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---SUPPORTING INFORMATION---

Complex H-bonded silanol network in zeolites revealed by IR and NMR spectroscopy combined with DFT calculations

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Zeolite Synthesis

The silicalite-1 zeolites were synthesized using clear precursor suspensions with different compositions, as outlined below. For the preparation of the suspensions, the total amounts of double deionized water and organic structure directing agent TPAOH (tetra n-propylammonium hydroxide, 20 wt. % in water solution, Alfa Aesar) were mixed for about 15 minutes by magnetic stirring. Then, the silicon source -TEOS (tetraethyl orthosilicate, 98%, Aldrich) was added dropwise to the previous mixture. After adding TEOS, the precursor solutions remained on magnetic stirring for one hour, before aging treatment in an orbital shaker for 18h at room temperature. Then, the hydrothermal treatment was carried out in Teflon-lined stainless-steel autoclaves under static conditions. After crystallization, the samples were removed from the oven, purified, dried overnight at 90 ° C and calcined at 550 ° C/ 5h in air.

Molar composition of the precursor suspensions used for the synthesis of the pure silica zeolites and the respective hydrothermal (HT) treatment conditions are as follows:
Sample MFI-50: 1SiO_2:0.28 TPAOH: 12.65 H_2O (HT for 28 h at 90 °C)
Sample MFI-100: 1SiO_2:0.28 TPAOH: 40 H_2O (HT for 48 h at 90 °C)
Sample MFI-2000: 1SiO_2:0.14 TPAOH: 40 H_2O (HT for 15 days at 140 °C).

Characterization

The crystallinity of the pure silica zeolite samples was investigated by powder X-ray diffraction (XRD) by a PANalytical XPert Pro diffractometer using Cu Kα radiation (λ = 1.5418 Å, 45 kV, 40 mA).

The crystal size and homogeneity of the sample were determined by scanning electron microscope (SEM) using a MIRA-LMH (TESCAN) equipped with a field emission gun using an accelerating voltage of 30.0 kV.

The FTIR spectra are acquired using a Nicolet Magna 550-FT-IR spectrometer (4 cm^{-1} optical resolution). The IR spectra were collected on activated samples at 350°C under vacuum in the in situ IR cell.

^{29}Si magic-angle spinning (MAS) NMR spectra were acquired at 99.3 MHz on a Bruker Avance III-HD 500 (11.7 T), using 4.0-mm outer diameter probe. Radiofrequency power of 36 kHz and a recycle delay of 20 s were used respectively.

^{1}H NMR Nuclear Magnetic Resonance: One dimensional ^{1}H magic-angle spinning (MAS) NMR spectra were acquired at 500.07 MHz on a Bruker Avance III-HD (11.7 T), using 1.9-mm outer diameter probes zirconia rotors spun at 40 kHz, a radiofrequency power of 114 kHz and a recycle delay of 10s. The modeling of ^{1}H NMR spectra is done using Lorentzian peaks in Dmfit software[1]. The ^{1}H NMR spectra of activated samples at 350°C under vacuum overnight were collected.

Table S1: Summary of the fits of ^{1}H NMR spectra of the three MFI samples*

	Chemical Shift (ppm)	**Relative Percentage (%)**
MFI-50		
Green silanols[1]	1.8	38.6
	2.0	10.7
Blue and pink silanols	3.9	29.5
	4.5	21.2
MFI-200		
Green silanols	1.7	11.0
	1.9	21.2
	1.8	31.5
Blue and pink silanols	3.3	10.2
	3.9	13.2
	5.3	12.9
MFI-2000		
Green silanols	1.9	4.5
	2.1	5.2
Blue and pink silanols	3.4	4.0
	3.8	71.8
	5.8	14.5

*The ^{1}H NMR signal corresponding to the Vespel caps of the 1.9 mm rotors was not considered in the fits.

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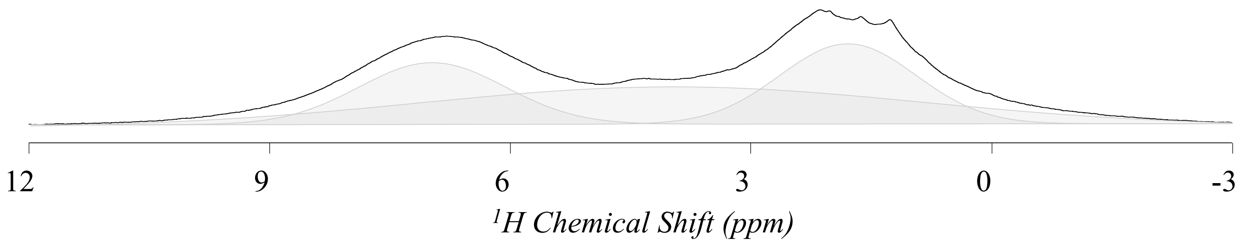
[1] The green silanols correspond to isolated and weak H bonded ones, the blue silanols correspond to medium H bonded ones and the pink silanols correspond to strong H bonded ones.


12
9
6
3
0
-3
^{1}H Chemical Shift (ppm)

Computational details

All calculations were performed with ORCA An Ab Initio, DFT and Semiempirical electronic structure package (vers. 4.1.2)[2,3] with hybrid gradient-corrected PBE0 exchange-correlation functional.[4] Geometry optimization was performed with def2-SVP basis set with utilization of def2/J auxiliary basis.[5,6] The positions of all atoms were allowed to relax without restrictions. The default convergence criteria for geometry optimization were used (energy change 5.0×10^{-06} Eh, maximal gradient 3.0×10^{-4} Eh/bohr, RMS gradient 1.0×10^{-4} Eh/bohr, maximal displacement 4.0×10^{-3} bohr, RMS displacement 2.0×10^{-3} bohr). The initial structures of the zeolite nanoparticles were cut from different parts of the periodic MFI structure (Fig. S4) as all terminal oxygen atoms were saturated by hydrogen atoms forming hydroxyl groups. In this way different parts of the MFI structure were exposed to the surface of the nanoparticles. This allowed us to simulate the structure and spectra of various silanols depending on their local surrounding and various types of hydrogen bonded moieties. All nanoparticle structures were optimized within the convergence criteria without any restrictions, neither atomic coordinates, nor interatomic distances or angles were fixed. Although the individual Si-O distances vary after the geometry optimization, the overall structure of the nanoparticles is preserved as it was in the periodic system.

The frequency calculations for all models were preformed numerically using the same computational method as for geometry optimization, however with tight SCF convergence criteria and larger grid. For the model ZNP-99 we also calculated analytical vibrational frequencies, which were found to differ from the numerically calculated values by at most 5 cm^{-1} for the frequencies higher than 1000 cm^{-1}. In order to correct the calculated vibrational frequencies for the anharmonicity and the shifts due to the computational method, all stretching vibrational frequencies of O-H groups in the silanols were scaled in standard fashion with a scaling factor 0.948. This value was obtained as a ration between experimental value of the stretching vibrational frequency of the trimethylsilanol, $(CH_3)_3SiOH$, 3735 cm^{-1},[7,8] and the corresponding calculated value with the computational method, described above. The obtained scaling factor is similar to those reported earlier for PBE0 exchange-correlation functional, 0.95-0.96.[9,10]

The calculations of the ^{1}H and ^{29}Si NMR chemical shifts were done with Gauge-Independent Atomic Orbitals (GIAOs) method,[11] as it is implemented in ORCA program package with the same computational method and basis as for the geometry optimization except the auxiliary basis, which was def2/JK. Fine grid, Grid4 FinalGrid5, and tighter SCF convergence criteria were used. The chemical shifts for protons and silicon atoms were obtained by subtraction from the calculated isotropic chemical shielding value for tetramethylsilane (TMS) for protons (averaged) and to silicon atom, respectively. Those values are reported and discussed in the manuscript.

For the ZNP-99 model, we also performed calculations of the NMR chemical shifts with larger basis set, def2-TZVP. The calculated ^{1}H chemical shifts, obtained with the smaller, def2-SVP, and with the larger, def2-TZVP, basis sets differ by at most 0.26 ppm with average absolute difference of 0.10 ppm. Taking into account that the variations of the calculated 1H NMR chemical shift are within 7 ppm, this difference does not affect the analysis and the conclusions, reported in the manuscript. For the ^{29}Si NMR chemical shifts the calculations with the two different basis sets differs at most by 4.0 ppm with average absolute difference of 2.3 ppm.

Table S2. Main features of the zeolite nanoparticle models (ZNP) used in the DFT calculations

Model	**Composition**	**Number of silanols**	**Si Q4**	**Si Q3**	**Si Q2**	**Si Q1**
ZNP-99	$Si_{22}O_{55}H_{22}$	22	5	12	5	0
ZNP-111	$Si_{25}O_{62}H_{24}$	24	7	12	6	0
ZNP-165	$Si_{37}O_{92}H_{36}$	36	8	22	7	0
ZNP-213	$Si_{47}O_{118}H_{48}$	48	17	14	14	2

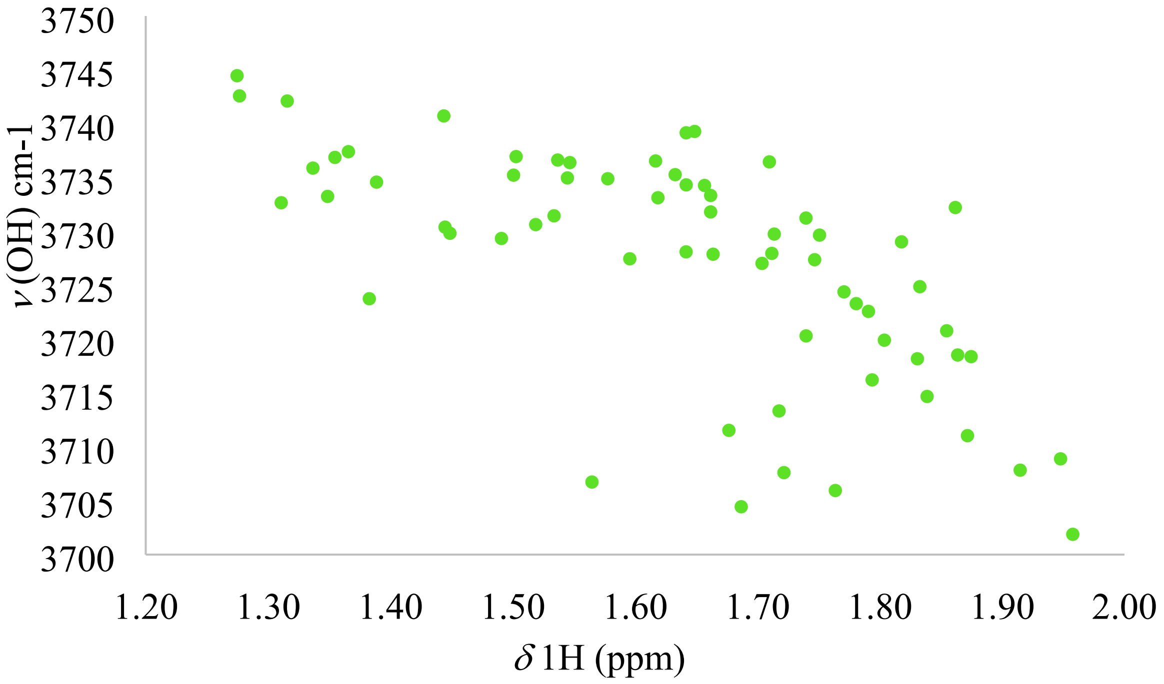
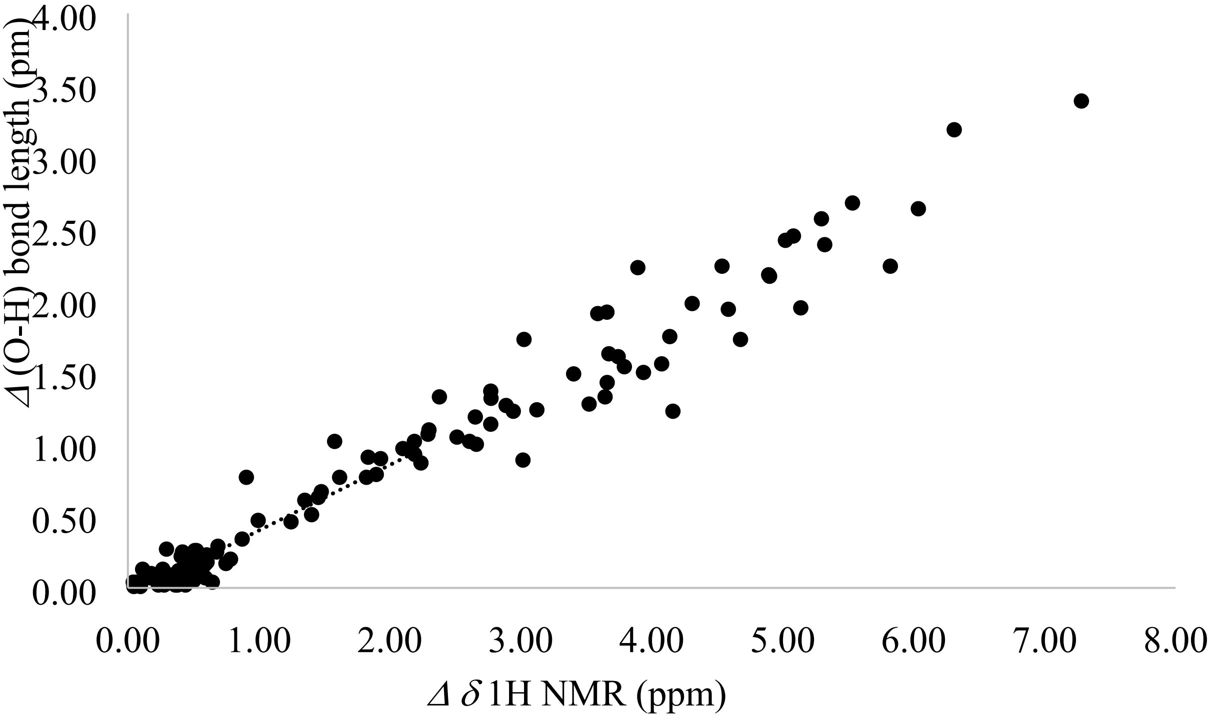
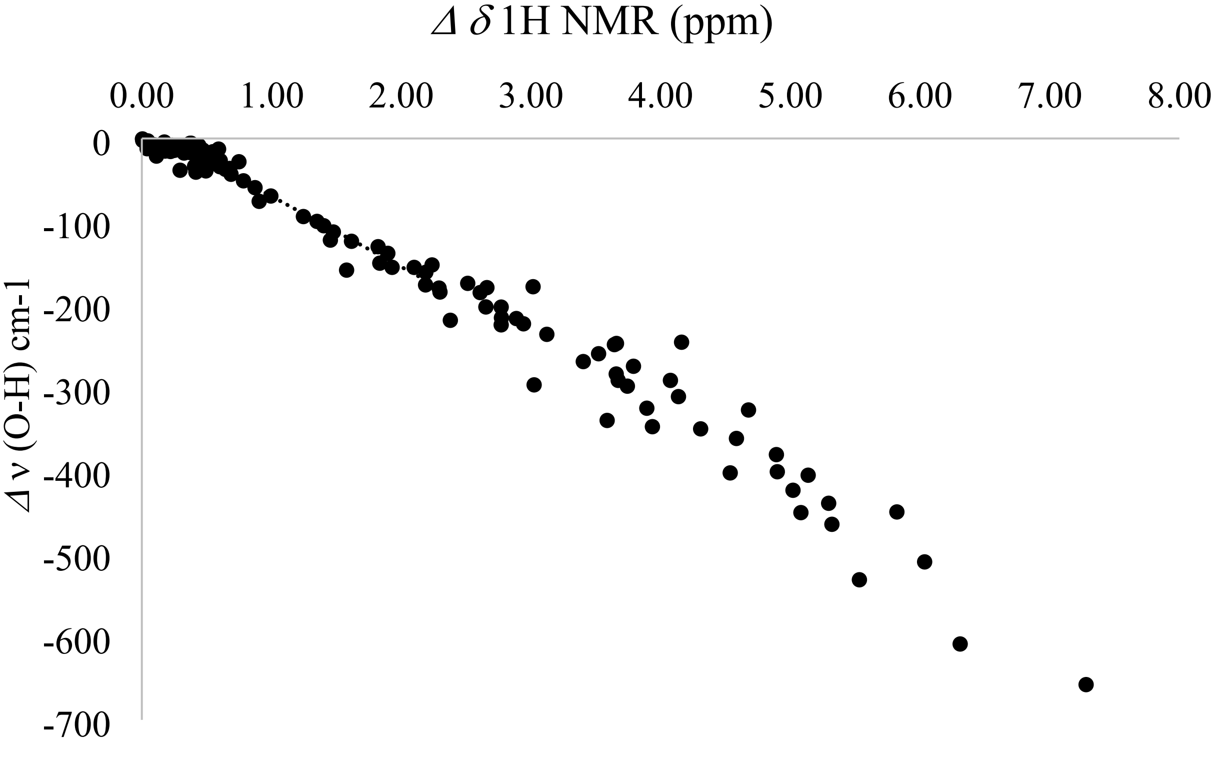


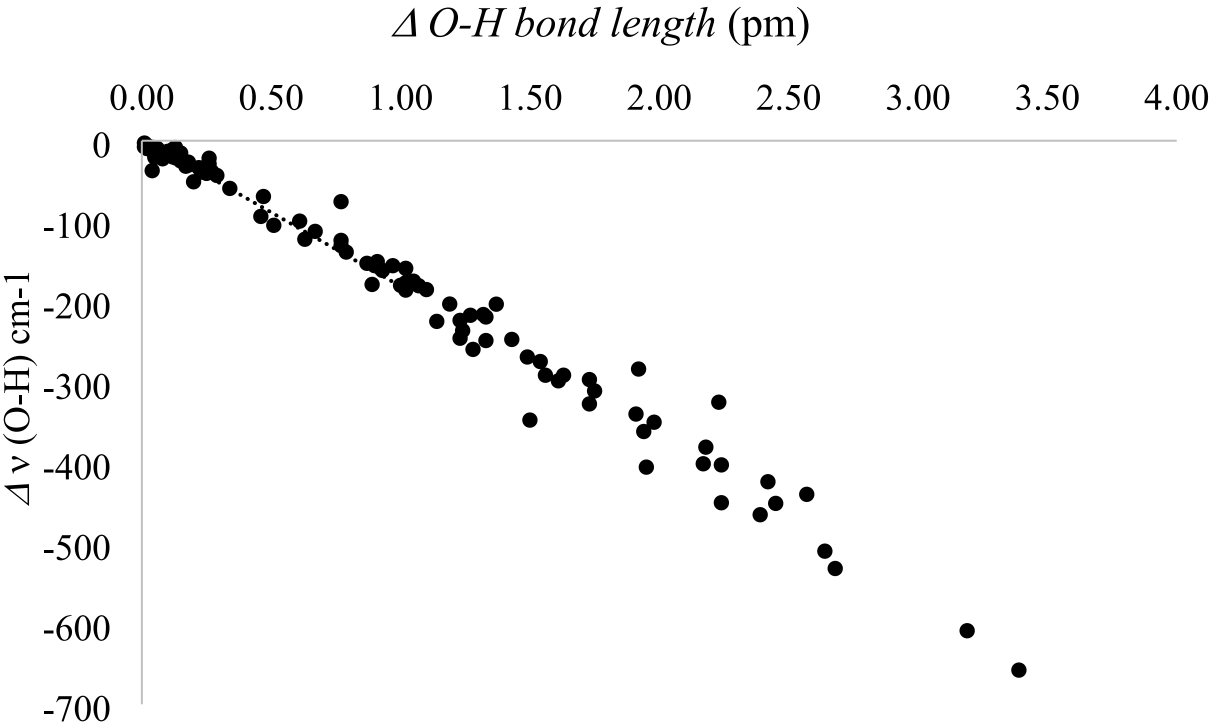
Figure S1. Correlation between calculated absolute values of the O-H stretching frequency and ^{1}H NMR chemical shift of the silanol groups in the modeled zeolite nanoparticles with ^{1}H NMR chemical shift between 1.2 and 2.0 ppm.

A


Δ (O-H) bond length (pm)
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
Δ δ 1H NMR (ppm)


Δ δ 1H NMR (ppm)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
0
-100
-200
-300
-400
-500
-600
-700
Δ ν (O-H) cm-1

B



C

Figure S2. Correlations between shifts of (A) the ^{1}H NMR chemical shift (in ppm) and R(O-H) bond length (in pm), (B) the ^{1}H NMR chemical shift and O-H vibrational frequency (in cm^{-1}), (C) the R(O-H) bond length and O-H vibrational frequency. The shifts are calculated with respect to the reference values for non-interacting silanol group: R(O-H) = 96.1 pm, ^{1}H NMR = 1.265 ppm, ν(O-H) = 3745 cm^{-1}. The correlation coefficients of the trend lines are 0.96, 0.97 and 0.98 for panels A, B, and C, respectively.

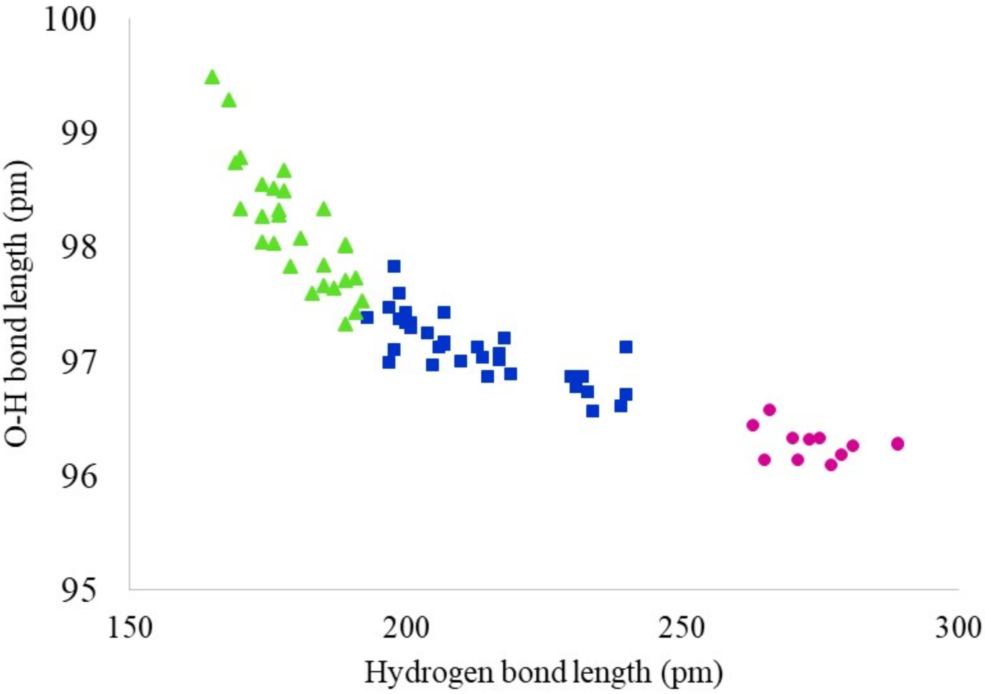
If we accept the discrimination of the three types of hydrogen bonds, for the regions of the strong and medium hydrogen bonds, we may obtain some general trends and corresponding linear relations connecting the hydrogen bond length, R(H-bond), and ^{1}H NMR chemical shift, O-H bond length, R(O-H), and stretching O-H vibrational frequency, ν(O-H). Most of those relations, however, in particular those for the medium hydrogen bonds, are with rather low correlation coefficient.

Correlations for the region of the strong hydrogen bonds:
^{1}H NMR = 25.390 - 0.108 * R(H-bond) (RMSD = 0.83)
ν(O-H) = 1229.5 - 11.857 * R(H-bond) (RMSD = 0.79)
R(O-H) = 108.37 – 0.0567 * R(H-bond) (RMSD = 0.71)
Correlations for the region of medium hydrogen bonds:
^{1}H NMR = 12.464 - 0.0419 * R(H-bond) (RMSD = 0.84)
ν(O-H) = 2935.7 + 2.9837 * R(H-bond) (RMSD = 0.68)
R(O-H) = 100.4 – 0.0154 * R(H-bond) (RMSD = 0.60)

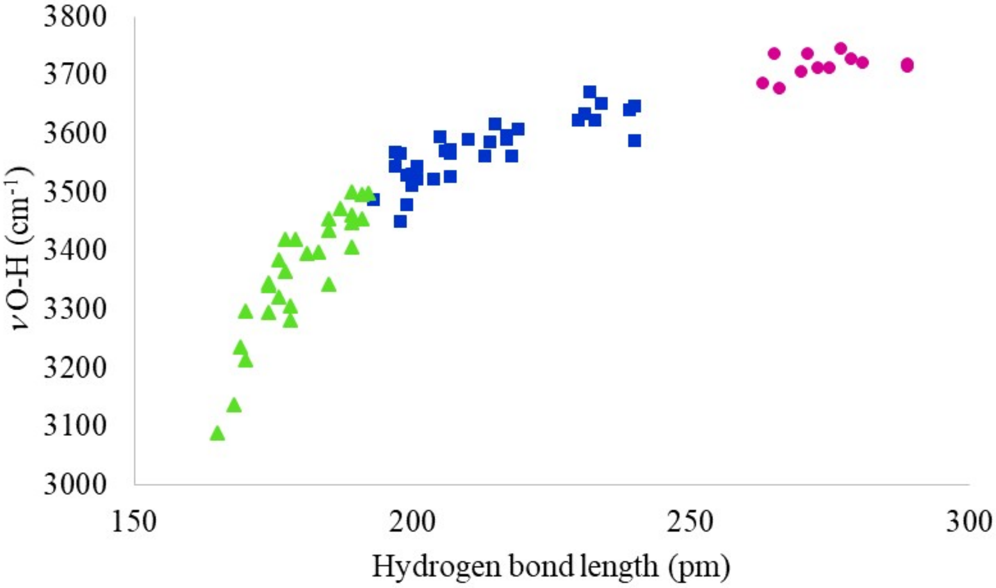
For the region of weak hydrogen bond, in which the R(H-bond) is longer than 260 pm, each of the characteristics, ^{1}H NMR chemical shift, O-H bond length, and stretching O-H vibrational frequency, essentially does not depend on the hydrogen bonded distance R(H-bond) and is likely influenced by other features of the local surrounding of the corresponding hydroxyl group.

Table S3. Regions of characteristic spectral features and distances for different types of non-H-bonded and H-bonded silanols obtained for the modeled zeolite nanoparticles: ^{1}H NMR chemical shift (in ppm), O-H vibrational frequency (in cm^{-1}), R(O-H) bond length (in pm), and the hydrogen bond length, R(H-bond) (in pm). The assignments are discussed in the text.

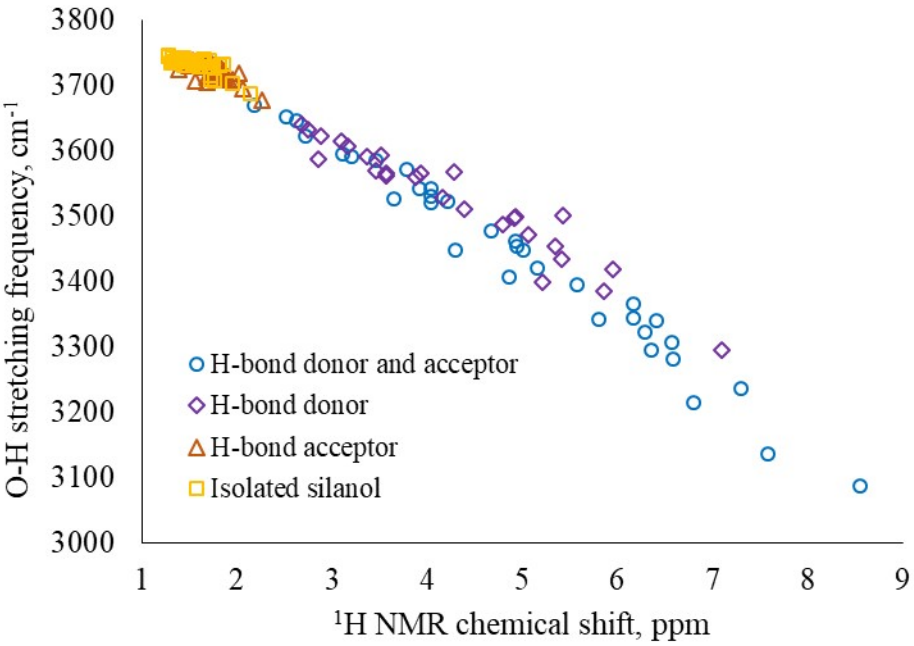
Type of H-bonds/silanols	**^{1}H NMR**	**ν(O-H)**	**R(O-H)**	**R(H-bond)**
Isolated silanols	1.27 – 1.96	3745 - 3702	96.1 - 96.3	-
H-bond acceptor	1.38 – 2.26	3737 - 3676	96.1 – 96.6	-
H-bond donor for weak H-bond	1.27 - 2.28	3745 - 3677	96.1 - 96.6	306 - 260
H-bond donor for medium H-bond	2.64 - 4.63	3670 - 3454	96.6 - 97.8	240 - 197
H-bond donor for strong H-bond	4.83 - 8.44	3500 - 3100	97.3 - 99.4	192 - 165
H-bond donor to very strong H-bond	9.70 – 15.18	2941 - 1956	100.6 – 106.9	167 - 141


100
99
98
97
96
95
O-H bond length (pm)
150
200
250
300
Hydrogen bond length (pm)

A

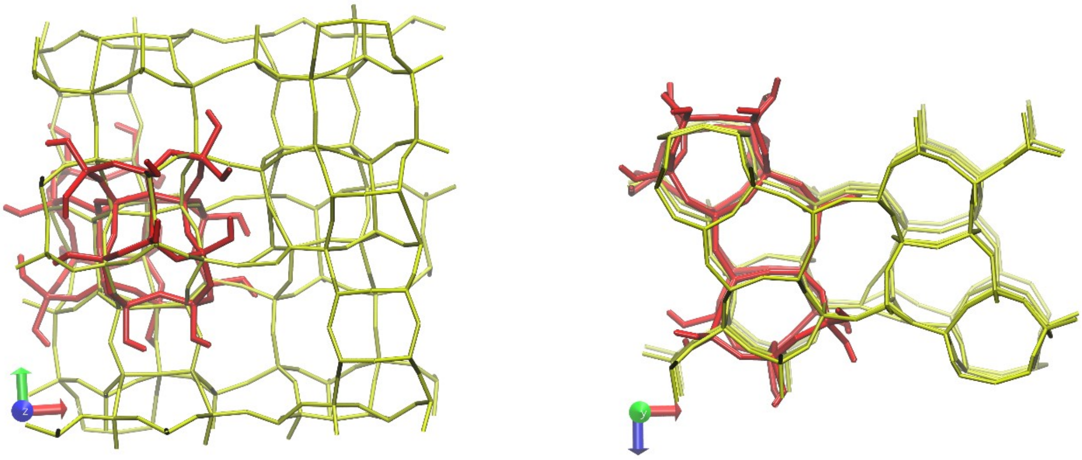

3800
3700
3600
3500
3400
3300
3200
3100
3000
νO-H (cm^{-1})
150
200
250
300
Hydrogen bond length (pm)

B

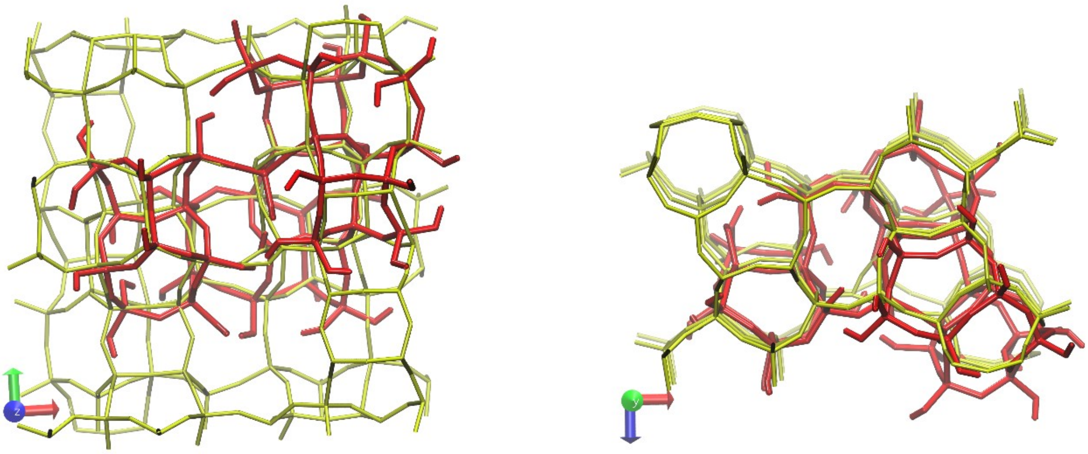


C

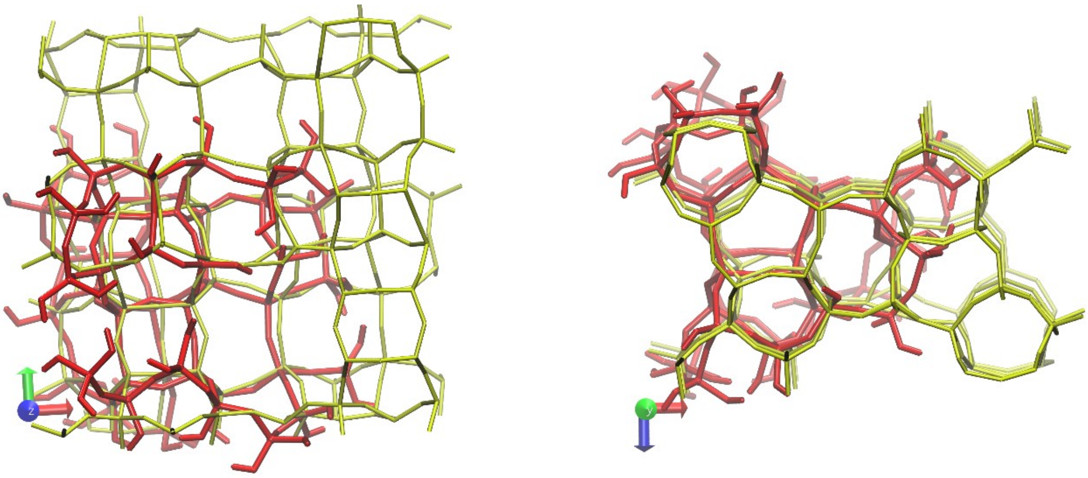
Figure S3. Plots of the hydrogen-bonded distance, R(H-bond), when the corresponding silanol group participates as proton-donor in a hydrogen bond versus R(O-H) bond length (panel A), and versus O-H stretching frequency (panel B). Tentative assignment of the data points to strong (pink rings), medium (blue squares) and weak (green triangles) hydrogen bonds is also shown. Panel C shows calculated O-H stretching frequencies of silanol groups depending on their participation in hydrogen bonds (see the legend inside the panel) versus their ^{1}H NMR chemical shifts.



ZNP-99



ZNP-165



ZNP-213

Figure S4. Positions of the fragments from the parent MFI type zeolite framework (containing only silicon T-atoms) used for zeolite nanoparticle models: ZNP-99, ZNP-111, ZNP-165 and ZNP-213. Left and right columns present views of the four models perpendicular to z- and y-directions, respectively.

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