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1. Introduction

The chemistry of CO_2 trapping, separation, and storage remains a critical task for modern and future researches in the domain

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A forgotten participant in pore deblocking of zeolites: dicarbonate in NaMeA zeolites, Me = Na, K, Rb, Cs†

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The dynamics of carbon dioxide, carbonate anion $(CO_3^{2^-})$, and dicarbonate anion $(C_2O_5^{2^-})$ in NaKA zeolite is studied at the DFT GGA level using *ab initio* molecular dynamics (AIMD). We show the easy formation of $C_2O_5^{2^-}$ dicarbonate from the reaction between $CO_3^{2^-}$ and CO_2 at high CO_2 loading and their equilibrium at low CO_2 loading. We have found that the dicarbonate anion can contact up to six cations (Me⁺ and Na⁺, Me = Na, K, Rb, Cs), which could reduce the separation properties of NaMeA zeolites relative to CO_2 mixtures. The K⁺ interaction with dicarbonate $C_2O_5^{2^-}$ species pushes the cation from 8R site in full analogy with the carbonate's deblocking studied earlier. The easy $C_2O_5^{2^-}$ formation in NaMeA is confirmed by modeling reaction of $C_2O_5^{2^-}$ formation at the DFT GGA (PBE-D3) and hybrid levels (B3LYP, HISS, HSE06) with cNEB. The calculated intensities for high and low frequency branches of valence vibrations in $C_2O_5^{2^-}$ are compared with calculated ones for Me₂C₂O₅ molecules and known IR spectroscopic data in the NaMeA zeolites. This new mechanism of deblocking could be important for a wide family of narrow pore zeolites (CHA, RHO, KFI, *etc.*) at room temperature where the carbonates are observed in the IR spectra.

of renewable carbon sources. An explosion of interest to the separation of CO₂ mixtures showed the cation gating¹ and breathing² mechanisms or their cooperative action^{3,4} as the effects, which can be directly confirmed by XRD data. The breathing or flexibility-driven mechanism is interpreted to be governed by the relative strength of the interactions of extra-framework cations with both the zeolite framework and the guest species.³ Cation gating appeared in different cationic form zeolites as cationic displacements in the presence of CO₂ or its mixtures.³⁻⁶ The flexibilitydriven effects are observed in the same systems in parallel. More precisely, the unusual growth of CH₄ adsorption of Me'MER zeolites (Me' = Na, K, Cs with different Si/Al modulus) after the minor addition of CO₂ to the gas has been interpreted as a consequence of the transformation of the 8R windows.4,6 The redistribution of Na and Cu cations in NaRHO between 6R windows (favorite for Cu) and 8R ones (favorite for Na) leads to the elliptic 8R deformation when it is occupied by a Na cation.⁵ Many effects related to the cation gating¹ (or blocking) and breathing² mechanisms were studied using narrow-pore cationic alkali RHO,1,2,5,7,8 KFI,9 and CHA10,11 forms. For all three frameworks, IR data showed the formation of carbonate species, *i.e.*, for RHO,^{1,7,8} for KFI,⁹ and for CHA.¹¹ It makes the participation of carbonates in the deblocking of narrowpore NaKA discussed earlier^{12,13} to be at least formally relevant for all these framework types.

Recent conclusion about a minor fraction of chemisorbed CO_2 species from IR spectra¹¹ compared to the total CO_2

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[†] Electronic supplementary information (ESI) available: Part S1 is related to the calculation of vibrational entropy at the PBE-D3 level (Table S1) and of the total entropy at the B3LYP level (Table S2) at separate points of AIMD trajectory. CRYSTAL17 output file 9_555.out is supplied for illustration of H-H coupling modes (at the time 9.555 ps) occurred in the entropy calculations (please see comments in Part S1). Simplified description of this study in a comparison with our previous works is given in Part S2 for more general picture. Thermal AIMD equilibration (K) for the reaction (3) with one CO_2 and one CO_3^{2-} species is shown in Fig. S1. Trajectories of Na and K cations, C and O atoms are shown for the reaction (3) with one CO_2 and one CO_3^{2-} species (low loading) in the course of AIMD run in Fig. S2. The "Naa_c2o5.avi" file with calculated reaction profile, the "NaKA_TS_all_freq. avi" file with all frequencies for transition state of C2O52formation in NaKA, and the "C2O5_new.mp4" file with the dynamics of $C_2O_5^{-2-}$ formation and the next drift K⁺ together with anion (to be viewed with any visualization software) are supplied. The CONTCAR.mol with initial coordinates of all atoms and CO2 molecules (and its version 1co3_7co2 as input for AIMD with the VASP code) at high CO₂ loading is given and can be seen via the MOLDRAW³⁴ code. See DOI: https://doi.org/10.1039/d3cp00433c

number per cell is in a general agreement with the earlier estimates of about 1-2 CO2 molecules chemisorbed per Me"X unit cage, Me'' = Na, Ca,¹⁴ and a respective decline of 8% of available porous space in an open FAU framework (NaX).¹⁵ For narrow-pore zeolites, however, new understanding could be obtained if the number of the carbonate species would be compared to the number of the cations, which can block the channels. It would be also constructive to evaluate the number of cations. which can contact with one carbonate anion. The answers to these questions can help understand the real significance of a small fraction of chemisorbed CO₂. Both queries could be easily studied with theoretical methods because it requires knowledge about precise position of the carbonate in each specific cationic form. Such information is difficult to extract by XRD or neutron scattering methods due to small concentrations^{11,14,15} and disordered positions of carbonates. Hence, theoretical methods could be thus useful to evaluate the role of chemisorbed CO2 in narrow-pore zeolites.11

The location of cations directly determines the separation properties of narrow-pore zeolites.^{1,6,16} The crucial influence of carbonates^{12,13} and bicarbonates^{13,17} on the positions of alkali cations in zeolites has been shown theoretically. Are they the only species throughout the products of CO₂ reactions that can modify the cationic positions? The results below demonstrate that the $C_2O_5^{2-}$ dicarbonate anion can also participate in cationic drift. This work considers for the first time the formation and the influence of dicarbonate anions on the behavior of heavy alkali cations, which block 8R windows in the alkaline forms of LTA zeolite. The feature of dicarbonates is the contact with two blocking cations at different 8R windows compared to the carbonates studied earlier,^{12,13,17} which contacts one such cation. To the best of our knowledge, it is the first work showing the existence and possible role of the dicarbonate anions in narrow pore zeolites.

After the presentation of computational details (Part 2), the results of AIMD run are given at high (Part 3.1.1) and low (Part 3.1.2) loadings. The activation barriers of the reaction (3) (Part 3.2) and IR frequencies/intensities (Part 3.2) are presented at low loading. The final part 3.4 of the results is devoted to the possible formation of tricarbonates at high loading.

2. Computational details

The pseudounit cell of NaMeA zeolite (12.305 Å, 12.305 Å, 24.610 Å, 90°, 90°, 90°) with chemical composition MeNa₂₃Al₂₄Si₂₄O₉₆, Me = Na, K, Rb, Cs, contains two α -cages divided by the 8R window (Fig. 1a) in which the unique Me⁺ cation is located¹² (details of the pseudounit cell construction with periodic boundary conditions are given in refs. 12 and 13). The AIMD of mixtures containing seven CO₂ and one CO₃⁻ (high CO₂ loading) or one CO₂ and one HCO₃⁻/CO₃²⁻ (low CO₂ loading) within one α -cage of total two is simulated at the PBE-D3 level in the VASP package.^{18,19} PBE functional²⁰ was combined with a



Fig. 1 (a) NaKA model and temporary dependences (ps) of the (b) K⁺ displacement along OZ-axis (blue arrow in a) relative to the 8R window (b, red dashed line at 12.20 Å) at high loading (seven CO₂ and one CO₃²⁻), (c) the C1-K⁺ and C2-K⁺ distances (green and light cyan lines) and O-K⁺ distance (purple line) relative to central O atom of C₂O₅⁻, (d) C1-O, C2-O, C1-C2 distances in C₂O₅⁻ (light cyan, green, and purple lines) (c) at 300 K.

plane wave basis set, the PAW pseudopotentials,²¹ as implemented in the VASP package.^{18,19} D3 semiempirical dispersion correction²² was used whose comparable accuracy for periodic systems was shown relative to the D4 level.²³ The kinetic electron energy cutoff was imposed at 500 eV. These simulations were run with a time step of 1 fs at 300 K in a Nose-Hoover thermostat^{24,25} with 40 fs thermal oscillations. Thermal equilibration was achieved after 1 ps (Fig. S1, ESI⁺). The simulation time was limited to 15 ps at high loading (seven CO₂ and one CO_3^{2-}) and 10 ps at low loading (one CO_2 and one CO_3^{2-} / HCO_3^{-}). The run was performed at temperature T = 300 K only. The effect of temperature on the results was not considered. The Brillouin zone sampling was restricted to the Γ -point. For the reaction path for C₂O₅²⁻ formation, climbing image nudged elastic band (cNEB) modeling²⁶ was applied at the PBE-D3 level. Both AIMD and cNEB modeling of the C₂O₅²⁻ formation (3) occur as the third stage of the reaction chain $\text{CO}_2 \rightarrow \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} \rightarrow \text{C}_2\text{O}_5^{2-}$.

$$H_2O + CO_2 \rightarrow HCO_3^- + H^+$$
(1)

$$HCO_3^- \to CO_3^{2-} + H^+$$
 (2)

$$\text{CO}_3^{2-} + \text{CO}_2 \to \text{C}_2 \text{O}_5^{2-}$$
 (3)

Despite the dehydration procedures of the zeolites before gas separation, a minor concentration of water remains in the cationic form zeolites after it to participate in reaction (1).^{16,27-31} Two alternative routes of carbonate formation are discussed in the Part 4. In our study, only one CO_3^{2-}/HCO_3^{-} was considered after reaction (1) irrespective of CO_2 loading (please see Part S2 for more details (ESI†)). The experimental formation of CO_3^{2-} was shown in a wide interval of CO_2 loading.²⁷ The time of its formation depends on the concentration of water, which remains nevertheless after the drying of the zeolite.²⁷

Regarding the constant temperature and pressure (one assumes that CO₂ pressure remains constant in the course of the reaction (3)), the variation of Gibbs energy $\Delta G_{ij} = \Delta H_{ij}$ – $T\Delta S_{ij}$ between the *i*- and *j*-points of the reaction profile or AIMD run was replaced by $\Delta U_{ij} - T\Delta S_{ij}$, ΔU_{ij} is calculated by DFT methods being usually larger (in absolute value) than $T\Delta S_{ii}$ values whose the variations were calculated along the reaction coordinate (2) and AIMD run. The frequencies and entropies were calculated (Tables S1 and S2 of ESI[†]) for fixed geometries at certain moments of AIMD modeling with the allowed movements of 16 or 17 atoms (other 161 or 160 atoms, respectively, were kept fixed). These 16 (with GGA DFT) or 17 (with hybrid DFT) atoms correspond to a reaction media. The comparison of the vibrational entropy was performed for low loading because the case of high loading is hindered owing to the numerous imaginary frequencies for CO₂ since they are not in the local minimum of the energy. Such a comparison between different points along the AIMD trajectory analysis becomes very complex due to the different imaginary frequencies of different CO₂ molecules (please see the last passage of Part S2 for more details (ESI[†])).

The exothermic step (1) has been already studied at the cNEB level earlier (heat of reaction is $-0.3 \text{ eV}^{13,32,33}$), while the

endothermic reaction (2) was considered with cNEB herein (Part 3.1.2). The reaction (3) was investigated using cNEB (Part 3.2) and AIMD (Part 3.1.2). Two different selections of initial geometries for AIMD were considered. For higher CO₂ loading, CO₂ molecules were manually added to the initial model (Fig. 1a). We added the file with initial coordinates of all atoms to the end of ESI[†] part in *mol format (and input file for VASP) where the positions and "crude" (nonoptimized) initial geometries of CO₂ molecules can be seen with the MOLDRAW³⁴ code. The AIMD started from these initial CO₂ positions while for the lower CO₂ loading it was initiated from the final products of the stage (2). After the stages (1) and (2) the zeolite framework contains one and two protons, respectively, and one CO32-. Only one CO32- per pseudocell was obtained after reaction (1) for both loadings basing on the experimental data^{14,15} (a brief discussion is presented at the end of the "Discussions" part). Different positions of protons relative to the reagents were tested either in remote positions of neighboring α -cage at high CO₂ loading, or in the same α -cage at low CO₂ loading. The IR intensities for $C_2O_5^{2-}$ in the IR spectra were calculated at the density functional perturbation theory (DFPT) level using Born charges, as realized with VASP (Part 3.3).35 Vibrational frequencies were calculated using the finite difference method as implemented in VASP. Small displacements (0.015 Å) of the atoms of interest were used to estimate the numerical Hessian matrix. The accuracy of the NaKA model for the solution of vibrational problem was earlier confirmed by a good agreement with KII⁺ frequencies measured for the weakly bonded KIII⁺ site of KX.13 The atomic charge density distribution was partitioned using Bader,³⁶ Mulliken, and Löwdin³⁷ schemes. A part of the computations with VASP was realized using GPU facilities.38,39

CRYSTAL17 code⁴⁰ was applied for single point computations along the reaction profiles (initial and final geometries, transition state) optimized using PBE-D3. Hybrid HF-DFT functionals, *i.e.*, global hybrid B3LYP, range-separated hybrids, namely, screened-coulomb HSE06⁴¹ and middle-range corrected HISS,^{42,43} were considered at the fixed geometries optimized at the PBE-D3 level. The atomic basis sets were involved as recommended in CRYSTAL: 86-511G*(K),⁴⁴ 8-511G(Na),⁴⁴ TZVP(Rb),⁴⁵ TZVP(Cs),⁴⁶ TZVP(H),⁴⁷ 8-411G*(O), 88-21G*(Si), 85-11G*(Al).⁴⁸

3. Results

3.1 AIMD simulations

The AIMD calculations showed the $C_2O_5^{2-}$ formation at higher or lower CO₂ loading irrespective of the NaKA model with the proton's positions in the neighboring α -cage (at high CO₂ loading) or in the same α -cage where the reaction takes place (at low CO₂ loading). In the last case, the equilibrium between CO_3^{2-} and $C_2O_5^{2-}$ is more shifted toward CO_3^{2-} in coherence with experiment¹⁶ according to respective intensities of their peaks assigned below for $C_2O_5^{2-}$. For the reaction at low CO₂ loading, the calculation of entropy contribution to the free energy was realized; thus, we consider the different loadings in two separate parts below.

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3.1.1 High CO₂ loading. *Ab initio* simulations show the easy formation of dicarbonate molecule from a reaction between CO_3^{2-} and CO_2 at 1.465 ps of the simulation captured as a movie (*mp4*-type illustration corresponding to a part ~5 ps of total run time ~14 ps in ESI†). The dicarbonate molecule was formed in the media (Fig. 2e) and remained stable throughout all the simulation of ~15 ps. Coherent motions of the K⁺ and dicarbonate can be outlined (Fig. 1c) as well as the essential K⁺ deviation from the plane of the 8R window (shown by red dashed line in Fig. 1b). The cation is nonsymmetrically coordinated to the anion so that the $C2\cdots K^+$ distance varies in a narrower range that for $C1\cdots K^+$ (Fig. 1c). The larger amplitudes of $C1-K^+$ motions illustrate a relative freedom of the dicarbonate "tail" relative to K⁺ in the course of diffusion together.

The respective AIMD movie deserves a short comment. For simplicity, only one α -cage with CO₃²⁻ and seven CO₂ are shown in the video file and Fig. 2, respectively. "Libretto" of the movie is the following: (1) CO₃²⁻ is shown by a circle beginning from 0 ps (Fig. 2a). During this initial step, CO₃²⁻ pulls the K⁺ cation from the 8R plane with especially large amplitude from 0.7 to 1.2 ps (Fig. 1b); (2) at 0.7 ps, the second circle depicts the CO₂ species, which will participate in the reaction with the CO₃²⁻ one; (3) the C₂O₅²⁻ anion is formed at 1.465 ps and steeply approaches the K⁺ cation. Despite a minor barrier of its formation, the C₂O₅²⁻ anion does not decompose during all the 15 ps (C1–C2 distance in Fig. 1d). The next process to be seen after C₂O₅²⁻ formation is the deviation of K⁺ together with C₂O₅²⁻ from its position in the 8R window. K⁺ is withdrawn from 8R window, thus deblocking it starting from 3.2 ps and to the end of the movie (5.465 ps).



Fig. 2 The 7 steps (time in ps is shown in left upper corner) of AIMD run at the PBE-D3 level. The circles depict CO_3^{2-} (4 first scans, a–d), CO_2 (3rd and 4th scans, c and d), and $C_2O_5^{2-}$ (3 last scans, e–g) species. The atomic colors are given in olive, red, blue, magenta, yellow, and cyan for C, O, Na, Al, Si, and K, respectively.

A conservation of the anion geometry can be checked from Fig. 1c and d.

The 8R deblocking effect can be evaluated from Fig. 1b. During the period from start to 3 ps the K⁺ cation moves with a large amplitude around coordinate Z = 11.2 Å (nearly 1.1 Å from 8R plane) and after this the amplitude decreases varying around a lower average Z = 11.0 Å (nearly 1.3 Å from 8R plane) up to 14 ps. This position can be compared with less effective action produced by one CO₃²⁻ in Fig. 1c¹³ or by HCO₃⁻ and 7 CO₂ in Fig. 1d.¹³ If the average K⁺ shift from 8R varies around of 11.4 Å at the presence of one CO₃²⁻, the longer shift (around 11.0 Å) is realized at the presence of HCO₃⁻ and seven coadsorbed CO₂. So, in both cases (at high loading here and with 7 CO₂ in ref. 13) additional CO₂ enhance the K⁺ drift from the 8R plane.

3.1.2 Low CO₂ loading. Together with the appropriate conditions for $C_2O_5^{2-}$ formation (7 CO₂ and one CO₃²⁻ thus imitating a high CO₂ loading in part 3.1.1) the reaction (3) was studied when only one CO₂ and one CO₃²⁻ participate that correspond to a lower CO₂ loading which is not the most favor route for the $C_2O_5^{2-}$ formation according to the experiment.^{16,28} This computation was extended for reaction (2) using the cNEB method. The final state of reaction (2) was used as the initial point for the AIMD study. The reagents and products were optimized showing a slight endothermic effect of 0.40 eV (Fig. 3), but a more stable geometry of the product was obtained in the course of the cNEB modelling (the lower inset in Fig. 3), thus shifting down the endothermic effect up to 0.17 eV (Fig. 3). While the $C_2O_5^{2-}$ formation was irreversibly obtained after 1 ps at high loading (Fig. 1c and d), the respective $C_2O_5^{2-}$ formation



at 6 ps was reversible at low loading transforming to CO_3^{2-} (when the C–O distance becomes more than 1.7 Å in Fig. 4) after 7.5 ps. The examples of C–O distances are shown in Fig. 4d, e and 5a.

We searched for the barrier of the reaction (2) using cNEB (Fig. 3). The experimental data point on easy CO_3^{2-} formation from HCO_3^{-} at room temperature (RT) in NAA and NaKA according to the presence of two close peaks with band splitting (BS) of about 20–60 cm⁻¹, which are often not resolved.^{16,28-30} The complexity of the reaction (2) is conditioned by its multiparticle character, *i.e.*, by the parallel motions of some Na⁺ cations to locally compensate the higher charge of CO_3^{2-} species instead of HCO_3^{-} . More precisely, two Na⁺ and one K⁺ are the closest cations relative to HCO_3^{-} compared to four Na⁺ and one



Fig. 4 (a) Temporary dependence (ps) of the C–O distance in $C_2O_5^-$ (Å) in the course of the AIMD run in NaKA according to eqn (3) at low loading (one CO₂ and one CO₃^{2–} per pseudocell) between O atom of CO₃^{2–} and C atom of CO₂ at 300 K. Respective geometries at different time moments are shown in (b–e). The arrows in (a) show the points where vibrational entropies were calculated (Table S1, ESI†).



Fig. 5 The geometries of (a) $C_2O_5^{2-}$ and (b) $C_3O_7^{2-}$ optimized in NaKA at high loading (from seven CO_2 and one CO_3^{2-} per pseudocell) at the PBE-D3 level. The ellipses depict the anions. The color agreement corresponds to that in Fig. 2. Respective upper frequencies and relative intensities (which are usually observables) are in Table 7. Relative energies are given in eV.

 K^{+} for CO₃²⁻ (the lowest and middle insets in Fig. 3, the quantities of the closest ions are determined by the condition $|Me^{*^+}-O_C| < 0$ 3 Å where Me^{*} = Na, K; O_C is the atom of carbonate group). The final barrier of 0.8 eV shown in Fig. 3 seems to be rather large (Table 1) for the reaction at RT conditions. An argument in favor of the crude estimations of activation energy $E^{\#}$ at higher levels (Table 1) comes from the frequency calculations at the B3LYP level for the reagents of the reaction (2) (1st line in Table S2, ESI[†]). Two imaginary frequency for the reagents of the reaction (2) were obtained at the B3LYP level for the geometry optimized at the GGA/PBE level. Hence, another geometry for the reagents is required at the B3LYP level and possibly for other hybrid DFT cases (Table 1) as well. Thus, one believes that we can consider the reaction (3) despite the overestimated barrier for the reaction (2) since the presence of the initial CO_3^{2-} product has been shown experimentally.^{16,28-31} The alternative variants of the reaction (2) are briefly discussed in the final part of the "Discussions".

To check the role of entropy at the steps (2) and (3), the vibrational S_{vib} entropy was evaluated as the most important part of entropy for the adsorbed molecules at the PBE-D3 level. It was calculated in two points (reagents and products) of the reaction (2) and in some selected points along the reaction path (3) studied with AIMD for low CO₂ loading (one CO₂ and one CO₃^{2–} per pseudocell). The constant number of 16 atoms (two H atoms, nearest seven surrounding cations plus the reactive species CO₂ and CO₃^{2–} or C₂O₅²) in each point was allowed to

Table 1 The activation $E^{\#}$ barriers (eV) of the reaction (2) with the GGA (PBE) and hybrid DFT methods (the basis set for the hybrid DFT is given in Part 2) for the geometry optimized at the PBE-D3/PAW level

Method	$E^{\#}$
PBE-D3	0.805
HISS	0.889
HSE06	0.869
B3LYP	0.842
PBE0	0.873

Table 2 The parameters (activation energy $E^{\#}$, heat of reaction ΔU , both in eV, imaginary frequencies of transition state, in cm⁻¹) of C₂O₅²⁻ formation reactions in the NaMeA zeolites, Me = Na, K, Rb, Cs, at DFT GGA (PBE) and hybrid (B3LYP, HISS, HSE06) theory levels

Method	$E^{\#}$	ΔU	$-i\omega$
PBE-D3	0.082	-0.293	59.1
B3LYP	0.117	-0.337	_
HISS	0.112	-0.645	_
HSE06	0.109	-0.486	—
PBE-D3	0.026	-0.265	85.2
	0.036^{a}	-0.220^{a}	
B3LYP	0.068	-0.279	_
HISS	0.084	-0.444	_
HSE06	0.063	-0.414	—
PBE-D3	0.034	-0.230	_
B3LYP	0.037	-0.275	_
HISS	0.049	-0.422	_
HSE06	0.033	-0.409	_
PBE-D3	0.026	-0.250	24.5
	0.035^{a}	-0.250^{a}	
B3LYP	0.018	-0.289	_
HISS	0.035	-0.434	_
HSE06	0.024	-0.419	_
	Method PBE-D3 B3LYP HISS HSE06 PBE-D3 B3LYP HISS HSE06 PBE-D3 B3LYP HISS HSE06 PBE-D3 B3LYP HISS HSE06	Method $E^{\#}$ PBE-D3 0.082 B3LYP 0.117 HISS 0.112 HSE06 0.109 PBE-D3 0.026 0.036 ^a B3LYP 0.068 HISS 0.084 HSE06 0.0031 PBE-D3 0.034 B3LYP 0.037 HISS 0.049 HSE06 0.033 PBE-D3 0.026 0.035 ^a B3LYP 0.018 HISS 0.026 0.035 ^a B3LYP 0.018 HISS 0.035	$\begin{tabular}{ c c c c c c } \hline Method & E'' & \Delta U \\ \hline PBE-D3 & 0.082 & -0.293 \\ B3LYP & 0.117 & -0.337 \\ HISS & 0.112 & -0.645 \\ HSE06 & 0.109 & -0.486 \\ \hline PBE-D3 & 0.026 & -0.265 \\ & 0.036^a & -0.220^a \\ B3LYP & 0.068 & -0.279 \\ HISS & 0.084 & -0.444 \\ HSE06 & 0.063 & -0.414 \\ \hline PBE-D3 & 0.034 & -0.230 \\ B3LYP & 0.037 & -0.275 \\ HISS & 0.049 & -0.422 \\ HSE06 & 0.033 & -0.409 \\ \hline PBE-D3 & 0.026 & -0.250 \\ & 0.035^a & -0.250^a \\ B3LYP & 0.018 & -0.289 \\ HISS & 0.024 & -0.419 \\ \hline \end{tabular}$

⁴ Starting cNEB from 1st point (left minimum in Fig. 7).

move while calculating the frequencies. The remaining remote atoms were fixed. The $S_{\rm vib}$ values were obtained at different N points either in the case of ${\rm CO_3}^{2-}$ or ${\rm C_2O_5}^{2-}$ geometries and compared relative to the $S_{\rm vib}$ (1) of the product (*i*), *i.e.*, $\Delta S_{\rm vib}(i) = S_{\rm vib}(i) - S_{\rm vib}(1)$, $i = 1, \dots, N$ (these points are depicted by arrows in Fig. 4a). The differences between $T\Delta S_{\rm vib}(i)$ values along the reaction paths (2) and (3) vary between -0.027 and 0.042 eV at T = 300 K, when RT = 0.026 eV (Table S1, ESI†). It cannot have a significant influence on the Gibbs energy $\Delta G = \Delta H - T\Delta S = \Delta U - T\Delta S$ (at fixed temperature and pressure) relative to the heats of the reaction (2) or (3) with $\Delta U = +0.17$ eV (see Fig. 3) or -0.265 eV (see Table 2), respectively.

At the B3LYP level the total entropy, TS(i) was calculated including the vibrational entropy at the same *i*-series of time moments using the CRYSTAL code and the same selected 16 atoms (plus one O atom) (Table S2, ESI[†]). The latter are allowed to move while other atoms are fixed in the agreement with the selected *i*-moment of the AIMD run. Similar evaluations of the entropy terms serve as the error boundaries (their maximal TS(i) changes between the *i*-points) for ΔG , *i.e.*, $\Delta G = -0.279 \pm$ 0.061 eV per cell at the B3LYP level instead of -0.265 ± 0.042 eV per cell at the PBE-D3 level for the NaKA case (0.061 and 0.042 correspond to the RMS deviations for $T\Delta S_{vibr}$ values in Table S2, ESI[†], respectively). It showed the reasonability of the enthalpy (or ΔU) consideration when kinetic modelling based on Gibbs energy could hardly give a new interpretation.

3.2. Activation energy of dicarbonate formation

3.2.1 NaKA zeolite. Despite the easy formation of dicarbonate in AIMD calculations, the additional analysis of its structure and the activation barrier of its formation is required in NaKA zeolites. cNEB computations of the reaction path of $C_2 O_5^{2-}$ formation (3) from CO_3^{2-} and CO_2 were performed. Respective reaction coordinate of C2O52- formation corresponds to the combined motion of angular vibration of O-C-O and of the center of mass of $K^+ + CO_2$ group toward the O_c atom of the CO_3^{2-} group. This process is visualized in the "NaKA TS all freq.avi" file (see ESI^{\dagger}). The small exothermic effect of -0.265 eV accompanies the reaction at the PBE-D3 level. To verify the cNEB results at the higher computational levels, the higher barriers and higher heats of the $C_2 O_5{}^{2-}$ formation were obtained with the hybrid methods than those obtained using GGA ones (Table 2). In the optimized products of reaction (3), the number of cations contacting with the anion increases from CO_3^{2-} to $C_2O_5^{2-}$. The CO_3^{2-} reagent has 5 nearest atoms (one KII and two NaI, NaIII, NaII located nearby from 2.224 to 2.390 Å within the α -cage in Fig. 6 and Table 3, the closest NaII' also blocks neighboring 8R window, $|NaII-O_C| =$ 2.224 Å to the nearest O_c atom of the CO_3^{2-} group as well as KII). The $C_2O_5^{2-}$ product conserves the same 5 contacts of CO_3^{2-}



Fig. 6 The geometries of isolated (a) Na₂C₂O₅ and (b) NaKC₂O₅ molecules whose parameters and frequencies are shown in Tables 4 and 5, respectively, and C₂O₅²⁻ geometries in NaMeA zeolite with one Me cation per pseudocell, where Me = (c) Na, (d) K, (e) Rb, (f) Cs, all optimized at the PBE-D3 level. The crystallographic types of the nearest cations (d, Table 3) and C-O bond lengths (f, Table 4) are shown (Å). The way to calculate the torsional O=C···C = O angle in C₂O₅²⁻ is shown in (a). The atomic colors are given in olive, red, blue, cyan, light green, and light magenta for C, O, Na, K, Rb, and Cs, respectively.

Table 3 The Na/Me–O_c distances (in Å) in the reagents (CO₃²⁻) and products (C₂O₅²⁻) of the reaction (3) in the NaMeA zeolites at the PBE-D3 theory level

	NaA		NaKA		NaRbA	NaCsA
Cation	$\mathrm{CO_3}^{2-}$	$C_2 O_5^{2-}$	$\overline{\mathrm{CO_3}^{2-}}$	$C_2 O_5{}^{2-}$	$\overline{{C_2 O_5}^{2-}}$	$C_2 O_5^{2-}$
NaI	2.364	2.478	2.342	2.452	2.409	2.411
		_	2.765	3.465	3.446	3.427
NaI′	2.307	2.492	2.390	2.554	2.404	2.379
NaI''		2.442	_	2.431	2.469	2.456
NaII/MeII	2.354	2.481	2.855	3.336	3.344	3.450
	2.537	3.272	2.685	2.852	3.172	3.364
		2.311	_	2.682	2.976	3.269
NaII'	2.294	2.438	2.224	2.392	2.360	2.343
NaIII	2.308	2.434	2.276	2.454	2.432	2.445
	_	2.331	_	2.279	2.285	2.269

(with similar Na-O_C distances) but can additionally achieve the third NaI" site at the $|NaI''-O_C| = 2.431$ Å (Table 3). One should take into account that these contacts are achieved due to large cationic shifts from their exact crystallographic positions. For example, one of three NaI cations becomes bi-coordinated to the framework Oz atoms of 6R ring in the NaCsA framework so that the Na–Oz distances increase up to 2.399, 2.4127, and 2.809 Å. Longer cationic drifts were obtained at the presence of CO_3^{2-} in NaX.^{32,49,50} We underline that the $C_2O_5^{2-}$ and CO_3^{2-} species contact the KII and NaII' atoms, which block two neighboring 8R windows. The behavior of the NaII' atom is very instructive during the AIMD run (shown by ellipse in Fig. S2, ESI⁺) because NaII' leaves the site in 8R while approaching the anion, thus fully deblocking the 8R ring. NaII does not block 8R for CO₂ passage (compared to K, Rb, Cs) due to the smaller radii but it holds its 8R site stronger due to the same size effect. Thus, another larger cation than Na must also deblock the 8R ring. This influence of one anion on two blocking cations could remain valid in the RHO type with the same α -cages and becomes even more actual in the CHA type due to the smaller sizes of the cages.

3.2.2 NaA zeolite. Admitting that the stronger attraction of Na⁺ cation to 8R window could hinder the stabilization of transition state such as for CO₂ hydrolysis,³³ we repeated the same reaction with all Na cations per the LTA pseudocell (Table 2). A small activation energy of 0.082 eV was also calculated for the exothermic process ($\Delta U = -0.293$ eV, the reaction profile can be seen in the "Naa_c2o5.avi" file in ESI†). The TS frequency was tested for closest mobile Na atoms that produces variation by only 0.3 cm^{-1} (up to 59.1*i* cm^{-1}). The barriers at the PBE-D3 level are smaller (in absolute value) than those calculated at the hybrid levels for NaA and NaKA, while for NaRbA and NaCsA, the results of using generalized gradient approximation and hybrid functionals are similar. The heats at the PBE-D3 level are lower (in absolute value) than those calculated at the hybrid levels for all NaMeA types (Table 2). The cation-O distances behave similarly with the increase in the number of the cationic neighbors of the anion after the reaction (3) from 5 to 6 such as in NaKA (Table 3). Hence, reaction (3) should take place at the absence of the heavier alkali atoms, which is in agreement with the IR spectra in NaA and NaKA. Two NaII cations are in contact with the CO_3^{2-} or $C_2O_5^{2-}$ anion, showing a possibility of parallel NaII shifts and deblocking the cage for gas passage (as NaII in Fig. S2 for NaKA, ESI \dagger) even if they do not present a barrier for CO₂.

The application of hybrid HF-DFT functionals is useful regarding the strong dependence of $C_2O_5^{2-}$ geometry on the total quantity and types of the cations, *i.e.*, on the electrostatic interactions (Table 4). The large torsional angle between C==O groups (Fig. 6a) corresponds to the angle between the planes with two nearly flat NaO₂C parts connected *via* one common O atom. For the NaMeA media, the $C_2O_5^{2-}$ approaches a flat structure (Table 4). The $C_2O_5^{2-}$ species thus shows a drastic change of the geometry between neutral NaKC₂O₅ and Na₂C₂O₅ molecules (Fig. 6a and b) and in the adsorbed state (Fig. 6c and d). The different presentation of exchange functional separately in short-range and long-range domains are realized in hybrid

Table 4 C–O bond lengths (Å), C–O–C angle (°), and O–C···C–O torsional angle^a (°, shown in Fig. 6a) for some $C_2O_5^{2-}$ species either as isolated Na₂C₂O₅ and NaKC₂O₅ molecules, or in NaA and NaCsA zeolites at the PBE-D3 level. The C–O bonds of the central C–O–C group are noted by a star

Parameter	Na ₂ C ₂ O ₅	NaKC ₂ O ₅	NaA	NaCsA
С-О	1.267	1.252	1.263	1.269
	1.267	1.247	1.237	1.223
	1.404*	1.450*	1.477*	1.498*
	1.398*	1.501*	1.437*	1.444*
	1.271	1.252	1.268	1.271
	1.268	1.247	1.253	1.247
O−C····C−O	59.3	6.8	0.1	9.9
C−O−C	119.9	117.3	126.7	126.4
Figure	Fig. 6a	Fig. 6b	Fig. 6c	Fig. 6f

DFT schemes (HISS, HSE06). However, the hybrid DFT control with HISS and HSE06 did not reveal a strong change in the reaction parameters (activation energy $E^{\#}$, heat of reaction ΔU) relative to that obtained at the GGA DFT (PBE-D3) level for all NaMeA cases.

3.2.3 NaRbA and NaCsA zeolites. The reaction profiles are unified for all alkali forms in Fig. 7 where the similarity can be seen for Na, Rb, and Cs forms. The presence of a new maximum at the reaction profile (at 0.4–0.5 Å along with OX in Fig. 7) is of minor importance. For example, restarting the cNEB in NaKA and NaCsA led to a variation of the barrier within 0.01 eV = 0.23 kcal mol⁻¹ (footnote "a" in Table 2), which is an acceptable accuracy with VASP. Two spatial parameters, *i.e.*, O–C–O angle in CO₂ and |C-O| distance (or R_{C-O}) between C atom of CO₂ and O_c atom of the CO₃^{2–} group, are shown along the reaction paths for all cationic cases (Fig. 8). For NaKA, two other



Fig. 7 Reaction profiles (eV) of $C_2O_5^{2-}$ formation *versus* reaction coordinate (Å) according to eqn (3) in NaMeA zeolites with one Me cation per pseudocell, where Me = Na (circles), K (triangles), Rb (crosses), Cs (squares), all constructed with cNEB at the PBE-D3 level.



Fig. 8 Energy U reaction (3) profiles (eV) of $C_2O_5^{2-}$ formation from CO_3^{-} and CO_2 (circles), the |C-O| distance (or R_{C-O} , Å, stars) between C atom of CO_2 and O_c atom of the CO_3^{2-} group, O-C-O angle (radian, triangles) in CO_2/CO_3^{2-} with cNEB computations in NaA (a), NaKA (b), NaRbA (c), and NaCsA (d) at the PBE-D3 level. Reagents and transition states are denoted as INT and TS, respectively.

profiles were selected relative to the one in Fig. 4, but respective O–C–O angle and R_{C-O} also reveal a deviation compared to the other alkali forms. The smooth behaviors of both O–C–O angle and R_{C-O} while passing the *TS* in the NaA, NaRbA, and NaCsA zeolites are in contrast with their drastic changes between *TS* and the next step in NaKA (Fig. 8). Hybrid DFT methods (B3LYP, HISS) show a decrease in the activation energy with increasing order of atomic radii from Na to Rb, while for GGA (PBE-D3), this trend is violated between K and Rb (Table 2).

3.3 Frequencies and intensities for comparison with the IR spectra

The presence of $C_2 O_5^{2-}$ in the NaKA zeolite can be supported by spectroscopic data. For this, all the modes and intensities were calculated for the K⁺ cation and C₂O₅²⁻ species at fixed coordinates of other framework atoms. The intensities can be calculated with VASP using the DFPT level using Born charges³⁵ while the frequencies can be obtained with PBE-D3 as well $(\nu' \text{ values in Table 5})$. Due to different approaches for the computations of the frequencies (ν in Table 5) and intensities using DFPT, the frequencies vary slightly relative to that obtained with DFT. The $\Delta \nu'$ values are smaller as much as by \sim 40 cm⁻¹ at the DFT-D3 level relative to the DFPT values. With both DFT and DFPT approaches, the calculated band splitting values between the upper frequency (UF) and low frequency (LF) $\Delta \nu = \nu_{\rm UF} - \nu_{\rm LF}$ of the most intensive valence modes are overestimated, *i.e.*, 569 cm⁻¹ (DFPT) and 535 cm⁻¹ (DFT/PBE) versus 480 cm⁻¹ from the experiment over 17% Na/K exchange.¹⁶ The largest intensities are calculated for the extreme right and left

Table 5 The frequencies (ν' , cm⁻¹) at the PBE-D3 level, frequencies (ν , cm⁻¹) and intensities (l, a.u., scaled relative to the most intensive peak) at the DFPT level for the valence vibrations of isolated gas species (Na₂C₂O₅, NaKC₂O₅) and C₂O₅²⁻ anion in NaKA. The maximal $\Delta\nu$ (cm⁻¹) is shown in the lowest row

Molecule			Anion in NaKA			
Na ₂ C ₂ O ₅		NaKC ₂ O ₅	NaKC ₂ O ₅		$C_2 O_5^{2-}$	
ν	Ι	ν	Ι	ν'	ν	Ι
1574.3	0.64	1716.7	1.00	1750.7	1732.0	1.00
1538.4	0.53	1688.2	0.01	1687.3	1658.9	0.23
1336.5	0.07	1272.6	0.05	1328.1	1288.0	0.01
1161.4	1.00	1143.8	0.24	1216.1	1162.7	0.57
412.9	—	572.9	—	534.6	569.3	—

peaks (Table 5). The pair of 1725 and 1249 cm⁻¹ ($\Delta \nu = 476$ cm⁻¹) in NaA transforms to the pair of 1721 and 1241 cm⁻¹ ($\Delta \nu = 480$ cm⁻¹) in NaKA (Table 6). A similar pair of IR peaks at 1715 and 1246 cm⁻¹ was recorded in ref. 28 and presented in Table 6 together with other literature data. An important feature is related to the "internal" peaks whose intensity becomes comparable to the one of the UF band (Table 5).

The geometries of dicarbonates in NaA and NaKA are quite similar (Fig. 6c and d) in agreement with the high and similar splitting values $\Delta \nu$ observed in both NaA and NaKA.^{16,28,31} Going to other frameworks, another number of contacting cations and their locations around C₂O₅²⁻ can change the geometries compared to the ones presented above (Fig. 2c-f). Constructive information can be extracted from the calculated spectra of respective neutral molecules $Me_2C_2O_5$, Me = Na, K, Rb, Cs (Table 5) considered as an extreme example for a higher Si/Al modulus and a minor cationic concentration. The high flexibility of the $C_2 O_5^{2-}$ anionic fragment due to the interaction with two different nearest cations (Fig. 6a and b) results in a wider variation of the $\Delta\nu$ and $\nu_{\rm UF}$ values than that obtained above for the products of the reaction (3) in the NaMeA forms. More precisely, $\Delta \nu$ shifts from 573 to 413 cm⁻¹ between NaKC₂O₅ and Na₂C₂O₅ molecules, while $\nu_{\rm UF}$ decreases in parallel as much as by 142 cm^{-1} . For both molecules, the UF and LF bands remain the most intensive ones from the group, but the intensity of the "internal" peaks becomes comparable to the one of UF band for Na₂C₂O₅. The drop of $\nu_{\rm UF}$ from 1717 to 1574 cm⁻¹ is important for the assignment of the dicarbonate's peaks, which can be effectively mixed with the bands of carbonate species. All these observations illustrate a complexity of observed spectra for another cationic media or zeolite. Thus, the UF and LF bands from 1734 to 1314 cm⁻¹ with $\Delta \nu = 420$ cm^{-1 11} are rather close to the values calculated for dicarbonates, which suggests the formation of $C_2 O_5^{2-}$ in nano-NaCHA.

Due to a large band splitting $\Delta\nu$ values calculated^{32,33,49,51-53} in HCO₃⁻ can be formally considered as the candidates to interpret the peaks related herein to dicarbonates. However, one cannot find a mechanism in the literature which allows the complete conversion of CO₃²⁻ to HCO₃⁻ under CO₂ loading. Another type of complexities with the band assignments to HCO₃⁻ was recently concerned regarding CaY.⁵¹ A small band splitting $\Delta\nu$ of 100 cm⁻¹ for bidentate HCO₃⁻ group was obtained at the bi-cationic site (H₂O)CaII···O₂COCH⁻···O(H)CaII⁵¹ closely to the experimental 60 cm⁻¹ in CaY.⁵² One should note that the

Table 6 Experimental UF and LF bands (in cm⁻¹) for carbonates and band splitting $\Delta \nu = \nu_{\text{UF}} - \nu_{\text{LF}}$ in the A type zeolites with Na or K cations when one could suspect a presence of dicarbonates

Cation	Ref.	$ u_{ m UF}$	$ u_{ m LF}$	$\Delta \nu$
NaA	16	1725, 1697, 1640, 1609	1381, 1364, 1249	476-201
	28 ^a	1740, 1725, 1693, 1638, 1640, 1580, 1456, 1390,	1356-1285, 1248	492-295
	29	1726, 1694, 1624	1365, 1250	476-331
	30 ^{<i>b</i>}	<i>1735</i> , 1675, 1568, 1506	1457 , 1384, 1373, 1359, <i>1245</i>	490, 49, 302
KA	28	1715, 1653	1359, 1246	469, 294
NaKA	16	1721, 1666, 1617, 1609	1381, 1365, 1241	480-228

^{*a*} The minor difference was found by the same group in the IR spectra measured later with the maximal $\Delta \nu = 488 \text{ cm}^{-1}$.^{31 *b*} The spectra were measured³⁰ at 30 °C after pretreatment at 350 °C.

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mono- and bidentate HCO_3^- groups are usually characterized in the literature by larger $\Delta\nu$ values of some hundreds cm⁻¹. Thus, the large band splitting $\Delta\nu$ values in HCO_3^- can be moderated at the presence of water. It also shows that the "mono- and bidentate carbonate" terms should be applied with caution.

3.4 The possibility of tricarbonate formation

The initial and final (after 12 ps run) geometries of the reaction (3) at high loading were optimized. In both cases new products were obtained in the course of the optimizations that illustrate rather small barriers of their formations, i.e., another coordination type of $C_2 O_5^{2-}$ toward K^+ from CO_3^{2-} (Fig. 5a) and new $C_3O_7^{2-}$ tricarbonate from $C_2O_5^{2-}$ dicarbonate (Fig. 5b). The $C_3 O_7^{2-}$ is however less stable by 0.263 eV than the dicarbonate coordinated by one carbonate group to K^+ (Fig. 5a) compared to that obtained after the AIMD run (both carbonate groups of $C_2O_5^{2-}$ are coordinated in Fig. 7d, 4d and e). The frequencies and intensities of the vibrational modes of carbonate groups were calculated, showing a wider range of BS value for tricarbonate compared to those of dicarbonate (Table 7). The highest intensities of the valence extreme peaks of the dicarbonate (1731, 1215.4 cm⁻¹ in Table 7) are in qualitative agreement with experiment $^{16,28-30}$ (Table 6). It is important to note the remote $C_3O_7^{2-}$ position relative to K⁺ coordinated by CO₂ (Fig. 5b). It shows a weaker probability of bulky $C_3 O_7^{2-}$ with the same -2echarge as CO_3^{2-} or $C_2O_5^{2-}$ to coordinate the K⁺ cation in 8R. But

Table 7 Frequencies^a ν (cm⁻¹) and intensities *I* (a.u.) of the symmetric (sym), asymmetric (as), and deformation (def) vibrations of carbonate groups obtained after optimization at the PBE-D3/PAW level of the reagents (seven CO₂ molecules and one CO₃²⁻ per pseudocell) and products (six CO₂ molecules and one C₂O₅²⁻) of the AIMD modelling of the reaction (3) (Fig. 1 and 2) (intensities are calculated at the DFPT level and scaled relative to the most intensive peak). Please see comments in Part 3.4

Species	ν	Ι	Type ^b
$C_2 O_5^{2-}$	1731.0	1.000	as(1)
	1667.2	0.376	as(2)
	1330.3	0.018	sym(1) + sym(2)
	1215.4	0.650	as(1)-as(2)
	864.3	0.304	sym(1)-sym(2)
	843.7	0.414	def(1) + sym(2)
	781.5	0.054	sym(1) + def(2)
	758.3	0.099	def(1) + def(2)
$C_{3}O_{7}^{2-}$	1887.3	1.000	as(1)
	1749.6	0.730	as(3)
	1684.1	0.626	sym(2)
	1351.0	0.120	sym(1) + as(2) + sym(3)
	1282.9	0.001	sym(1) + sym(3)
	1135.9	0.351	sym(1) + as(2) + sym(3)
	997.4	0.211	sym(2)
	812.5	0.945	def(1) + def(2)

^{*a*} For comparison, the frequencies were calculated for one CO_2 bicoordinated to Na (2.516 Å) and K (3.057 Å) cations (2377.0, 1341.2 cm⁻¹), which are close to the observed CO_2 values (2346, 1381 cm⁻¹ in NaKA¹⁶ and 2361–2351, 1382 cm⁻¹ in NaA³⁰). ^{*b*} Number in the brackets (vibration type in the right column) corresponds to the number of carbon atom whose mode dominates in the vibrational mode of the dicarbonate (C1–C2) or tricarbonate (C1–C2–C3).

such possibility requires more detailed analyses of different $C_3 O_7{}^{2-}$ locations.

4. Discussions

If a cation blocks a window for a passage of a gas molecule, the latter at a certain temperature (breakthrough temperature or $T_{\rm b}$) displaces the cation due to its kinetic energy, thus overcoming the barrier and penetrating the window. To possess an accurate model to estimate $T_{\rm b}$ for each gas at the presence of carbonates, one should have a model for interaction between the cation, anion, and gas molecule. This model is one of the future goals of our work. At the moment such a model "cationgas molecule" does not exist even without any anion. Rare computational attempts did not achieve yet an adequate picture (regarding their calculated barriers) using a kind of constrained AIMD in NaKA (the authors used the same pseudocell as herein⁵⁴) or DFT-D3 at partly fixed cations/framework atoms in substituted CHA types.55 While carbonates have been observed in cationic LTA forms, which have been known for more than 40 years, 56 their presence in MeCHA, Me = K, Rb, Cs, has been shown recently.¹¹ Their introduction into the system could be a realistic way to explain the gas separation of CO_2 mixtures. We showed herein that the carbonate can displace up to two cations at different SII sites (K⁺ in Fig. 1b and NaII⁺ in Fig. S2, ESI[†]), which control the gas passage. Thus, the low concentration of carbonates^{14,15} requires a care to neglect their presence for the separation of CO_2 gas mixtures.

The considered transformation (3) from CO_3^{2-} to $\text{C}_2\text{O}_5^{2-}$ can explain the similar IR results obtained by two independent grou*ps* by 2008²⁸ and 2019.²⁹ At RT and a moderate CO₂ pressure (1 bar), nearly symmetric CO_3^{2-} form with a minor BS disappears from IR spectra, but a new carbonate form with a large BS (named as a "labile" one²⁸) is observed. The IR results are extremely close between both works (Table 6). The transformation from CO_3^{2-} to $\text{C}_2\text{O}_5^{2-}$ corresponds to an exothermic process with a decrease in the total volume (one molecule appears instead of two). The equilibrium between CO_3^{2-} and $\text{C}_2\text{O}_5^{2-}$ should be inverted (to the direction of CO_3^{2-}) with the increase in the temperature and decrease in the loading in agreement with the experiment^{28,29} and Le Chatelier's principle.

The possibilities of 13 C MAS NMR were applied to the solution but the unique NMR spectra at the condition of the $C_2O_5{}^{2-}$ formation at 1 bar CO₂ remained unresolved between 162 and 172 ppm (only a wide shoulder).²⁹ This unresolved structure between 162 and 172 ppm seems to be the consequence of the variety of carbonate species at this pressure. $C_2O_5{}^{2-}$ formation was shown in the IR spectrum at 1 bar CO₂ (peaks at 1726 and 1250 cm⁻¹) from Fig. 5a in ref. 29, which corresponds to NMR spectrum being third from the bottom of Fig. 3 in ref. 29. Other NMR spectra were resolved in two cases at low pressure when $CO_3{}^{2-}$ dominates. As a result, this work²⁹ neither supports nor disproves the possibility of $C_2O_5{}^{2-}$ formation.

Earlier, the formation of dicarbonate $(C_2O_5^{2-})$ in molten eutectic mixture of carbonates was proposed to explain high

 CO_2 solubility in this system at high temperatures.⁵⁷ This experimental analysis was accompanied by theoretical computations of reaction heats (HF, MP2, QCI/SD computational levels).⁵⁸ Later, the $C_2O_5^{2-}$ intermediate was considered as unique explanation of ¹⁸O oxygen exchange between carbonate forms in water solutions.⁵⁷ Together with the possible role of dicarbonates in the molten carbonates⁵⁷ and water,⁵⁹ their stability in adsorbed state was modeled with the DFT+*U* approach at the surface of the $Ce_{21}O_{42}$ cluster.⁶⁰

The synthesis of dicarbonates was developed at low temperatures. The unique mention about synthetic route of di-*tert*-butyl dicarbonate addressed to the RT decomposition of tricarbonate prepared from phosgene and *tert*-butyl carbonate of potassium under low temperature (-5 to -15 °C).⁶¹ In the computational analyses of the tetra-carbonate chain neutralized by two protons at the ends, higher stability was assigned to 3-coordinated carbon chains.⁶² Nevertheless, both 3- and 4-coordinated carbon chains are less stable than free CO₂²⁸ in agreement with the low temperature (-5 to -15 °C) of dicarbonate synthesis.⁶¹ However, the alkali LTA zeolite is not an unique example when dicarbonate can be obtained at the RT conditions *via* the reaction (3) (Table 8).

From the review by Busca and Lorenzelli,⁶³ one could assume that any forms of alumina (α -, γ -, η -Al₂O₃ except of κ -Al₂O₃) are the other objects where dicarbonates could be stabilized because of a variety of "bidentate" or "bridged" ($\nu_{\rm UF} > 1700 \, {\rm cm}^{-1}$, 1100 $< \nu_{\rm LF} < 1300 \, {\rm cm}^{-1}$) carbonate groups observed, for example, over γ -Al₂O₃.^{64,65} Also, bridged carbonate groups were proposed on the basis of the assignment for the IR spectra on α -Fe₂O₃, α -Cr₂O₃, SnO₂, NiO, MgO.⁶³ However, later IR study of Al₂O₃ nanoparticles (NPs) did not record respective bands⁶⁶ though the NPs of Al₂O₃ permit a wider series of the facets and planes than more stable surfaces of bulk Al₂O₃. This result is coherent to the spectra without "bidentate" and "bridged" peaks of

Oxide	ν_{UF}	$ u_{ m LF}$	$\Delta \nu_{ m max}$	Ref.
Al ₂ O ₃ (Aerogel)	1850, 1820	1233, 1181	669	64
Al_2O_3 (Degussa)	1800	1233	567	
Al ₂ O ₃	1860, 1830	1240, 1200	660	63
TiO ₂	1773, 1750	1150	623	
ZrO_2	1780, 1760, 1740	1220, 1175, 1160	620	
MgO	1698	1292	406	
Fe ₂ O ₃	1720	1280	440	
α -Fe ₂ O ₃	1700	1230	470	65
CeO ₂	1732	1136	594^{a}	60
-	1722	1147	575 ^a	
	1755	1213	542^{bc}	
	1718	1171	547^{b}	
	1704	1133	571^{b}	
	1835	1120	715^{de}	
	1848	1161	687 ^{de}	

^{*a*} Experimental values. ^{*b*} Calculated at the DFT+*U* level for bidentate carbonate model. ^{*c*} Less stable than CO₂ and isolated CeO₂ cluster. ^{*d*} Calculated at the DFT+*U* level for dicarbonate. ^{*e*} Less stable than CO₂ and isolated carbonate/CeO₂ cluster but more stable than 2CO₂ and isolated CeO₂ cluster. carbonates deposited on gibbsite or γ -Al(OH)₃⁶⁷ and hematite.⁶⁸ Small models of Al(OH)₃ clusters with different number of water molecules did not result in a wide splitting between valence symmetric and asymmetric branches.

One of the widest series of carbonates, hydrocarbonates, and formates was modeled over the surface of CeO₂ clusters.⁶⁰ The possibility of carboxylate formation at various surface positions was not confirmed therein as well as by the authors in some zeolite forms.⁶⁹ In addition, the authors discriminated the carbonite's formation.⁶⁰ The authors observed stable pairs of IR peaks (below 373 K) 1732 and 1136 cm⁻¹ after CO₂ adsorption or 1722 and 1147 cm⁻¹ after CO adsorption.⁵⁸ They assigned both pairs to bidentate carbonates⁶⁰ since the presence of the Ce³⁺ signal after CO injection⁶⁰ indicates the possibility of partial CeO₂ reduction and CO oxidation. Hence, similar products were obtained upon CO and CO₂ adsorption. These $\nu_{\rm UF}$ and $\nu_{\rm LF}$ values are coherent to the results of our modeling at the DFPT level for dicarbonates (1732.0/1162.7 cm⁻¹ and 1716.7/1143.8 cm⁻¹ in Table 5) where similar intensities were also calculated. The small heat of dicarbonate formation (Table 2) agrees with the absence of the signal already at 373 K.⁶⁰ Analyzing the structures with the dicarbonates, the authors⁶⁰ obtained as much as twice lower stability than that of two corresponding (mono)carbonates. However, possible drastic difference can originate only from a partial bonding between the dicarbonate and CeO2 clusters. One term of every dicarbonate (Fig. 2q and r in ref. 60) was coordinated to the oxide particle. The total stabilization energy of the species was divided per two carbon atoms to be compared with respective energy of two adsorbed carbonates. Due to the limits imposed by the dicarbonate size and flexibility, the total interaction with oxide particle is smaller (in absolute energy), but the difference relative to respective energy of two adsorbed carbonates may be less emphasized.

The formation of $C_3 O_7^{2-}$ tricarbonate in the course of optimization (Part 3.4) allows proposing the possible mechanism of the denser CO₂ package than CO₂ multiadsorption, which is more strictly limited by CO2 molecular volume. More probably, it could be a combination of both of them because excessive CO2 cannot be deleted just by decreasing pressure. The convenience of polycarbonates is namely related to their easy decomposition (and CO₂ desorption) by decreasing pressure or increasing temperature. This goal can be provided via the selection of low silica zeolite with a sufficient concentration of the cations, which possesses a wide pore space to allow transport and the consequent addition of CO2 and conservation of Cn+1O2n+3²⁻ polycarbonates. For example, unusually higher CO₂ capacity of NaA zeolite with a lower internal volume relative to that of NaCaA (with a smaller number of the cations) could be interpreted due to the formation of polycarbonates in NaA (at least of dicarbonates) at some conditions.^{70,71} If the external surface of zeolite nanoparticles could be sealed, then they could conserve CO₂ at wider intervals of pressures and temperature.

In Part 3.1.2, the overestimated barrier for reaction (2) was obtained, which requires more careful determination but remains the most probable route for CO_3^{2-} formation. One should remark on the two imaginary frequencies at the B3LYP

level for the reagents of the reaction (2) obtained at the GGA/ PBE level (Table S2, ESI⁺), which signifies that another geometry for the reagents must be sought at the B3LYP level so that the $E^{\#}$ is not a reliable estimate at the fixed PBE-D3 geometry at least for B3LYP. The alternative routes are due to CO2 interaction with the third O atom extracted from: (A) zeolite framework;¹⁴ (B) oxide species such as Me_xO_y .^{69,72} The first possibility (A) was confirmed neither experimentally^{52,72-74} nor theoretically (ref. 69 and references therein). In one of the most detailed studies, the authors⁷⁴ did not find enough evidences in favor of special exceptional basicity of framework O atoms in NaKA and NaCaA forms and assigned this O-exchange to extraframework admixtures ($\sim 2\%$).⁷⁴ The exceptional basicity of any framework O atoms was not manifested via different O charges in cationic forms^{48,75} and all-siliceous^{48,76} zeolites. The second path (B) for alkaline forms is possible for impregnated zeolites (over-exchanged zeolites) when nonstoichiometric oxides can serve as the source of oxygen,^{77,78} which was not realized experimentally.^{16,28-31} Thus, an alternative route cannot be proposed under experimental conditions where dicarbonates are likely to be observed.

5. Conclusion

The transformation from CO_3^{2-} to $C_2O_5^{2-}$ was studied at the DFT GGA and hybrid levels with cNEB approach in a series of NaMeA zeolite models (Me = Na, K, Rb, Cs). The $C_2O_5^{2-}$ species showed a drastic transformation of the geometry between neutral Na₂C₂O₅ and NaKC₂O₅ molecules and in the adsorbed state. The $C_2 O_5^{2-}$ formation was characterized as exothermic process at all theory levels with a decrease in the total volume at the same conditions. The consideration of the $C_2O_5^{2-}$ formation in the terms of enthalpy was justified by calculations of the variations of vibrational entropy (at the GGA DFT level) or full entropy (at the hybrid DFT level) between certain points of AIMD run. The equilibrium between CO32- and C2O52- should be inverted (to the direction of CO_3^{2-} formation) with an increase in temperature and decrease in pressure in agreement with the experiment^{28,29} and Le Chatelier's principle. This equilibrium between CO_3^{2-} and $C_2O_5^{2-}$ can explain similar IR results obtained by two independent groups by 2008^{28} and 2019^{29} when the CO₃²⁻ and $C_2O_5^{2-}$ species dominate in the IR spectra at low and high CO₂ pressures, respectively. The AIMD run at the DFT GGA level was realized at low and high CO₂ loadings, showing higher C₂O₅²⁻ stability at higher CO_2 loading (no inverse reaction (3) was observed compared to lower CO2 loading) and its capability to deblock via withdrawing a cation from the 8R window. The latter directly worsens the separation of CO₂ gas mixtures.

If the first $CO_2 \rightarrow HCO_3^-$ step (1) in the reaction $CO_2 \rightarrow HCO_3^- \rightarrow CO_3^{2-} \rightarrow C_2O_5^{2-}$ sequence (1–3) was studied earlier in detail, ^{12,13,33} the second $HCO_3^- \rightarrow CO_3^{2-}$ step (2) was analyzed herein. The barrier of 0.8 eV is rather large, thus requiring a different site for H transfer in the NaKA to achieve better agreement with the experimental data, which confirms easy CO_3^{2-} formation from HCO_3^- at RT. Such a work is under way.

Alternative paths for CO_3^{2-} formation were discussed as less realistic compared to the reaction (2). The moderate heat of endothermic formation of the $\text{C}_3\text{O}_7^{2-}$ tricarbonate was evaluated by optimizing the $\text{C}_2\text{O}_5^{2-}$ with six CO_2 , which does not confirm its appearance in NaKA. But the possibility of the formation of higher $\text{C}_{n+1}\text{O}_{2n+3}^{2-}$ polycarbonates deserves future analysis in other wide pore low silica zeolites where these chemicals could be a tool for denser CO_2 concentration and package.

Finally, one could note that cation gating¹ and breathing² (i.e., changing the effective diameter and shape of a window being analogues of blocking/deblocking) mechanisms are interrelated since both are determined by cationic motions, leading to a distortion of 8R or D8R⁵² and thus creating a "breathing" effect. The cationic charge transfer seems to be a necessary step to provide the formation of negatively charged species in the negatively charged zeolite framework to minimize their Coulombic repulsion. This necessitates the cationic shifts³² and re-populations of their usual positions. The neutral unit cell and small number of relatively mobile cations limits the number of anionic species. One could propose that the cooperative effect of cation gating and deblocking upon CO₂ adsorption is based on the cationic interactions with various carbonate species as no reliable mechanism of strong CO₂ binding to cations was found to the best of our knowledge. The small fractions of $C_2O_5^{2-}$ and CO_3^{2-} species can be compensated by their contacts with 6 and 5 cations, respectively, including two of them which block two 8R windows. To the best of our knowledge, it is the first work where the formation of the dicarbonate anions in the zeolites is considered regarding the interactions with alkali cations, thus deblocking the 8R rings.

Conflicts of interest

There are no conflicts to declare.

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