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

Supporting Information
for

Cooperativity of Silanol Defect Chemistry in Zeolites

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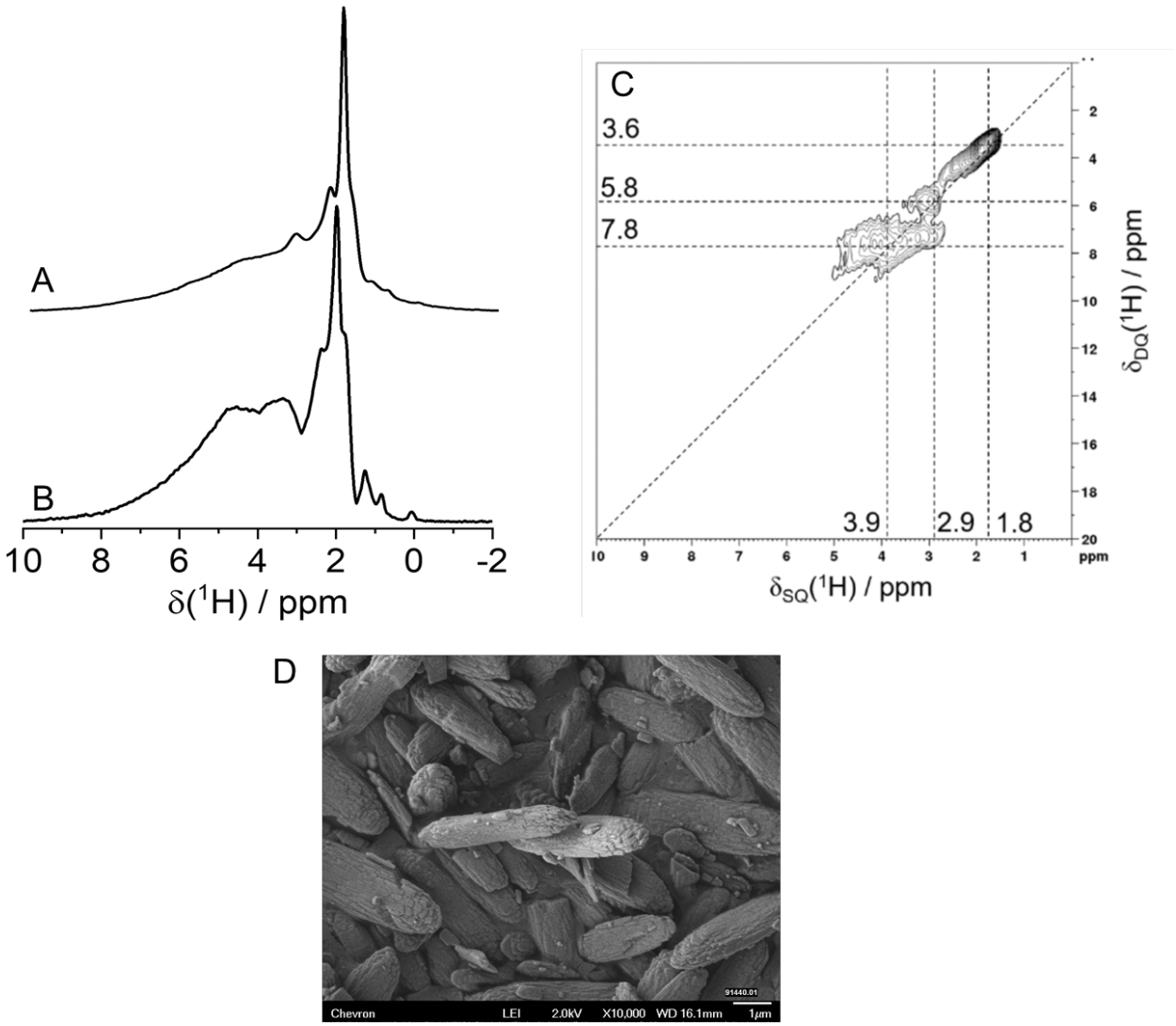

Fig. S1: (A) ^{1}H MAS NMR spectrum of deboronated SSZ-55, (B) SQ projection of ^{1}H DQ-SQ MAS NMR spectrum of deboronated SSZ-55 (Fig. 2), (C) ^{1}H DQ-SQ MAS NMR spectrum of SSZ-55 after Al insertion, (D) SEM image of SSZ-55.

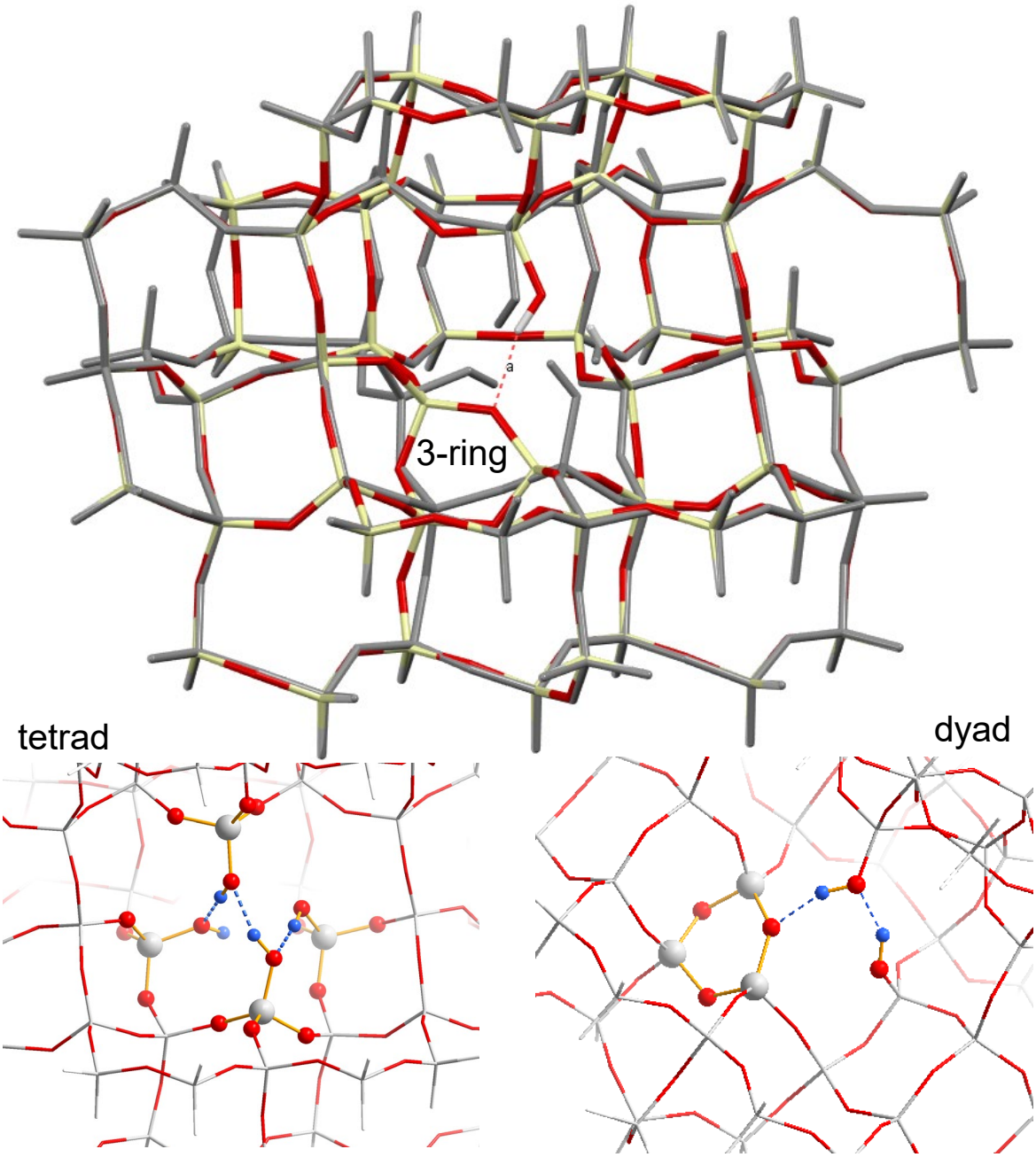

Fig. S2: Overlay of a cluster model with a tetrad nest in the center (grey) and a dyad model with two SiOH groups and a 3-ring formed by condensation of two silanols (colored), shown at the top. The clusters are built of 60 T atoms. The two clusters were terminated by hydrogen atoms at the boundaries, which were frozen in the optimization of the cluster geometry. The overlaying figures show that there are significant differences of the geometries near the cluster boundaries, which indicates that the relaxation of the strain caused by silanol condensation for the dyad model does not relax within the finite size of the models. For clarity, the tetrad and dyad model centers are shown at the bottom.

Table S1: Reaction energy per defect ΔE (kJ/mol) of N=1 for the defect site A.

Structure	ΔE
A12	196.6
A13[a]	167.9
A14	167.8[b]
A23	276.0
A24	278.6
A34	254.2

a) Structure A13 converged to structure A14.
b) The reaction energy per defect is 167.1 kJ/mol from single point B3LYP-D3//PBE calculations.

Table S2: Reaction energy per defect ΔE (kJ/mol) of N=2 for defect sites (A, B) (defects distance 8.4 Å).

Structure	ΔE	Structure	ΔE
A12-B12	227.4	A23-B12	237.1
A12-B13[a]	139.8	A23-B13[d]	207.4
A12-B14	177.8	A23-B14	208.7
A12-B23	174.2	A23-B23	227.5
A12-B24	207.7	A23-B24	279.9
A12-B34	139.8	A23-B34	207.4
A13-B12[b]	207.4	A24-B12	278.3
A13-B13[g]	402.6	A24-B13[e]	216.9
A13-B14	225.4	A24-B14	279.1
A13-B23[g]	298.6	A24-B23	207.7
A13-B24[g]	340.9	A24-B24	278.1
A13-B34[g]	316.4	A24-B34	202.1
A14-B12	207.4	A34-B12	208.7
A14-B13[c]	144.7	A34-B13[f]	201.8
A14-B14	219.0	A34-B14	211.8
A14-B23	139.8	A34-B23	177.8
A14-B24	202.2	A34-B24	253.8
A14-B34	182.3	A34-B34	198.7

a) Structure A12-B13 converged to structure A12-B34.
b) Structure A13-B12 converged to structure A14-B12.
c) Structure A14-B13 converged to structure A14-B23.
d) Structure A23-B13 converged to structure A23-B34.
e) Structure A24-B13 converged to structure A24-B23.
f) Structure A34-B13 converged to structure A34-B23.
g) Dangling Si-O bonds were formed.

Table S3: Reaction energy per defect ΔE (kJ/mol) of N=2 for defect sites (B, C) (defects distance 7.1 Å).

Structure	ΔE	Structure	ΔE
B12-C12[a]	180.9	B23-C12	162.8
B12-C13[h]	253.5	B23-C13[e]	144.3
B12-C14	424.2	B23-C14	179.2
B12-C23	167.7	B23-C23	154.7
B12-C24	236.1	B23-C24	216.2
B12-C34	191.9	B23-C34	136.7
B13-C12[b]	210.6	B24-C12[f]	226.6
B13-C13[c]	156.5	B24-C13[h]	339.3
B13-C14[h]	267.7	B24-C14	237.9
B13-C23[d]	153.1	B24-C23	214.2
B13-C24[h]	337.4	B24-C24	233.3
B13-C34	248.3	B24-C34	210.9
B14-C12	225.1	B34-C12[g]	173.6
B14-C13[h]	294.8	B34-C13[h]	320.1
B14-C14	290.4	B34-C14	182.5
B14-C23	225.6	B34-C23	181.1
B14-C24	260.8	B34-C24	227.0
B14-C34	165.8	B34-C34	188.7

a) Structure B12-C12 converged to structure B12-C23.
b) Structure B13-C12 converged to structure B23-C24.
c) Structure B13-C13 converged to structure B23-C34.
d) Structure B13-C23 converged to structure B23-C23.
e) Structure B23-C13 converged to structure B23-C34.
f) Structure B24-C12 converged to structure B24-C24.
g) Structure B34-C12 converged to structure B34-C23.
h) Dangling Si-O bonds were formed.

Table S4: Reaction energy per defect ΔE (kJ/mol) of N=2 for defect sites (B, D) (defects distance 6.8 Å).

Structure	ΔE	Structure	ΔE
B12-D12	293.6	B23-D12	190.5
B12-D13[a]	213.1	B23-D13	313.1
B12-D14	215.8	B23-D14	199.4
B12-D23	187.0	B23-D23	168.3
B12-D24	273.1	B23-D24	222.9
B12-D34	221.2	B23-D34	175.5
B13-D12[g]	292.0	B24-D12	241.4
B13-D13[g]	189.1	B24-D13	304.4
B13-D14[b]	154.4	B24-D14	246.1
B13-D23[c]	126.6[c]	B24-D23	206.3
B13-D24[g]	300.2	B24-D24	219.7
B13-D34[d]	182.4	B24-D34	221.2
B14-D12[e]	225.1	B34-D12	178.7
B14-D13[g]	265.8	B34-D13	211.0
B14-D14[f]	164.0	B34-D14	154.9
B14-D23	199.6	B34-D23	131.2
B14-D24	225.3	B34-D24	210.4
B14-D34	185.9	B34-D34	163.6

a) Structure B12-D13 converged to structure B12-D14.
b) Structure B13-D14 converged to structure B34-D14.
c) Structure B13-D23 converged to structure B34-D23. The reaction energy per defect is 125.7 kJ/mol from single point B3LYP-D3//PBE calculations.
d) Structure B13-D34 converged to structure B23-D34.
e) Structure B14-D12 converged to structure B24-D24.
f) Structure B14-D14 converged to structure B34-D14.
g) Dangling Si-O bonds were formed.

Table S5: Si-O-Si ring sizes after reaction (1) at each defect site.[a]

Silanol pair	Si-O-Si ring size	Silanol pair	Si-O-Si ring size	Silanol pair	Si-O-Si ring size	Silanol pair	Si-O-Si ring size
A12	3-ring	B12	5-ring	C12	5-ring	D12	5-ring
A13	none / 7-ring	B13	none / 7-ring	C13	none	D13	none / 7-ring
A14	3-ring	B14	5-ring	C14	5-ring	D14	5-ring
A23	5-ring	B23	3-ring	C23	3-ring	D23	3-ring
A24	5-ring	B24	none / 5-ring	C24	5-ring	D24	5-ring
A34	5-ring	B34	3-ring	C34	3-ring	D34	3-ring

a) In most cases, 3-rings and 5-rings are formed at defect sites. For distant pairs of silanol groups, in some cases dangling Si-O bonds remain (none). In rare cases, the 7-ring are formed.

Table S6: Reaction energy per defect ΔE (kJ/mol) of N=3 for defect sites (A, B, C).

Structure	ΔE
A12-B23-C34	149.7
A12-B34-C12	155.2
A12-B34-C14	153.6
A12-B34-C23	156.0
A12-B34-C34	147.2
A14-B23-C34	132.5
A23-B23-C34	156.3
A34-B23-C34	147.8

Table S7: Reaction energy per defect ΔE (kJ/mol) of N=3 for defect sites (A, B, D).

Structure	ΔE
A12-B34-D12	160.8
A12-B34-D14	124.4
A12-B34-D23	123.1[a]
A12-B34-D34	163.8
A14-B34-D23	151.7
A23-B34-D23	155.1
A34-B34-D23	152.3

a) The reaction energy per defect is 118.8 kJ/mol from single point B3LYP-D3//PBE calculations.

Table S8: Reaction energies per defect (kJ/mol) of *N*=3* for defect sites (A, B, D).

Structure	ΔE
A00-B34-D14	108.3
A00-B34-D23	88.6[a]
A12-B00-D14	116.5
A12-B00-D23	111.9
A12-B34-D00	104.8

a) The reaction energy per defect is 85.3 kJ/mol from single point B3LYP-D3//PBE calculations.

The ^{1}H NMR chemical shifts were calculated using the formula: $\delta = \sigma_{\mathrm{ref}} - \sigma + \delta_{\mathrm{ref}}$, where σ_{ref} and σ are the NMR shielding constants of the reference and calculated species, respectively. The reference species is tetramethylsilane (TMS) with $\delta_{\mathrm{ref}} = 0$. The same level of theory was used to calculate σ_{ref} and σ. Fig. S3 shows the correlation between the higher ^{1}H chemical shift value from the silanol group participating as a proton donor and the O-O distance between two silanol groups. All calculated ^{1}H NMR chemical shifts are summarized in Table S9. The ^{1}H chemical shift values of silanol dyads from the experiment are 3.4 and 4.6 ppm.

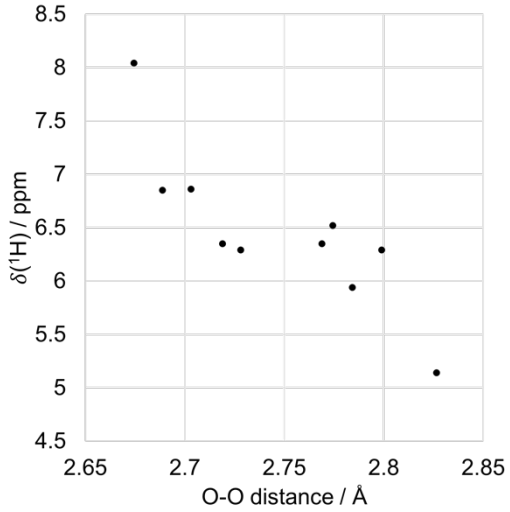

Fig. S3: Correlation between the higher ^{1}H chemical shift value from the silanol group participating as a proton donor and the O-O distance between two silanol groups.

Table S9: Calculated ^{1}H NMR chemical shifts (ppm).

Structure	Defect site	^{1}H NMR chemical shift	
		Hydrogen bond donor	Hydrogen bond acceptor
B34-D23	B	6.9	2.7
	D	6.3	3.3
A12-B34-D23	A	6.4	3.2
	B	6.5	2.6
	D	5.1	3.4
A12-B34-D14	A	5.9	2.7
	B	8.0	4.4
	D	6.3	2.9
A00-B34-D23	A	-	-
	B	6.9	2.7
	D	6.3	3.4

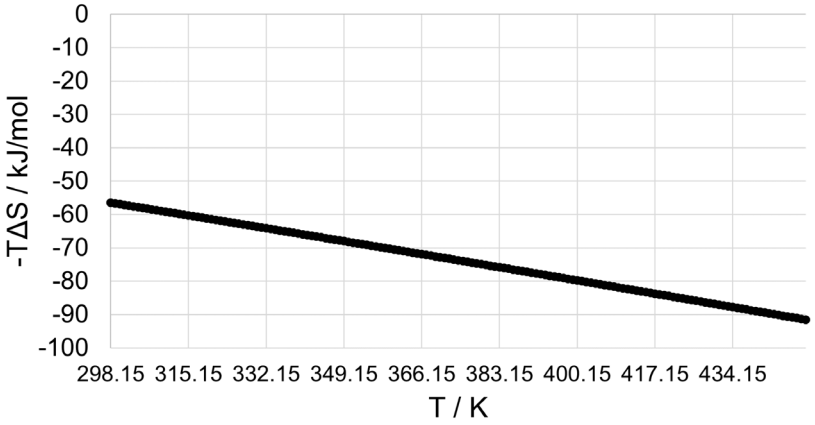

Fig. S4: Entropy contribution (-TΔS) of water molecule as a function of temperature.