Cobalt sandwich complex-based covalent organic frameworks for chemical fixation of CO₂

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ABSTRACT Carbon dioxide as a notorious greenhouse gas triggers severe global warming which is threatening the balance of ecosystem. In this respect, effectively capturing and transforming CO₂ into value-added chemicals are essential but still challenging tasks. As a kind of emerging crystalline porous material, covalent organic frameworks (COFs) have been demonstrated to be able to adsorb gases and function as catalysts to facilitate chemical transformations. Herein, we report an imine-linked, cobalt sandwich complex-based COF (Co-BD-COF) with high crystallinity and large surface area. Co-BD-COF can efficiently catalyze the transformation of CO₂ into cyclic carbonates due to abundant metal sites and high porosity. In addition, Co-BD-COF exhibits high catalytic selectivity toward small ethylene oxide derivatives in cycloaddition reaction due to the large steric hindrance around the cobalt complexes rendered by the peripheral phenyl moieties. This new metal sandwich-type building block provides a new strategy for improving catalytic selectivity of COFs.

Keywords: covalent organic frameworks, cobalt sandwich complex, carbon dioxide, heterocatalysis, catalytic selectivity

INTRODUCTION

Excessive emission of carbon dioxide has been a persistent environment issue due to the rapid development of industry and massive combustion of fossil fuels, which, however, has triggered huge threats to the whole world, such as global warming and the accompanied collapse of ecosystem. In this context, effectively reducing the concentration of CO₂ in the atmosphere is a critical and challenging task to be solved [1]. For carbon dioxide capture and utilization technology, capturing CO₂ and using it as a green C1 chemical raw material to produce value-added chemicals are sustainable methods to reduce CO₂ in the atmosphere and achieve a carbon-neutral energy cycle [2–6]. Cyclic carbonates are atom-economic non-reducing products; especially, cyclic carbonates substituted with shorter alkyl chains have many advantages in the electrolytes of lithium-ion batteries, such as high chemical stability and wide temperature range [7]. Various kinds of materials including ionic liquids [8], ammonium salts [9], metal-organic frameworks (MOFs) [10–12], and covalent organic frameworks (COFs) [13] have been developed for effi-

cient conversion of CO₂ into cyclic carbonates.

MOFs and COFs are heterogeneous catalysts [14], which can realize rapid recovery of the catalyst and inhibit the occurrence of polymerization in the reaction of catalyzing cyclocarbonate. Functional MOFs are ideal candidates for the chemical fixation of carbon dioxide, due to the active metal sites for gas adsorption and catalysis. However, the limited stability of MOFs inhibits their practical catalysis applications [10]. COFs represent an emerging class of crystalline porous materials featuring high stability and regular pore channels [15–18]. Although some COFs have already been used as heterogeneous catalysts in the chemical conversion of CO₂ [13,19,20], there still exists demands of building more effective COFs to control the product selectivity toward improving atom utilization and reduce purification costs during production. Selective catalysis can be achieved by reducing the pore size [21], but the effect of this strategy is not significant for improving the selectivity of COFs for CO₂ fixation [22,23]. Therefore, in order to achieve high catalytic performance and selectivity for CO₂ fixation, we expect to introduce sandwich-type metal complexes containing bulky organic ligands as selective catalytic centers between the layers of COFs to avoid the limitation of pore size [24]. Additionally, the unlimited pore size of COFs can facilitate mass transfer in catalytic reactions [25].

In this work, a metallocene analogous cobalt sandwich complex [(η⁵-cyclopentadienyl)(η⁴-cyclobutadiene)cobalt] ((η⁵-Cp)Co(η⁴-C₄Ph₄)) was employed as the building block to construct a metal-containing COF (Co-BD-COF). (η⁵-Cp)Co(η⁴-C₄Ph₄) obeys the Hückel's rule and exhibits high stability under air and moisture [26–28]. The cobalt complexes within the skeleton of the COF exist in the form of metallocene with a relatively large basal bulkiness, which might render enhanced catalytic selectivity due to the space confinement effects around Co centers. For the synthesis of Co-BD-COF, the aldehyde monomer (Co-CHO) was synthesized firstly (Scheme S1 and Figs S1–S3). Furthermore, linear and long benzidine (4,4'-biphenylenediamine, BD) was selected as the amino-functionalized monomer (Scheme 1). Two-dimensional (2D) crystalline Co-BD-COF was prepared by a Schiff base polycondensation between Co-CHO and BD, in which cobalt atoms were regularly arranged and precisely positioned within the 2D layers [15]. In addition, the uniformly dispersed Co within the framework of COF promised

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Scheme 1 Synthetic route and stacking mode of Co-BD-COF.

recyclable catalytic activity of the Co-BD-COF by effectively preventing the aggregation among Co atoms. Interestingly, the catalytic activity of COFs decreased sharply upon increasing the size of the substrates, indicating that COFs had a high selectivity to the molecular size of the substrate. These results suggest that sandwich-type COFs containing metal may serve as an excellent material for CO₂ fixation application due to their high efficiency and size selectivity.

EXPERIMENTAL SECTION

Preparation of Co-BD-COF

Co-CHO (12.1 mg, 0.02 mmol) and BD (7.36 mg, 0.04 mmol) were added to a 10-mL glass tube, and then 1.1 mL of a 5:5:1 (v/v/v) solution of *n*-butanol/mesitylene/acetic acid (6 mol L⁻¹) was added. The tube was degassed under vacuum at 77 K and sealed. Subsequently, the tube was heated at 120°C and kept for three days. After cooling to room temperature, the product was isolated by filtration and washed with tetrahydrofuran and acetone, and dried in vacuum, affording an orange powder in 89% yield.

Catalytic CO₂ cycloaddition with epoxides to produce cyclic carbonates

In a typical reaction, the catalyst (COF, 18 mg, 2 mol%), tetrabutylammonium bromide (TBAB, 0.05 mmol) and epoxides (1 mmol) were taken in a pre-dried Schlenk tube. After sealing and purging with CO₂ (1 atm), the Schlenk tube was placed in a preheated oil bath and stirred for 24 h at 40°C. After the reaction, the tube was cooled to room temperature. The reaction mixture was filtered off and washed thoroughly with dichloromethane to ensure complete extraction of the product. The collected filtrate contained both the product and co-catalyst (TBAB) which could be removed by washing with water. The remaining filtrate was evaporated under reduced pressure to obtain the product. Then the samples were analyzed by ¹H nuclear magnetic resonance (¹H NMR) spectroscopy. The recovered catalyst was dried under vacuum and reused for next cycles.

RESULTS AND DISCUSSION

Structure and physical characterization

Co-BD-COF was synthesized by solvothermal polycondensation of the monomers at 120°C in a mixed solvent of *n*-butanol/mesitylene/acetic acid (6 mol L⁻¹) for three days [29]. The crystallinity of Co-BD-COF was confirmed by powder X-ray diffraction (PXRD) analysis and the extended architecture of Co-BD-COF was modeled (Table S1). The experimental PXRD pattern of Co-BD-COF displayed an intense diffraction peak at 3.70° and two other signals at 6.55° and 11.00° (Fig. 1a), which were assigned to the (100), (200) and (300) facets, respectively. Co-BD-COF exhibited an eclipsed AA (Fig. 1b, c) rather than a staggered AB stacking mode (Fig. S4) by comparing the experimental PXRD patterns and the simulated results. Pawley refinement results indicated that the simulated structure matched well with the experimental data (*R*_{wp} = 6.70% and *R*_p = 5.02%). Interestingly, the metal atoms were uniformly located between rather than within the layers (Fig. 1c, d).

Fourier transform infrared (FT-IR) spectrum of the Co-BD-COF showed the characteristic peak for C=N linkages at 1624 cm⁻¹, significant disappearance of C=O (1692 cm⁻¹) and the N-H stretching vibrations (3439 and 3329 cm⁻¹) from the precursors, which indicated successful imine condensation (Fig. S5) [30,31]. To further verify the chemical structure of the COF, a model compound (Co-CHOA) was synthesized through a Schiff base reaction between Co-CHO and aniline (Scheme S2 and Figs S6–S8). Similarly, the same characteristic C=N stretching band at 1624 cm⁻¹ was observed for Co-CHOA (Fig. S5a) [32], which further proved that Co-BD-COF was connected by imine linkages. The chemical structure of Co-BD-COF was further characterized by the solid-state ¹³C cross polarization magic angle spinning (CP-MAS) NMR spectra. The characteristic signal at 158 ppm and significant attenuation of the signal of aldehyde carbon around 190 ppm for Co-BD-COF further confirmed the formation of C=N linkages (Fig. S9) [33], whereas the ¹³C CP-MAS NMR spectrum of Co-BD-COF displayed the carbon signals of cyclobutadiene (Cb) and cyclo-

Figure 1 (a) Experimental PXRD pattern (black) and Pawley refinement (red) of Co-BD-COF, their difference (orange), simulated profiles using the eclipsed AA arrangement (blue) and Bragg diffractions stacking modes (green). Top view (b) and side view (c) of the AA stacking modes for Co-BD-COF. (d) Side view of a unit cell of Co-BD-COF.

pentadienyl (Cp) moieties at 73 and 83 ppm, respectively [28]. In addition, the characteristic carbon signals of Co-BD-COF were consistent with those of Co-CHOA (Fig. S9). Moreover, elemental analysis of Co-BD-COF revealed that the contents of C, H and N were in good agreement with the theoretical values of $C_{61}H_{41}CoN_4$ for Co-BD-COF (Table S2). The content of Co atoms in Co-BD-COF was determined to be up to 7.51 wt% obtained from inductively coupled plasma optical emission spectrometry (ICP-OES, Table S3).

The morphology of Co-BD-COF was characterized through field emission scanning electron microscopy (FE-SEM). The images revealed Co-BD-COF appeared as lamellar particles (Fig. S10). More detailed characterization was implemented by using transmission electron microscopy (TEM). The images unveiled that the lamellar particles were composed of stacked COF layers (Fig. S11). Further elemental mapping analysis indicated a homogeneous distribution of C and Co elements on the nanosheets of Co-BD-COF. Thermogravimetric analysis indicated that Co-BD-COF was thermally stable up to 472°C (loss 5%) under nitrogen atmosphere (Fig. S12).

Porosity analysis

The permanent porosity of the Co-BD-COF was assessed by N_2 adsorption/desorption measurements at 77 K. As displayed in Fig. S13a, the N_2 sorption isotherms for Co-BD-COF suggested type IV characteristics, which indicated Co-BD-COF possesses mesopores. The Brunauer-Emmett-Teller (BET) surface area of Co-BD-COF was determined to be $1040 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of Co-BD-COF indicated a uniform pore size of 2.0 nm, which was simulated by the nonlocal density functional theory (NLDFT, Fig. S13b). The result was close to the d -spacing value as calculated from the PXRD pattern.

Chemical fixation of CO_2

Metallosalen (M-Salen) complex has been utilized to catalyze the cycloaddition reaction between carbon dioxide and epoxides to form cyclic carbonates, which has recently received increasing research interest [34]. Considering the porous architecture and high specific surface area of Co-BD-COF, the abundant Co sites anchored in the open channels of Co-BD-COF could accommodate guest molecules (e.g., CO_2) and serve as active sites to

mediate catalytic reactions [15,35]. To evaluate the CO_2 adsorption capacity of Co-BD-COF, CO_2 sorption isotherms were recorded at 273 K and the maximum uptake of CO_2 was found to be 1.17 mmol g^{-1} (Fig. S14). Therefore, we expected Co-BD-COF could function as a potential heterogeneous catalyst for cycloaddition reaction between epoxides and CO_2 [36]. Furthermore, Co-BD-COF maintained high thermal stability after being heated in CO_2 atmosphere for two days, as evidenced from the PXRD patterns of the COF samples (Fig. S15).

In order to systematically investigate the catalytic properties of Co-BD-COF, different epoxide derivatives were used as substrates in the cycloaddition reaction. Typically, all reactions were carried out at 40°C with a balloon of CO_2 (0.1 MPa) and TBAB as the co-catalyst (Table 1) [13]. The yields of the generated cyclic carbonates were calculated based on the 1H NMR spectroscopy. The cycloaddition reaction between CO_2 and epichlorohydrin was selected as a model reaction for comparison (Table S4), which achieved a yield of 95%. It disclosed that the yields were reduced to 36% and 9%, respectively, when Co-BD-COF or TBAB was absent. This indicated that both the COF and TBAB played indispensable roles in achieving high catalytic performance.

As summarized in Table 1, for 1,2-epoxybutane and 1,2-epoxypentane, the yields of cyclic carbonates reached 99% and 94%, respectively (entries 1 and 2). With elongating the alkyl chains, the yields decreased accordingly; for example, the yield dropped to 83% for 1,2-epoxyhexane (entry 3) and was further reduced to 43% for allyl glycidyl ether (entry 4). In general, the ethylene oxide derivatives with short alkyl chains could afford very high yields in this catalytic reaction. The high catalytic selectivity of Co-BD-COF toward less bulky epoxides could be ascribed to the special sandwich structures of the cobalt complexes in Co-BD-COF (Fig. 1d). This trend of catalytic selectivity was also observed for halogen-substituted substrates. For instance, the yield was 95% for chloropropene carbonate and was dropped to 82% for bromopropylene carbonate (entries 5 and 6). In addition, when more sterically hindered aromatic epoxides, i.e. styrene oxide and glycidyl phenyl ether were investigated, very low yields of ca. 11% and 32% were obtained, respectively (entries 7 and 8), probably due to the bulkiness of the substrates (Fig. S16) [37]. Moreover, it showed that the steric

Table 1 Catalytic cycloaddition of CO₂ with different epoxide substrates using Co-BD-COF as the catalyst

Entry	Epoxides	Catalysts	Co-catalysts	Temp. (°C)	Time (h)	Yields (%) ^a
1		Co-BD-COF	TBAB	40	24	99
2		Co-BD-COF	TBAB	40	24	94
3		Co-BD-COF	TBAB	40	24	83
4		Co-BD-COF	TBAB	40	24	43
5		Co-BD-COF	TBAB	40	24	95
6		Co-BD-COF	TBAB	40	24	82
7		Co-BD-COF	TBAB	40	24	11
8		Co-BD-COF	TBAB	40	24	32

a) Determined by ¹H NMR spectroscopic analysis.

Figure 2 (a) Recycling catalytic test of Co-BD-COF for the CO₂ cycloaddition with epichlorohydrin. (b) N₂ adsorption/desorption isotherms of Co-BD-COF before (black) and after (blue) the 5th run of cyclic reactions.

hindrance effect of aromatic rings was higher than that of chain substituents by comparing entries 4 and 8. Consequently, Co-BD-COF was demonstrated to exhibit high catalytic activity and selectivity toward small-size epoxides with low steric hindrance for effective chemical fixation of CO₂ [15].

To further evaluate the reusability of Co-BD-COF, the model reaction using epichlorohydrin as the substrate was studied [38,39]. The results showed that the yield of chloropropene carbonate remained 95% after three catalytic cycles and still maintained 90% after five repeated catalytic cycles (Fig. 2a and Table S5). In addition, the PXRD pattern and nitrogen sorption isotherms of Co-BD-COF were evaluated again after the catalytic cycles, and little changes in both crystallinity and specific surface area of Co-BD-COF were observed before and after the catalytic cycles (Fig. 2b and Fig. S17). In addition, the content of Co element in Co-BD-COF was measured again after the catalytic cycles and showed negligible change, which further proved the metal sites within the COF were intact during the catalytic cycles (Table S3). Thus, Co-BD-COF manifested high catalytic performance with good reusability toward CO₂ fixation [19,40–42].

To shed more lights into the effect of Co-BD-COF catalyst on the cycloaddition reaction between CO₂ and epoxides, a rea-

sonable mechanism is proposed by referring to the literature (Fig. 3) [15]. Firstly, the Co sandwich complexes interact with the oxygen atoms of the epoxides. The sandwich structure of (η⁵-Cp)Co(η⁴-C₄Ph₄) can prevent the bulky epoxides from interacting with the metal site. Next, a bromide from TBAB attacks one carbon atom of epoxide group from the less sterically-hindered side to form an oxyanion intermediate. Subsequently, the oxyanion attacks one CO₂ molecule to form an alkyl carbonate anion intermediate, which is followed by a cyclizing process to form the final carbonate and a release of Co-BD-COF for the next catalytic cycle [13,40].

CONCLUSIONS

An unprecedented cobalt sandwich complex-based imine COF (Co-BD-COF) was successfully developed, which showed high crystallinity, large surface area, and good stability. The metal active sites uniformly arranged in the Co-BD-COF skeleton could serve as the main catalytic centers to mediate effective fixation of CO₂ by cycloaddition reaction of CO₂ with epoxides in high yields. Meanwhile, Co-BD-COF as a heterogeneous catalyst was highly recyclable and exhibited superior activity and excellent selectivity toward small epoxide substrates with low

Figure 3 Proposed mechanism for the cycloaddition of CO₂ with epoxides catalyzed by Co-BD-COF.

steric hindrance. The current work not only enriches the diversity of metal-functionalized COFs, but also provides new insights into the design of COFs as effective heterogeneous catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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含钴夹层结构的共价有机框架用于二氧化碳的化学固定

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摘要 二氧化碳作为主要的温室气体导致了全球变暖, 并威胁着生态系统的平衡. 有效捕获二氧化碳并将其转化为增值化学品具有重要的意义, 但也充满挑战. 作为一种新兴的多孔晶态材料, 共价有机框架(COFs)不仅能有效吸附气体, 而且可作为化学转化催化剂. 本文报道了一种由亚胺连接的含钴夹层配合物的COF(Co-BD-COF), Co-BD-COF表现出较高的结晶度和较大的比表面积. Co-BD-COF还兼具丰富的金属位点和较高的孔隙率, 能有效地催化CO₂转化为环状碳酸酯. 此外, Co-BD-COF在环加成反应中表现出对小体积的环氧乙烷衍生物的高效选择性, 这种高效选择性来源于夹层钴配合物周围的苯基部分所形成的空间位阻作用. 将金属夹层配合物构筑到COF骨架, 为提高COFs的催化选择性提供了一种新的设计策略.