Selective Adsorption of CO₂ on Flexible Porous Coordination Polymers

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Introduction
To maintain fossil fuels as viable energy sources, carbon capture and storage technology is essential. Recent novel sorbents for CO₂ capture, including porous coordination polymers (PCPs), have attracted a lot of interests. Flexible PCPs have one attractive feature that their structure become dynamic only in the presence of suitable guests such as CO₂, CH₄, N₂, and H₂. These flexible materials can show interesting host-guest phenomena including crystal-crystal transformations and gated adsorption behaviors due to the structural transitions which occur between the guest free and guest-loaded states. Such dynamic host-guest behavior is particularly attractive for applications involving sorbent-based gas separations and selective adsorption such as CO₂ and CH₄ separations. In order to develop materials for these applications, a detailed understanding of the adsorption mechanisms of these flexible hosts is needed.

Materials and Methods
The material in this study is the linear chain coordination polymer catena-bis(dibenzo[4,4′]-bipyridylnickel(II)), or referred as “NiDBM-BPY”. The structure of NiDBM-BPY is shown in Figure 1 (right). This neutral one-dimensional polymer was propagated by a bridging 4,4′-bipyridine ligand bound to the z-axes of the nickel complexes which were bischelated in a planar fashion by two ancionic DBM ligands.

In this report, we used in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to investigate the gas adsorption mechanism in flexible porous coordination polymers. When conducted in situ with an IR active gas in a high pressure cell, the technique allows the positions and shapes of the host adsorption bands and adsorbed gas spectra to be directly correlated with the gas step-shape adsorption isotherm. This information aids in elucidating guest induced structure changes of these flexible hosts.

The d-spacing in the NiDBM-Bpy structure was measured by in situ SANS using the NG3 SANS instrument at the NIST Center for Neutron Research. Scattering data were collected on activated NiDBM-Bpy under vacuum, 17 bar of pure CO₂, 17 bar of pure N₂, and a 50/50 mixture containing 17 bar CO₂ and 17 bar N₂ (Ptot = 34 bar) at 30°C (303 K).

CO₂/N₂ breakthrough experiment was performed in a fixed-bed reactor with ID of 0.375” and a length of 12”. The average particle size of NiDBM-Bpy was around 100 μm to minimize external mass transfer limitations. The gas composition of effluent was analyzed by a Shimadzu GC.

Results and Discussion
In situ IR determined isotherms for 50/50 partial pressure mixtures (red) of CO₂/N₂ on NiDBM-Bpy as compared to pure CO₂ isotherms (black) are shown in Figure 1 (left). CO₂ uptake proceeds with a pronounced step beyond threshold pressures (Pth) and a large adsorption hysteresis for all mixtures studied. For the CO₂/N₂ mixtures, the partial CO₂ pressure (PCO₂) at Pth was equivalent to that of pure CO₂ (Figure a), indicating that CO₂ uptake is a function of PCO₂ rather than the total pressure (Ptot) for these mixtures. Multiple spectra taken at a saturation pressure (P) where NiDBM-Bpy is saturated with guest molecules, show that the CO₂ saturation coverage for the CO₂/N₂ mixtures is identical to what was obtained in pure CO₂. Because the normalized CO₂ coverage at saturation in the mixture matches that of pure CO₂, we conclude that NiDBM-Bpy preferentially adsorbs CO₂ over both N₂ without displacement of CO₂. No significant changes were observed in the position or line shape of the CO₂ v3 asymmetric stretch, indicating the environment for adsorbed CO₂ is unaltered in the mixture experiments. The fact that PCO₂ at Pth is independent of composition for the CO₂/N₂ mixtures suggests that N₂ has little impact initiating or stabilizing the NiDBM-Bpy structural transition at these conditions.

The lowest-angle (smallest Q) diffraction peak, corresponding to the largest d-spacing in the NiDBM-Bpy structure is indicated in Figure b. In the evacuated (guest-free) structure, the d-spacing was measured as (12.457±0.026)Å which corresponds to the (002) reflection observed in the X-ray powder diffraction for the guest free material. Upon saturation with pure CO₂ at 17 bar, the d-spacing shifts to (13.284±0.020) Å, confirming the guest-induced structural transition resulting from a lattice expansion. As expected from the IR and GC results, pure N₂ 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 CO₂/N₂ (PCO₂ =17, Ptot =17, and Ptot=34 bar) is equivalent to that of pure CO₂ at 17 bar, further verifying that N₂ has no effect on the CO₂-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 CO₂/N₂ mixture are initiated by CO₂. Pure N₂ 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 CO₂ illustrating that the presence of N₂ in the mixture has no effect on the porosity of the opened NiDBM-Bpy structure.

Since the IR data on the ligand vibrations will be sensitive to both interlayer spacing variations as well as conformational changes, the two sets of data clearly indicate that CO₂ is solely responsible for initiating and stabilizing the equilibrium structure of NiDBM-Bpy in CO₂/N₂ mixtures when PCO₂ is in excess of the same threshold pressure. 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 CO₂. This mechanism appears unchanged when comparing pure CO₂ adsorption to that occurring from mixtures.

The breakthrough curve of CO₂ from a fixed-bed reactor packed with NiDBM-Bpy showed a step-shape curve (Figure c), which also indicated the structure expansion above the Pth. The
selectivity (blue and green lines in Figure c) for CO₂ over N₂ was calculated from the binary mixture adsorption results and confirmed the sorbent’s affiliation to CO₂ than N₂.

![Image of Figure 1](https://via.placeholder.com/150)

**Figure 1.** The structure of NiDBM-Bpy (a, right) and dynamic structure change indicated by (a, left) isotherm, (b) the SANS, and (c) the breakthrough of CO₂/N₂ binary gas mixture.

**Significance**

In this study, we explained 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 \( P_{th} \) for CO₂ over NiDBM-Bpy have been verified by different techniques. Better understanding of this kind of new structure dynamic sorbents can help to design effective materials for adsorption/separation operation.

**References**