DOI: 10.1002/cctc.201300756



Pillared Cobalt–Amino Acid Framework Catalysis for Styrene Carbonate Synthesis from CO₂ and Epoxide by Metal–Sulfonate–Halide Synergism

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The sulfonate anion is proposed as a remarkable partaker in catalyzing epoxide– CO_2 cycloaddition for cyclic carbonate synthesis. The role is illustrated by the concerted action of a sulfonate-rich cobalt–amino acid framework catalyst [{Co(4,4'-bipy)(L-cys)(H_2O)}+H_2O]_n (2D-CCB) and a quaternary ammonium bromide co-catalyst in synthesizing styrene carbonate (SC) at a turnover number of 228. SC yield at atmospheric pressure is presumed to result from the activation of CO_2 by the sulfonate group. The involvement of SO_3^- anions as basic sites in 2D-CCB is ascertained from the initial rate (r_0) for catalyzing Knoe-

venagel condensation reactions and by using CO₂ temperature programmed desorption. Microwave pulses are used for synthesizing 2D-CCB at a rate that is 288-fold faster than conventionally employed solvothermal methods. Unambiguous evidence for the pulsating role-play of sulfonate groups in 2D-CCB is perceived by comparing the activity of an analogous metal organic framework (3D-CCB) in which the sulfonate oxyanions are jammed by coordination with cobalt. 2D-CCB is analyzed for heterogeneity, and reused four times.

Introduction

Increasing concerns over global warming have prompted researchers to develop strategies that could minimize the emission of carbon dioxide from industries and power plants as a byproduct. The quests for green technologies that utilize this greenhouse gas as a C1 feedstock for chemical manufacture would apparently triumph over the sequestration routes that inflict sewage liabilities. Recent years have witnessed the emergence of versatile catalysts that promote the transformation of CO₂ to products such as dimethyl carbonate, N,N'-disubstituted ureas, cyclic carbonates, cyclic urethanes, formic acid, and so forth.^[1] Amongst such processes, the cycloaddition of epoxides and CO₂ to produce cyclic carbonates is an atomically-economical reaction. Cyclic carbonates find applications as solvents, electrolytes in lithium-ion batteries, and as intermediates in the synthesis of ethylene glycol, acyclic carbonates, pharmaceuticals, and polymers.^[2]

Catalysts such as metal oxides, metal complexes, organometallic compounds, and ionic liquids are engaged as successful candidates in the cycloaddition of CO₂ and epoxides. Whereas most of them often fall short in fulfilling a viable post-catalytic recovery method; many easily recyclable ones often require more intense reaction conditions in achieving cyclic carbonates

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300756. at appreciable yields.^[3] Nevertheless, the harsh conditions are circumvented to some extent by immobilizing the ionic liquids or similarly active homogeneous species over heterogeneous materials such as silica, polymers, or biopolymers. More recently, metal-organic frameworks (MOFs)—an emerging class of porous, crystalline materials—are explored as materials that are capable of meeting specific needs; this includes catalysis,^[4] by a precise control of the coordination geometries and by judiciously choosing organic spacers in their construction. Thus, their customizability with a meticulous modulation of the constituent organic struts and/or metal-containing clusters contributes to the overwhelming interest in engaging MOFs or coordination polymers (CPs) as exquisite materials for versatile applications.^[5]

A few preeminent transition-metal-based porous di/tri-carboxylate bridged MOFs, zeolitic imidazolate MOFs (ZIFs) and so forth, with high CO2-adsorption capacities have been recently employed as catalysts for epoxide-CO₂ cycloadditions; this relies on the efficacy of various inherent functional groups such as hydroxyl or amine groups, or by post-synthetic modification (PSM) techniques.^[1h, 6] In our attempt to extend the study towards the influence of various functional groups of MOFs in catalysis, we noticed that the role of sulfonate anions remained scarcely explored.^[7] However, a few sulfonic acids have been explored as Lewis acid sites in several other catalytic processes.^[8] To the best of our knowledge, the role of the sulfonate anion has seldom been studied or employed in any cycloaddition reactions, which involve epoxides and CO₂, despite its efficiency as a leaving group. Other than ring-opening anions, the activation of epoxides toward ring opening is important for an efficient cycloaddition process. The literature suggests that a number of cobalt complexes have efficiently performed this function in the production of cyclic carbonates and polycarbonates from epoxides and CO_2 .^[9] This prompted us to combine both of these aspects for establishing an efficient catalytic system. Owing to the practicality in achieving reactive functional groups by a prudential alteration of its building blocks, a MOF class of material is selected as an appropriate candidate for encompassing both cobalt and reactive sulfonate (SO₃⁻) functional groups as synergistic participants for catalyzing cyclic carbonate synthesis. The α -amino acid L-cysteic acid in its deprotonated state is identified as a suitable spacer with a sulfonate source. A 2D cobalt–cysteate coordination polymer (2D-CCB)^[10] (Figure 1) is employed as the catalyst



Figure 1. Mercury diagram depicting parallel 2D rectangular grids in 2D-CCB (metal center and reactive functional groups shown in the ball-and-stick model).

for demonstrating the role of SO_3^- groups in the cycloaddition of styrene oxide (SO) and CO_2 in the presence of a tetra-*n*-butylammonium bromide (TBAB) co-catalyst. Microwave power is investigated as an energy-efficient tool for reducing the duration required for the synthesis of 2D-CCB to a more practical timeframe. A clearer perception about the contribution of the sulfonate moiety of 2D-CCB in affecting the cycloaddition of SO and CO_2 is sought by comparing its catalytic activity with an analogous MOF (3D-CCB) with a varied coordination state from the same building blocks that lack any sulfonate oxyanions.

Results and Discussion

Microwave-assisted synthesis of the catalyst

In synthesizing 2D-CCB by a solvothermal route, the need for considerable amounts of energy along with prolonged reaction durations: more than two days at the expense of an elevated temperature of 140 °C, stands as a major obstruction. However, a direct-mixing method or slow evaporation as alternative techniques may generally result in a significant fall in phase purity of 2D-CCB; this particularly owes to the insoluble nature of the basic cobalt carbonate precursor in the synthesis medium. The use of microwave energy addresses the above concerns by promoting efficient molecular collisions with significant reductions in time and energy by potentially offering a more rapid synthetic alternative. Our previous reports on mi-

crowave-mediated methods as a viable pathway for reducing the duration of catalyst syntheses and increasing catalytic efficiencies encouraged us to examine microwave energy irradiation for 2D-CCB synthesis.^[11] Previous reports on the microwave-assisted synthesis of MOFs by using high-boiling solvents such as N,N'-dimethylformamide (DMF) were performed at a controlled temperature below the boiling point. As a result, it takes a prolonged synthesis time, which extends even up to an hour in some instances.^[6k] Unlike MOFs that are synthesized in high-boiling solvents, the comparatively low boiling point of a water-methanol (1:1) mixture opens up the possibility of intrinsic temperature control wherein synthesis of 2D-CCB can be facilitated at a constant microwave power. Gratifyingly, a short time span of 10 min (at 100 W power) is enough for the synthesis of 2D-CCB(M), in the microwave (M=microwave).

Structural aspects and nature of the sulfonate anions

2D-CCB [{Co(4,4'-bipy)(L-cys)(H₂O)}, H₂O]_n exists as a 2D coordination polymer with a brick-wall topology. 2D-CCB contains SO₃⁻ groups that are oriented freely between adjacent rectangular grids, which are stacked by H-bonding interactions along the third dimension, forming the network (Figure 1). To study the variations in catalytic activity that occur as a result of the nature of the SO₃ groups—from anionic species (reactive functional groups) to a frozen state (coordinative functional groups), we chose a 3D framework, which was reported earlier by Huang et al.^[12] $[{Co_2(4,4'-bpy)_2(L-cys)_2(H_2O)_2} \cdot 3H_2O]_n$ (3D-CCB) is a 3D MOF with (4².8⁴)-intermediate value theorem topology, derived from the same constituent moieties of 2D-CCB namely, L-cysteic acid, the 4,4'-bipyridyl group, and cobalt. Despite their similarities and that the cobalt centers have distorted octahedral geometries; 3D-CCB has the oxyanion of the sulfonate group coordinated to cobalt (Scheme 1). Variations in their structures can be ascribed to the differences in synthesis time, pH, temperature, and nature of the counter anions (of the metal salt).

Characterization

To confirm the crystallinity, structural integrity, and bulk homogeneity of the microwave-synthesized catalyst 2D-CCB(M), its



Scheme 1. A representation of variations in the binding of L-cysteic acid with cobalt in 2D-CCB (left) and 3D-CCB (right). Sulfonate exists as an anion in the former, whereas it exists in a coordinated state to cobalt in the latter.

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Figure 4. TGA analyses of 2D-CCB(S) and 2D-CCB(M).

Figure 2. XRD patterns of 2D-CCB(S) and 2D-CCB(M) in comparison to the single crystal simulated pattern.

X-ray diffraction pattern (PXRD) is compared with that of the solvothermally prepared catalyst 2D-CCB(S), in which S = solvothermal, and its simulated X-ray diffraction pattern from the single crystal data analysis (Figure 2).^[10] The similarities in their patterns, particularly, the absence of any additional peaks with respect to the simulated pattern confirm that the bulk of 2D-CCB(S) and 2D-CCB(M) samples purely belong to the 2D-CCB phase.

Similarly, the FTIR bands of 2D-CCB(S) and 2D-CCB(M) establish the solvothermal and microwave catalysts as chemically identical (Figure 3). The FTIR peaks associated with the sulfonate group are observed in the 1200–1100 cm⁻¹ region,^[10,13] which corresponds to the S–O stretching frequencies of the sulfonate group.



Figure 3. FTIR spectra of 2D-CCB(S) and 2D-CCB(M).

Thermogravimetric analyses (TGA) are conducted after completely drying the samples in vacuo; therefore, their degradation curves do not reflect the loss of lattice water molecules (Figure 4). Hence, the first major weight loss is observed within 180–230 °C for both samples, which corresponds to the loss of coordinated water molecules. 2D-CCB begins to undergo framework degradation at approximately 300 °C for both sam-

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ples, which further corroborates the similarities in the thermal stabilities of 2D-CCB(S) and 2D-CCB(M).

Physical examinations of the catalysts' textural features are conducted by using field emission scanning electron microscopy (FESEM). As shown in Figure 5, the catalyst prepared in 10 min by the microwave-assisted method appears as an aggregation, in comparison to the large single crystals obtained by the solvothermal method (Figure 5a–d). However, further magnification reveals that 2D-CCB(M) is comprised of tiny crystals (Figure S1, Supporting Information).



Figure 5. FESEM images of the solvothermally synthesized (top) and microwave synthesized (bottom) 2 D-CCB samples. Images in the left side are of the order 100 μ m, whereas those in the right side are their respective magnifications in 20 μ m scale.

2D-CCB is a multifunctional catalyst that consists of a cobalt metal center, a sulfonate anion, and several lone pairs of electrons, which belong to O- and N-atoms of the framework. CO₂- and NH₃-temperature programmed desorption (TPD) is performed with 2D-CCB(M) for examining the acid–base characteristics and binding tendencies of CO₂ by basic sites (including sulfonate sites). Figure S2 (Supporting Information) depicts

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the CO₂-TPD profile and Figure S3 the NH₃-TPD profile. Table S1 (Supporting Information) accounts the weak/medium/strong acid-base sites of 2D-CCB in mmolg⁻¹. Kim et al.^[6j] have observed by using TPD that lone pair electrons in metal coordinated O- and N-atoms of MOFs can act as basic sites. MOFs such as Cu-BTC (BTC = benzene-1,3,5-tricarboxylic acid), MOF-5, UIO-66, Mg-MOF-74, MIL-101 and so forth, possess basic sites that range from $0-36.4 \text{ mmol g}^{-1}$ in concentration (CO₂-TPD). Though a direct comparison is not possible, we follow a similar pretreatment and program of CO₂-TPD for the 2D-CCB(M) catalyst observe 85.1 mmol g⁻¹ of basic and sites (21.2 mmolg⁻¹ weak, and 63.9 mmolg⁻ strong basic sites), which implies there are a higher number of basic sites that can also be attributed to sulfonate anions. NH₃-TPD shows that 2D-CCB(M) possesses a total acid site concentration of 133 mmol g^{-1} .

For a detailed understanding with experimental evidence on the acid and base sites available in the materials, we engaged the catalyst for acetalization

(acid site determination) and Knoevenagel condensation reactions (base site determination). The initial reaction rates (r_0) are estimated for the Knoevenagel condensation (base-site catalyzed) reaction between malononitrile and benzaldehyde, and the acid-site catalyzed acetalization between benzaldehyde and ethanol (Figure 6). Reactions are performed by using 2D-CCB and 3D-CCB on a comparative manner to unveil the role of the sulfonate groups. The acetalization reactions with 3D-CCB(S) and 2D-CCB(S) proceed at approximately the same rates, with r_0 values at 50.2×10^3 and 44.9×10^3 mol min⁻¹g⁻¹, respectively.

Thus, the acidic sites present in both catalysts can be assumed to be similar in number, which correspond to an approximately equivalent number of cobalt centers. Similarly, the rate determination of the 3D-CCB catalyst yields an r₀ value of 49.8×10^3 mol min⁻¹g⁻¹ for the Knoevenagel condensation, which reflects the number of basic sites. Even though anionic species are absent in 3 D-CCB, it is likely that heteroatoms containing lone pairs of electrons may contribute to the observed reactivity; similar to an observation by Cho et al.^[6k] for a cobalt-MOF surrounded with oxygen atoms. Surprisingly, for 2D-CCB, a threefold increase in the initial rate (169 \times 10^3 molmin⁻¹g⁻¹) in comparison with 3D-CCB is observed for the Knoevenagel condensation. This enhanced reaction rate, which is attributable to sulfonate oxyanions, demonstrates that the reactive sulfonate functional groups are capable of enabling high catalytic activities in base-catalyzed reactions.

Cycloaddition of SO and CO₂

The cycloaddition reaction of styrene oxide (SO) and CO_2 is performed at 0.1 MPa and 100 °C for 12 h with 0.4 mol% of catalyst (Table 1). In the absence of a catalyst, no styrene carbonate (SC) is yielded (entry 1). Cycloaddition with 2D-CCB(S) alone gives SO conversion of 18.5% with 65.2% selectivity for SC, whereas cycloaddition with TBAB alone shows 39.0% con-

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Figure 6. Comparison of acid–base sites by the initial rate (r_0) estimation from the Knoevenagel condensation (base-catalyzed) reaction and acetalization (acid-catalyzed) reaction by using 3 D-CCB and 2 D-CCB(S) as catalysts. 2 D-CCB(S) has an exceptional r_0 value for the Knoevenagel condensation, which is attributed to the basicity contributed by the reactive sulfonate groups in 2 D-CCB.

Table 1. Influence of various catalysts in the cycloaddition of SO and $\mathrm{CO}_2^{\mathrm{[a]}}$							
Entry	Catalyst ^[b]	Conversion of SO [%] ^[c]	Selectivity to SC [%] ^[c]				
1	none	0	0				
2	2 D-CCB(S)	18.5	65.2				
3	TBAB	39.2	99.9				
4	2 D-CCB(S)/TBAB	89.5	99.9				
5	2 D-CCB(M)/TBAB	91.1	99.9				
6	3 D-CCB	10.9	55.2				
7	3 D-CCB/TBAB	65.9	96.5				
[a] Reaction conditions: Styrene oxide = 25 mmol (2.85 mL at 25 °C), 0.1 MPa P_{CO2} , 12 h, 100 °C 600 rpm. [b] Catalyst mol % = 0.4 [c] Determined by GC							

version and over 99.9% selectivity (entries 2 and 3). Interestingly, a 1+1>2 sort of outcome (89.5% conversion, 99.9% selectivity) is achieved with a 2D-CCB(S)/TBAB system, which indicates a synergistic catalytic operation (entry 4). On the other hand, the microwave-synthesized counterpart 2D-CCB(M)/ TBAB shows 91.1% conversion with 99.9% SC selectivity (entry 5), which accentuates the competency of microwave energy not merely as a rapid catalyst synthesis technique, but also as an efficient route that produces catalysts that maintain the qualities of conventional catalysts.

Based on these observations, a rationalized mechanism for the cycloaddition of SO and CO₂ that involves the cobalt center and sulfonate groups of 2D-CCB in association with the bromide anions of TBAB is proposed herein (Scheme 2). The cycloaddition reaction commences with epoxide ring activation by the cobalt center of 2D-CCB, as in the case of a typical metal-center-catalyzed cycloaddition, whereby the epoxide ring is rendered susceptible to ring opening.^[9] Subsequent epoxide ring opening is achieved by the attack of the bromide anion of TBAB on the least hindered β -carbon atom of the epoxide ring.^[11] Previous reports of epoxide-CO₂ cycloaddition re-

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Scheme 2. Proposed mechanism for the cycloaddition of styrene oxide and CO_2 catalyzed by 2D-CCB/TBAB.

actions suggest that a contemporaneous presence of acid and base sites are desirable for a successful catalysis.^[6j] However, 2D-CCB facilitates the cycloaddition reaction in a more synergistic manner than two-component acid-base catalysis. The oxyanion of the sulfonate moiety of 2D-CCB attacks the carbon atom of CO₂, which is considered as one of the most oxidized states of carbon that induces its inertness. This attack results in the wreckage of its inertness, thereby forming a carbonate complex (intermediate-a); fortifying the cycloaddition reaction. In the subsequent step, the oxyanion of the ringopened intermediate (intermediate-b) attacks the carbon of the carbonate complex, thus detaching the SO₂-CO₃ linkage back to the SO_3^- anion; wherein a third intermediate (intermediate-c) is formed. This step is also favored because of the better leaving ability of the SO₃⁻ group compared to nucleophiles such as Br⁻ or Cl^{-.[14]} Finally, ring closure takes place with the elimination of a Br⁻ ion to generate SC, thus liberating TBAB and regenerating 2D-CCB, thenceforth moving to the next cycle of cycloaddition.

To gather further experimental evidence for the synergistic role of sulfonate groups involved in 2D-CCB, the analogous catalyst 3D-CCB with no reactive sulfonate group is employed as the catalyst under similar conditions. With the total conversion of SO by using 3D-CCB/TBAB (Table 1, entry 7) slightly exceeding the summation of its individual active centers (entries 3 and 6), a cooperative mechanism may be inferred to exist in this reaction as well. However, the 65.9% SO conversion is far less prominent against the conversion of 91.9% SO with 2D-CCB/TBAB under similar conditions, which sheds some light on the role that is performed by the sulfonate group. A plausible mechanism is illustrated in Scheme 3. Activation of the epoxide ring of SO followed by epoxide ring opening by the bromide anion takes place in a manner similar to the aforementioned mechanism of 2D-CCB/TBAB; however, the chance



Scheme 3. Cycloaddition of styrene oxide and CO_2 catalyzed by 3D-CCB/ TBAB, which proceeds in the absence of sulfonate anions.

for carbonate complex formation analogous to intermediateb (Scheme 2) does not prevail in this mechanism. Instead, intermediate-a' (Scheme 3) attempts a cycloaddition reaction directly with the CO_2 molecule to form intermediate-b'. Therefore, this step may proceed at a much slower rate than the addition to the carbonate complex step that is mentioned in 2D-CCB. This phenomenon is evidenced by the reduced SO conversions with 3D-CCB than 2D-CCB (Table 1, entries 4 and 7). The reduced SO conversion with 3D-CCB could serve as the experimental evidence for the involvement of sulfonate oxyanions of 2D-CCB in providing efficient SO conversions because the final ring-closure step is similar to that of the 2D-CCB catalyzed reaction.

The effects of varying catalyst concentration are examined for different ratios of 2D-CCB(M)/TBAB in the range 0.25– 0.1 mmol of catalyst/co-catalyst with 25 mmol of SC (0.1– 0.4 mol% catalysts) at 100 °C and a CO₂ pressure of 0.1 MPa for 12 h (Table 2). A steady increment in the SO yield is observed from 0.1 to 0.4 mol% for 2D-CCB(M) with a constant co-cata-

Table 2. Effect of 2D-CCB(M)/TBAB ratio in the yield of styrene carbona- te. ^[a]								
Entry	2 D-CCB(M) [mol %]	TBAB [mol %]	Ratio of 2 D-CCB(M)/TBAB	Yield of SC [%]				
1	0.1	0.4	1:4	21.5				
2	0.2	0.4	1:2	48.7				
3	0.3	0.4	3:4	79.4				
4	0.4	0.4	1:1	91.1				
5	0.4	0.3	4:3	82.3				
6	0.4	0.2	2:1	51.9				
7	0.4	0.1	4:1	24.7				
[a] Reaction conditions: Styrene oxide = 25 mmol (2.85 mL at 25 $^\circ$ C), 0.1 MPa P _{CO2} , 12 h, 100 $^\circ$ C.								

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lyst concentration of 0.4 mol% TBAB; for which the maximum conversion is observed at 0.4 mol% 2D-CCB (entries 1–4). Similarly, studies that use 0.1–0.4 mol% TBAB with 0.4 mol% of 2D-CCB(M) follow a similar trend; they show maximum conversion at 0.4 mol% TBAB (entries 4–8). Thus, 0.4 mol% of 2D-CCB(M) and TBAB (entry 4) are identified as the optimal catalyst ratios under the employed conditions (91.1% conversion and 99.9% selectivity).

The effect of reaction duration on the 2D-CCB(M)-catalyzed cycloaddition of SO and CO_2 is depicted in Figure 7. SO conversion increases with increasing reaction duration, in the range of 3 to 12 h, in which the highest conversion is obtained at 12 h. Prolonged reactions beyond 12 h do not give an appreciable increment in SC yields, which establishes the optimum reaction time as 12 h, whereby 91.9% SO conversion and 99.9% SC selectivity are obtained.



Figure 7. Effect of reaction time on the reactivity of SO and CO₂ by using 2D-CCB(M) as the catalyst at 0.1 MPa, 100 $^\circ$ C, and 0.4 mol% of catalyst.

Similarly, with the reaction temperature, the catalytic activity increases progressively from 40–100 °C, whereby an SC yield of 91.9% is reached in 12 h at 0.1 MPa pressure of CO₂ (Figure 8); no noticeable increase in activity is found up to 140 °C.

The effect of CO₂ pressure (0 to 2.0 MPa) on the yield of SC is depicted in Figure 9. For a 12 h long reaction at 100 $^{\circ}$ C,



Figure 8. Effect of reaction temperature on the reactivity of SO and CO_2 (12 h) by using 0.4 mol% of 2D-CCB(M) at 0.1 MPa pressure of CO_2 .



Figure 9. Effect of CO₂ pressure on the reactivity of SO and CO₂ by using 2D-CCB(M) in (a) 12 h and (b) 4 h, respectively at 100 $^{\circ}$ C and 0.4 mol% of catalyst.

91.9% SC yield is attained with an atmospheric pressure of CO_2 . This may be attributed to the easy formation of carbonate complex (intermediate-b) between the sulfonate group of 2D-CCB and CO_2 , thereby leading to facile cycloaddition. Further increase in CO_2 pressure up to 2 MPa apparently favors an increased SC formation, but the rise is insignificant. The effect of CO_2 pressure on the SC yield is also studied under shorter reaction durations (4 h). Although moderate SC formation is observed under atmospheric pressure of CO_2 , it is observed that SO conversion increases as a higher CO_2 pressure is applied (up to 2 MPa).

A comparison of the catalytic performances of various MOFs reported to catalyze the SO-CO₂ cycloaddition is shown in Table 3. For a sensible comparison, cycloadditions performed with 0.4/0.4 mol% of 2D-CCB(M)/TBAB at 100 $^\circ\text{C}$ under the conditions of (a) atmospheric pressure of CO₂ for 12 h and (b) 2 MPa CO₂ for 4 h are taken into account to match closely with the reported conditions. Based on the conversion per equivalent of metal ion, the former conditions furnish a turnover number (TON) of 228, whereas the latter provide a TON of 213. Turnover numbers are calculated for the reported catalysts in the cycloaddition of SO and CO₂ based on their respective formula weights available from the crystallographic information file from the Cambridge Structural Database. Even though a direct comparison with the reported catalysts is impractical, we attempt a comparison of the catalysts at the closest reaction conditions. Initially, the results of SO cycloaddition at mild pressures of CO₂ (0.1-1.0 MPa, entries 1-5) are compared to those of 2D-CCB/TBAB operated at atmospheric pressures (entry 6). MOF-5, affords a SC yield of 92% at 50°C under atmospheric pressures (entry 1), however this proceeded under a catalyst concentration of 2.5 mol%, which is much higher than the 0.4 mol% concentration with 2D-CCB(M). Moreover, even at a prolonged reaction duration of 15 h, MOF-5 gives a TON of 37. In comparison to MOF-5, the ZIF-8 catalyst gives a yield of 55% (entry 2) at 0.7 MPa CO₂, which presents an appreciable TON of 79. MIL-68-In-NH₂, Cr-MIL-101 and Co-MOF-74 (entries 3-5) give TONs less than the 2D-CCB/TBAB system though they use higher catalyst mol%, CO2 pressures (0.7**Table 3.** Comparison of the catalytic activities of 2D-CCB catalyst with previously reported MOF catalysts at the most matching conditions in styrene oxide– CO_2 cycloaddition. Entries 1–6 compare lesser CO_2 pressures, whereas 7–10 compare those at moderately higher pressures.

Entry	Catalyst	Catalyst [mol %] ^[a]	Co-catalyst [mmol] or solvent [mL]	<i>T</i> [°C]	CO ₂ Pressure [MPa]	<i>T</i> [h]	SC Yield [%]	TON ^[b]	Ref
1	MOF-5	2.5	TBAB (2.5 mmol)	50	0.1	15	92	37	[3d]
2	ZIF-8	0.7	-	100	0.7	5	55	79	[6d]
3	MIL-68(In)NH ₂	9.1	-	150	0.8	8	74	8	[6l]
4	Cr-MIL-101	1.2	TBAB (1.7 mmol)	70	0.8	24	33	28	[6e]
5	Co-MOF-74	1.6	CIC ₆ H ₅ (30 mL)	100	1	4	49	31	[6k]
6	2 D-CCB	0.4	TBAB (0.4 mmol)	100	0.1	12	91	228	this work
7	UIO-66-NH₂	2.1	CIC ₆ H ₅ (30 mL)	100	2	4	96	46	[6j]
8	Ni(salphen)	0.56	TBAB (2.0 mmol)	80	2	4	80	143	[6f]
9	Ni(saldpen)	0.75	TBAB (2.0 mmol)	80	2	4	86	115	[6m]
10	2 D-CCB	0.4	TBAB (0.4 mmol)	100	2	4	85	213	this work
[a] mo	[a] mol% of catalyst/cocatalyst to epoxide. MOF mol% calculated per equivalent of metal ion (formula weight as in crystallographic information, CIE). [b] moles of SO converted per mole of M^{n+} CIC-H ₂ - chorohenzene as								

as in crystallographic information, CIF). [b] moles of SO converted per mole of M^{n+} . CIC₆H₅ = chlorobenzene as solvent; TBAB = tetrabutylammonium bromide co-catalyst.

1 MPa) or solvents. Comparing the catalysts that operate at higher CO₂ pressures (2 MPa, entries 7–10), namely UIO-66-NH₂, Ni(salphen) and Ni(saldpen) MOFs, 2D-CCB(M)/TBAB achieves higher TONs, which demonstrates the competency of this catalyst system among reported MOFs.

a distinctively reduced conversion is observed in the fourth and fifth runs (87.7 and 85% SO conversions, respectively).

FTIR analysis was conducted on the recycled 2D-CCB(M) catalyst after each cycle until the end of the fifth run. The catalyst maintains its chemical integrity throughout the recycling process, which is determined by the similarity of the peaks from the first run until the fifth (Figure 11).

The recycled 2D-CCB(M) catalysts were also analyzed by PXRD technique (Figure 12). The major characteristic peaks of 2D-CCB(M) remain intact, which im-

plies that the catalyst maintains its structure throughout the process. An increase in noise is observed, which can be indicative of a slight decrease in crystallinity; however, a closer inspection of the XRD patterns of the recycled catalysts after the



MOFs such as ZIF-8 and Cu–BTC (BTC = benzene-1,3,5-tricarboxylic acid) have been reported^[6d,i] to pose recyclability problems in the cycloaddition of epoxide and CO₂ because of local structural disorder and/or active site/pore blocking by residual carbonaceous deposits. We performed catalyst recycling studies for 2D-CCB under an atmospheric pressure of CO₂ at 100 °C for 12 h (Figure 10). It is observed that SC selectivity (99.9%) in the first run is maintained throughout the first four cycles, whereas only a slight decrease in SO conversion is encountered in the first three runs (91.1 > 90.2 > 89.5%). However,



Figure 10. Catalyst recycling with 0.4 mol % 2D-CCB(M)/0.4 mol % TBAB at 100 °C, 0.1 MPa CO₂, and 12 h (99.9 % SC selectivity is maintained).



Figure 11. FTIR spectra of the recycled 2 D-CCB(M) catalyst.



Figure 12. XRD patterns of the recycled 2 D-CCB(M) catalysts.

third and fourth runs reveals the presence of an additional peak, which appears as a shoulder on the right side of the $2\theta = 20.8$ peak. This may be presumed as the blocking of catalytically active sites, and a possible explanation for the decrease in catalytic activities during the fourth and fifth cycload-dition runs.

We next evaluated the heterogeneity of 2D-CCB by using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of the filtrate for any metal leaching. The ICP-OES analysis reveals that only a miniscule amount of cobalt—as low as 0.2 ppm—is present in the filtrate, in comparison to 30–50 ppm metal concentrations reported with MOF catalysts.^[6e]

Conclusions

The sulfonate-functionalized 2D rectangular grid framework [{Co(4,4'-bipy)(L-cys)(H₂O)}·H₂O]_n, denoted as 2D-CCB, is demonstrated as the first example of a sulfonate-functionalized MOF catalyst that participates in the cycloaddition of epoxides and CO₂. The synergistic catalytic action of the oxyanionic sulfonate moiety and the cobalt center in association with the bromide anions of TBAB provides a TON of 228 in the cycloaddition of SO and CO₂ even at atmospheric pressure, which also yields SC at a high selectivity (99.9%). The oxyanion of the sulfonate group, which is proposed to form a carbonate complex with CO₂, facilitates the reaction even under an atmospheric pressure of CO₂, which further accelerates the reaction owing to the better leaving group ability of the sulfonate anion. An energy-efficient and time-saving synthesis of 2D-CCB is accomplished by microwave irradiation (100 W) in 10 min, which is 1/288th of the time required for conventional solvothermal synthesis, while maintaining its structural and catalytic qualities.

The role of the sulfonate group in catalysis is experimentally demonstrated by comparing its catalytic activity with a similar MOF 3 D-CCB, which is deprived of SO_3^- groups. The acid-base sites were compared by performing Knoevenagel condensation and acetalization reactions. The microwave-synthesized 2 D-CCB(M) catalyst is successfully reused up to four times without degradation of the covalent/coordinate linkage of the catalyst framework. The potential of sulfonate-functionalized MOFs can be extended to other processes also. Further explorations in the coordination modes, geometry, and functional group of MOFs in controlling the activity of MOF catalysts for cycloaddition reactions are in progress.

Experimental Section

Reagents and methods

L-Cysteic acid monohydrate (>99.0%) and 4,4'-dipyridyl (bipy; 98%) and styrene oxide (SO) were purchased from Aldrich, Korea and used as received. Cobalt(II) carbonate hydroxide was purchased from Junsei Chemical Co., Ltd. L-Cysteic acid was purchased from Tokyo Chemical Industry Co., Ltd. Doubly distilled water was used for the catalyst synthesis. Acetone, methanol, and dichloromethane (anhydrous, >99.8%), were purchased from Al-

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drich. CO_2 of 99.999% purity was used for the cycloaddition reactions without further purification.

Synthesis of the catalyst

Solvothermal synthesis (2D-CCB): [{Co(L-cys)(4,4'-bpy) (H₂O)]₇-H₂O]_n was synthesized solvothermally in a similar manner to a previous report by the author.^[9] Bipyridine (0.624 g, 4 mmol) dissolved in methanol (30 mL) was added drop wise to an aqueous dispersion (30 mL) of L-cysteic acid (0.677 g, 4 mmol) and basic cobalt carbonate (0.476 g, 2 mmol), and stirred for 15 min. The contents were transferred to a Teflon-lined autoclave (100 mL), sealed, and heated gradually to 140 °C. After 50 h, the oven was regressively cooled to room temperature whereby light pink block-like crystals of 2D-CCB(S) were obtained. FTIR (KBr): $\ddot{v} = 3580-3167$ (s), 1609(s), 1580 (m), 1419 (m), 1211(s), 1119 (m), 1046 (s), 817 (s), 723 (m), 570 cm⁻¹ (w). The catalyst was activated by immersing it in dry dichloromethane for 3 d with regular replenishment, followed by vacuum-drying at 70 °C for 12 h.

Microwave-assisted synthesis: 2D-CCB was synthesized under microwave irradiation in a Pyrex glass reactor tube (40 mL) fitted inside a multimode microwave reactor (KMIC-2 KW), which had a continuously adjustable power source (range 0-2 kW) with a 3stub tuner, operating at a frequency of 2.450 GHz. L-Cysteic acid (0.169 g, 1 mmol) was dissolved in water (10 mL, doubly distilled). Cobalt(II) carbonate hydroxide (0.119 g, 0.5 mmol) was suspended in this solution; 4,4'-bipyridine (0.156 g, 1 mmol) in methanol (10 mL) was added dropwise and stirred. The contents were transferred to the prepared Pyrex glass tube, sealed, and irradiated by microwaves at 100 W for 10 min. The reaction mixture was then allowed to cool gradually to room temperature. Pink crystals of 2D-CCB, denoted as 2D-CCB(M), were obtained in >75% yield upon cooling. FTIR (KBr): $\tilde{\nu} = 3578 - 3165$ (s), 1607 (s), 1578 (m), 1418 (m), 1207 (s), 1118 (m), 1046(s), 817(s), 723(m), 572 cm^{-1} (w). Activation of the catalyst was accomplished by a procedure similar to that used for 2D-CCB(S).

Synthesis of 3D-CCB: The six-day long solvothermal synthesis of $[{Co_2(L-cys)_2(4,4'-bipy)_2(H_2O)_2}\cdot 3H_2O]_n$ (3D-CCB) reported by Huang et al.^[12] was repeated with a slight modification as follows: a mixture of L-cysteic acid monohydrate (0.374 g, 2 mmol) and KOH (0.224 g, 4 mmol) in water (20 mL) was added dropwise to an aqueous solution (20 mL) of Co(NO_3)_2·6H_2O (0.582 g, 2 mmol). 4,4'-Bipyridine (0.312 g, 2 mmol) in methanol (20 mL) was added slowly to this mixture and stirred for 30 min, transferred and sealed in a Teflon-lined autoclave (100 mL), and heated at 100 °C for 6 d. Crystals of 3D-CCB(S) were obtained after slowly cooling the solution to room temperature. FTIR (KBr): $\tilde{\nu} = 3430$ (s), 1655 (s), 1642 (s), 1428 (m), 1227 (m), 1193 (m), 1039 (s), 852 (w), 723 (w), 605 cm⁻¹ (w).

Acknowledgements

This study was supported by the Korean Ministry of Education through the National Research Foundation (2012-001507), Global Frontier program and the Brain Korea 21 Project. The authors are grateful to KBSI for analysis.

Keywords: amino acids · cobalt · carbon dioxide fixation · metal–organic frameworks · microwave chemistry

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Received: September 11, 2013 Published online on December 11, 2013