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Covalent organic frameworks (COFs) with highly ordered crystalline structure and uniform microenvironment have potential applications in the field of catalysis, however, their application was restricted by the harsh synthesis conditions and multistep synthetic procedure. Herein, we reported the facile synthesis of a new COF-salen via in-situ salen skeleton formation by heating the aldehyde and amine precursors in air atmosphere. This COF-salen had AA stacking eclipsed layered crystalline structure, micro/macro hierarchical pore, high stability in acid or base medium and could be efficiently transferred to COFsalen-M (M = Co, Mn, Cu, Zn) with well retained ordered crystalline structure. The successful application of COF-salen-Co(III) and COF-salen-Mn respectively in the epoxide hydration which needs the cooperation of two salen-Co(III) and olefin epoxidation which involves the isolated salen-Mn as active site should be attributed to their unique layered crystalline structure that could efficiently isolate the active sites by restricting their mobility and generate the cooperation among the nearby active sites in the adjacent layers. The COF-salen-Co exhibited much higher activity and stability than corresponding amorphous polymers in cycloaddition reactions of epoxides with CO₂, demonstrating the advantage of crystalline structure in catalysis.

Introduction

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Covalent organic frameworks (COFs) are designable porous, crystalline materials that are constructed by organic monomers based on reversible chemical reactions, such as Schiff base reaction, boronic acid self-condensation or polycondensation with diols, C=C bond formation reaction, etc.¹⁻⁵ Nowadays, numerous COFs have been synthesized with different topologies such as two-dimensional (2D), three-dimensional (3D) and woven architectures.⁶⁻⁸ Due to their high surface area, periodic skeletons and ordered pores, and well-defined chemical structures, COFs have shown potential applications in the fields of gas storage and separation,⁹⁻¹⁰ sensors,¹¹⁻¹² photo devices, 13-14 and electronic proton conductions.15 heterogeneous catalysis¹⁶⁻¹⁸ and so on.

Generally, the COFs were synthesized under strict conditions such as vacuum/inert atmosphere, the narrow scopes of

solvents and so on, which impedes their practical applications. Recently, several groups have reported the synthesis of COFs under not very demanding conditions.¹⁹⁻²² For example, Dichtel's group reported the two-step synthesis of imine linked COFs using Lewis acid to catalyze the Schiff-base condensation in the first step, and supercritical CO₂ drying in the second step.¹⁹ Zhao and co-workers reported the successful synthesis of COF-LZU1, TpPa-1, and N₃-COF at room temperature using both batch and continuous flow.²⁰ COF-42, COF-43, and COF-LZU1 were synthesized under ambient conditions by Wang and co-workers.²¹ However, the facile synthesis of COFs is still limited to several types.

The "homogeneous" in "heterogeneous" catalysis has been a long term pursuit in the field of catalysis, however, still faces the big challenge.²³⁻²⁵ One of the challenges lies in the difficulty in the synthesis of solid catalysts with well-defined active sites that have identical local structure and microenvironment. The COFs are very attractive in bridging homogeneous and heterogeneous catalysts not only because of their solid nature in water/organic solvent which allows the easy separation and recovery, but also the possibility of integrating active sites in a uniform and identical microenvironment. Furthermore, recent progresses in the successful resolution of the crystal structure of COFs by a single crystal diffraction method made the detailed mechanism study during the catalytic process possible.²⁶⁻²⁷

The salen ligand which has [O,N,N,O] tetradentate bis-schiff base structure could coordinate with various kinds of metal ions to form stable salen-metal complexes which have been widely used in catalysis such as oxidation, CO_2 cycloaddition/copolymerization with epoxides, asymmetric alkene

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 $^{^{+}}$ Electronic Supplementary Information (ESI) available: FT-IR spectra, 13 C CP/MAS NMR spectrum, TGA data, XPS results, N $_2$ sorption isotherms & pore size distributions, SEM pictures, PXRD patterns, additional Tables and experimental sections. See DOI: 10.1039/x0xx00000x

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epoxidation/Diels-Alder reaction and so on.²⁸⁻³⁸ Different types of salen-M complexes generally involved different reaction pathways in catalysis.³⁹⁻⁴⁰ For example, salen-M (M = Ti, Al, Co, Cr) always needs the cooperation of two molecular catalysts to catalyze the reactions including epoxide hydration/asymmetric ring-opening reaction, cyanation of aldehyde, etc.^{33,41-42} For the olefin epoxidation reaction catalyzed by salen-Mn, the prevention of the dimer formation is required because the dimers are inactive for the reaction.43-45 Previously, salen-Co complexes were encapsulation in silica-based nanoreactor to facilitate the cooperation in the epoxide hydration reaction.³⁸ To prevent the dimer formation, salen-Mn was immobilized on the solid support or integrated in the molecular cages.⁴⁶⁻⁴⁸ For example, Cui and coworkers reported the enhanced activity and enantioselectivity over the homogeneous catalyst in chiral coordination cages derived from salen-Mn.48 However, the above strategies are hard to realize both the cooperation and

isolation effect simultaneously. The salen-based COE have been reported previously, but the cooperation and ዜሪን በረር ትርጉ ከትርጉ ከው ትርጉ ከትርጉ ከው ትርጉ ከው ት

Herein, we reported the facile synthesis of the COF-salen via heating 1,3,5-tris(3'-tert-butyl-4'-hydroxy-5'formylphenyl)benzene and ethylenediamine under air atmosphere. The COF-salen with AA stacking eclipsed layered crystalline structure had micro/macro hierarchical pore. The catalytic performance of COF-salen-M samples (M = Co, Mn, Cu, Zn) successfully generated by coordination of metal ions with COF-salen were investigated in epoxide hydration, olefin epoxidation and cycloaddition of CO₂ and epoxides with the emphasis on the elucidation of the cooperation and isolation effect. The advantageous of the crystalline COFs in catalysis was demonstrated with control experiments using corresponding amorphous polymers as catalysts.



Figure 1. (A) Schematic illustration for the synthesis of COF-salen and COF-salen-M, (B) and (C) PXRD patterns of COF-salen prepared under different conditions.

Results and discussion

Salen-based covalent organic framework, COF-salen was synthesized via facile heating of ethylenediamine and 1,3,5tris(3'-tert-butyl-4'-hydroxy-5'-formylphenyl)benzene

(TBHFPB) in organic solvents in the presence of 3 M aqueous acetic acid under air atmosphere (Figure 1A). Firstly, the synthesis conditions were optimized by screening the solvents while keeping the acetic acid concentration constant (detailed see Table S1). The yellow solids obtained using ethanol-dioxane, ethanol-THF and ethanol-DMF as solvent exhibited clearly the diffraction peaks at low 2-theta degree in their PXRD patterns, suggesting that all materials had crystalline structure (Figure 1B). Even without acetic acid, the crystalline materials could also be obtained as evidenced by the appearance of the diffraction peaks in the PXRD patterns (Figure 1C). This suggests the wide reaction conditions for the synthesis of COF-salen. Among all the conditions screened, the combination of acetic acid and mixed solvent of THF and EtOH was the best for the synthesis of COF-salen considering both the high crystallinity and the high yield (~86%).

The crystalline structure of COF-salen was resolved using powder X-ray diffraction (PXRD) combined with the computational structural simulations and Pawley refinement as conducted by Materials Studios version 8.0. Eclipsed AA stacking and staggered stacking (AB and ABC) models were built (Figure 2A and S1). It is found that the simulated PXRD patterns of the eclipsed AA stacking is in good agreement with the experimental obtained PXRD patterns with a P321 space group, as confirmed by the weak intensity of the difference plot in

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Figure 2A. COF-salen exhibited a set of strong PXRD peaks at 3.5°, 6.0°, 7.0° and 22.2°, which were assigned to the (100), (110), (200) and (001) facets, respectively. The Pawley refinement cell parameters are a = b = 29.86 Å, c = 4.18 Å, $\alpha = \beta$

= 90°, and γ = 120°, with R_{wp} = 4.37% and R_p = 3.06%. This result indicates that the COF-salen has well stacked structure. TA11058A



Figure 2. (A) Experimental, Pawley-refined, simulated PXRD patterns (AA stacking) and a difference plot of COF-salen, (B) top and side views of COF-salen showing the ideal eclipsed AA structure, (C) TGA curve of COF-salen under air atmosphere, (D) PXRD patterns of COF-salen after the treatment in different types of solvents.



Figure 3. (A) FT-IR spectra of COF-salen, COF-salen-Co and COF-salen-Co after the fifth recycle, (B) ¹³C CP-MAS NMR spectrum of COF-salen (* refers to spinning sidebands), (C) N₂ sorption isotherms (measured at 77 K) and (D) NLDFT pore size distribution curves of COF-salen (black) and COF-salen-Co (red).

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The formation of COF-salen was further characterized by Fourier-transform infra-red (FT-IR) and solid-state ¹³C CP MAS NMR spectroscopy (Figure 3). The FT-IR spectrum of COF-salen showed a strong vibration band at 1632 cm⁻¹ attributed to the stretching vibration of C=N, indicating the formation of imine bond (Figure 3A). The disappearance of the characteristic C=O stretching vibration at 1651 cm⁻¹ indicated the complete consumption of the aldehydes (Figure S2). In ¹³C CP MAS NMR spectrum of COF-salen (Figure 3B), the peak at 167.9 ppm assigned to C=N confirmed the formation of imine bond. The peak at 28.4 and 34.2 ppm was from the methyl and quaternary carbon of tert-butyl group of COF-salen, respectively. The peak at 61.4 ppm was from the carbons of methylene group, and the resonance at 159.9 ppm was from the carbon adjacent to the oxygen atom. The resonances from 118.6 ppm to 141.8 ppm were assigned to aromatic carbons. Furthermore, comparing with the ¹³C CP MAS NMR spectrum of the corresponding amorphous polymer POF-salen (Figure S3), the peaks widths of COF-salen were much narrower, indicating the more uniform chemical environment of COF-salen due to its ordered crystalline structure. The combined characterization results confirmed the successful formation of COF-salen via the reaction of TBHFPB and ethylenediamine.

The permanent porosity of COF-salen Was10haracterized5by the nitrogen sorption analysis at 77 K (Figure 3C, Table 1). The N₂ sorption isotherm of COF-salen was of type I with a sharp uptake at relative pressure $P/P_0 \leq 0.05$, showing that the material had microporous structure as clarified by IUPAC. COFsalen had the Brunauer-Emmett-Teller (BET) specific surface area of 1646 m²/g and pore volume of 1.07 cm³/g. The pore size distribution calculated based on nonlocal density functional theory (NLDFT) method was centered at about 1.86 nm, which agrees well with the theoretical data (1.9 nm) calculated by the AA stacking model of COF-salen (Figure 3D). This indicated COFsalen has very ordered reticular structure. Besides, some meso/macropores could be observed from the pore size distribution curve. High-resolution scanning electron microscopy (HR-SEM) revealed that COF-salen had microspherical morphology with diameter \sim 2 um. Further zooming in, we could see that the microspheres were constructed by aggregation of nanorods with thickness of ~ 30 to 60 nm to form large amounts of macropores (Figure 4). This indicated the meso/macropores are constructed from the packing of the nanorods, and the hierarchical porosity is an advantage for the mass diffusion especially during the catalytic process.

Table 1 Toxtural	properties and mota	contants of COE calon and COE calon M	
Table L. Textural	properties and meta	a contents of COF-salen and COF-salen-ivi.	

COF sample	BET surface area (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	Pore size (nm)	Theoretical metal content (wt%) ^a	Metal content analysed by ICP (wt%)
COF-salen	1646	1.07	1.86	-	-
COF-salen-Co	1065	0.66	1.59	12.2	11.9
COF-salen-Co(III)	836	0.54	1.36, 1.58	9.0	9.5
COF-salen-Mn	961	0.59	1.59	10.6	10.2
COF-salen-Cu	1258	0.77	1.59	12.9	10.9
COF-salen-Zn	1032	0.61	1.59	13.3	10.6
COF-salen-Co after 5th cycle	973	0.59	1.59	11.9	11.4

^a Theoretical metal content was calculated based on quantitative metalation of COF-salen.



Figure 4. HR-SEM pictures of (A-B) COF-salen and (C-D) COF-salen-Co (For A and C, scale bar is 1 μm; for B and D, scale bar is 100 nm) and (E) PXRD patterns of COF-salen-M.

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COF-salen could be stable up to 300 °C under air as revealed by thermal gravimetric analysis (TGA), which indicated the good thermal stability of COF-salen (Figure 2C). The chemical stability of COF-salen was assessed by dispersing COF-salen in water, DMF, methanol, 1 M HCl and 1 M NaOH solutions. The COFsalen was then collected by filtration and washed with methanol, water and THF, followed by drying under vacuum at 100 °C for 12 h. To our delight, the recovered COF-salen exhibited strong diffraction peaks in the PXRD patterns (Figure 2D), suggesting that COF-salen had high chemical and structure stability possibly due to the strong hydrogen bond and π - π stacking arrangement of the aromatic rings in COF-salen.

Inspired by the good chemical stability of COF-salen, we prepared the metal coordinated COF-salen-M (M = Co^{2+} , Mn^{2+} , Cu²⁺, Zn²⁺) by refluxing the corresponding metal acetate and COF-salen in EtOH for 3 days (Figure 1). The metal loading of COF-salen-M approached the theoretical value based on ICP-AES (inductively coupled plasma atomic emission spectrometry) measurement (Table 1). This shows that almost all salen units could be coordinated with metal ions attributed to the open and ordered porous structure of COFs. The formation of metalsalen was proved by the FT-IR spectroscopy (Figure 1 and S4). In the FT-IR spectra of COF-salen-M, a red shift of C=N vibration was observed, which indicated the successful coordination of metal ions with salen unit of COF-salen. For example, the C=N vibration of COF-salen-Co shifted from 1632 cm⁻¹ to 1613 cm⁻¹, accompanied with a new peak at 499 cm⁻¹ assigned to Co-N or Co-O vibration.51 TGA showed that all the COF-salen-M have good thermostability (Figure S5).

X-ray photoelectron spectroscopy (XPS) was also employed for the characterization of COF-salen-M using COF-salen-Co as a model (Figure S6). The XPS result showed the binding energy for Co (2p1/2) of COF-salen-Co and salen-Co respectively at 780.6 eV and 779.5 eV, showing that the Co species are in +2 state.⁵⁰ In comparison with the homogeneous counterpart, the blue shift in Co (2p1/2) binding energy of COF-salen-Co indicated the slight change in the local coordination structure of salen-Co possibly due to the increased rigidity of salen unit integrated in the framework of COFs.

The PXRD patterns of COF-salen-M are almost identical to those of Co-salen though the intensity of the diffraction peak decreased (Figure 4E). The N2 sorption isotherms of COF-salen-M were of type I similar to those of COF-salen (Figure S7). The BET surface areas of COF-salen-M were lower than those of COF-salen, but COF-salen-M still had high BET surface area varying in the range of 961 to 1258 m²/g. The pore diameter of COF-salen-M samples was the same and distributed at 1.59 nm, which was big enough for the free diffusion of most of organic compounds. The decrease in pore volumes and pore diameter after coordination of COF-salen with metal ions suggested the coordination of metal ions in the nanochannel of COF-salen. SEM and HR-SEM images showed that COF-salen-Co had similar morphology to COF-salen (Figure 3C-3D, Figure S8). The above results show that the crystalline structure of COF-salen was well retained after coordination with metal ions.

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COF-salen-Co was also transferred into COF salen-Co (III) 54a the oxidation of COF-salen-Co with air in the presence of ptoluenesulphonic acid. The appearance of the vibration peak at 1010 and 1125 cm⁻¹ assigned to –OTs in the FT-IR spectrum of COF-salen-Co(III) confirmed the incorporation of –OTs anions (Figure S9). COF-salen-Co(III) had crystalline structure as verified by the existence of diffraction peaks in its XRD patterns (Figure S10). The BET surface area, pore volume and pore diameter were slightly lower than those of COF-salen-Co due to the occupation of –OTs anions in the nanochannel (Figure S11, Table 1). The successful oxidation of COF-salen-Co to COF-salen-Co(III) indicated that COF-salen was robustness enough to survive the acidic oxidation process.

Table 2. The comparison of the catalytic performances of COF-salen-M and their homogeneous counterpart in EPH hydration, styrene epoxidation and cycloaddition of PO and CO_2 .

Deastion	Cataluct	Conv.	Sel.	TOF ^a	
Reaction	Catalyst	(%)	(%)	(h⁻¹)	
	COE-salen-Co(III)	98	>9	52	
EPH hydration ^b	cor-salen-co(m)	50	9	52	
		0.9	>9	07	
	salen-co(iii)	98	9	87	
Styrene	COF-salen-Mn	74	32	120	
epoxidation ^c	salen-Mn	58	24	33	
			>9	070	
CO₂ cycloadditio n reaction ^d	COF-salen-Co	91	9	972	
			>9	700	
	COF-salen-Zn	90	9	780	
		20	>9		
	COF-salen-Cu	20	9	67	
			>9		
	COF-salen-Mn	46	9	252	
			>9		
	POF-salen-Co	70	9	420	
			>9		
	salen-Co	25 ^e	9	41	
			>9		
	TBAB	9	9	-	

 $^{\rm a}$ TOF was calculated with conversion less than 30%. $^{\rm b}$ Reaction conditions: EPH (1 mmol), catalyst (20 μ mol), water (2 mmol), 40 °C, 3 h, 3-chloropropane-1,2-diol was the only product. c Reaction conditions: styrene (2 mmol), catalyst (10 μ mol), t-butyl hydroperoxide (6 mmol), acetonitrile (5 mL), 40 °C, 24 h. The products included benzaldehyde, styrene oxide, benzoic acid, etc. d Reaction conditions: PO (8 mmol), catalyst (8 μ mol), TBAB (80 μ mol), 100 °C, 2 MPa CO₂, 3 h. e Reaction time: 6 h.

The catalytic performance of COF-salen-M was tested in a series of reactions that have been previously catalyzed by homogeneous salen-M complexes (Table 2). Firstly, the catalytic

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performance of COF-salen-Co(III) was tested in the epoxide hydration for the production of glycol (an important intermediate in industry) to investigate the possibility of the cooperation of salen-Co(III) in the network of COFs because the efficient epoxide hydration needs the cooperation of two salen-Co(III) molecules.^{37,51-52} COF-salen-Co(III) could smoothly catalyze the epichlorohydrin (EPH) hydration to afford 98% conversion with >99% selectivity to 3-chloropropane-1,2-diol. This suggests that the successful cooperation of salen-Co(III) integrated in the network of COFs, possibly realized by the nearby Co-salen in the adjacent layers of the COFs. Under similar reaction conditions, the homogeneous counterpart (molecular structure see Scheme S1) with TOF of 87 h⁻¹ was more active than COF-salen-Co(III) with TOF of 52 h⁻¹. This indicates that cooperation of salen-Co(III) of COF-salen-Co(III) is not as free as in homogenous system due to the rigidity of the crystalline structure of the COFs.



Figure 5. (A) Kinetic curves for the epoxidation of styrene catalyzed by COF-salen-Mn and salen-Mn. Reaction conditions: styrene (2 mmol), catalyst (10 μ mol), t-butyl hydroperoxide (6 mmol), acetonitrile (5 mL), 40 °C. (B) Kinetic curves for the cycloaddition reactions of PO and CO₂ catalyzed by COF-salen-Co. Reaction conditions: PO (8 mmol), catalyst (8 μ mol), TBAB (80 μ mol), 100 °C, 2 MPa CO₂.

Salen-Mn is an efficient catalyst for epoxidation of olefins, but suffers the deactivation by forming dimer complexes during the catalysis.53-56 The integration of salen-Mn in the crystalline structure of COFs may inhibit the dimer formation. To investigate if the salen-Mn could be efficiently isolated in COFs, the catalytic performance of COF-salen-Mn was tested in the styrene epoxidation reactions (Table 2 and Figure 5A). As the kinetic curves showed, the styrene conversion increased sharply over COF-salen-Mn in the initial reaction time and about 50% conversion could be achieved in 1.5 h. After that, the reaction rate was slowed down, possibly due to the low concentration of styrene in the reaction system. The homogeneous salen-Mn afforded much slower reaction rate than COF-salen-Mn, about 58% conversion of styrene was achieved in 24 h. The TOF of COF-salen-Mn was ca 3.6 fold that of homogeneous counterpart, which indicated that the salen-Mn isolated in well-ordered pore channels of COFs was hard to form dimers due to the restricted movement during the catalysis. Moreover, the selectivity to styrene oxide over COFsalen-Mn is higher than that over salen-Mn, which further proved the crystalline structure could inhibit the deactivation, at least more effective than that of salen-Mn. The above results showed that salen-M integrated in the network of COTS could not only work cooperatively during catalysis⁰ but ⁸ also⁵ be effectively isolated to inhibit the dimer formation, which is mainly attributed to the unique layered structure of COFs. Owing to the rigidity of crystalline COFs, the cooperation effect is less efficient than the isolation effect during the catalytic process.

Functionalized five-membered cyclic carbonates have wide nonprotic solvents, applications precursors for as polycarbonate synthesis, intermediates in pharmaceuticals and fine chemicals synthesis.57-59 Salen-M complexes with Lewis acidity have been considered as promising catalysts in cycloaddition of CO2 and epoxides for the production of fivemembered cyclic carbonates with the aid of co-catalyst such as tetrabutylammonium bromide (TBAB).³¹ The catalytic performance of COF-salen-M was investigated in cycloaddition of CO₂ and propylene epoxide (PO) with TBAB as co-catalyst (Table 2). Almost no product could be detected using COF-Co without TBAB and only 9% conversion was obtained using only TBAB. The combination of COF-salen-Co and TBAB could smoothly catalyze the cycloaddition reaction to obtain 91% conversion with 99% selectivity to propylene carbonate (PC) (Figure 5B), showing that the efficient cycloaddition reaction needs the cooperation of Lewis acid and TBAB. A control experiment was performed with the combination of COF-salen and TBAB, but only 10% yield of PC was obtained. This confirms that salen-M was the active sites for the cycloaddition reaction.



Scheme 1. Proposed reaction mechanism for the cycloaddition reaction of CO₂ with PO over COF-salen-M in the presenece of TBAB.

A tentative mechanism of CO₂ cycloaddition reaction was illustrated in Scheme 1. Initially, PO was activated by coordination with COF-salen-M serving as a Lewis acid center. Then the Br⁻ of TBAB attacked on the less sterically hindered side of PO as a nucleophile, affording a ring-opening alkoxide intermediate. Subsequently, the M-carbonate intermediate formed by the insertion of CO₂ into the M-O bond of the alkoxide was converted to PC through a ring-closing step and COF-salen-M was regenerated. Under similar conditions, the activity increased in the order of COF-salen-Cu < COF-salen-Mn < COF-salen-Zn < COF-salen-Co. Considering that COF-salen-M had similar textural parameters and crystalline structure, the reaction sequence may be related with the Lewis acid strength Published on 05 February 2019. Downloaded by Iowa State University on 2/6/2019 10:02:29 PM

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and coordination ability of salen-M with ring-opening alkoxide intermediate.

The counter anions of the co-catalysts have great influence on the activity. Thus, apart from TBAB, potassium iodide (KI), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI) and tetraoctylammonium bromide (TOAB) were selected as nucleophilic co-catalysts. The activity decreased in the order of TBAB > TBAI > TOAB > TBAC > KI (Figure S12). Among the three tetrabutylammonium halides (TBAB, TBAC and TBAI), TBAB gave the highest activity, this result is a combination of nucleophilicity (CI⁻> Br⁻> I⁻) and leaving ability (I⁻ > Br⁻ > CI⁻). Encouragingly, TOAB with a much larger size could also give a high PO conversion of 76% with a TOF of 450 h⁻¹. This is possibly due to the uniform and large pore channels of COFsalen-Co, which benifits the transmission of co-catalyst with larger sizes.

The catalytic performance of COF-salen-Co was compared with that of corresponding amorphous polymer POF-salen-Co and the homogenous counterpart. POF-salen-Co with BET surface area of 860 m²/g, pore volume of 0.84 cm³/g and pore diameter of 0.85 nm has identical chemical composition to COFsalen-Co (Figure S13). Under similar conditions, POF-salen-Co afforded 70% conversion of PO. The TOF of COF-salen-Co was ca. 2.3 fold that of POF-salen-Co. The much higher activity of COF-salen-Co was mainly attributed to its ordered crystalline structure and large pore diameter. Homogeneous salen-Co with TOF of 41 h⁻¹ could only afford PO conversion of 25% after 6 h. The much higher activity of COF-salen-Co and POF-salen-Co than the homogeneous counterpart reflected the superiority of heterogenization of salen-Co, which is possibly related with increased rigidity of salen-Co complex in the network of COFs.

The PO conversion and TOF sharply increased with increasing reaction temperature over COF-salen-Co (Figure 6A). The TOF of COF-salen-Co as high as 1875 h⁻¹ could be obtained at 140 °C. This result indicated the good stability of COF-salen-Co at high temperature. Encouragingly, COF-salen-Co could smoothly catalyze the cycloaddition of epichlorohydrin (EPH) and CO₂ even under ambient conditions (25 °C and 1 bar of CO₂) to afford 96% conversion of EPH with a TOF of 26 h⁻¹ (Figure 6B). The high catalytic activity of COF-salen-Co under ambient conditions is not only attributed to the uniform distribution of salen-Co but also the enrichment effect of the porous structure for the low concentration CO₂. The activity of COF-salen-Co in cycloaddition reactions is comparable or higher than most reported solid catalysts, such as metal-organic frameworks (MOFs) and porous organic polymers (POPs) (Table S2).



Figure 6. (A) The catalytic performances of COF-salen_aCo in PO cycloaddition reactions at different temperatures?/(B) kinetic curve for the cycloaddition reactions of EPH and CO₂ catalyzed by COF-salen-Co at 25 °C and 1 bar CO₂.

	OCI	<u>^</u>	°			O	
Time (h)	3	8	8	8	12	24	
Conv. (%)	97	91	91	78	94	77	
Sel. (%)	99	95	99	93	99	99	
TOF (h ⁻¹)	1056	420	410	246	296	59	
Scheme 2	Cycload	dition of	differen	t types of	fepoxide	es with Co	02

catalyzed by COF-salen-Co.

We further investigated the substrate scope of COF-salen-Co and the results are summarized in Scheme 2. All the substrates employed could be converted to the corresponding carbonates. For the less steric hindrance substrates, such as EPH, COF-salen-Co afforded a high TOF of 1056 h⁻¹ and 97% of EPH conversion. The activity of COF-salen-Co decreased as the alkyl length of epoxides increased with an order of butyl glycidyl ether < 1,2epoxyhexane < propylene oxide. Styrene oxide with a large molecular size could be smoothly converted with a conversion of 78% and TOF of 246 h⁻¹. Surprisingly, a challenging substrate, 2-[(1-Naphthyloxy)methyl]oxirane (size of 0.8 * 0.9 nm²) could also be efficiently converted to corresponding cyclic carbonate with high conversion of 94% and TOF of 296 h⁻¹. The above results indicate that COF-salen-Co with uniform pore structure could accommodate large molecules. COF-salen-Co even could catalyse the most challenging internal epoxide, cyclohexene oxide (CHO), to afford 77% conversion and a TOF of 59 h⁻¹. These results confirmed that the COF-salen-Co has a wide substrate scope.





The stability of COF-salen-Co was investigated using cycloaddition reaction as a model. To confirm the heterogeneity of COF-salen-Co during the catalytic process, a hot filtration experiment was carried out by filtrating COF-salen-Co out of the reaction system after 3 h using 1,2-epoxyhexane as substrate when the conversion achieved up to 66%. No obviously increase in the conversion (67% vs 66%) was observed by stirring the filtrate under 2 MPa CO₂ for another 6 h, proving that the reaction is catalyzed by the solid catalyst. In contrast to COF-

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salen-Co, an obvious increase in the conversion from 38% to 47% FT-IR spectra in the range of 400-4000 cm⁻¹ were collected with was observed for amorphous POF-salen-Co in the same hot filtration experiment. This strongly proved the excellent stability of COFs comparing to amorphous polymers, possibly due to the ordered π - π stacking arrangement of the aromatic rings in the network of COFs. Furthermore, COF-salen-Co could be stably recycled for 5 times in CO₂ cycloaddition reaction with PO and no obvious decrement in PO conversion and selectivity was observed (Figure 7A). The cobalt content of COF-salen-Co after the fifth cycle analyzed by ICP was 11.4 wt%, which is comparable to the fresh sample (11.9 wt%). The BET surface area (1065 m²/g vs 973 m²/g) of the COF-salen-Co after five cycles only decreased slightly and pore size distribution was almost the same compared to the fresh one (Figure S14). The crystalline structure was well maintained even after five cycles (Figure 7B). Meanwhile, the morphology and FT-IR spectrum of the reused sample were almost identical to the fresh one (Figure S15 and 1A). The above characterization results of the reused COF-salen-Co confirmed its stability during the catalytic process.

Conclusions

In summary, we synthesized a new salen-based COF via a facile solvothermolysis under air. COF-salen has high surface area (1646 m²/g), uniform pore size (1.86 nm) and AA stacking eclipsed layered crystalline structure. After metalation with metals (Co, Mn, Cu, Zn), COF-salen-M with well-maintained high BET surface area and crystalline structure could be formed. In the EPH hydration reaction, COF-salen-Co(III) afforded a TOF of 52 h⁻¹, slightly lower than the homogeneous counterpart, indicating that salen-Co (III) in the adjacent layers of COFs could work cooperatively, but not as free as homogeneous counterpart. COF-salen-Mn exhibited much higher activity than salen-Mn in styrene epoxidation reaction, possibly due to the site isolation effect of COFs. Moreover, COF-salen-Co showed enhanced activity and recycling stability for cycloaddition reactions of epoxides with CO_2 (TOF up to 1875 h⁻¹) in comparison with amorphous POF-salen-Co, which demonstrated the advantages of COFs in catalysis. The synthesis of COFs with catalytic active sites in the network provides a new approach for the bridging "homogeneous" and "heterogeneous" catalysis.

Experimental section

Chemicals and Reagents.

All chemicals and solvents were used as received without any 1,3,5-Tris(3'-tert-butyl-4'-hydroxy-5'further purification. formylphenyl)benzene,60 N,N'-bis(3-tert-butylsalicylidene)ethanediamine cobalt (salen-Co (II)),⁵⁰ N,N'-bis(3-tertbutylsalicylidene)-ethanediamine manganese chloride (salen- $Mn)^{\rm 61}$ and POF-salen-Co $^{\rm 51}$ were synthesized according to the literature method.

Characterizations.

a Nicolet Nexus 470 IR spectrometer using KBr pellets As and state NMR spectra were performed on a Bruker 500 MHz spectrometer equipped with a magic-angle spin probe using a 4-mm ZrO2 rotor. ¹³C signals were referenced to Glycine (C₂H₅NO₂). The experimental parameters are as follows: 8 kHz spin rate, 5 s pulse delay, and 2500 scans. Scanning electron microscopy (SEM) was undertaken using a FEI Quanta 200F scanning electron microscope operating at an acceleration voltage of 2-30 kV. High-resolution scanning electron microscopy (HRSEM) was undertaken by using a HITACHI S5500

apparatus operating at an acceleration voltage of 30 kV. Before measurement, the samples were fully dispersed in ethanol and then deposited on a holey carbon film on a Cu grid. Powder Xray diffraction (PXRD) patterns of the samples were measured on a Rigaku RINT D/Max-2500 powder diffraction system operated at 40 kV and 200 mA using Cu Kα radiation (The scan rate of 5° min⁻¹ was applied to record the patterns in the range of 2 - 40°). The thermo gravimetric analysis (TGA) was performed from 25 to 900 °C under nitrogen atmosphere with a heating rate of 5°C/min using a NETZSCH STA 449F3 analyzer. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermofisher ESCALAB 250Xi apparatus by using AlK α (h $_{\lambda}$ = 1486.6 eV) as the excitation light source. The nitrogen sorption isotherms were performed on a Micromeritics ASAP 2020 system volumetric adsorption analyzer at 77 K. All samples were degassed at 100 °C for 6 h prior to the sorption measurements. The BET surface area was calculated from the adsorption data at a relative pressure P/P_0 in the range of 0.05-0.25. Pore size distributions were determined from the adsorption branches using nonlocal density functional theory (NLDFT) method. Metal content of the samples was determined using a PLASAM-SPEC-II inductively coupled plasma atomic emission spectrometry (ICP) by digesting the COFs in HNO_3/H_2SO_4 (1:1, v/v).

Synthesis of COF-salen.

1,3,5-Tris(3'-tert-butyl-4'-hydroxy-5'-formylphenyl)benzene (182 mg, 0.30 mmol) was dissolved in amixture of THF (6.4 mL) and EtOH (1.6 mL) in a 30 mL stainless autoclave. Then, 1.6 mL 3 M CH₃COOH and ethylenediamine (30 µL, 0.45 mmol) were added and the autoclave was placed in an oven and heated at 120 °C for 3 days. The resultant product was collected by fltration, washed extensively with ethanol, THF, CH₂Cl₂, water and DMF. Then the yellow powder was dried under vacuum at 60 °C for 12 h, the yield of COF-salen was estimated about 86%. Synthesis of COF-salen-Co.

In a 100 mL round flask, 200 mg of COF-salen (fully evacuated at 100 °C for 3 h before used) was added and dispersed in 12 mL ethanol, then a ethanol/water (6 mL/0.5 mL) solution of Co(OAc)₂·4H₂O (160 mg, 0.64 mmol) was added. The mixture was refluxed at 80 °C for 72 h under nitrogen atmosphere. After filtration, the obtained material was fully washed by ethanol, and then dried under vacuum at 60 °C for 12 h. The red powder was denoted as COF-salen-Co. The cobalt content was 11.9 wt% determined by ICP, the theoretical value was 12.2 wt%.

Synthesis of COF-salen-Mn.

200 mg of COF-salen (fully evacuated at 100 °C for 3 h before used) was dispersed in 20 mL DMF, then a 5 mL ethanol solution

of Mn(OAc)₂·4H₂O (229 mg, 0.93 mmol) was added. The mixture was stirred at 90 °C for 18 h under nitrogen atmosphere. Then a 5 mL ethanol solution of lithium chloride was added and the mixture was pumped with oxygen with a flow rate of 20 mL/min. The mixture was further stirred at 90 °C for 6 h. After filtration, the obtained material was fully washed by ethanol, DMF and water, then dried under vacuum at 60 °C for 12 h. The brown powder was denoted as COF-salen-Mn. The manganese content was 10.2 wt% determined by ICP, the theoretical value was 10.6 wt%.

Synthesis of COF-salen-Cu.

90 mg of COF-salen (fully evacuated at 100 °C for 3 h before used) was dispersed in 6 mL ethanol, then a 6 mL ethanol solution of $Cu(OAc)_2 \cdot H_2O$ (55 mg, 0.27 mmol) was added. The mixture was refluxed at 80 °C for 72 h under nitrogen atmosphere. After filtration, the obtained material was fully washed by ethanol, THF and then dried under vacuum at 60 °C for 12 h. The brown powder was denoted as COF-salen-Cu. The cooper content was 10.9 wt% determined by ICP, the theoretical value was 12.9 wt%.

Synthesis of COF-salen-Zn.

150 mg of COF-salen (fully evacuated at 100 °C for 3 h before used) was dispersed in 12 mL ethanol, then a ethanol/methanol (4 mL/2 mL) solution of $Zn(OAc)_2 \cdot 2H_2O$ (105 mg, 0.48 mmol) was added. The mixture was refluxed at 80 °C for 48 h under nitrogen atmosphere. After filtration, the obtained material was fully washed by ethanol, THF and then dried under vacuum at 60 °C for 12 h. The light yellow powder was denoted as COF-salen-Zn. The zinc content was 10.6 wt% determined by ICP, the theoretical value was 13.3 wt%.

Synthesis of COF-salen-Co(III).

280 mg of COF-salen-Co was dispersed in EtOH (10 mL) containing p-toluenesulfonic acid (150 mg) and the mixture was stirred under air atmosphere at room temperature for 12 h. The solid was collected by filtration, washed with EtOH and dried under vacuum at room temperature. The obtained brown powder was denoted as COF-salen-Co(III).

General procedure for the coupling reactions of $\ensuremath{\text{CO}}_2$ and epoxides.

The coupling of CO₂ and epoxides was performed in a highpressure stainless steel autoclave (15 mL) equipped with a magnetic stirrer. Typically, COF-salen-Co (4 mg, 8 µmol), TBAB (26 mg, 80 µmol) and propylene oxide (470 mg, 8 mmol) were put into the autoclave. After purging the autoclave with CO_2 to exclude air for three times, the reactor was pressurized with 2 MPa CO₂. Then the temperature of the autoclave was increased and maintained at 100 °C with a stirring speed of 550 rpm for a certain time. After reaction, the autoclave was guickly cooled by putting it into an ice-water bath. Then the gas was released slowly, the reaction mixture was added with ethyl acetate (EA) for dilution followed by the addition of butyl acetate as internal standard. After that, the catalyst was separated by centrifugation. The supernatant of the reaction was analysed by gas chromatography (GC). Similar procedure were utilized when using EPH, 1,2-epoxyhexane, butyl glycidyl ether, styrene oxide, cyclohexane oxide or 2-[(1-Naphthyloxy)methyl]oxirane as substrate. The yield of carbonate and conversion of 2-[(1For the room temperature reaction, epichlorohydrin (8 mmol), COF-salen-Co (8 μ mol), TBAB (80 μ mol) and the internal standard biphenyl were fixed in a Schlenk tube equipped with a magnetic stirrer. Then, the tube was purged with a balloon filled with CO₂ at 0.1 MPa and stirred at a speed of 550 rpm at 25 °C for 144 h.

For the hot filtration test, COF-salen-Co or POF-salen-Co was filtrated out of the system after 3 h of cycloaddition reaction using 1,2-epoxyhexane as substrate (Conditions: catalyst, 4 μ mol; TBAB, 40 μ mol; 1,2-epoxyhexane, 4 mmol; 100 °C, 2 MPa CO₂). The yield of corresponding carbonate was analyzed by GC. The filtration was put into the reactor and repressurized with 2 MPa CO₂. The reaction went on for another 6 h then analyzed using GC.

For catalyst recycling, COF-salen-Co obtained by centrifugation was washed three times using EA, dried under vacuum at 100 °C for 6 h and then reused directly for the next catalytic cycle (Conditions: catalyst, 8 μ mol; TBAB, 80 μ mol; PO, 8 mmol; 100 °C; 2 MPa CO₂; 2 h).

General procedure for the EPH hydration reactions.

COF-salen-Co(III) (20 μ mol), EPH (1 mmol), and H₂O (2 mmol) were added in a 10 mL schlenk tube, then the reaction mixture was stirred at 40 °C for 3 h. After cooling to room temperature, octanol (internal standard, 48 μ L, 40 mg) was added to the mixture and the solid catalyst was separated by filtration. The liquid phase was diluted with ethanol then analysed by GC to calculate the conversion of EPH and yield of diol.

General procedure for the styrene epoxidation reactions.

COF-salen-Mn (10 μ mol), styrene (2 mmol), t-butyl hydroperoxide (6 mmol) and 5 mL of acetonitrile were added into a 25 mL flask, then the reaction mixture was stirred at 40 °C for 24 h. After cooling to room temperature, biphenyl (as the internal standard) was added to the mixture and the solid catalyst was separated by filtration. The liquid phase was diluted with EA then analysed by GC to calculate the conversion of styrene and the yield of styrene oxide.

Conflicts of interest

There are no conflicts to declare.

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A facile synthesis of COF-salen via in-situ salen skeleton formation under air atmosphere is described herein. COFsalen-M prepared via metal ions coordination could efficiently catalyse chemical reactions, e.g. styrene epoxidation, epoxide hydration and cycloaddition reactions of epoxides with CO₂. More interestingly, both the cooperation and isolation effects are found in COF-salen-M.