

## Supporting Information

# Impact of Point Defects, of External Surfaces Sites and of the Si/Al Ratio on Al-O Bonds Hydrolysis Kinetics at the Initiation of Faujasite Dealumination

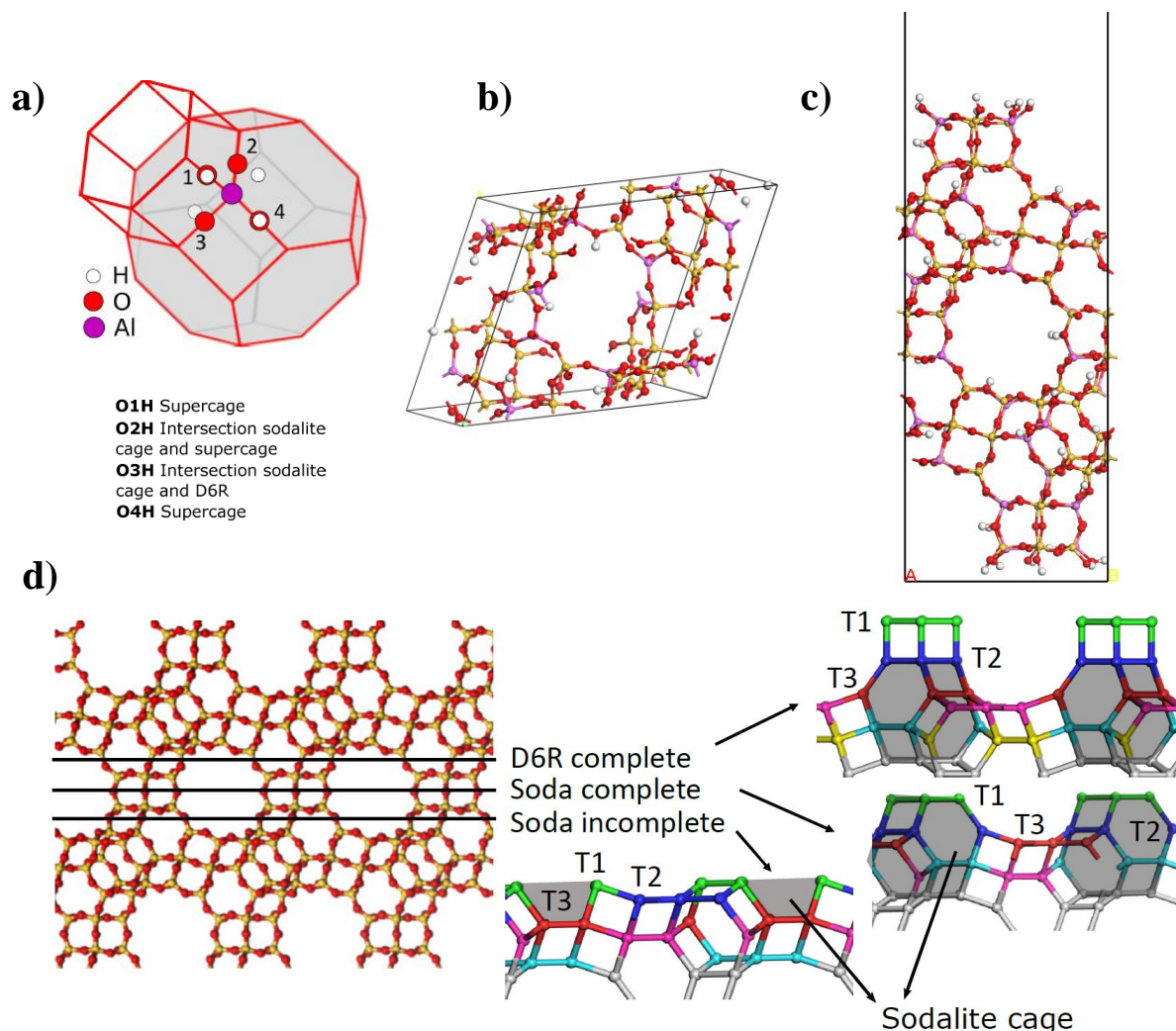
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### S1. Sites terminology and terminations of the surface models



**Figure S1.** a) Terminology of bulk sites of faujasite. b) Si/Al = 3 bulk cell modeled in the present work. c) Si/Al = 3 D6R complete surface cell modelled in the present work. d) (111) cleavage planes from the silicic bulk cell as it is looked from the [101] direction (left) and surface T sites nomenclature for the considered surface terminations (right). Adapted from ref. <sup>1</sup> with permission.

## S2. Energy data

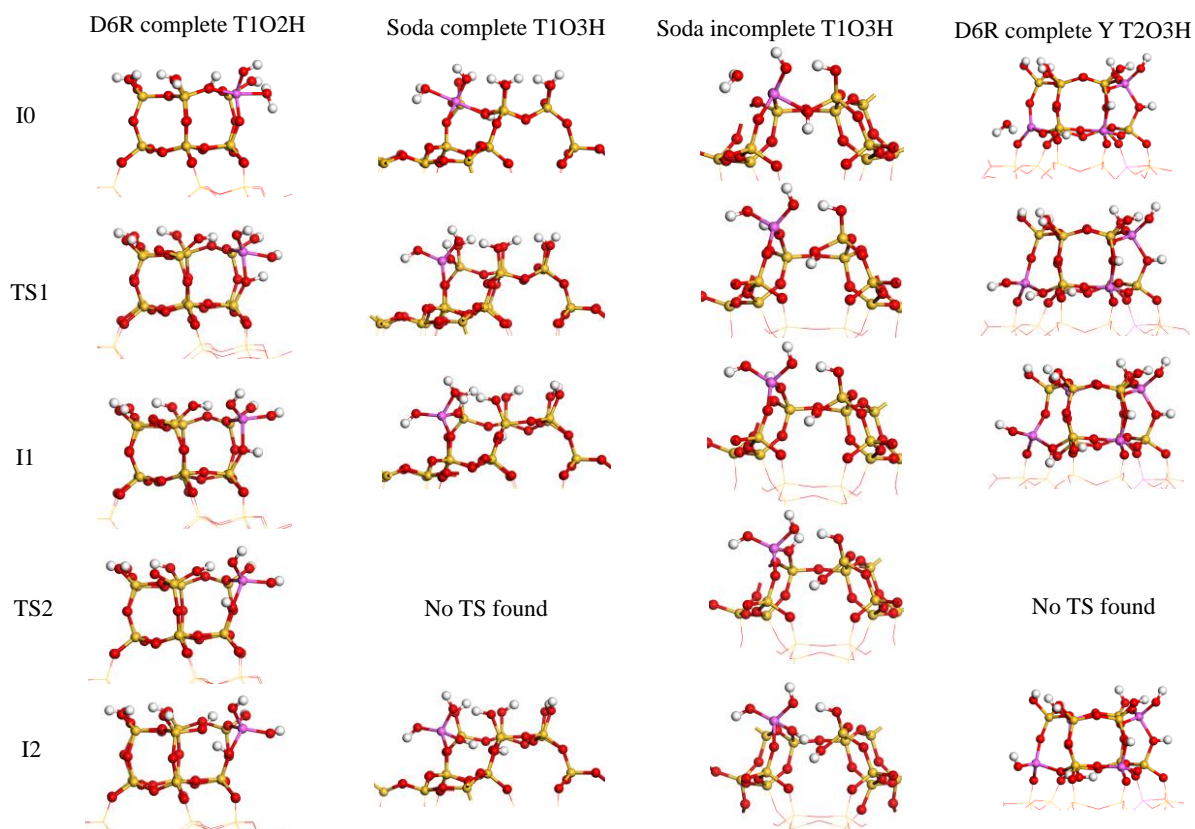
**Table S1.** Energy values  $\Delta E$  (kJ/mol) of the various intermediates and transition states discussed in the present work (referenced to the initial R state), for the systems exhibiting bridging OH groups, and dispersion components  $\Delta E_{\text{disp}}$  of these energies.

Systems	I0		TS1		I1		TS2		I2	
	$\Delta E$	$\Delta E_{\text{disp}}$	$\Delta E$	$\Delta E_{\text{disp}}$	$\Delta E$	$\Delta E_{\text{disp}}$	$\Delta E$	$\Delta E_{\text{disp}}$	$\Delta E$	$\Delta E_{\text{disp}}$
Bulk TO1H	-59	-30	45	-28	42	-30	44	-32	-7	4
Bulk TO3H #1	-54	-14	28	-8	24	-6	29	-7	-12	4
Bulk TO3H #2	-54	-14	20	-10	4	-8	10	-7	-17	6
Bulk Y TO1H	-71	-30	11	-26	-3	-30	-	-	-35	4
Bulk Y TO3H #1	-55	-16	17	-16	-2	-14	-	-	-12	4
Bulk Y TO3H #2	-46	-15	20	-13	18	-11	26	-9	-11	7
Bulk w/ def. O1H	-67	-27	13	-29	3	-30	-	-	-17	-1
Bulk w/ def. O3H	-52	-12	22	-9	7	-7	12	-6	-17	5
D6R comp. T2O3H	-53	-13	11	-9	-1	-7	8	-7	-16	3
D6R comp. T1O2H	-76	-7	-4	2	-24	-4	-19	0	-39	2
D6R comp. Y T2O3H	-41	-9	27	-9	3	-9	-	-	-9	2
Soda comp. T2O1H	-63	-26	27	-23	-1	-30	12	-29	-13	3
Soda comp. T1O3H	-69	-11	38	-6	26	-3	-	-	-28	-2
Soda incomp. T1O1H	-62	-16	-1	-15	-8	-18	0	-19	-48	-2
Soda incomp. T1O3H	-79	-19	-14	-16	-15	-16	-	-	-26	-3

**Table S2.** Free energy barriers (kJ/mol) for Al(T1)-H<sub>2</sub>O dissociation reactions at external surface models. Profiles are shown in figure 8 of the main text.

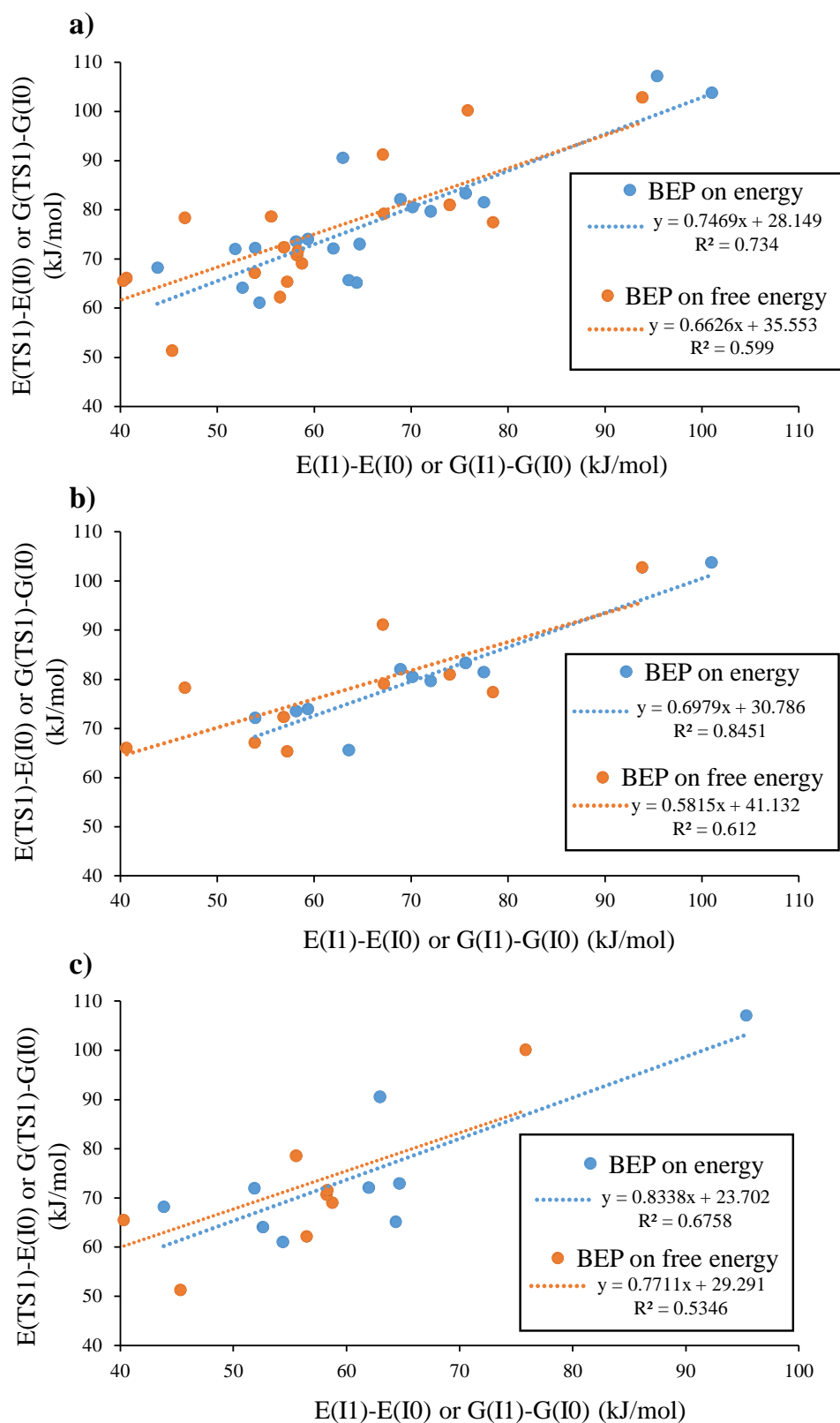
Systems	$G_b$	
	0K	450K
D6R complete	56	46
Sodalite complete	72	74

### S3. Additional structures



**Figure S2.** Intermediates and transition states along the dealumination path initiated from the T1O2H D6R complete, T1O3H sodalite complete and T1O3H sodalite incomplete sites, for cells containing a single Al, and for the D6R complete Y (Si/Al=3) T2O3H site. The color is the same as in figure 7 of the main text.

### S3. Brønsted-Evans-Polanyi relationships



**Figure S3.** Plots of the (free) energy barriers as a function of the reaction (free) energy (free energy computed at 450 K). A) all systems investigated, b) bulk systems only (including with defects), c) surface systems only.

## Reference

(1) Jarrin, T.; de Bruin, T.; Chizallet, C., Stability and Acidity of Sites at the External Surface and at Point Defects of Faujasite, *ChemCatChem* **2023**, *15*, e202201302.