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A copper-phosphonate network as high-performance heterogeneous catalyst for the CO₂ cycloaddition reactions and alcoholysis of epoxide

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A novel 3D copper-phosphonate network, with the general formula $Cu_7(H_1L)_2(TPT)_3(H_2O)_6$, namely compound **1**, has been synthesized using a rigid tetrahedral linker of tetraphenylsilane tetrakis-4-phosphonic acid (H₈L) and a nitrogen-containing ancillary ligand (TPT: [5-(4-(1H-1,2,4-triazol-1-yl)phenyl)-1H-tetrazole]) under hydrothermal conditions. The compound was fully characterized using PXRD, ICP, IR, TGA and elemental analysis. Compound **1** can be used as an efficient catalyst for the CO₂ coupling reaction that is greatly superior to many conventional MOF-based catalysts, where porosity always is mentioned and used. In addition, it shows excellent catalytic performance for ring-opening reaction with epoxides under ambient conditions. Additionally, compound **1** can be recycled at least three times without a significant compromise of the activity in the two catalytic reactions.

Introduction

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The class of materials known as coordination polymers (CPs) or metal-organic frameworks (MOFs) has drawn enormous research interests in recent years because of their appealing applications in different areas including ion exchange, gas storage, luminescence, nonlinear optics, catalysis and proton conduction.¹⁻⁶ In the broad domain of inorganic–organic hybrid materials research, since Alberti and coworkers reported the first metal-organophosphonates in 1978, the chemistry of metal phosphonates has attracted great attention due to their high chemical and thermal stability, which are important factors for their applications.⁷ In addition, the phosphonate linkers possess high number of oxygen atoms capable of bonding to metals to form different structural architectures while oxygen atoms may still be available to further serve as Hbond acceptors to generate protonated metal phosphonates by means of adjusting the pH conditions of reactions. However, networks based on phosphonate ligation are, by and large, less studied compared to carboxylate-based counterparts. One reason why has likely hampered extensive proliferation of their study as MOFs is the predisposition of metal phosphonate to a dense motif, thus largely decreasing opportunities for functions that rely on the porosity, for example, MOF materials, as the porous heterogeneous

catalysts, were deemed to catalyse the reaction within their channels, while metal phosphonate with dense network scarcely ever were employed as heterogeneous catalysts.^{8,9} As mentioned above, a more diverse set of applications for dense metal-phosphonate network still remain further to be explored.

In recent years, some MOFs have been demonstrated as efficient catalysts for the cycloaddition of carbon dioxide to epoxides and alcoholysis of epoxide. Coupling of CO₂ with epoxides to cyclic carbonate is a useful reaction, as the abundant C1 resource is conversed to value-added products both environmentally and practically attractive;¹⁰ the alcoholysis of epoxides with alcohols is a significant transformation in the synthesis of β -alkoxy alcohols, which are regarded as useful precursors for a wide range of pharmaceuticals.¹¹ On basis of the catalytic mechanism proposed in corresponding reports, Lewis acid metal sites and Brønsted acids sites play the dominant role in catalysis for CO₂ conversion and alcoholysis, respectively.^{12,13} However, hydrogen-bonding moieties between various catalysts and epoxides have also been demonstrated to promote CO2 cycloaddition reaction;¹⁴ epoxides can also undergo ringopening reactions in the presence of Lewis acid.¹⁵ Consequently, the protonated metal phosphonate, an effective combination of Lewis acids and Brønsted acids, would be a very promising heterogenous catalyst.

In this work, a protonated copper-phosphonate network, $Cu_7(H_1L)_2(TPT)_3(H_2O)_6$, namely compound **1**, was successfully prepared. The compound is assembled from a rigid tetrahedral linker of tetraphenylsilane tetrakis-4-phosphonic acid (H₈L), a nitrogen-containing ancillary ligand of 5-(4-(1H-1,2,4-tri azol-1yl)phenyl)-1H-tetrazole (TPT) and Cu(OAc)_2. In spite of a dense motif, the Lewis acid and Brønsted acid sites on the surface of the compound endowed the catalyst with high-performance

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Fig 1. (a) Ortep representation of the coordination environment in compound 1 with thermal ellipsoids set at 50% probability. Hydrogen atoms bonded to carbon atoms are omitted for clarity. (b) The layer formed by polyhedrons of Cu and P atoms. (c) The 3D view of compound 1 along the b-axis.

heterogeneous catalytic activity for the coupling of carbon dioxide with epoxides and the ring opening of epoxides with alcohols.

Experimental section

Materials and methods

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All the reagents and solvents were purchased commercially and used without further purification except for H_8L , which was synthesized according to a modified procedure documented previously.¹⁶

Synthesis of Cu₇(H₁L)₂(TPT)₃(H₂O)₆.(1): A mixture of Cu(OAc)₂ (14 mg, 0.07 mmol), H₈L(23 mg, 0.035 mmol), TPT (15 mg, 0.07 mmol) and H₂O (8.0 mL) was transferred into a 20mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 3 days, and then cooled to room temperature. The blue rodlike crystals were obtained by filtration, washed with distilled water several times and dried at ambient temperature; yield 14 mg (40% based on Cu²⁺ ions). Elemental analysis (%) Calcd for compound 1: C 36.87, H 2.13, N 12.04. Found: C 36.75, H 2.18, N 11.09. IR (KBr, cm⁻¹, Figure S2): 3134 (s), 3068 (s), 3012 (s), 1621 (m), 1531 (m),1459 (m), 1379 (m), 1288 (m), 1142 (vs), 1056 (vs), 971 (s), 920(s), 849 (m), 814 (m), 764 (m), 668(m), 588 (vs).

Cycloaddition of CO₂ to epoxides. Crystalline samples 1 were grinded into powders to be used in the reaction. In a typical procedure, epoxide (20 mmol), tetrabutylammonium bromide (TBAB, 97 mg, 0.3 mmol), and the compound **1** (5 mg, 2 µmol) were placed in a 10 mL stainless steel autoclave. The reactor was purged with carbon dioxide up to 1MPa under a solvent-free environment at 100 $^{\circ}$ C. The yields of the product carbonates were calculated by ¹H NMR spectroscopy.

Ring opening of epoxides with alcohols. Crystalline samples **1** were grinded into powders to be used in the reaction. In a typical procedure, a mixture of catalyst (5 mg, 2 μ mol) and toluene (27 mg, serving as an internal standard) was added to a solution of styrene oxide (0.2 mmol) in MeOH (2 mL), and then the mixture was stirred at ambient temperature. The reaction was monitored for the required time by GC-7900 equipped with a capillary column (TM-FFAP, 50m × 0.25 mm × 0.25 µm) and a flame ionization detector.

Results and discussion

Structure description. Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in monoclinic space group

P2₁/n, and consists of three and a half crystallographically independent Cu(II) ions, one protonated[HL]7- ligand, one and a half nitrogen-containing ancillary ligands and three water molecules in the asymmetry unit. Cu1 is in a trigonal bipyramid geometry, surrounded by four O atoms from one water molecule and three different phosphonate groups, and one N atom from TPT ligand. Cu2 and Cu3 are both five-coordinated by three O atoms from three different phosphonate groups and two N atoms from two TPT ligand, wherein the two metal ions are bridged by phosphonate O atom in a vertex-sharing manner. Cu4 has a half occupancy factor and is four-coordinated by two water molecules and two O atoms from two phosphonate ligands, thereby forming a rectangle (Fig. 1a). The silicon-based phosphonate ligand links ten copper atoms through unidentate moieties in two μ^2 : $\eta^1 \eta^1$, one μ^3 : $\eta^2 \eta^1$ and one μ^3 : $\eta^1 \eta^1 \eta^1$ coordination modes (Fig. S1). The three trianglebipyramids centered by Cu1, Cu2, Cu3 ions share P atoms to form one-dimensional (1D) chains. The chains are further connected with Cu4-centered rectangle to assemble the layers (Fig. 1b), which are further filled and linked by [HL]⁷⁻ linkers and TPT ligands to form a three-dimensional extended dense structure (Fig. 1c).

Coupling reaction of carbon dioxide with epoxides. Styrene oxide was chosen as the model substrate for the chemical conversion of CO₂ into carbonates to probe the optimized catalytic reaction conditions (Fig. S7-9). The corresponding results are summarized in Table 1. Firstly, the reactions were performed using 2 µmol of compound 1 (5 mg, 0.1 mol ‰ based on catalyst) and 0.3 mmol of co-catalyst TBAB with 0.1 MPa CO2 at room temperature for different reaction time: 12h, 24h and 48h. The yields of the corresponding cyclic carbonate were 1.6%, 2.4% and 4.1%, respectively (entries 1, 2 and 3 in Table 1). The yields are too low under those conditions. Then reaction pressure was increased to 1 MPa, only 2.4% yield was obtained. When the temperature was increased to 60 °C, the yield reached 35.7% as shown in entry 5. Subsequently, the temperature was raised to 100 °C, keeping the pressure to 1 MPa, the substrates were almost completely converted to the cyclic carbonates after 12 h of reaction (entry 6). Besides, the yield of 4-phenyl-1,3-dioxolan-2-one was very low In the absence of TBAB, indicating that TBAB was imperative for the reaction (entry 7). Comparably, only 59% yield was obtained using 0.3 mmol TBAB without compound 1 under the same conditions, the results providing experimental evidence of the important role of the catalyst 1 in this reaction (entry 8). Accordingly, the

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Table 1. The coupling reactions of styrene oxide with CO_2 under various reaction conditions



Entry	T(°C)	P(MPa)	t(h)	Yield(%)	
1	25	0.1	12	1.6	
2	25	0.1	24	2.4	
3	25	0.1	48	4.1	
4	25	1.0	12	2.4	
5	60	1.0	12	35.7	
6	100	1.0	12	> 99	
7	100	1.0	12	1.9	
8	100	1.0	12	59	
9	100	1.0	12	76.9	
10	100	1.0	12	75.2	

Reaction conditions: styrene oxide (2.4g, 20 mmol), catalyst (5mg, 2 μ mol) and TBAB (97mg, 0.3 mmol) under various conditions. Yields were determined by ¹H NMR spectroscopy.

optimized reaction condition was found to be 2 μ mol of catalyst and 0.3 mmol of TBAB co-catalyst in solvent-free conditions at 100 $^{\circ}$ C under 1 MPa CO₂ reaction atmosphere.

Then, a series of different types of the epoxides substrates were employed to check the catalytic generality of compound 1 for the chemical conversion of CO₂ to form cyclic carbonates under the optimized reaction conditions (Fig. S10-15 and Fig. S7a, g). As listed in Table 2, the small-sized epoxide substrates of glycidol and epichlorohydrin provided an almost complete conversion in 3 hours with corresponding turnover frequency (TOF) values of 476 per mole of metal per hour. Relatively, the reaction time for the large substrates of styrene oxide and 1, 2-epoxy-3-phenoxypropane is prolonged to about 12 hours with TOF of 119. It is worthwhile to note that the turnover number (TON) and TOF values of compound 1 for all employed epoxides are much higher than most previously reported conventional MOF-based catalysts, where porosity always is mentioned and used (Table S2-5). With the same embedded Lewis acid metal sites, HKUST-1 was also employed as a heterogeneous catalyst in these reactions for the sake of comparison. Although the complete conversions for the epoxide substrates of glycidol, epichlorohydrin and 1, 2-epoxy-3-phenoxypropane were equal to those catalyzed by compound 1, a lower yield of 84% for styrene oxide was obtained, which indicates that the Brønsted acids-containing 1 possesses higher catalytic performance than HKUST-1 in chemical fixation of CO₂ (Figures S18-21).

Recyclability is another crucial parameter for the heterogeneous catalysts to be considered for practical applications in industry. The reusability of compound **1** was carried out by using styrene oxide as the reaction substrate. The reaction was performed at 100 °C using 2 μ mol of catalyst for 12 h. After the reaction, the catalyst was isolated by centrifugation, washed with dichloromethane for three times and dried in air. The recovered catalyst was reused in the following reactions under the same conditions as the first run. After three circles, the conversion slightly decreased on account of an unavoidable loss of catalyst during the recyclable reactions, indicating that the catalytic reactivity of compound **1** was still

maintained. The powder X-ray diffraction (PXRD) of the third run is in good agreement with the PXRD patter of the structural integrity of the compound. The result reveals that the structural integrity of the compound **1** was retained after cyclic experiment (Fig. S5).

Moreover, to obtain an insight into the heterogeneous nature of the compound **1**, a filtration test was carried out by removing the catalyst after 6 hours of reaction, and then the reaction was further conducted under the same reaction condition

Table 2. Coupling Reaction of CO ₂ with Epoxides							
	R	CO ₂	T, P	ر 			
Entry	Substrate	t(h)	Yield(%)	TON	TOF		
1	А́∩он	3	>99	1429	476		
2	<u>گ</u> م	3	>99	1429	476		
3		12	>99	1429	119		
4		12	>99	1429	119		

Reaction conditions in this work: epoxide (20 mmol), catalyst (2 μ mol) and TBAB (0.3 mmol) under CO₂ (1 MPa), 100°C. The repeated experiments after three successive runs, wherein the TBAB was added each time when compound **1** was recycled.

(Fig. S16-17 and Fig. S7a, g). As recorded in Fig. 2, a slight increase in the formation of the cyclic carbonate was probably due to the existence of co-catalyst TBAB, which can also catalyze this reaction by itself. At the end of the catalytic reaction, inductively coupled plasma (ICP) analysis was conducted to detect the reaction mixture filtrate. No Cu leaching demonstrates that the reaction catalyzed by compound **1** was indeed heterogeneous.



Fig. 2. Time-conversion plot for the filtration test of CO_2 cycloaddition reactions; Insert: Recycle experiments with styrene oxide for the cycloaddition reaction of CO_2 with compound **1**.

To explore the mechanism of CO_2 cycloaddition reaction, $Cu(OAc)_2$ and H_8L were employed for the catalysis in the presence of TBAB; the yields are 76.9% and 75.2%, respectively (entries 9 and 10 in Table 1), manifesting that both Lewis acids and Brønsted acids promote the coupling of carbon dioxide with epoxides. Based on the above results and previous literatures,¹⁷ a plausible mechanism for the CO_2 cycloaddition reaction was proposed. As illustrated in

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Scheme 1, the catalytic reaction is initiated via the coordination of the metal to the oxygen atom from the epoxide substrate and the Brønsted acid simultaneously forms hydrogen bonding with epoxide, which assists in activating the epoxy ring. Then the Br⁻ from TBAB attacks the less sterically hindered carbon atom of the activated epoxide, leading to the formation of opened epoxy ring. Subsequently, the CO₂ reacts with the oxygen anion of the open ring to form the epoxide intermediate, which is then converted into the final cyclic carbonate by the ring closing step. At the same time, the catalyst is regenerated.



Scheme 1. Proposed mechanism of the CO_2 cycloaddition reaction with catalyst **1** and TBAB as co-catalyst.

Ring-opening reaction with epoxides. Up to now, there are only few metal-phosphonate materials which are used as catalysts for this reaction reported. The catalytic performance of compound **1** was investigated in the ring-opening reaction of styrene oxide. The results are summarized in table 3. In the absence of catalyst, no reaction occurred after 12 hours. When the compound **1** was loaded at 2 µmol (5 mg, 1 mol% based on catalyst), the reaction gave an excellent conversion (99%) and regioselectivity (>99%) to β-alkoxy alcohol after 12 hours at room temperature. Compound **1** showed higher selectivity to β-alkoxy alcohol compared to Cu- and Fe-based MOFs reported in previous literatures for the ring-opening reaction with epoxides.^{11c,11e} Besides, compound **1** exhibits higher catalytic activity that is greater than documented metal phosphonates material catalysts for ring–opening reaction with styrene oxide under the similar conditions.^{11d,13}

To study the mechanism of catalytic reaction, $Cu(OAc)_2$ and H_8L as catalysts for the ring-opening reaction with epoxides were carried out under the similar condition. The conversions are 38% and 99%, respectively. The results suggested that the Brøndsted acid plays a more dominant role and there is a co-catalytic effect of the Lewis acid to promote this catalytic reaction. Besides, it is worth noting that H_8L as homogeneous catalyst, although it exhibits superior activity in this reaction, is limited in separation and reusability, indicating that this 3D network **1** cannot be replaced by the ligand.

The recyclability of catalyst **1** was examined. Prior to reuse, the catalyst was centrifuged, washed with dichloromethane and dried in air. After three circles, the conversion and selectivity keep almost

the same as the original ones (Fig. S4). And the $P\!XRD_{ri}patterns$ showed that the recovered catalyst were consistent with the recovered catalyst were consistent were catalyst were consistent were catalyst were catalyst were consistent were catalyst were catalyst

 Table 3. Ring opening of styrene oxide with MeOH

Entry	Catalyst	Time/h	Conversion/%	selectivity/%		
1		12				
2	1	12	99	>99		
3	Cu(OAc) ₂	12	38	>99		
4	H ₈ L	0.5	99	>99		
reaction condtions: styrene oxide (24 mg, 0.2 mmol), catalyst (5 mg, 2						
umol) 25°C MeOH (2 ml)						

sample, indicating that the catalytic activity of **1** was still maintained during the recycle experiments (Fig. S5).

Conclusion

In summary, a novel three-dimensional copper phosphonate network was successfully prepared by a hydrothermal process. It exhibits prominently catalytic activity for the cycloaddition of carbon dioxide to epoxides that is superior to many conventional MOF-based catalysts, where porosity always is mentioned and used. Besides, it is used as a highly active and selective heterogeneous catalyst in the ringopening reaction with epoxides under ambient conditions. Considering the high efficiency and the easy preparation of this catalyst system, compound **1** can be an appealing candidate for many acid-catalyzed reactions in future.

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