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Article

Series of M-MOF-184 (M = Mg, Co, Ni, Zn, Cu, Fe) Metal–Organic Frameworks for Catalysis Cycloaddition of CO_2

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ABSTRACT: In light of the chemical exploitation of CO₂, new reusable materials for efficiently catalyzing the cycloaddition of CO₂ and epoxides under moderate conditions are needed. Herein, a new series of isostructural metal–organic frameworks (MOFs) $M_2(EDOB)$ [EDOB^{4–} = 4,4'-(ethyne-1,2-diyl)bis(2-oxidobenzoate), M = Mg, Ni, Co, Zn, Cu, Fe], known as M-MOF-184, analogous to a well-studied MOF-74 structure, were synthesized and fully characterized. The M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks exhibit accessible mesopore channels (24 Å) and high porosity. Among them, Mg-MOF-184 demonstrated the most upper surface area (>4000 m² g⁻¹) in any reported MOF-74-type frameworks. Furthermore, Co-MOF-184 revealed the highest CO₂ uptake (73 cm³ g⁻¹, at 298 K), and Zn-MOF-184



showed the highest catalytic activity upon the cycloaddition of CO_2 (96% conversion, 86% selectivity, and 82% yield) under mild conditions (1 atm CO_2 , 80 °C, 6 h, and solvent-free). Notably, the catalytic performance of Zn-MOF-184 outperformed that of the original M-MOF-74 (M = Mg, Co, Zn) materials and various Zn-based MOFs. To evaluate the acidity and basicity of a series of M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks, the interaction of these MOFs with acetonitrile vapor was investigated by vapor adsorption and ATR-FTIR spectroscopy measurements. As such, Zn-MOF-184 showed the strongest Lewis acidity derived by Zn cations, which was correlated to the highest catalytic activity upon the cycloaddition of CO_2 . Interestingly, the 2-oxidobenzoate anions from Co-MOF-184 showed the strongest basicity among the series, which was associated with the highest saturated acetonitrile uptake (544 cm³ g⁻¹ at 298 K). Our findings suggest that the integration of Lewis acidic and basic sites, high surface area, and large accessible pores into the framework can facilitate the CO_2 fixation reaction.

INTRODUCTION

Given the utilization of CO_2 emission, the chemical conversion of CO₂, a significant greenhouse gas, to fine chemicals has emerged as an environmental and attractive approach.^{1,2} In this respect, the cycloaddition of CO₂ and epoxides to form cyclic carbonates is a highly atom-economical process that has been extensively studied due to wide applications in the pharmaceutical and fine chemical industries of the carbonate products.^{3–5} Although many homogeneous catalysts have been extensively studied in the synthesis of cyclic carbonates, the reactions often have difficulties in the separation of catalyst and product.⁵ In contrast, the CO₂ fixations catalyzed by heterogeneous catalysts such as ionic liquid-supported solids,^{6,7} polymers,^{8,9} and porous organic frameworks^{10,11} have the advantages of facile separation and regeneration of the catalyst. However, these solid catalysts often required harsh conditions (high CO_2 pressure/temperature) due to a lack of accessible surface area for accelerating interactions of CO₂ and reagents with active sites.^{3,5,12} Therefore, new heterogeneous catalysts which efficiently promote this reaction under mild conditions are still highly desirable.

Metal–organic frameworks (MOFs) are a class of crystalline porous materials constructed by inorganic and organic building units via strong bonds.¹³ Due to their structural and chemical tunability, MOFs can possess high surface area, multiple active sites (e.g., acid and base sites), and variable chemical functionalities, which can be beneficial for improving the efficiency of the CO₂ cycloaddition reaction.^{14–20} In particular, MOFs consisting of both acidic and basic sites have been demonstrated to potentially catalyze the cycloaddition reaction.^{21–24} In general, Lewis acid metal centers and Brønsted acid groups promote the activation of the epoxide ring, while the basic functions (e.g., amine, pyridine, imidazole, triazole, tetrazole, and amide groups) improve the CO₂ affinity inside the pore or halide nucleophiles facilitate the opening

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process of epoxide ring. For instance, Co-MOF-74 and Mg-MOF-74 replete with Lewis metal acid and basic O²⁻ sites exhibited outstanding conversions of styrene oxide (95%) in the presence of chlorobenzene solvent at 100 °C under 2 MPa CO₂ and without cocatalyst.^{25,26} In addition, the composite polyILs@MIL-101 catalyst,²¹ formed by the polymerization of imidazolium-based poly(ionic liquid)s into the MIL-101 structure, revealed excellent catalytic activity toward CO₂ cycloaddition with the use of acetonitrile solvent under mild conditions (<1 bar CO₂ pressure, \leq 70 °C) due to the synergic effects of Lewis acid sites (Cr³⁺) and basic sites (Br⁻) from polyILs. Nevertheless, the bifunctional MOFs still have disadvantages of solvent use,^{21,25,26} long reaction times,^{22–24} and high temperature.^{25,26}

To overcome these challenges, we attempted to develop new MOF-based catalysts in which the acidic and basic sites, high surface area, and accessibly large aperture functionalized by polarized moieties can synergistically promote CO₂ fixation at a short reaction time under ambient CO₂ pressure and moderate temperature without the use of solvent. We envisioned that the polarized pore is able to enrich the concentration of substrates within the framework, and the large pore diameter offers an accessible space for the chemical reactions. As a result, the surface interactions among MOFs, CO₂, and reagent molecules can be improved, which makes MOFs reach the demand for mild conditions. To date, only a few reported MOFs exhibit these desired properties in combination with a high surface area and can be synthesized via a one-pot reaction. Specifically, a well-established M-MOF-74 (M_2 (DOBDC), DOBDC⁴⁻ = 2,5-dioxidobenzenedicarboxylate, also known as CPO-27-M) family^{27,28} has emerged as a promising framework for heterogeneous catalysis. The MOF-74 structure is composed of metal oxo chains $M_3[(-O)_3(-CO_2)_3]_{\infty}$ (M²⁺ = Mg, Ni, Co, Zn, Cu, Mn, Fe) connected by organic DOBDC4- units, resulting in highly porous structures with accessible hexagonal channels. The infinite rod units contain a high density of open metal sites serving as Lewis acid sites and the 2-oxidobenzoate anions acting as basic sites, which have been demonstrated as highly active nodes capable of gas adsorption^{29,30} and catalytic processes.³¹⁻³³ Furthermore, the MOF-74 prototype also takes advantage of creating isostructural frameworks with three strategies including altering the metal components, extending the length of the organic unit, and modifying chemical functional groups within the organic unit.^{28,34}

In view of exploring the acidity and basicity of heterogeneous catalysts, infrared spectroscopy (IR) on materialadsorbed acetonitrile has often been used to determine the surface properties of many solids such as metal oxides and zeolite.^{35–38} Acetonitrile with a nitrogen electron lone pair acting as a soft Lewis base coordinates to an open metal ion (Lewis acid site), and the proton in the methyl group serves as a weak Brønsted acid interacting with the basic oxygen anion, resulting in carbanion and/or acetamide species.³⁶ By FTIR analysis using acetonitrile as the probe molecule, there are some studies devoted to determining the Lewis acidity of MOFs;^{39–41} however, no study on characterizing the basicity property of MOFs has been reported.

In this article, we report the synthesis of the $M_2(EDOB)$ series, also known as MOF-184⁴² (where M = Mg, Ni, Co, Zn, Cu, and Fe; $EDOB^{4-} = 4,4'$ -(ethyne-1,2-diyl)bis(2-oxidobenzoate)), with analogous expansion to MOF-74 (Figure 1). The extended $EDOB^{4-}$ linker contains two phenyl rings joined



Figure 1. Crystal structure of M-MOF-184. Infinite, rod-shaped metal clusters, $M_3[(-O)_3(-CO_2)_3]_{\infty}$ (where M = Mg, Co, Ni, Zn, Cu, Fe), are joined with EDOB^{4–} linkers to form M-MOF-184. Atom colors: C, gray; O, red; and metals, blue. H atoms are omitted for clarity.

by a rigid $C \equiv C$ spacer that can minimize the flexibility of the organic backbone,⁴³ resulting in robust mesopore structures with a high surface area⁴⁴ and a polarizable environment induced by π systems from phenyl rings and alkyne bonds. In principle, these π systems can interact with a metal (cationic or neutral), an anion, and another π system by electrostatic interaction, which can improve the surface affinity of the MOF framework for all of the reactants such as epoxide, CO_2 , and the cocatalyst. By taking advantage of the large surface area, the conjugated π system within the robust structure, and the high concentration of accessibly acidic metal and basic 2oxidobenzoate anion sites, the M-MOF-184 structure achieves efficient and heterogeneous catalysis to convert CO₂ to cyclic carbonates under ambient conditions. In previous work, two M-MOF-184 (M = Mg, Ni) compounds constructed from the EDOB⁴⁻ linker had been obtained through large-scale semitechnical routes.⁴² However, the quality of experimental PXRD data of Mg-MOF-184 had not been allowed for structural elucidation, and the BET surface areas of the M-MOF-184 frameworks were nonoptimal ($S_{BET} = 3154$ and 2449 m² g⁻¹ for Mg- and Ni-MOF-184, respectively), possibly due to the possible presence of impurity phases. Herein, we proposed that the employment of a small-scale solvothermal reaction in the synthesis of M-MOF-184 will be a potential strategy for achieving the pure phase of the crystalline framework endowed with optimal surface areas and accessible pore apertures.^{45,46} As expected, our activated M-MOF-184 (M = Mg, Co, Ni, Zn) materials had high surface areas $(S_{BET} >$ 3200 m^2 g⁻¹), and Mg-MOF-184 represented one of the highest BET surface area values reported for isoreticular MOF-74 structures (>4000 m² g⁻¹). Specifically, Co-MOF-184 had the highest CO₂ uptake at 298 K, and Zn-MOF-184 revealed the best catalytic activity upon cycloaddition of CO₂ among the series. The vapor acetonitrile adsorption at 298 K on four M-MOF-184 frameworks (M = Mg, Co, Ni, Zn) followed by FTIR spectroscopy was accordingly studied to determine the relative strength of acidity and basicity of these M-MOF-184 frameworks. As expected, the FTIR analysis revealed the strongest Lewis acidity of the Zn-MOF-184 framework, which was correlated to the highest catalytic performance on CO₂ fixation. Also, the 2-oxidobenzoate anions constructed in the Co-MOF-184 structure revealed the strongest basicity in the series, which complemented the highest saturated acetonitrile and CO₂ uptakes at 298 K. This work demonstrated the importance of the high surface area, accessible pore channel, and presence of both Lewis acid and base sites within the MOF structure, which are suitable for efficiently catalyzing the chemical fixation of CO_2 under mild conditions. To the best of our knowledge, we first presented the employment of vapor acetonitrile adsorption combined with FTIR spectroscopy as an appropriate strategy for investigating the nature of acidic and basic sites of MOFs.

EXPERIMENTAL SECTION

Materials and Analytical Techniques. All of the information for materials, general procedures, and analytical instruments are described in the Supporting Information (SI). Briefly, the H₄EDOB linker was synthesized via four consecutive steps (Supporting Information, Scheme S1). Full synthesis details are provided in the SI, Section S2.

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance II 500 MHz spectrometer. Powder Xray diffraction data were collected using a Bruker D8 Advance diffractometer in reflectance Bragg-Brentano geometry at 40 kV and 40 mA for Cu K α radiation (λ = 1.54178 Å). Thermogravimetric analysis (TGA) was carried out using a TA Q500 thermal analysis system. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were recorded on a Bruker Vertex 70 system by accumulating 100 scans at 2 cm⁻¹ resolution. A dried MOF sample (~2 mg) was placed on a diamond crystal plate and well-flatted with a spatula. All of the ATR-FTIR spectra were measured at least four times, and the output signals are described as follows: vs, very strong; s, strong; m, medium; sh, shoulder; w, weak; vw, very weak; and br, broad. Elemental microanalyses for activated samples were performed on a LECO CHNS-932 analyzer. Low-pressure N2 and CO2 adsorption isotherms were volumetrically recorded on a Micromeritics 3Flex instrument. The products of catalytic reactions were identified with an Agilent 19091s-433 gas chromatography (GC) system equipped with an Agilent 5973N mass spectrometry detector (GC-MS), and the catalytic conversions, selectivities, and yields were determined using an Agilent 123-0132 GC system equipped with a flame ionization detector (GC-FID) in the presence of biphenyl as an internal standard.

Vapor acetonitrile (CH₃CN) isotherms were measured with a BEL Japan BELSORP-aqua3. To ensure the reproducibility of acetonitrile sorption, all of the measurements were recorded three times and the results obtained with standard deviations of ± 0.1 , ± 0.1 , ± 0.2 , and $\pm 0.1\%$ for Mg-, Co-, Ni-, and Zn-MOF-184, respectively. For the evaluation of acidity and basicity properties, M-MOF-184 samples after the acetonitrile adsorption were evacuated under a dynamic vacuum to achieve a pressure of 10 Torr at room temperature, followed by performing ATR-FTIR spectroscopy.

Synthesis and Structural Determination of M-MOF-184. Full synthesis and characterization details of each M-MOF-184 framework can be found in the SI, Section S3.

M-MOF-184 (M = Mg, *Co*, *Ni*, *Zn*). A hydrated metal nitrate (M = Mg, Co, Ni, Zn) and the H₄EDOB linker were added to different mixtures of *N*,*N*-dimethylformamide (DMF) and methanol (MeOH)/ethanol (EtOH)/water (H₂O). The reaction mixture was placed in a scintillation vial, sealed with a PTFE-lined cap, sonicated until affording a clear solution, and held at 120 °C for 24 h. The resulting M-MOF-184 solid was washed with anhydrous DMF, immersed in anhydrous MeOH, and held at 100 °C under dynamic vacuum.

M-MOF-184 (M = *Cu, Fe).* The syntheses of Cu and Fe frameworks were conducted under an inert atmosphere of N₂. By using a cannula, a solvent mixture of anhydrous DMF and anhydrous isopropanol/anhydrous MeOH was transferred to a Schlenk tube, which was preloaded with hydrate copper nitrate or anhydrous iron(II) chloride and H₄EDOB linker. The mixtures were flash frozen and evacuated at least three times to remove O₂, followed by stirring and heating at an appropriate temperature under a N₂-filled balloon. Upon completion, the brown-red (for Fe-MOF-184) and greenish (Cu-MOF-184) solids were produced at the bottom of the tube. The resulting Cu- and Febased solids were washed with anhydrous DMF, immersed in

anhydrous MeOH, and activated at elevated temperature under dynamic vacuum. Specifically, due to the facile oxidation of Fe²⁺, the solvent exchange and activation for the Fe compound were conducted with an air-free technique and N₂ flow. The solvent-exchange and activation procedure of the Cu compound were similar to those of other M-MOF-184 (M = Mg, Co, Ni, Zn) species.

Even after exhaustive attempts, we were not able to find suitable conditions for obtaining single-crystalline materials; therefore, experimentally obtained PXRD patterns were used to determine the crystal structure. Initial structural models of M-MOF-184 were built by using Materials Studio 7.0 (Accelrys Software Inc.) software⁴⁷ (Section S4), in which the trigonal space group (R3) and inorganic connectivity unit of the MOF-74 structure remained. The DOBDC⁴⁻ ligand of the MOF-74 structure was replaced by the EDOB⁴⁻ linker. Accordingly, geometry optimization was performed by using the universal force field implemented in the Forcite module, and the unit cell parameters were optimized until energy convergence was achieved (10^{-4} kcal/mol). As for the preparation for the powder Xray diffraction (PXRD) measurement, only the Fe-MOF-184 sample was placed on an airtight specimen holder in a glovebox to avoid oxidation of the powder sample. The others were mounted on a zero background holder under an ambient environment. PXRD measurements were collected with the 2θ range from 3 to 50°, a step size of 0.02°, and a fixed count time of 2 s per step. The predicted M-MOF-184 structures were also validated with the Pawley refinements using the Reflex module in which the PXRD patterns of activated samples are matched with those calculated from crystal models. Full details are described in the Supporting Information, Section S4.

Catalytic Studies of M-MOF-184 for the Cycloaddition of **CO**₂ and **Epoxide**. In a model experiment, epoxide (5 mmol), activated MOF catalyst (1.2 mol % ratio based on active metal sites), and tetrabutylammonium bromide (nBu₄NBr, 1.5 mol %) were inserted into a 25 mL Schlenk tube in a N₂-filled glovebox. The tube was flash frozen under a liquid N2 bath and subsequently evacuated (3 \times 5 min) before being connected to a CO₂ balloon. The reaction was stirred, heated to 80 °C, and regularly monitored by GC analysis of sample aliquots. After completion, the reaction was cooled in an ice bath, the unreacted CO₂ was vented, and the MOF catalyst was removed by centrifugation. The catalytic conversion, selectivity, and yield of the reaction were determined by GC-FID analysis of an aliquot of the reaction using biphenyl as the internal standard. For the recycling experiment, the recovered MOF catalyst was washed with anhydrous MeOH $(3 \times 3 \text{ mL})$ for 24 h, activated with the same procedure of parent MOF, and then reused for successive cycles. The procedure for the cycloaddition reaction under high CO₂ pressure was conducted in a Parr high-pressure reactor. The autoclave reactor was evacuated $(3 \times 5 \text{ min})$, purged with CO₂, and then placed under the desired pressure of CO₂ for 15 min to allow the system to equilibrate. Then the reactor was allowed to stir and set at 80 °C for 6 h. At the end of the reaction, the reactor was placed in an ice bath for 20 min, and the unreacted CO_2 was vented before the reactor was opened. All catalytic experiments were performed at least three times. As for the FTIR studies on MOFs in contact with the reactants, all recovered MOF samples were swiftly soaked in anhydrous MeOH (2 mL) after the adsorbed experiments, and then dried under vacuum (0.03 Torr) at room temperature.

RESULTS AND DISCUSSION

Structural Characterization of M-MOF-184. The successful synthesis of microcrystalline M-MOF-184 frameworks was confirmed by PXRD analysis of the experimental samples in comparison with the predicted patterns from the crystal models (SI, Section S4). The PXRD patterns of asprepared M-MOF-184 frameworks showed good agreement in peak position with the predicted patterns (Figures S5–S10). Accordingly, full profile matching Pawley refinements were performed and achieved good matches of the initial and refined unit cell parameters (Figure 2) (SI, Section S4). The refined

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Figure 2. Pawley refinement of Mg-MOF-184. Shown are the experimental (red), refined (black), and difference (green) patterns. The Bragg positions are marked as pink bars, and the patterns calculated from the crystal models are shown in blue.

M-MOF-184 structures exhibited unit cell parameters that were nearly equivalent to the predictions with good agreement factors and low convergence residuals ($R_{wp} = 2.29-5.84\%$, R_p = 1.45-4.07%) (Section S4, Tables S1-S6). The variant of the void volumes, lattice parameters, and unit cell volumes for the refined M-MOF-184 structures could account for the different ionic radii of these divalent cations (Tables S1-S6). The pore channels of M-MOF-184 have larger diameters $(23 \times 25 \text{ Å}^2)$ compared to those of M-MOF-74 ($10 \times 13 \text{ Å}^2$).²⁸ We noticed that the unit cell volumes of M-MOF-184 (9862-10656 Å³) were nearly 3 times greater than those of M-MOF-74 (3067-4066 $Å^3$) (Table 1). Interestingly, the calculated crystal densities from the refined structure of Mg-MOF-184 with or without coordinated water $(0.53/0.48 \text{ cm}^3 \text{ g}^{-1}, \text{ respectively})$ were lower than those of IRMOF-74-III(Mg) (0.58/0.53 cm³ g^{-1} , respectively), even though Mg-MOF-184 has smaller aperture diameters than IRMOF-74-III(Mg) (22.2 \times 27.3 $\dot{A^2}$).²⁸

The thermal gravimetric analysis (TGA) of activated M-MOF-184 showed no weight loss up to 150 °C, implying the absence of guest molecules in the pores (Figure S19). The major weight loss for each compound associated with the framework degradation was observed at 200 °C (Fe), 250 °C (Cu), 300 °C (Co, Ni), and 350 °C (Mg, Zn) (Figure S19). An analysis of the weight percent of residual metal oxide for Mg (21.8%), Co (37.1%), Ni (33.6%), Zn (38.1%), Cu (37.0%), and Fe (30.3%) variants was found to be in good

agreement with the calculated values derived from EA (21.8, 37.3, 33.4, 38.3, 37.0, 30.3%, respectively). The singular morphology of stick-shaped crystallites observed for assynthesized M-MOF-184 samples through the scanning electron microscopy (SEM) images confirmed the phase purity of as-made M-MOF-184 (Figures S20–S25).

Porosity and CO₂ Adsorption Properties. The permanent porosity of all activated M-MOF-184 compounds was evaluated by measuring the N2 isotherms at 77 K. The resulting profiles displayed a type IV isotherm with full reversibility, which is typical of a mesoporous material. The isotherms showed steep increases in the range of $P/P_0 = 0.05 -$ 0.07 without hysteresis, which was attributed to the pore filling in regular mesopores (Figure S26). From these isotherms, Brunauer-Emmett-Teller (BET)/Langmuir surface areas for Mg, Co, Ni, Zn, Cu, and Fe compounds were estimated to be 4050/4240, 3250/3580, 3250/3470, 3750/3450, 2460/2200, and 3020/2450 m² g⁻¹, respectively (Table 1). The experimental surface areas and pore volumes for Cu- and Fe-MOF-184 have proven challenging due to the low crystallinity (for Cu) and high oxidation (for Fe) upon conventional activation, thus Cu and Fe variants will not be further evaluated. Notably, our BET specific surface area values for Mg- and Ni-MOF-184 were higher compared to the previously reported data for Mg- and Ni-MOF-184 (3154 and 2449 m² g^{-1} , respectively).⁴² The pore volumes estimated at $P/P_0 =$ 0.15 from the N₂ isotherms for Mg-, Co-, Ni-, and Zn-MOF-184 (1.41, 1.18, 1.10, and 1.12 cm³ g⁻¹, respectively) were 2 times higher than those of Mg-, Co-, Ni, and Zn-MOF-74 (Table 1). The experimental surface areas and pore volumes for Mg-, Co-, Ni-, and Zn-MOF-184 compounds well matched the theoretical van der Waals values calculated from the refined crystal structures with open metal sites (Table S7), indicating the complete desolvation and structural robustness of four frameworks upon conventional activation. Moreover, the pore size distributions were estimated to be around 22-23 Å and exhibited good agreement with the mesopore nature obtained from crystallographic data (Figure S27). It was worth noting that the surface areas for M-MOF-184 (M = Mg, Co, Ni, Zn) compounds were greater than those of the $M_2(dobpdc)$ compounds $(S_{BET} = 3000 - 3900 \text{ m}^2 \text{ g}^{-1})^{48}$ and IRMOF-74-III-R (R = H, CH₃, NH₂, $S_{BET} = 2440-2720 \text{ m}^2 \text{ g}^{-1}$).⁵¹ Remarkably, the surface area of representative Mg-MOF-184 $(S_{\text{BET}} = 4050 \text{ m}^2 \text{ g}^{-1})$ is one of the highest values reported for isoreticular MOF-74 structures $[S_{BET} = 3270 \text{ m}^2 \text{ g}^{-1} \text{ for} \text{Mg}_2(\text{dobpdc}),^{52} S_{\text{Langmuir}} = 5770 \text{ m}^2 \text{ g}^{-1} \text{ for } \text{Mg}_2(\text{dotpdc})^{53}].$ We systematically investigated the low-pressure CO₂ uptake

property of M-MOF-184 (M = Mg, Co, Ni, Zn). The CO_2

Table 1. Comparison of Pore Structure and Gas Adsorption Properties between the Refined M-MOF-184 (M-MOF-74) Framework Families

М	$d_{\rm cryst}/{\rm cm}^3~{\rm g}^{-1a}$	unit cell volume/% ^a	void space/% ^a	$S_{\rm BET}/m^2 {\rm g}^{-1}$	$V_{\rm pore}/{\rm cm}^3~{\rm g}^{-1b}$	CO ₂ uptake/cm ³ g ^{-1c}	$Q_{\rm st}/{\rm kJ}~{\rm mol}^{-1d}$
Mg	0.53 (0.91)	10 656.10 (3964.72)	75.6 (60.5)	4050 (1603) ^e	1.41 (0.60) ^e	68	35
Co	0.64 (1.17)	10 396.06 (3967.06)	74.2 (58.7)	3250 (1572) ^e	1.18 (0.57) ^e	73	33
Ni	0.68 (1.19)	9861.76 (3909.02)	74.3 (60.3)	3250 (1351) ^e	$1.10 (0.53)^{e}$	71	36
Zn	0.64 (1.22)	10 698.49 (3981.47)	74.6 (58.2)	3750 (1279) ^e	$1.12 (0.47)^{e}$	43	21
Cu	0.68 (1.31)	9992.66 (3663.26)	74.9 (58.8)	2460 (1369) ^f	0.65		
Fe	0.65 (1.12)	10 186.40 (4065.85)	74.4 (58.8)	3020 (1360) ^g	0.82		

^{*a*}Calculated from the refined crystal structures of M-MOF-184 and the reported crystal structures of M-MOF-74. ^{*b*}The pore volume was calculated at $P/P_0 = 0.15$ from the N₂ isotherm (77 K). ^{*c*}At 800 Torr and 298 K. ^{*d*}The isosteric heat of CO₂ adsorption was calculated at zero coverage. ^{*e*}Reference 48. ^{*f*}Reference 49. ^{*s*}Reference 50.

adsorption behaviors of these four MOF-184 frameworks differed from that of the metal component. In such, the initial uptakes in the low-pressure region for Mg, Co, and Ni at 298 K were much steeper than those observed for Zn (Figure 3),



Figure 3. CO_2 isotherms at 298 K for M-MOF-184 (M = Mg, Co, Ni, Zn). Adsorption and desorption branches are marked by filled and open symbols, respectively. The connecting curves are guides for the eye.

indicative of the high affinity of Mg, Co, and Ni frameworks to CO₂. Except for Zn-MOF-184 revealing the smallest total CO₂ uptake at 298 K, the capacities for Mg, Co, and Ni frameworks were slightly different from each other, in which the greatest CO_2 uptake observed for Co-MOF-184 (73 cm³ g⁻¹) was a bit higher than the uptake value of Ni-MOF-184 (71 cm³ g⁻¹), followed by Mg-MOF-184 (68 cm³ g⁻¹).⁵⁴ The variabletemperature CO₂ adsorption properties were recorded at 273, 283, and 298 K (Figures S28-S30), and the isosteric heat of CO_2 adsorption (Q_{st}) was subsequently calculated by fitting the respective isotherms using a virial-type expansion (Figure S32). The higher Q_{st} values for Ni, Mg, and Co (36, 35, and 33 kJ mol⁻¹, respectively) compared to that of the Zn variant (21 kJ mol⁻¹) led to strong interactions of CO_2 with the exposed Ni^{2+} , Mg^{2+} , and Co^{2+} metal centers. The lowest Q_{st} value of the Zn framework could be attributed to its fully 3d¹⁰ electron configuration.55 With the empirical Irving-Williams series for high-spin octahedral divalent cations, the trend in Q_{st} values (Ni > Mg > Co > Zn) tracked inversely well with the ionic radius of the high-spin divalent metal cation (Ni < Mg < Co < Zn).

Catalytic Studies of M-MOF-184 for the Cycloaddition of CO₂ and Epoxide. Motivated by the structural features of M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks including a high density of different Lewis acidic and basic sites, high surface area, and an accessible mesopore channel, we sought to explore their catalytic activity on the cycloaddition of CO₂. To obtain an optimized reaction condition, we first used styrene oxide (5 mmol) as an example epoxide, activated M-MOF-184 (1.2 mol %, calculated on the basis of metal sites) materials, and *n*Bu₄NBr (1.5 mol %), solvent-free, at 80 °C under atmosphere CO₂ pressure for 6 h. Under the model conditions, four M-MOF-184 materials exhibited moderate conversions of styrene oxide (>60%) (Figure S36) and a high selectivity of styrene carbonate formation (>80%) (Table S8). Among this series, Zn-MOF-184 displayed the highest catalytic performance in the formation of styrene carbonate with highly epoxide conversion (96%), selectivity (85%), and yield (82%) in a solvent-free environment at 80 °C for 6 h (Table 2, Figure 4). The media catalyzed by Zn-MOF-184 were used for up to



Figure 4. Time-dependent yield of styrene carbonate catalyzed by M-MOF-184 (M = Mg, Co, Ni, Zn, Cu, Fe). Error bars indicate the range of data based on three repeat experiments.

8 h and observed to have no significant increase in carbonate, implying the completeness of reaction at 6 h (Figure S37). Mg, Co, and Ni compounds exhibited high selectivities of styrene carbonate (>82%) but lower conversions of styrene oxide (62–73%). The turnover number (TON) and turnover frequency (TOF) for the Zn compound (20, 10 h⁻¹, respectively) were also found to be at least 2 times higher

Table 2. Catalytic Performance of M-MOF-184 for the Cycloaddition of Styrene Oxide and CO_2^{a}

			R	$\frac{O}{2} + \frac{O}{2} - \frac{1}{n}$	M-MOF-184 Bu₄NBr, 80 °C,	1 atm R ²				
no.	M-MOF-184	con./% ^b	TON ^c	TOF/h ^{-1d}	con./% ^e	TON ^c	TOF/h^{-1d}	con./% ^f	TON ^c	TOF/h^{-1d}
1	Zn-MOF-184	62	20	10	86	28	6.9	96	31	5.1
2	Mg-MOF-184	35	11	5.5	54	19	4.8	72	23	3.8
3	Co-MOF-184	28	10	5.0	54	19	4.8	72	23	3.8
4	Ni-MOF-184	14	4.6	2.3	35	12	3.0	61	21	3.5

^{*a*}Reaction conditions: styrene oxide (5.0 mmol), MOF catalyst (1.2 mol % metal active site), nBu_4NBr (1.5 mol %), 1 atm CO₂ (balloon pressure), 80 °C, and 6 h. ^{*b*}Conversion determined by GC–FID analysis of the crude reaction mixture after 2 h. ^{*c*}TON = (moles of product)/(moles of metal in the catalyst). ^{*d*}TOF = TON/reaction time. ^{*e*}Conversion determined by GC–FID analysis of the crude reaction mixture after 4 h. ^{*f*}Conversion determined by GC–FID analysis of the crude reaction mixture after 4 h. ^{*f*}Conversion determined by GC–FID analysis of the crude reaction mixture after 6 h.

https://dx.doi.org/10.1021/acs.inorgchem.0c02807 Inorg. Chem. XXXX, XXX, XXX–XXX than those of others (Table 2), implying the high catalytic activity of the Zn-based framework. The reaction in the absence of MOF catalyst afforded only a 12% yield of carbonate, indicating the significant impact induced by M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks on the chemical transformation of CO₂.

To demonstrate the potential and applicability of the Zn-MOF-184 system, the substrate scope was also studied on other epoxides including propylene oxide, epichlorohydrin, and cyclohexene oxide (Figure 5). Propylene oxide and epichlor-



Figure 5. Catalytic performance during the synthesis of different cyclic carbonates catalyzed by Zn-MOF-184. Error bars indicate the range of data based on three repeat experiments.

ohydrin had the highest conversions (100%) compared with styrene oxide (96%) and cyclohexene oxide (69%) owing to the faster diffusion of small substrates rather than large substrates into the MOF's pores. In particular, the large epoxide substrates restrict the diffusion into the MOF pores, which limit the access of reactants (e.g., epoxides, CO₂, nBu₄NBr) to the active sites (e.g., Lewis metal sites, 2oxidobenzoate anions), resulting in the low conversion.^{14,56–58} Epichlorohydrin exhibited slightly lower selectivity and yield in the formation of carbonate than propylene oxide, attributed to the electron-withdrawing effect of the -Cl group reducing the electron density of the epoxide oxygen. The lower conversion of styrene oxide in comparison to propylene oxide and epichlorohydrin was associated with the low reactivity of its β carbon attributed to the conjugation between the benzene ring and the epoxy group. Among the epoxides examined, cyclohexene oxide exhibited the lowest catalytic performance (yield of 59%) owing to steric hindrance originating from the two rings of the substrate, which restricts the ring opening. We noticed that large substrates cyclohexene oxide and styrene oxide exhibited higher selectivities in the formation of respective carbonates (88 and 86%, respectively) than did small substrates propylene oxide and epichlorohydrin (70 and 72%, respectively). These observations indicated that Zn-MOF-184 exhibited the high catalytic conversion of small substrates and remarkably catalytic selectivity of large substrates in the CO₂ fixation reaction.

Furthermore, the reusable nature of Zn-MOF-184 was evident when the leaching and recycling experiments were performed. At the outset of the 1 h catalysis reaction, the Zn-MOF-184 catalyst was isolated by centrifugation, and filtration was allowed to continue under the same condition. As shown in Figure S37, there were insignificant increases in the formation of styrene carbonate (an increase of 8.6% yield). Moreover, only a trace amount of Zn^{2+} leached from the framework into the filtrate, as confirmed by ICP analysis (the concentration of $Zn^{2+} < 0.043$ ppm). For the recycling study, there were insignificant decreases in the catalytic performance after five consecutive runs of the experiments (Figure S38). The structural stability of Zn-MOF-184 after several reactions was accordingly evaluated by PXRD, BET, and FTIR analyses of the reused Zn-MOF-184 samples after the sixth cycled reaction. As expected, the PXRD pattern revealed the unimportant change in the peak intensity and position, indicating the stability of the Zn-based framework (Figure \$39). The BET surface area presented a slight decrease, indicative of the insignificant degradation of Zn-MOF-184 (Figure S40). Additionally, the IR spectra for recovered Zn-MOF-184 after activation and the parent Zn-MOF-184 showed a good in-line profile, implying that the structural integrity remained after several catalysis reactions (Figure S41).

The catalytic activity of the heterogeneous Zn-MOF-184 framework was further compared with other homogeneous and heterogeneous Zn-based catalysts. As depicted in Table S9 (entries 1-4), homogeneous metal salts $Mg(NO_3)_3 \cdot 6H_2O_1$ $Co(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_3 \cdot 6H_2O$, and $Zn(CH_3COO)_2 \cdot$ 2H₂O and heterogeneous solids Zn and ZnO facilitated lower catalytic performances (9.6-57% yield) compared to that of Zn-MOF-184. We found that the TOF values at 6 h of reaction time catalyzed by these nonporous homogeneous and heterogeneous metal-based catalysts $(0.6-3.6 h^{-1})$ were lower than that of Zn-MOF-184 (5.1 h^{-1}), indicative of the outperformed activity of the porous Zn-MOF-184 framework. Interestingly, neither the Zn precursor $[Zn(NO_3)_2 \cdot 6H_2O]$ nor the H₄EDOB linker resulted in low conversions of styrene oxide (37 and 25%, respectively) and moderate selectivities of styrene carbonate formation (63 and 52%, respectively) under similar conditions (Table S9, entries 4 and 6). Also, the mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and the H₄EDOB linker afforded a slight increase in the styrene oxide conversion (45%) but with less selectivity toward the styrene carbonate (50%) (Table S9, entry 7). This evidence supported the high catalytic activity of the porous Zn-MOF-184 framework constructed from the coordination between the infinite rod Zn-oxo cluster and the H₄EDOB linker. Furthermore, as shown in Table S9 (entries 14-16), two isostructural Mg- and Co-MOF-74 frameworks with the same topological network, smaller pore aperture sizes, and lower porosities promoted the lower conversions of styrene oxide (27 and 31%, respectively) compared to that of Zn-MOF-184 under the same condition (1.2 mol % catalyst, calculated on the basis of metal sites). Interestingly, Zn-MOF-184 and Zn-MOF-74 had activities than outperformed Mgand Co-MOF-74 frameworks, implying the strong Lewis acidity derived from the infinite Zn-oxo rod unit. It was worth noting that Zn-MOF-184 with the larger aperture size exhibited higher conversion and selectivity in the formation of styrene carbonate than did Zn-MOF-74 (Table S9), suggesting the important role of large pore structure in catalytic performance.

To further validate the large pore function on the cycloaddition reaction, the catalytic performances of propylene oxide, epichlorohydrin, styrene oxide, and cyclohexene oxide were also evaluated on the Zn-MOF-74 catalyst (Figure 6). As



Figure 6. Conversions and yields of various cyclic carbonates generated from CO_2 cycloadditions catalyzed by Zn-MOF-184 (dark colors) and Zn-MOF-74 (light colors). Error bars indicate the range of data based on three repeat experiments.

expected, the catalytic conversions of these epoxides catalyzed by Zn-MOF-74 (aperture size of 11 Å) were lower than those catalyzed by Zn-MOF-184 (aperture size of 22 Å) under the same condition (1.2 mol % catalyst, calculated on the basis of metal sites). Yields of generated cyclic carbonates catalyzed by Zn-MOF-74 were only 52% for propylene oxide, 48% for epichlorohydrin, 50% for styrene oxide, and 38% for cyclohexene oxide, which were poorer (average of 20%) than those of Zn-MOF-184. We also found that the selectivity in the formation of cyclohexene carbonate catalyzed by Zn-MOF-74 (only 63%) was lower than that catalyzed by Zn-MOF-184 (88%), confirming the outperformed catalytic selectivity attributed to the larger pore function of Zn-MOF-184. The outstanding effect of the large pore feature within the Zn-MOF-184 framework on the catalytic performance of CO₂ fixation was worth noting.

To demonstrate the superior activity of the infinite Zn-oxo chain cluster, model reactions proceeding by other Zn-based MOFs such as MOF-5,⁵⁹ MOF-177,⁶⁰ ZIF-8,⁶¹ and MOF-508⁶² were carried out (Table S9, entries 17–20). These MOFs constructed by representative cluster types—octahedral (Zn₄O(CO₂)₆ for MOF-5 and MOF-177), tetrahedral (Zn₄ for ZIF-8), and paddle-wheel (Zn₂N₂(CO₂)₄ for MOF-508) geometries—promoted a lower catalytic transformation than did Zn-MOF-184. This result indicated the high catalytic activity of the infinite rod of Zn₃[O₃(CO₂)₃]_∞ units. Moreover, we noticed that the surface area and CO₂ uptake properties of Zn-VNU-74 (S_{BET} = 3750 m² g⁻¹/CO₂ uptake = 43 cm³ g⁻¹) were lower than those of other MOFs such as Mg-MOF-184 (4050 m² g⁻¹/120–130 cm³ g⁻¹, respectively), and MOF-5 (970 cm³ g⁻¹/56 cm³ g⁻¹, respectively), indicating the

more significant impact of the structural function of the Zn-MOF-184 framework in comparison to the high surface area and high CO_2 uptake properties in catalyzing CO_2 fixation.

Due to the quadrupole moment of CO₂, the phenolate anions in the MOF-74 (CPO-27)-type structure acting as basic sites can activate CO₂ in the cycloaddition reaction, resulting in CO₂-phenolate nucleophiles. These CO₂-phenolate nucleophiles then undergo the ring-opening process of epoxide, followed by yielding the cyclic carbonate product.⁶³ This consequence had been established from the experimental works in which the cycloaddition reaction catalyzed by M-MOF-74 (CPO-27, M = Mg, Co) in the absence of the *n*Bu₄NBr cocatalyst (the Br⁻ anion of the *n*Bu₄NBr cocatalyst can lead to nucleophilic attack on the epoxide, leading to ringopening progress) had produced the carbonate product with a yield of >95% under a CO₂ pressure of 2 MPa.^{25,26} To explore the role of the phenolate anions in our MOF-184 platform, we also employed the cycloaddition reaction without using nBu₄NBr cocatalyst under two CO₂ conditions: ambient pressure and 2 MPa. The results showed that there was no carbonate product formed under either reaction condition. We accordingly characterized the Zn-MOF-184 catalyst after the cocatalyst-free reactions (named SO/CO₂@Zn) by using FTIR analysis, and the results exhibited the emergence of two peaks at 1490 and 1517 cm⁻¹ associated with two ν carbonate CO_3^{2-} vibrations attributed to the formation of CO_2 -phenolate (Figure S46).^{38,64} However, as stated above, none of the carbonate product was found, indicating that the CO₂-phenolate nucleophiles derived from Zn-MOF-184 do not proceed with the ring-opening process, thus the cocatalystfree reaction catalyzed by Zn-MOF-184 cannot produce the cyclic carbonate product. This result was attributed to the large distance between the CO2-phenolate nucleophile and the epoxide ring (Figure S47), resulting in an impossible attack on the CO₂-phenolate nucleophile and epoxide ring. Motivated by this evidence, we demonstrated that the phenolate anions constructed in the M-MOF-184 network are not involved in the important catalytic sites which directly promote the ringopening epoxide process in the formation of cyclic carbonate. We noted that the effect of phenolate anions enhances the surface affinity of MOF's pore wall for CO₂.

To investigate the surface interaction of reactants and the Zn-MOF-184 framework, ATR-FTIR analysis was carried out on the Zn-MOF-184 samples in contact with styrene oxide (termed SO@Zn) and after 4 h of reaction under the model condition (named Sub@Zn).⁶⁵ As depicted in Figure S48, the emergence of weak peaks at 2176 and 2150 cm⁻¹ ascribing to stretching vibrations of $C \equiv C$ bonds was observed for both SO@Zn and Sub@Zn samples. In general, the C \equiv C stretching absorptions (near 2100 cm⁻¹) for symmetrically internal alkyne are weak or absent due to the minimal dipole of the C \equiv C bond. Indeed, the C \equiv C stretching modes were not found in activated Zn-MOF-184 material (Figure S48). However, both SO@Zn and Sub@Zn samples showed the occurrence of these C \equiv C stretching vibrations, indicating that the dipole moment of $C \equiv C$ bonds was increased due to the surface interaction between the EDOB⁴⁻ linker and the reactants. Moreover, the presence of new peaks at 1129 and 1070 cm⁻¹ was observed in SO@Zn owing to the characteristic peaks of alkoxide C-O-C stretching vibrations of styrene oxide.^{66,67} The intensity of absorbed bands at 1103 and 1029 cm⁻¹ associated with alkoxy C–O stretching vibrations of the 2-oxidobenzoate anion was increased in the Sub@Zn sample.

These results implied the high affinity of the Zn-MOF-184 framework for organic substrates.

In comparison with the MOF-74 structure, the ATR-FTIR analysis was also evaluated on the activated Zn-MOF-74 material adsorbed on styrene oxide (named SO@Zn-MOF-74). As shown in Figure S49, there were unimportant differences in the intensities of the absorbed bands (1129-1026 cm^{-1}) associated with alkoxy C–O stretching vibrations of styrene oxide and the 2-oxidobenzoate anion of the activated Zn-MOF-74 and SO@Zn-MOF-74 samples, implying the weak interactions between the Zn-MOF-74 structure and epoxide. These observations further demonstrated the high polarity of the Zn-MOF-184 framework attributed to the incorporation of the C \equiv C bond in the EDOB⁴⁻ linker, resulting in the high affinity of Zn-MOF-184 for the reactants.

Accordingly, a plausible mechanism for the cycloaddition of CO₂ catalyzed by Zn-MOF-184 was proposed (Figure 7).^{14–17}



Figure 7. Proposed reaction mechanism for the cycloaddition of CO_2 with epoxides catalyzed by Zn-MOF-184.

First, the epoxide ring is activated by an O atom through interaction with Zn sites. Second, the Br nucleophile generated from the nBu₄NBr cocatalyst triggers the C atom of epoxide and engages in ring-opening, resulting in a Znbromoalkoxide. Subsequently, O²⁻ of the Zn-bromoalkoxide interacts with CO₂ enriched in the pore, forming a Znalkycarbonate intermediate. Finally, a carbonate product is obtained through a ring-closure step accompanied by the regeneration of the Zn-MOF-184 catalyst and Br⁻ nucleophile.

Characterization of Acidity and Basicity Properties. While the surface areas, aperture sizes, and unit cell parameters of the four M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks were relatively similar, their catalytic performance on CO2 fixation was dramatically different. Moreover, M-MOF-184 structures replete with both Lewis acidic (open metal center) and basic 2-oxidobenzoate anion sites, large pore apertures, and high surface areas engage the chemical interactions with acetonitrile. Motivated by these features, we sought to investigate the relative strength of acidity and basicity using an ATR-FTIR study on M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks with adsorbed vapor acetonitrile.

As depicted in Figure 8 and Table 3, the acetonitrile isotherms at 298 K for four M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks showed several steps and a hysteresis loop with high saturation capacities (>480 cm³ g⁻¹, 0.88 g g⁻¹). The saturated acetonitrile uptake capacities for four M-MOF-184

(M = Mg, Co, Ni, Zn) frameworks were slightly different from

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each other, probably due to their same topological network and similar structural functions of unit cell volume, void space, and porosity (Table S10). Interestingly, Co-MOF-184 reached the highest uptake (548 cm³ g⁻¹, 1.00 g g⁻¹) with the broadest hysteresis loop ($P/P_0 = 0.20-0.35$), and Mg-MOF-184 exhibited second-order saturation uptake with the narrowest hysteresis loop $(P/P_0 = 0.20 - 0.25)$. As for this series, we found the saturated capacities to follow the trend of Co > Mg > Ni \approx Zn, while the volumetric uptakes were arranged in the order Co > Ni > Zn > Mg (Table 3). Steeply increased uptakes below $P/P_0 = 0.05$ were observed, which was possibly associated with the coordination of the metal centers to the nitrogen atom of acetonitrile. Depending on the metal ions, the capillary condensations induced in two different pressure regions $(P/P_0 = 0.1-0.2 \text{ and } 0.2-0.35)$ and hysteresis loops were observed with various extensions (defined in percentage, Section S8) in the order Co (26%) > Zn (19%) > Ni (12%) > Mg (4%). These findings suggested distinguishing surface interactions between M-MOF-184 frameworks and vapor acetonitrile.

For comparison, acetonitrile adsorption isotherms were conducted on Co-MOF-74, Basolite C300 (HKUST-1), Basolite Z1200 (ZIF-8), and BPL carbon (Figure S50). As shown in Table 3, the maximum uptake capacity of Co-MOF-184 (0.99 g g⁻¹) was 2 times higher than that of Co-MOF-74 (0.48 g g⁻¹), BPL carbon (0.44 g g⁻¹), Basolite Z1200 (0.41 g g⁻¹), and Basolite C300 (0.32 g g⁻¹). The volumetric maximum capacity for Co-MOF-184 (348 cm³ cm⁻³) was also higher than that of Co-MOF-74 (308 cm³ cm⁻³), Basolite C300 (60 cm³ cm⁻³), Basolite Z1200 (78/70 cm³ cm⁻³), and BPL carbon (105 cm³ cm⁻³). We noted that Basolite C300 and Basolite Z1200, well-known MOFs endowed with Lewis acid sites (Cu²⁺ and Zn²⁺ ions, respectively), and BPL carbon, a microporous material with an absence of the acid and base sites, exhibited smaller acetonitrile adsorption properties compared to those of Co-MOF-184 and Co-MOF-74. Among these comparative MOFs, Co-MOF-74 revealed a larger acetonitrile uptake compared to those of Basolite C300, Basolite Z1200, and BPL carbon even though the lowest surface area was noted for Co-MOF-74 (Table S10), suggesting the significant structural function of the accessibly infinite rod-based structure containing both Lewis acid and base sites. Furthermore, the aperture diameters of Co-MOF-184 are larger than those of Co-MOF-74, resulting in the higher acetonitrile uptake capacity for Co-MOF-184, indicative of the important impact of large aperture diameter on the acetonitrile adsorption. Accordingly, ATR-FTIR analysis on M-MOF-184 (M = Mg, Co, Ni, Zn) samples after the vapor acetonitrile adsorption were conducted to characterizing the acidic and basic sites of four frameworks (Figure 9).⁶⁸⁻⁷⁰ In such, Mg, Zn, Co, and Ni frameworks showed an absorption band corresponding to the $\nu(C \equiv N)$ vibrational mode of acetonitrile (2252 cm^{-1}), which shifted to higher frequencies of 2256, 2257, 2275, and 2281 cm⁻¹, respectively, indicating the presence of coordination between nitrogen atoms to open metal sites (Figure 9A). The largest magnitude of intensity for the shift was found in the Zn compound, followed by the order Mg > Ni > Co, implying that the Zn framework has the strongest Lewis acidity in the series.³⁹⁻⁴¹ This evidence confirmed the best performer to be Zn-MOF-184 for the catalysis cycloaddition of CO₂.



Figure 8. Acetonitrile isotherms at 25 $^{\circ}$ C for (A) Mg, (B) Co, (C) Ni, and (D) Zn materials. Closed and open circles represent the adsorption and desorption branches, respectively. The connecting line is provided as a guide.

Table 3. Acetonitrile Adsorption Properties for M-MOF-184 in Comparison with Representative MOFs/Adsorbents^a

no.	material	uptake capacity/g g^{-1}	uptake capacity/cm ³ cm ⁻³			
1	Mg-MOF-184	0.96	278			
2	Co-MOF-184	0.99	348			
3	Ni-MOF-184	0.89	330			
4	Zn-MOF-184	0.88	309			
5	Co-MOF-74	0.48	308			
6	Basolite C300	0.32	60			
7	Basolite Z1200	0.41	78			
8	BPL	0.44	105			
^{<i>a</i>} The maximum uptake was calculated at $P/P_0 = 0.9$.						

On the other hand, the characterization of the basicity property through surface interactions of the basic 2oxidobenzoate anions with acetonitrile was evaluated. In such, the peaks that appeared at about 2230 and 2210 cm⁻¹ (Figure 9A) related to the C \equiv N vibrational modes in the formation of physisorbed CH₃CN species and the polymerization of (CH₂CN)⁻ carbanions, respectively,⁷¹ were examined in each framework (Figure 9A). As for this series, Co-MOF-184 had the highest intensity for these bands, following the order Ni > Mg \approx Zn. Furthermore, four M-MOF-184 compounds exhibited the occurrence of new absorption bands relating to the formation of (CH₂CN)⁻ carbanions (2020–2033 cm⁻¹) whose C \equiv N stretching bands were observed at about 2038–2046 cm⁻¹ (Figure 9B), in which the largest intensity of two bands was noted in Co and Zn variants, followed by Mg and Ni (Figure 9B). Furthermore, the presence of new peaks ascribing to the scissor and asymmetric vibrations of C-H bonds (1482-1468 cm^{-1}) and C-H bending movements (~1307 cm^{-1}) associated with the formation of (CH₂CN)⁻ carbanionic species of the basic O^{2-} sites to the H atoms of $-CH_3$ groups was noted for Co, Ni, and Mg materials (Figure 9C),³⁵⁻³⁷ in which the relative intensities of these absorption bands were found to follow the order Co > Ni > Mg > Zn. All of this evidence indicated that the greatest number of (CH₂CN)⁻ carbanions created within Co-MOF-184 resulted from the coordinative interactions of the CH₃CN-Co framework and the polymerization of CH₃CN-CH₃CN.³⁷ This was attributed to the strongest basicity of the 2-oxidobenzoate anions sites coordinating to the Co centers. Interestingly, we noted that Co-MOF-184 presented the strongest basicity and the highest acetonitrile uptake, which were also correlated to the highest CO_2 uptake property, a wide probe molecule used for characterizing basic sites.^{72–74} Our results suggested that the use of acetonitrile adsorption and corresponding ATR-FTIR analysis on MOF's adsorbed acetonitrile was an appropriate method for evaluating the acidity and basicity of MOF's structure consisting of Lewis acidic and basic sites.

SUMMARY

The synthesis and full characterization of an isostructural series M-MOF-184 (M = Mg, Co, Ni, Zn, Cu, Fe) were reported. In this series, the Co framework showed the highest low-pressure

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Figure 9. ATR-FTIR spectra of acetonitrile (CH₃CN) adsorbed on M-MOF-184 (M = Mg, Co, Ni, Zn) frameworks.

 CO_2 uptake (73 cm³ g⁻¹, at 800 Torr, 298 K), and Ni presented the highest isosteric heat of adsorption (36 kJ mol⁻¹). Zn-MOF-184 revealed the highest catalytic performance upon cycloaddition of CO2 (conversion of 96%, selectivity of 86%, and yield of 82%) under mild reaction conditions (solvent-free, balloon pressure of CO₂, 80 °C, 6 h). The catalysis performance of Zn-MOF-184 outperformed that of homogeneous, heterogeneous catalysts, the M-MOF-74 (M = Mg, Co, Zn) series, and other Zn-based MOFs. Through FTIR analysis of these MOFs after acetonitrile adsorption, the relative acidity and basicity of four M-MOF-184 members were determined. Accordingly, the Lewis acid Zn sites in the Zn structure and the basic 2-oxidobenzoate anions derived from the Co framework were proven to have the strongest acidity and basicity, respectively. These results were found to be in agreement with the best catalytic activity of Zn-MOF-184 on cycloaddition of CO₂ and the highest CO₂ and acetonitrile uptakes of Co-MOF-184. Our contribution paves the way for the future development of MOFs applicable to catalysis cycloaddition of CO₂ and provides a convenient guideline for the characterization of MOFs replete with both Lewis acidic and basic sites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02807.

Full details for linker and MOF synthesis and characterizations (PXRD, TGA curves, FTIR, and gas adsorption), catalytic reactions, vapor sorptions details (PDF)

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Notes

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