Cs-RHO Goes from Worst to First As Water Enhances Equilibrium CO₂ Adsorption

Le Xu, Alexander Okrut, Gregory L. Tate, John Meynard M. Tengco, Ryouji Onishi, Kun-Lin Wu, Ambarish Kulkarni, Takahiko Takewaki, John R. Monnier, Alexander Katz

† Department of Chemical and Biomolecular Engineering, University of California Berkeley, CA 94720, United States
‡ Department of Chemical Engineering, University of South Carolina, SC 29208, United States
§ Department of Chemical Engineering, University of California Davis, CA 95616, United States
∥ Inorganic Functional Material Lab, Mitsubishi Chemical Group, Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

ABSTRACT: Zeolite adsorbents often suffer a challenge of capturing CO₂ from flue gas, because the co-existence of H₂O would be significantly detrimental to their equilibrium CO₂ capacity. Herein, we observed a unique cooperative adsorption mechanism between H₂O and CO₂ on Cs-RHO zeolite, wherein the presence of H₂O favors the adsorption of CO₂. Cs-RHO adsorbs 3-fold higher amount of CO₂ relative to that under dry conditions, on dehydrated Cs-RHO, at the same temperature and CO₂ pressure. In-situ powder X-ray diffraction indicates a new phase with Im-3m symmetry appears after H₂O saturation and is responsible for enhanced CO₂ uptakes under humid conditions. A systematic investigation of alkali-cation-exchanged RHO zeolites with Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ cations showed Cs-RHO to be unique in its increase of CO₂ adsorption under wet versus dry conditions, although a mixed cation exchanged NaCs-RHO exhibited similar phase transitions after humid CO₂ adsorption. We found no evidence of cooperativity with Na⁺ cations in adsorption, when using this latter zeolite, as adsorption amounts for H₂O and CO₂ as well as humid CO₂ could be described by a simple linear superposition of Na-RHO and Cs-RHO values. We hypothesize based on previous Rietveld refinements of CO₂ adsorption in Cs-RHO zeolite that this phase change is related to solvation of extraframework Cs⁺ cations by water, which favors the migration of Cs⁺ from their original D8R position to SBR sites. This movement allows a trapdoor mechanism by which CO₂ can interact with Cs⁺ at SBR sites to access the α-cage.

A promising approach for dealing with rising levels of CO₂ is sequestration from flue gas. Zeolites are structurally well-defined materials that adsorb CO₂ (such as zeolite LTA, RHO, CHA, KFI, MER and FAU etc.), while exhibiting excellent stability (thermal, hydrothermal, and mechanical), high volumetric-based CO₂ adsorption capacity, and low cost. However, an ongoing challenge with the design of zeolite adsorbents is that flue gas always contains H₂O – a highly competitive adsorbate. The design of zeolites that retain significant equilibrium CO₂ adsorption capacity from humid gas mixtures remains a grand challenge, which cannot be addressed by studies of single-component CO₂ adsorption. The conventional belief is that humidity always results in a significant decrease of the equilibrium CO₂ adsorption capacity of a zeolite, e.g., demonstrated by previous studies based on large pore as well as small pore zeolites, and justified by the much higher heat of adsorption for H₂O compared to CO₂. This has led to proposals for combating this decreased CO₂ capacity under humid conditions by employing energy-intensive approaches, such as flue gas pre-drying. Here, in this manuscript, we demonstrate unique cooperativity in adsorption between H₂O and CO₂, wherein H₂O facilitates the adsorption of CO₂ on Cs-containing RHO zeolite. By solvating extra-framework Cs⁺ cations and causing a phase transition, the interaction between Cs⁺ and H₂O moves Cs⁺ cations away from positions where they would block the entrance of α-cages and make those cages inaccessible for CO₂ adsorption at low pressure. Using a combination of ab-initio molecular dynamics and experiment we demonstrate that this results in an unprecedented higher equilibrium CO₂ adsorption capacity on Cs-RHO under wet (5% relative humidity) rather than dry conditions.

We investigated a comparative series of cation-exchanged RHO zeolite samples comprising H⁺, Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺ as well as a hydrothermally synthesized NaCs-RHO zeolite for CO₂ adsorption under wet and dry conditions. Single-component CO₂ physisorption isotherms of dehydrated materials are shown in Figures S2-S8 and are summarized in Table S1. Among these, the material with the highest limiting CO₂ uptake is Na-RHO (4.9 mmol/g at 1 bar and 30 °C, Figure S3, Supporting Information). Even at a low CO₂ pressure of 0.1 bar, Na-RHO adsorbs 3.65 mmol/g CO₂, which is higher than the uptake observed at 1 bar for Li-RHO and NaCs-RHO, and much higher than those for Rb-RHO and Cs-RHO (Table S1). We observe similar CO₂ adsorption isotherms as well as limiting values of uptake at 1 bar CO₂ pressure compared with prior literature reports for H-RHO, K-RHO, and Rb-RHO (see Figures S5, S7, and S8, respectively, Supporting Information).
These data are consistent with the known strong interaction between the Na\(^+\) cations and CO\(_2\) under dry conditions, and it spans a variety of different framework types.\(^7,\)\(^6\)

Consistent with prior literature, the single-component CO\(_2\) uptake observed for Cs-RHO is the lowest amongst the cation-exchanged series investigated (only 0.46 mmol/g at 1 bar and 30 °C; see Figure S4 and Table S1, Supporting Information). This should be contrasted with prior literature data at significantly higher single-component CO\(_2\) pressures, which demonstrate that Cs-RHO zeolite is capable of adsorbing much higher amounts of CO\(_2\) (3.4 mmol/g at 4 bar and 25 °C).\(^8\) These higher CO\(_2\) uptakes for Cs-RHO at pressures above 1 bar demonstrate that there is sufficient space within the zeolite channels that is not being

![Figure 1: Single-component equilibrium adsorption amounts of (navy blue) H\(_2\)O at 5% relative humidity relative to (light blue) CO\(_2\) at 1 bar on H-RHO, Li-RHO, Na-RHO, K-RHO, Rb-RHO, Cs-RHO and NaCs-RHO zeolites.](image1)

![Figure 2: Equilibrium CO\(_2\) adsorption amounts during (navy blue) single-component physiosorption under dry conditions versus (light blue) CO\(_2\) physiosorption under wet conditions (5% relative humidity) on H-RHO, Li-RHO, Na-RHO, K-RHO, Rb-RHO, Cs-RHO and NaCs-RHO zeolites.](image2)

NaCs-RHO also holds for H\(_2\)O as well as CO\(_2\) under humid conditions.

Using TGA, we compared cation-exchanged RHO zeolites for humid CO\(_2\) adsorption, by first saturating the dehydrated zeolites with H\(_2\)O at a fixed relative humidity of 5% at 30 °C, followed by conducting humid CO\(_2\) adsorption at the same relative humidity and temperature. The first H\(_2\)O saturation experiment allows measurement of the H\(_2\)O saturation capacity of all zeolites, whereas the subsequent humid CO\(_2\) treatment at the same relative humidity (5% at 30 °C) as H\(_2\)O saturation measures the amount of CO\(_2\) adsorption under wet conditions. Comparing results from the latter with single-component CO\(_2\) adsorption measurements under dry conditions informs on the role of H\(_2\)O in CO\(_2\) adsorption. H\(_2\)O is expected to in general reduce equilibrium CO\(_2\) uptakes due to its much higher absolute enthalpy of adsorption relative to CO\(_2\).\(^5\) Indeed, because of the latter, the presence of CO\(_2\) is assumed not to alter equilibrium H\(_2\)O adsorption amounts.

All cation-exchanged RHO zeolites adsorb H\(_2\)O at 5% relative humidity and 30 °C (Figures S10-S16, Supporting Information), H-RHO, Li-RHO and Na-RHO show similarly high H\(_2\)O uptakes ranging from 9.26 - 9.77 mmol/g in Table S1 and Figure 1. We observe that the presence of large cations such as K\(^+\), Rb\(^+\) and Cs\(^+\) exchanged in RHO zeolite results in decreased H\(_2\)O uptakes of 2.97 - 7.41 mmol/g in Table S1 and Figure 1. The observed trends of exchange cations controlling H\(_2\)O adsorption in zeolite RHO demonstrate a decreased adsorption capacity as the row of the alkali metal cation increases, with Cs-RHO notably having the lowest H\(_2\)O uptake of 2.97 mmol/g, which is consistent with its chaotropic rather than kosmotropic nature in the Hofmeister series.\(^1\)

Zeolite NaCs-RHO exhibits an intermediate affinity to H\(_2\)O adsorption (7.27 mmol/g H\(_2\)O), which follows a linear superposition of the pure-cation-exchanged Na-RHO and Cs-RHO data, weighted by the relative molar Na\(^+\) and Cs\(^+\) compositions of the NaCs-RHO zeolite (Figure S17, Supporting Information). Based on these data, as well as our data for pure-component Cs\(^+\), we conclude that for both CO\(_2\) and H\(_2\)O as pure components, Na\(^+\) and Cs\(^+\) cations in NaCs-RHO do not work together in causing adsorption, but rather function as independent entities, coordinating water on their own separately as opposed to a mixed complex involving both metals.

Equilibrated humid CO\(_2\) uptakes following H\(_2\)O saturation on all zeolites are summarized in Table S1 and Figures 1 and 2. Despite H-RHO, Li-RHO and Na-RHO having comparable H\(_2\)O saturation capacities, the humid CO\(_2\) capacities of these zeolites drops drastically as the exchange cations change from H\(^+\) (1.09 mmol/g) to Li\(^+\) (0.44 mmol/g) to Na\(^+\) (0.49 mmol/g). The latter is significantly lower than the humid CO\(_2\) uptake exhibited by NaCs-RHO of 0.78 mmol/g. We surmise that partial replacement of Na\(^+\) by Cs\(^+\) guest cations in RHO zeolite favors CO\(_2\) adsorption under humid conditions.

Crucially, among all investigated materials, Cs-RHO’s CO\(_2\) capacity of 1.45 mmol/g under humid conditions is much higher than that of all other univalent cation exchanged RHO zeolites after H\(_2\)O saturation. This equilibrated CO\(_2\) uptake on hydrated Cs-RHO is 3-fold higher relative to the
value observed under dry conditions, on dehydrated Cs-RHO, of 0.46 mmol/g at the same temperature and CO₂ pressure in Figure 2. We conclude that H₂O acts cooperatively with the Cs⁺ cation to facilitate CO₂ adsorption. This role of H₂O is diametrically opposed to the conventional one in the literature, of H₂O serving as a competitive adsorbent in situations involving humid CO₂ adsorption.²⁻³

When comparing humid CO₂ adsorption capacities in Table S1 and Figure 2, we observe that Na-RHO, the material with the highest CO₂ uptake under dry conditions, is also the material with nearly the lowest CO₂ uptake under humid conditions. In contrast, Cs-RHO was the material with the lowest CO₂ uptake under dry conditions. The mixed exchanged-cation material NaCs-RHO has a humid CO₂ uptake of 0.78 mmol/g, which is close to a linear superposition of Na-RHO and Cs-RHO humid CO₂ uptakes weighted by their respective molar composition (calculated to be 0.54 mmol/g). These data further underscore the lack of cooperativity between Na⁺ and Cs⁺ guest cations in RHO in adsorbing CO₂ under humid conditions.

To gain further insight into the unprecedented increase in adsorption capacity on Cs-RHO zeolite under humid compared with dry conditions, we investigated Cs-RHO, NaCs-RHO, and Na-RHO zeolites using in-situ PXRD, at the different stages of the TGA experiment above, corresponding humid CO₂ adsorption. However, we observe an increase in the lattice parameter corresponding to I-43m symmetry after H₂O saturation, which is consistent with the expansion of the Na-RHO unit cell as a result of H₂O filling the zeolite micropores. During subsequent humid CO₂ adsorption, the unit cell dimension only changes slightly, commensurate with the low amount of CO₂ adsorbed for Na-RHO zeolite under humid conditions (0.49 mmol/g, Figure 2). This is contrasted with the high amount of CO₂ adsorbed for Na-RHO under dry conditions (4.90 mmol/g, Figure 2).

To access the α-cage, before migrating back once the CO₂ has diffused in.
Table 1: Crystallographic information of Na-Rho, NaCs-Rho and Cs-Rho series materials.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Space group and lattice parameter (Phase 1)</th>
<th>Space group and lattice parameter (Phase 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydrated Na-Rho</td>
<td>I-43m, 14.3421 Å</td>
<td>-</td>
</tr>
<tr>
<td>Hydrated Na-Rho</td>
<td>I-43m, 14.5540 Å</td>
<td>-</td>
</tr>
<tr>
<td>Hydrated Na-Rho with CO₂</td>
<td>I-43m, 14.5538 Å</td>
<td>-</td>
</tr>
<tr>
<td>Dehydrated NaCs-Rho</td>
<td>I-43m, 14.5442 Å</td>
<td>-</td>
</tr>
<tr>
<td>Hydrated NaCs-Rho</td>
<td>I-43m, 14.5752 Å</td>
<td>Im-3m, 14.9756 Å</td>
</tr>
<tr>
<td>Hydrated NaCs-Rho with CO₂</td>
<td>I-43m, 14.5438 Å</td>
<td>I-43m, 14.5540 Å</td>
</tr>
<tr>
<td>Dehydrated Cs-Rho</td>
<td>I-43m, 14.5879 Å</td>
<td>-</td>
</tr>
<tr>
<td>Hydrated Cs-Rho</td>
<td>Im-3m, 14.9668 Å</td>
<td>I-43m, 14.6024 Å</td>
</tr>
<tr>
<td>Hydrated Cs-Rho with CO₂</td>
<td>Im-3m, 14.9854 Å</td>
<td>-</td>
</tr>
</tbody>
</table>

Although dehydrated NaCs-RHO has the same initial crystal symmetry (I-43m) as dehydrated Na-RHO in Table 1, the symmetry of hydrated NaCs-RHO changes into a mixture of two phases after hydration at 30 °C (5% relative humidity), as indicated by the appearance of a new phase with Im-3m symmetry (Figure 3e). Furthermore, this new phase with Im-3m symmetry becomes the one with the greater intensity in the in-situ PXRD pattern after subsequent CO₂ adsorption (Figure 3f). The same phase transition from I-43m to Im-3m has been previously reported in NaCs-RHO, upon single-component CO₂ adsorption above 200 kPa, and has been used to explain high CO₂/CH₄ selectivity in this zeolite.²

We also observe the same phase transition from I-43m to Im-3m in Cs-RHO, which, like Na-RHO and NaCs-RHO, initially exhibits I-43m symmetry in the dehydrated state but transitions to an almost pure phase with Im-3m symmetry after the first H₂O saturation process (the PXRD intensity of the original I-43m becomes very weak) in Figure 3h. Following the second humid CO₂ adsorption stage, we observe exclusively Im-3m phase in Cs-RHO zeolite in Figure 3i and Table 1.

Previously, the interaction between CO₂ and dehydrated Cs-RHO was investigated using Rietveld refinement of in-situ PXRD data by Wright and coworkers.¹⁰ Dehydrated Cs-RHO possessed I-43m symmetry, but this symmetry changes upon single-component CO₂ adsorption at 4 bar to 100% Im-3m symmetry (50% change at 2 bar and 20% change at 1 bar). This prior refinement study shows that in dehydrated Cs-RHO, Cs⁺ cations have two locations corresponding to the D8R and S6R sites, whereas after single-component CO₂ adsorption at 4 bar, under dry conditions, the Cs⁺ cations were found to be in the same S6R as before CO₂ equilibration, along with a new position, corresponding to the S8R, just outside of the D8R.¹⁰ These data elucidate the low CO₂ uptake of dehydrated Cs-RHO at 1 bar under dry conditions (Figure S4). This is because the large Cs⁺ cations at the D8R sites block the entrance and prevent CO₂ from accessing the α-cage. The observed phase change from I-43m to Im-3m symmetry is commensurate with the opening of the D8R entrance to the α-cage by moving Cs⁺ from the D8R to S8R position. This unblocking effect allows a trapdoor mechanism by which CO₂ can interact with Cs⁺ at S8R sites to access the α-cage, at higher CO₂ pressures (where Cs-RHO uptake of CO₂ under dry conditions

Figure 4: Two-dimensional histograms of the Cs⁺ cation distances with Al atoms in (a) dry and (b) wet conditions to identify the occupancies of the (c) various high symmetry sites. (d) Two-dimensional histogram of the Cs⁺ cation distances with the center of the D8R site and the oxygen atom of the water molecules. (e) Representative image showing the formation of a hydrogen bonding network with the S8R Cs⁺ cations and the water molecules in the α-cage (green highlight). Color scheme: O (red), H (white), Cs (purple). The zeolite framework is represented using lines for better clarity.
increases in excess of 4 mmol/g by 9 bar), akin to that described above for Na-RHO.

Based on our results in this study, we hypothesize that H$_2$O solvates Cs$^+$ guest cations and acts as a lubricating solvation layer, which decreases the energy barrier for unblocking access to the α-cage via Cs$^+$ migration, according to a similar trapdoor mechanism. Similar roles of solvation relating to the movement of guest cations in zeolites have been previously described, and, in particular, demonstrated for H$_2$O in cation-exchanged RHO zeolites.

Under this proposed scenario, a small amount of H$_2$O (5% relative humidity) in Cs-RHO would move Cs$^+$ cations away from their original D8R sites in the dehydrated Cs-RHO zeolite, thereby facilitating CO$_2$ access. This small amount of H$_2$O is insufficient to cause competitive adsorption with CO$_2$ in the confines of the α-cage of the RHO zeolite, leading to a greater equilibrated CO$_2$ uptake for Cs-RHO under humid rather than dry conditions.

To support the hypothesis above, we have quantified the differences of the dynamics of Cs$^+$ cations in dry and wet conditions using ab-initio molecular dynamics simulations (CP2k code, PBE functional, 10 ps production run, 1 fs timestep). The zeolite composition (i.e., Cs$_{10}$Al$_{12}$Si$_{38}$O$_{100}$), water uptake (i.e, 13H$_2$O/unit cell), and unit cells (dry: 1-43m, wet: 1m-3m) are consistent with the experimental samples. Figure 4a and b presents a 2-dimensional histogram of the distances of the Cs$^+$ cations from the D8R site and the Al atoms in dry and wet conditions. Although all three high-symmetry sites are populated (Fig. 4c), our AIMD calculations suggest preferential occupation of D8R sites (66% of Cs$^+$ cations) under dry conditions. In contrast, the addition of water (~1.3 water/Cs$^+$ cation, similar to experiment) results in a significant redistribution of the cations. Specifically, while less than 10% of the Cs$^+$ occupy S8R sites under dry conditions, in presence of water, the Cs$^+$ cations preferentially migrate (60%) to the S6R sites. Furthermore, as evidenced by Cs$^+$-O$_{H2O}$ and the Cs-D8R center 2-dimensional distance histograms, this site redistribution arises due to the solvation of the Cs$^+$ cation by the water molecules. We observe an average Cs$^+$-O$_{H2O}$ bonding distance of ~3.2 Å, in agreement with Cs$^+$ hydration. Note that the few Cs+ atoms in the D8R sites (yellow dashed oval in Fig 4d) do not interact with the water molecules. These AIMD simulations provide additional insights into the driving force underlying the above re-distribution of cations. Specifically, the migration of the Cs+ cations to the S8R sites (which are exposed to the α-cages) enables the formation for a strong hydrogen bonding network with the water molecules in the α-cages (Fig 4e), and would be a critical step in the hypothesized trapdoor mechanism – vide supra.

Our observations here lead to a previously unrecognized role of H$_2$O acting cooperatively to facilitate CO$_2$ adsorption – a mechanism that is impossible to achieve under single-component CO$_2$ conditions. Our results motivate the need to investigate CO$_2$ adsorption in materials under wet conditions characteristic of flue gas. We are currently in the process of proving this hypothesized mechanism by conducting a Rietveld refinement of in-situ PXRD data in parallel with advanced ab-initio metadynamics simulations.

**ASSOCIATED CONTENT**

**Supporting Information.** Experimental, characterization and physisorption, TGA data are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**  
*askatz@berkeley.edu  (A. Katz)

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Funding Sources**

Any funds used to support the research of the manuscript should be placed here (per journal style).

**ACKNOWLEDGMENT**

Generally the last paragraph of the paper is the place to acknowledge people (dedications), places, and financing (you may state grant numbers and sponsors here). Follow the journal’s guidelines on what to include in the Acknowledgement section.

**REFERENCES**


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