Flexible metal-organic framework compounds: *in situ* studies for selective CO₂ capture

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Abstract: Results are presented that explore the dynamic structural changes occurring in two highly flexible nanocrystalline metal-organic framework (MOF) compounds during the adsorption and desorption of pure gases and binary mixtures. The Ni(1,2-bis(4-pyridyl)ethylene)[Ni(CN)₄] and catena-bis(dibenzoylmethanato)-(4,4'-bipyridyl)nickel(II) chosen for this study are 3-D and 1-D porous coordination polymers (PCP) with a similar gate opening pressure response for CO₂ isotherms at 303 K, but with differing degrees of flexibility for structural change to accommodate guest molecules. As such, they serve as a potential model system for evaluating the complex kinetics associated with dynamic structure changes occurring in response to gas adsorption in flexible MOF systems. Insights into the crystallographic changes occurring as the MOF pore structure expands and contracts in response to interactions with CO₂, N₂, and CO₂/N₂ mixtures have been obtained from *in situ* small-angle neutron

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scattering and neutron diffraction, combined with *ex situ* X-ray diffraction structure measurements. The role of structure in carbon capture functionality is discussed with reference to the ongoing characterization challenges and a possible materials-by-design approach.

Keywords: composite materials; nanostructured materials; gas-solid reactions; microstructure; phase transitions; neutron diffraction

1. Introduction

The development of new low-cost strategies for separating and adsorbing carbon dioxide from flowing gas streams is central to current worldwide efforts to mitigate carbon release into the environment. Indeed, the low cost capture of carbon dioxide from coal or natural gas fired electrical power generation, through the use of adsorption-based separations and multi-scale porous solid sorbent materials, could significantly reduce net carbon emissions from stationary sources.^[1-4] In this context, the emergence of new solid sorbent compounds is of particular importance. Presently available solid sorbent materials do not have sufficient carbon capture efficiency and selectivity, adsorption/desorption cycle life, or cost-effective scale-up potential. However, current research is providing new insights into how porous solid sorbents can be better designed and tailored to optimize their carbon dioxide sorption characteristics.^[5-12] Their incorporation into separation membranes (to separate carbon dioxide from hydrogen, methane, nitrogen, oxygen or water vapor) may offer the potential for scale-up to industrial applications. One family of highly tailorable porous solid sorbents are metal-organic frameworks (MOFs) otherwise known as porous coordination polymers (PCPs).^[13-27] These compounds are

constructed by bridging metal ions through organic linkers into extended coordinate-covalent networks. The diversity offered in the design of PCPs comes from the ability to alter the coordination geometry and organic linker properties in a myriad of combinations to create porous networks of widely varied size and chemical nature.

Flexible PCPs, or structurally dynamic MOFs, are an interesting class of solid sorbents that exhibit large reversible changes in porosity in response to the adsorption and desorption of solvent or gas guest molecules. This structural flexibility can arise through a number of mechanisms including, for example, bond rotations in the organic linkers, weak intermolecular bonding interactions between structural components in the PCP, and changes in bonding angles of the coordination complexes within the network. These changes may be subtle, involving small shifts in atom or functional group positions that open access to a pore or channel within the structure, or may be quite significant leading to rather dramatic changes in the overall crystal lattice. The nanoscale porosity of these flexible materials is typically gas specific over a wide temperature and pressure range and, as such, often proposed to be exploitable for gas separation applications. The great structural versatility, together with the ability to control the structure and microstructure of structurally dynamic MOFs, offers prospects to tailor these materials for selective gas adsorption applications.^[28-35]

In practice, a predictive understanding of how structurally dynamic MOFs or flexible PCPs can be functionalized to optimize specific gas selectivity is difficult to achieve. This is due to the complex interplay of thermodynamics associated with guest–host interactions and phase transitions, the stabilizing effects of guest adsorption on the host sorbent (including mechanical

stress relief in the host crystal), and other nucleation effects, all of which dictate the degree of structural change and amount of gas adsorption within these systems. This situation is further complicated by the multi-component interactions between the host solid and competing gas species in a mixture, including possible cooperative phenomena involving multiple gases and the host matrix.^[8, 36-58] The interplay of these various factors remains not fully understood with MIL-53 being the only flexible MOF system probed in appreciable detail.^[53-58] Determining the precise nature of molecular- and nanoscale microstructural changes occurring during selective adsorption of both pure and mixed gas systems is critical for advancing the field and designing new sorbent systems for light gas separations. Among many complementary methods, neutron and X-ray scattering methods provide an array of suitable techniques for addressing this challenge, including small-angle neutron and X-ray scattering and diffraction (SANS and SAXS, ND and XRD) inelastic neutron scattering (for physical gas adsorption) and extended or near-edge X-ray absorption fine-structure analysis (for chemical gas adsorption).^[59-69]

In this paper, we present *in situ* SANS and *in situ* ND measurements made during the adsorption of pure CO₂ and CO₂/N₂ mixtures to gain insight into the complex structural changes occurring when gases adsorb in two structurally dynamic flexible MOF compounds. One, known to exhibit a high level of CO₂ adsorption/desorption, is effectively an extended 3D Hofmann clathrate analogue: a pillared Ni(1,2-bis(4 pyridyl)ethylene)[Ni(CN)₄] compound (NiBpeneNiCN), here simply denoted “NiBpene”.^[70] The other, believed to exhibit a high degree of selectivity for CO₂ adsorption over other gases, is a flexible linear chain (1D) coordination polymer: catenabis(dibenzoylmethanate)-(4,4'-bipyridyl)nickel(II) polymer, abbreviated here as “NiDBM-Bpy” (where DBM stands for dibenzoylmethanate, and Bpy stands

for 4,4'-bipyridyl). It is recognized as one of the “DBM” class of MOFs, elegantly described by Soldatov.^[71-76] Interestingly, both of these materials have nearly identical gate opening pressure responses to CO₂ at 303 K. This coincidence in CO₂ adsorption behavior between two highly contrasted crystallographic structures with very different degrees of freedom available for structure transitions during gas adsorption make these two materials an ideal model system for investigating how structures respond and evolve to the adsorption of guest molecules. Furthermore, the selective CO₂ adsorption properties of the NiDBM-Bpy system have recently been elucidated, revealing how the dynamic structure can potentially be harnessed for practical gas separations.^[77] Elsewhere, single-crystal XRD has been combined with powder XRD to achieve *a priori* structure determinations of NiBpene.^[78] Here, using *in situ* SANS and ND measurements with a gas-pressure cell, we seek new insights into these dynamic structured materials that would help advance the development of new gas separation compounds.

2. Experimental

2.1. Sample Preparation

All chemicals were purchased from Sigma-Aldrich^{‡§}, St. Louis, MO, and used as received. The Ni(1,2-bis(4 pyridyl)ethylene)[Ni(CN)₄] compound (NiBpene) was prepared as previously described.^[78] The catenabis(dibenzoylmethanate)-(4,4-bipyridyl)nickel(II) polymer (NiDBM-Bpy) compound was prepared by reaction of anhydrous bis(dibenzoylmethanato)nickel(II) (Ni(DBM)₂) with 4,4-bipyridine in dry tetrahydrofuran (THF) as previously described.^[79] The

[‡] Certain commercial materials and equipment are identified in this paper only to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

[§] Reference in this work to any specific commercial product is to facilitate understanding and does not necessarily imply endorsement by the US Department of Energy.

sample purity for both compounds was verified by determination of the mass fraction of residual NiO in dry air at 773 K (500 °C) using thermal gravimetric analysis (TGA), by C, H, and N elemental analysis (Robertson Microlit Laboratories, Ledgewood, NJ), and powder XRD. ^[78,79]

2.2. Adsorption Isotherm Measurements

High pressure pure CO₂ and N₂ adsorption-desorption isotherms were collected for both NiBpene and NiDBM-Bpy powders at 303 K (30 °C) on a pressure-composition isotherm measurement system (Advanced Materials Corporation, Pittsburgh, PA) for pressures up to 20 bar for pure CO₂, and up to 50 bar for N₂/CO₂. CO₂ isotherms were collected at 273 K (0 °C), 258 K (13 °C) and 303 K (30 °C), and N₂ isotherms were collected at 204 K (-69 °C), 214 K (-59 °C), and 303 K (30 °C). This instrument is designed on the basis of a conventional Sievert apparatus. Prior to the isotherm measurements, $\approx$ 800 mg of each compound was degassed under vacuum at 383 K (110 °C) overnight. All other sample pre-activation was performed using CO₂ at the measurement temperature. Mixed gas adsorption isotherms on NiBpene and NiDBM-Bpy up to 16 bar total pressure at 273 K (0 °C) were collected on 25 mg samples using a Hiden IGA gravimetric instrument (Hiden Isochema, Warrington, UK). The lower temperature was required to get the transition pressure for the mixture within the 20 bar pressure range of the instrument. A 50/50 mixture by volume of CO₂/N₂ was mixed prior to injection into the sample chamber using high purity source gases delivered in the appropriate ratio using mass flow controllers. Buoyancy effects were minimized by the use of a counterweight assembly on the sampling balance. Any residual buoyancy (< 250 μ g at 16 bar) effects remaining from the small mismatch in counterweight and sample side volumes were corrected for using gas density values calculated from the NIST software, *REFPROP* (NIST, Boulder, CO). Thermogravimetric analyses were performed on $\approx$ 5 mg samples using a Perkin-Elmer TGA7 thermogravimetric analyzer under a

dry air purge of 100 mL/min (Perkin-Elmer, Akron, OH). The samples were ramped to 828 K (550 °C) at a rate of 15 K/min.

2.3. Powder X-ray Diffraction

Lab-based powder XRD data were measured under ambient conditions, and used to investigate the phase purity, establish the phase relationships, and obtain preliminary cell parameters for these nanocrystalline materials. These experiments were carried out using a Phillips X-ray powder diffractometer (Panalytical, Westborough, MA) with Cu K α radiation (X-ray energy = 8.048 keV, wavelength = 0.15406 nm). The diffractometer was equipped with a series of Soller slits and a scintillation counter. The 2θ scanning range was 5° to 71° and the step interval was 0.03°. Data were analyzed using the software package, GSAS.^[80-83] However, refinement attempts were not successful for the diffraction patterns from the dried samples under ambient conditions. Instead, peak assignments were based on consistency checks with previous single crystal diffraction data for these and similar materials.^[76,78]

2.4. Neutron Diffraction:

In situ neutron powder diffraction (NPD) data for NiBpene were collected at the NIST Center for Neutron Research on the high-resolution powder neutron diffractometer (BT1), with monochromatic neutrons of wavelength 0.2079 nm produced by a Ge(311) monochromator. The collimation angle widths before and after the monochromator, and after the sample, were (60, 20 and 7) arc minutes full-width-at-half-maximum (FWHM), respectively. Reduced temperatures were used in order to minimize the Debye-Waller factor broadening of the diffraction peaks, hence improving the resolution. Data were collected over a 2θ range of 2° to 166° with a step

size of 0.05° at 20 K (-253 °C) and at 10 K (-263 °C) in the guest-free state and with toluene adsorbed to saturation, respectively. Measurements were then made during a CO₂ adsorption / desorption cycle at 258 K (-15 °C) for which we had accompanying adsorption isotherm measurements. Refinement attempts of the nuclear structure were carried out by applying the Rietveld refinement technique to the NPD using the software *GSAS*, just as for the powder XRD analysis discussed above.^[80-83] The neutron scattering lengths used in the refinements are (1.030, 0.665, 0.936, 0.581 and -0.374) $\times 10^{14}$ m for Ni C, N, O and H, respectively.

2.5. Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) was measured both to give the profile, $I(Q)$, measured as a function of the magnitude of the scattering vector, Q , where $Q = (4\pi/\lambda)\sin(\phi/2)$, λ is the neutron wavelength, and ϕ is the scattering angle (i.e., $\phi = 2\theta$ in the diffraction notation above), and to determine the position and intensity of the small-angle diffraction peaks associated with the flexible MOF d -spacing that is most sensitive to the presence of adsorbed guest molecules. SANS measurements were carried out using the NIST/NSF NG3 SANS instrument, as well as the NIST/ExxonMobil/University of Minnesota NG7 30 m SANS instrument at the NIST Center for Neutron Research (NCNR), Gaithersburg, MD^[84,85]. In both cases, $\lambda = 0.51$ nm and up to 3 instrument configurations were used in order to obtain scattering intensity data over a Q range from as low as 0.04 nm^{-1} to 6.0 nm^{-1} . While this Q range was sufficient to characterize much of the powder morphology present, only the data in the $(3 < Q < 6) \text{ nm}^{-1}$ range are relevant to the small-angle diffraction results reported here. Data were recorded on a two-dimensional detector, corrected for detector sensitivity, electronic and parasitic background effects, and sample absorption, then calibrated against the incident beam flux and normalized to unit sample volume.

Finally, the data were circularly averaged to obtain absolute scattered intensity $I(Q)$ data *versus* Q . This was done using the NCNR SANS analysis software package developed using Igor Pro [85]. For the small-angle diffraction peak observed, the linker d -spacing was obtained from the peak position in Q , Q_{PK} , by $d = 2\pi/Q_{PK}$. *In situ* data were collected for both activated NiBpene and NiDBM-Bpy under vacuum, at 17 bar of pure CO₂, 17 bar of pure N₂, and a 50/50 mixture containing 17 bar CO₂ and 17 bar N₂ ($P_{tot} \approx 34$ bar) at 303 K (30 °C). With the relatively small amount of NiBpene or NiDBM-Bpy sample in the chamber (≈ 0.11 g), the large headspace volume (≈ 2 L), and the resulting large number of moles of CO₂ at 17 bar (1.35 moles CO₂) the change in headspace composition of the CO₂/N₂ mixture due to selective CO₂ adsorption is negligible (0.016 %) in these SANS measurements.

3. Results and Discussion

3.1. Structural Changes due to Adsorption and Desorption of Guest Species

To provide baseline characterization information for the CO₂ sorption behavior of the two solid sorbents being considered here, **Figure 1** shows CO₂ adsorption / desorption isotherms for the NiBpene and NiDBM-Bpy materials at 303 K (30 °C). (Repeated measurements show these data to be reproducible.) The **Supplementary Material (Figure S1 and Figure S2)** presents corresponding isotherm curves for a series of lower temperatures, and shows these to be generically similar to those at 303 K, except that the pressure scale is reduced for lower temperature isotherms and the hysteresis in adsorption and desorption decreases at reduced temperatures. At 303 K, both materials show hysteresis, exhibit adsorption threshold pressures of ≈ 10 bar CO₂, and show maximum CO₂ adsorption at ≈ 17 bar applied pressure. The only significant differences are that NiBpene adsorbs approximately three times as much CO₂ per unit

mass (or about twice as much CO₂ per mole) as NiDBM-Bpy does when each powder is subjected to 17 bar applied pressure of CO₂, and there are prominent step-like features in the desorption curve for NiBpene, whereas such features are much reduced in the desorption isotherm for NiDBM-Bpy. Such step-like features have been associated with phase transformations in the sorbent, whether during desorption as seen here, especially for NiBpene^[78], or during adsorption as seen elsewhere for interpenetrating MOFs.^[86] Meanwhile, as shown in the **Supplementary Material (Figure S3)**, gravimetrically measured adsorption isotherms at 273 K using a 50/50 CO₂/N₂ mixture by volume (and pressure) suggest that similar behaviors (with no steps) occur during adsorption in both compounds studied here in a mixed gas environment. **Figure 1a** indicates a maximum CO₂ adsorption in NiBpene of just over 3 CO₂ molecules per formula unit at 303 K.^[70,78] **Figure 1b** indicates a maximum CO₂ adsorption in NiDBM-Bpy of ≈ 1.5 CO₂ molecules per formula unit at 303 K. This difference partly reflects the fact that NiBpene has more pore volume per unit cell in its structure than does NiDBM-Bpy. In what follows, we have applied diffraction-based methods, including small-angle scattering, to investigate possible underlying structural and microstructural changes that occur during the adsorption and desorption of CO₂ and CO₂/N₂ mixtures.

Previous work has established the crystal structures of the open pore guest-loaded phases of the NiBpene and NiDBM-Bpy structures.^[78,79] In the case of NiBpene, dimethyl sulfoxide (DMSO) solvent loaded NiBpene structure^[78] adopts a monoclinic unit cell with space group $P2_1/m$, $a = 1.35941(12)$ nm, $b = 1.43621(12)$ nm, $c = 1.42561(12)$ nm, $\beta = 96.141(2)^\circ$, $V = 2.7674(4)$ nm³, $Z = 4$, $D_c = 1.46$ g cm⁻³. **Figure 2** depicts the open-pore structure (with additional Bpene ligands in the open pore and disordered DMSO solvent and water molecules not shown). The guest solvents and guest Bpene molecules are removed by a solvent extraction process and degassing

procedure prior to gas adsorption measurements to give a guest free material.^[78,79] The framework is based on a 2-D infinite layer-like tetracyanonickelate $[\text{Ni}(\text{CN})_4]^{2-}$ planar complex. The layers are pillared by the Bpene ligands, which occupy the axial positions of the $[\text{NiN}_6]$ octahedron. These Bpene ligands further bridge together the 2-D $\text{Ni}[\text{Ni}(\text{CN})_4]$ sheets to form the 3-D pillared-layered structure. **Figure 3a** shows the schematic of the 3D porous structure formed by pillaring planar nickel cyanide networks with a quasi-linear bidentate ligand, 1,2-bis(4-pyridyl)ethylene (Bpene). Accompanied by other more general structural changes, the interlayer spacing (*d*-spacing) expands or contracts on adsorption or desorption of CO_2 gas molecules.

NiDBM-Bpy is another interesting class of smart sorbent that exhibits wide variability in structure and displays selectivity among guest molecules. The structure of NiDBM-Bpy consists of a ladder-and-platform motif (shown in **Figure 2**) that gives rise to an efficient parallel packing of the 1-D parallel chain, yet it provides space for accommodating guest species. The DBM ligands or fragments correspond to the disks (paddle wheels) in **Figure 2b**. The DBM fragment has a flexible architecture that can be easily converted from one structure to another (can be planar, twisted, or bent depending on the guest molecules present).^[71-76,79] The guest species fill the residual pocket space between the DBM fragments and form van der Waals contact with each other and with the host. The disks are linked by the Bpy molecules.

From the general structures of NiBpene and NiDBM-Bpy, it can be seen that the dimensionality and degree of structural freedom, which can change in response to guest incorporation, differ dramatically for the two systems, even though they have comparable shapes in their CO_2 isotherms at 303 K. For example, as an interconnected three-dimensional network, the NiBpene

compound might be expected to expand and contract through a more complex mechanism involving changes in bond angles between network components. In this situation, a change in one part of the structure may force a change in an entire domain due to the bonding requirement of the interconnected network. In contrast, the NiDBM-Bpy compound, which has a series of independent one-dimensional chains interacting through weaker van der Waals forces, might be expected to expand through a more random swelling mechanism where independent chains simply move apart to allow the inclusion of guests. The complex thermodynamics involved with the guest adsorption and structure transition in a flexible compound ultimately must influence the adsorption selectivity of that compound. Thus, study of the contrasting structure transition mechanisms in NiBpene and NiDBM-Bpy can provide insights into how the nature of the structure transitions influences material performance. In this connection, and building on the previous structure characterizations ^[78,79], an initial assessment of the crystal structure transitions occurring between the open pore guest-loaded phases and the closed pore guest-free phases in NiBpene and NiDBM-Bpy was made using *ex situ* laboratory-based X-ray diffraction (XRD).

Figure 4 presents XRD data for dry (previously evacuated) NiBpene and NiDBM-Bpy under ambient conditions, together with the proposed Bragg peak *hkl* index assignments for the main peaks measured. (Note: *all* peaks measured were accounted for in both XRD patterns.) The small angle diffraction peaks marked with red arrows are those most directly associated with lattice spacings that expand and contract, respectively, during adsorption and desorption of molecular guests within the structure. However, in principle, the entire structures can exhibit changes and even phase transformations during the adsorption and desorption of guest molecules. The NiBpene index assignments correspond to those from a recent single-crystal *a priori* structure determination using synchrotron-based XRD measurements of a small single-crystal

sample that was successfully grown, containing dimethyl sulfoxide (DMSO) guest molecules, work reported elsewhere.^[78] To date, it has not been possible to obtain small single crystals of NiDBM-Bpy sufficient in size for a similar *a priori* structure determination. As a result, the NiDBM-Bpy XRD indexing here is derived from unit cell parameters previously found for NiDBM-Bpy containing dimethyl formamide guest molecules.^[76] While the absolute lattice parameters and bond angles are measurably different for the NiBpene and NiDBM-Bpy structures, measured under ambient conditions without solvent, we assume these structures comprise reasonable low-pressure starting points for our *in situ* CO₂ adsorption studies.

A summary of our working assumptions for the low-pressure NiBpene and NiDBM-Bpy structures are given in **Table 1**. Using these lattice parameter values, the *d*-spacing corresponding to the first Bragg diffraction peak (001) marked in **Figure 4** for NiBpene in the dry state is ≈ 1.14 nm. For NiDBM-Bpy, the corresponding *d*-spacing for the first peak (002) in the dry state is ≈ 1.25 nm. With reference to **Figure 3**, we note that diffraction measurements of either compound in a truly evacuated state might reveal modifications to these structures, due to a complete collapse of the pillars in NiBpene, or a full coalescence of the chains in NiDBM-Bpy.

3.2. *In Situ* Neutron Diffraction Results

Figure 5a presents *in situ* neutron diffraction patterns for NiBpene during progressive CO₂ desorption at 258 K (−15 °C) together with the corresponding sorption isotherm curves.

Measurements were first made under vacuum at 20 K (this condition is optimum for data quality with the smallest Debye-Waller factor, giving well-defined Bragg peaks), then at 258 K under 5 bar CO₂ (sufficient to give the maximum CO₂ adsorption measured at 258 K), and then we

progressively reduced the CO₂ pressure to show the changes during desorption. The corresponding isotherm curve at 258 K is shown for comparison in **Figure 5b**. To date, attempts to index and fit these patterns to pertinent structure models, as a function of CO₂ adsorbed or desorbed, have not succeeded due to the diffraction peaks being few and the peak widths being broad (even though some peaks can be associated with those indexed in **Figure 4a**, as shown, especially for the 0.5 bar CO₂ data). It has not been possible to arrive at satisfactory structural refinement results in general. These must await further synchrotron-based single-crystal X-ray diffraction *in situ* studies of both NiBpene and NiDBM-Bpy under realistic CO₂ gas pressure conditions. For now we note that, qualitatively, the diffraction patterns shown in **Figure 5a**, labeled 1, 2, 3, 4, can be associated with the correspondingly numbered places on the desorption isotherm. We also note that several structural changes affecting the whole diffraction pattern can be discerned during desorption, and that these correspond to different features in the desorption curve. The three lowest angle small-angle diffraction peaks are indicated. One of these, the lowest angle peak for the sample under vacuum at 20 K, suggests that the prevalent NiBpene structural phase under vacuum and low CO₂ pressure transforms to a different phase (where this peak appears much suppressed) in the presence of significant adsorbed CO₂. The other two peaks demonstrate a decrease in lattice spacing as CO₂ is desorbed, but also a decrease in intensity. We note that the 001 peak is absent for the fully evacuated case, possibly associated with a collapse in the pillar structure shown in **Figure 3a**.

It was not possible to obtain *in situ* neutron diffraction patterns for NiDBM-Bpy during progressive CO₂ desorption. This is because of the much weaker neutron diffraction peak intensities compared to NiBpene. Fortunately, preliminary *in situ* X-ray diffraction data have been obtained recently from NiDBM-Bpy powder for the case of CO₂ desorption at 303 K

(30 °C). These data have been obtained at the ultra-small-angle X-ray scattering (USAXS) facility at the Advanced Photon Source (APS), Argonne National Laboratory, IL.^[87,88] (See **Supplementary Material, Figure S4**). As with NiBpene, it is possible to associate the observed peaks at low CO₂ pressures with those indexed in **Figure 4b**. These data indicate that, unlike the case of NiBpene, several peaks of NiDBM-Bpy simply shift in scattering angle during CO₂ desorption. Some peaks may split in the presence of adsorbed CO₂, and there is clearly a modification in the overall structure during desorption as the CO₂ pressure is reduced from 8 bar to 6 bar, which corresponds to the minor step feature in the NiDBM-Bpy desorption curve (**Figure 1b**). However, the more comprehensive phase transformations, indicated by the NiBpene data of **Figure 5a**, are less evident.

3.3. *In Situ Small-Angle Neutron Scattering Results*

In situ SANS measurements were performed to follow the behavior of the lowest angle diffraction peaks through the adsorption/desorption cycles of both materials. **Figure 6** shows changes in the first small-angle neutron diffraction peak (occurring at the lowest scattering angle) as a function of pure CO₂ adsorption and desorption for NiBpene (**a, b**) and for NiDBM-Bpy (**c, d**). These measurements were carried out at 303 K (30 °C), consistent with the isotherm measurements of **Figure 1**. The *d*-spacing and intensity variations derived from **Figure 6** are compared with the adsorption isotherms in **Figure 7**, again for NiBpene (**a, b**) and for NiDBM-Bpy (**c, d**). It is immediately clear from these plots that, even though the pressure ranges associated with the isotherm curves of NiBpene and NiDBM-Bpy are similar, NiBpene exhibits a greater range of variation both in Bragg peak intensity and in the range of *d*-spacing variation, particularly during desorption.

Figure 7 shows that the NiBpene *d*-spacing does not follow the sorption isotherms as would be expected for a simple expansion and contraction of the pore structure to accommodate guest molecules, whereas the Bragg peak intensity does do so, at least qualitatively. Once the pressure is sufficient for CO₂ adsorption, the inter-layer *d*-spacing for NiBpene increases from ≈ 1.24 nm at 6 bar to ≈ 1.30 nm at 17 bar where the maximum amount of CO₂ is adsorbed. However, on desorption, the *d*-spacing can be followed down to as low as 1.17 nm at 5 bar, indicating there is a strong hysteresis effect in NiBpene desorption. Meanwhile, the NiBpene Bragg peak (001) intensity is significantly enhanced by the presence of adsorbed gas molecules following the onset of the adsorption gate opening process at ≈ 6 bar CO₂. Indeed, there is a significant increase in Bragg peak intensity, directly related to the amount of CO₂ gas adsorbed, with a corresponding decrease during desorption. These results are consistent with the ND results of **Figure 5**, which also show the (001) *d*-spacing varies in a similar quantitative fashion during CO₂ desorption. Allowing for the different temperatures used in the measurements, the diffraction patterns (1, 2, 3, 4) measured during desorption at 258 K correspond to CO₂ applied pressures of ≈ 15 bar, 9 bar, 6 bar and 4 bar, respectively, at 303 K. Consistent with **Figure 5** at 258 K, the (001) diffraction peak position at 303 K, shown in **Figure 6** and **Figure 7**, indicates a *d*-spacing that remains > 1.15 nm for CO₂ pressures > 2 bar. These numbers are also consistent with the XRD results of **Figure 4** indicating a *d*-spacing of 1.14 nm under ambient dry conditions. In the NiBpene SANS results, the (001) Bragg peak intensity all but disappears for the evacuated case, consistent with the previous result for ND under vacuum (**Figure 5a**). This suggests that the pillar structure visualized in **Figure 3a** may indeed collapse in the complete absence of guest molecules within the structure. Despite the changes in Bragg peak intensity, measurable broadening of the Bragg peak width can only be discerned at intermediate CO₂ pressures during desorption.

Taken collectively these data suggest a complex set of structural changes occur during CO₂ adsorption and desorption. Instead of the simple expansion and contraction of the (001) *d*-spacing with correlated tilting of aligned NiBpene organic spacer molecules to transition between the α - and β -phases shown in the idealized picture of **Figure 3**, we anticipate that orientational ordering of the ligands occurs with the (001) expansion, together with other structural changes (including those associated with guest interactions with framework molecules). The lattice parameters of the powder NiBpene sample without DMSO molecules were determined to be $P2_1/m$, $a = 1.377(4)$ nm, $b = 1.473(7)$ nm, $c = 1.239(3)$ nm, $\beta = 113.0(2)^\circ$, $V = 2.3144$ nm³. While the lattice parameters of those of the single crystal NiBpene with inclusion of DMSO and water ($a = 1.35941(12)$ nm, $b = 1.43621(12)$ nm, $c = 1.42561(12)$ nm, $\beta = 96.141(2)^\circ$, $V = 2.7674(4)$ nm³) are similar, the β angles of the two monoclinic unit cells are significantly different. The β angle decreases from $113.0(2)^\circ$ to $96.141(2)^\circ$ with guest inclusion. The proposed schematic model of a flexible crystal structure (α -phase) opening up the unit cell as guest molecules are included (β -phase) is shown in **Figure 3a**.^[70,78] While the details of such a mechanism need to be further tested, this type of transformation could lead to the significant changes in (001) *d*-spacing observed, as well as the increased Bragg peak intensity after the structural gate opens to adsorb CO₂. Future work will focus on more detailed, *in situ*, studies to confirm the proposed schematic mechanism.

Some of the unexpected trends observed for NiBpene may be attributable to the presence of a residual amount of “free-Bpene” ligand within the NiBpene unit cell, as discussed earlier using single-crystal XRD.^[78] While the extraction and activation procedure is quite effective at

removing guests from the structure, complete extraction of low volatile guests from porous compounds is a well-known problem and as such, the presence of traces of residual guests in the material must be considered. The presence of any residual free Bpene ligand would occupy potential CO₂ adsorption sites and would add a stabilizing force to form small domains of the expanded structural phase that would modify some of the effects observed. The effects of different structural phases transforming among themselves during adsorption and desorption also should not be neglected. In this connection, we note that the four neutron diffraction patterns occurring for NiBpene CO₂ desorption at 258 K, 1, 2, 3 and 4, shown in **Figure 5**, appear to represent three distinct structural phases occurring during desorption at 5 bar CO₂ (1), 1 bar CO₂ (3), and under vacuum, with the diffraction patterns at 1.5 bar CO₂ (2) and 0.5 bar CO₂ (4) indicating mixed phases. The transformations occur at higher desorption pressures at 303 K. On comparing **Figure 1a** and **Figure 5b** the corresponding CO₂ desorption pressures at 303 K would be: (1) 15 bar, (2) 9 bar, (3) 6 bar, and (4) 4 bar.

In contrast to NiBpene, the lowest angle NiDBM-Bpy *d*-spacing probed by small angle neutron diffraction (**Figure 6**) follows the sorption isotherm curve closely. This *d*-spacing increases reversibly from ≈ 1.24 nm for evacuated DBM to ≈ 1.33 nm for full CO₂ adsorption – a comparable increase to that found for NiBpene during adsorption, although less than the change observed during desorption in NiBpene. The variation in Bragg peak intensity correlates only approximately to the isotherm curve and it remains significant for all CO₂ pressures, as apparent in **Figure 6** and **Figure 7**. These observations suggest that the structure varies more uniformly with regard to CO₂ adsorption/desorption, perhaps with no major phase transformations during either adsorption or desorption. These findings are interesting in comparison to those for NiBpene where the *d*-spacing and intensity trends are the opposite of the NiDBM-Bpy case. The

d-spacing results clearly illustrate the role of the lattice expansion and contraction in gate opening for CO₂ adsorption in NiDBM-Bpy. The 1-D structure of the NiDBM-Bpy chains affords significant degrees of freedom for lattice contraction in the 002 direction, while the general crystal ordering is not expected to change much due to the relatively rigid nature of the Bpy linkers. Thus, the mechanism for NiDBM-Bpy appears to be more of a gradual swelling as the 1D chain separation increases with CO₂ uptake. Based on previous *in situ* Fourier Transform – infrared (FT-IR) studies, this mechanism proceeds through conformational changes in the DBM ligand as CO₂ is adsorbed.^[79] It is quite likely that CO₂ is adsorbing into similar adsorption sites as those occupied by dimethylformamide (DMF) molecules in the crystal structure of [NiDBM-Bpy]·(DMF), and thereby initiating an expansion along the *c*-axis in the crystal lattice shown in **Figure 2b**.

While it is expected that the CO₂ adsorption properties of NiBpene and NiDBM-Bpy depend primarily on their internal structures, which potentially offer an extremely high surface area for CO₂ adsorption ($\approx 1000 \text{ m}^2/\text{cm}^3$), the fineness of the powder grain morphology may also play a significant role when liquids, e.g., water or water vapor are present, and the powder grains are pressed together under pressure. Ability to purge the sorbent structure of impurity molecules may also depend on powder grain morphology. In the **Supplementary Material (Figure S5 and Figure S6)**, combined SANS and ultrasmall-angle neutron scattering (USANS) results over a scattering vector magnitude, Q , range from 0.0003 nm^{-1} to $> 3 \text{ nm}^{-1}$ are presented, together with size distribution results derived from applying the entropy maximization routine, MaxEnt, to the data.^[89] These results show that NiBpene possesses a significantly finer grain morphology than does NiDBM-Bpy, but both systems contain significant fine structure and porosity within the powder grains. Recently, combined SAXS and ultra-small-angle X-ray scattering (USAXS) *ex*

in situ studies of loosely packed powders have confirmed these points and suggest even finer structures that extend continuously down in scale to the crystalline structures proposed in **Figure 2** (see **Supplementary Material, Figure S4** and **Figure S7**).^[87,88] Future *in situ* SAXS measurements hold promise for measuring several low-angle diffraction peaks at once, at least over part of the adsorption pressure range of interest. For the present we confine the remainder of our discussion to our *in situ* SANS results.

3.4. Results for Dual Gas CO₂/N₂ Adsorption / Desorption Isotherms

In situ SANS measurements of the small-angle diffraction peaks were also made under pressure using a mixed 50/50 CO₂/N₂ gas atmosphere to quantify how the structures of NiBpene and NiDBM-Bpy respond compared to the case of pure CO₂ adsorption. These measurements elucidate the role of structure on the selective adsorption recently documented for the NiDBM-BPy system.^[77] Since the adsorption of guests in the structure is known to stabilize the open pore network,^[30-33,42-49,90,91] different guests can be expected to show discernible structural differences when adsorbed into the pore system. Such an effect is well demonstrated when comparing the XRD results reported for NiDBM-Bpy loaded with CH₄^[75] to the SANS results reported here for NiDBM-Bpy loaded with CO₂. For NiDBM-Bpy(CH₄), the adsorption of CH₄ results in a splitting of the (002) diffraction peak, with the original peak position preserved and a new peak appearing with ≈ 0.1 nm larger *d*-spacing. As the CH₄ is desorbed, the larger *d*-spacing peak maintains its position, only losing intensity and eventually vanishing as all of the CH₄ is desorbed. The adsorption and desorption of CO₂, however, follows a different mechanism as shown in **Figure 6**, which indicates a gradual shift of ± 0.1 nm in the (002) peak

lattice spacing during adsorption and desorption of CO₂. Similar differences might occur between pure and mixed gas adsorption and provide insight into the adsorption selectivity.

Figure 8 presents small-angle diffraction peaks measured *in situ* under 17 bar CO₂, 17 bar N₂, and a mixed 35 bar of equimolar CO₂/N₂ pressure conditions at 303 K (30 °C) for both NiBpene and NiDBM-Bpy. In NiBpene the increase in linker *d*-spacing to accommodate the CO₂ guest molecules is reduced in a 50/50 CO₂/N₂ mix from that measured for pure CO₂ with the same partial pressure. The Bragg peak intensity is also reduced. In NiDBM-Bpy the full increase in linker *d*-spacing is observed for the given CO₂ partial pressure, and the Bragg peak intensity is not diminished from that found under 17 bar of CO₂ alone. We also note that pure N₂ does not initiate the opening of either structure for adsorption at these pressures at 303 K.

The *d*-spacing and intensity changes noted for the NiBpene peak indicate different structural changes are occurring as a result of mixture adsorption in comparison to pure gas adsorption. This suggests that the presence and adsorption of an equimolar gas mixture containing 17 bar CO₂ and 17 bar N₂ fundamentally changes how the crystal structure opens and is stabilized compared to adsorption of pure CO₂ at 17 bar. Barrer ^[42-44] and Coudert ^[45-47] have both illustrated how guest adsorption lowers the thermodynamic potential of structurally dynamic sorbents, thus stabilizing higher porosity states in the solid. Our data seem to indicate that we are seeing this mechanism manifest itself during the adsorption of CO₂ and N₂. Further experiments at NETL will evaluate whether or not these structural changes impact the selective adsorption of CO₂ from mixtures with N₂.

The comparative absence of major structural phase changes in NiDBM-Bpy during mixed gas adsorption (as in pure CO₂ adsorption) also provides important insights regarding the gas mixture dynamics within this material. The data in **Figure 8b** show no discernible phase changes affecting the DBM linkers for the system during adsorption of pure CO₂ or mixtures of CO₂/N₂. Previous *in situ* FTIR studies have also shown a similar lack of conformational change in the DBM linkers during dynamic adsorption either of pure CO₂ or of CO₂ mixtures with N₂, CH₄, and N₂O.^[79] Collectively, the SANS and *in situ* FTIR point to a NiDBM-BPy compound whose structural gate-opening and subsequent stabilization of the open pore framework are relatively insensitive to gas mixtures, being driven predominately by CO₂ partial pressure. This result is significant because it suggests the open pore network is well-stabilized by CO₂ adsorption, and this could underlie selective CO₂ adsorption from mixtures in this system.

4. Conclusions

In this paper we have analyzed the CO₂ adsorption/desorption behavior of two flexible MOFs with very different coordination networks but similar CO₂ adsorption threshold pressures and broadly similar desorption hysteresis (apart from the different prominence of the step features). While their CO₂ adsorption/desorption isotherms are similar in basic shape, the expanded 3-D network of NiBpene affords a larger ultimate pore volume than the 1-D NiDBM-Bpy material where guest adsorption occurs within interstitial spaces between polymer chains. Despite their nearly identical isotherm threshold pressures, *in situ* SANS and neutron diffraction measurements indicate that their respective adsorption mechanisms are fundamentally different. This difference likely results from the available degrees of freedom and the chemical nature of the framework material within the two structures. For simplicity, the 1-D chain structure of

NiDBM-Bpy can proceed through a smoother swelling process where the relative crystal coherence of the material changes little as the amount of CO₂ adsorbed increases and only the *d*-spacing between the lattice planes is significantly affected. The rigid interlinked 3D network of NiBpene, however, shows evidence of domain growth and ligand reorientation occurring throughout the adsorption process. This results in a higher degree of structural coherence once saturated with CO₂. Furthermore, SANS measurements using binary gas mixtures of CO₂/N₂ indicate that the different mechanisms operating within NiDBM-Bpy and NiBpene materials may be influencing the gas adsorption selectivities of the two compounds. The diffraction peak for NiDBM-Bpy is identical in shape and position under the same partial pressures of CO₂ in pure and CO₂/N₂ mixtures. However, the diffraction peak shape and position of NiBpene is different under the same partial pressures of CO₂ in pure and CO₂/N₂ mixtures, indicating some degree of co-adsorption of N₂. These intriguing differences in mechanisms between the two materials with such similar CO₂ adsorption/desorption isotherms offer an opportunity to study the influence of structure on adsorption selectivity in flexible MOFs.

We conclude by noting that both NiBpene and NiDBM-Bpy belong to material classes where aspects of the structure can be adjusted in a controllable way.^[70-76] Controllable aspects include the length of the linker *d*-spacing and consequent size of the void spaces available for CO₂ adsorption, the fineness of the powder grain morphology, and the concentration of synthetically incorporated impurity guest species that reduce the dynamically available space for CO₂ adsorption/desorption. Such materials and material classes can be optimized through a materials-by-design approach. Currently lacking is a sufficiently powerful numerical modeling capability to relate the complex multiple-gas adsorption and desorption properties to equally

complex, dynamically variable material structures. Once such modeling capabilities are fully established, measurements of CO₂ adsorption efficiency and selectivity could be combined with diffraction-based crystal structure and *in situ* microstructure characterization to gain insights leading to optimized CO₂ solid sorbent design.

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Table 1. Crystal symmetries and lattice parameters for NiBpene and NiDBM-Bpy.

Symmetry and lattice parameters	NiBpene dry	NiDBM-Bpy dry
Symmetry:	monoclinic, <i>P21/m</i>	monoclinic, <i>C2/m</i>
<i>a</i> [nm]:	1.377(4)	1.1441(2)
<i>b</i> [nm]:	1.473(7)	1.1988(1)
<i>c</i> [nm]:	1.239(3)	2.5610(1)
α :	—	—
β :	113.0(2)°	110.17(1)°
γ :	—	—
<i>V</i> [nm ³]:	2.314(14)	3.297(1)
<i>Formula</i> :	C ₁₆ H ₁₀ N ₆ Ni ₂	C ₄₀ H ₃₀ N ₂ O ₄ Ni
<i>Molecular mass</i> (g)	403.68	661.38

¹Computed or estimated standard deviation uncertainties are given in parentheses in least significant digits.

Figure Captions:

Figure 1. Pure CO₂ mass adsorption and desorption isotherms at 303 K (30 °C) for (a) NiBpene and (b) NiDBM-Bpy. Measurement uncertainties at each data point are smaller than the symbols used. Sample uncertainties are likely to be larger. At 303 K NiBpene adsorbs up to ≈ 3.25 CO₂ molecules per sorbent formula unit while NiDBM-Bpy adsorbs up to ≈ 1.5 CO₂ molecules per sorbent formula unit.

Figure 2. Crystal structures of the expanded phase of (a) NiBpene^[78] and (b) NiDBM-Bpy^[76]. Guest molecules in both structures are removed for clarity. The *d*-spacings that vary with guest loading are indicated by arrows. In (b) the structure on the left shows the single chain structure of NiDBM-Bpy, while the image on the right is a view down the Ni-Bpy chain axis showing the layered arrangement of parallel chains.

Figure 3. Schematic showing the proposed guest induced structure transition in (a) NiBpene and (b) NiDBM-Bpy. The one dimensional chain structure of NiDBM-Bpy provides more degrees of freedom for structure expansion than the rigid interconnected structure of NiBpene.

Figure 4. Lab-based XRD patterns for (a) NiBpene and (b) NiDBM-Bpy under ambient conditions with proposed Bragg peak index assignments shown for the main peaks. All peaks measured were accounted for in both patterns. The lowest angle diffraction peaks, marked with the red arrows, are those most directly associated with the expanding and contracting lattice spacings during adsorption/desorption of molecular guests within each structure, and these are the peaks followed in the SANS measurements. The *Q* ranges plotted correspond to 2θ angular ranges of 5° to 45° for NiBpene, and 5° to 40° for NiDBM-Bpy.

Figure 5. (a) *In situ* neutron diffraction patterns during progressive CO₂ desorption for NiBpene at 258 K (−15 °C) together with (b) adsorption/desorption isotherm curves for NiBpene at the same temperature. Note the changes in diffraction pattern, 1, 2, 3, 4, corresponding to different parts of the desorption isotherm, as labeled. In (a) some peaks that can be associated with those indexed in **Figure 4a** are indicated. The red arrow indicates the peak followed in the SANS measurements.

Figure 6. Small-angle neutron diffraction peak variations as a function of pure CO₂ adsorption and desorption, measured *in situ* at 303 K (30 °C) for (a, b) NiBpene and (c, d) NiDBM-Bpy. The plots have been displaced vertically for greater clarity. Measurement uncertainties at each data point, determined by standard SANS data reduction procedures, are consistent with the scatter in the data. Overall uncertainties due to sample or isotherm variations may be greater.

Figure 7. Variations in expandable linker *d*-spacing and associated Bragg peak intensity compared to CO₂ adsorption/desorption isotherms for (a, b) NiBpene and (c, d) NiDBM-Bpy. All measurements made at 303 K (30 °C). The vertical bars at each data point represent the estimated or measured standard deviation uncertainties but, for the *d*-spacing measurement, these uncertainties are frequently smaller than the symbol at each data point – as evident in (b) and (c).

Figure 8. Small-angle diffraction peaks under 17 bar CO₂, 17 bar N₂, and mixed 35 bar CO₂/N₂ pressure conditions, *in situ* at 303 K (30 °C) for (a) NiBpene and (b) NiDBM-Bpy.^[77] Once again the plots have been displaced vertically for greater clarity, measurement uncertainties at each data point are consistent with the scatter in the data shown. Overall uncertainties due to sample or isotherm variations may be greater. (Despite initial pressure cycling of both samples, the data for NiBpene in vacuum exhibits a small peak, suggesting that some guest molecules, adsorbed when the sample was exposed to ambient conditions have not been removed.)

Flexible metal-organic framework compounds: *in situ* studies for selective CO₂ capture

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Graphical Abstract Synopsis:

We present *in situ* small-angle neutron scattering results for two flexible metal-organic frameworks (MOFs). The figure shows that for one (NiBpene, high CO₂ adsorption) the intensity of the Bragg peak for the expandable *d*-spacing most associated with CO₂ adsorption varies approximately with the isotherm, while for the other (NiDBM-Bpy, high CO₂ selectivity) the *d*-spacing, itself, varies with the isotherm. The cartoons show the proposed modes of structural change.

(a)

(b)

(a)

(b)