

Supporting Information:

Carbonate Promoted Drift of Alkali Cations in Small Pore Zeolites: the AIMD Study of CO₂ in NaKA Zeolite

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S1. Carbonate formation

Several mechanisms of carbonate and hydrocarbonate formation have been discussed in.^{S1-S4} It has been found recently that the activation energy of the formation of hydrocarbonate (HCO₃⁻) from CO₂ and H₂O in MeX zeolites is rather small (a few kcal/mol) for Me = K, Rb, Cs in agreement with their formation at room temperature.^{S5} As zeolites usually contain water one can assume that formed HCO₃⁻ withdraws cations from their sites in the 8R windows and let other CO₂ pass through. Alternative route of carbonate and hydrocarbonate formation was shown in alkaline earth zeolites where MeO_XMe clusters, Me = Mg – Ba, and X varies from 1 to 4 depending on Me. Therein, the MeO_XMe clusters can react with CO₂ immediately^{S3} or after CO oxidation to CO₂ at these clusters.^{S1,S2} We should

note that previous studies of this carbonate phenomenon did not deal with dynamics and suggested only geometry optimizations^{S6} and climbing-image Nudged Elastic Band (ciNEB) calculations.^{S1-S4}

S2. The pseudo-unit cell of NaKA zeolite

Because of the large NaKA unit cell, we reduced the cell model up to two α -cages which contains only 1/4 atoms of true NaKA unit cell. In order to do this, the Al-O-Al alternation^{S7} was allowed at some remote positions from the central 8R window between two α -cages of the pseudo-unit cell where the K^+ cation under study was positioned. The acceptance of non-Loewenstein model for such comparable analysis is based on thermodynamic reason of its lower stability without anomalous electrostatic properties.^{S8} The perturbed Si-O-Al alternation cannot result in enhanced artificial electrostatic effects because very close Si and Al charge values were obtained with accurate basis sets at the B3LYP level with the $q(Al)/q(Si)$ ratio between 0.911 and 0.990,^{S9} being pretty close to 0.975 from X-ray electron spectroscopy.^{S10} As an indirect confirmation of this, the activation energy for the HCO_3^- formation obtained in the present article is of the same order as in the MeX faujasites with $Si/Al = 1$ ^{S5} and a conservation of the Loewenstein rule.^{S7}

S3. The role of ion-quadrupole K^+ -CO₂ interaction energy

The ion-quadrupole (K^+ -CO₂) interaction energy is realized for long $|C-K^+| > 5 \text{ \AA}$ distances (Fig. 3). The sum of the half of kinetic CO₂ diameter ($1/2 \times 3.3 \text{ \AA}$ ^{S11}) and K^+ ionic radii ($1.37 \text{ \AA}$ ^{S12}) is equal to $3.02 \text{ \AA}$ that is smaller than CO₂- K^+ distance of $5 \text{ \AA}$ (Fig. 3, S4). This allows using the central quadrupole CO₂ moment for an evaluation of ion-quadrupole K^+ -CO₂ interaction energy. Even overestimating charge $q(K^+)$ as +1 and taking gas phase CO₂ quadrupole $\Theta = -3.3 \text{ e} \times \text{a.u.}^2$,^{S13} one can get approximately (in a.u.): $q(K^+) \times \Theta \times R^{-3} = (-3.3) \times (5/0.5292)^{-3} \approx -3.8 \times 10^{-3} \text{ hr} = -2.5 \text{ kcal/mol}$ for the attraction between CO₂- K^+

separated by $R = 5 \text{ \AA}$ (Fig. 3, S4). This small value allows classifying the $\text{CO}_2\text{-K}^+$ interaction as a weak one in agreement with the results^{S14,S15} especially as compared to the large energy barriers required for a partial cation shift from the 8R plane.^{S16} Such small value explains the conservation of the K^+ position in the 8R plane irrespective of either three (Fig. S4), or seven (Fig. 3) adsorbed CO_2 per one α -cage.

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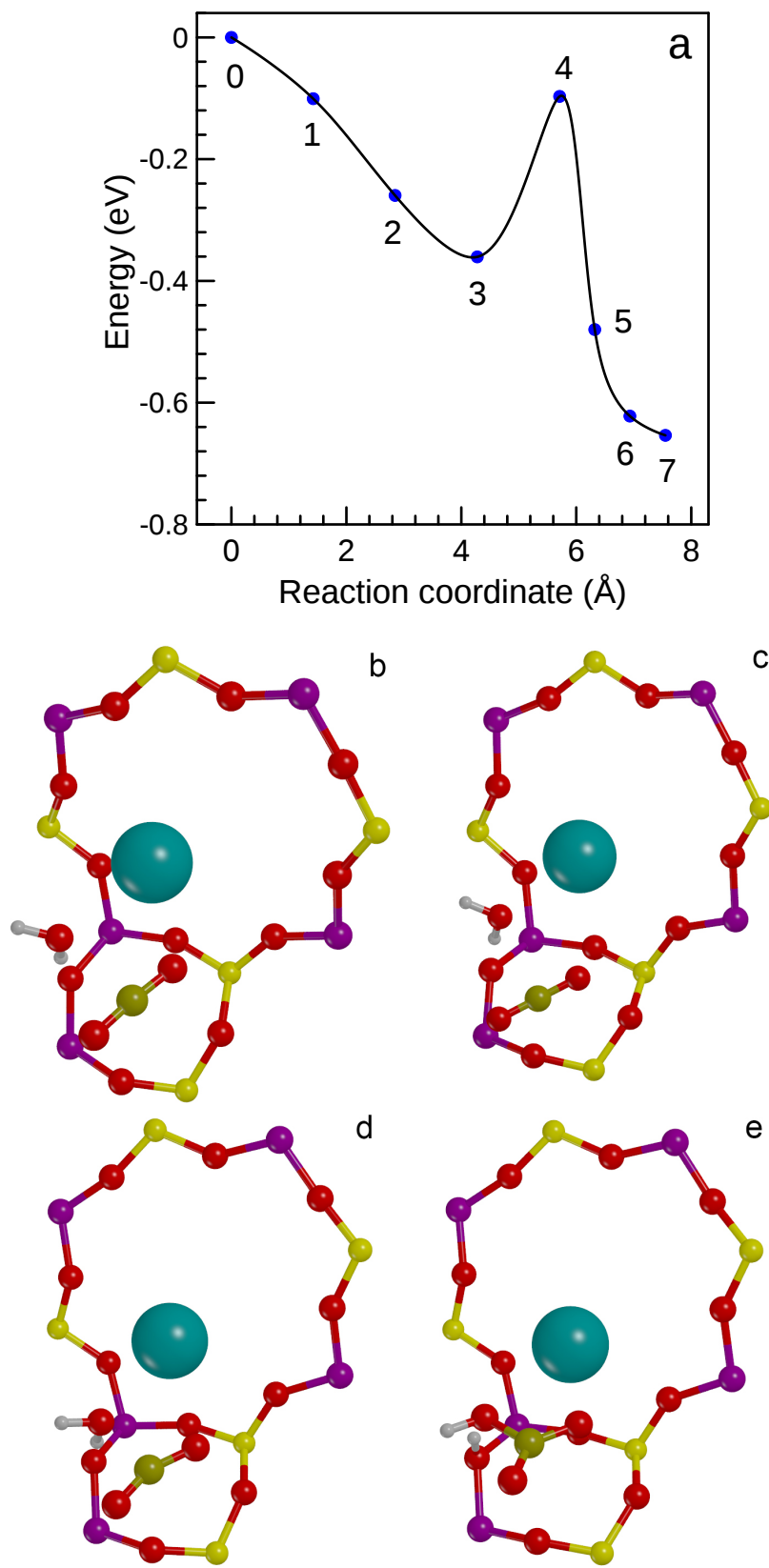


Figure S1: Reaction profile (a) and respective geometries of reagents (0-b), minimum (3-c), transition state (4-d), and products (7-e) calculated at the PBE-D2/PAW level.

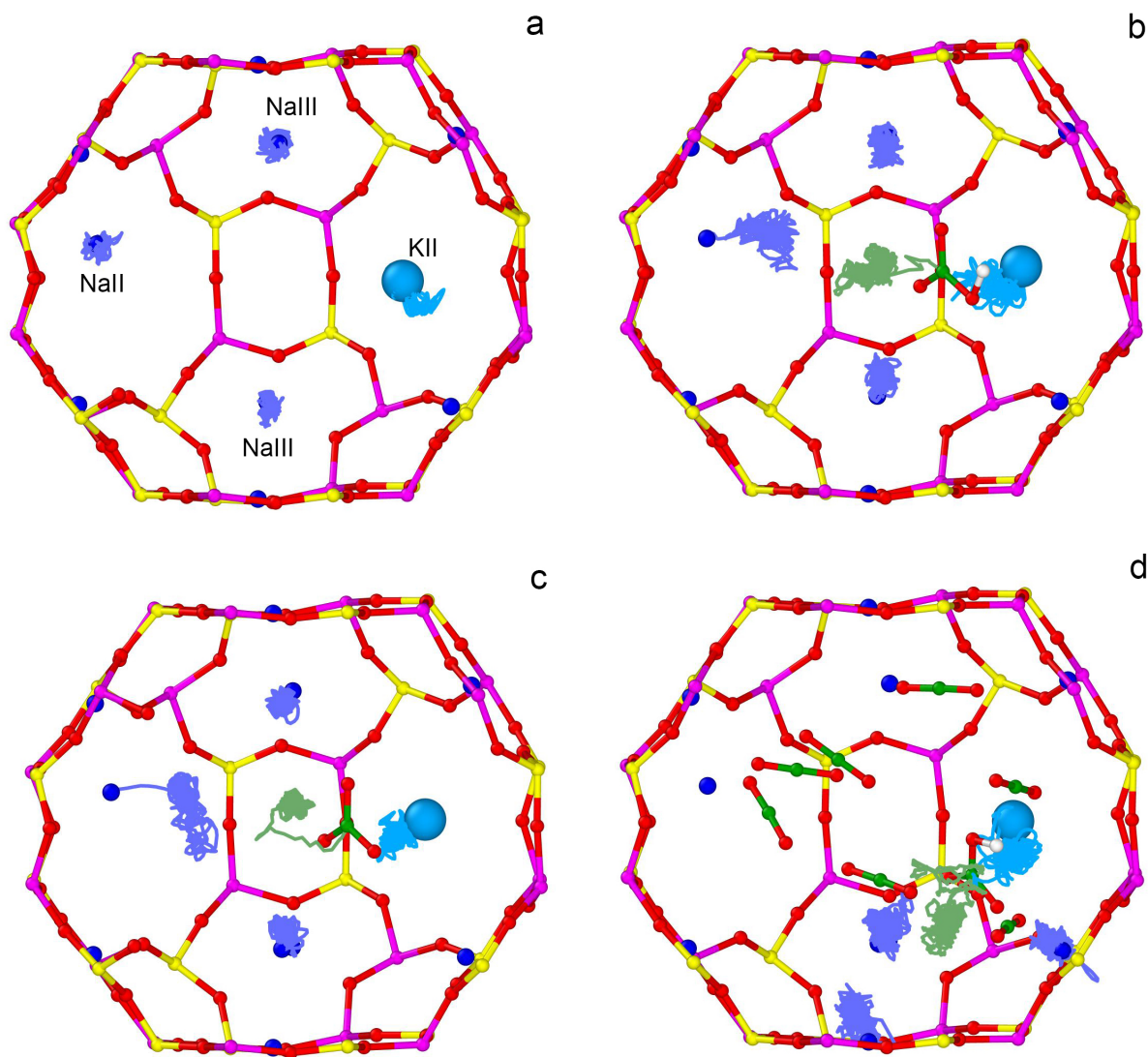


Figure S2: Representative atomic trajectories from *ab initio* molecular dynamics for NaKA zeolite. The trajectories of some Na (dark blue) and one K (blue) atoms in empty NaKA (a), including the trajectories of C (green) atom of HCO_3^- (b), CO_3^{2-} (c) and the mixture of seven CO_2 and one HCO_3^- (d). The cases (a-d) correspond to Figs. 2a-d, respectively, at 300 K.

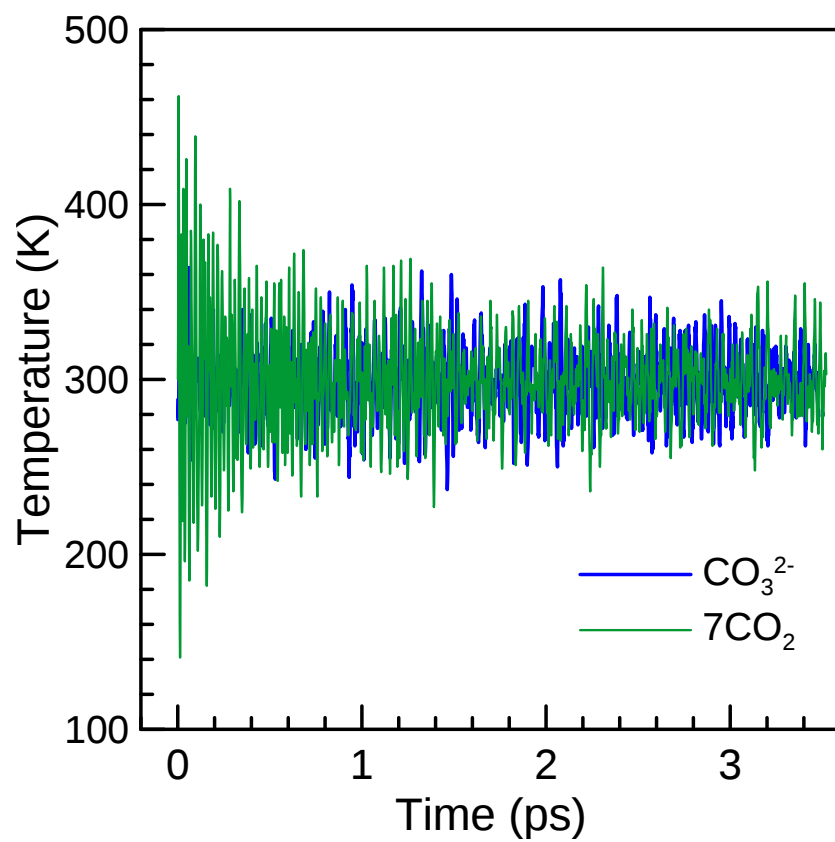


Figure S3: Temperature (K) equilibration towards 300 K with CO_3^{2-} (blue, Fig. 2c) and 7 CO_2 (green, Fig. 3) per one α -cage of two α -cages in pseudo-unit cell of NaKA (Fig. 1).

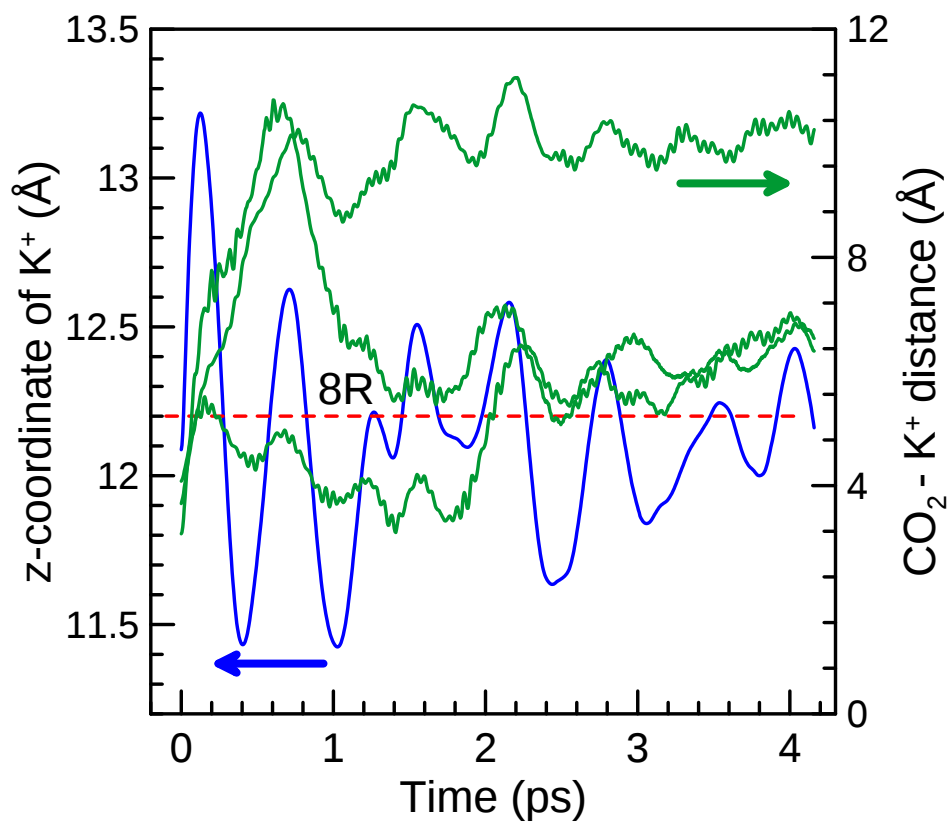


Figure S4: Time dependences (ps) of the K⁺ displacement along OZ-axis (blue line, left axis) and the C-K⁺ distance (green line, right axis) in NaKA with 3 CO₂ per one α -cage at 300 K.