

Carbonate-Promoted Drift of Alkali Cations in Small Pore Zeolites: Ab Initio Molecular Dynamics Study of CO₂ in NaKA Zeolite

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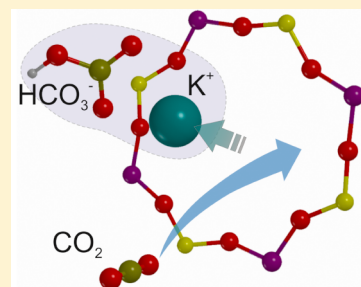
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Supporting Information

ABSTRACT: An effect of deblocking of small size (8R, D8R) pores in zeolites due to cation drift is analyzed by using ab initio molecular dynamics (AIMD) at the PBE-D2/PAW level. The effect of carbonate and hydrocarbonate species on the carbon dioxide uptake in NaKA zeolite is demonstrated. It is shown that a hydrocarbonate or carbonate anion can form strong complexes with K⁺ cation and withdraw it from the 8R window, so that the probability of CO₂ diffusion through 8R increases. For the first time, correlations between cationic and HCO₃⁻/CO₃²⁻ positions are demonstrated in favor of their significant interaction leading to the cationic drift from 8R windows. This phenomenon explains a nonzero CO₂ adsorption in narrow pore zeolites upon high Na/K exchange. In a gas mixture, such deblocking effect reduces the separation factor because of the possible passage of both components through the plane of partly open 8R windows.



Effective separation of gas mixtures containing carbon dioxide is one of the central problems of carbon capture and storage.¹ During the study of the separation of carbon dioxide from dry CO₂/N₂ gas mixtures, it was found that NaKA zeolites with low and moderate contents of K have an exceptionally high selectivity for CO₂.² Similar separation effects were also manifested for other alkali form zeolites with 8R windows or D8R prisms on the basis of individual isotherms for the gas components (ETS-4,³ CHA,^{4–8} ZK-5,^{9–11} RHO,^{12–16} KFI,^{10,17} LEV,¹⁷ ETS-10,¹⁸ etc.). The kinetic diameter of an adsorbate, the size of alkali cation, and Si/Al modulus were already discussed as the important factors which should be taken into account to determine the pore-blockage temperature in MeCHA zeolites.⁷ However, the specific feature of CO₂ molecules forming carbonates^{2,5,10} has not been discussed. The usual disregard is based on a small CO₂ fraction (a few percent) which transforms into carbonates, but even a small amount of carbonate anions concentrated in the areas such as 8R windows or D8R prisms can significantly change the gas penetration. We will consider more precisely the case of the NaKA zeolite.²

When the Na/K exchange increases up to about K⁺/(Na⁺ + K⁺) = 33%, it becomes sufficient to “close” the 8R windows (site II) in the NaKA crystal as the K⁺ cations replace first the NaIII⁺ and NaII⁺ cations near 4R and in the 8R windows (Figure 1), respectively, because of a weaker binding to their sites. We recall that one KIII⁺ and three KII⁺ per each α-cage result in K⁺/(Na⁺ + K⁺) = (1 + 3)/12 * 100% = 33% while one NaII⁺ or KII⁺ is shared between two neighbor α-cages. When the NaA zeolite, with a free diameter around of 4.1 Å for 8R window,²² is transformed into NaKA at 40% K⁺/(Na⁺ + K⁺) the free diameter of the 8R window reduces to 3 Å. In such a

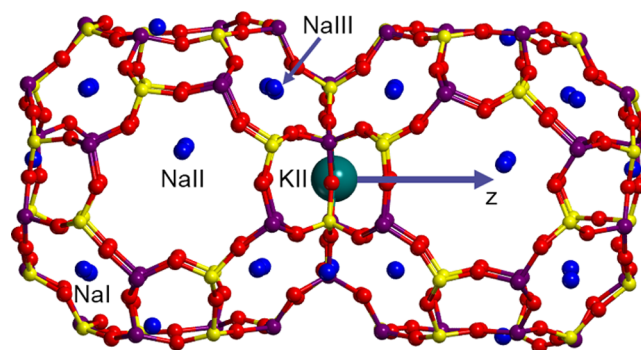


Figure 1. Pseudounit cell of NaKA zeolite used in the computations.^{19–21} OZ direction is perpendicular to 8R plane. The atomic colors are given in gray (small spheres), red, blue, magenta, yellow, and green for H, O, Na, Al, Si, and K, respectively.

case, adsorption of neither CO₂ nor N₂ is expected as their kinetic diameters are larger than 3 Å (3.3 and 3.64 Å, respectively²²). In reality, the CO₂ uptake is essentially nonzero at K⁺/(Na⁺ + K⁺) even higher than 40%.²

Atomistic simulations have been used to elucidate several mechanisms that explain how CO₂ can penetrate through “closed” 8R windows. The authors⁴ proposed the “molecular trapdoor” mechanism. By using nudged elastic band (NEB) calculation with density functional theory (DFT), they found that several CO₂ can displace an extra-framework cation from

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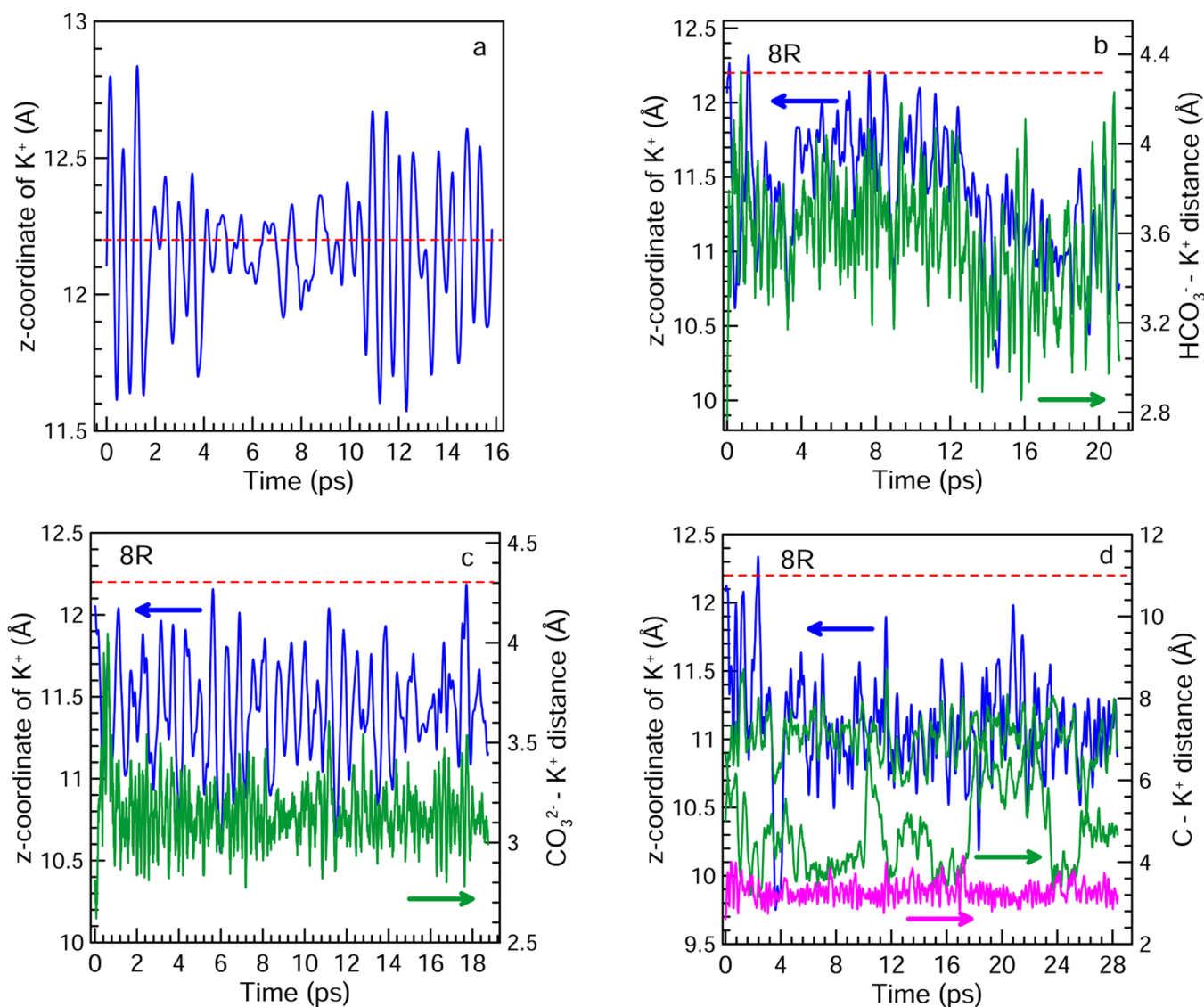


Figure 2. Time dependences (ps) of the K^+ displacement along OZ-axis (blue line, left axis) in empty NaKA (a) and the C- K^+ distance (green line, right axis in panels b–d); NaKA with HCO_3^- (b), CO_3^{2-} (c), and HCO_3^- and 7 CO_2 (d) per one α -cage at 300 K. The position of the 8R plane corresponds to 12.20 Å and is shown by a dashed line. Green and pink lines (d) represent C- K^+ distances for some CO_2 and HCO_3^- , respectively. Respective 3D trajectories of cationic and anionic species in (a–d) are presented in Figure S2a–d.

its position, and the next CO_2 can pass through below blockage temperature T_c related to the gas breakthrough. However, it has not been confirmed by recent ab initio molecular dynamics (AIMD)/DFT calculations^{12,20} and thermodynamic calculations.²³ No evidence was obtained from the chemical potentials upon CO_2 adsorption in NaA that a weak interaction between the CO_2 and Na^+ cations can displace cations from their crystallographic sites.²³ On the basis of the calculation of the free-energy profile of CO_2 entering 8R windows, the authors¹² proposed that the amplitude of thermal motion of extra-framework cations is large enough and that CO_2 is able to squeeze while the gate is open. This idea deviates from the hypothesis⁴ proposed for N_2 and CH_4 passing through 8R above threshold temperature T_s , which corresponds to the activation of cation migration. These propositions,^{4,12} however, do not explain nonzero CO_2 uptake in NaKA after a high Na/K exchange.

The CO_2 adsorption leads to a formation of chemisorbed carbonates that has been observed in Fourier transform

infrared (IR) measurements in many works.^{2,5,9,10,24–27} Recently, powder neutron diffraction allowed the measurement of the cationic shifts from their sites after CO_2 adsorption in NaA.²⁸ Earlier, only cationic drifts were assigned to CO_2 influence including the case of Mg shift from D6R site observed by Lobo et al. in MeZK-5¹⁰ where carbonates were also observed. The mechanism of CO_2 uptake associated with the carbonate formation from CO_2 and H_2O have been proposed in ref 21 in parallel with the “molecular trapdoor” mechanism.⁴ (A short discussion of other routes of carbonate formation in zeolites^{29–32} is in section S1 of the Supporting Information). This assumes that negatively charged carbonate species can withdraw cations from the windows by strong Coulomb interaction.²¹ The relevance of CO_3^{2-}/HCO_3^- channels for CO_2 capture mechanism by liquid amines³³ and amines deposited over various supports³⁴ was recently confirmed via ^{13}C NMR spectra.

This Letter provides analysis of the influence of carbonate species on the K^+ behavior in the course of CO_2 adsorption in

NaKA zeolite by AIMD. The pseudocell of NaKA zeolite (chemical composition $\text{KNa}_{23}\text{Al}_{24}\text{Si}_{24}\text{O}_{96}$) contains two α -cages divided by the 8R window (Figure 1) in which unique K^+ cation is located^{20,21} (details of the pseudocell construction are given in section S2 of the Supporting Information). The AIMD dynamics of mixtures containing 3 and 7 CO_2 , HCO_3^- , CO_3^{2-} , and 7 CO_2 plus HCO_3^- within one α -cage is simulated using PBE functional³⁵ combined with a plane wave basis set, the PAW pseudopotentials,³⁶ and D2³⁷ semiempirical dispersion corrections as implemented in the VASP package.^{38,39} The kinetic electron energy cutoff was imposed at 500 eV. These simulations were run with a time step of 1 fs for 1–30 ps at 300 K in a Nose–Hoover thermostat^{40,41} with 40 fs thermal oscillations.

IR spectroscopy demonstrated the presence of hydrocarbonate or/and carbonate anions in NaKA.² The modeling of the reaction between CO_2 and H_2O in the optimized NaKA cell by the climbing-image NEB method (Figure S1) reveals a minor barrier of 0.15 eV (imaginary frequency of the transition state is 298.8 i cm^{-1}). The small value of the barrier justifies the appearance of hydrocarbonate anion in our models. The exothermic effect of carbonate formation in various zeolites including NaA was evaluated earlier.^{21,42}

In the picosecond scale, the amplitude of K^+ cation motion relative to its equilibrium position in the plane of the 8R window of NaKA zeolite (Figure 1) is compared without (Figures 2a and S2a) and with one (Figures 2b and S2b) hydrocarbonate or (Figures 2c and S2c) carbonate anion in one of two α -cages of NaKA which are connected by the 8R window (Figure 1). The z -coordinate of K^+ remains around the 8R plane at the absence of any carbonate anion (near 12.20 Å in Figure 2a), while in the presence of hydrocarbonate, the average deviation is around 1.2 Å (near 11.0 Å in Figure 2b) after 17 ps. The period of K^+ vibrations in empty NaKA (Figure 2a) is around 0.5–0.64 ps, which corresponds to the frequencies of $52\text{--}67\text{ cm}^{-1}$ and is in a good agreement with 54 cm^{-1} ¹⁴³ or 58 cm^{-1} ¹⁴⁴ at low coordinated KIII site of the KX zeolite. During the equilibration (see quick temperature relaxation in Figure S3), either carbonate or hydrocarbonate is located near adjacent 6R (NaI^+), 4R (NaIII^+), and 8R (the last one with KII^+) windows. The carbonate anion interacts more tightly with 3 Na^+ and K^+ because of its higher charge, and after 2 ps no significant movement from that place is observed. In contrast, one can see that hydrocarbonate starts to displace K^+ further away from 8R window at 12 ps (Figures 2b and S2b) which results in the shift of 1.9 Å (reaching 10.3 Å in Figure 2b at 14 ps). Because of the weaker interaction with cations, hydrocarbonate has a higher mobility than carbonate, and it can migrate between the adjacent 6R windows (Figure 2b). The carbonate anion does not reproduce the same scale of motions, as it is in more tight contact with the cations (Figure S2c). To ensure this, one could compare the amplitudes of the IC– K^+ variations at the same conditions (in the absence of CO_2), i.e., for HCO_3^- in Figure 2b and for CO_3^{2-} in Figure 2c. Regarding different C– K^+ scales of Figure 2b,c on the one hand and of Figures 2d or S4 on the other hand, the longer time-of-life in both hydrocarbonate or carbonate complexes with K^+ seems to be evident versus that in $\text{K}^+\text{--CO}_2$. At the same time, neither 3 CO_2 (Figure S4) nor 7 CO_2 (Figure 3) can withdraw K^+ from the 8R window without hydrocarbonate or carbonate. The respective mobility of K^+ is quite similar to the case of the empty NaKA. The average position is still around the 8R window, and the amplitudes are 0.3–0.4 Å. The

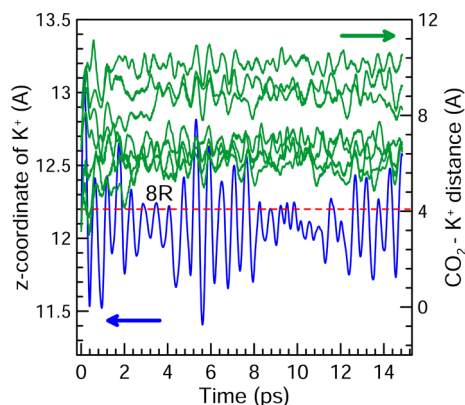


Figure 3. Time dependences (ps) of the K^+ displacement along the OZ-axis (blue line, left axis) and the C– K^+ distance (green line, right axis) in NaKA with 7 CO_2 at 300 K.

CO_2 molecules do not form complexes with K^+ as the distance between CO_2 and K^+ is greater than 4.2 Å (Figures 3 and S4).

The authors⁷ evaluated that a partially opened 8R window is sufficient for the admission of various adsorbed molecules, i.e., with the K^+ shift between 2.04 Å (H_2) and 3.00 Å (CH_4). These shifts can be hardly compared to respective shifts in other zeolites because (1) they are measured relative to one O atom of 8R window and (2) the 8R windows are differently distorted in other zeolites. Nevertheless, the similar order of cation shifts is obtained in Figure 2c,d. The largest distance between the K^+ atom and the respective oxygen of 8R window reaches 5.3 Å in the presence of hydrocarbonate. The strong Coulomb attraction with carbonates provides an energy gain for cationic drift according to our AIMD results. This gain was possibly the reason for the Mg shift from the stable D6R site observed by Lobo et al. in MgZK-5^5 or of the Na/K displacements from 8R in NaKA.²⁸ The drift of several angstroms is in agreement with calculated displacements of cations toward the carbonate formed in the RHO form (Figure 2e in ref 42).

This AIMD result is coherent to our earlier static calculations in which we obtained the series of stable minima of the K^+ positions along with carbonate outside the plane of the 8R window of NaKA.²¹ The long K^+ shift (Figure 2b–d) explains the nonzero CO_2 adsorption in NaKA with the Na/K exchange being higher than 33% when CO_2 cannot pass all 8R windows because its kinetic diameter is greater than 3 Å.² It seems that the microscopic model of carbonates should be taken into account while interpreting the breakthrough experiments with CO_2 mixtures.^{7,8} Such deblocking will anyhow reduce the separation factor in the gas mixture because of the possible passage of both gas components through the partly open 8R windows.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b00519.

Reaction profile between CO_2 and H_2O in the optimized NaKA cell (Figure S1), trajectories of the carbonate species (Figure S2), temperature relaxation (Figure S3), and some evaluations of the ion–quadrupole ($\text{K}^+\text{--CO}_2$) interaction energy (section S3) (PDF)

XDATCAR files (VASP format) with the dynamics of K^+ displacements upon the carbonate influences (to be viewed with OVITO or other visualization software) (ZIP)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Chu, S. Carbon Capture and Sequestration. *Science* **2009**, *325*, 1599–1599.
- (2) Liu, Q.; Mace, A.; Bacsik, Z.; Sun, J.; Laaksonen, A.; Hedin, N. NaKA sorbents with high CO_2 -over- N_2 selectivity and high capacity to adsorb CO_2 . *Chem. Commun.* **2010**, *46*, 4502–4504.
- (3) Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacobinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. A titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules. *Nature* **2001**, *412*, 720–724.
- (4) Shang, J.; Li, G.; Singh, R.; Gu, Q.; Nairn, K. M.; Bastow, T. J.; Medhekar, N.; Doherty, C. M.; Hill, A. J.; Liu, J. Z.; et al. Discriminative Separation of Gases by a “Molecular Trapdoor” Mechanism in Chabazite Zeolites. *J. Am. Chem. Soc.* **2012**, *134*, 19246–19253.
- (5) Pham, T. D.; Hudson, M. R.; Brown, C. M.; Lobo, R. F. Molecular Basis for the High CO_2 Adsorption Capacity of Chabazite Zeolites. *ChemSusChem* **2014**, *7*, 3031–3038.
- (6) Shang, J.; Li, G.; Singh, R.; Xiao, P.; Liu, J. Z.; Webley, P. A. Determination of Composition Range for “Molecular Trapdoor” Effect in Chabazite Zeolite. *J. Phys. Chem. C* **2013**, *117*, 12841–12847.
- (7) Li, G. K.; Shang, J.; Gu, Q.; Awati, R. V.; Jensen, N.; Grant, A.; Zhang, X.; Sholl, D. S.; Liu, J. Z.; Webley, P. A.; et al. Temperature-regulated guest admission and release in microporous materials. *Nat. Commun.* **2017**, *8*, 15777.
- (8) Du, T.; Fang, X.; Liu, L.; Shang, J.; Zhang, B.; Wei, Y.; Gong, H.; Rahman, S.; May, E. F.; Webley, P. A.; et al. An optimal trapdoor zeolite for exclusive admission of CO_2 at industrial carbon capture operating temperatures. *Chem. Commun.* **2018**, *54*, 3134–3137.
- (9) Liu, Q.; Pham, T.; Porosoff, M. D.; Lobo, R. F. ZK-5: A CO_2 -Selective Zeolite with High Working Capacity at Ambient Temperature and Pressure. *ChemSusChem* **2012**, *5*, 2237–2242.
- (10) Pham, T. D.; Hudson, M. R.; Brown, C. M.; Lobo, R. F. On the Structure-Property Relationships of Cation-Exchanged ZK-5 Zeolites for CO_2 Adsorption. *ChemSusChem* **2017**, *10*, 946–957.
- (11) Remy, T.; Peter, S. A.; Van Tendeloo, L.; Van der Perre, S.; Lorgouilloux, Y.; Kirschhock, C. E. A.; Baron, G. V.; Denayer, J. F. M. Adsorption and Separation of CO_2 on KFI Zeolites: Effect of Cation Type and Si/Al Ratio on Equilibrium and Kinetic Properties. *Langmuir* **2013**, *29*, 4998–5012.
- (12) Coudert, F.-X.; Kohen, D. Molecular Insight into CO_2 “Trapdoor” Adsorption in Zeolite Na-RHO. *Chem. Mater.* **2017**, *29*, 2724–2730.
- (13) Lozinska, M. M.; Mangano, E.; Mowat, J. P. S.; Shepherd, A. M.; Howe, R. F.; Thompson, S. P.; Parker, J. E.; Brandani, S.; Wright, P. A. Understanding Carbon Dioxide Adsorption on Univalent Cation Forms of the Flexible Zeolite Rho at Conditions Relevant to Carbon Capture from Flue Gases. *J. Am. Chem. Soc.* **2012**, *134*, 17628–17642.
- (14) Lozinska, M. M.; Mangano, E.; Greenaway, A. G.; Fletcher, R.; Thompson, S. P.; Murray, C. A.; Brandani, S.; Wright, P. A. Cation Control of Molecular Sieving by Flexible Li-Containing Zeolite Rho. *J. Phys. Chem. C* **2016**, *120*, 19652–19662.
- (15) Pera-Titus, M.; Palomino, M.; Valencia, S.; Rey, F. Thermodynamic analysis of framework deformation in Na,Cs-RHO zeolite upon CO_2 adsorption. *Phys. Chem. Chem. Phys.* **2014**, *16*, 24391–24400.
- (16) Lozinska, M. M.; Mowat, J. P. S.; Wright, P. A.; Thompson, S. P.; Jorda, J. L.; Palomino, M.; Valencia, S.; Rey, F. Cation Gating and Relocation during the Highly Selective “Trapdoor” Adsorption of CO_2 on Univalent Cation Forms of Zeolite Rho. *Chem. Mater.* **2014**, *26*, 2052–2061.
- (17) Yang, J.; Zhao, Q.; Xu, H.; Li, L.; Dong, J.; Li, J. Adsorption of CO_2 , CH_4 , and N_2 on Gas Diameter Grade Ion-Exchange Small Pore Zeolites. *J. Chem. Eng. Data* **2012**, *57*, 3701–3709.
- (18) Park, S. W.; Yun, Y. H.; Kim, S. D.; Yang, S. T.; Ahn, W. S.; Seo, G.; Kim, W. J. CO_2 retention ability on alkali cation exchanged titanium silicate, ETS-10. *J. Porous Mater.* **2010**, *17*, 589–595.
- (19) Mace, A.; Hedin, N.; Laaksonen, A. Role of Ion Mobility in Molecular Sieving of CO_2 over N_2 with Zeolite NaKA. *J. Phys. Chem. C* **2013**, *117*, 24259–24267.
- (20) Mace, A.; Laasonen, K.; Laaksonen, A. Free energy barriers for CO_2 and N_2 in zeolite NaKA: an ab initio molecular dynamics approach. *Phys. Chem. Chem. Phys.* **2014**, *16*, 166–172.
- (21) Larin, A. V.; Mace, A.; Rybakov, A. A.; Laaksonen, A. Carbonate “door” in the NaKA zeolite as the reason of higher CO_2 uptake relative to N_2 . *Microporous Mesoporous Mater.* **2012**, *162*, 98–104.
- (22) Breck, D. W. *Zeolite molecular sieves: structure, chemistry and use*; Krieger, 1984.
- (23) Guo, X.; Wu, L.; Navrotsky, A. Thermodynamic evidence of flexibility in H_2O and CO_2 absorption of transition metal ion exchanged zeolite LTA. *Phys. Chem. Chem. Phys.* **2018**, *20*, 3970–3978.
- (24) Pirngruber, G. D.; Raybaud, P.; Belmabkhout, Y.; Čejka, J.; Zúkal, A. The role of the extra-framework cations in the adsorption of CO_2 on faujasite Y. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13534–13546.
- (25) Montanari, T.; Busca, G. On the mechanism of adsorption and separation of CO_2 on LTA zeolites: An IR investigation. *Vib. Spectrosc.* **2008**, *46*, 45–51.
- (26) Delaval, Y.; de Lara, E. C. Study of physisorption of carbon dioxide on naa zeolite. Part 1.—Experimental results obtained by infrared spectroscopy. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 869–877.
- (27) Rzepka, P.; Bacsik, Z.; Smeets, S.; Hansen, T. C.; Hedin, N.; Wardecki, D. Site-Specific Adsorption of CO_2 in Zeolite NaK-A. *J. Phys. Chem. C* **2018**, *122*, 27005–27015.
- (28) Rzepka, P.; Wardecki, D.; Smeets, S.; Müller, M.; Gies, H.; Zou, X.; Hedin, N. CO_2 -Induced Displacement of Na^+ and K^+ in Zeolite —NaK—A. *J. Phys. Chem. C* **2018**, *122*, 17211–17220.
- (29) Zhidomirov, G. M.; Larin, A. V.; Trubnikov, D. N.; Vercauteren, D. P. Ion-Exchanged Binuclear Clusters As Active Sites of Selective Oxidation over Zeolites. *J. Phys. Chem. C* **2009**, *113*, 8258–8265.
- (30) Larin, A. V.; Zhidomirov, G. M.; Trubnikov, D. N.; Vercauteren, D. P. Ion-exchanged binuclear Ca_2O_X clusters, $X = 1–4$, as active sites of selective oxidation over MOR and FAU zeolites. *J. Comput. Chem.* **2009**, *31*, 421–430.
- (31) Larin, A. V.; Rybakov, A. A.; Zhidomirov, G. M.; Mace, A.; Laaksonen, A.; Vercauteren, D. P. Oxide clusters as source of the third

oxygen atom for the formation of carbonates in alkaline earth dehydrated zeolites. *J. Catal.* **2011**, *281*, 212–221.

(32) Larin, A.; Bryukhanov, I.; Rybakov, A.; Kovalev, V.; Vercauteren, D. Theoretical identification of carbonate geometry in zeolites from IR spectra. *Microporous Mesoporous Mater.* **2013**, *173*, 15–21.

(33) Kortunov, P. V.; Siskin, M.; Baugh, L. S.; Calabro, D. C. In Situ Nuclear Magnetic Resonance Mechanistic Studies of Carbon Dioxide Reactions with Liquid Amines in Aqueous Systems: New Insights on Carbon Capture Reaction Pathways. *Energy Fuels* **2015**, *29*, 5919–5939.

(34) Chen, C.-H.; Shimon, D.; Lee, J. J.; Mentink-Vigier, F.; Hung, I.; Sievers, C.; Jones, C. W.; Hayes, S. E. The “Missing” Bicarbonate in CO₂ Chemisorption Reactions on Solid Amine Sorbents. *J. Am. Chem. Soc.* **2018**, *140*, 8648–8651.

(35) Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(36) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(37) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.

(38) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *47*, 558–561.

(39) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169–11186.

(40) Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* **1984**, *81*, 511–519.

(41) Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Phys. Rev. A: At., Mol., Opt. Phys.* **1985**, *31*, 1695–1697.

(42) Larin, A. Deblocking effect of carbonates and hydrogen carbonates in the alkali form zeolites with narrow pores. *Microporous Mesoporous Mater.* **2014**, *200*, 35–45.

(43) Brodskii, I. A.; Zhdanov, S. P. Spectral properties of interionic vibrations in synthetic zeolites. *J. Appl. Spectrosc.* **1980**, *33*, 999–1003.

(44) Butler, W. M.; Angell, C. L.; McAllister, W.; Risen, W. M. Far-infrared study of cation motion in dry and solvated mono- and divalent cation containing zeolites X and Y. *J. Phys. Chem.* **1977**, *81*, 2061–2068.

(45) Sadovnichy, V.; Tikhonravov, A.; Voevodin, V.; Opanasenko, V. In *Contemp. High Perform. Comput. From Petascale Towar. Exascale*; Vetter, J. S., Ed.; CRC Press: Boca Raton, FL, 2013; pp 283–307.