

# Molecular understanding of high CO<sub>2</sub> adsorption capacity in chabazite zeolites

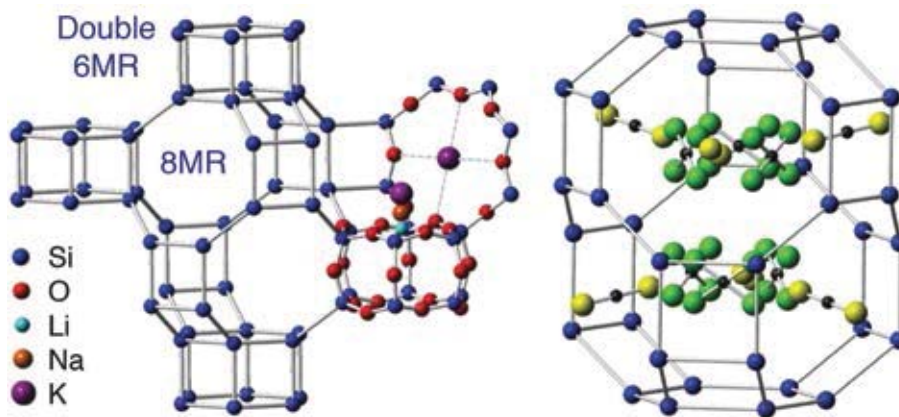
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The large-scale capture and sequestration of carbon dioxide (CO<sub>2</sub>) from pre-combustion, post-combustion, and natural gas mixtures have become important technological and environmental targets to mitigate the effect of greenhouse gases on global climate change. Conventional CO<sub>2</sub> capture using primary alkanolamine scrubbers consumes large amounts of energy for regeneration. Nanoporous materials such as carbon molecular sieves, zeolites, and MOFs have been studied for CO<sub>2</sub> separations and capture because of their high internal surface area, high micropore volume, chemical tunability, fast adsorption/desorption kinetics, and low heats of adsorption [1].

Chabazite (CHA) is a small pore zeolite consisting of a double 6-membered ring (D6R) as the basic building unit with one large ellipsoidal cavity accessed by six 8-membered ring windows (8MR). CHA-type zeolites provide improved hydrothermal stability over other zeolites, an important property in the selective catalytic reduction of NO<sub>x</sub> and moist flue-gas applications. CHA has also been shown to have high selectivity for light olefins in the conversion of methanol to olefins process and demonstrated potential in gas separations, such as CO<sub>2</sub> from N<sub>2</sub> in flue gas mixtures. Extra-framework cations present in Al-exchanged zeolite frameworks play important roles in determining the adsorption properties. Adsorption measurements reveal that the CHA samples with higher aluminum content have higher adsorption capacity. We considered the adsorption properties and site-specific adsorption properties of CO<sub>2</sub> in pure, high, and medium silica CHAs (Si/Al = ∞, = 12, = 6, respectively) with varied cation-exchange (Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>). These insights were obtained by combining in-situ X-ray (XRPD) and neutron powder diffraction (NPD) methods using Fourier difference

mapping to locate the adsorbed CO<sub>2</sub> and correlating the results with adsorption measurements. This allows us to elucidate the atomic origin of the adsorption properties across a series of cationexchanged zeolites, which aids in the engineering of improved CO<sub>2</sub> adsorbents [2].

Figure 1 depicts the locations of alkali metal cations typically observed in highsilica CHAs. From Rietveld refinement of powder diffraction data, we observed Li and Na at the 6MR window, as expected as this coordination environment is the most favorable in CHA for small cations. In this position, each Li<sup>+</sup> or Na<sup>+</sup> is effectively coordinated with 3 oxygen atoms of the framework. Due to ionic radii difference ( $r_{\text{Na}^+} = 1.16 \text{ \AA}$ ,  $r_{\text{Li}^+} = 0.73 \text{ \AA}$ ), Na<sup>+</sup> lies higher above the plane of the 6MR ( $\approx 22^\circ$ ) measured from the Si in the ring compared to Li-CHA-6 ( $\approx 9.6^\circ$ ). These angles are slightly larger in Li- and Na-CHA-12. On the other hand, the larger K<sup>+</sup> cation sits preferentially in the middle of the 8MR where it is coordinated with 4 oxygen atoms of the zeolite framework. In addition, K<sup>+</sup> is observed on a position above the 6MR where it is only coordinated with 3 oxygen atoms of the zeolite framework.



**FIGURE 1:** (Left) Illustration of the CHA structure and typical cation locations in the zeolites. (Right) CO<sub>2</sub> adsorption sites in Si-CHA with framework oxygen atoms omitted for clarity. Site A: 8MR, yellow CO<sub>2</sub> oxygen atoms; Site B: cage, green CO<sub>2</sub> oxygen atoms.

Dispersive interactions are the primary contributors to the adsorption energy in CHA and are determined by the distances between the carbon and oxygen atoms of

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CO<sub>2</sub> molecule to the surrounding oxygen atoms of the framework. The refinement of XRPD and NPD patterns of CO<sub>2</sub> on pure silica CHA resulted in the identification of two adsorption sites for CO<sub>2</sub>: (1) locating in the 8MR and (2) in the ellipsoid cages of CHA framework (Fig. 1). In the CHA 8MR, the preferred adsorption site (A) is the center of the CHA window in which each carbon atom in CO<sub>2</sub> molecule has maximal close contacts with the 8 oxygen atoms of the 8MR such that two O<sub>8MR</sub> across the ring from each other give an angle O<sub>8MR</sub>-C<sub>CO<sub>2</sub></sub>-O<sub>8MR</sub> = 180°. From XRPD refinement of CO<sub>2</sub> in Si-CHA, the CO<sub>2</sub> – 8MR oxygen atom distances were determined to be from 3.129(6) Å to 3.410(4) Å, and with  $d(O_{CO_2}-O_{CHA})$  between ca. 3.18 Å to 3.98 Å. Another CO<sub>2</sub> adsorption site (B) in pure silica CHA is inside the ellipsoidal cage where the carbon atom has the most effective contact distances with 4 framework oxygen atoms and the CO<sub>2</sub> oxygen atoms also have effective contact distances with 4 to 5 framework oxygen atoms each. Overall, these considerations explain the high occupancy of CO<sub>2</sub> at site A in CHA zeolites, or indeed in 8MR zeolites in general.

Two CO<sub>2</sub> adsorption sites were determined in Li-CHA and Na-CHA zeolites by Fourier analysis (Fig. 2). The distance between Na<sup>+</sup> and O<sub>CO<sub>2</sub></sub> in site A (3.605(0) Å) is much shorter than that for the Li<sup>+</sup> (4.307(0) Å) leading to a more effective electrostatic interaction. The CO<sub>2</sub> second site in these zeolites is end-on coordination with the cation, M<sup>+</sup>...O=C=O, at distances of 2.68(7) Å (Na<sup>+</sup>) and 2.3(2) Å (Li<sup>+</sup>). The linear CO<sub>2</sub> molecule is tilted toward the 4MR window to achieve closer contact with framework oxygen atoms. This adsorption site can be viewed as B' being a rotation and translation of the all-silica site (B). Since the Li<sup>+</sup>...O=C=O distance is shorter than that in Na<sup>+</sup>-CHA, the CO<sub>2</sub> contact angle is more acute,  $\angle Li^+ \dots O=C=O \approx 144^\circ$  vs.  $\angle Na^+ \dots O=C=O \approx 163^\circ$ , having more effective dispersive interaction with the framework. Because the interaction energy of the large quadrupole moment of CO<sub>2</sub> ( $14.3 \times 10^{-40}$  C m<sup>2</sup>) with an inhomogeneous electric field of zeolite is highest in 8MR zeolites, site A (8MR) is still a major adsorption site in alkali-exchanged CHA even though open metal cations provide an additional strong binding site in the cage (B') through enhanced electrostatic interaction.

In solid CO<sub>2</sub>, molecules of CO<sub>2</sub> are arranged in their lowest energy configuration where an O atom of one CO<sub>2</sub> molecule is in close contact with more than 10 oxygen atoms and C atom also has close contact with 6 oxygen atoms of other CO<sub>2</sub> ( $d_{C-O} \approx 3.11$  Å), which is the distance we found in the 8MR. Further, in the cases of Li- and Na-CHA-12 at low CO<sub>2</sub> doses, there is an overall similarity of

the positions and occupancies of the two CO<sub>2</sub> sites (A, B') with  $\angle Li^+ \dots O=C=O \approx 142^\circ$  and  $\angle Na^+ \dots O=C=O \approx 166^\circ$  and the cation-CO<sub>2</sub> distance are identical to those in CHA-6 at 2.302(5) Å (Li<sup>+</sup>) and 2.59(8) Å (Na<sup>+</sup>).

Refinement of the K-CHA-12 data show that K<sup>+</sup> behaves quite similarly to Cu<sup>2+</sup> in which the majority of the CO<sub>2</sub> is found in the 8MR and only a small fraction of the adsorbate is found with an end-on CO<sub>2</sub> coordination with the cations. Interestingly, in K-CHA-6 with the higher concentration of K<sup>+</sup> partially blocking more of the 8MR window, the occupancy of the second CO<sub>2</sub> site (C) in the cage is significantly increased. The increase in interaction energy is due to the CO<sub>2</sub> coordination to two K<sup>+</sup> cations (across 6MR-6MR or 6MR-8MR) being more efficient in lower silica K-CHA-6 with a K<sup>+</sup>...O=C=O distance approx. 3 Å. In this configuration, the oxygen and carbon atoms also have a number of attractive interactions with framework oxygen atoms.

Structural properties of Chabazite zeolites dosed with CO<sub>2</sub> were determined from in-situ powder X-ray and neutron diffraction measurements. The 8MR (A) was identified as the major CO<sub>2</sub> adsorption site in pure silica CHA due to the high number of close contacts to the framework oxygen atoms to the CO<sub>2</sub>. The exchanged cations in charged CHA frameworks are open metal ions providing strong binding sites through induced polarizability of CO<sub>2</sub>. CO<sub>2</sub> is coordinated end-on to cations with the molecular axis tilted to the framework to maximize its dispersion interaction. The population of the direct coordinated adsorption sites of CO<sub>2</sub> with these metal cations decreases with the hardness of cation, except for K-CHA-6, where the bridged complexes of CO<sub>2</sub> and two K<sup>+</sup> cation sites were formed with higher interaction energy than a single cation adsorption site. Additionally, a major CO<sub>2</sub> adsorption site in the 8MR, previously determined in Cu-CHA [3], was still observed in these cation-exchanged CHAs due to high van der Waals and quadrupole interactions. The type of structural determination completed here is essential in the understanding and design of better adsorbent materials for CO<sub>2</sub> capture and separation technologies.

## References

- [1] T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown, J. R. Long, *Energy Environ. Sci.* **6**, 138 (2013).
- [2] M. R. Hudson, T. D. Pham, C. M. Brown, R. F. Lobo, *ChemSusChem* **7**, 2959 (2014).
- [3] M. R. Hudson, W. L. Queen, J. A. Mason, D. W. Fickel, R. F. Lobo, C. M. Brown, *J. Am. Chem. Soc.* **134**, 1970 (2012).