Deconvolution of metal apportionment in bulk metal-organic frameworks

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We report a general route to decipher the apportionment of metal ions in bulk metal-organic frameworks (MOFs) by solid-state nuclear magnetic resonance spectroscopy. We demonstrate this route in Mg1−xNi−x-MOF-74, where we uncover all eight possible atomic-scale Mg/Ni arrangements through identification and quantification of the distinct chemical environments of 13C-labeled carboxylates as a function of the Ni content. Here, we use magnetic susceptibility, bond pathway, and density functional theory calculations to identify local metal bonding configurations. The results refute the notion of random apportionment from solution synthesis; rather, we reveal that only two of eight Mg/Ni arrangements are preferred in the Ni-incorporated MOFs. These preferred structural arrangements manifest themselves in macroscopic adsorption phenomena as illustrated by CO/CO2 breakthrough curves. We envision that this nondestructive methodology can be further applied to analyze bulk assembly of other mixed-metal MOFs, greatly extending the knowledge on structure-property relationships of MOFs and their derived materials.

INTRODUCTION

The preparation of bulk chemicals via mixing precursors in the liquid phase, followed by heating to produce solids, has been well established since antiquity. The resulting solid product is presumed to have stoichiometry simply related to the solution mixtures, e.g., ions distributed randomly throughout the product. The apportionment of structural elements, however, remains an important question in materials science, as the spatial distribution of components in a solid may well affect properties. The question of apportionment is particularly important in the chemical synthesis of metal-organic frameworks (MOFs), where properties can be facilely tuned by introducing heterogeneity into MOFs using mixed-organic linkers (the multivariate MOFs) or mixed-metal ions (the mixed-metal MOFs) (1–3). The organic linkers in multivariate MOFs have been apportioned by nondestructive solid-state nuclear magnetic resonance (SSNMR) spectroscopy in combination with computational screening (4). The order of linkers with identical chemical structure but different configurations in MOF superstructure is resolved in a similar way (5). A recent SSNMR work uncovers the arrangement of metal ions within trimers of MIL-100(Al,Fe) (6). However, the experimental identification of metal apportionment is much more challenging for MOFs with infinite number of metal permutations, and the only successful attempt to date was accomplished from destructive atom probe tomography study of mixed-metal MOF-74 single crystals (7). Here, we demonstrate that SSNMR reveals atomic-scale metal apportionment within bulk mixed-metal MOFs as evidenced by our analyses of Mg1−xNi−x-MOF-74 (x = 0.00 to 1.00). Assignment of individual NMR peaks to specific local bonding configurations proceeds from ferromagnetic (FM) and antiferromagnetic (AFM) susceptibility measurements, bond pathway analyses, and density functional theory (DFT) calculations. We illustrate that these structural details are responsible for the superior performances of mixed-metal MOFs compared to their monometallic counterparts in applications, such as the adsorption of industrially important CO gas. We envision that this proposed SSNMR strategy (Fig. 1) will enrich the current knowledge and complement methodology in design, synthesis, characterization, and application of new functional materials.

RESULTS

SSNMR measurements

We used a one-pot approach (8) to synthesize phase pure Mg1−xNi−x-MOF-74 samples (fig. S1), which are constructed by infinite metal-oxygen chains and 2,5-dihydroxyterephthalate (DHTP) linkers interconnected via oxygen atoms (fig. S2), where methanol exchange was used before subsequent structural studies (9). The metal apportionment of mixed-metal MOFs at macroscopic and microscopic length scales (Fig. 2) is typically measured by elemental analysis such as inductively coupled plasma optical emission spectroscopy (ICP-OES) and energy-dispersive x-ray spectroscopy (EDS) (8), respectively. We performed these two characterizations accordingly. The results reveal homogenous Mg/Ni apportionment at macroscopic (table S1) and microscopic (figs. S3 to S11 and table S2) length scales but do not assess apportionment at atomic scale. We surmise that SSNMR measurements will identify Mg/Ni apportionment at atomic scale via the distinguishable 13C chemical shifts engendered from binding of carboxylate to paramagnetic Ni2+ ions (S = 1), which are fingerprints of Mg/Ni stoichiometry and sequence along metal-oxygen chains (Fig. 1) (10). The chemical shift changes induced by paramagnetic ions have been shown effective in probing the local bonding configuration of atoms proximate to metal ions in oxides and hydroxides (11–13), as well as SSNMR studies of monometallic MOFs (14–21). Here, we 13C-labeled carboxylate groups of

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Mg$_{1-x}$Ni$_x$-MOF-74 samples (fig. S12) to visualize the effects of paramagnetic Ni$^{2+}$ ions so as to probe the spatial distribution of metal ions. In particular, we take advantage of isotopic enrichment at the carboxylate groups [98 atomic % (at %) $^{13}$C] to provide an enhancement of $\sim$90 in sensitivity of carboxylate over natural abundance (1.07 at %) $^{13}$C associated with the remaining carbons of DHTP.

In particular, we relied on $^{13}$C magic angle spinning (MAS) NMR to analyze the chemical shifts of carboxylate moieties, thus discerning the Mg/Ni apportionment. As shown in Fig. 3A and fig. S13, the $^{13}$C NMR spectrum of (pure magnesium) Mg-MOF-74 features a narrow peak at 175 parts per million (ppm) (22). The incorporation of Ni into Mg-MOF-74 results in a set of additional four narrow peaks at 230, 210, 203, and 144 ppm and another class of three broad peaks centered at 817, 715, and 197 ppm. The identification of five narrow and three broad peaks was further confirmed by deconvoluting NMR spectra (figs. S14 to S18) and repeating SSNMR measurements and analyses at a different MAS frequency (figs. S19 to S24). The correlation of these peaks with solvent molecules (methanol) trapped in MOF channels is excluded (fig. S25). These preliminary observations unambiguously verify that our approach is very sensitive to the changes in the Ni content, and multiple local chemical environments of carboxylate can be probed and distinguished.

**Atomic-scale metal apportionment**

Zooming into the local chemical environments of carboxylate, each carboxylate is bonded to three metal ions via one $\mu_1$-O and one $\mu_2$-O, and the three metal ions are characterized by a $3_1$ skew axis parallel to the crystallographic c axis (the sequence of three metal ions is hereafter referred to as the Mg/Ni arrangement; Fig. 3B). Together, there are eight possible arrangements (from $\mu_1$-O to $\mu_2$-O) for the

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**Fig. 1.** Schematic illustration of uncovering the atomic-scale Mg/Ni apportionment in bulk Mg$_{1-x}$Ni$_x$-MOF-74 samples by SSNMR and using this information to understand their macroscopic properties.

**Fig. 2.** Schematic illustration of measuring Mg/Ni apportionment in Mg$_{1-x}$Ni$_x$-MOF-74 at macroscopic and microscopic length scales. SEM, scanning electron microscopy.
Ni six peaks. The two broad peaks at 817 and 197 ppm correspond to served NMR spectra of monometallic MOF-74 samples. We then with a 13C-carboxylate.

crystallite surface. These carboxylates are not affected by Ni2+ but exhibit similar 13C chemical shift as that of Mg-MOF-74. (gions (the full spectra are shown in fig. S13). The weak peak at 175 ppm in the spectrum of Ni-MOF-74 is due to defects such as dangling carboxylates at the terminal crystallite surface. These carboxylates are not affected by Ni2+ but exhibit similar 13C chemical shift as that of Mg-MOF-74.

We first assigned the broad peak at 715 ppm and the narrow peaks within selected regions (the full spectra are shown in fig. S13). The weak peak at 175 ppm in the spectrum of Ni-MOF-74 is due to defects such as dangling carboxylates at the terminal crystallite surface. These carboxylates are not affected by Ni2+ but exhibit similar 13C chemical shift as that of Mg-MOF-74.

We thus postulate that five narrow and three broad peaks shown in SSNMR results are corresponding to the eight modes of Mg/Ni arrangements. The distinct 13C NMR chemical shifts and linewidths are expected to originate from different magnetic coupling schemes, i.e., the type of interaction between unpaired electrons of paramagnetic Ni2+ ions and adjacent or even remote unpaired electrons of other Ni2+ ions. Both FM (i.e., electronic spins are parallelly aligned) coupling and AFM (i.e., electronic spins are antiparallelly aligned) coupling of Ni2+ are witnessed in (pure nickel) Ni-MOF-74, whereas the FM coupling is stronger (23). We suspect that the Ni2+ ions in Mg1−xNi−x-MOF-74 samples interact with each other in a similar manner on the basis of magnetic susceptibility measurements (figs. S26 to S31). As a result, the Mg/Ni arrangement in which Ni2+ ions are FM-coupled induces broad 13C NMR peaks, characteristic of paramagnetic solids, and the Mg/Ni arrangement in which Ni2+ ions are AFM-coupled generates much narrower 13C NMR peaks with similar spectral features to those found in diamagnetic Mg-MOF-74 (6, 16, 17).

We first assigned the broad peak at 715 ppm and the narrow peak at 175 ppm to the carbon in Ni−μ1−O−13C−μ2−O−Ni(−Ni) and Mg−μ1−O−13C−μ2−O−Mg(−Mg), respectively, based on the observed NMR spectra of monometallic MOF-74 samples. We then used the two magnetic coupling schemes to assign the remaining six peaks. The two broad peaks at 817 and 197 ppm correspond to Ni−μ1−O−13C−μ2−O−Ni(−Mg) and Mg−μ1−O−13C−μ2−O−Ni(−Ni) arrangements due to the FM coupling between two adjacent Ni2+ ions, whereas the four narrow peaks at 230, 210, 203, and 144 ppm are attributed to Ni−μ1−O−13C−μ2−O−Mg(−Ni), Ni−μ1−O−13C−μ2−O−Mg(−Mg), Mg−μ1−O−13C−μ2−O−Ni(−Mg), and Mg−μ1−O−13C−μ2−O−Mg(−Ni) arrangements, with AFM-coupled Ni2+ ions.

Assignment of 13C peaks within each magnetic coupling scheme can be empirically accomplished by examining the role that unpaired electrons play in contributing to the 13C chemical shifts. Here, we follow the precedent wherein chemical shift changes are additive through bonds and are sensitive to the distance between the paramagnetic ion and the observed NMR nucleus (13). Figure 4A illustrates the spatial distribution of metal ions relative to carboxylate groups, from which we analyzed the distances and bond angles between Ni2+ ion at different positions (M2 to M4) and the 13C nucleus of carboxylate (C4). The distances are found to be M2−C4 < M4−C4 < M3−C4, and the metal-oxygen-carbon angles are also ordered as M2−O−C4 < M4−O−C4 < M3−O−C4. Considering that the effect of unpaired electrons at the carboxylate carbon decreases with increasing through-bond distance, we estimate the magnitude of chemical shift change induced by paramagnetic Ni2+ ions (i.e., chemical shift of paramagnetic substance − chemical shift of diamagnetic analog) and then assign the NMR peaks accordingly. For the FM-coupled scheme of 13C chemical shifts, the arrangement with two adjacent Ni2+ ions at M2 and M3 positions results in greater chemical shift changes [Ni−μ1−O−13C−μ2−O−Ni(−Mg): |817 ppm − 175 ppm| > Ni−μ2−O−13C−μ3−O−Ni(−Ni): |197 ppm − 175 ppm|]. Turning to the four narrow 13C peaks within the AF-coupled scheme, they may also be assigned according to the distance of the 13C nuclei from unpaired electrons in the following order: Ni−μ1−O−13C−μ2−O−Mg(−Ni) ([230 ppm − 175 ppm]) > Ni−μ1−O−13C−μ2−O−Mg(−Mg) ([210 ppm − 175 ppm]) > Mg−μ1−O−13C−μ2−O−Mg(−Ni) ([144 ppm − 175 ppm]) > Mg−μ1−O−13C−μ2−O−Ni(−Mg) ([203 ppm − 175 ppm]). We also notice that the differences between observed chemical shifts of paramagnetic
The two broad peaks at 817 and 197 ppm and the four narrow peaks at 230, 210, 203, and 144 ppm have to be assigned separately because of their distinct magnetic coupling schemes. According to our DFT analyses, the chemical shifts are predicted to be 4333 ppm for Ni–µ1-O–13C–µ2–O–Ni(–Mg) and 766 ppm for Mg–µ1-O–13C–µ2–O–Ni(–Ni), respectively. Using the order of calculated chemical shift as a guide, we assigned the peak at 817 ppm to Ni–µ1-O–13C–µ2–O–Ni(–Mg) and the peak at 197 ppm to Mg–µ1-O–13C–µ2–O–Ni(–Ni). Similarly, the order of calculated chemical shifts is 252 ppm [Ni–µ1-O–13C–µ2–O–Mg(–Ni)] > 204 ppm [Ni–µ1-O–13C–µ3–O–Mg(–Mg)] > 190 ppm [Mg–µ1-O–13C–µ2–O–Ni(–Mg)] > 184 ppm [Mg–µ1-O–13C–µ2–O–Mg(–Ni)] for the other Mg/Ni arrangements, and the four narrow peaks at 230, 210, 203, and 144 ppm were assigned accordingly. Assignment from the computational approach is consistent with that from the empirical approach (table S6), and the results are shown in Fig. 4B.

We then calculated the abundance of each Mg/Ni arrangement in Mg1-xNi-x-MOF-74 samples (Fig. 4C), considering that the NMR peak area is proportional to the number of 13C nuclei in corresponding chemical environment (figs. S34 to S35). After Ni incorporation, the compositional contribution of Mg–µ1-O–13C–µ2–O–Mg(–Mg) gradually decreases from 100 to 0%, as expected. The Mg–µ1-O–13C–µ2–O–Ni(–Ni) and Ni–µ1-O–13C–µ2–O–Ni(–Ni) arrangements, featuring the “Ni–µ1-O–Ni” bonding mode, are unexpectedly predominant in atomic-scale metal heterogeneity in nearly all MOF samples (Fig. 4D). The two arrangements together constitute more than 80% of all eight arrangements when x > 0.39 and more than 70% of seven Ni-containing arrangements even in the sample of x = 0.10 (fig. S36). Specifically, the Mg–µ1-O–13C–µ2–O–Ni(–Ni) arrangement dominates in the region of x = 0.10 to 0.39, whereas the Ni–µ1-O–13C–µ2–O–Ni(–Ni) arrangement dominates in the region of x = 0.50 to 0.93. This important observation is contrary to the common notion that solution mixing of starting materials in one-pot synthesis will yield random metal apportionment in mixed-metal MOFs. The dominance of two Mg/Ni arrangements among all eight arrangements is attributed to the marked effect of FM coupling in stabilizing the Ni–µ2–O–Ni-type environments (fig. S37).

Macrosopic adsorption phenomena

The SSNMR analysis here provides a unique yet reliable approach to create a direct correlation between the controllable atomicscale material preparation and the previously inaccessible atomic-scale metal apportionment. We anticipate that this correlation may be further extended to the macroscopic properties of mixed-metal MOFs. Toward this end, we explored the relationship between metal apportionment and macroscopic properties by monitoring gas adsorption, as it is one of the most important applications of MOFs (31). Carbon monoxide (CO) was chosen as a representative example because it is highly valuable and its use is essential in the production of many chemicals (32). It has been demonstrated that the adsorption behavior of CO/CO2 on activated Ni-MOF-74 is distinct from activated Mg-MOF-74 (33, 34): CO adsorption is preferential on Ni-MOF-74 via the formation of strong Ni–C bonds, whereas the pore surface of Mg-MOF-74 is primarily covered by CO2 through weak physical adsorption. We thus postulate that fine-tuning of atomic-scale metal apportionments in Mg1-xNi-x-MOF-74 samples, mainly the compositional change in Mg–µ1-O–13C–µ2–O–Ni(–Ni) and Ni–µ1-O–13C–µ2–O–Ni(–Ni) arrangements, may yield different CO adsorption behavior compared to their monometallic

A

B

C

D

Fig. 4. Speciation and quantification of local bonding environments in Mg1-xNi-x-MOF-74. (A) Schematic illustration of the connectivity between carboxylate groups and metal ions in Mg1-xNi-x-MOF-74. The carboxylate and metal ions of interest and corresponding M–C distances and M–O–C angles are highlighted in red. (B) Assignment of 13C NMR peaks to corresponding atomic-scale Ni/Mg arrangements. (C) Abundance of each 13C NMR peak as a function of the Ni content. The three peaks at 175, 197, and 715 ppm are labeled for clarity. The abundance of other peaks is always less than 10% for all compositions. The estimated error is ±0.2%. (D) Abundance of two peaks at 197 and 715 ppm as a function of the Ni content.

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counterparts. In addition, this strategy may allow for effective separation of CO from gas stream containing certain amounts of CO₂, making a more facile CO recovery process.

We test this postulation by first performing DFT calculations to elucidate the adsorption behavior of CO on model clusters representing Mg-μ₁-O-13C-μ₂-O-Ni(−Ni) and Ni-μ₁-O-13C-μ₂-O-Ni(−Ni) arrangements, respectively (Fig. 5A). According to our computational results, CO molecule prefers to adopt strong chemical adsorption on Ni²⁺ via “terminal binding” in both arrangements, whereas the physical adsorption of CO on Mg²⁺ is remarkably weaker (33–36). The Mg-μ₁-O-13C-μ₂-O-Ni(−Ni) arrangement, however, allows for “bridge binding” of the second CO molecule on each Ni²⁺. This binding mode is thermodynamically stable, as reflected by a mean CO adsorption energy of −44 kJ/mol. It is worth mentioning that the Ni²⁺ and Mg²⁺ ions involved in the bridge binding mode are related by the 3₁ axis and thus are exposed to the same MOF channel (fig. S38). In contrast, further DFT explorations suggest that the incorporation of bridge binding CO molecules is perturbed by two adjacent terminal binding CO molecules in Ni-MOF-74 (fig. S39).

We conducted breakthrough experiments to gain insights into CO/CO₂ adsorption as a consequence of tuning atomic-scale metal apportionment. Before these adsorption measurements, the MOFs were activated to evacuate methanol and yield open metal sites (9). We monitored the concentrations of eluents immediately after the gas stream passed through a column packed with activated MOFs as a function of retention time (Fig. 5B and fig. S40). The CO₂ uptake by Mg-MOF-74 (x = 0.00) is preferential, as reflected by a long breakthrough time of 8.20 min, whereas observation of a very short breakthrough time of 0.75 min is indicative of ineffective CO adsorption on Mg²⁺ (table S7) (34). Nevertheless, the breakthrough time of CO becomes noticeably longer when Ni is incorporated and surpasses that of CO₂ when the Ni content is beyond 21%. All recorded CO

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**Fig. 5. CO/CO₂ gas mixtures adsorbed onto Mg₀.₇₉Ni₀.₂₁-MOF-74.** (A) The adsorption configurations of CO on model clusters representing Mg-μ₁-O-13C-μ₂-O-Ni(−Ni) (left) and Ni-μ₁-O-13C-μ₂-O-Ni(−Ni) (right) arrangements, respectively. (B) Selected breakthrough curves of CO/CO₂ in a CO/CO₂/Ar/He flow (5:5:1:89 volume %) for activated Mg₀.₇₉Ni₀.₂₁-MOF-74 samples. The Ar and He were introduced as internal reference and carrier gas, respectively. (C) CO/CO₂ adsorption capacity as a function of the Ni content. (D) CO coverage per Ni as a function of the Ni content. (E) Schematic illustration of the mechanism of higher CO coverage per Ni allowed for Mg₀.₆₁Ni₀.₃₉-MOF-74 than Ni-MOF-74.
breakthrough curves of Mg$_{1-x}$Ni$_x$-MOF-74 samples ($x > 0.21$) exhibit a roll-up feature, which resembles the characteristics found in CO/CO$_2$ breakthrough experiment of Ni-MOF-74 (33, 34). These results strongly support our hypothesis that the predominant atomic-scale Mg$_{1-x}$-13C$_x$-Ni$_{1-x}$-13C$_x$-O-Ni(−Ni) and Ni$_{1-x}$-13C$_x$-13C$_x$-O-Ni(−Ni) arrangements in these MOF samples (Fig. 4D) are crucial in determination of the macroscopic CO adsorption performance.

We then calculated the adsorption capacity of CO/CO$_2$ as a function of the macroscopic material composition (Fig. S41 and table S7) to better interpret breakthrough data. As shown in Fig. 5C, CO$_2$ adsorption on Mg$_{1-x}$Ni$_x$-MOF-74 is not governed by any particular atomic-scale metal apportionment but, alternatively, by the averaged macroscopic composition, as evidenced by the linearly decreasing CO$_2$ adsorption capacity with increasing Ni content. This observation is consistent with the notion that incorporation of more Ni into the MOFs results in less available Mg$^{2+}$ sites for CO$_2$ adsorption. Unlike the case of CO$_2$, CO adsorption capacity of measured MOF sample notably and nonlinearly grows with increasing Ni content. These CO capacity results can be interpreted by splitting the full compositional scale into two regions of the atomic-scale Mg$_{1-x}$-13C$_x$-13C$_x$-O-Ni(−Ni) and Ni$_{1-x}$-13C$_x$-13C$_x$-O-Ni(−Ni) arrangements: For the region of $x < 0.4$, the emergence of Mg$_{1-x}$-13C$_x$-13C$_x$-O-Ni(−Ni) enables drastically improved CO adsorption; for the region of $x > 0.4$, Ni$_{1-x}$-13C$_x$-13C$_x$-O-Ni(−Ni) becomes the major (or predominant) in all atomic-scale arrangements and CO adsorption capacity of corresponding Mg$_{1-x}$Ni$_x$-MOF-74 gradually resembles that of monometallic Ni-MOF-74. Hence, only a slight difference in CO capacity is observed with the Ni content ranging from 0.4 to 1.0. We converted CO adsorption capacity to CO coverage per Ni (Fig. 5D) and observed that the coverage ramp up from 1.06 ($x = 0.10$) to its maxima of 1.64 ($x = 0.39$) and then steadily declines to the value comparable to that of Ni-MOF-74 ($x = 0.89$; $x = 1.00$) (35, 36). This decline results from the steric hindrance from two terminal binding CO molecules on adjacent Ni$^{2+}$ ions within the same channel, and the perturbation is further amplified by the wobbling of CO molecules about the time-averaged position at ambient temperature (Fig. 5E) (36, 37).

**DISCUSSION**

We have uncovered nonrandom atomic-scale metal apportionment in mixed-metal MOFs by SSNMR and further establish the relationship between metal apportionment and macroscopic observables by breakthrough experiments. Moreover, we exploit apportionment assessment to propose a new functional material (Mg$_{0.61}$Ni$_{0.39}$-MOF-74) for potential industrial application of CO adsorption. This specific metal composition and apportionment result in a higher atom economy of Ni than Ni-MOF-74, requiring only half of Ni$^{2+}$ for the same amount of adsorbed CO gases. Note that the substitution of Ni with earth-abundant and nontoxic Mg in Mg$_{0.61}$Ni$_{0.39}$-MOF-74 also improves the humidity tolerance of MOFs during gas adsorption (38, 39) and yields enhanced catalytic activity and stability in reactions such as (de)hydrogenation of alcohols (40). The SSNMR-accessible atomic-scale metal apportionment thus fills the gap between rational design of macroscopic scale material preparation and creation of superior macroscopic scale performance of mixed-metal MOFs. We envision that this nondestructive SSNMR methodology can be further applied to analyze bulk assembly of other mixed-metal MOFs such as Mg$_{1-x}$Co$_x$-MOF-74. The preliminary results shed light on the unique magnetic properties of these samples, and we will report the thorough work in the future.

**MATERIALS AND METHODS**

**Sample preparation**

Hydroquinone ($\geq 99\%$), potassium carbonate-$^{13}$C (98 at % $^{13}$C), potassium formate ($99\%$), sodium sulfite ($\geq 98\%$), 2,5-dihydroxyterephthalic acid (H$_2$DHTP; 98%), magnesium nitrate hexahydrate (99.999% trace metal basis), nickel(II) nitrate hexahydrate (99.999% trace metal basis), hydrochloric acid (37%; ACS reagent), and ethanol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Anhydrous CO$_2$ ($\geq 99.999\%$ purity) was obtained from EMD Millipore Chemicals. Ultra-high-purity grade CO gas (99.999% purity) was obtained from Praxair. All starting materials and solvents, unless otherwise specified, were used without further purification.

The synthesis of 13COOH-labeled H$_2$DHTP (H$_2$DHTP-$^{13}$C$_2$) is modified from the published procedure (41). A glass branched seal tube was filled with a mixture of hydroquinone (0.714 g, 6.48 mmol), $^{13}$C-labeled potassium carbonate (1.00 g, 7.18 mmol), and potassium formate (1.60 g) and flushed for three cycles (vacuum/CO$_2$). The reaction mixture was then heated to 200°C under CO$_2$ atmosphere for 4 hours. The yellow product was slowly cooled down to room temperature before adding to 30 ml of 0.5 weight % sulfuric sodium sulfite aqueous solution. The yellow product was precipitated with hydrochloric acid (37%), washed with water (10 ml x 3), filtered off, and dried under vacuum at 50°C to give H$_2$DHTP-$^{13}$C$_2$ a bright solid yellow color (yield: 0.653 g, 3.26 mmol, 50%).

Methanol-exchanged Mg$_{1-x}$Ni$_x$-MOF-74 samples were synthesized following the published procedure (8). Typically, H$_2$DHTP or H$_2$DHTP-$^{13}$C$_2$ (40.0 mg, 0.200 mmol) and a stoichiometric (table S1) mixture of Mg(NO$_3$)$_2$-6H$_2$O and Ni(NO$_3$)$_2$-6H$_2$O (0.617 mmol in total) were dissolved in DMF/ethanol/H$_2$O (15 ml/1 ml/1 ml) and placed in a 20-ml scintillation vial, which was heated to 120°C for 20 hours. The precipitate was collected, washed, and immersed in 20 ml of anhydrous DMF for 3 days, during which time the DMF was refreshed three times per day. The DMF-exchanged compound was filtered off and immersed in 20 ml of anhydrous methanol for 3 days, during which time the methanol was also refreshed three times per day. Natural abundance samples were used in ICP-OES, scanning electron microscopy, EDX, magnetic susceptibility, and breakthrough measurements, while 13COO$^-$-labeled samples were used in SSNMR measurements.

**Characterizations**

The details of PXRD, ICP-OES, scanning electron microscopy, EDS, SSNMR, magnetic susceptibility, CO/CO$_2$ breakthrough measurements, and DFT calculations are provided in the Supplementary Materials.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.add5503

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