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Modulation the Acidic and Basic Site Concentration of the Metal-organic Framework Derivatives to Promote the Carbon Dioxide Epoxidation Reaction

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Abstract: Metal-organic Framework (MOF) is an ideal precursor/template for porous carbon, and its active components are uniformly doped, which can be used in energy storage and catalytic conversion fields. Metal-organic framework PCN-224 with carboxylporphyrin as ligand was synthesized, and then Zn^{2+} and Co^{2+} ions were coordinated in the center of the porphyrin ring by post-modification. Here, PCN-224-ZnCo with different ratios of bimetallic Zn^{2+}/Co^{2+} ions were used as the precursor, and the metal-nitrogen-carbon(M-N-C) material of PCN-224-ZnCo-950 was obtained by pyrolyzing the precursor at 950 °C in Ar. Because Zn is easy to volatilize at 950 °C, the formed M-N-C materials can reflect different Co contents and different basic site concentrations. The formed material still maintains the original basic framework. With the increase of Zn^{2+}/Co^{2+} ratio in precursor, the concentration of N-containing alkaline sites in pyrolysis products gradually increase. Compared with the precursor, PCN-224-ZnCo$_1$-950 with Zn^{2+}/Co^{2+}=1:1 has greatly improved basicity and suitable acidic/ alkaline site concentration. It can be efficiently used to carbon dioxide absorption and catalyze the cycloaddition of CO_2 with epoxide. More importantly, the current method of adjusting the acidic/basic sites in M-N-C materials through volatilization of volatile metals can provide an effective strategy for adjusting the catalysis of MOF derivatives with porphyrin structure.

Introduction

As we all know, the global warming caused by CO_2 is becoming more and more serious, so the use of CO_2 as carbon source has been widely concerned in the research.[1] On this premise, cycloaddition of epoxide and CO_2 to form cyclic carbonate is an atom-economic method to obtain high-yield cyclic carbonate.[2] Metal-organic framework materials have received extensive attention in the past decades due to their designable structure and different physical and chemical properties. Metal-organic framework materials have attracted extensive attention in the past decades because of their designable structures and different physical and chemical properties.[3] Various application fields including gas storage, separation and catalysis have been explored and developed, including the adsorption and fixation of carbon dioxide.[4] The cycloaddition of carbon dioxide and epoxy compounds to form cyclic carbonates is an atomic economic process,[5] and cyclic carbonates are used as an electrolytes for lithium ion batteries and intermediates for the synthesis of fine chemicals. However, under mild conditions, the kinetic inertia and stability of CO_2 are greatly limited in its utility as a C1 source.[6] To promote the adsorption of carbon dioxide, the MOF can be designed with different metal ions/clusters and different organic linking groups to provide advanced features,[7] such as high CO_2 absorption,[8] permanent porosity and active catalytic sites.[9] Zinc-based ZIF MOF (ZIF-8, ZIF-90, ZIF-68, etc.) and its derivatives are first used as MOF catalysts for the preparation of cyclic carbonates by CO_2 conversion from epoxides for the first time.[10] However, the pore size of this type of MOF is extremely small, the ability to adsorb CO_2 is extremely weak, and the small particles of ZIF require complicated purification steps to be separated from the reactants.[11]

MOF catalysts based on porphyrin structural units, such as PCN-224, have large pore size and relatively stable performance, with a pore size of about 19.1Å.[12] More and more researchers begun to study the pore size of MOF and tried to improve the catalytic reaction by increasing the pore size of MOF.[13]

PCN-224 (Co) is a kind of PCN-224 MOF with Co metal ions coordinated in the porphyrin center. As an acidic site, Co can effectively promote the ring opening of the epoxy compounds and greatly enhance the addition efficiency of CO_2 in the reaction. However, the N base active site in porphyrin is occupied, which greatly weakens the absorption of CO_2 by the N active site.[14] Therefore, balancing the catalytic activity of acid-base active centers is an important task to improve porphyrin MOF catalyst.[15] In addition, the catalyst can be simply and effectively separated from the reaction mixture by using the magnetism of cobalt,[16] which is beneficial to the recycling of the catalyst.[17]

In this study, based on PCN-224 coordinated with two metals, Zn and Co, the bimetallic PCN-224 is pyrolyzed at a proper temperature to volatilize Zn, which can not only release part of basic N sites,[18] but also produce some high-activity defects and increase the content of coarse pores and mesopores. This can greatly improve the activity and reaction efficiency of the catalyst. Pyrolysis of MOF can provide porous carbon with high surface area and uniform heteroatom distribution. For example, ZIF-MOF can provide high N content and/or CoNx active sites in products.[19] After pyrolysis of porphyrin-based MOF, MNx species of different metals will be stabilized in the carbon matrix to ensure high dispersion and show synergistic effect in catalysis.[20]

According to the literature reports,[21] metalloporphyrin is easier to generate PCN-222 than PCN-224, while metalloporphyrin is difficult to generate metalized PCN-224. Therefore, in order to obtain bimetal (Zn and Co) PCN-224-ZnCo, we first synthesized PCN-224 without metal in the center of porphyrin ring, and then post modified PCN-224 with $ZnCl_2$ and $CoCl_2{\cdot}6H_2O$ to obtain bimetal (Zn and Co) PCN-224-ZnCo.

Experimental Section

All chemicals are purchased from Shanghai Aladdin Bio-Chem Technology Co, LTD and used without any further purification.

Synthesis of organic ligands: According to previous reports,[22] tetrakis(4-carboxyphenyl) porphyrin (H_2TCPP) was synthesized with minor modifications according to previous reports. Generally, pyrrole (3.0 g, 0.043 mol) and methyl p-formylbenzoate (6.9 g, 0.042 mol) are added into a three-necked flask, and then 100 mL of propionic acid is slowly added to the three-necked flask in a fume hood. The solution is heated to 160°C, refluxed for 12 hours, and then cooled to room temperature. The resulting solution is filtered in a fume hood. The solid is washed with ethanol, ethyl acetate and tetrahydrofuran respectively, and dried in a vacuum oven for 10 h to obtain (TPPCOOMe). Then put the obtained solid (1.95 g) into a three-necked flask, dissolve it with tetrahydrofuran (60 mL) and methanol (60 mL), and then add a solution of KOH (6.82 g) in H_2O (60 mL). The mixture solution is heated to 80 °C, refluxed for 12 hours, and then cooled to room temperature. H_2O is added to ensure that the solid is completely dissolved, and then the solution is adjusted to Ph=3 with 1 mol/L HCl, and no more purple precipitate is produced. The purple solid is filtered, washed with 100 mL of water, and dried in a vacuum drying oven to obtain a blue-purple solid (H_2TCPP).[23]

Synthesis of PCN-224: A few modifications have been made to the synthesis of PCN-224 according to the latest reports.[24] Typically, $ZrCl_4$(120 mg), H_2TCPP (50 mg) and benzoic acid (1200 mg) are dissolved ultrasonically in DMF (8 mL) in a 20 mL Pyrex vial. The mixture is heated in an oven at 120 °C for 24 h. After cooling to room temperature, cubic dark purple crystals are collected by filtration.

Synthesis of PCN-224-ZnCo$_1$: Putting 1.125mmol of $ZnCl_2$ and 1.125mmol of $CoCl_2{\cdot}6H_2O$ (the molar ratio of Zn to Co is 1:1) into a three-necked flask filled with 30mL DMF, then add 200mg of PCN- 224, heat to 120°C to react for 12 hours, and then centrifuge the mixture. Pour out the liquid, wash the remaining solid twice with fresh DMF and twice acetone with low-boiling point, and finally put it into a vacuum drying oven and dried at 70 C for 8h to obtain PCN-224-ZnCo$_1$.

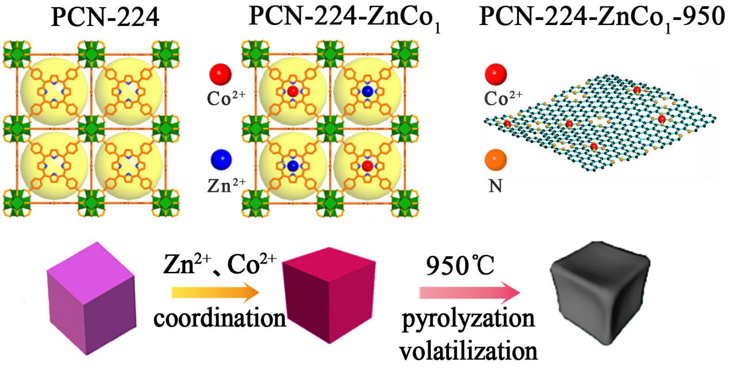
Synthesis of PCN-224-ZnCo$_1$-950: PCN-224-ZnCo$_1$ powder (100mg) was placed in a tubelar furnace and heated to 950 °C at a rate of 5 °C/min under flowing argon. The porous carbon composite PCN-224-ZnCo1-950 was obtained by pyrolyzing the powder at 950 °C for 2h and then naturally cooling to room temperature. The product was vacuum dried at 80 °C for 24 hours before use.

Catalytic Performance: The catalyst is used to catalyze the cycloaddition reaction of CO_2 and epoxy compounds, which can obtain cyclic carbonate with high efficiency. The typical experimental procedure is as follows: Add PCN-224-ZnCo$_1$-950 (10 mg) and tetra-n-butylammonium bromide (0.216 mmol) cocatalyst are added into a solvent-free schlenk tube, and a balloon filled with carbon dioxide is placed at the nozzle. Evacuate the test tube, and then continue to add epoxides (propylene oxide, epichlorohydrin, 1,2-epoxy octane, n-butyl glycidyl ether and epoxy propylene, etc. 5 mmol) to the schlenk tube. Schlenk tube was putted into an oil bath at 50 °C for 20 h. After the reaction, the mixture was cooled to room temperature and separate the catalyst from the mixture with a high-speed centrifugation. Chloroform was added to small amount of supernatant to gain the reaction mixture. Use ^{1}H NMR ($CDCl_3$, TMS as internal standard) to analyze and calculate the conversion rates of the epoxy carbonates. The separated catalyst was washed several times with acetone, and then dried in a vacuum drying oven for 10 hours before being stored for the next reaction.

Results and Discussion

Morphology and Structure Characterization

With reference to Zhou's literature and many improvements,[25] Zr-based porphyrin MOF (PCN-224)with high stability was synthesized, based on six-linked Zr_6 clusters and tetra(4-carboxyphenyl) porphyrin (TCPP).Porphyrin ligands form mesoporous MOF, and then active Zn^{2+} and Co^{2+} are introduced into the center of the porphyrin ring. The molar ratio of the two metals is 1:1, so the bimetallic PCN-224 in the text is named as PCN-224-ZnCo$_1$ (Scheme 1). Finally, after pyrolysis at 950 °C, the structure with highly dispersed ZnN_X and CoN_x is transformed into porous carbon nanocubes (Figure 1).The image of the electron microscope shows that under pyrolysis at a high temperature of 950 °C, the original cube frame did not collapse, and some crystals even appeared hollow structures. With the increase of mesopores and macropores, the active sites of the catalyst are fully contacted with reactants, which reduces the mass transfer resistance and greatly shortens the reaction time. Moreover, there is a synergistic effect between Co and exposed N active sites. Calcination increases the concentration active sites of basic N and promotes the degree of graphitization, thereby increasing the activity and stability of the catalyst.



Scheme 1. The main synthesis process of PCN-224-ZnCo$_1$-950.

We use pyrolysis to remove Zn from PCN-224-ZnCo$_1$, so it thereby releases thereby releasing higher alkaline active sites. The concentration of alkaline active center formed in the raw material with ratio of Zn/Co=1:1 is reasonably matched with the concentration of acidic sites formed by Co and Zr in the same raw material (PCN-224-ZnCo$_1$-950), which produces the best catalytic effect in the epoxidation of carbon dioxide (Table 2).

Fourier transform infrared (FTIR) spectrum is shown in Figure 2. Compared with H_2TCPP ligand, the asymmetric vibrational absorption intensity of the C-OH and C=O groups is greatly reduced after the Zr^{4+} coordinated with the -COOH group in PCN-224. By post-modifying PCN-224 with Zn and Co ions, it can be observed that the synthesized PCN-224-ZnCo$_1$ has no N-H bond absorption peak. In addition, PCN-224-ZnCo1 has Co-N and Zn-N absorption peaks at 1004cm^{-1} and 1008cm^{-1} (Figure 2b, Figure 2c), which further reflects the metallization of porphyrin ring with Zn and Co, and then PCN-224-ZnCo$_1$ is pyrolyzed at a temperature of 950 ℃, the disappearance of the Zn-N bond (Figure 2c) is sufficient to prove the disappearance of Zn.

Similarly, we analyzed PCN-224-ZnCo$_1$-950 by X-ray photoelectron spectroscopy (XPS), and further determined the chemical state of each element. As shown in Figure 3a, XPS spectrum clearly depicts the presence of C, N, O, Co, while the existence of Zn is not detected, which illustrates the absence of Zn. In order to further verify the lack of Zn, the true contents of zinc and cobalt were determined by ICP-AES. It can be seen that the actual Zn and Co contents in PCN-224-ZnCo$_1$-950 are 0.03 and 0.59wt%, respectively (Table S1). The high-resolution N 1s XPS spectrum can fit four sub-peaks, indicating that there are four different types of N, namely pyridine N, graphitized N, pyrrole N, and oxide N. The peak positions are 398eV and 400.9eV, 399.3eV and 404.5eV. It can be seen from Figure 3b that the highest content of pyrrole N is generated after the volatilization of Zn in the ZnNx structure of the protoporphyrin unit. It has the dual characteristics of basic sites and defects formed in PCN-224-ZnCo1-950 with pyrolysis, which is also an important reason for the high catalytic activity.

Peak of PCN-224-ZnCo1-950 at 789.5eV corresponds to $3p_{3/2}$ of Co element. In the high-resolution 2p spectrum of Co, 781.5eV indicates that there are Co-N species in the sample, which proves the interaction between Co and N. In the C 1s spectrum, it shows that there are four types of C atoms, including C=C, C-N, C-O and C=N.PCN-224 is chosen because it has 3D porous structure, very high surface area, and most importantly, the hollow porphyrin center is easy to metallize. Through controlled the process of pyrolysis,[26] PCN-224-ZnCo$_1$-950 was obtained. It can be seen from the electron micrograph that the morphology of PCN-224-ZnCo$_1$-950 is similar to that of PCN-224 before modification, showing a concave cubic shape (Figure 1).

From the pore size and specific surface analysis results, it can be seen that PCN-224-ZnCo$_1$-950 shows a high BET surface area (1240 m^{-2}g^{-1}), and the pore size is mesopores (S5-S7) concentrated in about 3 nm. However, from the comparison of pore sizes before and after pyrolysis, it can be seen that after pyrolysis (Figure S6,7), a relatively large pore size of about 10-20 nm has been appeared, indicating that pyrolysis has formed a graded pore distribution, which is conducive to the diffusion of substances in the catalytic process, thus promoting the cycloaddition efficiency.[27] During the pyrolysis process, the Co species of PCN-224-ZnCo$_1$-950 has a better diffusion coefficient which can better diffuse to the outer surface, and then the pyrolysis product of organic ligands are graphitized around the outer Co.[28] When the carbon shell exceeds the critical thickness that can stabilize it, the structural collapse, thus forming a hollow structure of porous carbon (Figure 1f).

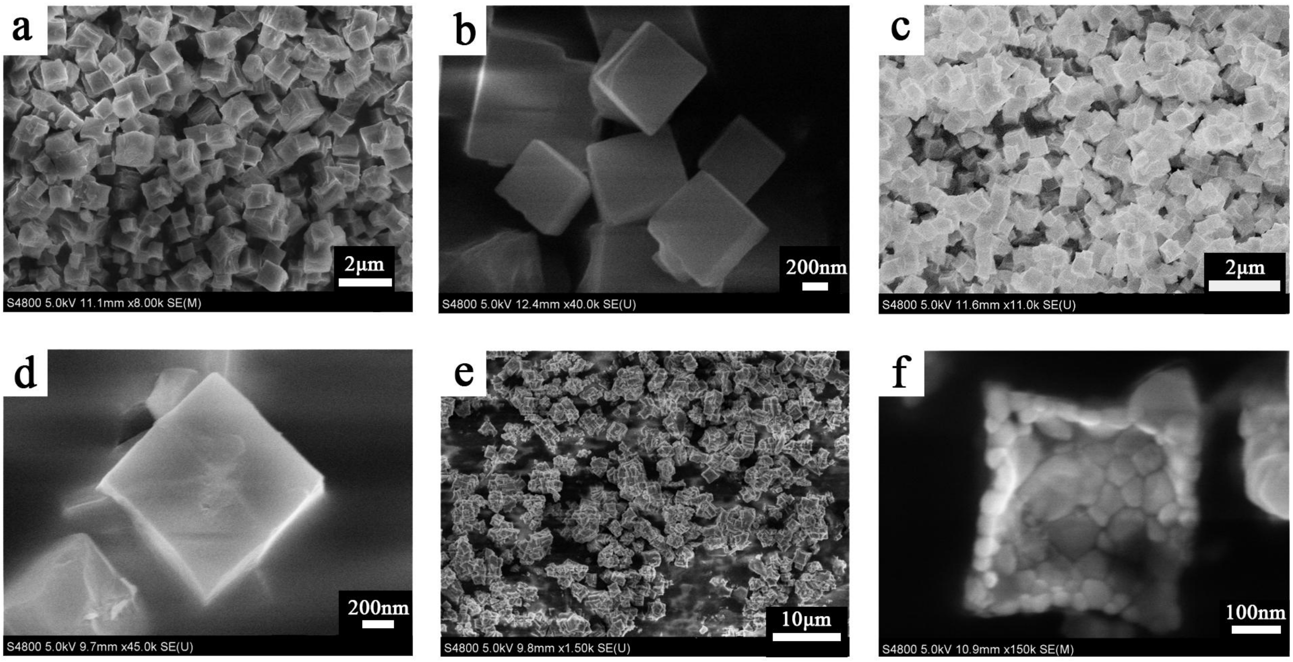


Figure 1. SEM images of (a), (b) PCN-224, (c), (d) PCN-224-ZnCo$_1$ and (e), (f) PCN-224-ZnCo$_1$-950.

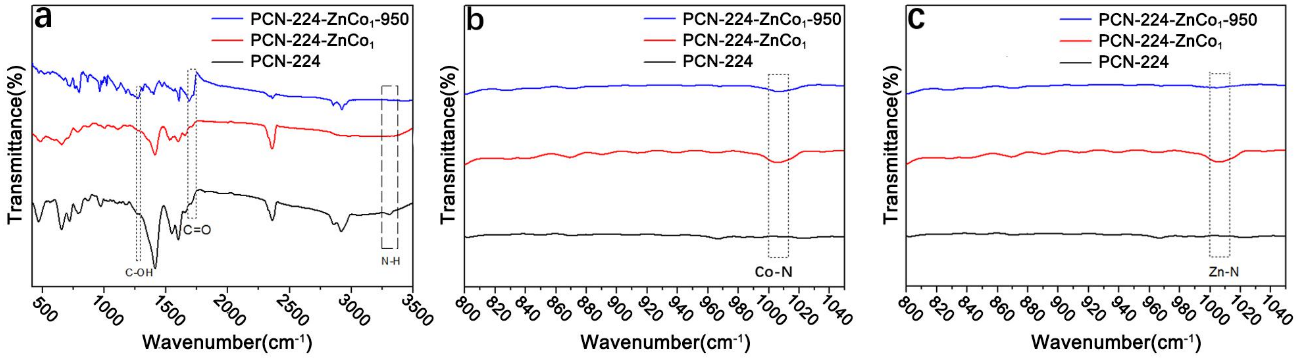


Figure 2. (a) FTIR spectra of PCN-224ZnCo$_1$-950, PCN-224-ZnCo$_1$ and PCN-224; (b), (c) The magnified FTIR spectra of PCN- 224-ZnCo$_1$-950, PCN-224-ZnCo$_1$ and PCN-224.

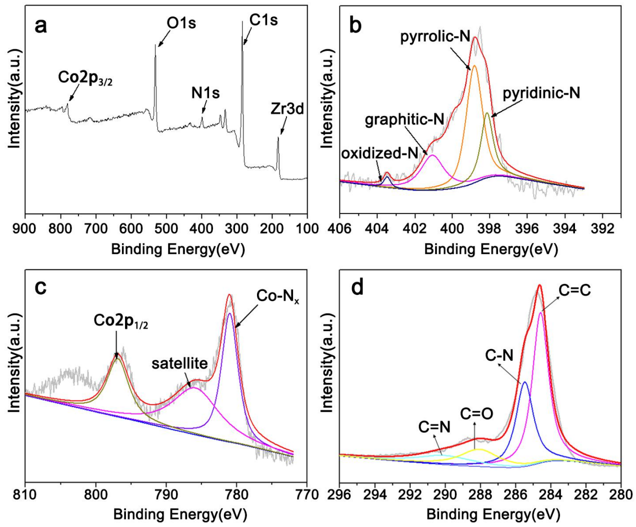


Figure 3. (a) PCN-224-ZnCo$_1$-950 XPS total spectrum. The high-resolution XPS spectra of (b) N 1s, (c) Co 2p and (d) C 2s in the PCN-224-ZnCo$_1$-950 sample.

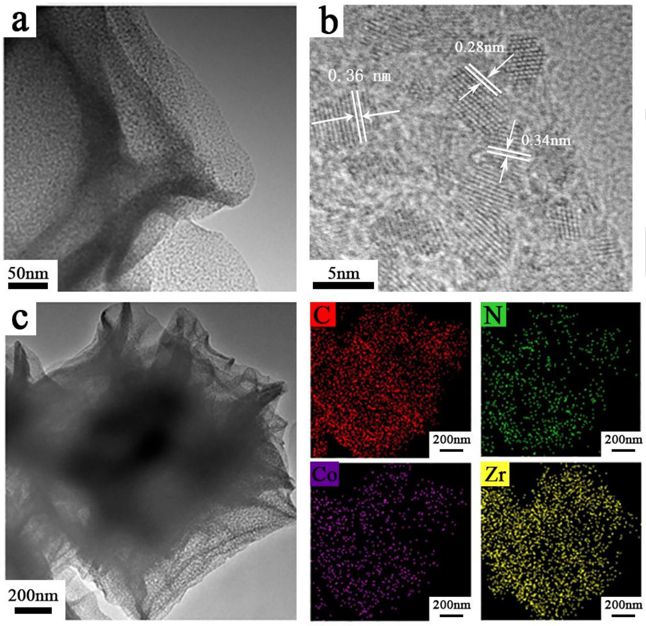


Figure 4. (a), (b), TEM of PCN-224-ZnCo$_1$-950. (c) TEM of PCN-224-ZnCo$_1$-950 and corresponding C, N, Co, and Zr elemental mappings for PCN-224-ZnCo$_1$-950.

The formation of pyrolysis products with partial hollow structure is very beneficial to promote catalytic reaction kinetics. During pyrolysis process, the Zn/Co species can catalyze graphitization of organic structures. The HRTEM images clearly show the lattice stripes of graphitized carbon and Co_2O_3 metal clusters. The interplanar spacing is 0.34 nm, corresponding to the (002) carbon plane of graphite carbon (Figure 4b),which is consistent with the peak value of θ=25.8°in PXRD pattern (Figure S4).

After pyrolysis, cobalt exists in the form of Co_2O_3 nanoclusters with a diameter of 2-3nm and is uniformly embedded in the network of nitrogen-carbon materials. From the HTEM image, the lattice fringe spacing of Co_2O_3 is 0.28, corresponding to the (225) crystal plane, which is consistent with the peak at θ=44.2° in the PXRD image. The nano-ZrO_2 structure appeared in the material was formed after the pyrolysis of the node ZrO_6 cluster. The lattice fringe spacing of ZrO_2 is 0.3nm, corresponding to the (101) crystal plane, which is consistent with the peak at θ=43° in the PXRD pattern (Figure S4).

The degree of graphitization of PCN-224-ZnCo$_1$-950 can be further characterized by Raman scattering spectrum (Figure S9). The D and G band at 1322 and 1560 cm^{-1} correspond to disordered and sp^2 hybrid graphitized carbon, respectively. The smaller the ratio, the higher the degree of graphitization in the carbon materials. According to the test, the I_D/I_G of the material is 1.06. The graphitization process further adjusts the electronic structure of the PCN-224-ZnCo$_1$-950 material, which also promotes the catalytic reaction.

Catalytic Performances for CO_2 cycloaddition

The acidity and alkalinity of the catalysts play a very important role in catalyzing the addition reaction of carbon dioxide and epoxide to form cyclic acid esters. In this paper, the acidity and alkalinity characteristics of catalytic materials are measured by temperature program desorption (TPD) technology, using NH_3 (NH_3-TPD) and CO_2 (CO_2-TPD) as probe gases. Tests of CO_2-TPD and NH_3-TPD clarified the concentration of alkalinity and acidity in pyrolyzed PCN-224-ZnCo$_1$-950 material (Figure 5, Table 1).MOF composed of zinc porphyrin units is pyrolyzed at high temperature, and the N-site generated by the zinc metal volatilization process becomes a non-coordinating basic site, which plays a very important role in the adsorption and activation of CO_2 and can interact synergistic catalysis occurs at acidic sites. It can be seen from Figure 5 and Table 1 that the PCN-224-ZnCo$_1$-950 obtained after pyrolysis has higher alkalinity and lower acidity than the precursor PCN-224-ZnCo$_1$. It can be known from the subsequent catalytic results (Figure 6, Table 2) that PCN-224-ZnCo$_1$-950 has excellent catalytic performance for the cycloaddition reaction of carbon dioxide and epoxy compounds. Before pyrolysis, the ratio of alkalinity/acidity in PCN-224-ZnCo1 is 0.0092. After pyrolysis, the ratio of alkalinity/acidity in PCN-224-ZnCo$_1$-950 is 0.0267, which has increased by nearly 3 times.

As can be seen from Figures 3 and 4, after PCN-224-ZnCo$_1$ pyrolyzed, it showed well-dispersed Co_2O_3 nanoclusters in the N-doped porous carbon matrix. The mechanism of heterogeneous catalyst to catalyze the cycloaddition of CO_2 in an N-doped carbon matrix can be attributed to the synergistic effects of basic sites derived from the activated N compounds (N-doped carbon matrix) with Co sites. The acidic site properties of Co will activate the ring opening of the epoxide (Figure 6). In addition, the existence of well-dispersed Co species surrounded by protective carbon walls may contribute to binding and activating the epoxides (substrates). The alkalinity of N-compound formed by the volatilization of zinc can not only activate the carbon dioxide, but also enhance its adsorption, thus promoting the catalytic reaction. From the above-mentioned alkalinity to acidity concentration ratio, it can be seen that in a good cycloaddition catalyst, the concentration of acidic sites is still much higher than the alkali site concentration, reaching more than 37 times (Table 1), which is not a simple one-to-one relationship.

To test TPD, we used Micromeritics Chemisorb 2750 automation system and ChemiSoft TPx software to perform temperature programmed desorption (TPD) on all samples. The sample was pretreated at 250 °C for 1 h under carrier gas helium, and then cooled to the adsorption temperature of 25 °C. NH_3 and CO_2 are introduced into the sample as detection gases by continuous flow. The probe gas is adsorbed to saturation at an adsorption temperature of 25 °C, which can be observed from the stable signal of the TCD detector. Then the sample is flushed with helium until a stable transcranial Doppler signal is obtained, and the physically adsorbed gas on the sample is removed and use the TCD detector to measure the desorption temperature of the program, and the temperature will rise to 270 °C at a rate of 10 °C / min.

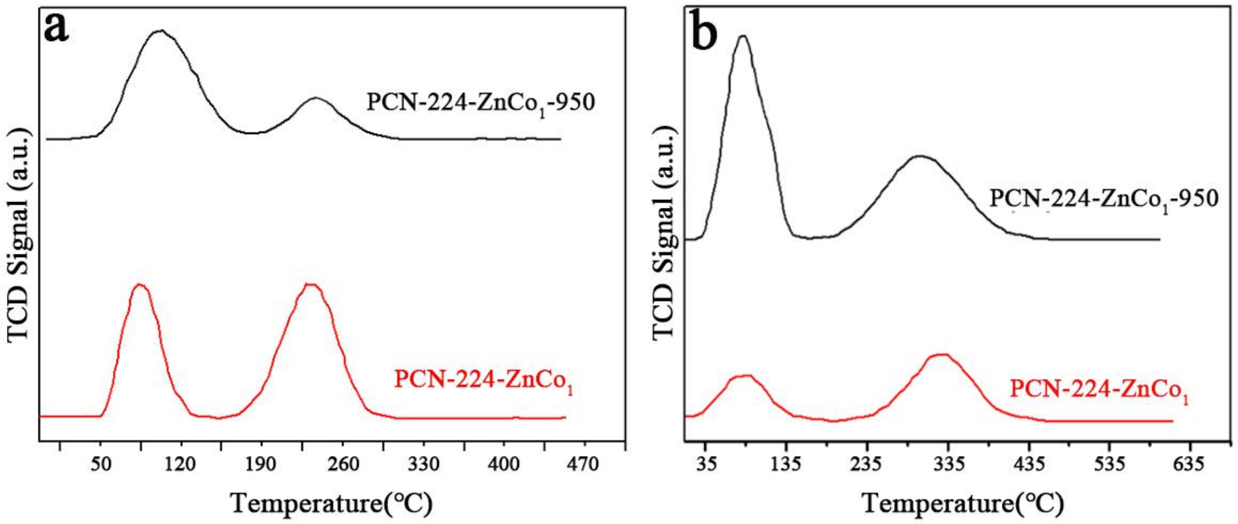


Figure 5. Temperature program desorption curve of PCN-224-ZnCo$_1$-950: (a) NH_3-TPD. (b) CO_2-TPD.

Table 1 Concentration of acidic and basic sites in PCN material [a]

Samples	Acidic* (mmol/g)	Basic* (μmol/g)
	NH3-TPD	CO_2-TPD
PCN-224-ZnCo$_1$	0.429	3.96
PCN-224-ZnCo$_1$-950	0.264	7.06

[a]: Acidic/basic concentrations were obtained by area integration of the peak area of CO_2-TPD and NH_3-TPD, respectively

It can be seen from the above discussion that the ratio of the basic sites of N to acidic sites of cobalt will affect the conversion rate of the CO_2 reaction. If the basic sites of N increase greatly and the acidic sites are reduced, will the catalytic performance continue to improve? Although there are many basic sites that can greatly absorb the acidic gas CO_2, not enough acid sites will also affect the progress of the reaction. We mixed different content of Zn/Co metal salt (mol%, Zn:Co=1:2, Zn:Co=2:1, Zn:Co=1:1) and reacted with PCN-224 to obtain several kinds of metalized PCN-224 with different Zn^{2+}/Co^{2+} contents. Then calcine these samples in a tube furnace at 950 °C in an argon atmosphere respectively. The products were applied to catalyze the reaction of CO_2 with 1,2-epoxyoctane, the reaction time 8h. The measured catalysts were PCN-224-ZnCo$_3$-950 (Zn:Co=1:2), PCN-224-ZnCo$_2$-950 (Zn:Co=2:1), PCN-224-ZnCo$_1$-950 (Zn:Co= 1:1). The product is cyclic octane carbonate, and the conversion rates of 1,2-epoxyoctane are 43.7%, 40.5%, and 55.8% respectively (see Table 2). It can be seen that the Zn/Co ratio is higher than 1 or less than 1, the catalytic activity is not as good as the catalyst PCN-224-ZnCo1-950 with the Zn/Co ratio equal to 1. In addition, PCN-224 containing no metal and PCN-224-Co containing only cobalt were further calcined at 950 °C. After strict heat treatment, two calcination catalysts PCN-224-950 and PCN-224-Co-950 were obtained, and their catalytic performance was tested. The CO_2 and 1,2-epoxyoctane were used in the ring reaction, and the reaction was carried out at 45 °C for 8h. The catalytic conversion rates of PCN-224-950, PCN-224-Co-950, and PCN-224-ZnCo$_1$-950 to 1,2-epoxyoctane were 36.2%, 48.1%, and 55.8%, respectively (Table 2). It can be seen that the catalytic effect of metal-free catalyst (equivalent to full zinc content and then all volatilization) and catalyst containing total cobalt acidic sites is not as good as PCN-224-ZnCo$_1$-950 with a ratio of Zn/Co=1:1. The substrate for catalyzing the reaction is enlarged. Different substrates were used to test the catalytic performance of PCN-224-ZnCo$_1$-950 (Table 3). The reaction conditions:

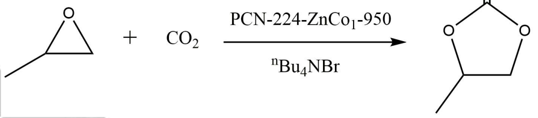
catalysts 10 mg, 5 mmol of epoxy compound, 0.216 mmol of cocatalyst nBu4NBr,[29] 50 °C, 1 bar CO_2 and 16h. The results are shown in Table 3. It can be seen from Table 3 that the catalyst also has a very significant catalytic epoxidation effect on epoxy compounds with long carbon chains, which benefits (for forming) from its larger pore structure and graded pore characteristics. Compared with the catalysts reported in literature (Figure S8), PCN-224-ZnCo$_1$-950 has obvious advantages. After the reaction was completed, the used catalyst was washed three times with methanol, and then dried in vacuum at 80 °C for 6h. The results of repeated use experiments showed (Figure S10) that after 8 times of repeated use, the catalytic performance has changed little.

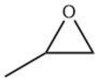
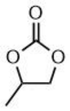
Table 2: Catalytic activities of different catalysts [a]

Entry	Catal.	Sub.	Temp.(°C)	Cyclic Carbonate Yield (%)
1	PCN-224	Epoxy octane	45	26.4
2	PCN-224-Co	Epoxy octane	45	32.8
3	PCN-224-ZnCo$_1$	Epoxy octane	45	33.6
4	PCN-224-ZnCo$_3$-950	Epoxy octane	45	43.7
5	PCN-224-ZnCo$_2$-950	Epoxy octane	45	40.5
6	PCN-224-950	Epoxy octane	45	36.2
7	PCN-224-Co-950	Epoxy octane	45	48.1
8	PCN-224-ZnCo$_1$-950	Epoxy octane	45	55.8

[a]:Reaction conditions: Epoxy octane(5 mmol), catalyst (10 mg), nBu_4NBr (0.216 mmol), 45 °C,8 h, 1 atm CO_2.

Table 3 PCN-224-ZnCo$_1$-950 catalyzed the cycloaddition reaction of various substrates with carbon dioxide



Entry	Epoxide	Product	Yield (%)
1			100

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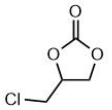
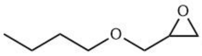
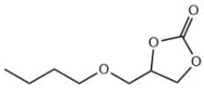
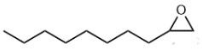
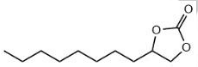
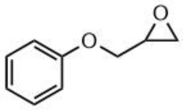
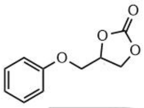
2			98
3			67
4			62
5			59

Reaction condition: expoxides (5 mmol), PCN-224-ZnCo$_1$-950 catalyst (10 mg), ^{n}Bu$_4$NB$_r$ (0.216 mmol), 50 °C, 16h, 1 bar CO$_2$. Conversion was determined by ^{1}H NMR spectroscopy.

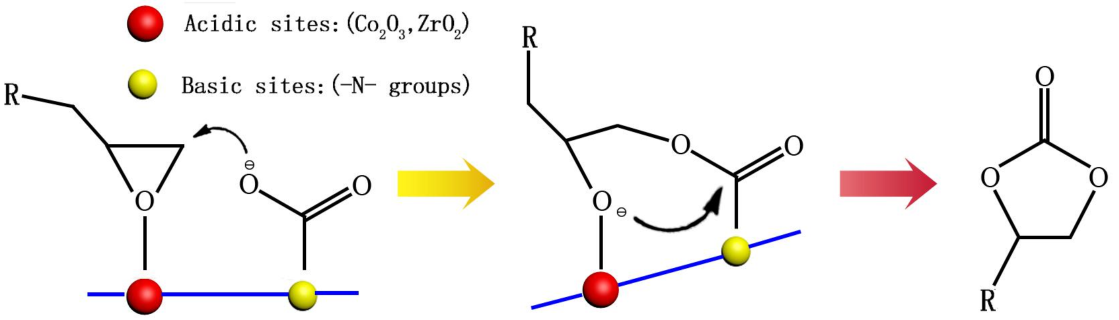


Figure 6. Diagram of the reaction process of carbon dioxide cycloaddition.

According to the research results above and relevant data in reference,[30] the process of PCN-224-ZnCo$_1$-950 catalyzing the cycloaddition reaction of carbon dioxide can be deduced, as shown in Figure 6. First, acidic sites, such as metallic Co nanoclusters, coordinate with the O of the epoxide to activate epoxy compounds. At the same time, basic sites, such as pyridine nitrogen or pyridine nitrogen, can easily capture and adsorb CO$_2$. The lone pair attacks the carbonyl group of CO$_2$ and activates CO$_2$. Afterwards, negatively charged O in CO$_2$ attacks the C in epoxide and opens the ring. While C-O bond are formed, the coordination bonds between metal clusters and O are broken. Finally, the intramolecular O anion attacks the C in CO$_2$, the C-N bond broken, and the ring closed. Thus, the corresponding cyclic carbonate is obtained. During the reaction process, the mobile electrons in nitrogen-carbon structure plays a significant role in promoting the intramolecular charge transfer during the acid/base co-catalysis process. The hollow structure, larger pore size and hierarchical pore structure can promote the raw material adsorption and the product diffusion; the volatilization of zinc and the diffusion, migration and fusion of cobalt particles will produce some unsaturated defect structures, which also have an important role in promoting the cycloaddition reaction of carbon dioxide.

CONCLUSION

Metal-organic framework PCN-224 MOF with porphyrin ligand as structural unit was synthesized. Zn and Co metal ion solutions were added to metallization in different proportions, and then pyrolyzed into stable catalyst under argon atmosphere for CO$_2$ conversion reaction. Due to the low melting point of Zn, it can be volatilized at 950 °C, thereby releasing abundant basic sites to improve the conversion rate of the carbon dioxide cycloaddition. As the ratio of Zn/Co in the precursor increases, the concentration of N-containing basic sites in the pyrolysis product gradually increases. Among them, PCN-224-ZnCo$_1$-950 with Zn/Co=1:1, is a catalyst whose basicity is greatly improved compared with that of the precursor. It has a suitable acid/basic site concentration ((acid site concentration)/ (basic site concentration) =37.4), and can efficiently catalyze the cycloaddition reaction of carbon dioxide and epoxide. Thanks to its macroporous and hierarchical pore structure, the catalyst has an excellent catalytic effect on epoxy compounds with longer carbon chains. Better than most catalysts reported in the literature. After PCN-224-ZnCo$_1$ was pyrolyzed, it showed well-dispersed Co$_2$O$_3$ nanoclusters in the N-doped porous carbon matrix. The mechanism of the heterogeneous catalyst to catalyze the cycloaddition of CO$_2$ in an N-doped carbon matrix can be attributed to the synergistic effects of basic sites derived from the activated N compounds (N-doped carbon matrix) with Co sites (Co$_2$O$_3$ nanoclusters).Firstly the acidic sites coordinate with the O of the epoxide and activate the epoxy compound. At the same time, the basic N-containing active sites are easy to capture and adsorb CO$_2$, and its lone pair of electrons attack the carbonyl group of CO$_2$ to make CO$_2$ activated. Then activated CO$_2$ reacts with activated epoxy compound to generate corresponding cyclic carbonate. These results provide a reasonable strategy for the adjustment of acidic/basic sites in porous metal-nitrogen-carbon materials. The catalyst of this structure has broad application prospects in catalyzing the cycloaddition reaction of carbon dioxide.

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Keywords: PCN-224 derivative; pyrolysis; metalloporphyrin; carbon dioxide conversion; cycloaddition

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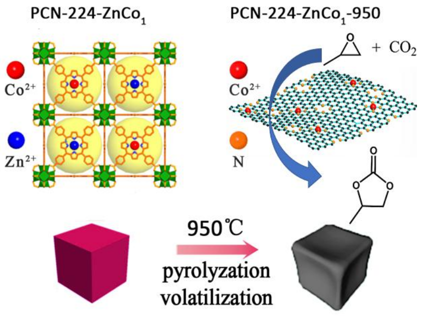

We successfully synthesized PCN-244-ZnCo$_1$, which was then pyrolyzed to the target product PCN-224-ZnCo$_1$-950 at 950 °C. The physical structure of PCN-224-ZnCo$_1$-950 did not change much as judged by SEM and N_2 adsorption and desorption. Due to the volatilization of Zn, PCN-224-ZnCo$_1$-950 has greatly improved basicity and suitable acidic/alkaline site concentration compared with the precursor. It can be efficiently used to carbon dioxide absorption and catalyze the cycloaddition of CO_2 with epoxides.