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Chemical reduction of the elastic properties of zeolites: a comparison of the formation of carbonate species *versus* dealumination

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S1. The BS evaluation from the calculated BS(δ) dependencies for the NaCsRHO models [32, 33].

According to the parameters of linear BS(δ) function for the carbonates

$$BS(\delta) = 5.58 + 2571.4\times\delta \qquad (S1)$$

taken from the bottom line of Table 2 from ref. [32] the δ = 0.020 Å value for the carbonate should result in BS values of 57.0 cm^{-1} which is close to the experimental value of 60 cm^{-1} [27, 28]. In ref. [33] the curve

$$BS(\delta) = 201.9 + 933.02\times\delta \qquad (S2)$$

had been fitted over 8 points for HCO_3^- species in the NaCsRHO zeolites optimized at the same PBE/PAW level as (S1). It had been obtained in a reasonable agreement with two HCO_3^- species with BS of 297.7 cm^{-1} (LDA/NaX($2CO_3^{-2}$)) and 318.3 cm^{-1} (B3LYP/6-31G* for the Na_2CO_3(6R+4R) cluster) and the asymmetry parameters of 0.134 and 0.155 Å, respectively, optimized earlier [32]. The curve (S2) results in the BS of 388.5 and 385.7 cm^{-1} for δ = 0.200 and 0.197 Å, respectively, for the (153, 149) and (155, 151) models at the PBE/PAW level. The predicted BS values can be compared to the calculated 332.7 and 385.9 cm^{-1} (Table 1). The first predicted BS value of 388.5 cm^{-1} for δ = 0.200 Å seems to be overestimated relative to the calculated 332.7 cm^{-1} but the reason of the deviation is very simple. Both the LDA and PBE (153, 149) models involve the strong HBs (Fig. 2b). The short HB length for the PBE (153, 149) model is 1.799 Å that explains the low calculated BS value. In the absence of strong HBs like in the (155, 151) models (Table 1), *i.e.*, HB length in the PBE model is 2.349 Å, the predicted value of 385.7 cm^{-1} is in a nice agreement with calculated BS of 385.9 cm^{-1} (Table 1).

S2. The ΔU extrapolation from the calculated dependencies for the NaCsRHO models [25].

The parameters of the linear ΔU (eV) functions [33] *versus* R = Si/Al have been estimated as $\Delta U = -0.861 + 0.223\times R$ for carbonates and as $\Delta U = -1.532 + 0.098\times R$ for hydrocarbonates over the studied interval $2.43 < R < 7.0$ for Na_XCsRHO models, where *X* depends on R (Fig. 2 in ref. [33]). Hence, the ΔU extrapolation to R = 1 leads to ΔU = -0.638 and -1.434 eV, respectively. Their difference gives the value 0.796 eV for NaX (Si/Al = 1) which is discussed in the main text.

S3. The estimation of the Coulomb energy between two carbonate species

We can confirm that the variation of the repulsive Coulomb energy between two carbonate species cannot be the reason of different stabilities of the zeolite models with two carbonate/(hydro)carbonate species. First, the inter-carbonate distances R_{cc} (if one uses the distances between the C atoms of the anions) do not correlate with the relative stability within the ordered series of the models (Table S4). Second, two first lines with (155, 151) and (156, 152) in the Table 2 at the LDA level are the most illustrative because of the distance variation and hydrocarbonate formation in the first case with the largest R_{cc} = 11.104 Å and the carbonate-carbonate pair with the shortest R_{cc} = 8.902 Å. If one assumes that they have the formal charge -2*e* for carbonate and -1*e* for hydrocarbonate then it leads to respective variation of Coulomb energy only 0.161 eV between them that is much smaller than ΔU = 1.005 eV calculated for this pair of the models (Table S9). The estimate 0.161 eV also demonstrates as an upper boundary for the repulsion energy between (153, 149) and (155, 151) models that this term cannot invert their relative stabilities (Fig. 3b) as a consequence of the closer R_{cc} distances and smaller Coulomb repulsion than in the selected example.

S4. The carbonate shielding in the NaX and NaKX zeolites

The series of the neutral and charged cluster models (Fig. S2 and Table S6) shows more effective shielding by two K cation than by two Na ones using the Mulliken charges. It is confirmed by the smaller (in absolute value) charge of the K_2CO_3 species which are embedded to the neutral all siliceous (Fig. S2a, b) or charged as -2 *e* (with 2 Al atoms in Fig. S2c) cluster. The total charge of Na_2CO_3 (Fig. S2a, c) is far from neutral (-0.696 and -0.622 *e* in Table S6) as compared to that of the K_2CO_3 one (only -0.137 *e* in Table S6). The comparison of the $M\ldots O_c$ distances with the sum of covalent radii of O_c (1.35 Å [39]) and M atoms (0.99 and 1.37 Å for Na and K, respectively [39]) shows the different number of the tight $M\ldots O_c$ contacts, *i.e.*, shorter than 2.33 and 2.72 Å for $Na\ldots O_c$ and $K\ldots O_c$, respectively, is obtained in the NaX and NaKX (Table S7). We have observed one such a bond for HCO_3^- and three for CO_3^{-2} in NaX, while three and four short bonds are for CO_3^{-2} in NaKX (Table S7). This picture is in agreement with the higher number of the K cations around the CO_3^{-2} species in NaKX (five K cations around every CO_3^{-2} species in Fig. 2c, d) than in NaX (three and four Na cations around HCO_3^- and CO_3^{-2} species in Fig. 2a, b).

Table S1. MeII…O$_z$ distances (Å), where O$_z$ belongs to 6R window, and their difference ΔR (Å) with and without one carbonate species per UC of the NaX or NaKX models optimized at the PBE and LDA levels. ΔR corresponds to Me = Na in NaX and to Me = K in NaKX (negative sign of ΔR corresponds to decrease of the MeII…O$_z$ distance).

Me	NaX (LDA)			NaX (PBE)			NaKX (PBE)		
	no CO_3	+ CO_3	ΔR	no CO_3	+CO_3	ΔR	no CO_3	+CO_3	ΔR
149	2.191	2.263	0.072	2.247	2.263	0.016	2.553	2.721	0.168
	2.205	2.295	0.090	2.255	2.295	0.040	2.539	2.672	0.133
	2.190	2.304	0.114	2.243	2.304	0.061	2.566	2.736	0.170
150	2.195	2.300	0.105	2.263	2.415	0.152	2.534	2.702	0.168
	2.205	2.415	0.210	2.247	2.463	0.216	2.553	2.709	0.156
	2.193	2.420	0.227	2.242	2.456	0.214	2.560	2.712	0.152
151	2.206	2.297	0.091	2.258	2.383	0.125	2.555	2.687	0.132
	2.218	2.284	0.066	2.278	2.357	0.079	2.565	2.656	0.091
	2.212	2.209	-0.003	2.265	2.269	0.004	2.553	2.676	0.123
152	2.200	2.278	0.078	2.255	2.452	0.197	2.553	2.708	0.155
	2.200	2.275	0.075	2.254	2.407	0.153	2.554	2.693	0.139
	2.187	2.220	0.033	2.239	2.568	0.329	2.546	2.740	0.194

Table S2. MeII…O$_z$ distances (Å), where O$_z$ belongs to 6R window, and their difference ΔR (Å) with and without two carbonate species per UC of the NaX or NaKX models optimized at the PBE and LDA levels. ΔR corresponds to Me = Na in NaX and to Me = K in NaKX (negative sign of ΔR corresponds to decrease of the MeII…O$_z$ distance).

Me	NaX (LDA)			NaX (PBE)			NaKX (PBE)		
	no CO_3	+ CO_3	ΔR	no CO_3	+CO_3	ΔR	no CO_3	+CO_3	ΔR
153-149	2.191	2.257	0.066	2.247	2.291	0.044	2.553	2.706	0.153
	2.205	2.209	0.004	2.255	2.276	0.021	2.539	2.695	0.156
	2.190	2.202	0.012	2.243	2.300	0.057	2.566	2.700	0.134
	2.209	2.202	-0.007	2.275	2.355	0.080	2.553	2.686	0.133
	2.193	2.217	0.024	2.251	2.396	0.145	2.551	2.719	0.168
	2.189	2.229	0.040	2.257	2.370	0.113	2.571	2.712	0.141
154-150	2.195	2.283	0.088	2.263	2.350	0.087	2.534	2.705	0.171
	2.205	2.407	0.202	2.247	2.376	0.129	2.553	2.700	0.147
	2.193	2.325	0.232	2.242	2.343	0.101	2.560	2.705	0.145
	2.211	2.234	0.023	2.271	2.365	0.094	2.556	2.634	0.078
	2.227	2.274	0.047	2.284	2.357	0.073	2.547	2.584	0.037
	2.188	2.295	0.107	2.239	2.395	0.156	2.570	2.636	0.066
155-151	2.206	2.346	0.140	2.258	2.333	0.075	2.555	2.627	0.072
	2.218	2.275	0.057	2.278	2.332	0.054	2.565	2.666	0.101
	2.212	2.236	0.024	2.265	2.246	-0.019	2.553	2.676	0.123
	2.148	2.220	0.072	2.205	2.311	0.106	2.562	2.695	0.133
	2.146	2.217	0.071	2.210	2.373	0.163	2.558	2.649	0.091
	2.196	2.247	0.051	2.253	2.313	0.060	2.549	2.763	0.214
156-152	2.200	2.278	0.078	2.255	2.373	0.118	2.553	2.626	0.073
	2.200	2.308	0.108	2.254	2.366	0.112	2.554	2.643	0.089
	2.187	2.212	0.025	2.239	2.391	0.152	2.546	2.587	0.041
	2.205	2.417	0.212	2.253	2.362	0.109	2.548	2.564	0.016
	2.206	2.383	0.177	2.252	2.436	0.184	2.558	2.581	0.023
	2.202	2.440	0.238	2.243	2.504	0.261	2.554	2.689	0.135

Table S3. The energy variation ΔU (in eV) relative to the most stable energy U_N (in eV) for each series with *N* carbonate species per UC, $\Delta U = U - U_N$, bulk (B), shear (S) modulus in the Voight (B_V), Reuss (B_R), and Hill (B) forms (in GPa), their variations ΔB_V, ΔB_R, ΔB, ΔS (in %, in brackets), in the NaX and NaKX models (the numbers of the Na or K cations being closest to the carbonates, are shown in brackets, first column) optimized at the PBE and LDA levels (negative sign in the brackets corresponds to decrease of the modulus). The * signifies the hydrocarbonate formation.

N	$\Delta U^{c)}$	B_V (ΔB_V)	B_R (ΔB_R)	B (ΔB)	S (ΔS)
NaX, LDA (U_0 = -1285.675, U_1 = -1325.703, U_2 = -1366.649 eV)					
0	-	26.50 (0.0)	26.29 (0.0)	26.39 (0.0)	14.00 (0.0)
1(151)	0.0	26.08 (-1.6)	25.52 (-2.9)	25.80 (-2.2)	12.29 (-12.2)
1(152)	0.145	26.88 (+1.4)	26.04 (-1)	26.46 (+0.3)	12.63 (-9.8)
1(149)	0.163	24.70 (-6.8)	23.74 (-9.7)	24.22 (-8.2)	11.42 (-18.4)
1(150)	1.679	24.98 (-5.7)	24.13 (-8.2)	24.55 (-7.0)	11.38 (-18.7)
2(155,151)*	0.0	24.00 (-9.4)	22.98 (-12.6)	23.49 (-11.0)	10.99 (-21.5)
2(153,149)*	0.305	-	-	-	-
2(156,152)	1.005	24.75 (-6.6)	24.37 (-7.3)	24.56 (-6.9)	11.19 (-20.1)
2(154,150)	1.133	-	-	-	-
NaX, PBE (U_0 = -1177.86, U_1 = -1215.161, U_2 = -1253.441 eV)					
0	-	38.41 (0.0)	38.39 (0.0)	38.40 (0.0)	19.86 (0.0)
1(151)	0.0	37.52 (-2.3)	37.49 (-2.4)	37.50 (-2.3)	19.29 (-2.9)
1(149)	0.115	37.67 (-1.9)	37.53 (-2.2)	37.60 (-2.1)	19.27 (-3.0)
1(152)	0.735	36.46 (-5.1)	36.38 (-5.2)	36.42 (-5.2)	19.35 (-2.6)
1(150)	1.042	35.29 (-8.1)	35.04 (-8.7)	35.17 (-8.4)	18.93 (-4.7)
2(153,149)*	0.0	36.72 (-4.4)	36.66 (-4.5)	36.69 (-4.5)	18.68 (-5.9)
2(155,151)*	0.347	36.46 (-5.1)	36.33 (-5.4)	36.39 (-5.2)	18.91 (-4.8)
2(154,150)	0.810	36.89 (-4.0)	36.50 (-4.9)	36.69 (-4.5)	18.68 (-6.0)
2(156,152)	1.072	37.79 (-1.6)	37.65 (-1.9)	37.72 (-1.8)	18.94 (-4.7)
NaKX, PBE (U_0 = -1177.283, U_1= -1214.421, U_2 = -1252.200 eV)					
0	-	34.24 (0.0)	34.20 (0.0)	34.22 (0.0)	17.33 (0.0)
1(151)	0.0	34.29 (+0.2)	34.20 (0.0)	34.25 (+0.1)	17.80 (+2.7)
1(149)	0.016	35.90 (+4.8)	35.83 (+4.8)	35.86 (+4.8)	17.48 (+0.8)
1(150)	0.111	33.98 (-0.8)	33.83 (-1.0)	33.91 (-0.9)	18.06 (+4.2)
1(152)	0.331	32.52 (-5.1)	33.34 (-5.5)	32.43 (-5.2)	17.82 (+2.8)
2(156,152)	0.0	28.84 (-15.8)	28.49 (-16.7)	28.66 (-16.3)	17.57 (+1.4)
2(154,150)	0.409	33.83 (-1.2)	33.70 (-1.5)	33.76 (-1.3)	17.79 (+2.6)
2(155,151)	0.448	32.75 (-4.4)	32.60 (-4.7)	32.68 (-4.5)	18.17 (+4.8)
2(153,149)	0.540	33.08 (-3.4)	32.86 (-3.9)	32.97 (-3.7)	17.17 (-0.9)

Table S4. The carbonate - carbonate distances (R_{cc}), energies calculated using LDA and GGA PBE functionals with two carbonate species per UC in the NaX or NaKX zeolites, the N_1 and N_2 numbers of the Me = Na or K cations, being closest to the carbonates, are shown in the third column.

Form	Method	N_1, N_2[a)]	ΔU	R_{cc}
NaX	LDA	155,151*	0.000	11.104
		153,149*	0.305	9.954
		156,152	1.005	8.902
		154,150	1.133	9.418
	PBE	153,149*	0.000	10.963
		155,151*	0.347	11.302
		154,150	0.810	9.698
		156,152	1.072	10.604
NaKX	PBE	156,152	0.000	9.331
		154,150	0.409	9.686
		155,151	0.448	9.774
		153,149	0.540	9.463

[a)] * signifies the hydrocarbonate formation

Table S5. The Bader type charges q(X) and $|C/H\ldots O_c|$ distances of carbonate and hydrogen carbonates in NaX and NaKX zeolites calculated using GGA PBE functionals with two carbonate species per UC (hydrogen carbonates are given in the columns 4 and 5 for two first models) in the NaX or NaKX zeolites, the N_1 and N_2 numbers of the Me = Na or K cations, being closest to the carbonates, are shown in the third column. The * signifies the hydrocarbonate formation.

Form	N_1, N_2	X	q(X)	$\lvert C/H\text{-}O_c \rvert$	q(X)	$\lvert C\text{-}O_c \rvert$
1	2	3	4	5	6	7
NaX	153,149*	C	1.890	-	1.939	-
		O	-1.261	1.274	-1.275	1.304
		O	-1.254	1.252	-1.279	1.319
		O	-1.187	1.413	-1.268	1.302
		H	0.346	1.001	-	-
		CO_3	-1.466^*	-	-1.883	-
	155,151*	C	1.898	-	1.920	-
		O	-1.262	1.273	-1.281	1.305
		O	-1.231	1.251	-1.270	1.300
		O	-1.159	1.410	-1.287	1.320
		H	0.369	0.982	-	-
		CO_3	-1.385*	-	-1.918	-
NaKX	156,152	C	1.922	-	1.925	-
		O	-1.273	1.318	-1.276	1.323
		O	-1.275	1.311	-1.284	1.301
		O	-1.282	1.299	-1.269	1.307
		CO_3	-1.908	-	-1.904	-

Table S6. The Mulliken type charges q (*e*) of the X groups containing one Na- or K-carbonate in the clusters with *n* atoms of Al per the cluster and total charge Q (*e*) optimized at the B3LYP/6-31G* level. Respective figure numbers are shown.

Cluster/n	Q	X	q(X)
6R+4R/0 Fig. S2a	0	CO_3	-1.272
		Na1	0.459
		Na2	0.117
		Na_2CO_3	**-0.696**
6R+4R/0 Fig. S2b	0	CO_3	-1.258
		K1	0.728
		K2	0.393
		K_2CO_3	**-0.137**
8R/2 Fig. S2c	-2	CO_3	-1.394
		Na1	0.335
		Na2	0.364
		Na_2CO_3	**-0.622**

Table S7. The Bader type charges q(M) and M…O_c distances between the M cation and O_c atoms of carbonate and hydrocarbonates in NaX and NaKX zeolites calculated using GGA PBE functionals with two carbonate species per UC in the NaX or NaKX zeolites, the N_1 and N_2 numbers of the Me = Na or K cations, being closest to the carbonates, are shown in the third column. The * signifies the hydrocarbonate formation. The M…O_c distances which are smaller than sum of ionic radii (2.34 and 2.73 Å for Na…O_c and K…O_c, respectively) are shown in bold.

Form	N_1, N_2	Type	M	q(M)	$\|M-O_c\|$
NaX	153,149*	CO_3	Na117	0.872	2.472, 2.988
			Na122	0.890	**2.338**, 2.360
			Na125	0.892	**2.312**, 2.352
			Na126	0.894	**2.315**, 2.366
		HCO_3	Na113	0.887	2.407
			Na128	0.908	**2.234**
			Na131	0.901	2.372, 2.372
NaKX	156,152	CO_3	K164	0.847	2.905
			K171	0.886	**2.577**
			K175	0.883	**2.648**, 2.832
			K178	0.889	**2.574**
			K179	0.901	2.754
		CO_3	K168	0.847	2.763, 2.768
			K169	0.889	**2.645**, 2.988
			K172	0.902	**2.684**
			K173	0.904	**2.650**
			K177	0.890	**2.607**

Table S8. The variations of the cell parameters, volume (ΔV, Å^3) for each series with N carbonate species per UC in the NaX and NaKX models (the numbers of the Me = Na or K cations, being closest to the carbonates, are shown in brackets, second column) optimized at the DFT/PAW levels (negative sign in the brackets corresponds to decrease of the parameters/volumes). The * signifies the hydrocarbonate formation.

Me (DFT)	N	$a(\Delta a)$	$b(\Delta b)$	$c(\Delta c)$	α	β	γ	$V\,(\Delta V)$
Na (LDA)	0	17.500 (0.00)	17.470 (0.00)	17.453 (0.00)	59.94	60.06	60.17	3783.24 (0.00)
	1(151)	17.541 (0.23)	17.406 (-0.37)	17.553 (0.57)	59.71	59.76	60.43	3805.39 (0.58)
	1(152)	17.461 (-0.22)	17.532 (0.35)	17.505 (0.30)	59.87	60.03	60.57	3805.61 (0.59)
	1(149)	17.575 (0.43)	17.538 (0.39)	17.584 (0.75)	59.55	59.74	60.15	3819.53 (0.96)
	1(150)	17.450 (-0.29)	17.372 (-0.56)	17.501 (0.28)	59.51	60.31	61.03	3790.52 (0.19)
	2(155,151)*	17.541 (0.23)	17.406 (-0.37)	17.553 (0.57)	59.99	59.76	60.43	3805.39 (0.58)
	2(153,149)*	17.763 (1.50)	17.836 (2.10)	17.763 (1.78)	59.23	59.65	59.65	3911.51 (3.39)
	2(156,152)	17.412 (-0.50)	17.544 (0.42)	17.472 (0.11)	59.99	60.05	60.72	3799.2 (0.42)
	2(154,150)	17.428 (-0.64)	17.383 (-0.50)	17.453 (0.0)	59.51	60.75	61.26	3781.53 (-0.04)
Na (PBE)	0	17.811 (0.0)	17.783 (0.0)	17.742 (0.0)	59.78	59.9	60.41	3983.76 (0.0)
	1(151)	17.815 (0.02)	17.788 (0.03)	17.734 (-0.05)	59.68	59.74	60.56	3983.21 (-0.01)
	1(149)	17.847 (0.20)	17.805 (0.12)	17.828 (0.48)	59.53	59.70	60.28	3995.84 (0.30)
	1(152)	17.776 (-0.20)	17.766 (-0.10)	17.745 (0.02)	59.75	59.92	60.69	3982.81 (-0.02)
	1(150)	17.778 (-0.19)	17.668 (-0.65)	17.846 (0.59)	59.66	60.32	60.51	3987.15 (0.08)
	2(153,149)*	17.847 (0.20)	17.805 (0.12)	17.828 (0.48)	59.45	59.70	60.28	3995.84 (0.30)
	2(155,151)*	17.838 (0.15)	17.717 (-0.37)	17.773 (0.17)	59.80	59.85	60.48	3993.95 (0.25)
	2(154,150)	17.750 (-0.34)	17.660 (-0.69)	17.904 (0.91)	59.65	60.36	60.64	3989.85 (0.15)
	2(156,152)	17.794 (-0.10)	17.773 (-0.06)	17.732 (-0.06)	59.74	59.97	60.88	3992.58 (0.22)
K (PBE)	0	17.852 (0.00)	17.859 (0.00)	17.878 (0.00)	60.25	60.22	60.23	4048.63 (0.00)
	1(151)	17.852 (0.00)	17.859 (0.0)	17.878 (0.00)	60.31	60.22	60.22	4048.63 (0.0)
	1(149)	17.946 (0.53)	17.836 (-0.13)	17.890 (0.07)	59.90	60.01	60.11	4050.16 (0.04)
	1(150)	17.836	17.871	17.899	60.27	60.28	60.27	4054.72

		(-0.09)	(0.07)	(0.12)				(0.15)
	1(152)	17.822 (-0.17)	17.947 (0.49)	17.876 (-0.01)	60.38	60.18	60.21	4059.12 (0.25)
	2(156,152)	17.774 (-0.44)	17.967 (0.60)	17.699 (-1.0)	60.32	59.89	60.92	4031.02 (-0.43)
	2(154,150)	17.820 (-0.18)	17.824 (-0.20)	17.917 (0.22)	60.21	60.31	60.37	4048.74 (0.00)
	2(155,151)	17.955 (0.58)	17.727 (-0.74)	17.776 (-0.57)	60.40	60.41	59.80	4025.42 (-0.57)
	2(153,149)	17.873 (0.12)	17.869 (0.06)	17.821 (-0.32)	60.07	60.06	59.92	4015.69 (-0.81)

[a] * Signifies the hydrocarbonate formation

Table S9. The energy variation ΔU (in kcal/mol) relative to the most stable energy U_N (in eV) for each series with *N* carbonate (and hydrocarbonate if any) species, $\Delta U = U - U_N$, Young's modulus (YM) components E_x, E_y, E_z (in GPa), their variations ΔE_i (in %, in brackets), YM in Hill's form *E* (in GPa), and its variations ΔE (in %, in brackets) in the NaX and NaKX models (the numbers of the Na or K cations, being closest to the carbonates, are shown in brackets, first column) per UC optimized at the PBE/PAW level (negative sign in the brackets corresponds to decrease of the modulus). The * signifies the hydrocarbonate formation.

N	ΔU[c)]	E_x (ΔE_x)	E_y (ΔE_y)	E_z (ΔE_z)	E (ΔE)
NaX, LDA (U_0 = -1285.675, U_1 = -1325.703, U_2 = -1366.649 eV)					
0	-	39.31 (0.0)	38.28 (0.0)	34.22 (0.0)	35.68 (0.0)
1(151)	0.000	32.97 (-16.1)	35.86 (-6.3)	29.87 (-12.7)	31.82 (-10.8)
1(152)	0.145	36.31 (-7.6)	31.84 (-16.8)	32.57 (-4.8)	32.68 (-8.4)
1(149)	0.163	32.65 (-16.9)	26.41 (-31.0)	26.32 (-23.1)	29.62 (-17.0)
1(150)	1.679	25.69 (-34.7)	29.41 (-23.2)	30.64 (-10.4)	29.57 (-17.1)
2(155,151)*	0.000	33.88 (-13.8)	27.26 (-28.7)	27.52 (-19.6)	28.51 (-20.1)
2(153,149)*	0.305	-	-	-	-
2(156,152)	1.005	28.07 (-28.6)	31.65 (-17.3)	28.13 (-17.8)	29.13 (-18.3)
2(154,150)	1.133	-	-	-	-
NaX, PBE (U_0 = -1177.86, U_1 = -1215.161, -1237.263[c)], U_2 = -1253.441, -1275.869[c)] eV)					
0	-	52.47 (0.0)	58.08 (0.0)	52.12 (0.0)	50.82 (0.0)
1(151)	0.000 0.000[c)]	51.21 (-2.4)	56.47 (-2.8)	49.72 (-4.6)	49.39 (-2.8)
1(149)	0.115 0.112[c)]	51.00 (-2.8)	54.57 (-6.1)	51.74 (-0.7)	49.38 (-2.8)
1(152)	0.735	50.51(-3.7)	57.53 (-0.9)	51.05 (-2.1)	49.31 (-3.0)
1(150)	1.042	50.77 (-3.2)	52.08 (-10.3)	51.04 (-2.1)	48.16 (-5.2)
2(153,149)*	0.000 0.000[c)]	50.03 (-4.7)	52.54 (-9.5)	50.96 (-2.2)	48.13 (-5.3)
2(155,151)*	0.347 0.249[c)]	51.06 (-2.7)	53.99 (-7.0)	49.82 (-4.4)	48.35 (-4.9)
2(154,150)	0.810	49.83 (-5.0)	49.58 (-14.6)	51.98 (-0.3)	47.91 (-5.7)
2(156,152)	1.072	50.10 (-4.5)	55.89 (-3.8)	50.28 (-3.6)	48.66 (-4.3)
NaKX, PBE (U_0 = -1177.283, U_1= -1214.421, -1235.422[c)], U_2 = -1252.200, -1273.665[c)], -1253.770[b)], -1274.972[b,c)] eV)					
0	-	47.91 (0.0)	51.40 (0.0)	45.18 (0.0)	44.49, (0.0) 45.96[c)]
1(151)	0.000 0.280[c)]	48.37 (1.0)	-50.16 (-2.4)	-44.68 (-1.1)	45.52 (2.3)
1(149)	0.016 0.000[c)]	47.65 (-0.5)	49.6 (-3.5)	45.81 (1.4)	45.10 (1.4)
1(150)	0.111	47.18 (-1.5)	51.89 (1.0)	45.59 (+0.9)	46.01 (3.4)
1(152)	0.331	46.07 (-3.8)	51.40 (2.0)	44.13 (-2.3)	45.18 (1.6)
2(156,152)	0.000 0.000[c)]	46.01 (-3.9)	54.67 (6.4)	43.20 (-4.4)	43.77 (-1.6)
2(154,150)	0.409, 0.616[c)] -[b)], [b,c)]	47.51 (-0.8)	48.89 (-4.9)	46.79 (3.6)	45.39 (2.0)
2(155,151)	0.448,	49.82 (4.0)	48.72 (-5.2)	46.43 (2.7)	46.00 (3.4)

	$1.176^{b)}$, $1.133^{b,c)}$				
2(153,149)	0.540 $0.852^{b)}$, $1.118^{b,c)}$	47.11 (-1.6)	49.85 (-3.0)	44.15 (-2.3)	43.90 (-1.3)

[a)] * Signifies the hydrocarbonate formation; [b)] Initial introduction of the HCO_3^-/CO_3^{-2} pair instead of two CO_3^{-2} moieties; [c)] DFT-D2

Table S10. Minimal and maximal values of Young's modulus (E), shear modulus (S), the Cartesian components of linear compressibility, Poisson's ratio (ν), and respective asymmetries $A_X = X_{max}/X_{min}$, X = E, S, in the NaX and NaKX models with *N* carbonate (and hydrogen carbonate, if any) species (the numbers of the Na or K cations, being closest to the carbonates, are shown in third column, the same notation as in the Tables S8, S9) and in the HY(D) form after Al extraction from 4R fragment as $AlOH^{+2}$ of with different number of water molecules (the same notation as in the Table 2) optimized at the DFT/(LDA or PBE) levels. The * signifies the hydrocarbonate formation.

Type	DFT	N	E_{max}	E_{min}	A_E	S_{max}	S_{min}	A_S	β_x	β_y	β_z	ν_{max}	ν_{min}
NaX	LDA	0	38.93	31.11	1.25	16.40	12.15	1.35	13.0	11.5	13.5	0.40	0.14
		1(151)	34.22	29.01	1.18	14.75	10.73	1.38	12.9	12.7	13.5	0.42	0.13
		1(152)	38.65	29.28	1.32	14.91	10.50	1.42	11.4	15.4	11.6	-	-
		1(149)	33.31	25.45	1.31	14.05	8.88	1.58	10.9	16.3	14.9	0.48	0.06
		1(150)	34.88	26.75	1.3	13.59	8.69	1.56	13.6	16	11.9	0.52	0.16
		2(155,151)*	35.60	25.76	1.38	12.63	7.79	1.62	9.7	18.7	15.2	0.52	0.11
		2(153,149)*	-	-	-	-	-	-	-	-	-	-	-
		2(156,152)	35.30	22.94	1.54	14.08	8.41	1.67	15.0	13.0	13.0	0.50	0.16
		2(154,150)	-	-	-	-	-	-	-	-	-	-	-
NaX	PBE	0	58.63	40.14	1.46	25.04	15.23	1.64	8.8	8.6	8.7	0.44	0.09
		1(151)	54.96	39.04	1.41	23.59	15.13	1.56	8.5	9.1	9.0	0.43	0.12
		1(149)	57.62	39.12	1.47	23.90	14.73	1.62	9.1	9.2	8.3	0.42	0.12
		1(152)	57.65	39.75	1.45	23.22	14.95	1.55	9.7	8.7	9.1	0.42	0.12
		1(150)	56.43	38.51	1.47	23.50	14.45	1.63	8.8	10.5	9.2	0.41	0.12
		2(153,149)*	55.50	40.55	1.37	22.64	14.84	1.53	9.3	9.3	8.7	0.42	0.12
		2(155,151)*	54.11	39.35	1.37	22.53	15.20	1.48	9.3	10.1	8.1	0.44	0.14
		2(154,150)	57.38	38.41	1.49	23.18	14.72	1.57	8.7	9.8	9.1	0.39	0.15
		2(156,152)	56.06	41.18	1.36	22.55	14.55	1.55	9.0	8.7	8.9	0.45	0.15
NaKX	PBE	0	51.43	34.66	1.48	20.95	13.39	1.56	9.5	9.6	10.2	0.43	0.14
		1(151)	50.50	36.53	1.38	21.25	14.24	1.49	8.8	9.9	10.5	0.42	0.16
		1(149)	49.92	36.25	1.38	21.27	13.73	1.55	8.9	9.4	9.6	0.43	0.14
		1(150)	52.02	36.07	1.44	21.94	14.47	1.52	9.6	9.4	10.6	0.43	0.14
		1(152)	52.83	35.46	1.49	21.32	14.20	1.50	10.1	9.6	11.2	0.42	0.13
		2(156,152)	46.78	37.95	1.23	21.12	14.66	14.66	12.0	10.3	12.8	0.34	0.13
		2(154,150)	49.47	36.54	1.35	21.62	14.36	14.36	9.5	10.2	10	0.40	0.14
		2(155,151)	49.53	39.18	1.26	21.57	15.06	15.06	9.4	10.9	10.4	0.43	0.13
		2(153,149)	50.21	34.39	1.46	20.48	13.20	13.20	9.7	9.3	11.3	0.41	0.16
HY(D)	PBE	HY	58.91	47.28	1.25	22.72	17.69	1.28	6.9	6.9	6.9	0.40	0.22
		+2H_2O	38.53	30.33	1.27	16.79	12.47	1.35	9.2	16.1	13.4	0.40	0.09
		+3H_2O	40.57	32.63	1.24	17.14	12.69	1.35	8.9	13.6	12.6	0.41	0.12
		+4H_2O	39.30	32.17	1.22	17.23	12.51	1.38	8.6	12.3	13.4	0.42	0.15

Figure S1. Energy variation ΔU per UC (eV) calculated using Catlow (circles) and Sauer-Sierka (triangles, diamonds) FFs *versus* $\Sigma_{i=1,\,3}\Delta R_{Me\text{-}Oi}$, (Å) displacements of Me cations upon the influence of one carbonate species per UC relative to their sites in the NaX, Me = Na (circles, triangles), or NaKX, Me = K (diamonds), zeolites without carbonates.

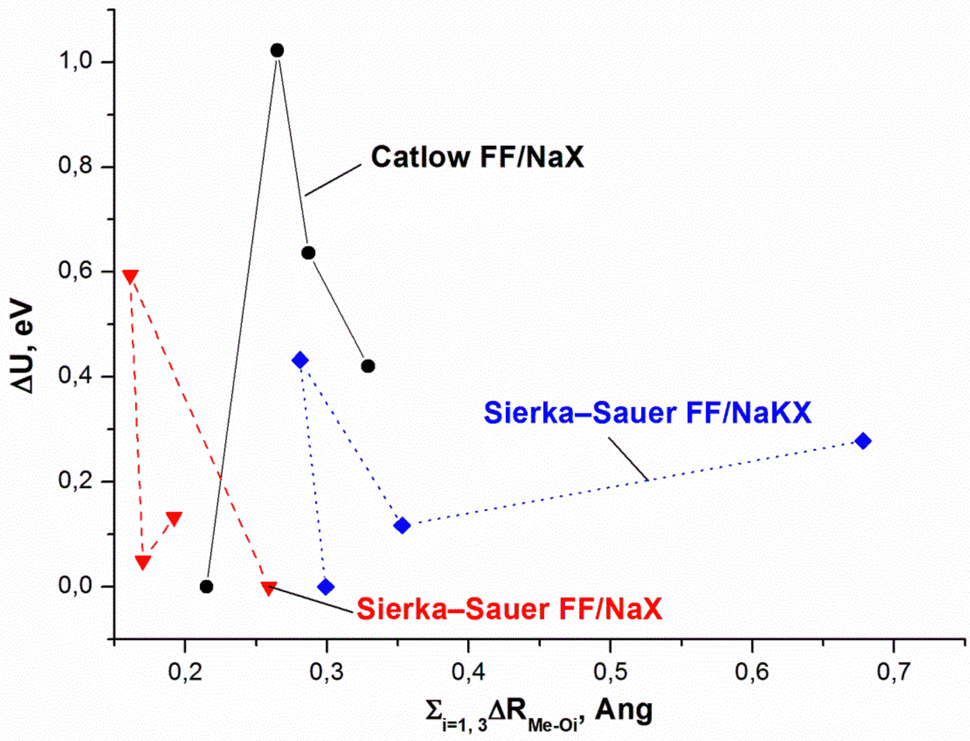


Figure S2. The geometries of the Na- (a, c) or K-carbonates (b) in the neutral (a, b) or charged (c, -2*e*) clusters with (c) or without (a, b) atoms of Al optimized at the B3LYP/6-31G* level. The Mulliken charges are given in Table S6. The atomic colors are given in cyan, blue, red, yellow, magenta, and grey for K, Na, O, Si, Al, and H, respectively.

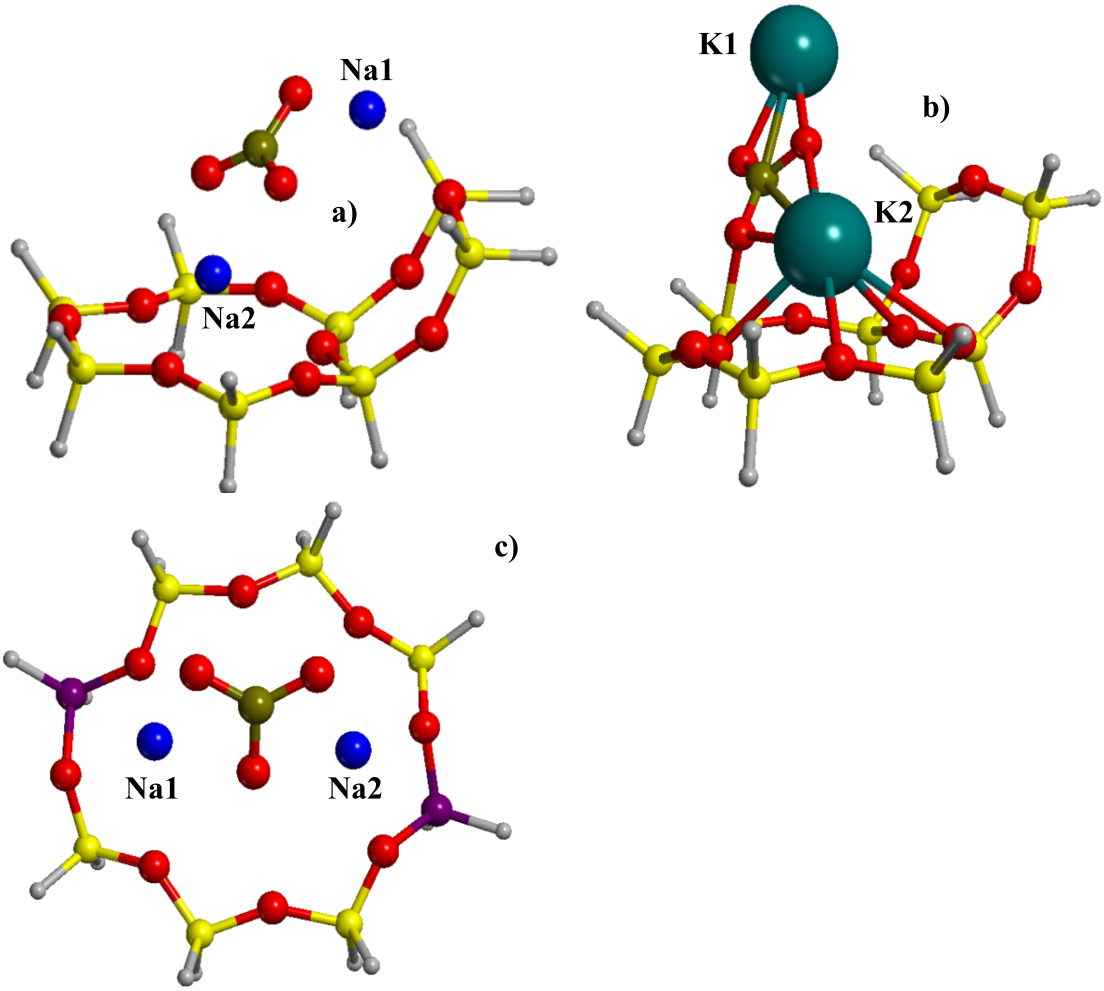
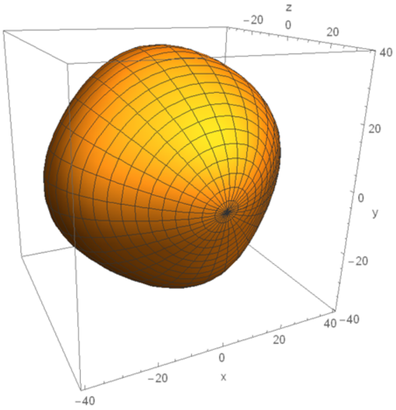
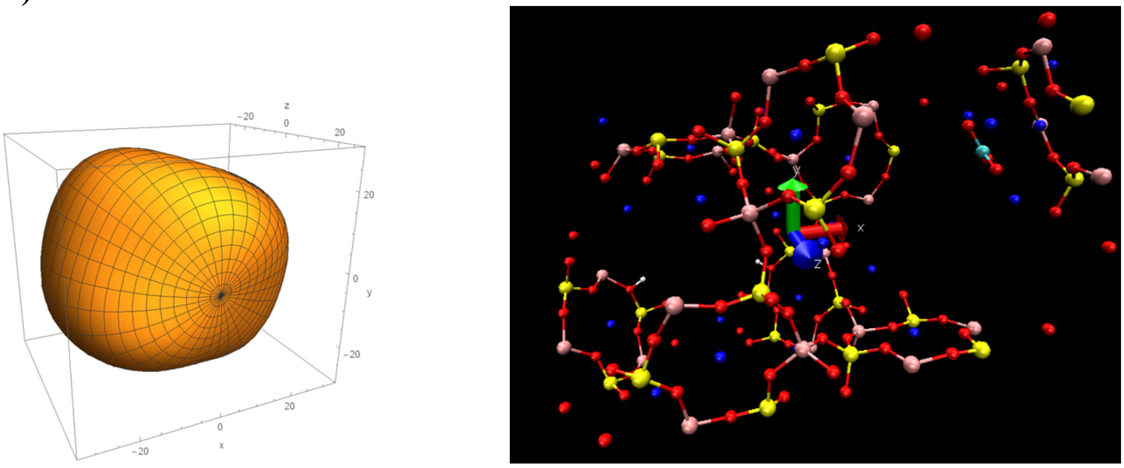


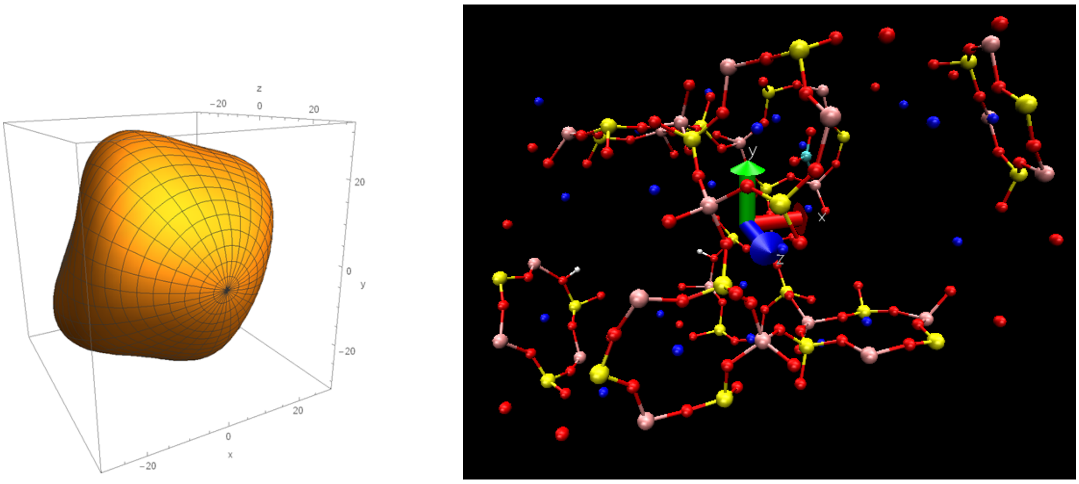
Figure S3. Asymmetry of Young *modulus* (according to Hill's form) in Cartesian coordinates (GPa) calculated at the DFT/LDA level in (a) empty NaX zeolite (the color version is on-line) upon carbonate (b-d, f, g) and hydrocarbonate (e) formation. The * signifies the hydrocarbonate formation. The cases correspond to the Table S9. The color agreement is the same as in the Figure S2, only Al is given in ochre. **a) no carbonates**



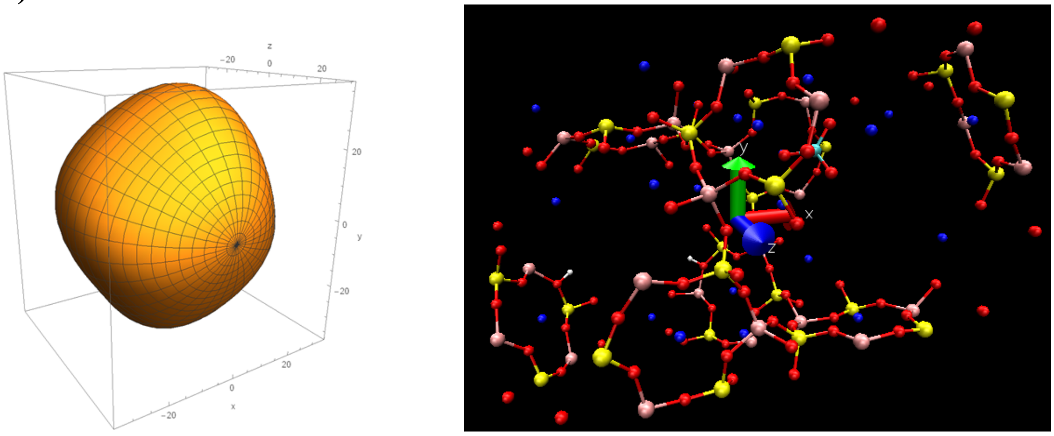
b) 149



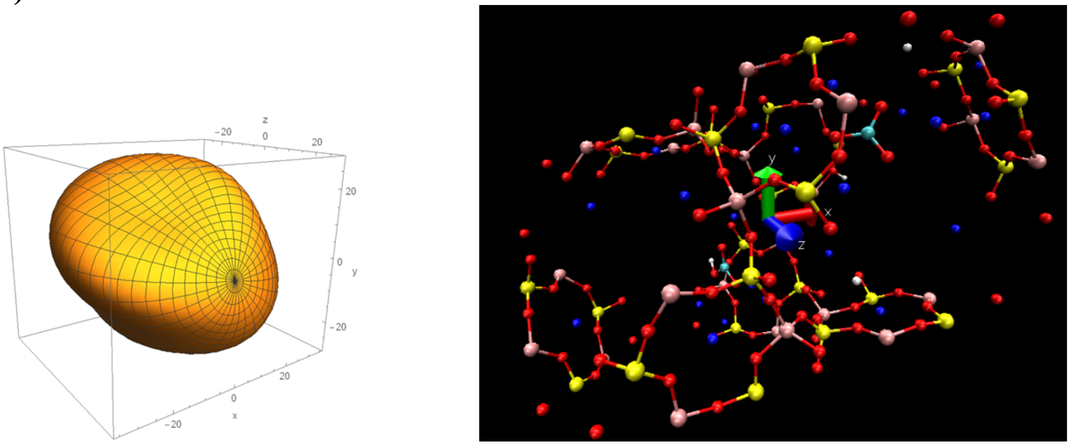
c) 150



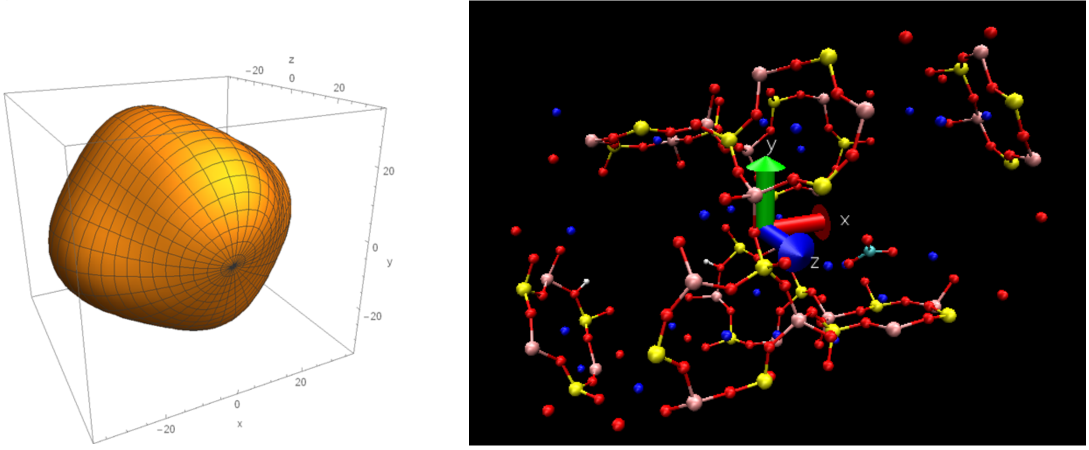
d) 151



e) 151+155*



f) 152



g) 152+156