Supporting Information for

Acidity and Local Confinement Effect in Mordenite Probed by Solid-State NMR Spectroscopy

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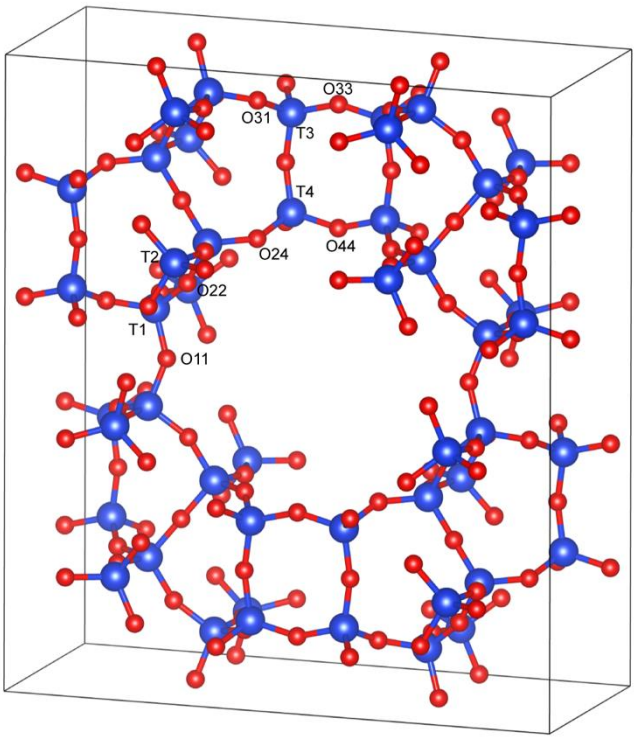

Figure S1. T sites and oxygen sites in MOR zeolites.

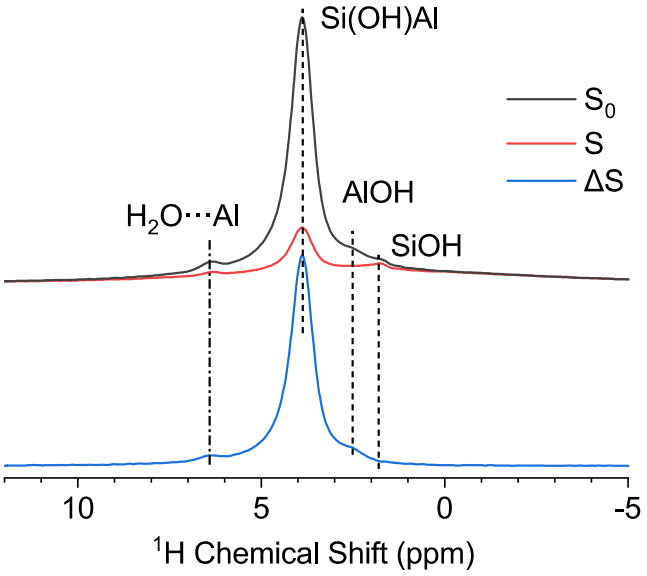

Figure S2. ^{1}H $\{^{27}Al\}$ S-RESPDOR of dehydrated H-MOR, S, S_0 stand for the spectra with and without ^{27}Al irradiation, ΔS stands for the difference spectrum, the recoupling time is 0.9 ms.

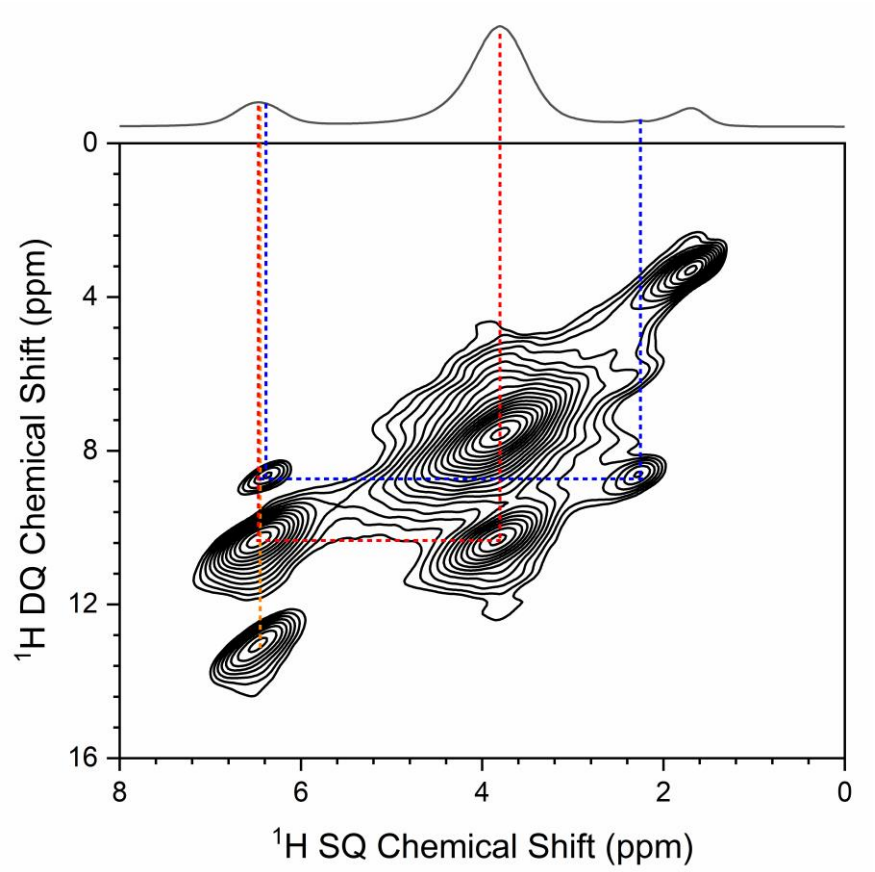

Figure S3. ^{1}H POST-C7 DQ-SQ NMR spectrum of dehydrated H-MOR. Orange, red and blue dash lines indicate the space proximity of ^{1}H atom of adsorbed water with itself, with BASs and with AlOH, respectively.

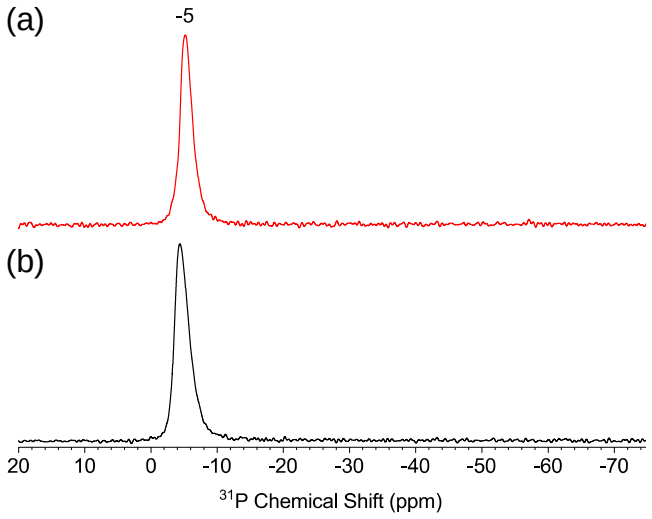

Figure S4. ^{31}P SP MAS NMR spectra of H-MOR adsorbed with TMP before (a) and after (b) CD_3CN adsorption, with ^{1}H decoupled.

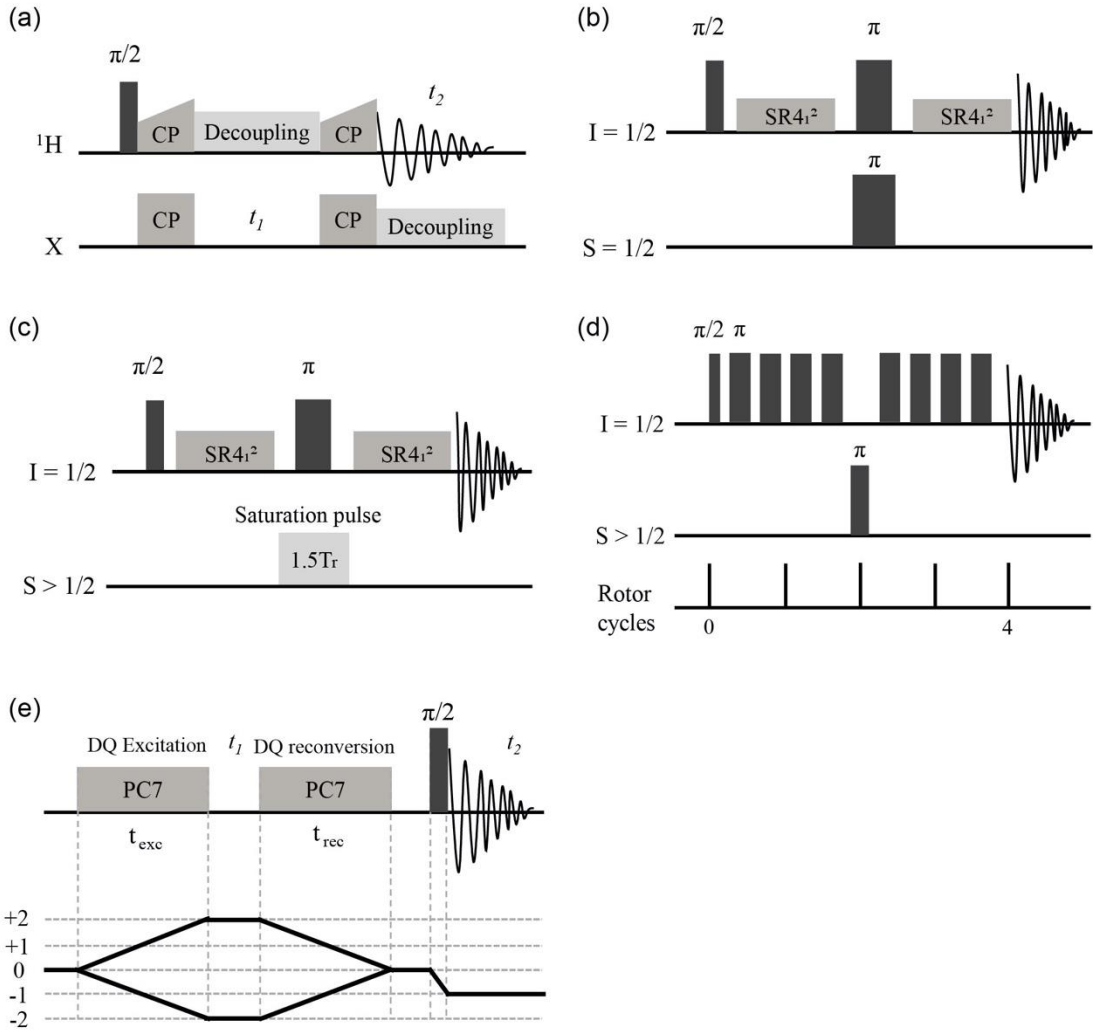

Figure S5. Pulse sequences of NMR experiments used in this article: (a) the proton detected {^{1}H-}X-^{1}H CP HETCOR experiments; (b) S-REDOR experiments; (c) S-RESPDOR experiments; (d) REAPDOR experiments; (d) POST C7 DQ-SQ correlation experiments.

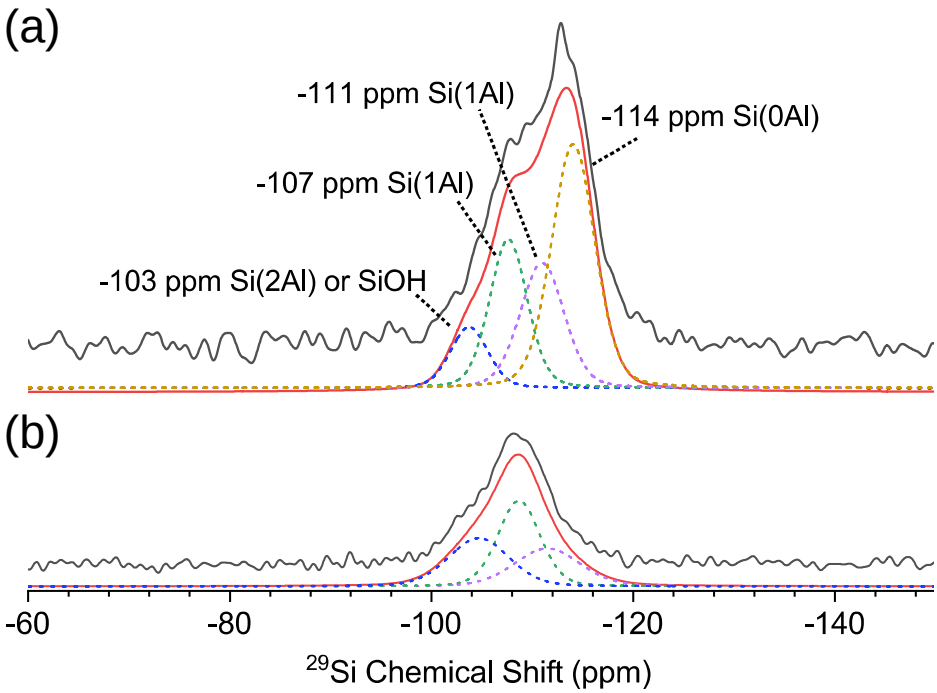

Figure S6. ^{29}Si SP and CP NMR spectra of H-MOR after CD_3CN adsorption with deconvolution according the {^{1}H-}^{29}Si-^{1}H CP HETCOR spectrum shown in **Figure 3g**.

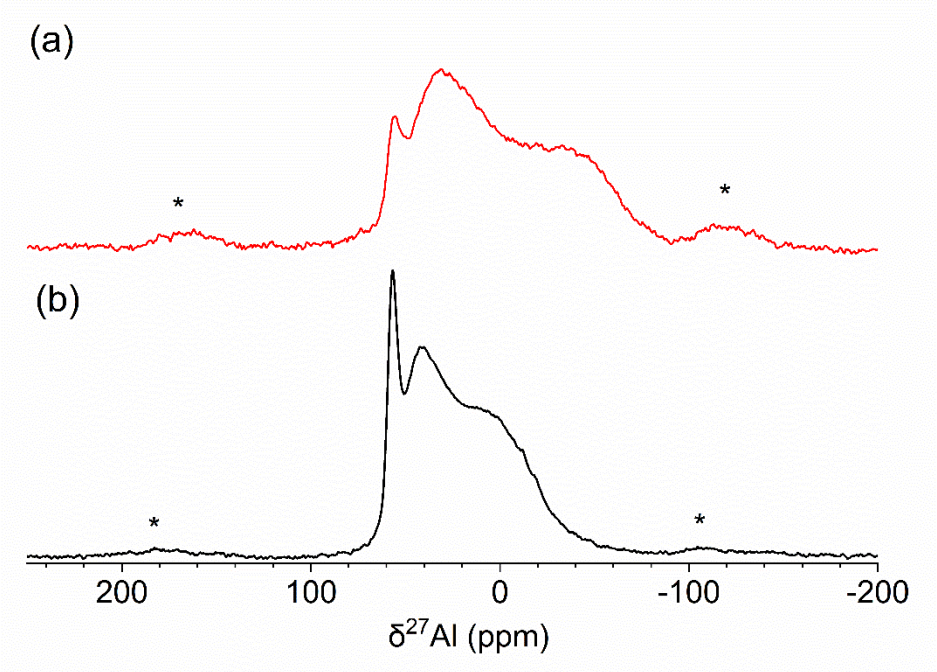

Figure S7. ^{27}Al MAS NMR spectra of dehydrated H-MOR zeolites before (a) and after (b) CD_3CN adsorption.

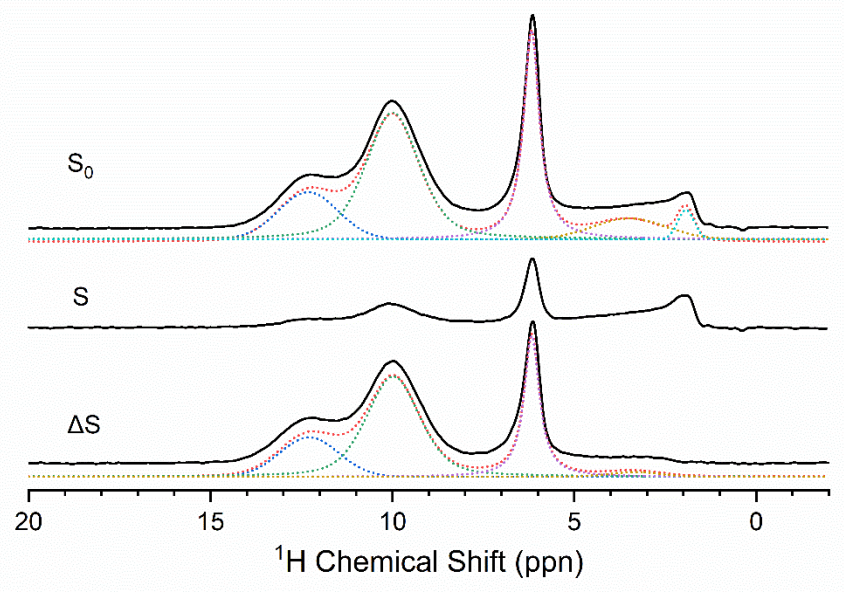

Figure S8. ^{1}H {^{27}Al} S-RESPDOR of dehydrated H-MOR after CD_3CN adsorption with deconvolution, S, S_0 stand for the spectra with and without ^{27}Al irradiation, ΔS stands for the difference spectrum, the recoupling time is 0.9 ms.

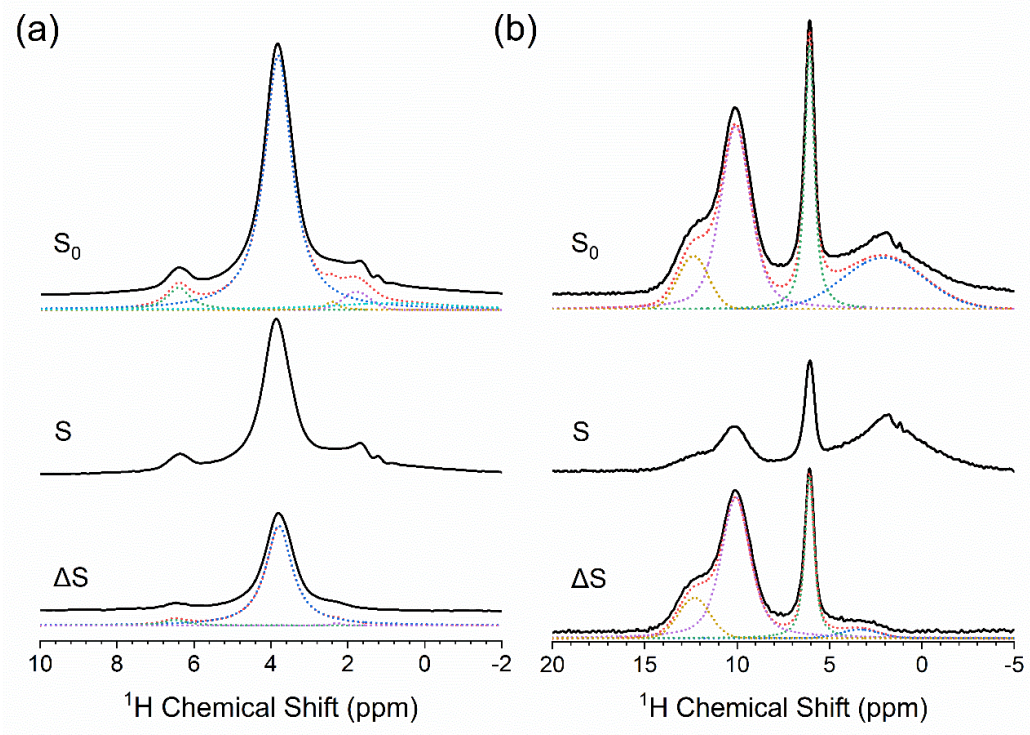

Figure S9. ^{1}H {^{27}Al} REAPDOR of dehydrated H-MOR before (a) and after (b) CD_3CN adsorption with deconvolution. S, S_0 stand for the spectra with and without ^{27}Al irradiation, ΔS stands for the difference spectrum, the recoupling time is 1.83 ms with 2 MHz (a) and 0.5 MHz (b) offset of ^{27}Al.

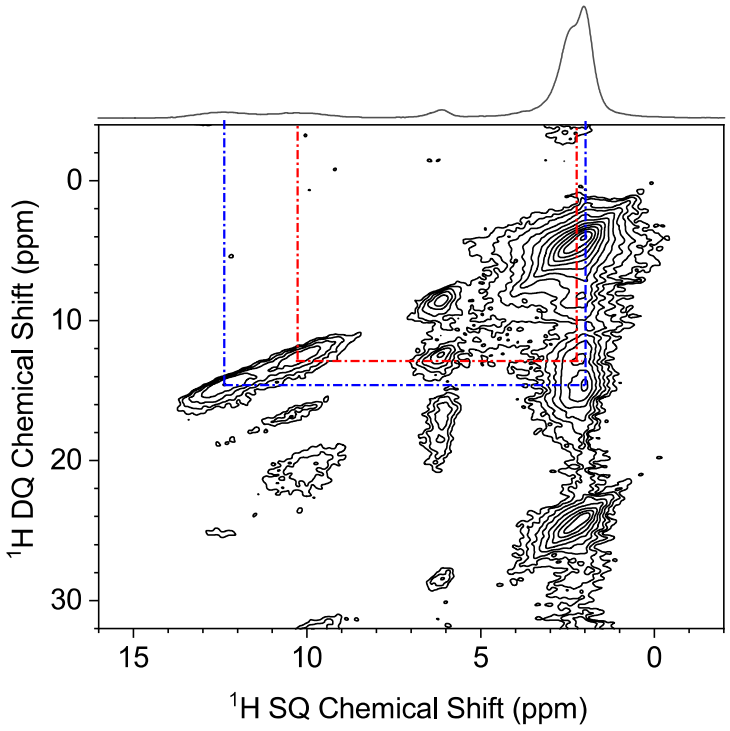

Figure S10. ^{1}H POST-C7 DQ-SQ NMR spectrum of H-MOR after ^{15}N-CH_3CN adsorption.

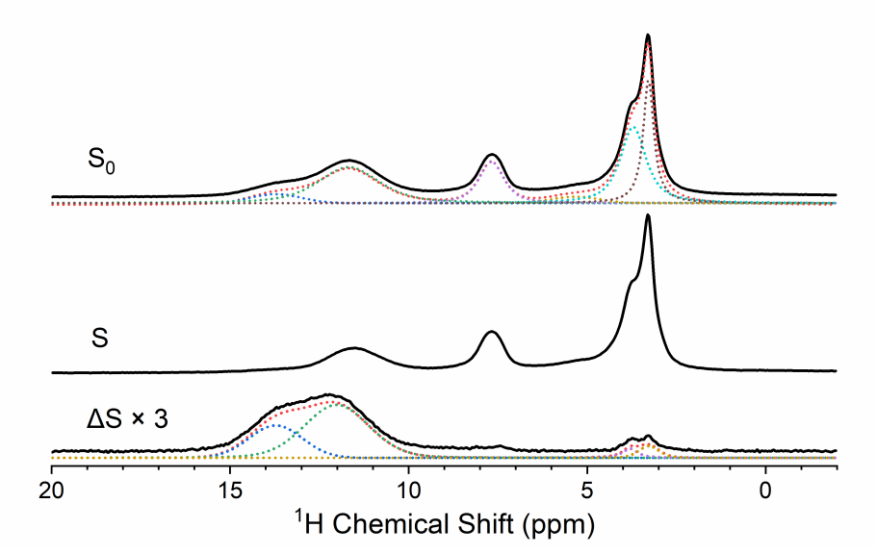

Figure S11. ^{1}H {^{15}N} S-REDOR of dehydrated H-MOR after CD_3CN adsorption at 293 K with deconvolution. S, S_0 stand for the spectra with and without ^{27}Al irradiation, ΔS stands for the difference spectrum, the recoupling time is 1 ms.

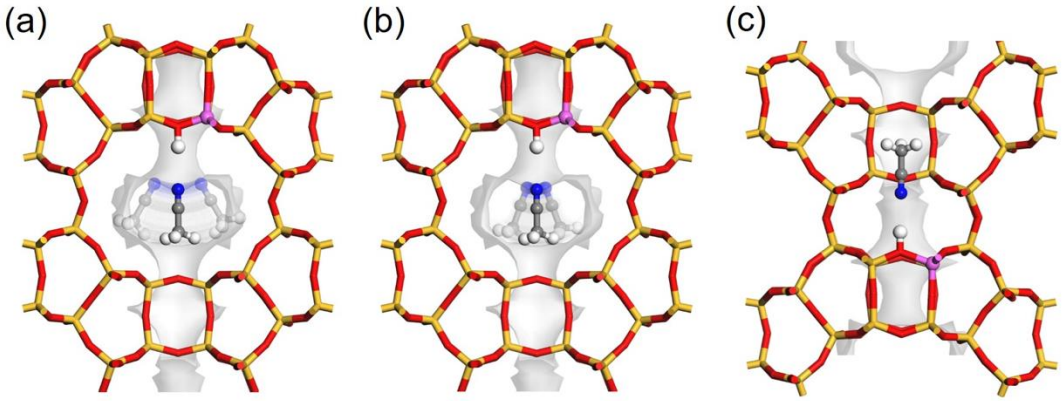

Figure S12. Schematic of (a) highly flexible acetonitrile in 12MR channels, (b) partially restricted acetonitrile in 12MR channels and (c) restricted acetonitrile in 8MR channels.

Table S1. Acquisition parameters for CP NMR experiments.

Experiment	**^{29}Si CP**	**^{15}N CP**	**^{1}H-^{15}N-^{1}H CP[a]**
B_0(T)	9.4	14.1	14.1
Number of scans	1024	2000	64
Recycle delay (s)	2	2	2
ω_R (kHz)	12	12	12
^{1}H RF field for 90° pulse (kHz)	81	48	48
Contact time (ms)	3.5	5	5
^{1}H RF amplitude ramp for contact pulse	ramp90.110.1000[b]	ramp90.110.1000[b]	amp90.110.1000[b]
^{1}H RF field during contact pulse (kHz)	71	44	44
X RF field during contact pulse (kHz)	52	32	32
^{1}H RF field for SPINAL64 decoupling pulses (kHz)	81	48	48

[a] Same CP acquisition parameters are used for the first ^{1}H-^{15}N CP and second ^{15}N-^{1}H CP.

[b] ^{1}H contact RF field is swept from 90 to 110% of the set ^{1}H RF field linearly with 1000 steps during contact pulse.

Table S2. Acquisition parameters for 2D and double-resonance NMR experiments.

Pulse sequence	**CP-HETCOR[a]**		**REAPDOR**	**S-RESPDOR**	**DQ-SQ**	**S-REDOR**
Nuclei	{^{1}H}-^{29}Si-^{1}H	{^{1}H}-^{15}N-^{1}H	^{1}H {^{27}Al}	^{1}H {^{27}Al}	^{1}H	^{1}H {^{15}N}
B_0 (T)	9.4	14.1	9.4	14.1	14.1	14.1
Number of scans	400 - 800	400	32	-[c]	32	-[c]
t1 increments (us)	125	3000	-	-	41.67	-
t1 points	50	32	-	-	160	-
Recycle Delay (s)	2 – 5[b]	2	2 – 5[b]	2 – 5[b]	2	2
ω_R (kHz)	8	12	12	22	24	20
o.d. rotor (mm)	4	4	4	3.2	3.2	3.2
Ramp CP						
Contact time (ms)	3.5	3	-	-	-	-
^{1}H Channel RF field (kHz)	77	43	-	-	-	-
X Channel RF field (kHz)	69	31	-	-	-	-
^{1}H π/2 & π pulse (us)	3.25	6.5	3.35 & 6.7	3.2 & 6.4	3.0 & 6.6	3.05 & 6.1
^{15}N π pulse (us)	-	-	-		-	13
^{27}Al RF field for saturation pulse / kHz	-	-	98	92	-	-
Recoupling pulse	-	-	-	SR4	POST-C7	SR4
Recoupling time (ms)	-	-	1.83	0.18 – 2.3	0.083	0.2 – 4.2

[a] Same CP acquisition parameters are used for the first ^{1}H-X CP and second X-^{1}H CP.

[b] Recycle delay 2 s for dehydrated H-MOR and 5 s for H-MOR after CD_3CN adsorption decided by ^{1}H T1.

[c] The scan number was dependent on the sensitivity of corresponding ^{1}H MAS NMR spectra with different dephasing (mixing) times.