Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information

Acidity of two-dimensional zeolites

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Table S1 Deprotonation energies (in kJ/mol) of SiH_3OH and $2T_{6OH}$ molecules calculated with different methods in TURBOMOLE and VASP programs.

System	B3LYP/def2-TZVP	CCSD(T)/CBS(D,T)[a]	PW91/pw[b]
SiH_3OH	1525.4	1524.7	1487.5
$2T_{6OH}$	1313.2	1306.3	1287.7

[a] Calculations done with extrapolation to the complete basis set (CBS), on the basis of extrapolation between aug-cc-pVDZ and aug-cc-pVTZ basis sets. Structures of the protonated and the deprotonated forms of molecules were optimised with B3LYP/def2-TZVP

[b] Deprotonation energies calculated with VASP using the PW91 functional, planewave basis set with energy cutoff of 400 eV and projector augmented wave (PAW) method. Deprotonation energies are extrapolated to infinitely large unit cell (gas phase limit).

Table S2 Unit cell parameters (in pm and degrees) of the systems studied.

Model	a	b	c	α	β	γ
H-CHA	945.3	944.1	938.7	93.958	94.835	95.377
H-2dH(Al/Si=1/63)	2141.4	1854.4	-	90.000	-	-
H-2dH(Al/Si=1/7)	1071.7	932.5	-	90.000	-	-
H-2dH(Al/Si=1/3)	1083.0	932.0	-	90.000	-	-

Table S3 Geometric parameters (pm and degrees) of protonated and deprotonated Brønsted sites, calculated with different cluster models of the H-CHA zeolite embedded in a 2×2×2 supercell.

	Protonated				Deprotonated		
Model	$\angle$(AlOSi)	r(AlO)	r(SiO)	r(OH)	$\angle$(AlOSi)	r(AlO)	r(SiO)
MM	135.6	190.3	169.6	98.5	147.1	175.0	158.6
$8T_{12OH}$	131.5	191.9	170.3	96.8	143.0	174.1	157.7
$12T_{12OH}$	131.5	191.3	170.5	97.0	143.0	173.9	157.7
$16T_{16OH}$	133.3	191.9	170.4	96.8	143.3	174.1	157.7
$33T_{34OH}$ [a]	133.9	191.3	170.2	96.7	144.2	173.9	157.7
$44T_{34OH}$ [a]	134.0	191.3	170.2	96.8	144.7	173.9	157.6

[a] cluster models embedded in a 3×3×3 supercell

Table S4 Fitted parameters A (kJ×Å /mol) and B (kJ×Å^3/mol) together with the correction energy, $E_{\mathrm{corr}}(\mathrm{kJ/mol})$ calculated using these parameters (eqn (8)) for H-2dH zeolite models with different Al/Si ratio.

Al/Si	Model	$\Delta E_{\mathrm{DP}}^{\infty}$	A	B	E_{corr} [x]	$A/\langle r\_\_\rangle$ [x]	$B/\langle r\_\_\rangle^3$ [x]
1/63 [a]	MM	836.1	-1752.1	-23657	- 44.3	-43.9	-0.4
	1D6R	1032.1	-1696.9	-22783	-42.9	-42.5	-0.4
	3D6R	1041.0	-1834.7	41611	-45.3	-46.0	0.7
	4D6R	1041.5	-1685.6	9727	-42.1	-42.3	0.2
1/7 [b]	MM	870.5	-1667.7	-49835	-42.5	-41.7	-0.8
	1D6R$_{+2T}$	1049.3	-1472.4	-70558	-37.9	-36.8	-1.1
	2D6R$_{+4T}$	1072.1	-1839.8	106148	-44.3	-46.0	1.7
	4D6R	1068.9	-1442.7	-37162	-36.7	-36.1	-0.6
	7D6R$_{+4T}$	1071.8	-1565.4	76842	-37.9	-39.1	1.2
1/3 [b]	MM	890.3	-1648.2	-52858	-41.8	-41.0	-0.8
	1D6R$_{+4T}$	1069.6	-1669.0	16221	-41.3	-41.5	0.2
	4D6R$_{+4T}$	1090.6	-1789.9	99372	-43.0	-44.5	1.5

[a] Cell sizes used in the fit: 1×1, 2×2, 3×3

[b] Cell sizes used in the fit: 2×2, 3×3, 4×4

[x] Calculated for 2×2 cell for Al/Si=1/63 and 4×4 cell for Al/Si=1/7 and 1/3

Table S5 Geometric parameters (pm and degrees) of protonated and deprotonated Brønsted sites calculated with different embedded cluster models for the H-2dH zeolite

		Protonated				Deprotonated		
Al/Si	Model	$\angle$(AlOSi)	r(AlO)	r(SiO)	r(OH)	$\angle$(AlOSi)	r(AlO)	r(SiO)
1/63 [a]	MM	133.9	191.1	171.8	98.5	141.4	175.6	158.6
	1R6	133.8	191.5	171.2	97.1	139.9	173.7	157.5
	2R6	135.6	192.0	170.9	97.0	141.0	174.0	157.5
	3R6	135.3	192.1	170.9	97.0	140.4	174.1	157.5
	4R6	134.8	191.9	170.8	97.0	139.7	174.0	157.5
	5R6	134.9	192.0	170.8	97.0	139.7	174.2	157.6
	6R6	135.0	192.2	170.8	97.0	139.8	174.1	157.6
	7R6	134.9	192.0	170.8	97.0	139.8	174.1	157.6
1/7 [b]	MM	132.8	183.0	175.7	98.0	138.0	172.4	160.6
	1D6R$_{+2}$	131.7	184.4	172.7	97.8	134.7	170.9	158.7
	2D6R$_{+4}$	132.7	185.1	172.7	96.8	136.0	171.4	158.8
	3D6R$_{+2}$	132.7	185.2	172.7	96.8	135.6	171.5	158.9
	4D6R	132.7	185.2	172.7	96.8	136.2	171.4	158.9
	7D6R$_{+4}$	132.7	185.3	172.8	96.8	136.3	171.5	158.9
1/3 [b]	MM	129.8	183.3	175.5	97.4	133.1	173.3	161.2
	1D6R$_{+4}$	128.6	184.7	174.4	96.8	129.6	171.6	160.1
	4D6R$_{+4}$	130.5	185.2	174.4	96.7	132.2	171.8	160.0

[a] Results for 2×2 cell

[b] Results for 4×4 cell

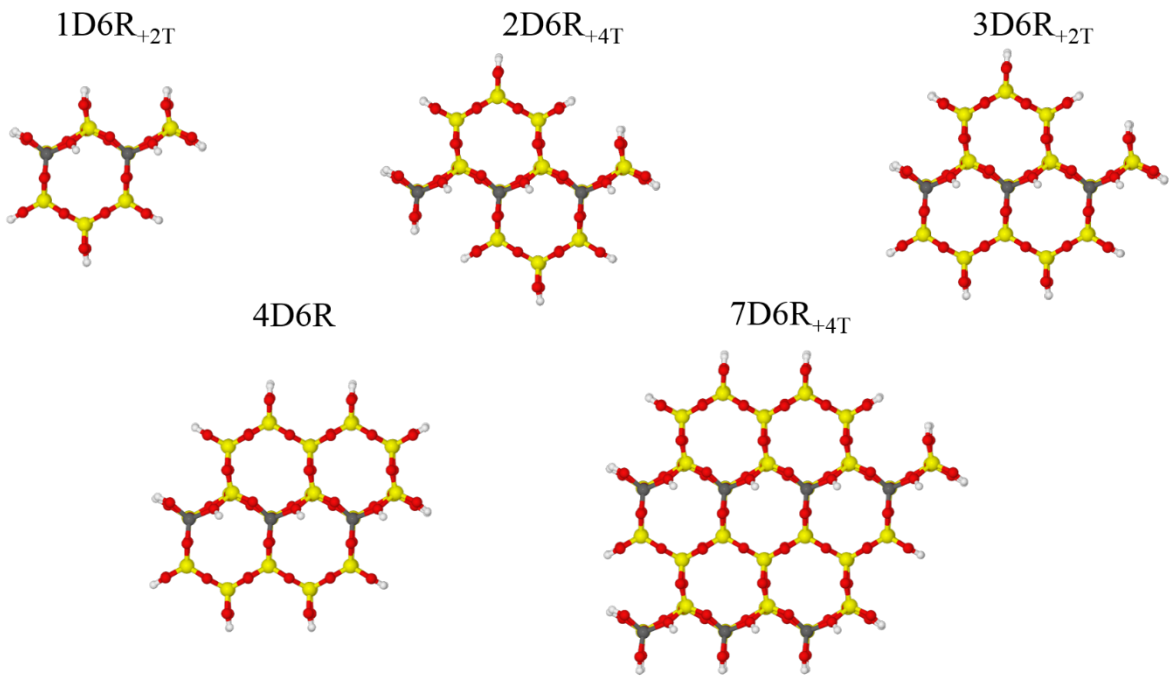

Fig. S1 Cluster models applied in QM/MM calculations of the H-2dH deprotonation energy (Al/Si=1/7).

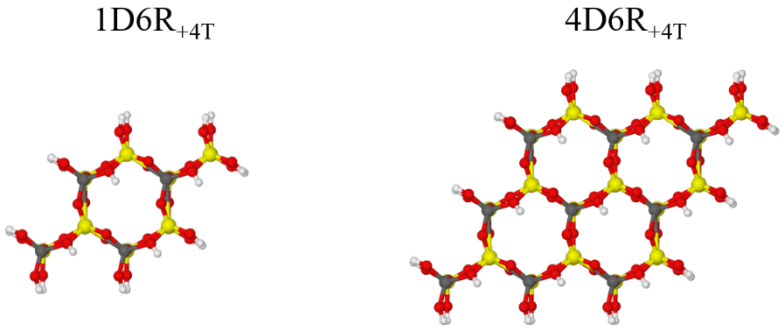

Fig. S2 Cluster models applied in QM/MM calculations of the H-2dH deprotonation energy (Al/Si=1/3).

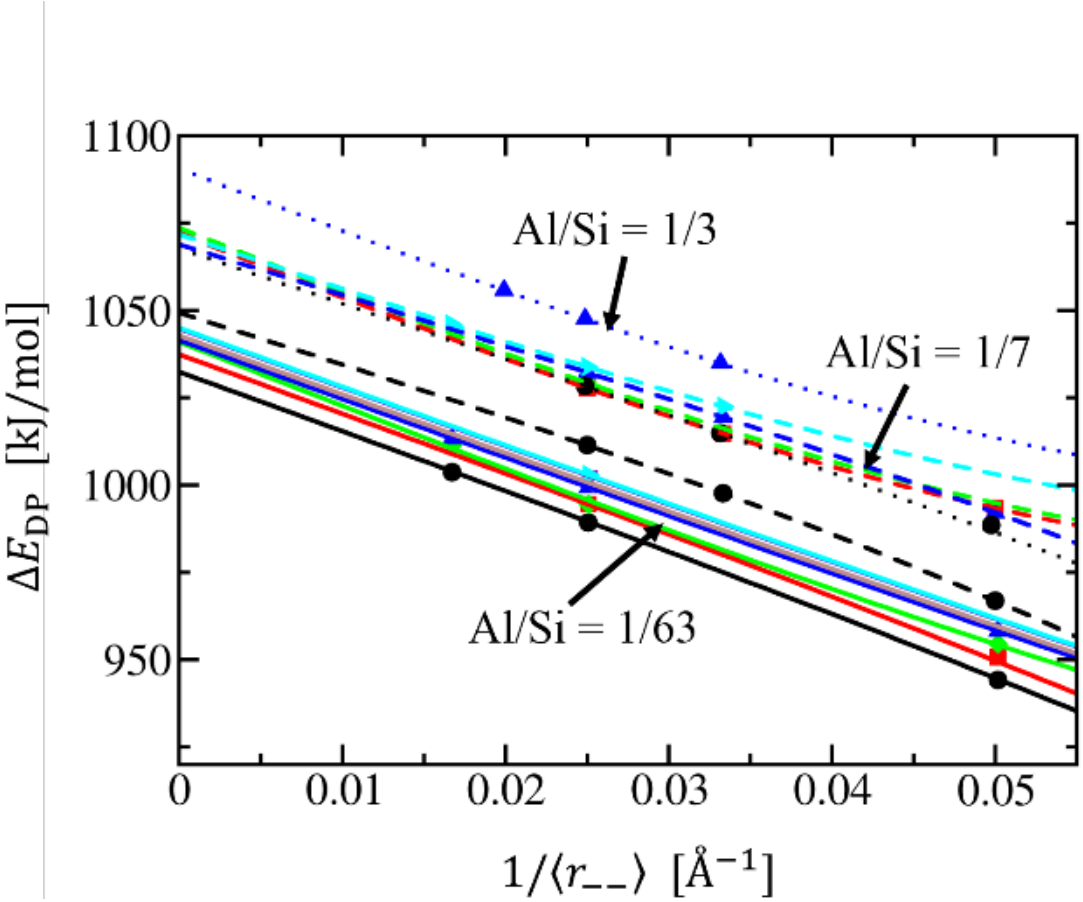

Fig. S3 Deprotonation energy of different embedded models of H-2dH zeolites (symbols), and fitted extrapolation curves (lines), as a function of the inverse of the average anion-anion distance, $\langle r\_\_\rangle$. Different embedded cluster models are depicted with colours: 1D6R – black, 2D6R – red, 3D6R – green, 4DR4 – blue, 5D6R – brown, 6D6R – violet, 7D6R – magenta. Different Al/Si ratios are indicated by various line types: 1/63 (solid lines), 1/7 (dashed lines) and 1/3 (dotted line). Fitting curve parameters (eqn (8)) are presented in Table S4.

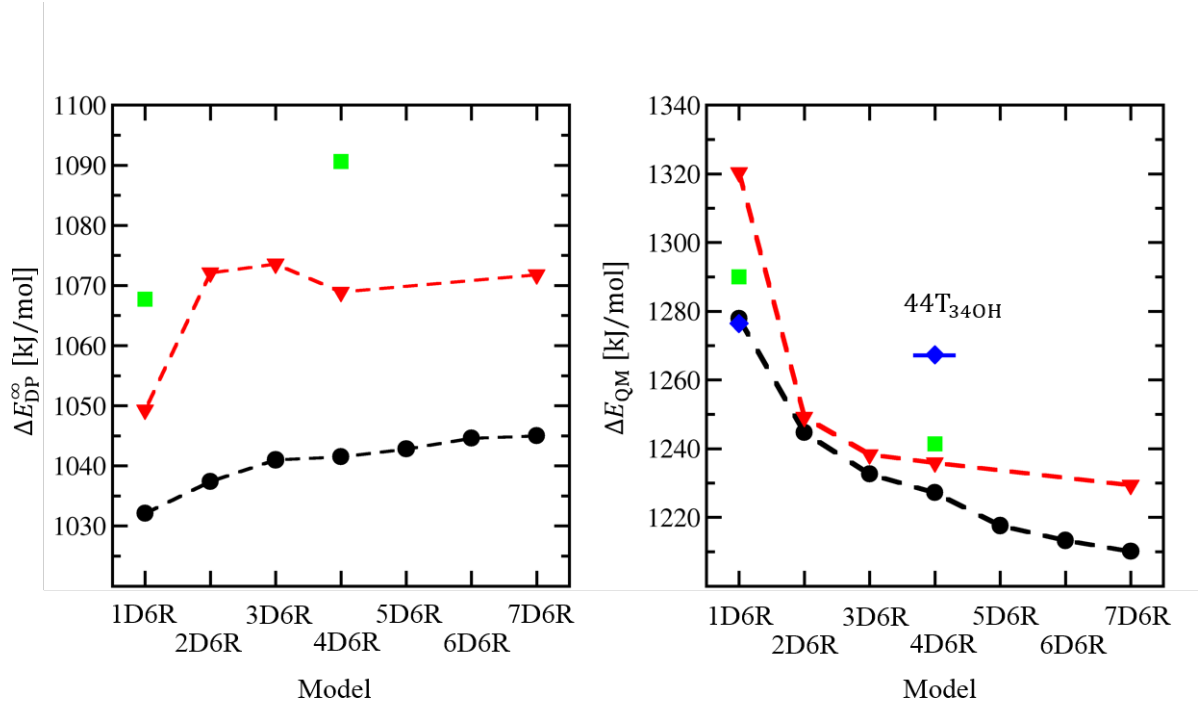

Fig. S4 Corrected deprotonation energy (left) and QM part of the deprotonation energy (right) of different embedded models of H-2dH zeolites with different Al/Si ratios: 1/63 (black dots), 1/7 (red triangles) and 1/3 (green squares). For comparison, the QM part of the deprotonation energy of H-CHA models is presented by blue diamonds.