CO_2-Selective Adsorption

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Selective Adsorption of CO_2 from Light Gas Mixtures by Using a Structurally Dynamic Porous Coordination Polymer**

*Kristi L. Kauffman, Jeffrey T. Culp, Andrew J. Allen, Laura Espinal, Winnie Wong-Ng, Thomas D. Brown, Angela Goodman, Mark P. Bernardo, Russel J. Pancoast, Danielle Chirdon, and Christopher Matranga**

Gas separations are important to many diverse areas of fossil energy including pre- and post-combustion CO_2 capture and fuel cell applications. The need for efficient gas purification processes has led to interest in adsorption-based separations and new sorbent materials. Porous coordination polymers (PCPs), commonly referred to as metal–organic frameworks (MOFs), lend a great deal of structural versatility to such applications.[1] A combination of organic and inorganic building blocks, these multi-dimensional hosts can be tailored for selective adsorption of one guest over another through methods such as pore-size exclusion, mesh-size adjustable sieving, and guest-dependent structural dynamics.[1,2]

The numerous reports on structurally dynamic PCPs illustrate the potential of these materials for adsorption applications yet there are only a few reports demonstrating actual gas separations.[1,3] A structural breathing phenomenon in the MIL-53 family of MOFs was found to have a significant role in the ability of this sorbent to separate CO_2 and CH_4.[3b,4] Despite the detailed studies of MIL-53, there are currently no experimental or theoretical methodologies to predict gas selectivities in other structurally dynamic systems or to indicate how generally applicable the MIL-53 separation mechanism may be. Additional studies with actual gas mixtures are needed to advance our theoretical and empirical understanding of structurally dynamic PCPs.

Much of the literature on selective adsorption in PCPs is based on the prediction of a separation extrapolated from pure gas isotherms or calculations from the ideal adsorbed solution theory (IAST), not from actual experimental observations.[1] Recent publications point out that the use of IAST to predict selectivies in structurally dynamic PCPs can be complicated by the possibility of cooperative adsorption effects, indicating the need for new fundamental insight into how specific structurally dynamic PCPs selectively adsorb gases.[1b,5] While one computational study has investigated the role of stepped isotherms in the separation of CO_2/N_2 mixtures,[6] most models only address single-component adsorption. Recent reviews highlight the lack of fundamental understanding of gas-selective adsorption in these sorbents, indicating the need for experiments and theoretical calculations to shed light on this important phenomenon.[1]

Perhaps the most crucial mechanistic issue to address in structurally dynamic systems surrounds what happens to gas interactions with the sorbent before and after the transition between states of differing porosity. The gas- and temperature-dependent threshold pressures (P_{th}), above which a rapid rise in gas uptake is noted in most structurally dynamic PCPs, has led many to hypothesize this process could be used to selectively adsorb gases. Yet others have cautioned it could lead to cooperative adsorption where one gas initiates and stabilizes the structural transition, allowing all other gases in the mixture equal access to the open pore network, thus negating the selective aspect of the threshold pressure/temperature.[1,5] In short, there is uncertainty in the literature about whether or not the mere presence of a threshold pressure or "gate opening effect" for one gas species at a given pressure/temperature guarantees selectivity over another gas which does not initiate this "gate opening" at the same pressure/temperature. Currently, there are no theoretical or empirical formalisms which can be used to predict when cooperative adsorption may occur.

The data presented here indicates that selectivity results from the structural transition in catena-bis(dibenzoylmethanato)-(4,4′-bipyridyl)nickel(II), referred to as "NiDBM-Bpy" (Figure 1, right, and Figure S1 in the Supporting Information), for the CO_2, N_2, and CH_4 mixtures reported here. There

[*] Dr. K. L. Kauffman, Dr. J. T. Culp, T. D. Brown, Dr. A. Goodman, M. P. Bernardo, R. J. Pancoast, D. Chirdon, Dr. C. Matranga
National Energy Technology Laboratory, United States Department of Energy
P.O. Box 10940, Pittsburgh, PA 15236 (USA)
E-mail: christopher.matranga@netl.doe.gov
Dr. J. T. Culp
URS, P.O. Box 618, South Park, PA 15129 (USA)
Dr. A. J. Allen, Dr. L. Espinal, Dr. W. Wong-Ng
National Institute of Standards and Technology
United States Department of Commerce
Gaithersburg, MD 20899 (USA)

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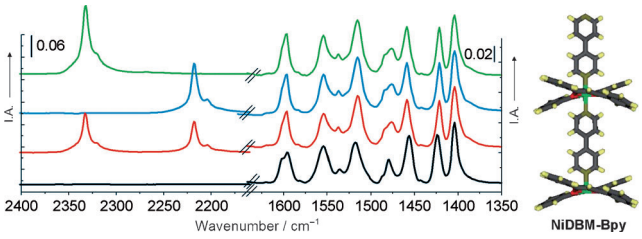

Figure 1. Left: Representative spectra of the ν_3 antisymmetric stretching region (2400–2200 cm^{-1}) of adsorbed gases and the aromatic bending mode (1650–1350 cm^{-1}) of NiDBM-Bpy at 30 °C (303 K) and P_s: vacuum (black), 50/50 CO_2/N_2O (red), N_2O (blue), CO_2 (green). I.A. = integrated area. Right: A view showing an isolated chain of NiDBM-BPY. C, gray; H, yellow; O, red; N, orange; Ni, green.

appears to be a thermodynamic driving force for the selective inclusion of CO_2 into NiDBM-Bpy over both N_2 and CH_4. An understanding of the mechanism behind this selectivity will help researchers determine the structural, energetic, and mechanistic reasons for this behavior, thus enabling the development of new dynamic sorbent systems for separation applications.

NiDBM-Bpy was chosen because of its dynamic behavior[7] and our previous in situ FTIR investigations show a structural transition accompanies the rapid rise in gas uptake at P_{th}.[8] In situ FTIR (Supporting Information)[9] allows guest and sorbent vibrations to be probed simultaneously (Figure 1). Adsorption isotherms can be generated using the integrated area (I.A.) of the CO_2 (2333 cm^{-1}) or N_2O (2218 cm^{-1}) ν_3 anti-symmetric mode normalized to characteristic sorbent bands (1328–1650 cm^{-1}) (Figure 1). In situ IR determined isotherms for 50/50 partial pressure mixtures (red) of CO_2/N_2, and CO_2/CH_4 on NiDBM-Bpy as compared to pure CO_2 isotherms (black) are shown in Figure 2. Observed P_{th} values are summarized in Table S1 (Supporting Information). CO_2 uptake proceeds with a pronounced step beyond P_{th} and a large desorption hysteresis for all mixtures studied. For the CO_2/N_2 and CO_2/CH_4 mixtures, the partial CO_2 pressure (P_{CO_2}) at P_{th} was equivalent to that of pure CO_2 (Figure 2 a,b), indicating that CO_2 uptake is a function of P_{CO_2} rather than the total pressure (P_{tot}) for these mixtures. Conversely, if the isotherms are plotted as a function of the total pressure, the threshold pressures for these mixtures are roughly double that of pure CO_2 (Figure 2 c,d and Table S1). Multiple spectra taken at a saturation pressure (P_s) where NiDBM-Bpy is saturated with guest molecules, show that the CO_2 saturation coverage for both the CO_2/N_2 and CO_2/CH_4 mixtures is identical to what was obtained in pure CO_2 (Table S2). Because the normalized CO_2 coverage at saturation in the mixture matches that of pure CO_2, we conclude that NiDBM-Bpy preferentially adsorbs CO_2 over both N_2 and CH_4 without displacement of CO_2. No significant changes were observed in the position or line shape of the CO_2 ν_3 asymmetric stretch, indicating the environment for adsorbed CO_2 is unaltered in the mixture experiments. The fact that P_{CO_2} at P_{th} is independent of composition for both the CO_2/N_2 and CO_2/CH_4 mixtures suggests that N_2 and CH_4 have little impact initiating or stabilizing the NiDBM-Bpy structural transition at these conditions.

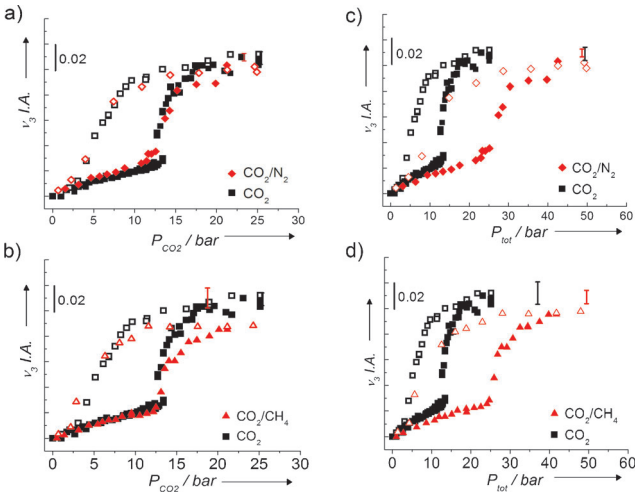

Figure 2. IR adsorption (solid) and desorption isotherms (open) at 30 °C (303 K) generated from the normalized integrated area (I.A.) of the CO_2 ν_3 anti-symmetric stretch for 50/50 binary mixtures of a,c) CO_2/N_2 (red diamonds) and b,d) CO_2/CH_4 (red triangles) as compared to pure CO_2 (black squares). Panels (a) and (b) are plotted versus CO_2 partial pressure (P_{CO_2}), while panels (c) and (d) are plotted versus total pressure (P_{tot}). In this and following figures, the vertical bars represent standard deviation uncertainties ($N = 5$) at the saturation pressure (P_s).

The IR adsorption isotherm for a 50/50 mixture of CO_2/N_2O on NiDBM-Bpy at 30 °C (303 K) is shown in Figure 3. The CO_2 ν_3 band was used to generate the isotherm displayed in Figure 3 a while panel b shows the N_2O ν_3 band of the mixture compared to the isotherm of pure N_2O (blue). In contrast to that of pure CO_2 and N_2O, the normalized saturation coverage from the mixture is significantly less than the pure feed (Table S2). In fact, the integrated intensities at saturation for CO_2 and N_2O are both approximately half that of their pure gas values. The IR generated isotherms illustrate that both CO_2 and N_2O coadsorb in this framework in a competitive fashion. N_2O was chosen to test the limits of selectivity in NiDBM-Bpy because it is similar to CO_2 in size and physical properties. The kinetic diameter of both gases is 3.3 Å. The critical temperature for N_2O is 309.57 K and 304.14 K for CO_2 while the boiling point of N_2O is −88.5 °C (184.7 K) and the sublimation temperature for CO_2 is

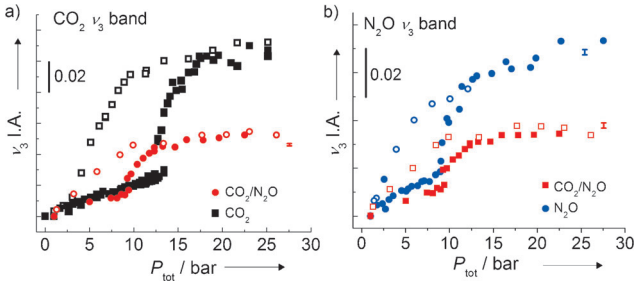

Figure 3. IR adsorption (solid) and desorption isotherms (open) at 30 °C (303 K) generated from the normalized integrated area (I.A.) of the a) CO_2 and b) N_2O ν_3 anti-symmetric mode for a 50/50 mixture of CO_2/N_2O (red) compared to pure CO_2 (black squares) and N_2O isotherms (blue circles).

−78.5 °C (194.7 K).[10] There is also the benefit that N_2O and CO_2 are both IR active, allowing them to be directly monitored using FTIR (Figure 1). The similarity of interaction thermodynamics with NiDBM-Bpy is reflected in the comparable P_{th} of the two gases[1] at 30 °C (303 K), 9.1 and 12.7 bar for N_2O and CO_2, respectively, with a P_{th} of 9.4 bar for the 50/50 mixture. In comparison, neither pure N_2 nor CH_4 are able to initiate the structure change at 30 °C (303 K) in the pressure range studied. However, both N_2 and CH_4[8] exhibit favorable interactions with NiDBM-Bpy at lower temperatures as demonstrated by step-shaped isotherms (Figure S4).

Further verification of the selective adsorption noted during in situ IR measurements was established using gas chromatography (GC) of the headspace composition before and after equilibration with the sorbent (Supporting Information). The change in headspace composition after equilibrium with NiDBM-Bpy for 50/50 mixtures of CO_2/N_2, CO_2/CH_4, and CO_2/N_2O is shown in Figure 4 (see Table S3). Similar results for 80/20 mixtures are shown in the Supporting Information (Figure S6, Table S4). The amount of CO_2 in the

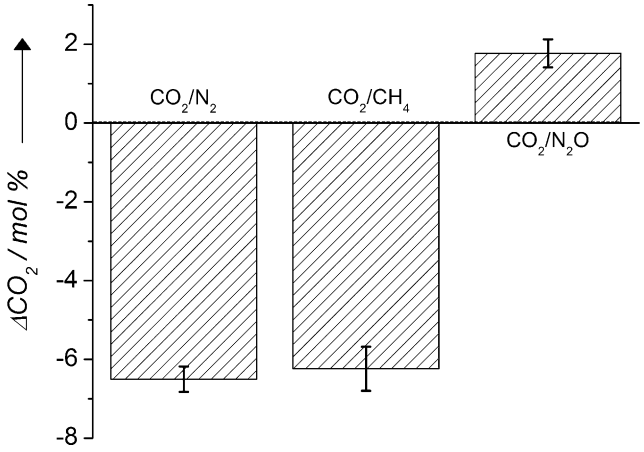

Figure 4. The change in mole percent of CO_2 (ΔCO_2) in the headspace after equilibrium exposure of gas mixtures (as indicated) to NiDBM-Bpy at 30 °C (303 K) and P_s.

headspace decreased for mixtures of CO_2 with N_2 and CH_4, indicating preferential adsorption of CO_2 from the gas phase into the NiDBM-Bpy pore network. Mixtures of 80/20 CO_2/CH_4 and CO_2/N_2 showed complementary decreases in CO_2 composition. Conversely, changes in the headspace composition were not statistically significant for the 50/50 and 80/20 mixtures of CO_2/N_2O, confirming the highly competitive adsorption process between CO_2 and N_2O noted in Figure 3. Results from the GC measurements were in agreement with the predicted equilibrium CO_2 composition (Table S5) for all three mixtures investigated, further confirming the behavior of this sorbent system.

Representative NiDBM-Bpy vibrational bands under pure gases and mixtures at P_s are shown in Figure S7. Changes in the NiDBM-Bpy spectrum at 712, 694, 683 cm^{-1} were observed at pressures above P_{th} for both pure gases and mixtures and have been attributed to conformational rearrangements of ligands during the transition to a high porosity state with an associated adsorption of CO_2.[8a] Favorable thermodynamics between the guest and the framework help stabilize conformational changes of the dibenzoylmethane (DBM) ligand (see Figure S8), resulting in the observed increase in gas uptake at P_{th}.[8a] The spectra in Figure S7 indicate the structural transition is independent of gas composition as long as either P_{N_2O} or P_{CO_2} is greater than P_{th} for CO_2/N_2, CO_2/CH_4, and CO_2/N_2O mixtures. In situ FTIR of the NiDBM-Bpy lattice bands illustrate that the ligand environment above P_{th} in mixtures of CO_2/N_2 and CO_2/CH_4 appears unchanged from pure CO_2 environments, indicating CO_2 helps stabilize the ligand confirmation in the open pore structure.

The lowest-angle (smallest Q) diffraction peak, corresponding to the largest d-spacing in the NiDBM-Bpy structure as indicated in Figure S1, was measured by in situ SANS using the NG3 SANS instrument at the NIST Center for Neutron Research.[11] Scattering data were collected on activated NiDBM-Bpy under vacuum, 17 bar of pure CO_2, 17 bar of pure N_2, and a 50/50 mixture containing 17 bar CO_2 and 17 bar N_2 ($P_{tot} \approx 34$ bar) at 30 °C (303 K) (Figure 5). In the evacuated (guest-free) structure, the d-spacing was measured

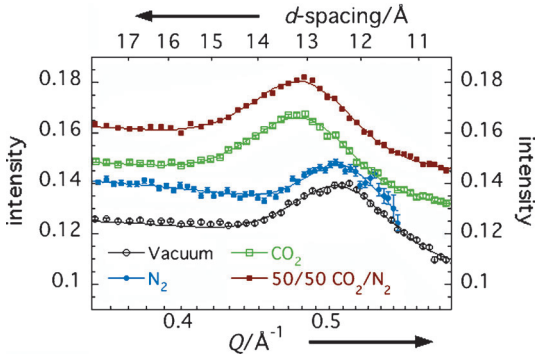

Figure 5. SANS diffraction peak data plotted versus both Q and d-spacing of NiDBM-Bpy under vacuum (black open circles), 17 bar N_2 (blue solid circles), 17 bar CO_2 (green open squares), and a mixture containing 17 bar CO_2 and 17 bar N_2 (red solid squares) at 30 °C (303 K). Vertical bars are the measurement standard deviation uncertainties for each point.

as (12.457 ± 0.026) Å which corresponds to the (002) reflection observed in the X-ray powder diffraction for the guest-free material (Figure S1 and S11). Upon saturation with pure CO_2 at 17 bar, the d-spacing shifts to (13.284 ± 0.020) Å, confirming the guest-induced structure transition resulting from a lattice expansion. As expected from the IR and GC results, pure N_2 does not initiate any obvious changes in structure or porosity at 17 bar, yielding a d-layer spacing of (12.364 ± 0.035) Å, which is nearly identical to that obtained for the evacuated structure. Equilibrium adsorption of a 50/50 mixture of CO_2/N_2 (P_{CO_2} = 17, P_{N_2} = 17, and P_{tot} = 34 bar) is equivalent to that of pure CO_2 at 17 bar, further verifying that N_2 has no effect on the CO_2-induced structural transition in NiDBM-Bpy. The in situ SANS data, in combination with the results above, confirm that changes in the lattice spacing and porosity of NiDBM-Bpy brought about by the CO_2/N_2

mixture are initiated by CO_2. Pure N_2 is not capable of initiating or stabilizing a structural transition at these pressures and temperatures. The SANS result for the 50/50 mixture of these gases shows no change from that of pure CO_2, illustrating that the presence of N_2 in the mixture has no effect on the porosity of the opened NiDBM-Bpy structure. Since the IR data on the ligand vibrations (Figure S7) will be sensitive to both interlayer spacing variations as well as conformational changes, the two sets of data clearly indicate that CO_2 is solely responsible for initiating and stabilizing the equilibrium structure of NiDBM-Bpy in CO_2/N_2 mixtures when P_{CO_2} is in excess of P_{th}. Furthermore, the adsorption and separation mechanism involves a lattice expansion in the (002) direction with associated conformational rearrangement of DBM ligands to accommodate the expansion and selective incorporation of CO_2. This mechanism appears unchanged when comparing pure CO_2 adsorption to that occurring from mixtures.

The guest-dependent phase change and resulting adsorption of gas provides selectivity for CO_2 over N_2 and CH_4. Volumetric isotherms show pure CO_2, N_2, and CH_4 can all initiate and stabilize the phase change, albeit at very different temperatures and pressures. However, CO_2 and N_2O initiate structural transitions under similar conditions. It is likely the selectivity in this system is driven by the overall thermodynamics of the adsorption process which initiates both the phase change and subsequent uptake of gas. Previous theoretical works by Barrer,[12] Coudert,[4c–e] and others[4f,13] have pointed to the complicated interplay of thermodynamics describing the phase transition, guest-host interactions, stabilizing effects of the guest on the sorbent, relief of mechanical strain in the crystal, and nucleation effects, as being key physical events dictating phase change and gas adsorption conditions in dynamic guest–host systems. We hypothesize that the details of these thermodynamics for each dynamic sorbent system under specific experimental conditions (e.g., temperature, pressure, gas mixture composition) will dictate how efficiently gas separations will occur.

On a final note we stress that the selective adsorption of CO_2 over N_2 and CH_4 in the NiDBM-Bpy system does not imply that all structurally dynamic systems will exhibit similar behavior. As has been pointed out in the literature, the mere presence of a "gate opening effect" or stepped isotherm for one gas species at a pressure/temperature where there is no observation of "gate opening" for another gas, does not imply or guarantee selective adsorption will occur due to the possibility of cooperative adsorption effects.[1,5] The systems and conditions where this cooperative adsorption may occur remain unresolved in the literature. Detailed studies of the NiDBM-Bpy system will help unravel the complicated energetics leading to the selective adsorption observed in our work.

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