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Title: Formation of cyclic carbonates from CO₂ and epoxides catalysed by a cobalt coordinated conjugated microporous polymer

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Formation of cyclic carbonates from CO₂ and epoxides catalysed by a cobalt coordinated conjugated microporous polymer

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Abstract: A cheap and effective cobalt coordinated conjugated microporous polymer (Co-CMP-2) was synthesized by the ethanediamine-based salen ligand cross-linked with 1, 3, 5-triethynylbenzene. Co-CMP-2 exhibited extremely high catalytic efficiency in product of cyclic carbonates from CO₂ and epoxides, which is superior to previous Co-CMP. The TOF of Co-CMP-2 could reach 23300 h⁻¹ for ethylene carbonate. Moreover, it can be reused more than 10 times without significant loss in its catalytic activity.

Introduction

The CO₂ emission has attracted attention because it is widely considered as a primary factor to the changes in global climate.^[1] However CO₂ itself is an excellent C₁ resource.^[2] Therefore, the conversion of CO₂ into useful chemicals became an important strategy for reducing CO₂ emission.^[3] One of these useful chemicals is cyclic carbonate that has wide applications in chemical industries. The cyclic carbonates were formed by the cycloaddition reaction of CO₂ with epoxides. Up to now, plenty of catalyst systems^[4] for this reaction have been reported. For instance, salen,^[5] metal salts,^[6] ionic liquids^[7] and porphyrin complexes^[8] were effective catalysts. However these catalysts were homogeneous catalysts with difficulties to be separated. Other metal oxides immobilized catalyst^[9] as heterogeneous catalysts also have been claimed but suffering the problem of low catalytic activities. It remains a challenge^[10] for the development of the synthesis of cyclic carbonate in heterogeneous catalyst at mild conditions.

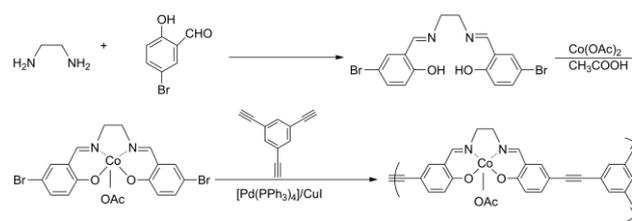
Conjugated microporous polymers (CMPs) discovered by Cooper group^[11] are of great interest because they have lots of excellent properties. These CMPs can be tailored for various applications including catalysis,^[12] gas sorption,^[11,13] superhydrophobic separations,^[14] sensors^[15] and supercapacitors.^[16] In recent years, several metal functionalized CMPs were reported to have the combination of various properties together such as the combination of gas sorption and catalytic activity. In this field, we developed a cobalt/aluminium functionalized CMPs which can capture CO₂ and convert CO₂ into cyclic carbonates at room temperature and atmospheric pressure.^[17] Because of high CO₂ capture ability, the metal

coordinated CMPs have a superior performance to corresponding homogeneous catalyst as heterogeneous catalysts^[18].

In this work, we extended the previous research and obtained a cheaper but more effective cobalt coordinated conjugated microporous polymer (Co-CMP-2). This polymer was synthesized by easily available ethylenediamine and 5-Bromosalicylaldehyde. Moreover, its catalytic activity has been significantly improved for the coupling reaction of CO₂ and epoxides. For the reaction of propylene oxide and CO₂, the TON of Co-CMP-2 is 236, which is higher than that of previous Co-CMP (201).^[17] Moreover, the TOF of Co-CMP-2 can reach 23300 h⁻¹ at mild conditions for ethylene carbonate, which is the best among literature reports to the best of our knowledge.^[19] This polymer still remains the significant recyclability for the coupling reaction, remaining a yield of 96.2% after 10 times of regeneration.

Results and Discussion

To prepare Co-CMP-2, first we synthesized dibromo-functionalized precursor monomers (Salen-Co) prepared by a complexation reaction of Salen^[20] and cobalt acetate (Co(OAc)₂). After removing impurities, we produced the Co-CMP-2 (Scheme 1) catalysed by Pd(PPh₃)₄ and CuI with 1, 3, 5-triethynylbenzene in toluene under reflux. The synthesis details are given in the Supplementary Information. Like other CMPs, the polymer, Co-CMP-2, was also completely insoluble in any organic solvents and exhibited high thermal stabilities, of which pyrolysis temperature is about 300 °C shown in Figure S1.



Scheme 1. Synthesis of Co-CMP-2

Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) were used to record the morphological structure of Co-CMP-2. The SEM images shown in Figure 1 a and b reveal that the Co-CMP-2 network morphologically consists of submicron spheres with porous features and it can be also observed from the HR-TEM pictures (Figure 1 c and d) that the Co-CMP-2 show finely ordered micropores with roughly 0.5 nm in diameter. According to these images, the polymer was featureless at those length scales.

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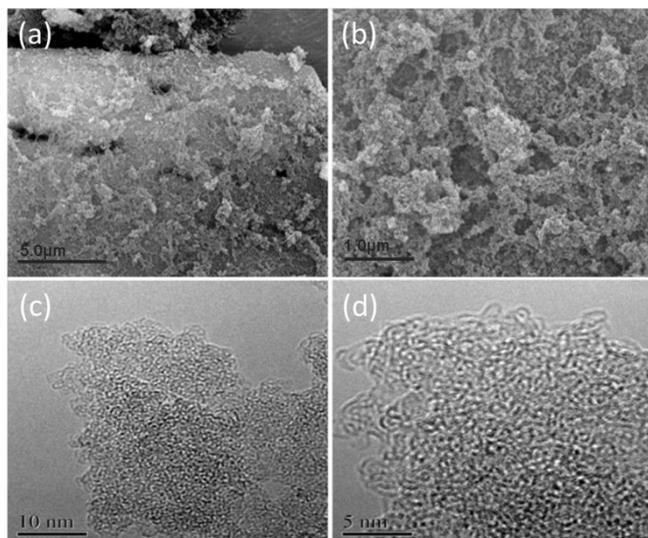


Figure 1. SEM images of Co-CMP-2 with different scan bars of 5 μm (a) and 1 μm (b); HR-TEM images of Co-CMP-2 with different scan bars of 10 nm (c) and 5 nm (d).

Moreover, nitrogen sorption isotherms were measured to investigate the porosity of Co-CMP-2 and the results are further demonstrated that the Co-CMP-2 network is porous. As summarized in Table 1, the Co-CMP-2 shows a high Brunauer-Emmett-Teller (BET) surface area of 475 m^2/g and total pore volume of 0.918 cm^3/g . According to IUPAC classification, Co-CMP-2 gave rise to type I isotherms (Figure S2), indicating that the material consisted of both micropores and mesopores. Metal (Co) content distributed in the polymer network is determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and 6.15 wt% of Co is detected, less than the theoretical value of 10.07 wt%. FT-IR result with characteristic peaks at around 3425 cm^{-1} , attributed to the O-H vibrations, indicated the existence of the Salen units in the Co-CMP-2 framework without Co-coordinated (Figure S4). The solid-state NMR data of Co-CMP-2 is in Supplementary Figure S3.

Table 1. Physical properties for Co-CMP-2.

Parameter	value
S_{BET} (m^2/g) ^[a]	475
V_{tot} (cm^3/g) ^[b]	0.918
M_{calc} (wt%) ^[c]	10.07
M_{ICP} (wt%) ^[d]	6.15
CO_2 uptake (mg/g) ^[e]	64.6

[a] Brunauer-Emmett-Teller (BET) surface area was calculated in the pressure range of (p/p_0) 0.05–0.3; [b] Total pore volume was measured at $p/p_0 = 0.99$; [c] Data was calculated based on 100% reaction of salen unit; [d] Data was obtained by inductively coupled plasma-optical emission spectroscopy (ICP-OES); [e] Volumetric CO_2 -adsorption-desorption isotherms were measured for Co-CMP-2 at 298 K.

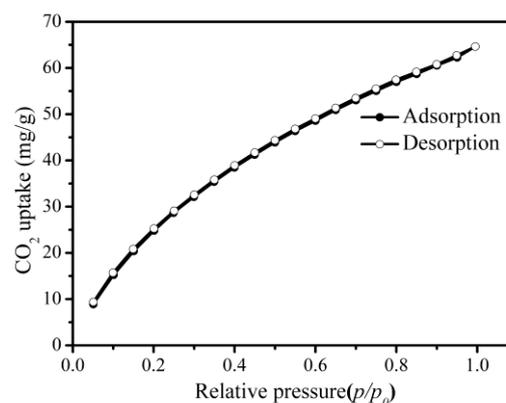


Figure 2. CO_2 -adsorption and desorption isotherm for polymer Co-CMP-2 at 298K

CO_2 adsorption was measured at 298K and 1bar using volumetric methods. As given in Figure 2, Co-CMP-2 shows a good CO_2 adsorption quantity of 64.6 mg/g , much higher than reported CMPs^[21]. The CO_2 uptakes of the tetrahedrally linked CMPs were 59.4 mg/g , 36.1 mg/g and 55.4 mg/g under the same condition, although they have higher surface area than that of Co-CMP-2. The excellent uptake capacity is ascribed to the good porosity of Co-CMP-2. On the other hand, the metal centres distributing in the CMP-2 network can function as active sites to attract CO_2 molecule, facilitating to the CO_2 adsorption.

Table 2. Cycloaddition of CO_2 with ethylene oxide

Entry	Co-CMP-2 (mol%)	TBAB (mmol)	Yields ^[a] (%)	TOF (h^{-1})
1 ^[c]	0	0.9	18.6	10.35
2 ^[b]	0.1	0.9	99.2	990
3 ^[b]	0.05	0.9	88.5	1710
4 ^[b]	0.01	0.9	81.8	8180
5 ^[b]	0.005	0.9	63.2	12600
6 ^[b]	0.0025	0.9	58.4	23300

Reaction conditions: EO (50mmol, 2.2g), 100 °C, 3.0 MPa initial CO_2 pressure, 1h, 40mL autoclave. [a] Yields of isolated product obtained after column chromatography. [b] TOF = mol of EC produced per mol of Co catalytic center per hour. [c] TOF = mol of EC produced per mol of Br⁻ per hour.

Co-CMP-2 was used as solid catalyst for CO_2 transformation in this work. The Co-CMP-2 exhibits exceptional catalytic activity towards the cycloaddition of CO_2 and ethylene oxide with *n*-tetrabutylammonium bromide (TBAB) as co-catalyst. Using 0.1 mol% of Co-CMP-2 and 0.9 mmol of TBAB, a yield of 99.2% was achieved with a TOF=990 h^{-1} (entry 2, Table 2). However,

the reaction catalysed by the co-catalyst TBAB only gave a yield of 18.6% with a TOF=10.35 h⁻¹(entry 1, Table 2) in the absence of Co-CMP-2. The results indicate that the Co-CMP-2 polymer exhibited high catalytic activity for CO₂ transform. With the use of reduced amounts of Co-CMP-2 (entry 3-6, Table 2), considerable yields could still be achieved. Especially, when the amount of Co-CMP-2 reduced to just 0.0025 mol% of the ethylene oxide, an extremely high TOF up to 23300 h⁻¹ per mole of Co loading can be obtained, indicating that the Co-CMP-2 has a superior catalytic ability for the CO₂ transformation(entry 6, Table 2).

To further demonstrate the superiority of Co-CMP-2, we next carried out reactions to compare with previous Co-CMP (Table 3). As for ethylene carbonate, Co-CMP-2 gave excellent yield (99.1%) at the relatively high temperature(100 °C) and CO₂ pressures (3MPa)(Entry 1, Table 3). For the reaction to produce propylene carbonate, the TON of Co-CMP-2 exhibited 236 with yield 98.7% (Entry 2, Table 3), which is better than that of previous Co-CMP (TON 201 with yield 98.1%).^[17]

Table 3. Cycloaddition of CO₂ with various epoxides.

Entry	Substrate	Product	T/°C	P/MPa	Yield ^[a] /%	TON ^[d]	TOF ^[e] /h ⁻¹
1 ^[b]	EO	EC	100	3.0	99.1	237	237
2 ^[c]	PO	PC	100	3.0	98.7	236	236

[a] Yields of isolated product obtained after column chromatography. [b] EO=ethylene oxide, EC=ethylene carbonate, reaction conditions: Co-CMP-2(100mg), EO (25mmol), co-catalyst (TBAB) 1.8mmol, 1h. [c] PO=propylene oxide, PC=propylene carbonate, reaction conditions: Co-CMP-2(100mg), PO (25mmol), TBAB 1.8mmol, 1h. [d] TON = (moles of product)/(moles of metal in the catalyst). [e] TOF = mol of product produced per mol of Co catalytic center per hour.

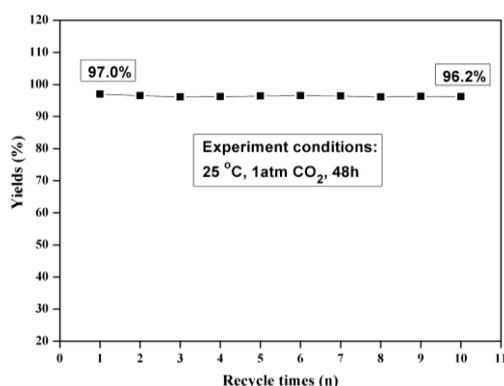


Figure 3. Recycled experiment of Co-CMP-2 for the cycloaddition of CO₂ and propylene oxide

To investigate the recycle stability of Co-CMP-2, multiple experiments were repeated using the regenerated Co-CMP-2 polymers. We found that the Co-CMP-2 could be reused more than 10 times without significant loss in catalytic activity under atmospheric pressure and room temperature as shown in Figure 3. Given the easy regeneration, excellent reusable ability and the low cost because of the ethylenediamine and 5-

Bromosalicylaldehyde materials, the CO-CMP-2 catalyst can be used as a promising candidate in industrial application.

Conclusions

In conclusion, the Co-CMP-2 polymer can not only capture CO₂ but also transform CO₂ with high efficiency under atmospheric pressure and room temperature. A significantly high TOF was achieved for the cycloaddition of CO₂ and ethylene oxide. Besides, the low cost of the Co-CMP-2 is also favourable for the real application. This work provides a cost-effective heterogeneous catalyst and new strategy for CO₂ conversion.

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Experimental Section

The procedure for the synthesis of Co-CMP-2: Salen-Co-OAc(scheme 1, 0.6mmol), 1, 3, 5-triethynylbenzene (1.2mmol), copper(I) iodide (50 mg) and tetrakis-(triphenylphosphine) palladium(0) (100 mg) were dissolved in a mixture of toluene (15 mL) and triethylamine (6 mL). The reaction mixture was heated to 40 °C and stirred for 1 hour under an argon atmosphere (to exclude oxygen and prevent any homocoupling of the alkyne monomers). Next, the reaction mixture was heated to 80 °C, stirred for 72 hours, then cooled to room temperature. The insoluble precipitated polymer was filtered and washed four times with dichloromethane, methanol, water, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol and dichloromethane (volume ratio = 1:1) for 48 hours. The product was dried in a vacuum for 24 hours at 70 °C and isolated as a brown powder (yield: 79.6%).

The procedure for the synthesis of cyclic carbonates at room temperature and atmospheric pressure (Propylene oxide as an example): A mixture of Bu₄NBr (1.8 mmol, 600 mg) and Co-CMP-2 (100 mg) was placed in a vacuum tube reaction. Propylene oxide (25 mmol, 1.75 ml) was added to the tube using a syringe, and CO₂ (at atmospheric pressure) was introduced. After being stirred for 48 hours at 25 °C, the reaction mixture was dissolved with ethyl acetate (30 ml), and the insoluble solid material was filtered. Removing the solvent from the filtrate yielded a pale yellow oily substance. Further purification of the crude product was carried out by column chromatography (yield: 97.0%).

Keywords: carbon dioxide • cyclic carbonates • heterogeneous catalysis • cost-effective • high-efficiency

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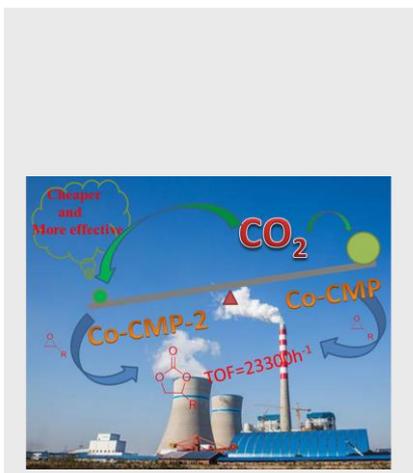
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Layout 1:

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**Formation of cyclic carbonates from
CO₂ and epoxides catalysed by a
cobalt coordinated conjugated
microporous polymer**

Layout 2:

FULL PAPER

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