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Privileged zeolitic sites for humid CO_2 adsorption: K^+ in double eight-membered rings

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Humid CO_2 adsorption in K^+-exchanged zeolites featuring double-eight membered ring (D8R) structures results in CO_2 outcompeting and desorbing dimeric water under equilibrated conditions, which is not observed for either the H^+-form of the same zeolites or larger-pore zeolites.

In an effort to combat global warming, there has been a strong focus on capturing CO_2 from post-combustion sources such as flue gas.[1, 2] Zeolites, microporous crystalline aluminosilicates, have been extensively investigated in this regard.[3-7] However, an ongoing challenge is the typical observed decrease in CO_2 adsorption capacity due to competitive adsorption by H_2O,[5, 8] which generally has a significantly higher heat of adsorption than CO_2.[8, 9] Approaches for solving this challenge benefit from selective adsorption sites that preferentially bind quadrupolar CO_2 over dipolar water.[10] Previously, in elegant research that identified key supramolecular interactions involving small-pore zeolite host and CO_2 guest, Lobo et al. demonstrated that (i) framework O in eight-membered rings bonds to C atoms of CO_2 by *pushing* electron density through its lone pairs, and (ii) exchange cations bond to the O atom of CO_2 by *pulling* electron density and generating an induced dipole in the latter.[11] We posit that cations filling double eight-membered ring (D8R) secondary building units in zeolites have the prospect of fulfilling both (i) and (ii) above, and in doing so, could provide a selective environment for bonding of CO_2 over water, though the structural details of such an environment are currently unavailable. In particular, we demonstrated sites in K^+-exchanged MER zeolite (K-MER) that desorb a water dimer for each CO_2 adsorbed under humid conditions corresponding to 5% relative humidity (RH), with a combined thermogravimetric analysis (TGA) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) approach.[12] These sites were inferred to consist of K^+ cations in D8Rs of K-MER zeolite, which can accommodate either one water dimer or one CO_2 molecule within their volume. Here, we investigate the generality of this last result by studying humid CO_2 adsorption in three new types of zeolites: (i) RHO (Si/Al=3.7), (ii) MER (Si/Al=2.9), and (iii) PAU (Si/Al=3.6) (see Fig. S1, Supporting information). These three frameworks were chosen because they contain D8R structures and represent slightly different variations on the symmetry of those structures.[13] TGA data in Fig. 1 show gravimetric profiles upon equilibrated H_2O and humid CO_2 adsorption (5% RH, 1 bar of CO_2 for Step II, 30 °C) in these three K^+ ion-exchanged zeolites (Table S1, Supporting information). Separate H_2O (in Step I) and CO_2 (in Step II) uptake in the zeolites was initially evaluated on

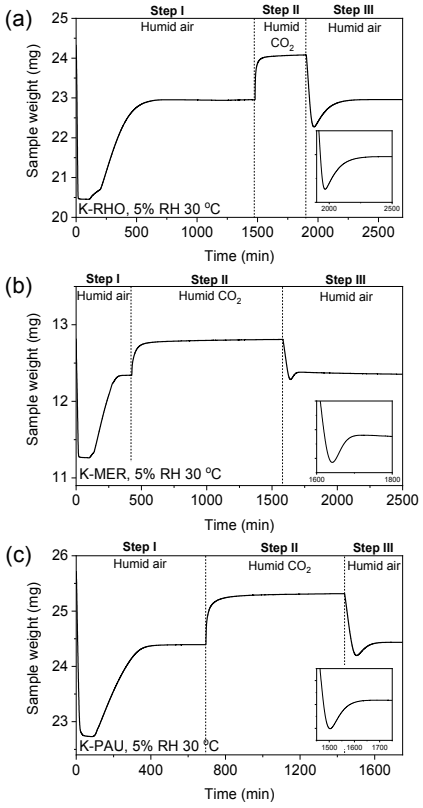

Fig 1. TGA profiles of (a) K-RHO, (b) K-MER and (c) K-PAU zeolites during gas adsorption under humid air (step I), humid CO_2 (step II) and humid air (step III) conditions at fixed 5% RH and 30 °C.

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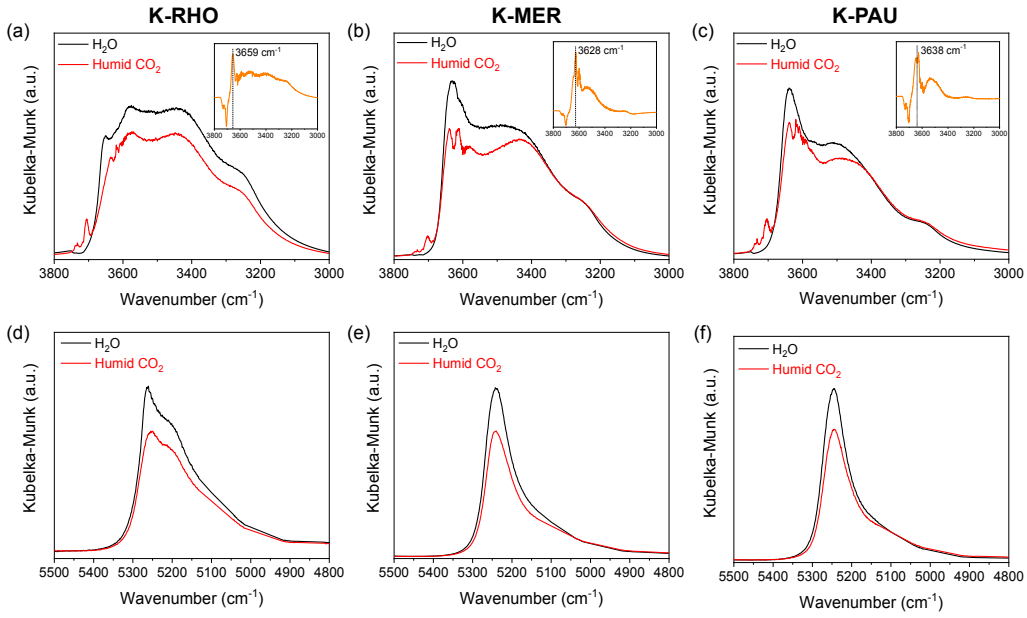

Fig. 2. (a-c) DRIFT spectra of –OH stretching IR band for adsorbed H_2O in K-RHO, K-MER and K-PAU, respectively, after equilibrated under humid air (H_2O, black) and subsequent humid CO_2 conditions (Humid CO_2, red) at 5% RH and 30 °C. (d-f) DRIFT spectra of combination IR band of H_2O in K-RHO, K-MER and K-PAU, respectively, under the same conditions.

the basis of the observed weight increases ("TGA only" in Fig. S2, Supporting information). These calculated gravimetric uptakes reflect an implicit assumption that CO_2 does not desorb pre-equilibrated H_2O, which will be investigated below (*vide infra*). Interestingly, during the desorption of adsorbed CO_2 under humid air (5% RH, 30 °C) in Step III, we observe a pronounced overshoot during Step III in the TGA profiles for all three K^+-exchanged zeolites (insets in Fig. 1). We previously ascribed such an overshoot to be a manifestation of H_2O desorption during humid CO_2 adsorption in Step II (i.e. the overshoot is a consequence of the kinetically slower water readsorption compared to CO_2 desorption in Step III). When we compare TGA data of three zeolites between sequential versus simultaneous adsorption of H_2O and humid CO_2, the results show a path independence in humid CO_2 adsorption, which demonstrates that the system is under thermodynamic control (see Fig. S3, Supporting Information).

We characterized humid CO_2 adsorption in K^+ exchanged RHO, MER and PAU zeolites with in-situ DRIFTS. Fig. 2 shows DRIFT spectra of each zeolite after H_2O saturation in air (Step I; H_2O, spectra in black), and subsequent humid CO_2 adsorption (Step II; humid CO_2, spectra in red) at a fixed relative humidity and temperature (5% RH, 30 °C) under equilibrium control. Focusing first on –OH stretching (ν) IR bands at 3800–3000 cm^{-1}, which characterize the amount of adsorbed H_2O, data shown in Fig. 2a-c show subtraction spectra that minimize overlap and interference from gas-phase CO_2 $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ combination bands (see Fig. S4, Supporting information). These DRIFTS data demonstrate a decrease in the intensity of –OH stretching bands upon humid CO_2 adsorption (Step II), when compared with air at the same RH (Step I). We conclude that CO_2 outcompetes H_2O in these three zeolites.

The insets in Fig. 2a-c show subtraction spectra that characterize the nature of the water desorbed during humid CO_2 adsorption (Step II). Characteristic IR bands of such H_2O species in K-MER, K-RHO, and K-PAU are observed at 3659-3628 cm^{-1} along with a broader band at lower wavenumbers. In view of more hydrogen bonding leading to a lower wavenumber and lower extinction coefficient for –OH stretching,[14] our data demonstrate that water species with less (or the least amount of) hydrogen bonding are the ones selectively desorbed during CO_2 adsorption. Such characteristic IR bands in this spectral region (3659-3628 cm^{-1}) have been previously assigned to dimeric H_2O species that are not associated with the hydrogen bonding network of bulk water clusters.[15, 16] The subtlety of the underlying effects is demonstrated by our previous data showing no H_2O desorption upon humid CO_2 desorption in Cs-RHO, which exhibited no adsorbed dimeric water in Step I, in contrast with our results here with the same zeolite exchanged with K^+ cations.[12] These results emphasize the importance of dimeric water, which involves a reduced hydrogen bonding environment and enthalpy of vaporization (i.e. when considering water as a purely Van der Waals fluid, in the limit of no hydrogen bonding, its enthalpy of vaporization is expected to be about half of the value for bulk water[17]).

The data above emphasize the generality of CO_2 outcompeting dimeric H_2O in zeolites possessing K^+-D8R structures, and suggest such structures as privileged structural motifs for selective CO_2 adsorption under humid conditions. To elucidate the role of K^+ cations and D8R structures in facilitating selective CO_2 adsorption in the presence of H_2O, we performed DRIFTS on the framework (T–O–T) vibration region of all three zeolites after H_2O adsorption. We observe negative IR bands at 949-962 cm^{-1} (see data in Fig. S5, Supporting Information). We observe further perturbation to those bands after subsequent humid CO_2 adsorption. Our prior DRIFTS study[12] proved that such IR band perturbations reflect the migration of K^+ cations from their initial position in the center of the D8R, out to the

single 8-ring (S8R) site, as caused by adsorption of a H_2O dimer and/or CO_2.[18] We surmise that when CO_2 replaces dimeric H_2O dimer in the D8R in K-RHO, K-MER, and K-PAU, the further negative increases in the framework vibration (T-O-T) bands indicate that CO_2 adsorbs to the same cationic site in the D8R and pushes the cation further out away from the center. This result identifies the privileged CO_2 adsorption site as a K^+ cation located within the D8R structure of these three zeolites.

Next, we combine DRIFTS and TGA to independently quantify adsorbed water and CO_2 adsorption during Step II in K^+-D8R zeolites. DRIFT spectra in Fig. 2d–f exhibit a combination IR band ($\nu+\delta$) of adsorbed H_2O in the spectral region of 5500–4800 cm^{-1}, and the integrated area of this band reflects the amount of H_2O adsorbed in zeolite.[19] By comparing the areas of IR band before and after humid CO_2 adsorption in Steps I and II, we quantify the amount of desorbed H_2O during humid CO_2 adsorption in Step II to correspond to 22%, 19%, and 16% of the total equilibrated H_2O uptake in Step I, in humid air, for K-RHO, K-MER and K-PAU, respectively (Fig. 2d–f and see Fig. S6 and S7, Supporting information). Combining this with TGA data in Fig. 1 and Fig. S2, we rigorously quantify H_2O and CO_2 uptakes in K^+-D8R zeolites, corresponding to humid CO_2 uptakes of 1.18 – 1.85 mmol/g (see "IR corrected" in Fig. S2, Supporting information). The 1.85 mmol/g humid CO_2 uptake corresponding to K-RHO is the highest one that we have observed to date at 5% RH. This is, a zeolite that does not appear to be all that impressive for humid CO_2 uptake when analysis is based on TGA data alone coupled with conventional heuristics.[8, 12] Comparing K-MER zeolites having different Si/Al ratios in our current and previous[12] study (Si/Al=2.9 vs 2.0, respectively), their humid CO_2 uptakes do not show significant difference at 5% RH and 30 °C (1.35 mmol/g vs 1.27 mmol/g, respectively). This similarity was unexpected given the 3.5-fold higher dry CO_2 uptake (at 1 bar) for the K-MER zeolite at the higher Si/Al ratio (see Fig. S8, Supporting information).

We quantify transient H_2O and CO_2 adsorption profiles via combined TGA and time-resolved DRIFTS. The profiles clearly demonstrate H_2O desorption by CO_2 adsorption in Step II and reversible H_2O re-adsorption upon CO_2 desorption, under humid air, in Step III (see in Fig. S9a–c, Supporting Information). Parametric (phase) plots in Fig. S9d–f demonstrate direct relationships between amounts of H_2O readsorption and CO_2 desorption during Step III, ranging from 1.85 (±0.06)–2.29 (±0.13) H_2O per CO_2. We conclude that within uncertainty each molecule of CO_2 desorbed during Step III is replaced with a single H_2O dimer. This macroscopic quantification connects with the qualitative microscopic observation in DRIFTS in Fig. 2 showing selective desorption of dimeric H_2O upon humid CO_2 adsorption in Step II.

To better understand the role of K^+ cations, we compared H^+-exchanged forms of both RHO and PAU zeolites under humid CO_2 conditions (the structure of H-MER zeolite was unstable[20]). In stark contrast to TGA data for K^+-zeolites in Fig. 1a and b, corresponding TGA data for the H^+ form of RHO and PAU zeolites in Fig. S10a-b lacks a characteristic overshoot in the gravimetric profiles at Step III, which was present for K-RHO and K-PAU zeolites. This observation couples with the IR bands of

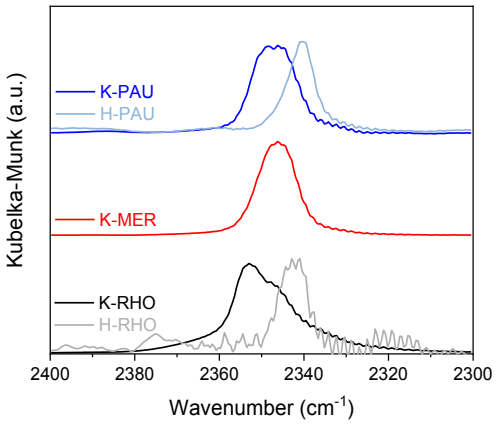

Fig. 3. DRIFT spectra of adsorbed CO_2 in K^+-D8R zeolite (K-RHO, K-MER and K-PAU) and H^+-D8R zeolites (H-RHO and H-PAU). The spectra were obtained during CO_2 desorption under humid air conditions at 5% RH and 30 °C after humid CO_2 adsorption at the same conditions.

H_2O in H-RHO and H-PAU zeolites not appreciably changing before and after humid CO_2 adsorption (i.e. between Steps I and II; see Fig. S11, Supporting information). We conclude that humid CO_2 adsorption during Step II does not result in desorption of H_2O from Step I in the H^+-exchanged forms of the zeolites. This underscores the important role of K^+-D8R structures as H_2O resilient sites for humid CO_2 adsorption in zeolites.

DRIFTS data in Fig. 3 demonstrate asymmetric stretching (ν_3) IR bands of adsorbed CO_2 in zeolites, which are acquired during a desorption cycle in humid air during Step III. These IR bands are observed at 2353 cm^{-1}, 2346 cm^{-1}, and 2347 cm^{-1} for K-RHO, K-MER and K-PAU, respectively. In comparison, the same IR bands for H-RHO and H-PAU are located at a much lower frequency of 2342 and 2341 cm^{-1}, respectively. These observed frequency shifts between the K^+- and H^+-exchanged forms of the zeolite can be rationalized on the basis of the Stark effect.[21] This effect has been previously invoked to elucidate blue shifts in the IR stretching bands of adsorbed CO and CO_2 in zeolites, with the extent of blue shift shown to increase with exchange-cation charge density.[21, 22] We conclude that the magnitude of the blue shifts observed above by DRIFTS are evidence of strong ion-dipole interactions involving CO_2 and K^+-D8R sites. The same reasoning predicts a lower vibrational frequency (weakening of C-O bond) in the absence of alkali cations, which is controlled solely by the negative charge of the zeolite framework,[23] resulting in CO_2 vibrational frequencies in the H^+-exchanged zeolites above, which are significantly lower than that of gas phase CO_2 (2349 cm^{-1}). We also observe a lower vibrational frequency for humid versus dry conditions as a result of water competitive adsorption in all three zeolites (see Fig. S12, Supporting Information).

From the perspective of H_2O, both the K^+- and H^+-exchanged forms of the zeolite have nearly the same water uptakes (see Fig. S2 and S10, Supporting Information). However, a significant difference is that the DRIFT spectra of the –OH stretching IR bands of adsorbed H_2O show exclusively hydrogen-bonded water and, in particular, no dimeric H_2O for the H^+-exchanged zeolites (see Fig. 1a–c and Fig. S11, Supporting information). We

conclude that K^+-exchange cations in the D8R structures facilitate the synthesis of dimeric H_2O. We surmise that this is the result of two effects: (i) K^+ cations in the S8R physically isolate the H_2O dimer inside of the D8R from bulk H_2O clusters on the outside, in the alpha cage, by acting as a physical barrier, and (ii) H^+ in the D8R acts as a bridge that facilitates extended hydrogen bonding of H_2O in the zeolite, without the opportunity to site isolate a less hydrogen bonded dimeric H_2O species. A consequence of K^+-D8R structures that lead to the synthesis of dimeric water in Step I, which desorbs upon humid CO_2 adsorption in Step II, is a higher CO_2 uptake compared to the corresponding H^+-exchanged zeolites (see Fig. S2 and S10, Supporting Information). To further understand the importance of D8R zeolite confinement, we also investigated humid CO_2 adsorption in K-FER zeolite (Si/Al=8.8), which consists of S8R sites that open up to a ten-membered ring (10MR) in the alpha cage. K-FER lacks the confinement afforded by K^+-D8R sites described above as those that are active for humid CO_2 adsorption.[24] While we observe a weakly hydrogen-bonded H_2O species at 3650 cm^{-1} in K-FER, which is in the range for dimeric H_2O in K^+-D8R zeolites above, both TGA and DRIFTS results of K-FER zeolite do not show evidence of H_2O being desorbed during humid CO_2 adsorption (i.e. neither a characteristic overshoot in TGA nor a decrease in IR band intensity of H_2O is observed; see Fig. S13, Supporting Information).

To understand why this isolated H_2O species in K-FER is not desorbed upon humid CO_2 adsorption, we investigated the adsorbed CO_2. DRIFT spectra in Fig. S14, which show a red shift in the CO_2 IR band of K-FER (main IR band shown at 2345 cm^{-1}) compared with that in K-RHO. This red shift reflects the greater confinement within the K^+-D8R structure compared to K-FER, consistent with greater confinement in zeolites causing a more blueshifted CO_2 vibrational frequency, as a consequence of more polarization and stronger ion-dipole interactions between cations and CO_2.[24] We conclude that the more open site in K-FER is ultimately responsible for weaker cation-CO_2 interactions, thereby causing a lack of competitiveness of CO_2 over a similar isolated dimeric H_2O species in K-FER. This rationalizes the higher humid CO_2 uptake in K-RHO (1.85 mmol/g) compared with K-FER (1.05 mmol/g).

It is intriguing that CO_2 outcompetes H_2O in our three cation-rich zeolites under equilibrium control, particularly when K^+ cations are known to interact strongly with water (i.e. they are kosmotropic in the Hofmeister series),[8] as evidenced by their significant water uptakes at the 5% RH chosen for this study. However, our results demonstrate that the local environment destabilizes dimeric H_2O in the confined K^+-D8R site compared to the more open sites in K-FER. Our work is the first demonstration of the generality of the K^+-D8R as a privileged structure for humid CO_2 adsorption, and more broadly motivates rational molecular design strategies that exploit cation-containing D8Rs for selective humid CO_2 adsorption in zeolites.

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Data availability

The data supporting this article have been included as part of the ESI.

Conflicts of interest

There are no conflicts to declare.

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Data availability

The data supporting this article have been included as part of the ESI.