Q.; Xu, T.-T.; Xin, J.-Y.; Zhang, S.-J. Superbase/cellulose: An environmentally benign catalyst for chemical fixation of carbon dioxide into cyclic carbonates. *Green Chem.* **2014**, *16*, 3071–3078. [CrossRef]
- 76. Chen, J.-X.; Jin, B.; Dai, W.-L.; Deng, S.-L.; Cao, L.-R.; Cao, Z.-J.; Luo, S.-L.; Luo, X.-B.; Tu, X.-M.; Au, C.-T. Catalytic fixation of CO₂ to cyclic carbonates over biopolymer chitosan-grafted quarternary phosphonium ionic liquid as a recylable catalyst. *Appl. Catal. A* 2014, 484, 26–32.
- 77. Chen, W.; Zhong, L.-X.; Peng, X.-W.; Sun, R.-C.; Lu, F.-C. Chemical fixation of carbon dioxide using a green and efficient catalytic system based on sugarcane bagasse-an agricultural waste. *ACS Sustain. Chem. Eng.* **2015**, *3*, 147–152. [CrossRef]
- Wu, X.-H.; Wang, M.-P.; Xie, Y.-Z.; Chen, C.; Li, K.; Yuan, M.-M.; Zhao, X.-G.; Hou, Z.-S. Carboxymethyl cellulose supported ionic liquid as a heterogeneous catalyst for the cycloaddition of CO₂ to cyclic carbonate. *Appl. Catal. A* 2016, 519, 146–154. [CrossRef]
- 79. Ma, Y.; Chen, C.; Wang, T.-F.; Zhang, J.-S.; Wu, J.-J.; Liu, X.-D.; Ren, T.-G.; Wang, L.; Zhang, J.-L. Dialkylpyrazolium ionic liquids as novel catalyst for efficient fixation of CO₂ with metal- and solvent-free. *Appl. Catal. A* 2017, 547, 265–273. [CrossRef]
- 80. Jose, T.; Cañellas, S.; Pericàs, M.A.; Kleij, A.W. Polystyrene-supported bifunctional resorcinarenes as cheap, metal-free and recyclable catalysts for epoxide/CO₂ coupling reactions. *Green Chem.* **2017**, *19*, 5488–5493. [CrossRef]
- 81. Biswas, T.; Mahalingam, V. g-C₃N₄ and tetrabutylammonium bromide catalyzed efficient conversion of epoxide to cyclic carbonate under ambient conditions. *New J. Chem.* **2017**, *41*, 14839–14842. [CrossRef]
- 82. Ravi, S.; Puthiaraj, P.; Ahn, W.S. Cyclic carbonate synthesis from CO₂ and epoxides over diamine-functionalized porous organic frameworks. *J. CO*₂ *Util.* **2017**, *21*, 450–458. [CrossRef]
- 83. Velázquez, H.D.; Pantoja, J.G.; Ruiz, E.M.; León, R.G.D.; Palou, R.M. Efficient synthesis of organic carbonates to the multigram level from CO₂using a new chitin-supported catalyst. *Catal. Lett.* **2017**, *147*, 2260–2268. [CrossRef]
- 84. Peng, J.; Wang, S.; Yang, H.-J.; Ban, B.-R.; Wei, Z.-D.; Wang, L.-H.; Lei, B. Chemical fixation of CO₂ to cyclic carbonate catalyzed by new environmental-friendly bifunctional bis-β-cyclodextrin derivatives. *Catal. Today* **2019**, *330*, 76–84. [CrossRef]
- 85. Wang, S.; Peng, J.; Yang, H.-J.; Ban, B.-R.; Wang, L.-H.; Lei, B.; Guo, C.-Y.; Hu, J.-C.; Zhu, J.-J.; Han, B.-X. β-cyclodextrin/quaternary ammonium salt as an efficient catalyst system for chemical fixation of CO₂. *J. Nanosci. Nanotechnol.* 2019, *19*, 3263–3268. [CrossRef] [PubMed]
- 86. Natongchai, W.; Pornpraprom, S.; D'Elia, V. Synthesis of bio-based cyclic carbonates using a bio-based hydrogen bond donor: Application of ascorbic acid to the cycloaddition of CO₂ to oleochemicals. *Asian J. Org. Chem.* **2020**, *9*, 801–810. [CrossRef]
- 87. Bai, D.; Duan, S.; Hai, L.; Jing, H. Carbon dioxide fixation by cycloaddition with epoxides, catalyzed by biomimetic metalloporphyrins. *ChemCatChem* **2012**, *4*, 1752–1758. [CrossRef]
- Ema, T.; Miyazaki, Y.; Shimonishi, J.; Maeda, C.; Hasegawa, J.Y. Bifunctional porphyrin catalysts for the synthesis of cyclic carbonates from epoxides and CO₂: Structural optimization and mechanistic study. *J. Am. Chem. Soc.* 2014, 136, 15270–15279. [CrossRef] [PubMed]
- Zhou, Q.-S.; Peng, X.-W.; Zhong, L.-X.; Li, X.-H.; Chua, W.-T.; Sun, R.-C. Xylan/DBU as an efficient and green catalyst for chemical fixation of CO₂. *Fuel Process. Technol.* 2018, 176, 146–152. [CrossRef]
- Song, J.-L.; Zhang, Z.-F.; Han, B.-X.; Hu, S.-Q.; Li, W.-J.; Xie, Y. Synthesis of cyclic carbonates from epoxides and CO₂ catalyzed by potassium halide in the presence of β-cyclodextrin. *Green Chem.* 2008, 10, 1337–1341. [CrossRef]
- 91. Li, K.; Wu, X.-H.; Gu, Q.-W.; Zhao, X.-G.; Yuan, M.-M.; Ma, W.-B.; Ni, W.-X.; Hou, Z.-S. Inclusion complexes of organic salts with β-cyclodextrin as organocatalysts for CO₂ cycloaddition with epoxides. *RSC Adv.* **2017**, *7*, 14721–14732. [CrossRef]
- 92. Muderawan, I.W.; Ong, T.T.; Tang, W.-H.; Young, D.J.; Ching, C.-B.; Ng, S.C. Synthesis of ammonium substituted β-cyclodextrins for enantioseparation of anionic analytes. *Tetrahedron Lett.* **2005**, *46*, 1747–1749. [CrossRef]
- Cheng, W.-G.; Fu, Z.-Z.; Wang, J.-Q.; Sun, J.; Zhang, S.-J. ZnBr₂-based choline chloride ionic liquid for efficient fixation of CO₂ to cyclic carbonate. Syn. Commun. 2012, 42, 2564–2573. [CrossRef]
- 94. Wei, R.-J.; Zhang, X.-H.; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Synthesis of bis(cyclic carbonate) and propylene carbonate via a one-pot coupling reaction of CO₂bisepoxide and propylene oxide. *RSC Adv.* **2013**, *3*, 17307–17313. [CrossRef]
- 95. Han, L.; Li, H.; Choi, S.J.; Park, M.S.; Lee, S.M.; Kim, Y.J.; Park, D.W. Ionic liquids grafted on carbon nanotubes as highly efficient heterogeneous catalysts for the synthesis of cyclic carbonates. *Appl. Catal. A* **2012**, *429*, 67–72. [CrossRef]

- Sun, J.; Cheng, W.-G.; Fan, W.; Wang, Y.-H.; Meng, Z.-Y.; Zhang, S.-J. Reusable and efficient polymer-supported task-specific ionic liquid catalyst for cycloaddition of epoxide with CO₂. *Catal. Today* 2009, 148, 361–367. [CrossRef]
- 97. Ulusoy, M.; Çetinkaya, E.; Çetinkaya, B. Conversion of carbon dioxide to cyclic carbonates using diimineRu(II) complexes as catalysts. *Appl. Organomet. Chem.* 2009, 23, 68–74. [CrossRef]
- Yao, R.; Wang, H.; Han, J. Polyethylene glycol-supported ionic liquid as a highly efficient catalyst for the synthesis of propylene carbonate under mild conditions. *Front. Chem. Sci. Eng.* 2012, *6*, 239–245. [CrossRef]
- 99. Xie, Y.; Zhang, Z.-F.; Jiang, T.; He, J.-L.; Han, B.-X.; Wu, T.-B.; Ding, K.-L. CO₂cycloaddition reactions catalyzed by an ionic liquid grafted onto a highly cross-linked polymer matrix. *Angew. Chem. Int. Ed.* **2007**, *46*, 7255–7258. [CrossRef]
- 100. Xiao, L.-F.; Li, F.-W.; Peng, J.-J.; Xia, C.-G. Immobilized ionic liquid/zinc chloride: Heterogeneous catalyst for synthesis of cyclic carbonates from carbon dioxide and epoxides. *J. Mol. Catal. A* 2006, 253, 265–269. [CrossRef]
- Bai, D.-S.; Jing, H.-W.; Wang, G.-J. Cyclic carbonate synthesis from epoxides and CO₂ over cyanocobalamin/n-Bu₄NI. *Appl. Organomet. Chem.* 2012, 26, 600–603. [CrossRef]
- Wang, J.-Q.; Sun, J.; Cheng, W.-G.; Dong, K.; Zhang, X.-P.; Zhang, S.-J. Experimental and theoretical studies on hydrogen bond-promoted fixation of carbon dioxide and epoxides in cyclic carbonates. *Phys. Chem. Chem. Phys.* 2012, 14, 11021–11026. [CrossRef] [PubMed]
- North, M.; Quek, S.C.Z.; Pridmore, N.E.; Whitwood, A.C.; Wu, X. Aluminum(salen) complexes as catalysts for the kinetic resolution of terminal epoxides via CO₂coupling. ACS Catal. 2015, 5, 3398–3402. [CrossRef]
- 104. Leng, Y.; Lu, D.; Zhang, C.-J.; Jiang, P.-P.; Zhang, W.-J.; Wang, J. Cover picture: Sandmeyer-type trifluoromethylthiolation and trifluoromethylselenolation of (Hetero) aromatic amines catalyzed by copper. *Chem. Eur. J.* **2016**, *22*, 1–9.
- 105. Wang, J.-Y.; Liang, Y.-T.; Zhou, D.-G.; Ma, J.-P.; Jing, H.-W. New crown ether complex cation ionic liquids with N-heterocycle anions: Preparation and application in CO₂ fixation. *Org. Chem. Front.* **2018**, *5*, 741–748. [CrossRef]
- 106. Chen, F.; Liu, N.; Dai, B. Iron(II) bis-CNN pincer complex-catalyzed cyclic carbonate synthesis at room temperature. ACS Sustain. Chem. Eng. 2017, 5, 9065–9075. [CrossRef]
- 107. Lee, S.D.; Kim, B.M.; Kim, D.W.; Kim, M.; Roshan, K.R.; Kim, M.K.; Won, Y.S.; Park, D.W. Synthesis of cyclic carbonate from carbon dioxide and epoxides with polystyrene-supported quaternized ammonium salt catalysts. *Appl. Catal. A* 2014, 486, 69–76. [CrossRef]
- 108. Zhang, Q.; Yu, P.; Lei, B.; Yang, H.-J.; Hu, J.; Wang, L.; Zhou, T.; Jiang, Q.; Zhu, J.; Han, B. Efficient solvent-free synthesis of cyclic carbonates from the cycloaddition carbon dioxide and epoxides catalyzed by new imidazolinium functionalized metal complexes under 0.1 MPa. *Catal. Lett.* 2020, 150, 2537–2548. [CrossRef]
- 109. Yang, H.; Nie, H.; Wen, Q.; Ban, B.; Hu, J. Reaction study on CO₂ with amines catalyzed by N,N-dimethylethanolamine. J. Xuzhou Inst. Technol. (Nat. Sci. Ed.) **2022**, 1, 9–13.
- Bivona, L.A.; Fichera, O.; Fusaro, L.; Giacalone, F.; Buaki-Sogo, M.; Gruttadauria, M.; Aprile, C. A polyhedral oligomeric silsesquioxane-based catalyst for the efficient synthesis of cyclic carbonates. *Catal. Sci. Technol.* 2015, *5*, 5000–5007. [CrossRef]
- Wang, J.-Q.; Song, W.-H.; Yi, G.-S.; Zhang, Y.-G. Imidazolium salt-modified porous hypercrosslinked polymers for synergistic CO₂ capture and conversion. *Chem. Commun.* 2015, *51*, 12076–12079. [CrossRef] [PubMed]
- 112. Guan, J.; Song, Y.-H.; Lin, Y.; Yin, X.-Z.; Zuo, M.; Zhao, Y.-H.; Tao, X.-L.; Zheng, Q. Progress in study of non-isocyanate polyurethane. *Ind. Eng. Chem. Res.* 2011, *50*, 6517–6527. [CrossRef]
- 113. Sheng, X.-F.; Ren, G.-J.; Qin, Y.-S.; Chen, X.-S.; Wang, X.-H.; Wang, F.-S. Quantitative synthesis of bis(cyclic carbonate)s by iron catalyst for non-isocyanate polyurethane synthesis. *Green Chem.* **2015**, *17*, 373–379. [CrossRef]
- 114. Carré, C.; Ecochard, Y.; Caillol, S.; Avérous, L. From the synthesis of biobased cyclic carbonate to polyhydroxyurethanes: A promising route towards renewable non-isocyanate polyurethanes. *ChemSusChem* **2019**, *12*, 3410–3430. [CrossRef] [PubMed]
- 115. Sheng, X.-F.; Wang, Y.; Qin, Y.-S.; Wang, X.-H.; Wang, F.-S. Aluminum porphyrin complexes via delicate ligand design: Emerging efficient catalysts for high molecular weight poly(propylene carbonate). *RSC Adv.* **2014**, *4*, 54043–54050. [CrossRef]
- Sheng, X.-F.; Guo, H.-C.; Qin, Y.-S.; Wang, X.-H.; Wang, F.-S. A novel metalloporphyrin-based conjugated microporous polymer for capture and conversion of CO₂. RSC Adv. 2015, 5, 31664–31669. [CrossRef]
- 117. Qin, Y.-S.; Guo, H.-C.; Sheng, X.-F.; Wang, X.-H.; Wang, F.-S. An aluminum porphyrin complex with high activity and selectivity for cyclic carbonate synthesis. *Green Chem.* **2015**, *17*, 2853–2858. [CrossRef]
- Büttner, H.; Lau, K.; Spannenberg, A.; Werner, T. Bifunctional one-component catalysts for the addition of carbon dioxide to epoxides. *ChemCatChem* 2015, 7, 459–467. [CrossRef]
- 119. Cheng, W.-G.; Xiao, B.-N.; Sun, J.; Dong, K.; Zhang, P.; Zhang, S.-J.; Ng, F.T.T. Effect of hydrogen bond of hydroxyl-functionalized ammonium ionic liquids on cycloaddition of CO₂. *Tetrahedron Lett.* **2015**, *56*, 1416–1419. [CrossRef]
- 120. Zhang, W.-H.; He, P.-P.; Wu, S.; Xu, J.; Li, Y.-X.; Zhang, G.; Wei, X.-Y. Graphene oxide grafted hydroxyl-functionalized ionic liquid: A highly efficient catalyst for cycloaddition of CO₂ with epoxides. *Appl. Catal. A* **2016**, *509*, 111–117. [CrossRef]
- 121. Wu, S.; Wang, B.-S.; Zhang, Y.-Y.; Elageed, E.H.M.; Wu, H.-H.; Gao, G.-H. Phenolic hydroxyl-functionalized imidazolium ionic liquids: Highly efficient catalysts for the fixation of CO₂ to cyclic carbonates. *J. Mol. Catal.* **2016**, *418*, 1–8. [CrossRef]
- 122. Samanta, S.; Srivastava, R. A novel method to introduce acidic and basic bi-functional sites in graphitic carbon nitride for sustainable catalysis: Cycloaddition, esterification, and transesterification reactions. *Sust. Energy Fuel* 2017, *1*, 1390–1404. [CrossRef]

- 123. Steinbauer, J.; Longwitz, L.; Frank, M.; Epping, J.; Kragld, U.; Werner, T. Immobilized bifunctional phosphonium salts as recyclable organocatalysts in the cycloaddition of CO₂ and epoxides. *Green Chem.* **2017**, *19*, 4435–4445. [CrossRef]
- 124. Ren, Y.-W.; Chen, J.-G.; Qi, C.-R.; Jiang, H.-F. A new type of Lewis acid–base bifunctional M(salphen) (M = Zn, Cu and Ni) catalysts for CO₂ fixation. *ChemCatChem* **2015**, *7*, 1535–1538. [CrossRef]
- 125. Monica, F.D.; Vummaleti, S.V.C.; Buonerba, A.; De Nisi, A.; Monari, M.; Milione, S.; Grassi, A.; Cavallo, L.; Capacchione, C. Coupling of carbon dioxide with epoxides efficiently catalyzed by thioether-triphenolate bimetallic iron(III) complexes: Catalyst structure-reactivity relationship and mechanistic DFT study. *Adv. Synth. Catal.* **2016**, *358*, 3231–3243. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.