Unconventional, Highly Selective CO₂ Adsorption in Zeolite SSZ-13
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ABSTRACT: Low-pressure adsorption of carbon dioxide and nitrogen was studied in both acidic and copper-exchanged forms of SSZ-13, a zeolite containing an 8-ring window. Under ideal conditions for industrial separations of CO₂ from N₂, the ideal adsorbed solution theory selectivity is >70 in each compound. For low gas coverage, the isosteric heat of adsorption for CO₂ was found to be 33.1 and 34.0 kJ/mol for Cu- and H-SSZ-13, respectively. From in situ neutron powder diffraction measurements, we ascribe the CO₂ over N₂ selectivity to differences in binding sites for the two gases, where the primary CO₂ binding site is located in the center of the 8-membered pore window. This CO₂ binding mode, which has important implications for use of zeolites in separations, has not been observed before and is rationalized and discussed relative to the high selectivity for CO₂ over N₂ in SSZ-13 and other zeolites containing 8-ring windows.

One of the most pressing issues facing the energy sector is the mitigation of greenhouse gases implicated in global warming through pre- and postcombustion capture applications. Efficient and selective capture of CO₂ from industrial flue gas streams is of particular interest as the current strategy, involving absorption in alkanolamine solutions, suffers a lack of corrosion control and significant energy requirements for regeneration. Typical flue gas streams have low concentrations of CO₂: typical N₂:H₂O:CO₂ ratios of 6.5:1:1 by weight and up to 15% CO₂ by volume at pressures of ~1 bar. The high gas flow rates make porous materials, such as zeolites, metal–organic frameworks (MOFs), and activated carbons, promising options for future separation/sequestration of CO₂. These framework materials typically exhibit high internal surface areas, allowing them to physiosorb significant amounts of gas. While adsorption capacity is important, high selectivity and facile regeneration are pertinent properties for postcombustion capture. Many physisorption materials offer moderate to weak flue gas–adsorbent interactions, allowing removal at close to or slightly above room temperature. Additionally, the selectivity of a porous adsorbent can be due to a number of effects such as exclusion due to the size/shape of the pores, adsorbent–

adsorbate surface interactions, and varying diffusion rates between different components in a gas mixture. Although increasing in numbers, recent reports of physisorption materials that exhibit a high selectivity for CO₂ over N₂ at ambient pressure and temperature are not common. While gas uptake measurements offer a single view of a specific material’s potential for gas storage/separation, comparisons between different analogues can afford further insight into the optimization of properties, such as adsorption capacities, binding energies, and selectivities, that are crucial in the design of new, advanced materials for energy-related applications. Cu-exchanged zeolites have shown improved hydrothermal stability over other copper-exchanged zeolites, an important property for postcombustion capture of CO₂ in flue streams with water present. Here, we report an investigation of low-pressure CO₂/N₂ sorption in acidic and copper-exchanged derivatives of zeolite SSZ-13, giving deeper insights into the site-specific adsorption properties obtained utilizing neutron powder diffraction (NPD) combined with in situ CO₂ and N₂ adsorption. Gas uptake measurements indicate that the low-pressure CO₂ capacity and the ideal adsorbed solution theory (IAST) selectivity relative to N₂ are not significantly impacted upon exchanging Cu cations into the host SSZ-13 framework. We further determine key structural features of the host framework that result in high uptake and selectivity using NPD. Langmuir surface areas for Cu- and H-SSZ-13 were determined from 77 K N₂ uptake measurements to be 710 and 764 m²/g, respectively, with a micropore volume of 0.25 and 0.27 cm³/g, respectively, agreeing with previously reported values (see Supporting Information (SI)). The CO₂ and N₂ adsorption data for H- and Cu-SSZ-13 are presented in Figure 1. The maximum uptake at 1 bar is lower for the Cu²⁺-exchanged derivative, 3.75 mmol/g (14.2 wt%), compared to the acidic form, 3.98 mmol/g (14.9 wt%), as expected on a gravimetric basis. In terms of the number of moles of CO₂
adsorbed at standard temperature and pressure, H- and Cu-SSZ-13 are in line with the best sorbents for CO2 uptake and only significantly ousted by Mg-MOF-74 (5.4 mmol/g at 0.1 bar).\textsuperscript{8} IAST adsorption selectivities for CO2 over N2 were calculated for an idealized flue gas mixture of 0.15 bar CO2 and 0.75 bar N2 to be 72.0 and 73.6 for Cu- and H-SSZ-13, respectively.

Materials with high overall CO2 uptake capacity and high selectivity for CO2 over N2 generally have high isosteric heats of adsorption ($Q_0$) over a range of surface coverages. This can be a critical parameter, depending on the target separation application. By fitting the adsorption isotherms measured at 298, 308, and 318 K for each material to dual-site Langmuir application. By fitting the adsorption isotherms measured at 298 K.

The SSZ-13 zeolites used in this study were determined to have SiO2/Al2O3 = 12, with the copper derivative having Cu2+/ Al = 0.35 (SI section S1). SSZ-13 is composed of corner-sharing Al/SiO4 tetrahedra that form double six-membered-ring cages, which stack in an ABC-type sequence. The cages are further connected to form a cavity with 8-membered windows found in the larger 8-membered ring window coordinated to O(2) and O(4) with distances between 2.0 and 2.25 Å. Important for high uptake capacity of SSZ-13 zeolites, site I in the 6-ring window has been determined to be the only copper location through powder X-ray diffraction (XRD).\textsuperscript{3d} The high Si/Al ratio results in a low concentration of charge-balancing Cu2+ cations, with a site I occupancy of only ∼25%. Rietveld refinement of our NPD data on bare Cu-SSZ-13 indicated nuclear scattering density only in the region of site I (Figure 3), with a Cu−O(1) distance of 2.24(1) Å to the three coordinate oxygen atoms and a refined Cu2+ occupancy of 0.26(2). This value is lower than the ∼0.36 determined by XRD\textsuperscript{3d} but agrees well with measured Al content.

NPD data were further collected at sequential, in situ loadings of 0.5, 0.75, 1.0, 1.5, and 4.0 CO2 molecules per Cu2+

Figure 1. CO2 (squares) and N2 (circles) adsorption isotherms for Cu-SSZ-13 (green, blue traces) and H-SSZ-13 (red, orange traces) at 298 K.

Figure 2. Representative NPD Rietveld refinement of the in situ gas-loaded zeolite at a loading of 0.5 CO2 per Cu2+ at 4 K (final goodness-of-fit $\chi^2 = 1.048$). Additional diffraction patterns and structural parameters can be found in the SI.
comparable to those of the framework oxygens and site A CO2 atoms, while the displacement parameters of the remaining site B CO2 atoms are large. Since NPD data give averaged structural information, and the refined molecular unit is a statistical representation of all site B molecules, the larger ADPs are likely indicative of static disorder or a shallow local potential. To further refine this model, we attempted several other descriptions of the CO2 units, including site B with multiple CO2 sites that are slightly rotated about the Cu2+-O axis, requiring a highly constrained molecular structure. None of these approaches was satisfactory, and no detailed structural information about the bond distances and angles of the CO2 can be determined from the data over that of the isotropic ADP model. We postulate that site B disorder is likely the result of competing interactions between the partially occupied CO2 sites A and B as well as between site B CO2 and the framework directly around the Cu2+.

To determine specifics of the separation properties, we performed additional in situ N2 diffraction for a loading of 1.5 N2 per Cu2+. The N2 is located to the side of the window at an angle of ~128° (O(4)−N2−O(ri8)), while the CO2 is centered (i.e., 180°, Figure 3). The closest N2-framework interactions are N1−O(3) at ~3.1 Å and N1−O(4) at ~3.5 Å. The N2 molecules, unlike CO2 molecules, do not orient perpendicular to the symmetry center of the 8-ring window. The ADPs for N2 are again large, as with the high loading for CO2, suggesting there is more disorder in the location of the N2 outside of the center of the pore window for high N2 loadings (Table S11). There is no evidence of a secondary N2−Cu2+ adsorption site based on the data with this loading.

The overall high affinity for CO2 versus N2 in both forms of the zeolites determined here may stem from several key factors: (1) the small pore size in zeolite SSZ-13 restricts diffusion, (2) the pore window is an ideal diameter for adsorption of CO2 and unoccupied by cations, and (3) the electrostatic interactions differ between the gases and both the H+ and Cu2+ frameworks. Grand canonical Monte Carlo simulations by Krishna and van Baten considered the selectivity of several 8-ring window zeolite frameworks and suggested that framework flexibility, i.e., lattice dynamics, does not influence the diffusion selectivity in a variety of 8-ring window zeolites, regardless of composition.11 In SSZ-13, the 3.8 Å pore window is too small for easy diffusion of N2 (kinetic diameter 3.64 Å), while CO2 (3.30 Å) can more freely diffuse into the pores. This, coupled with the fact that the framework−CO2 interaction is the ideal distance for adsorption in the window sites based on van der Waals radii,12 leads to very high CO2:N2 selectivity in SSZ-13. We can calculate the potential energy surface using isolated-molecule DFT calculations for the gas on a central trajectory through the 8-ring window (SI section S4). The minimum energy is found with CO2 in the center of the window, correlating with the simulations and our NPD data. This is favored by 46.5 kJ/mol compared to any arrangement where CO2 oxygen atoms are asymmetric with respect to the window.

The energy minima for N2 on a central trajectory through the 8-ring window are both in the center of the ring and outside the plane of oxygen atoms in the ring with an O(ri8)−(N2)−O(ri8) angle of 120°. N2 is favored in the center of the ring by only 8 kJ/mol compared to the side of the window site when on a central trajectory, suggesting there is no energetic reason for locating in the ring as opposed to the side of the window as determined by NPD. Krishna and van Baten also calculated the probability for adsorption at the window site in CHA and found that CO2 had ~30–40% probability of being located in the pore windows, while N2 had a <10% likelihood of locating there; they suggested it is the length of the CO2 molecule that makes this location ideal.11a If we consider the difference in quadrupole interactions between framework and CO2 (quadrupole moment = 13.4 × 10−40 C m2, polarizability = 26.3 × 10−25 cm3), and N2 (quadrupole moment = 4.7 × 10−40 C m2, polarizability = 17.7 × 10−25 cm3) over the "length" of the guest molecule, the result is much stronger affinity for CO2 over N2 in the window site (SI).

This new-found knowledge of CO2−framework interaction directly mediated in the center of the 8-ring window may have broad applicability. The quadrupolar interactions should also be valid in the description of other zeolites with high selectivities and 8-ring windows. In the analogous zeolite CHA, albeit at
differing Si/Al ratios, the CO$_2$ and N$_2$ adsorption in the Li-, Na-, and K-exchanged derivatives follows a trend based on the properties of the cations (size and polarizability), with Li-CHA having the highest and K-CHA the lowest CO$_2$ and N$_2$ uptakes. It is known that K$^+$ preferentially locates in the 8-ring window, while Li$^+$ prefers to exchange into the center of the 6-ring pore. In the case of Na-CHA, Na$^+$ prefers the 8-ring window site at low and the 6-ring site at high Na$^+$ content. It is plausible that the availability of window sites in Li- versus place of Cu$^{2+}$, as a copper-cation-based zeolite should have preferentially adsorb at the Cu$^{2+}$ site. From our NPD data, the suffering to the same extent from humidity effects that other on storage ability. Since water preferentially adsorbs at the Mg analogue, one of the leading separation materials based humidity, only 16% of the initial uptake capacity is retained in overall uptake of the sieving media. This is especially noticeable material is favored since water can significantly impact the ability, making Cu-SSZ-13 an ideal candidate for practical CO$_2$/

**REFERENCES**


