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Influence of carbonate species on elastic properties of NaX and NaKX zeolites



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Bryukhanov I.A.^a, Rybakov A.A.^b, Kovalev V.L.^a, Larin A.V.^{b,*}

^a Department of Mechanics and Mathematics, Moscow State University, Leninskie Gory, Moscow, GSP-2, 119992, Russia ^b Chemistry Department, Moscow State University, Leninskie Gory, Moscow, GSP-2, 119992, Russia

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ABSTRACT

The inter-relation between chemical and mechanical properties is demonstrated regarding Young's modulus variation of the NaX and NaKX (83% exchange Na/K) zeolites upon carbonate formation or CO₂ adsorption. The force field (FF) approach is based on the combination of known FFs for the zeolite atoms, alkali cations, CO₂, and carbonate atoms. Contrary variations of the Young's modulus are obtained in NaX upon CO₂ adsorption (increase far from CO₂ condensation conditions) or carbonate formation (decrease). Higher decreases of the Young's and bulk moduli are predicted for K-exchanged form that was not yet tested experimentally.

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1. Introduction

The requirement of high mechanic resistance and thermal stability remains the important condition of successful application of aluminosilicate zeolites or aluminophosphates upon hard conditions of many industrial catalytic processes. However, these mechanic properties are less systematically studied till now that is partly a consequence of their complex and expensive measurements [1,2 and Refs. therein]. Another difficulty of experimental studies is the absence of the anisotropy in the modulus measured and the absence of the possibility to exactly assign respective variations of the modulus (Young's, bulk, shear) to any specific phenomenon in the oriented zeolite structure. The complexity of zeolite synthesis is due to the necessity of numerous high temperature steps, i.e., burning of template molecules, dehydroxylation, etc., each of them could produce various defects. But the relative impact of each type of defect on the mechanic resistance and thermal stability is not yet classified or evaluated comparing to other possible reasons of modulus variations upon the reaction conditions. As the example we can consider the structural changes due to the impact of adsorbed species like pyridine [3], water [4–6], alcohols [2], carbon dioxide [7,8], halocarbons [9–11], etc. Such changes can be also a consequence of an adsorbate penetration into the framework [2]. However, some of the molecules

(pyridine, water) stimulate redistribution of cations between the available cationic sites. Evidently, the possibility of recoding such changes depends on characteristic residence times. Exchange between the cationic positions with new methods like PFG NMR self-diffusion measurements shows rather small time-of-life of cations in different positions, *i.e.*, between 40 and 150 ms for Li [12], that is too fast to be recorded during the measurements of LiZ-SM-5 modulus. Could the cation drift with respective adsorbate redistribution be the reason of increased or decreased bulk, shear, or Young's modulus? In order to influence various zeolite moduli and to allow their measurement, the cation must possess much longer residence time at the new position.

In the relevant work [13] the drift of Na cations from SIII' sites in NaX and from SII and SI' sites in NaY was interpreted due to only CO_2 influence. Detailed consideration of the important work [13] is presented in the Discussion. The authors admitted that CO_2 is physisorbed in the NaY and NaX zeolites at 400 K according to the molecular dynamics (MD) calculation. This assumption is justified for NaY [14] but not for NaX [15,16]. The presence of symmetric CO_3^{-2} species has been quantitatively shown in the NaX zeolite up to 573 K [15,16]. To summarize, the arguments in [13] do not prove that NaIII cations diffuse together with CO_2 in NaX. In addition, one can ask the following question: can the carbonates cause a cation displacement? The Na⁺ and CO_3^{-2} ionic species are linked by stronger Coulomb forces and could demonstrate the higher stability and the longer time-of-life as compared to the "Na⁺-CO₂" complex. Then common drift of the cation and carbonate can be

^{*} Corresponding author. Tel.: +7 495 9393952; fax: +7 495 9328846. E-mail address: Nasgo@yandex.ru (A.V. Larin).

the reason of cation displacement from its crystallographic position and of a bad balance of the electrostatic forces between the cations and the framework. The latter can lead to a weakening of the whole system. This phenomenon can be accompanied by bulk (BM) and Young's (YM) moduli variations. Such YM change owing to the chemical reasons, *i.e.*, carbonate formation, has not yet been studied, while the YM drop due to physical processes, for example, upon carbon dioxide adsorption close to critical conditions for CO₂ condensation in pores, was recorded [7]. We believe that this YM change [7] can be discussed in the same terms as presented for the shortage of NaX crystals [17] using NLDFT method [18,19]. Some arguments about the similar origins of both results [7,17] are presented in the Part S1 of Supplementary Materials. The data in the publication [7] related to the YM variation upon carbon dioxide could serve as a landmark for the influence of carbonate formation. The carbonates can be both symmetric and asymmetric in NaX [15].

Asymmetric carbonate species are not an exclusive feature of the NaX zeolite. In NaCaY they are formed if Ca exchange is higher or equal than 46% [14]. In alkali MeETS-10 forms the band splitting of asymmetric carbonates is as large as in NaX ($350 \text{ cm}^{-1} = 1715 \text{ cm}^{-1} - 1365 \text{ cm}^{-1}$ [16]). The high catalytic activity of MeETS-10 with supported Pt in aromatization reaction of hexane is connected with the quantity of CO₂ desorbed [20]. The desorption at temperatures of 422 K (Me=Li) or 503 K (Me=Cs) can be caused by carbonate forms whose high and low frequency peaks of CO_3^{-2} vibration bands in the MeETS-10 are strongly split, *i.e.*, show the highest interval between the peaks of 312 cm^{-1} for Li and $325/362 \text{ cm}^{-1}$ for Cs [20]. According to the direct relation [21] between the band splitting (BS) and distortion of carbonate species

$$\delta = \sum_{i=1,3} (|| \mathbf{C} - \mathbf{O}|_i - | \mathbf{C} - \mathbf{O}|_{\text{aver}}|) \tag{1}$$

where $|C-O|_{aver} = (\Sigma_{i=1}^{-3}|C-O|_i)/3$, one could predict that these BS values correspond to asymmetric species with δ around 0.13–0.15 Å using the linear function fitted with any computational approach [21]. Two types of the bi-dentate species were successfully observed *via* IR spectroscopy in Rb- and Cs-forms but thermo-desorption showed two peaks of desorbed species for all the forms [20].

Some anomalies in the adsorption by cationic form zeolites upon CO₂ adsorption allow discussing the participation of the carbonate species. The CO₂ adsorption was observed at the K/Na exchange higher than 17% which should already exclude the CO₂ penetration due to blocking of the 8R windows by K cations of larger radii [22]. Earlier [23], we have demonstrated that K cation moves from its crystallographic position KII in 8R of the NaKA zeolite as a result of the interaction with carbonates. Such displacement effectively opens the 8R window and provides CO₂ passing as well as any gas component of appropriate kinetic diameter if an activation barrier of adsorption is small at the temperature of the study. In the experiments with binary mixtures both components should pass the window if the sieve effect is not involved owing to different sizes. The presence of carbonate species was approved in the NaKA system via IR technique [22] while a possible presence of both mono- and bi-coordinated carbonates in NaX was first experimentally shown in 1963 [15]. In accordance with our recent work [21] we would like to use the terms of symmetric and asymmetric carbonate species (instead of mono- and bi-coordinated ones) whose distortion is measured by the splitting of the symmetric and asymmetric bands of carbonate vibrations and whose equilibrium can be driven by external pressure of any gas [15]. Asymmetric carbonates were optimized in NaKA in accordance with experimental IR data (band shift or BS and intensity ratio) [23]. However, the NaKA model can be applied for comparative adsorption studies being constructed with pseudo unit cell locally violating the Loewenstein rule [23]. That is why the YM values cannot be properly calculated in NaKA to estimate its relaxation in the presence of asymmetric carbonates. If the cations are more effectively displaced from their positions upon the influence of asymmetric species than upon that of symmetric ones, then the YM calculation in the presence of symmetric carbonates will provide the lower boundary for possible influence of asymmetric species on the Young's modulus. To obtain the lower boundary, the influence of symmetric carbonates on the NaX cations could be tested and compared with that of the asymmetric ones in NaKA.

In the earlier work [23] we have shown using density functional theory (DFT) with periodic boundary conditions that K cations can be displaced by asymmetric carbonates from their crystallographic positions in NaKA zeolite. In this work we have undertaken such analysis to check the influence of symmetric carbonates at the level of empirical force fields (FFs). In the next parts we have described the computational details and the selected models. Then carbonate geometries and cationic displacements are compared as well as Young's moduli for selected models.

2. Computational details

The FAU structure was constructed first using the spatial subgroup F23 and subsequently shifting the crystallographic origin from (0, 0, 0) to (1/8, 1/8, 1/8) [24,25]. Then it was allowed to relax without symmetry (P1 group). Hence, we have worked with the primitive cell of smaller volume as much as 4 times. Empirical core-shell FFs with GULP3.4 code [26] have been applied using periodic boundary conditions. The final FF is the combination of the Catlow [27-29] or Sierka-Sauer [30,31] FFs for the framework atoms, Bush FF for alkali cations [32], Maurin FF for CO₂ [33], and the Rohl-Wright-Gale for carbonates [34,35]. The latter contains three- and four-term potentials that control the O-C-O angular distortions and deviations of the carbonate anion from planarity, respectively, Bush FF delivers the parameters of Buckingham potential between alkali cations (Na, K cores) and the shell of the O framework atoms of the T–O–T^{\prime} type, where T or T^{\prime} = Si and/or Al [32]. Additionally, we made only necessary assumptions to unify the FFs. We accepted: (1) A, ρ , C parameters of Buckingham potentials $Ae^{-r/\rho}-C/r^6$, between three possible O types¹, *i.e.*, carbonate (or CO₂) oxygen shell, hydroxyl oxygen Al-O(H)-Si core, and framework oxygen T-O-T' shell, are the same for all pairs with the parameters from Ref. [29,32]; (2) the alkali cations (core only) interact with all O shells (carbonate oxygen shell or framework oxygen T-O-T' type shell) via the same potential as with hydroxyl oxygen Al-O(H)-Si core. This combined FF [27-29,32,34,35] was applied to the case of none, one, or two carbonate species adsorbed per unit cell (UC) of the NaX zeolite. Carbonate was modeled as a product of the reaction between water and CO₂ so that two protons were located at the framework that also provided a neutral UC. Calculated elastic moduli for NaX with CO2 or with carbonates were compared to the experimental data [7] and discussed.

The NaKX zeolite model was constructed by 83% (5/6) exchange of the Na cations at the II, II', and III positions by K ones while a part of NaI (in double 6R prisms) remains at their positions where they do not contact with carbonate (or CO₂) species. It is a usual practice due to a hard exchange of the NaI cations by the others. The final NaKX and NaX formulae correspond to Na₄K₂₀Si₂₄Al₂₄O₉₆×nH₂CO₃ and Na₂₄Si₂₄Al₂₄O₉₆×nH₂CO₃, respectively, n = 0-2.

 $^{^1}$ In the case of Catlow FF: A = 22764 eV, ρ = 0.149 Å $^{-1}$, C = 27.879 eV \times Å 6 , if 0 < r < 12 Å.

3. Results

3.1. Cell geometries

The optimized cell parameters of all the models are shown in Table 1 with and without carbonates. The variations of the respective Cartesian cell parameters as well as the cell stabilities upon addition of one carbonate species can deviate substantially for the similar cationic positions. It shows the complexity of the surface of potential energy of interaction between carbonate and zeolite that can produce different changes of cell parameters. The drastic difference between NaX and NaKX is the increase and decrease, respectively, of the cell volumes upon the carbonate formation that can be correctly compared within the same FF approach. The NaX cell volume varies using Sierka–Sauer FF within the same interval while adding one (0.22–0.45%) or two (0.26–0.44%) carbonate species *per* cell. The volume growth of

NaX obtained with Catlow FF is larger with two (from 0.68% to 0.87%) than with one (from 0.32% to 0.76%) carbonate species. Similarly, the decrease of NaKX volume with Sierka–Sauer FF is larger with two (from -0.72% to -1.58%) than with one (from -0.29% to -0.36%) carbonate moiety *per* cell. We should emphasize that the cationic Na displacements are generally larger with Catlow FF than the ones obtained using Sierka–Sauer FF (Table 2). Therefore, the larger volume increase with Catlow FF correlates with the larger cationic Na displacements. In both systems there was no correlation with their stability (the total energy, see Table 3).

3.2. Geometry of carbonate anions

For all optimized geometries (Table S1) symmetric carbonates with small deviations from the equilibrium carbonate geometry imposed by FF [34] ($|C-O| = 1.20 \text{ Å}, \angle O-C-O = 120^\circ$) have been obtained irrespective of starting at the NaI or NaII positions,

Table 1

Cell parameters (Å, °) and volumes (V, Å³) of the MeX zeolites and their variations (%, in the brackets) with N carbonates per primitive cell optimized using GULP code with (B) Catlow [28,29] or (A) Sierka–Sauer [30,31] FFs (in brackets).

Me (FF)	Ν	a	b	С	α	β	γ	$V(\Delta V)$
Na(A)	0	17.93 (0.0)	17.93 (0.0)	17.96 (0.0)	60.07	60.07	60.00	4086.72 (0.0)
	1(151)	18.09	17.96	17.77	60.02	60.35	59.99	4095.81 (0.22)
		(0.89)	(0.16)	(-1.05)				(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
	1(149)	18.05	17.97	17.92	59.94	59.82	59.82	4097.45 (0.26)
		(0.67)	(0.22)	(-0.22)				
	1(152)	17.95	17.95	17.95	60.31	59.90	60.35	4105.29 (0.45)
		(0.11)	(0.11)	(-0.01)				
	1(150)	17.94	17.88	17.94	60.38	60.39	60.29	4103.39 (0.41)
		(0.0)	(-0.27)	(-0.11)				
	2(154,150)	17.95	17.88	17.99	60.77	60.60	59.32	4102.38 (0.38)
		(0.11)	(-0.28)	(0.16)				
	2(153,149)	18.04	18.12	17.98	59.30	59.60	59.43	4104.57 (0.43)
		(0.61)	(1.06)	(0.11)				
	2(155,151)	18.12 (1.06)	17.89	17.75	60.25	60.31	60.30	4097.38 (0.26)
			(-0.22)	(-1.16)				
	2(156,152)	17.87	18.06	17.85	60.69	59.97	60.33	4104.86
		(-0.33)	(0.72)	(-0.61)				(0.44)
Na (B)	0	17.56	17.60	17.61	60.24	60.23	60.21	3872.14 (0.0)
		(0.0)	(0.0)	(0.0)				
	1(150)	17.60	17.62	17.72	60.24	60.23	59.94	3901.43 (0.76)
		(0.22)	(0.11)	(0.61)				
	1(152)	17.63	17.69	17.59	60.41	59.76	59.98	3884.61 (0.32)
		(0.40)	(0.51)	(-0.11)				
	1(151)	17.75	17.60	17.63	59.85	59.91	59.97	3889.02 (0.44)
		(1.1)	(0.0)	(0.11)				
	1(149)	17.66	17.64	17.71	59.80	59.83	59.71	3885.31 (0.34)
		(0.56)	(0.11)	(-0.01)				
	2(154,150)	17.58	17.59	17.75	60.70	59.83	60.34	3903.86 (0.82)
		(0.11)	(-0.01)	(0.79)				
	2(156,152)	17.49	17.78	17.71	59.72	59.94	60.60	3901.06 (0.75)
		(-0.39)	(1.02)	(0.56)				
	2(155,151)	17.83	17.58	17.61	59.70	60.34	59.95	3905.97 (0.87)
	0(150 1 10)	(1.53)	(-0.11)	(0.0)	50.00	50.44	50.50	2000 42 (0.00)
	2(153,149)	17.68	17.72	17.77	59.68	59.41	59.56	3898.42 (0.68)
	0	(0.68)	(0.68)	(0.90)	CO 02	CO 02	CO 02	415450(00)
K (A)	0	18.04	18.04	18.04	60.03	60.03	60.03	4154.59 (0.0)
	1(140)	(0.0)	(0.0)	(0.0)	50.75	50.02	50.96	(120.01 (0.25)
	1(149)	(0.11)	10.00	18.05	59.75	59.95	59.60	4159.91 (-0.55)
	1(151)	(-0.11)	(0.22)	(-0.01)	60.02	60.25	60.26	<i>(</i> 120.72 (0.26)
	1(151)	(0.16)	(0.16)	(0.44)	00.05	00.55	00.20	4159.75 (-0.50)
	1(150)	(-0.10)	(-0.10)	(-0.44)	60.19	60.35	60.09	<i>A</i> 1 <i>A</i> 2 67(0.20)
	1(150)	(-0.50)	(-0.22)	(0.01)	00.15	00.55	00.05	4142.07(-0.23)
	1(152)	17.96	18.08	17.94	60.33	60.18	60 19	4139 89 (_0 35)
	1(152)	(-0.44)	(0.22)	(-0.55)	00.55	00.10	00.15	4155.05 (-0.55)
	2(155 151)	18 15	17.71	17.69	60 54	60.91	60.84	4089.04 (-1.58)
	2(133,131)	(0.61)	(-1.82)	(-1.94)	00.51	00.51	00.01	1005.01(1.50)
	2(154 150)	17 92	17.81	18 10	60.65	59 75	60.03	4099 88 (-1 32)
	2(10.,100)	(-0.67)	(-1.27)	(0.33)	00.00	22.75	22.05	1000.00 (1.02)
	2(153,149)	18.03	18.02	18.01	59.95	59.74	59.88	4124.59 (-0.72)
	_(,- 10)	(-0.01)	(-0.11)	(-0.22)	100			
	2(156.152)	18.00	17.92	17.78	60.92	60.63	60.14	4107.61(-1.13)
	((-0.22)	(-0.67)	(-1.44)				
			,					

Table 2

MeII...O_z distances (in Å), where O_z is oxygen atom of 6R, with (+CO₃) and without (no CO₃) carbonates and its increase (ΔR , in Å) in the MeX zeolite as calculated using GULP code with Catlow [28,29] or Sierka-Sauer [30,31] FFs. The ΔR correspond to Me=Na in the NaX and Me=K in NaKX.

Me	NaX (Catlow)			NaX (Sierka-Sauer)			NaKX (Sierka	NaKX (Sierka-Sauer)	
	no CO ₃	+CO3	ΔR	no CO ₃	+CO3	ΔR	no CO ₃	+CO3	ΔR
Me152	2.251	2.372	0.121	2.382	2.436	0.054	2.682	2.773	0.091
	2.257	2.374	0.117	2.389	2.450	0.061	2.680	2.790	0.110
	2.271	2.362	0.091	2.379	2.456	0.077	2.675	2.755	0.080
Me149	2.274	2.357	0.083	2.382	2.469	0.087	2.681	2.767	0.086
	2.272	2.381	0.109	2.379	2.398	0.021	2.678	2.806	0.128
	2.284	2.357	0.073	2.389	2.451	0.062	2.677	2.762	0.085
Me150	2.255	2.325	0.070	2.355	2.419	0.064	2.679	2.986	0.307
	2.257	2.347	0.090	2.355	2.407	0.052	2.676	2.930	0.254
	2.256	2.311	0.055	2.355	2.400	0.045	2.683	2.800	0.117
Me151	2.271	2.375	0.104	2.389	2.452	0.063	2.684	2.777	0.093
	2.276	2.370	0.094	2.379	2.466	0.087	2.678	2.805	0.127
	2.280	2.369	0.089	2.382	2.491	0.109	2.676	2.809	0.133

Table 3

The energy variation ΔU (in kcal/mol) relative to the most stable *N* case with the total energy U_N (in eV) for each series, $\Delta U = U - U_N$, Young's modulus (YM) components^a E_x , E_y , E_z (in GPa), their variations ΔE_i (in %, in brackets), and average $E = (E_x 2 + E_y^{-2} + E_z^{-2})^{1/2}/3^{1/2}$ YM value in the NaX and NaKX models with *N* carbonate species (the serial numbers of cations Me=Na, K, being closest to the carbonates, are shown in brackets, first column) *per* primitive unit cell optimized with GULP (negative ΔE_i sign in the brackets corresponds to decrease of the modulus).

Ν	ΔU^{c}	$E_x (\Delta E_x)$	$E_y (\Delta E_y)$	$E_z (\Delta E_z)$	$E(\Delta E)$	
NaX, Catlow FF ($U_0 = -5360.381$, $U_1 = -5399.792$, $U_2 = -5437.624 \text{ eV}$)						
0	-	55.75 (0.0)	55.58 (0.0)	64.64 (0.0)	58.81 (0.0)	
1(150)	0.00	57.43(+3.0)	52.00 (-6.5)	57.65(-10.8)	55.75 (-5.2)	
1(152)	9.68	57.5 (+3.3)	47.19 (-13.3)	62.29 (-3.6)	56.02 (-4.8)	
1(151)	14.67	56.9 (+2.0)	52.30(-5.9)	62.75 (-2.9)	57.48 (-2.3)	
1(149)	23.57	53.77 (-3.5)	51.91 (-6.6)	59.37 (-8.2)	55.11 (-6.3)	
2(154,150)	0.00	51.52 (-7.6)	50.44 (-9.3)	57.93 (-10.4)	53.40 (-9.2)	
2(156, 152)	2.05	52.34 (-6.1)	48.85 (-12.1)	60.47 (-6.5)	54.11 (-8.0)	
2(155, 151)	5.37	46.43 (-16.7)	44.45 (-20.0)	56.36 (-12.8)	49.36 (-16.1)	
2(153, 149)	13.69	40.12 (-28.0)	48.08 (-13.5)	62.73 (-3.0)	51.17 (-13.0)	
NaX, Sierka-Sauer FF ($U_0 = -5348.677, U_1 = -$	$-5429.040, U_2 = -5510.236 \text{ eV}$				
0	-	50.46 (0.0)	50.45 (0.0)	51.14 (0.0)	50.69 (0.0)	
1(151)	0.0	46.27(-8.3)	44.11 (-12.6)	45.57 (-10.9)	45.33 (-10.6)	
1(149)	1.13	44.82 (-11.2)	45.07 (-10.7)	50.54 (-1.1)	46.88 (-7.5)	
1(152)	3.04	47.85 (-5.2)	46.39 (-8.0)	50.28 (-1.7)	48.20 (-4.9)	
1(150)	13.69	48.57(-3.7)	46.31 (-8.2)	54.00 (+5.6)	49.73 (-1.9)	
2(154, 150)	0.0	47.76 (-5.4)	47.22 (-6.4)	55.33 (+8.2)	50.24 (-0.9)	
2(153, 149)	16.02	38.82 (-23.1)	42.86 (-15.0)	51.22 (0.0)	44.60 (-12.0)	
2(155, 151)	21.11	47.21 (-6.4)	43.58 (-13.6)	45.55 (-10.9)	45.47 (-10.3)	
2(156, 152)	26.05	45.95 (-8.9)	41.55 (-17.6)	49.99 (-2.2)	45.96 (-9.3)	
NaKX, Sierka–Sauer FF	$F(U_0 = -5330.037, U_1 =$	$= -5411.071, U_2 = -5492.549 \text{ eV}$				
0	-	50.45 (0.0)	53.46 (0.0)	56.53 (0.0)	53.54 (0.0)	
1(149)	0.0	40.13 (-20.5)	44.43 (-16.9)	52.20 (-7.7)	45.86 (-14.3)	
1(151)	2.69	39.34 (-22.0)	44.24 (-17.2)	54.14 (-4.2)	46.32 (-13.5)	
1(150)	6.41	43.44 (-13.9)	46.49 (-13.0)	55.76 (-1.3)	48.85 (-8.8)	
1(152)	9.96	42.97 (-14.8)	46.63 (-12.8)	54.22 (-4.1)	48.17 (-10.0)	
2(155, 151)	0.0	43.82 (-13.1)	37.57 (-29.7)	52.92 (-6.4)	45.21 (-15.6)	
2(154, 150)	6.48	39.68 (-21.3)	43.41 (-18.8)	53.47 (-5.4)	45.89 (-14.3)	
2(153, 149)	18.81	35.57(-29.5)	37.12 (-30.6)	46.65 (-17.5)	40.08 (-25.1)	
2(156, 152)	20.29	46.48 (-7.9)	40.92 (-23.5)	52.52 (-7.1)	46.88 (-12.4)	

^a The variations of the bulk or shear modulus are shown in Table S1 of SM.

imposed FF for cations and zeolites, and initial distorted (asymmetric) CO_3^{-2} geometry. Three cases corresponding to the lowest energies of carbonates near the NaII positions are presented in Table S1 in the order of increasing energy. The maximal deviations of \angle O–C–O and \angle O–O–O–C *versus* 120° and 0°, respectively, do not exceed 2° (Table S1).

Earlier, we showed that K remains in the 8R plane of NaKA in the absence of CO_3^{-2} and deviates from it, if K is linked to CO_3^{-2} . The latter moves together with the nearest Na and K cations in the course of full geometry optimization. The final stable position of K does not coincide with its crystallographic site observed without carbonate. The new K position corresponds to the larger distances towards the zeolite framework oxygen atoms (O_z) [23]. The distances between the K cation in the 6R and the nearest framework O_z atoms at the level of FF (NaX) modeling (Table 2) are shorter, *i.e.*, 2.755–2.986 Å, than those between the K cation in the 8R and the nearest framework O_z atoms (Table 6 in Ref. [23]) obtained at the level of periodic DFT (neutral MOR cell in Ref. [23]), *i.e.*, 2.954–3.461 Å. These larger K... O_z distances are caused by the larger K displacements upon carbonate asymmetric coordination. If the K coordination by asymmetric CO_3^{-2} in NaKA leads to the K displacements around 0.2–0.3 Å [23], respective elongations of the K... O_z distances in the presence of symmetric CO_3^{-2} species in NaKX do not exceed 0.12–0.16 Å using Sierka–Sauer FF approach with the exception of the position near K(150) (Table 2).

To compare the coordination of Na cation one could address to Fig. 1. DFT with periodic boundary conditions (Fig. 1c) leads to the



Fig. 1. K...O_{carb}, Na...O_{carb}, and C—O_{carb} distances in the presence of CO₃⁻² species in (a) NaX optimized with GULP and Sierka–Sauer FF (case 152 in Tables 1–3), (b) NaKX optimized with GULP and Sierka–Sauer FF (case 149 in Tables 1–3), (c) pseudo-NaKA form optimized with VASP (PBE functional using PAW method) [23]. The Na types are shown in the NaKA form. The color code is: Si in yellow, Al in violet, H in gray, O in red, Na in blue, K in dark cyan, C in brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4

The Young's modulus (YM) components^a E_x , E_y , E_z (in GPa), their variations ΔE_i (in %), average $E = (E_x^2 + E_y^2)^{1/2}/3^{1/2}$ YM value, cell volume (V, in Å³), and their variations ΔE and ΔV (in %) versus M carbon dioxide molecules per primitive unit cell of the NaX models optimized with GULP and Catlow FF [27,29] (positive sign of ΔE_i corresponds to increase of the modulus).

М	$E_x (\Delta E_x)$	$E_y (\Delta E_y)$	$E_z \left(\Delta E_z \right)$	$E(\Delta E)$	$V(\Delta V)$
0	55.75 (0.0)	55.58 (0.0)	64.64 (0.0)	58.81 (0.0)	3872.1 (0.0)
2	56.49 (1.33)	52.84 (-4.93)	63.08 (-2.41)	57.63(-2.01)	3869.1 (-0.08)
5	54.16 (-2.85)	53.08 (-4.50)	65.53 (1.38)	57.86 (-1.61)	3878.1 (0.15)
8	56.73 (1.76)	52.59 (-5.38)	61.31 (-5.15)	56.99 (-3.10)	3875.6 (0.09)
12	56.71 (1.72)	52.86 (-4.89)	63.06 (-2.44)	57.70 (-1.89)	3872.5 (0.01)
16	60.04 (7.70)	59.34 (6.77)	63.71 (-1.44)	61.06 (3.83)	3870.5 (-0.04)
20	61.37 (10.08)	59.03 (6.21)	66.51 (2.89)	62.38 (6.07)	3886.7 (0.38)
22	56.98 (2.21)	58.69 (5.60)	67.90 (5.04)	61.38 (4.37)	3886.5 (0.37)
24	59.95(7.53)	58.14 (4.61)	67.81 (4.90)	62.11 (5.61)	3887.6 (0.40)

shorter Na...O_c distances, where O_c is the O atom of carbonate species, than those obtained with GULP/Sierka–Sauer FF (Fig. 1a for NaX). DFT also provides shorter K...O_c distance of 2.557 Å in NaKA (Fig. 1c) as compared to the range between 2.915 and 3.239 Å (Fig. 1b) in NaKX. These closer contacts explain the stronger distortion of the carbonate anion in NaKA [23], which can be evaluated *via* parameter δ (1). Partly, the difference of the Me...O_c distances is the result of the different computational levels.

3.3. Young's modulus variation upon CO₂ influence

Young's modulus (YM) of 38.7 ± 1.7 GPa of NaX in vacuum was experimentally determined [7]. Additionally, the bulk modulus of NaCaX was evaluated between 38 and 46 GPa using different adsorbates (Xe, Kr) and NLDFT method [19]. We remind that bulk modulus is usually smaller than Young's modulus. The calculations with GULP resulted in the overestimated values of YM Cartesian components (Table 4) in vacuum between 50.45 and 51.14 GPa (average *E* = 50.69 GPa) with Sierka–Sauer FF and between 55.58 and 64.64 GPa (average *E* = 58.81 GPa) with Catlow FF instead of 38.7 ± 1.7 GPa [7]. The calculated bulk modulus of NaX varies slightly between 45.10 and 43.87 GPa with Sierka–Sauer FF (Tables S3 and S4) and between 45.10 and 45.13 GPa with Catlow FF (Tables 5 and S2).

In order to interpret the experimental Young's moduli in CO_2 atmosphere [7], the coverage value has to be determined. Moreover, carbonate presence in NaX was confirmed many times [15,16,22], therefore the experimental YM in CO_2 [7] can correspond to the unified influence of both CO_2 and CO_3^{-2} species. But at the moment we do not have a balanced FF that can be applied to consider simultaneously both CO_2 and CO_3^{-2} moieties in NaX.

Table 5

The bulk modulus according to Reuss (B_R), Voigt (B_V), Hill (B_H) (in GPa), their variations ΔB_i (in %) in the NaX models *versus* M carbon dioxide molecules *per* primitive unit cell optimized with GULP and Catlow FF [27,29] (positive ΔB_i sign corresponds to increase of the modulus).

М	$B_R (\Delta B_R)$	$B_V \left(\Delta B_V \right)$	$B_H (\Delta B_H)$
0	45.10 (0.0)	45.13 (0.0)	45.11 (0.0)
2	44.54 (-1.24)	44.65(-1.06)	44.60 (-1.13)
5	46.49 (3.08)	46.54 (3.12)	46.52 (3.13)
8	47.80 (5.99)	47.86 (6.05)	47.83 (6.03)
12	48.11 (6.67)	48.26 (6.94)	48.18 (6.81)
16	49.39 (9.51)	49.51 (9.71)	49.45 (9.62)
20	52.49 (16.39)	52.72 (16.82)	52.61 (16.63)
22	51.32 (13.79)	51.87 (14.93)	51.60 (14.39)
24	51.92 (15.12)	52.03 (15.29)	51.97 (15.21)

As a result, we have estimated separately the influence of CO_2 and carbonate species on the Young's moduli. First, we will consider the impact of CO_2 on the YM and BM values.

Regarding available adsorption isotherms of CO₂ in the Fig. 4 from the ref. [7] for 302.9 and 315.2 K, we can estimate that the resulting adsorption is around 4.5 mmol/g at these conditions (0.61 atm, 298 K) for the minimum in the Young's modulus [7]. This value gives ~60 CO₂ molecules *per* conventional cell if one accepts that the limit is ~9 mmol/g [17] or 120 CO₂ molecules (Table 5.9 in Ref. [36]). Our primitive cell possesses the smaller volume that is 4 times less as compared to the conventional cell. Hence, the adsorption for the measured YM value [7] corresponds to ~15 CO₂ molecules *per* primitive cell. We have performed the calculations up to 24 CO₂ molecules adopting the FF for CO₂ from [33] and using the Catlow FF for NaX atoms (Table 4).

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The cell volume varies slightly ($|\Delta V/V| < 0.15\%$ in Table 4) at less than 20 CO₂ molecules per primitive cell and grows significantly at higher filling ($\Delta V/V > 0.37\%$). The YM and BM behaviors with the CO_2 quantity are different. The adsorption of less than 16 CO_2 molecules leads to the YM decrease (Table 4, Fig. 3), while BM decreases only at small coverage (less than 2 CO₂ molecules). At the total *M* number of 22 CO₂ the average YM and BM similarly decrease and again slightly grow again if 22 < M < 24. The applied Catlow FF was not scaled to describe the condensation process and re-packing of the molecules, but this YM decrease can show such a possibility. We shall not discuss these details of the YM behavior closely to the condensation limit. For us the most important result is the growth of YM (Table 4) and BM (Table 5) due to CO₂ adsorption relative to the free (without adsorbate) NaX zeolite. The BM increase with CO₂ was obtained in silicalite at room temperature [37] using different FFs for CO₂ [38] and silicalite [39] (the last one is similar to BKS FF [40]) as compared to those used herein [27-31,34,35]. In parallel with the BM growth, the cell volume of silicalite decreases at the smaller coverage and grows for the higher coverage [37] resembling the volume variation in Table 4. The complex character of the cell volume like "expansion-contraction-expansion" versus adsorption was assigned to the main role of repulsive "solid-fluid" interactions at the smallest and highest pore filling regarding heptane in MCM-41 silica pores [41]. These data on the strains in MCM-41 are in partial agreement with the results of Ref. [19], but the latter showed only "contraction-expansion" sequence with pressure of both Kr and Xe adsorbates [19]. Experimental strains for CO₂ in NaX [17] showed a variety of the "expansion-contraction-expansion" (305, 353, and 423 K), "contraction-expansion" (195 K), and "contraction" (273 K) types with temperature. All the relative strains are of the same order $\sim (2-6) \times 10^{-4}$ for all Kr, Xe, and CO₂ gases. Now we will consider the impact of CO_3^{-2} on the YM and BM values.

3.4. Young's modulus variation upon carbonate influence

The adsorption of one carbonate anion (without CO₂) per primitive cell (or four anions per conventional UC) results in a general decrease of the Young's modulus for the most stable obtained geometries (Table 4). One should note that an increase can be observed in one of the Cartesian directions being smaller than 3.3 and 5.6% with Catlow and Sierka-Sauer FF, respectively, than the decreases along the other coordinates (<13.3% in absolute value). The presence of two carbonate groups per cell leads to the increase of one z-component in one case only (8.2%) with Catlow FF (the favor case for Na154 and Na150 in Table 3). The variations of the respective Cartesian cell parameters (Table 1) and the components of Young's modulus (Table 3) do not reveal a common trend (the same trend is justified between BM and cell volume, Tables S2-S4). The YM decrease is emphasized in NaKX zeolite compared to that in NaX being in agreement with higher mobility of heavier K and Cs cations already noted in the literature [23,40].

From the results above one could conclude that CO_2 and CO_3^{-2} species lead to opposite changes of the Young's modulus values. The similar YM changes (in absolute value) can be achieved however by different concentrations of respective species. The YM decrease of around -10% is created by one carbonate anion per cell (or 4 anions per conventional UC) while the YM increase of 6% is produced by sixteen CO_2 molecules or 64 per conventional UC (Table 4). Taking into account that the carbonate species are formed at small CO_2 concentrations in the presence of traces of water [15], carbonate moieties change YM in the wider range of CO_2 concentrations. The displacements of cations (Table 2) are characterized by the change of bulk and shear moduli (see them in Table S2–S4 of Supplementary Materials).

4. Discussion

All the results above are related to the symmetric CO_3^{-2} moleties. As we have applied the FF developed for symmetric carbonate [34,35] we have not obtained asymmetric form in NaX starting from different initial carbonate geometries at the NaI or NaII positions. Both asymmetric CO_3^{-2} forms, *i.e.*, with non-equivalent C–O bond lengths, and nearly symmetric CO_3^{-2} form, are presented in NaX at room temperature [15] and should change the NaX modulus. Their presence is supported by the IR spectra with two band splitting (BS) values from 350 to 200 cm^{-1} [15] which can lead to the asymmetry parameter δ (1) around 0.075 and 0.12 Å according to the "BS $-\delta$ " ratio (1) [21]. It is instructive to evaluate which carbonate form, either symmetric, or asymmetric one, is more effective to attract the cations. It could help to understand the influence on Young's modulus of both carbonate forms together in NaX and thus to propagate quantitatively the evolution of the Young's modulus calculated herein while adding the asymmetric CO_3^{-2} form to NaX. For comparison with asymmetric forms, we could address to the model of MOR zeolite where the symmetric and asymmetric forms were compared [23]. It was illustrated by the longer Me...O_z distances for any Me=Na or K (Table 6 in Ref. [23]) in the case of asymmetric form which was obtained from symmetric one varving the total charge of the MOR unit cell between 0 (all-siliceous cell with Na₂CO₃ inside) and -2e (two Si atoms were replaced by Al atoms in the same cell). This charge re-distribution seems to be very effective for a change of the cation–carbonate interactions. The distortion δ (1) varies between 0.085 and 0.066 Å for more asymmetric species and between 0.026 and 0.017 Å for symmetric ones. These δ (1) values for the asymmetric moieties result in the band splitting between 230 and 170 cm^{-1} [23]. These values are smaller than 350 cm^{-1} for NaX which reveals a higher distortion (1) of the asymmetric form in NaX than in NaKA. Hence, the asymmetric carbonate should trap Na more effectively compared to the symmetric form. Hence, we can predict that the impact of asymmetric ones on the cations should be even stronger than calculated herein (Table 3).

The possibility to get asymmetric carbonates with the FF oriented favoring symmetric ones should be accompanied by refitting of both zeolite and carbonate FFs to allow a domination of the factors leading to the CO_3^{-2} distortion at some determined conditions. Alternatively, other FF should be developed to provide equilibrium geometry of pre-selected asymmetric CO_3^{-2} species. In NaX symmetric CO_3^{-2} species (possessing the peaks at 1485 and 1425 cm^{-1}) leave the NaX zeolite only around 573 K [15,16]. Asymmetric coordinated species are formed immediately after loading but steeply transform to the symmetric ones with time. The asymmetric species seem to be less stable and exist below 323 K [15]. The formation of asymmetric carbonates is modulated by high partial pressure of any adsorbed gas [15]. Hence, the existence of asymmetric carbonates can be controlled using the additional adsorbed gas that could fill the cages and could be used for pressure simulation. The problem is that one should have the parameters of interaction potentials between the atoms of such gas molecule, carbonate, and zeolite atoms. The FF for such gas model was not available for us. Hence, the selection of appropriate gas component is in progress.

Alternative explanation of Na⁺ drift in NaX was proposed on the basis of MD simulation in the absence of chemisorbed CO₂. The curves on the mean square displacements (MSD) of Na(SIII') cation in Fig. 6b for NaX from the ref. [13] demonstrate a small difference with time irrespective of CO₂ loading (21, 42, 78 molecules per UC). We want to stress that Na(SIII') is the one only mobile cation type in NaX according the results of the work [13]. The MSD curves for 21 and 78 molecules per UC nearly coincide within the



Fig. 2. The CO_3^{-2} species as optimized with GULP and Sierka–Sauer FF approach for one (a, case Na151 in Tables 1–3) or two (b, case (Na153, Na149) in Tables 1–3, and c, case (Na155, Na151) in Tables 1–3) species per cell. The color code corresponds to that in Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conventional period less 400 ps, on one hand, and with the curve for 42 molecules per UC, on the other hand. The higher NaIII mobility at 78 molecules (at the coverage 78/120 = 0.65) than at 21 ones at the longer run (more than 400 ps) is an unexplained feature which has not been compared to the computation error of the method (if available). Such comparison for NaY zeolite [13] may be useful to interpret the drastic qualitative difference between the MSD curves for 25 and 71 molecules, on one hand, and for 50 and 92 molecules, on the other hand. In the first group of the runs, the Na(SI) cations remain strictly fixed (Fig. 2a and c for 25 and 71 CO₂ in the Ref. [13]), while their thermal displacements $(1-2 Å^2)$ are "allowed" in the second group (Fig. 2b and d for 50 and 92 CO₂ in the Ref. [13]).

Finalizing this discussion, we would like to note that the MD confirmation of the specific CO_2 influence could come from the evaluation of a long residence time near Na(SIII') for some selected CO_2 molecules. This time-of-life of Na⁺-CO₂ complex have to be comparable to the observed scale of 400 ps. Because no long time-of-life for Na⁺-CO₂ was demonstrated, CO₂ gas starts displacing the most mobile Na(SIII') cations to facilitate the exchange between cationic sites. Such influence should be similar for other gases such as N₂ and cannot thus explain the known features for CO_2/N_2 separation [22]. These arguments cannot thus prove yet that Na(SIII') cation diffuses together with CO₂. Such cation drift due to a complex formation with CO₂ seems to be less probable



Fig. 3. Average Young's (filled circles) modulus (GPa) $E = (E_x^2 + E_y^2 + E_z^2)^{1/2}/3^{1/2}$ where E_x , E_y , E_z are its components and bulk (open symbols) modulus (open symbols according to Reuss (circles), Voigt (triangles), Hill (diamonds) in GPa) modulus *versus M* carbon dioxide molecules *per* unit cell of NaX optimized with GULP and Catlow FF [27,29].

due to the weak cation– CO_2 interaction. The interaction energy is determined by the main "charge–quadrupole moment" term of electrostatic interaction. The arguments in the Ref. [13] cannot assure thus that Na(SIII') cation diffuses only together with CO_2 in NaX.

Another "trapdoor" scenario of the CO_2 influence on the cationic positions has been recently proposed [42] to explain anomalous separations factors for the CO_2 mixtures. The authors [42] emphasized the formation of favored complex of large alkali cations (K, Cs) with three CO_2 molecules to demonstrate possible cation displacement from its crystallographic position. We have already analyzed this approach in our previous work [21]. We believe that this model cannot provide the explanation to observed phenomenon both for calculations from the isotherms of isolated gas components and for the binary CH_4/CO_2 mixture where sieve effect seems to be valid.

5. Conclusions

Using periodic boundary conditions with combined empirical force fields we have succeeded to optimize carbonate CO_3^{-2} moleties with plane symmetric geometry and very close C-O bond lengths. For the first time it was shown that symmetric carbonates lead to efficient detachment of Na and K cations from the framework oxygens. The larger Na...O bond elongations upon the carbonate influence with the Catlow FF correlate with the stronger decrease of Young's modulus (YM) of NaX than using Sierka-Sauer FFs. Regarding the large Na...O distances obtained with the FF optimization relative to those obtained earlier with plane wave computations in NaKA [23], the FF model of "Nacarbonate" interactions has to be the lower boundary for the evaluation of carbonate influence on the NaX structural properties. We have estimated the influence of carbonate species formed in NaX zeolite on the Na positions in the latter. In the case of NaX with symmetric CO_3^{-2} species the lower YM was calculated relative to the respective system without CO_3^{-2} formation. The YM varies in more emphasized way in the NaKX zeolite that is in agreement with higher mobility of heavier K cations already analyzed in the literature. The YM change increases with the number of the CO_3^{-2} moieties. The extent of the modulus change depends on the relative positions of the carbonates in the cell.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014. 04.036.

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