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Efficient Fixation of CO₂ by a Zinc-Coordinated Conjugated Microporous Polymer

Yong Xie,^[a, b] Ting-Ting Wang,^[b] Rui-Xia Yang,^[b] Nian-Yu Huang,^[a] Kun Zou,^{*,[a]} and Wei-Qiao Deng^{*,[b]}

Zinc-coordinated conjugated microporous polymers (Zn-CMPs), prepared by linking salen zinc and 1,3,5-triethynylbenzene, exhibit extraordinary activities (turnover frequencies of up to 11600 h⁻¹), broad substrate scope, and group tolerance for the synthesis of functional organic carbonates by coupling epoxides with CO₂ at 120 °C and 3.0 MPa without the use of additional solvents. The catalytic activity of Zn-CMP is comparable to those of homogeneous catalysts and superior to those of other heterogeneous catalysts. This catalyst could be reused more than ten times without a significant decrease in performance.

In recent years, concerns about global warming have boosted interest in the chemical fixation of CO₂, which can be regarded as the most environmentally abundant C₁ building block available.^[1] More specifically, the cycloaddition of CO₂ to epoxides, which yields useful cyclic or polycarbonate products,^[2] is of particular interest as it represents a much greener alternative to the use of phosgene. Cyclic carbonates are an important class of chemical products used for various purposes, for example, as electrolytes in lithium-ion batteries, as raw material for plastics, as valuable raw materials and intermediates in the production of pharmaceutical and fine chemicals, and as environmentally friendly nontoxic solvents; therefore, a variety of industrial processes for the production of these carbonates have been developed. However, their preparation often suffer from low catalyst reactivity with turnover frequencies (TOFs) rarely > 200 h⁻¹ even at elevated temperatures (> 130 °C), air sensitivity, and the use of additional solvents, high pressure, and high temperature conditions.^[3]

Recently, several efficient homogeneous catalysts have been reported in this area. North and co-workers used a bimetallic aluminum (salen) complex, which could catalyze the reaction of CO₂ with propylene oxide (PO) at room temperature and atmospheric pressure.^[4] The Sakai group developed a magnesium-based porphyrin (Mg-porphyrin) that catalyzed a terminal epoxide at 120 °C and 1.7 MPa with TOFs at as high as 12000 h⁻¹.^[5] A more recent work reported by Kleij et al. identified an aluminum complex that showed high activity (TOFs up to 36000 h⁻¹) and broad substrate scope even for internal epoxides.^[6] Although significant progress has been made, two major challenges remain in this area. First, the efficient homogeneous catalysts suffer from separation problems whereas the heterogeneous catalysts have low catalytic activities for this reaction; thus, an efficient heterogeneous catalyst is highly demanded. Second, to the best of our knowledge, the reported heterogeneous catalysts were only effective for terminal epoxides; therefore, it is a big challenge to develop a catalyst that can transform internal epoxides.

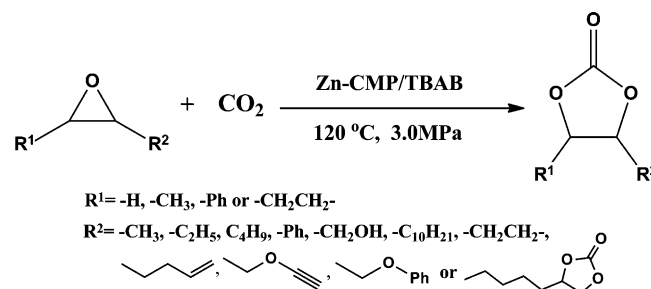
Conjugated microporous polymers (CMPs)^[7] are highly flexible porous materials that may be tailored for various applications such as catalysis,^[8] gas storage,^[9] light harvesting^[10] luminescence,^[11] sensors,^[12] superhydrophobic separations,^[13] and supercapacitors.^[14] On combining these various properties, we expect to obtain new functionalities for CMPs. For example, we have developed a cobalt-functionalized CMP that can capture CO₂ and catalyze its conversion at room temperature and atmospheric pressure.^[15]

Herein, we report a highly efficient heterogeneous catalyst, a zinc-coordinated conjugated microporous polymer (hereafter referred to as Zn-CMP), which is synthesized by linking salen zinc with 1,3,5-triethynylbenzene. This Zn-CMP exhibits extraordinary catalytic activity (TOFs up to 11600 h⁻¹) towards the coupling of CO₂ and epoxides, including terminal and internal

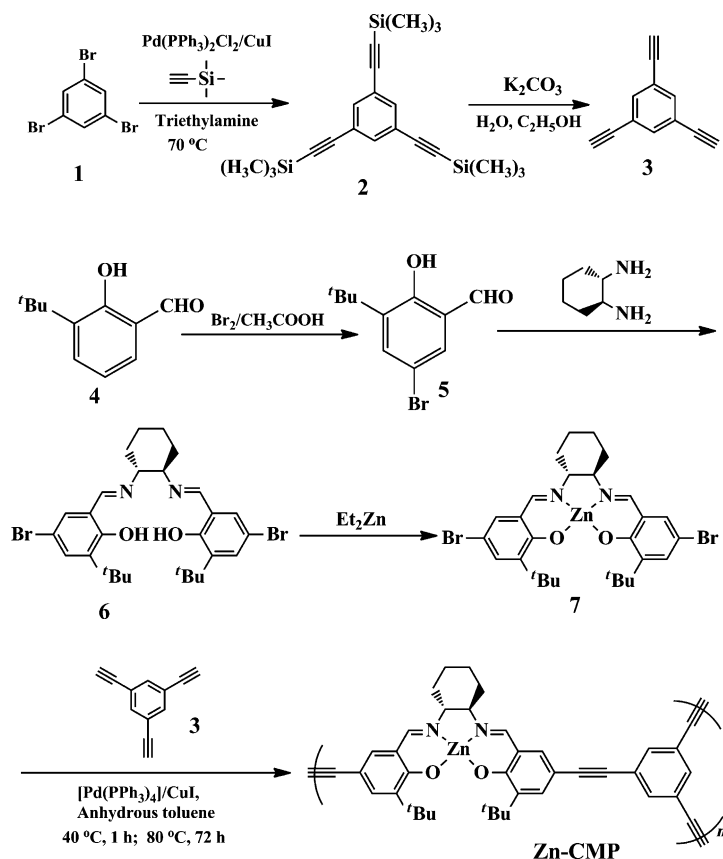
[a] Y. Xie, Dr. N.-Y. Huang, Prof. Dr. K. Zou
Hubei Key Laboratory of Natural Products Research
College of Chemistry and Life Sciences,
China Three Gorges University
Yichang 443002 (PR China)
E-mail: kzou@ctgu.edu.cn

[b] Y. Xie, T.-T. Wang, R.-X. Yang, Prof. Dr. W.-Q. Deng
State Key Laboratory of Molecular Reaction Dynamics
Dalian National Laboratory for Clean Energy
Dalian Institute of Chemical Physics
Chinese Academy of Science
457 Zhongshan Road, Dalian 116023 (PR China)
Fax: (+86)411-84675584
E-mail: dengwq@dicp.ac.cn

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Scheme 1. Synthesis of functional organic carbonates from CO₂ and epoxides.



Scheme 2. Synthesis route for Zn-CMP.

derivatives and is the most efficient heterogeneous catalyst reported thus far (Scheme 1). The catalytic activity remains high even after more than ten reuses.

To prepare Zn-CMP, we first synthesized the dibromo-functionalized precursor monomers salen zinc by a complexation reaction of (*R,R*)-*N,N'*-bis(5-bromo-3-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (salen) and ZnEt_2 (1.0 M solution in hexane). The resulting precursor was co-polymerized with 1,3,5-triethynylbenzene in toluene under reflux to produce Zn-CMP (Scheme 2). The synthetic details are given in the Supporting Information. Zn-CMP is insoluble in almost all of organic solvents and stable in strong acids and bases (Supporting Information, Table S1). Its pyrolysis temperature is higher than 300 °C (Figure S1).

Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) were used to record the morphological structure of Zn-CMP. The SEM image shown in Figure 1a reveals that Zn-CMP consists of submicron spheres, and HR-TEM picture (Figure 1b) shows that the pores on the polymer surface are roughly 0.5 nm in diameter. According to these images (additional images are shown in Figure S2), the polymer was featureless at those length scales. ^1H - ^{13}C cross-polymerization/magic angle spinning (CP/MAS) solid-state nuclear magnetic resonance (NMR) was used to identify the structures of Zn-CMP (Figure S3). The peaks at 120.0–150.0 ppm corresponded to the C–C sites of the polymer's benzene rings. The peaks at 70.0–100.0 ppm were ascribed to

sp^1 -hybridized $-\text{C}\equiv\text{C}-$ sites. The peaks at 40.0–60.0 ppm were ascribed to sp^3 -hybridized $-\text{CH}_2$ sites and $-\text{CH}$ sites in the cyclohexane moiety. The peak with the lowest intensity, at 10.0–20.0 ppm, was ascribed to $-\text{CH}_3$ groups.

Zn-CMP also exhibits excellent material properties, and the results are summarized in Table S2. The porosity in the polymer was investigated by N_2 adsorption analyses at 77.4 K (See Figure S4). The Brunauer–Emmett–Teller (BET) surface area determined from the N_2 sorption data is $791 \text{ m}^2 \text{ g}^{-1}$, and the total pore volume of Zn-CMP is $1.81 \text{ cm}^3 \text{ g}^{-1}$, which is substantially larger than that of many high-pore-volume metal organic frameworks (MOFs), including NOTT-112 ($[(\text{Cu}_3(\text{L})-(\text{H}_2\text{O})_3)]\cdot 8\text{DMSO}\cdot 15\text{DMF}\cdot 3\text{H}_2\text{O}$) ($1.62 \text{ cm}^3 \text{ g}^{-1}$)^[16a] and Mg-MOF-74 ($0.62 \text{ cm}^3 \text{ g}^{-1}$).^[16b] Because of its high BET surface area and pore volume, Zn-CMP exhibits an excellent CO_2 adsorption capacity as shown in Table S2. According to adsorption isotherms, the uptake of CO_2 reached 58.4 mg g^{-1} at room temperature and atmospheric pressure (Figure S5). The CO_2 adsorption capacity of Zn-CMP is comparable to those of the CMPs reported (59.4 , 36.1 , 71.3 , 66.0 , and 55.4 mg g^{-1} for **1**, **2**, **3**, **4** and **5**,^[17] respectively; detailed structures are shown in Figure S6). The comparison indicates that Zn-CMP is a good CO_2 adsorption material among CMPs. We expect that the CO_2 adsorption ability of this polymer would enhance the local concentration of CO_2

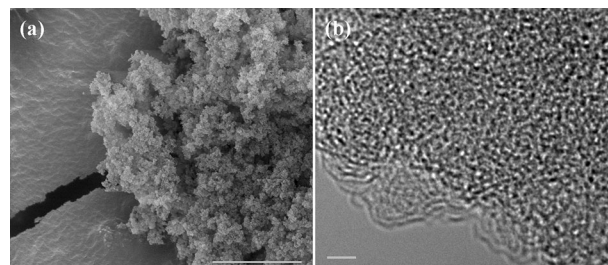


Figure 1. (a) SEM image of Zn-CMP (scale bar: 2.0 μm). (b) HR-TEM image of Zn-CMP (scale bar: 2.0 nm).

around the catalytic centers inside the polymer and thus improve its catalytic activity. The content of zinc in the polymer is 6.60 wt%, which is less than the theoretical value 9.56 wt% (Table S2). The presence of O–H vibrations (3280 and 1440 cm^{-1}) in FTIR spectra of Zn-CMP indicates that some parts of the salen units in the polymer are not coordinated to the zinc ions (Figure S7), which may be caused by metal leaking during the synthesis procedure.

Zn-CMP was initially used as a solid catalyst for the cycloaddition of CO_2 to PO with *n*-tetrabutylammonium bromide (TBAB) as co-catalyst. At a Zn-CMP loading of 0.2 mol% and a TBAB loading of 1.8 mol%, a 94.1% yield of propylene carbonate was achieved with $\text{TOF} = 470 \text{ h}^{-1}$ (entry 5, Table 1), which is higher than that achieved by using the corresponding

Table 1. Synthesis of propylene carbonate from CO₂ and PO.^[a]

Entry	Amount added [mol%]		Yield ^[b] [%]	TOF ^[c] [h ⁻¹]
	Zn-CMP	TBAB		
1 ^[d]	salen zinc (0.2)	1.8	72.5	362
2	0.2	0	10.2	51
3 ^[e]	0	0.9	11.5	13
4 ^[f]	CMP	1.8	30.9	
5	0.2	1.8	94.1	470
6	0.1	1.8	74.8	748
7	0.05	1.25	55.3	1100
8	0.02	1.25	47.1	2350
9	0.01	1.25	43.4	4340
10	0.0075	1.25	38.1	5080
11	0.005	0.9	35.7	7140
12	0.0025	0.9	29.0	11 600
13 ^[g]	0.2	1.8	76.1	8

[a] Reaction conditions: PO (50.0 mmol, 2.90 g), 120 °C, 3.0 MPa initial CO₂ pressure, 1 h, 40 mL autoclave. [b] Yields of isolated product obtained after column chromatography. [c] TOF = mol of PC produced per mol of Zn catalytic center per hour. [d] Zn-CMP was replaced with [(*R,R*)-*N,N'*-bis(3-*tert*-butyl-salicylidene)-1,2-cyclohexanediamine] (salen zinc). [e] TOF = mol of PC produced per mol of Br⁻ per hour. [f] 100 mg CMP. [g] Reaction conditions: PO (50.0 mmol, 2.90 g), 25 °C, 0.1 MPa initial CO₂ pressure, 48 h.

homogeneous catalyst salen-zinc (362 h⁻¹; entry 1, Table 1). The possible reason for such enhancement of catalytic activity is that the nanopores inside the polymer absorb CO₂ and enrich the local concentration of CO₂ near the catalytic centers resulting in a high catalytic performance of Zn-CMP. The enhancements of catalytic activities caused by nanopore confinement have been reported in other systems.^[18] In the absence of a co-catalyst, only a yield of 10.2% propylene carbonate was obtained (entry 2, Table 1). In the absence of Zn-CMP, the cycloaddition catalyzed by the co-catalyst TBAB alone gave rise to a yield of 11.5–17.6% (entry 3, Table 1 and entries S1–S3, Table S3). The salen unit without zinc showed a weak catalytic activity (entry 4, Table 1). With the use of reduced amounts of Zn-CMP and co-catalyst (entries 6–12, Table 1), considerable conversions could still be achieved, resulting in high TOFs of up to 11 600 h⁻¹ per mole of zinc loading (entry 12, Table 1). Moreover, at a Zn-CMP loading of 0.2 mol% and a TBAB loading of 1.8 mol%, a 76.1% yield of propylene carbonate was achieved with TOF 8 h⁻¹ at room temperature and atmospheric pressure. (Entry 13, Table 1). This TOF is comparable to that of the homogeneous bimetallic aluminum (salen) catalyst, which was 2–10 h⁻¹ calculated from experimental data in Ref [8b] under the same conditions.

To the best of our knowledge, Zn-CMP is the most active heterogeneous catalyst for the reaction of CO₂ and epoxides reported thus far. To make a comparison to the reported catalysts, we summarized representative homogeneous catalysts in Table S4 and heterogeneous catalysts in Table S4. As shown in Table S3, the catalytic activity of Zn-CMP is even comparable to the most active homogeneous catalyst systems, such as Mg-porphyrin,^[5] aluminum-based complexes (Al-complex),^[6] zinc-based complexes (Zn-complex),^[19a] or zinc-containing ionic liquids.^[19b] The catalyst Al-complex/PPN-Br [PPN = bis-(triphenyl-

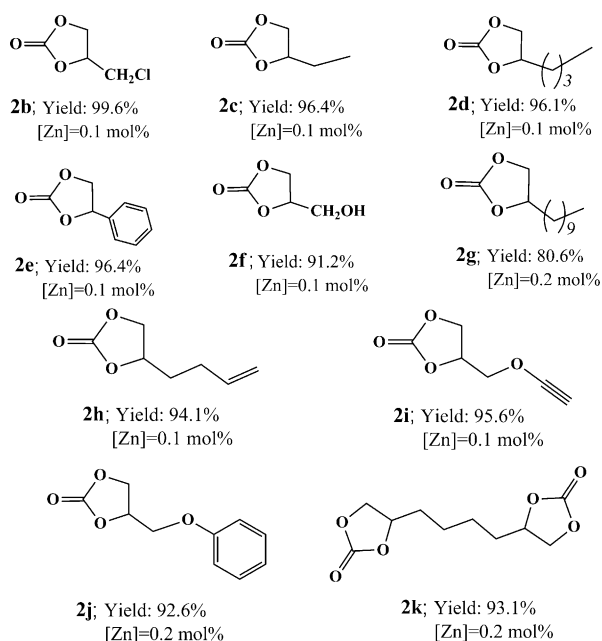
phosphine) iminium] exhibited the highest TOF (36 000 h⁻¹) for 4-butyl-1,3-dioxolan-2-one formation from 1,2-epoxyhexane at 90 °C and 1.0 MPa CO₂ pressure. For the same reaction, the TOF for using Mg-porphyrin as catalyst could reach 12 000 h⁻¹ at 120 °C and 1.7 MPa CO₂ pressure. The TOF using Mg-porphyrin as catalyst was only 3300 h⁻¹ for the reaction of PO with CO₂, which indicated that the reaction of 1,2-epoxyhexane with CO₂ is easier than that with PO. The homogeneous catalyst Zn-complex (Ni(PPh₃)Cl₂/PPh₃/Zn)^[19a] and zinc-containing ionic liquid ([EMIm]₂[Br₂Zn(Et₂PO₄)₂])^[19b] were also good catalysts for the synthesis of propylene carbonate with the TOFs up to 3544 and 2362 h⁻¹, respectively. The ZnBr₂/hexabutylguanidinium bromide catalyst^[19c] exhibited an activity (TOFs up to 8670 h⁻¹) for the coupling reaction of CO₂ with PO. We found that Zn-CMP exhibited an activity (TOFs up to 11 600 h⁻¹) comparable to that of most reported homogeneous catalysts for this reaction.

Table S5 shows the comparison between Zn-CMP and the representative heterogeneous catalysts. These catalyst systems, including zeolites and MOFs, showed good catalytic activities for the cycloaddition of CO₂ with PO or styrene oxide. Zeolites such as beta^[20a] and MCM-41^[20b] were reported to have decent catalytic activities in the cycloaddition reaction of CO₂ with PO to form propylene carbonate at 120 °C and 0.69 MPa CO₂. A long reaction time (5 h) was needed to obtain decent yields of propylene carbonates (> 90%). Several MOFs, such as Mg-MOF-74^[16b] and Co-MOF-74,^[20c] also exhibited good catalytic activities in the cycloaddition of CO₂ with styrene oxide to form styrene carbonate at 2.0 MPa CO₂ and 100 °C with > 95.0% yields. To compare Zn-CMP and Mg-MOF-74, we carried out experiments under the same experimental conditions and found that the reaction catalyzed by Zn-CMP required 3 h whereas Mg-MOF-74 needed 4 h to achieve the same yields.

To investigate the recycling stability of Zn-CMP, the experiments were repeated with a large number of iterations. We found that Zn-CMP could be reused more than ten times without significant decrease of catalytic activity (yields decreased slightly from 98.2% to 93.1%) at 120 °C and 3.0 MPa CO₂ (Figure S8).

After establishing the high catalytic activity of Zn-CMP for propylene carbonate formation (Table 1), we then investigated its reactivity for the cycloaddition of CO₂ into various highly functionalized terminal epoxides to form the organic carbonates **2b–2k** (Scheme 3). Generally, a low loading of Zn-CMP (0.1–0.2 mol%) with co-catalyst TBAB (3.6 mol%) was used to catalyze the reaction at 120 °C and 3.0 MPa CO₂. All corresponding carbonates (**2b–2k**) could be obtained with decent yields (> 90%) and high selectivity (> 99%). This result indicates that Zn-CMP has a high versatility towards cycloaddition of CO₂. In addition to alkanes, alkenes, alkynes, alkyl halides, alcohols, ethers, and aryl groups (**2b–2j**), Zn-CMP could even mediate the formation of the cyclic carbonate product **2k**. From these combined results we could clearly conclude that Zn-CMP is an excellent catalyst for the conversion of highly functional terminal epoxides.

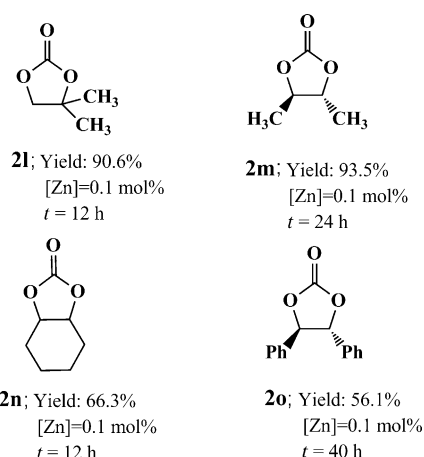
Zn-CMP was further investigated as catalyst for catalyzing the cycloaddition of CO₂ with internal epoxides (Scheme 4,



Scheme 3. Reaction Scope for terminal epoxides. Cyclic (bis-)carbonates (**2b–2k**) obtained from their corresponding epoxides using Zn-CMP/TBAB as catalytic system. General conditions are epoxides (50.0 mmol), Zn-CMP (quantity indicated), TBAB (3.6 mol%), 120 °C, 3.0 MPa initial CO₂ pressure, reaction times 1 h for **2b–2e** and 2 h for **2f–2k**, 40 mL autoclave. Yields of isolated product obtained after column chromatography.

synthesis of **21–2o**), which are widely considered as difficult substrates with few achieved successful conversions. The corresponding organic carbonates (**21–2o**) have been successfully produced by increasing the reaction time at 120 °C and 3.0 MPa CO₂. To obtain reasonable yields of product **21**, a prolonged reaction time of 12 h was required (90.6%). A decent yield of 93.5% was achieved for **2m** after 24 h. When epoxy cyclohexane was used as a substrate, the corresponding carbonate **2n** was obtained with a 66.3% yield after 12 h. The carbonate **2o** has been rarely synthesized through catalytic cycloaddition of CO₂ with stilbene oxide.^[6] However, Zn-CMP can provide a reasonable yield of 56.1% after 40 h. The *trans*-disposition of both substituents in carbonates **2m** and **2o** can be determined by ¹H NMR and ¹³C NMR spectroscopy (Figures S22 and S23).

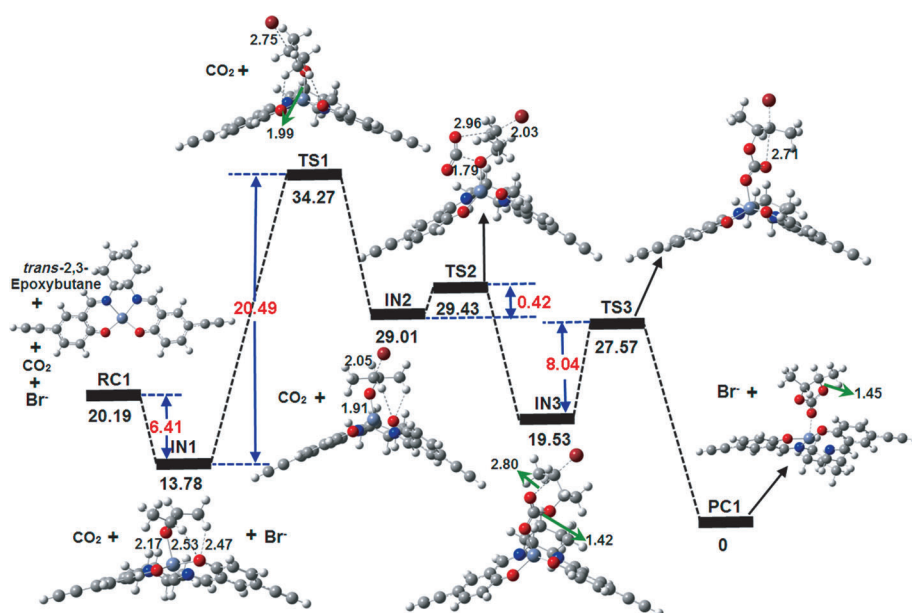
The salen-zinc center played a key role for the reaction, thus a possible catalytic cycle was proposed in Figure S24. The function of co-catalyst, quaternary ammonium salt (*n*Bu₄NBr), is to open the ring of the internal epoxide. Consequently, CO₂ mol-



Scheme 4. Reaction scope for internal epoxides. Cyclic carbonates (**21–2o**) obtained from their corresponding epoxides using Zn-CMP/TBAB as catalytic system. General conditions are epoxides (50.0 mmol), Zn-CMP (quantity indicated), TBAB (3.6 mol%), 120 °C, 3.0 MPa initial CO₂ pressure, 40 mL autoclave. Yields of the isolated product obtained after column chromatography. Further details: for **2o** 3.0 mL methyl ethyl ketone (MEK) was used in reaction; for **2o** the corresponding epoxide was 25 mmol.

ecule was coordinated to the zinc ion and an intramolecular rearrangement occurred to form the zinc carbonate (PC1), which could cyclize to form the internal carbonate and regenerate the salen zinc center and co-catalyst.

Density functional theory (DFT) calculations were performed to investigate this mechanism. Based on the proposed mechanism, five intermediates and three transition states were optimized as listed in Tables S6–S13. The energy profiles (in kcal mol⁻¹, 1 cal = 4.2 J) of these structures (in Å) are depicted in Scheme 5. The reaction was presumed to occur in four steps, starting from the adsorption of *trans*-2,3-epoxybutane to the salen zinc to form an intermediate (IN1 in Scheme 5) as an exo-



Scheme 5. Calculated energy profiles (in kcal mol⁻¹) and optimized structures (in Å) of species for the catalytic mechanism.

thermic reaction ($\Delta E = -6.41 \text{ kcal mol}^{-1}$). The next step was the ring opening of epoxybutane induced by the nucleophile (Br^-), which was considered as the most difficult step in the reaction with the highest activation energy (TS1, $\Delta E^\ddagger = 20.49 \text{ kcal mol}^{-1}$). The third step was the insertion of the CO_2 molecule, which is an intramolecular rearrangement process with a minimum activation energy (TS2, $\Delta E^\ddagger = 0.42 \text{ kcal mol}^{-1}$). The last step was the formation of the product, which is a backbiting reaction (TS3, $\Delta E^\ddagger = 8.04 \text{ kcal mol}^{-1}$). The calculation results confirmed that the catalytic procedure occurred easily as the highest activation energy of the entire catalytic reaction was only $20.49 \text{ kcal mol}^{-1}$.^[21]

In summary, we demonstrated the use of a zinc-conjugated microporous polymer (Zn-CMP) as a highly active and versatile heterogeneous catalyst for organic carbonate formation. In the presence of *n*-tetrabutylammonium bromide (TBAB), the turnover frequency (TOF) of the catalytic reaction can reach $11\,600 \text{ h}^{-1}$ at 120°C and 3.0 MPa CO_2 . The catalytic activity of Zn-CMP is comparable to that of the homogeneous catalysts and better than that of the best heterogeneous catalyst. Moreover, Zn-CMP is so far the only efficient heterogeneous catalyst suitable for internal epoxides. This polymer can be reused more than ten times without significant loss of its catalytic activity.

Experimental Section

The Supporting Information contains experimental details as well as Tables and Figures referred to in the text.

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Keywords: CO_2 fixation • cyclic carbonates • heterogeneous catalysis • turnover frequencies • polymers

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