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Ni(salphen)-based metal-organic framework for the synthesis of cyclic carbonates by cycloaddition of CO_2 to epoxides†

*Yanwei Ren, Yanchao Shi, Junxian Chen, Shaorong Yang, Chaorong Qi and Huanfeng Jiang**

A well-defined homogeneous molecular catalyst Ni(salphen) was introduced as "metalloligand" in MOF, providing an efficient and recyclable heterogeneous catalyst for the synthesis of cyclic carbonates by cycloaddition of CO_2 to epoxides under relatively mild conditions.

Introduction

Although carbon dioxide (CO_2) is a nontoxic, non-flammable and abundant C1 building block, the scope of the synthetic applications of CO_2 is limited because of its inert nature. The development of efficient synthetic methods for CO_2 fixation is therefore an important and challenging subject.[1] Among them, cyclic carbonates derived from the coupling reactions of CO_2 with epoxides are promising target molecules since it can be widely used for various purposes, such as electrolytes in lithium-ion batteries, raw materials for polycarbonate, and polar aprotic solvents.[2]

Various homogeneous metal complexes catalysts, such as M(salen) complexes[3] have been developed for the cycloaddition of CO_2 and epoxides. Although these homogeneous catalysts usually exhibit high activity and selectivity at mild temperature in the presence of co-catalysts, their practical application remain limited because of catalyst instability and difficulty in catalyst/product separation. Immobilization of homogeneous catalysts can facilitate its recovery and reuse and therefore is of considerable interest to academia and industry.[4] According to this strategy, various heterogeneous catalysts have been developed for coupling reaction CO_2 with epoxides, such as functional polymers,[5] ion-exchange resins,[6] and quaternary ammonium or phosphonium supported on SiO_2.[7] Recently, based on the great potential as adsorbents/catalysts due to extremely large surface area and well-ordered porous structure, several metal-organic frameworks (MOFs) heterogeneous catalysts have been studied for CO_2 fixation.[8] However, these studies rely on the intrinsic catalytic activity (e.g., weak Lewis acidity) of the metal-connecting points. A more rational strategy than such an "opportunistic" approach is to introduce well-defined homogeneous molecular catalysts (or precatalyst) into the MOF structures.[9] Until now, a few MOFs based on M(salen) ligands with an additional functional group such as carboxylates,[10] *p*-benzoic acid groups,[11] and *p*-pyridyl groups[12] in the *para* or *meta* position to the OH group have been studied as new generation of heterogeneous catalysts that are capable of catalyzing more advanced and value-added reactions. Surprisingly, no MOF catalyst employing this synthetic strategy for CO_2 fixation has been reported so far. Herein we report a new dicarboxyl-functionalized nickel salphen complex Ni-H_2L (Scheme 1) as bridging metalloligand incorporating into a 3D MOF as self-supported heterogeneous catalyst for coupling reaction CO_2 with epoxides in the presence of quaternary ammonium salts. To our knowledge, it will be the first occasion to demonstrate that a M(salen)-based MOF material can be efficient both as a CO_2 adsorbent and as a catalyst for its chemical fixation.

Results and discussion

The Ni(salphen) ligand Ni-H_2L was synthesized by a Schiff base condensation reaction between *o*-phenylenediamine and (E)-3-(3-tert-butyl-5-fomyl-4-hydroxyphenyl)acrylic acid and then metalated with $Ni(OAc)_2{\cdot}4H_2O$. Reaction of $CdCl_2$ and with Ni-H_2L in dimethylformamide (DMF)/H_2O at 80 ℃ for 96 h afford brown block single crystals of $[Cd_2(Ni\text{-}L)_2(H_2O)_4]{\cdot}3DMF$ (**1**) in good yield. The product was stable in air and insoluble in water and common organic solvents and was formulated on the basis of elemental analysis, IR spectroscopy, and thermogravimetric analysis (TGA). Phase purity of the bulk sample was established by comparison of their observed and simulated powder X-ray diffraction (PXRD) patterns (Supporting information, Fig S1).

Single-crystal X-ray diffraction study showed that **1** adopts a 3D nanoporous framework and crystallizes in the triclinic space group P-1 with two Ni-L units, two Cd ions and four coordination H_2O molecules in the asymmetric unit. Basic building block, dinuclear Cd_2 clusters C-I and C-II (Fig 1a) with a C_2 axis passing through two bridging oxygen atoms, clustered by two bidentate and two tridentate carboxylate groups of four Ni-L units. In the two Cd_2 clusters, one of the independent Cd ions is coordinated by five oxygen atoms from three carboxylate groups, and two coordination water molecules (with *trans*-position in C-I, *cis*-position in C-II). Ni-L units exhibit two coordination modes including bis-bidentate chelating mode and bis-tridentate chelating-bridging carboxylate groups (Fig S2). Each Ni ion is coordinated in a nearly square-planar geometry with two nitrogen atoms and two oxygen atoms form the **L** ligand ($Ni\text{-}O_{avg}$ = 1.839 Å, $Ni\text{-}N_{avg}$ = 1.850 Å). Each Cd_2 cluster in **1** is thus linked by four Ni-L ligands, and each Ni-L ligands is linked to two Cd_2 cluster to generate a porous 2D network along *a*-axis (Fig S3). All thick lamellar networks are stacked together via supermolecular interaction to form a 3D nanoporous framework with 1D ellipse-shape channels cross section of ~ 1.0×1.4 nm along *b*-axis, which are filled with DMF molecules (Fig 1b). Therefore, the channel surfaces are uniformly stacked with Ni-L units with coordinatively unsaturated Ni^{2+} ions, and the Ni-Ni distance of adjacent Ni-L layers is about 5.128 Å, which are accessible to guest molecules and available for cooperative double-Lewis acidic activation. PLATON calculation[13] reveals that **1** has 41.3% of the total volume available for guest inclusion. TGA revealed that the coordination water and DMF molecules could be readily removed in the temperature range 30-120 ℃, and the framework are stable up to 150 ℃ (Fig S4). After a sample of **1** was ground and heated at 100 ℃ for 5 h under vacuum to obtain activated **1**, PXRD of the resultant powder showed a broad diffraction pattern similar to that of the pristine sample. This result indicates that the nanoporous framework was maintained after removal of solvent molecules. To determine the permanent porosity of **1**, 77 K N_2 adsorption was carried out on the evacuated framework (Fig S5). A type I isotherm was observed, indicating that **1** is microporous, and the apparent surface area was calculated using the Langmuir method to be $358 m^2/g$ ($245 m^2/g$ BET). The CO_2 adsorption measurement of the activated **1** showed that up to 25 $cm^3 g^{-1}$ of CO_2 uptake was obtained at 273 K and 1.0 atm (Fig S6), a moderate adsorption capacity of lower-pressure CO_2 as compared to reported MOFs,[14] indicating its potential application for CO_2 capture and conversion.

The moderate stability and uptake for CO_2 of the Ni(salphen)- based MOF **1** prompted us to explore its utilization as a heterogeneous catalyst for the synthesis of cyclic carbonates by cycloaddition of CO_2 to epoxides, since M(salen) complexes are promising catalysts for CO_2 fixation reaction.[3a] The activity of various catalysts was tested at 80 ℃ and 2 MPa using the reaction of propylene oxide (PO) and CO_2 to produce propylene carbonate (PC). As shown in Table 1, the catalytic performance of activated **1** depends strongly on the ammonium salts used, and highest activity was observed using NBu_4Br (entries 1-4). Theoretically, iodide is the best promoter in accordance to the increasing nucleophilicity, but in the presence of microporous MOF the diffusion of the large iodide might be hampered, thus explaining the slightly reduced activity compared to the bromides. When the catalyst was not used, the yield of PC was very low (12%), indicating Lewis acid activation of PO was necessary for the reaction (entry 5). To answer the question whether the reaction was catalyzed by Ni-L units or the coordinatively unsaturated Cd active sites exposed in the 1D channel of activated **1**, we performed the tests reaction under standard conditions using Ni-H_2L and $[Cd(bpdc)]_n$ (H_2bpdc = 4,4'-biphenyldicarboxylic acid),[15] respectively as the catalysts (entries 6 and 7, the molar amounts of Ni-L and Cd were the same as in **1**). Results revealed the yield of PC was all higher than no catalyst test, but significantly lower than **1**, clearly indicating that synergistic and/or additive activation of two kinds of Lewis acid in **1** occurs during the reaction process. Another reason for the higher activity of this MOF catalyst is that it is a porous material, which is favourable for the increasing of CO_2 uptake, and facilitates the access of reactants to the active sites and product diffusion through open channels. At the same time, we found the amount of NBu_4Br had a great influence on the reaction. Increasing the amount of NBu_4Br from 1 mol% to 3 mol% could enhance the yield of PC significantly (entries 6, 8 and 9). The PC yield was also increased with an increasing reaction temperature or time (entries 10-12), but higher temperature reactions were not investigated, because this catalyst is unstable more than 150 ℃. The results of the recycling experiments showed no obvious decrease in activity of the catalyst after being used three times (entries 13 and 14). Furthermore, the solid catalyst recovered from the catalytic reaction exhibited the same PXRD as the pristine solid of MOF **1** (Fig S1), unambiguously supporting the stability of the MOF framework during the catalytic reactions. The good recyclability may be due to that this catalyst was synthesized by the solvothermal method and therefore resisted moderate temperature and pressure. This catalytic capability of the self-supported Ni(salphen) MOF catalyst can compare to that of other MOF based heterogeneous catalysts reported in the literatures for the cycloaddition reaction of CO_2 to epoxide (Table 2).

Table 3 summarized the coupling reactions of CO_2 with different epoxides catalyzed by **1**/ NBu_4Br system, and the data show that the catalytic system could convert epoxides 2a-2d to the corresponding cyclic carbonates effectively under the same conditions. The conversion for 2e is lower partly because it has bulky space size, reducing its diffusion rate in the 1D open channel of solid catalyst. This result further suggests that the catalytic reaction took place in the channel not on the catalyst surface. Indeed, when extended reaction time to 24 h, the yield reach to 82 %.

Based on above analysis, a plausible Lewis acidic activation mechanism is proposed for this CO_2 fixation reaction, which is similar to that of the homogenous catalytic system with Co(salen)X complexes as catalysts and quaternary ammonium salts as co-catalysts.[16] First of all, the porosity and polar nature of **1** favors the CO_2 uptake and further increases the local concentration of CO_2 in the channel. The coupling reaction is initiated through the coordination of the coordinatively unsaturated Ni^{2+} (or Cd^{2+}) in **1** to the oxygen atom of the epoxide, and this step can activate the epoxy ring. Secondly, the Br^- generated from NBu_4Br attacks the less-hindered carbon atom of the coordinated epoxides, followed by the ring opening step. Then, the oxygen anion of the opened epoxy ring interacts with CO_2, forming an alkylcarbonate anion, which is converted into the corresponding cyclic carbonate through the ring closing step. Simultaneously, the catalyst is regenerated.

Conclusions

In summary, we introduced a well-defined homogeneous Ni(salphen) catalyst as “metalloligand” in a porous MOF. The Ni(salphen) units and coordinatively unsaturated Cd active sites accessible via the open MOF channels were utilized to generate an efficient heterogeneous catalyst for the coupling reactions of CO_2 with epoxides under relatively mild conditions. The MOF catalyst features a high local density of coorperative layer Ni(salphen) motifs, exhibiting improved catalytic performance relative to the monomeric homogeneous catalyst. This solid catalyst can be easily recycled and reused without any apparent loss of catalytic activity after being used three times. This work established a new strategy in the rational design of effective self-supported MOF catalysts for CO_2 absorption and *in situ* fixation based on functional metallosalens or metalloprophyrins.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Nos. 20932002 and 21172076), the National Basic Research Program of China (973 Program) (No. 2011CB808600), the Natural Science Foundation of Guangdong Province, China (No. 10351064101000000), and the Fundamental Research Funds for the Central Universities (No. 2011ZM0044) for the financial support.

Notes and references

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† Electronic supplementary information (ESI) available: Synthesis and characterization of Ni-H_2**L** ligand and MOF **1**, X-ray crystallography, PXRD data, TGA data, nitrogen and carbon dioxide adsorption isotherms, and catalytic reaction. CCDC: 900477.

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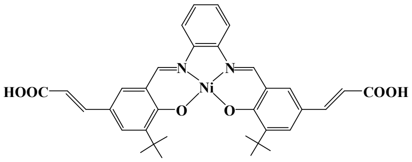


Scheme 1. Schematic representation of Ni-H_2L.

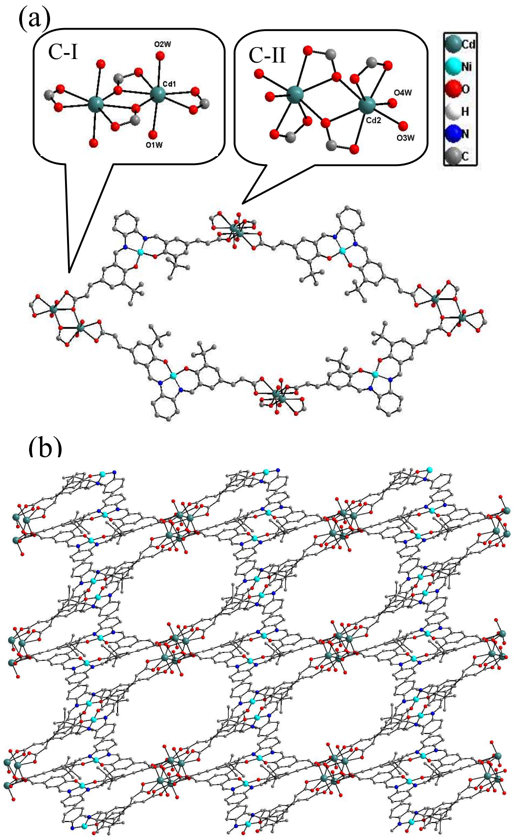


Fig.1 (a) Building block in **1** and (b) view of 3D porous structure of **1** along the *b*-axis.

Table 1. Reaction of CO_2 and PO used by different catalysts and ammonium salts at various conditions[a]

Entry	Catalyst	Ammonium salt	Yield [%][g]
1	**1**	None	0
2	**1**	NBu_4Cl	26
3	**1**	NBu_4Br	80
4	**1**	NBu_4I	72
5	None	NBu_4Br	12
6	Ni-H_2L	NBu_4Br	38
7	$[Cd(bpdc)]_n$	NBu_4Br	25
8[b]	**1**	NBu_4Br	56
9[c]	**1**	NBu_4Br	75
10[d]	**1**	NBu_4Br	85
11[e]	**1**	NBu_4Br	82

12[f]	**1**	NBu_4Br	86
13(2nd)	**1**	NBu_4Br	80
14(3rd)	**1**	NBu_4Br	78

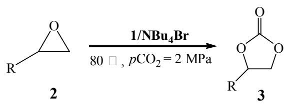
[a] Typical reaction conditions: PO (10 mmol), ammonium salts (3 mol %), catalyst (0.05 g), CO_2 pressure (2 MPa), reaction temperature (80 ℃), reaction time (4 h). [b] 1 mol % NBu_4Br was used. [c] 2 mol % NBu_4Br was used. [d] Reaction temperature is 100 ℃. [e] Reaction time is 10 h. [f] Reaction temperature is 100 ℃ and reaction time is 24 h. [g] The yields were determined by GC with an internal standard.

Table 2. Comparison with other MOF based heterogeneous catalytic systems on cycloaddition reaction of CO_2 to epoxide.

Catalyst	Co-catalyst	Pressure (MPa)	Temperature (□)	Time (h)	Yield (%)	Ref.
MIXMOF-5[a]	NEt_4Br	3.0	140	3	63.0[b]	8a
MOF-5	NBu_4Br	1.0	50	4	97.6[b]	8b
Ni(salphen)-MOF	NBu_4Br	2.0	80	4	80.0[b]	Present work
ZIF-8	-	0.7	80	4	52.0[c]	8e
ZIF-8-f[d]	-	0.7	80	4	73.1[c]	8e
Co-MOF-74	-	2.0	100	4	96.0[e]	8c
Mg-MOF-74	-	2.0	100	4	95.0[e]	8d
F-IRMOF-3[e]	-	2.0	140	5	84.0[e]	8f

[a] MIXMOF-5 represent mixed-linker MOF-5 with general formula $Zn_4O(BDC)_x(ABDC)_{3-x}$, in which BDC is benzene-1,4-dicarboxylate, ABDC is 2-aminobenzene-1,4-dicarboxylate. [b] Epoxide in this cycloaddtion reaction is propylene oxide. [c] Epoxide in this cycloaddtion reaction is chloropropylene oxide. [d] ZIF-8-f represent the grafting of ethylene diamine in the ZIF-8 framework. [e] epoxide in cycloaddtion reaction is styrene oxide.

Table 3. Various carbonates synthesis catalyzed by **1** in the presence of NBu_4Br[a]



Entry	**2**	R	Time/h	Yield(%)
1	2a	Me	4	80
2	2b	CH_2Cl	4	84
3	2c	Ph	4	81
4	2d	CH_2Ph	4	76
5	2e	CH_2OPh	4	55
6	2e	CH_2OPh	24	82

[a] reaction conditions: see Table 1.