The Chemistry of CO₂ Capture in an Amine-Functionalized Metal–Organic Framework under Dry and Humid Conditions

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Supporting Information

ABSTRACT: The use of two primary alkylamine functionalities covalently tethered to the linkers of IRMOF-74-III results in a material that can uptake CO₂ at low pressures through a chemisorption mechanism. In contrast to other primary amine-functionalized solid adsorbents that uptake CO₂ primarily as ammonium carbamates, we observe using solid state NMR that the major chemisorption product for this material is carbamic acid. The equilibrium of reaction products also shifts to ammonium carbamate when water vapor is present; a new finding that has impact on control of the chemistry of CO₂ capture in MOF materials and one that highlights the importance of geometric constraints and the mediating role of water within the pores of MOFs.

Metal–organic frameworks (MOFs) are emerging as effective materials for selective CO₂ chemisorption with high uptake due to the ease with which they may be tuned by the pre- and post-synthetic modification of their building units.1–3 To date, the most successful MOFs for CO₂ capture have included alkylamine-functionalized (R,NHR₂, or RNH₂) pores. These alkylamines have been shown to selectively react with CO₂, forming covalent C=N bonds, yielding great low-pressure (<100 Torr) uptake and selectivity, yet only ammonium carbamate is reported as the product of CO₂ capture.4–6 Previously, we demonstrated that the pores of IRMOF-74-III {Mg₂(3,3'-dioxido-[1,1'-4',1'-terphenyl]-4,4'-dicarboxylate)} can be designed and functionalized with one primary alkylamine covalently attached to each linker leading to enhanced CO₂ capture.6 Here, we report on a new, diamine-functionalized MOF system, IRMOF-74-III-(CH₂NH₂)₂(Mg₂(2,5'-bis(aminoethyl)-3,3'-dioxido-[1,1'-4',1'-terphenyl]-4,4'-dicarboxylate)), and demonstrate its framework chemistry with CO₂ under dry and humid conditions. This study contributes to the fundamental understanding of CO₂ capture in MOFs under conditions relevant to those required in practice. Although examples of carbamic acid formation in organic molecular crystals, surface modified silica, and porous silica are reported, control of the CO₂-binding chemistry has not been demonstrated.11–15 We show that the equilibrium of chemisorbed CO₂ shifts at the time when CO₂ is introduced to the system from primarily carbamic acid to ammonium carbamate depending upon the absence or presence of water, respectively. Accordingly, understanding this chemistry is crucial to achieving control over which of the two chemisorption products is formed, as each species’ unique properties may make it desirable for specific carbon capture applications.14,15

The synthesis and characterization of organic linkers and extended structure, IRMOF-74-III-(CH₂NH₂)₂, was carried out according to previously reported conditions [see Supporting Information (SI), Sections S2 and S3].6 Because the presence of free amines on the organic struts disrupts the synthesis of the extended structure, the two primary amine functional groups were incorporated into IRMOF-74-III as Boc-protected (–Boc = tert-butylcarbonyl) derivatives.16 The quantitative removal of the –Boc protecting groups from the framework structure by microwave irradiation (SI, Section S4) was confirmed by solid state cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR), and Fourier transform infrared spectroscopy (FT-IR), as well as solution phase NMR of the acid-digested material (SI, Sections S5, S6, and S7). Powder X-ray diffraction (PXRD) and nitrogen adsorption isotherm experiments confirmed that the framework maintained its structural integrity and porosity after post-synthetic deprotection of the –Boc groups (SI, Sections S8 and S9).

To confirm that CO₂ binds in a chemisorptive fashion and that it can be removed afterwards, CO₂ isotherms for IRMOF-74-III-(CH₂NH₂)₂ were measured at 25 °C (Figure 1). This compound shows similar capacity (67 cm³ g⁻¹) to the

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previously reported IRMOF-74-III-CH₂NH₂ (75 cm³ g⁻¹) at 800 Torr, indicating similar physisorption behavior of the materials. In the low pressure range (<100 Torr), however, the IRMOF-74-III-(CH₂NH₂)₂ compound significantly out-performs its monoamine counterpart, collecting 2.33 times the amount of CO₂ per gram of material at identical pressures (SI, Section S10), indicative of enhanced chemisorption. The behavior of the material after different activation conditions was also studied (Figure 1). After the first CO₂ isotherm measurement, three separate experiments were conducted: first, a subsequent isotherm was measured without any activation of the material. Investigation of this isotherm reveals a ca. 17% drop in CO₂ uptake at 800 Torr, and a ca. 83% drop in CO₂ uptake at 0.8 Torr, compared to the as-synthesized, activated material. This suggests that the amine moieties capture the CO₂ by covalent bond formation. The next isotherm was measured after activating the material under dynamic vacuum at 25 °C for 12 h. Investigation of this isotherm reveals a 12% drop in CO₂ uptake at 800 Torr, and a 61% drop in CO₂ uptake at 0.8 Torr. This indicates that only a portion of the amine-CO₂ bonds are broken simply by applying vacuum as shown in Figure 2. Finally, an isotherm was measured after activating the material under vacuum for 2 h at 120 °C. This isotherm showed no drop in CO₂ uptake in both the high and low pressure regions, indicating full regeneration of the material.

The nature of the covalent bond being formed upon CO₂ chemisorption was examined by solid state ¹³C and ¹⁵N CP-MAS NMR of 50% ¹⁵N-enriched IRMOF-74-III-(CH₂NH₂)₂ (Figure 2). The ¹³C spectrum (Figure 2a) shows the carbonyl phenoxide peaks at 173 and 166 ppm respectively, as well as the aromatic peaks between 110 and 150 ppm. Of particular note is the CH₂ resonance with two features at 48.6 and 44.0 ppm. Though only one resonance here is expected, this pair of peaks was consistently observed with similar intensity ratios across several tested samples. Likewise, a pair of amine peaks is observed in the ¹⁵N spectrum at 30.3 and 25.4 ppm (Figure 2d), where only one amine resonance is expected. These two peaks are surmised to emanate from two distinct conformations of the linkers based on the torsional angle of the central phenyl ring, yielding two distinct amine positions with slightly different chemical shifts. To characterize the chemisorption products of CO₂, samples were exposed to 675 Torr of ¹³CO₂ (99% ¹³C atom basis) in a sealed dosing apparatus for 24 h. (SI, Section S5). The appearance of a highly intense peak in the ¹³C spectrum (Figure 2b, in red) with a maximum at 160.3 ppm
and right-shoulder features at ca. 158 and 156 ppm confirmed that the \(^{13}\text{CO}_2\) was adsorbed by reaction with the primary amines to form a new species. In contrast to our previous study in which a broad peak spanning 164–160 ppm was assigned to a mixture of carbamate and carboxylic acid, this sharp, narrow peak is assigned as primarily carboxylic acid. This assignment is consistent with chemical shifts observed and/or calculated for carboxylic acid in various structural configurations in other solid \(\text{CO}_2\) sorbents.\(^{6,12,14,17}\) The full width at half-maximum line width of 350 Hz and asymmetric shape of this resonance suggest an inhomogeneous broadening arising from multiple overlapping carbamic acid sites, with each site likely varying slightly in its configuration and hydrogen bonding environment.

Further support of the assignment of this resonance as carboxylic acid was gathered via \(^{15}\text{N}\) CP-MAS NMR (Figure 2 in red, SI, Section S5). The presence of two residual amine peaks at 30.3 and 25.4 ppm was observed, indicating that complete saturation of the alkylamine moieties was not achieved upon exposure to \(^{13}\text{CO}_2\) at 675 Torr. Two peaks at 92.7 and 87.7 ppm appear at the expense of the amine peaks, suggesting that this difference in chemical shift, arising from conformations of the linkers, carries over to the chemisorbed products as well. Critically, as no major peak is observed that can be assigned as ammonium, we assign these two downfield peaks as carbamic acid \(^{15}\text{N}\) sites. However, when the MOF was exposed to 95% relative humidity (RH) conditions prior to loading with \(^{13}\text{CO}_2\), a significant new peak at 36.6 ppm is observed along with a peak at 90.1 ppm (Figure 2f, blue). Though these CP-MAS spectra are not quantitative with respect to integration, their similar magnitudes suggest that the species observed here is ammonium carbamate, with the peak at 36.6 ppm being ammonium. The assignment of the adsorbed species as ammonium carbamate is supported by the change in the \(^{13}\text{C}\) chemical shift maximum for the 95% RH-treated material to 164.0 ppm (Figure 2c, blue), consistent with previous reports of the \(^{13}\text{C}\) chemical shift of carbamate.\(^{12,14,17,18}\) Though some small portion of this \(^{13}\text{C}\) signal may be attributable to bicarbonate, as has been discussed in studies of amine-tethered porous silicas,\(^{18}\) the \(^{15}\text{N}\) spectrum enables us to assert that the dominant amine-\(\text{CO}_2\) chemisorption product in humid conditions is ammonium carbamate. The peak splitting observed in the dry adsorption spectrum is lost upon exposure to 95% RH, suggesting that the inter-linker interaction required to produce the ion pair ammonium carbamate alters the torsional angle of the central phenyl ring on the linkers to result in one major structural conformation. This shift to ammonium carbamate from carboxylic acid occurs as a function of the amount of water vapor present, with MOF samples exposed to atmospheric moisture (50% RH) exhibiting signal contributions from both carboxylic acid and carbamate (SI, Section S5).

Although the role of water is critical to this chemistry, initial examination in modeled IRMOF-74-III-(CH\(_2\)NH\(_2\))\(_2\) the separation between primary amines points to geometric constraints within the pores as also being operative. To further understand the amine-amine distances and their contribution to this unique chemistry, we modeled the conformation of the linkers (Figure 3, SI Section S11) in IRMOF-74-III-(CH\(_2\)NH\(_2\))\(_2\). Because the amines are introduced to the material as their \(\text{Boc}\) protected counterparts, steric hindrance plays a significant role in their final orientation. When considering amine geometries that would facilitate formation of carboxylic acids, two possible intermethylene distances (staggered amine conformation), 5.3 and 8.3 Å, were of particular interest since similar intermethylene distances have been found in molecular carboxylic acids (5.982(4) Å, and 8.017(1) Å).\(^{11,15}\) The similarities between these distances and those in IRMOF-74-III-(CH\(_2\)NH\(_2\))\(_2\) support the notion of carboxylic acid formation in the absence of a proton-transfer species (in the present case, water) which would generate ammonium carbamate.

For additional experimental support of these two species, FT-IR (SI, Section S6), combined thermogravimetric analysis, differential scanning calorimetry, mass spectrometry (TGA-DSC-MS, SI Section S12), and breakthrough measurements (SI, Section S13) were performed. Samples of IRMOF-74-III-(CH\(_2\)NH\(_2\))\(_2\) exposed to \(\text{CO}_2\) were also analyzed using TGA-DSC-MS. The sample lost 12 mass % of \(\text{CO}_2\) (m/z = 44) at relatively low temperature (onset at 47 °C) after exposure to dry \(\text{CO}_2\). Humidified (95% RH) samples of IRMOF-74-III-(CH\(_2\)NH\(_2\))\(_2\), that were exposed to \(\text{CO}_2\) exhibit a mass loss of 10 mass % corresponding to \(\text{CO}_2\) (m/z = 44) and \(\text{H}_2\text{O}\) (m/z = 18) at higher temperature (onset at 65 °C). The results of the thermal analysis indicate \(\text{CO}_2\) is more strongly bound as ammonium carbamate as opposed to carboxylic acid under wet and dry conditions, respectively. Additionally, the decrease in mass loss under humid conditions supports the conclusion of two amines participating in ammonium carbamate formation versus one amine forming carboxylic acid upon reaction with \(\text{CO}_2\). The dynamic adsorption capacity, as measured by breakthrough time, remained the same under dry (900 ± 10 s g\(^{-1}\), 1.2 mmol g\(^{-1}\)) and 65% RH (890 ± 10 s g\(^{-1}\), 1.2 mmol g\(^{-1}\)) conditions (SI, Section S13). This appears counterintuitive given the TGA-DSC-MS results, but is justified by the fact that at 50% RH (SI, Section S5) we observe a mixture of carbamate and carboxylic acid in the solid state NMR. This mixture would likely be the result of initial carboxylic acid generation, with subsequent proton transfer to form ammonium carbamates, and thus the kinetics of \(\text{CO}_2\) capture would be dictated by the formation of the former species.

To investigate the difference in thermal properties between ammonium carbamate and carboxylic acid in IRMOF-74-III-(CH\(_2\)NH\(_2\))\(_2\) and their impact on regeneration of the material, vacuum was applied for 24 h at room temperature to the NMR samples previously exposed to \(^{13}\text{CO}_2\) and solid state CP-MAS NMR was performed. Under dry loading conditions, the \(^{13}\text{C}\) carboxylic acid resonance at 160.3 ppm is significantly reduced after vacuum (Figure 2b, gray), and the \(^{15}\text{N}\) carboxylic acid...
resonances at 92.7 and 87.7 ppm decrease as the two amine peaks at 30.3 and 25.4 ppm rise in intensity (Figure 2e, gray). For the sample exposed to both 95% RH and $^{13}$CO$_2$, room temperature vacuum activation appears much less effective (Figure 2c,f), with only minor loss of signal observed for the carbamate resonance in both the $^{13}$C and $^{15}$N spectra. This is consistent with the TGA-DSC-MS results, where the onset point of CO$_2$ desorption as carbamate occurs 18 °C higher than for carbamic acid.

**ASSOCIATED CONTENT**

* Supporting Information

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Methods and additional data (PDF)

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Notes

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