Electronic Supplementary Information (SI)

Hydronium Ion and Water Complexes *vs.* Methanol on Solid Catalyst Surfaces: How Confinement Influences Stability and Reactivity

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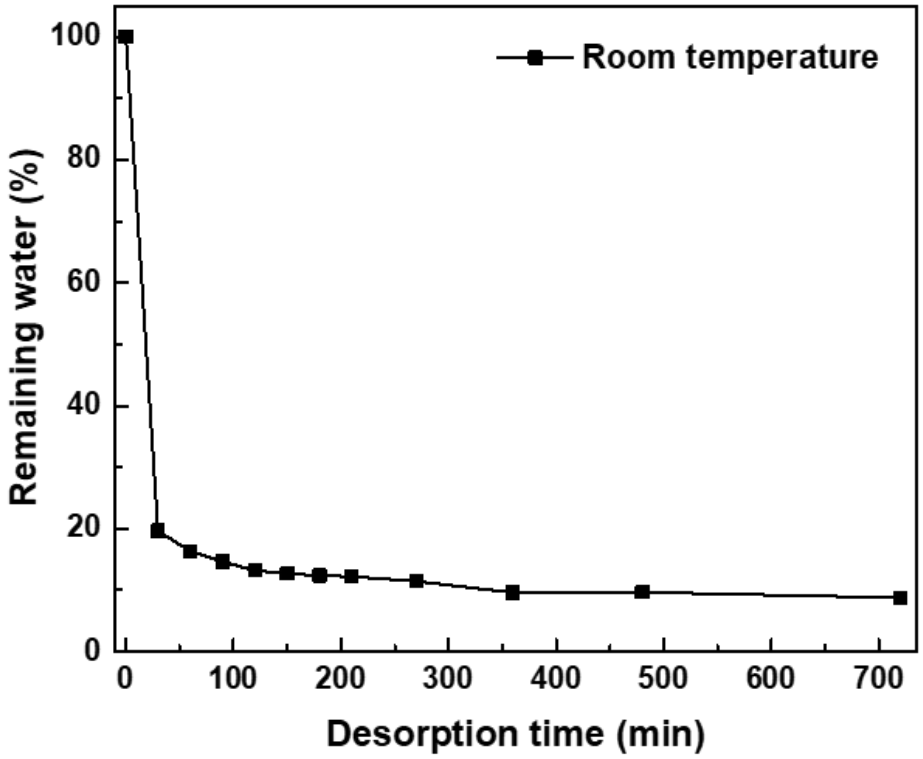

Figure S1: Desorption of water from zeolite H-ZSM-5 in vacuum over time at 298 K.

Table S1: Data from the physicochemical characterization of the materials under study.

Material	Si/Al ratio[a)]	Na^+ density (mmol/g)[a)]	Si(OH) density (mmol/g)[b)]	BAS (H^+) density (mmol/g)[b)]	BET surface [m^2/g]	V_{micro} [ml/g]	V_{meso} [ml/g]	Pore diameter [nm]
Silicalite	>800	-	0.66	-	350	0.12	0.10	<0.56 [d)]
Na-ZSM-5	24	0.6	0.08	-	345	0.12	0.06	<0.56 [d)]
H-ZSM-5	24	-	0.19	0.49	372	0.13	0.07	<0.56 [d)]
SBA-15	>1600	-	2.20	-	870	0.14	0.93	7.1 [e)]
Na-[Al]SBA-15	12	0.86	1.14	-	522	0.05	0.75	6.7 [e)]
H-[Al]SBA-15	12	-	0.59	0.19	442	0.03	0.72	6.8 [e)]
A200	>1600	-	0.39	-	198	-	0.76	-
H-STA@A200	12[c)]	-	0.57	0.34	120	-	0.49	-
Na-STA@A200	12[c)]	0.25	0.52	0.09	123	-	0.56	-

a) Determined by ICP-OES with experimental accuracy of ±10%.

b) Determined by ^{1}H MAS NMR (BAS after NH_3 adsorption).

c) Si/W ratio for STA@A200.

d) according to the IZA database (Baerlocher, C.; McCusker, L. B. Database of Zeolite Structures; http://www.izastructure.org/databases/)

e) Calculated from physisorption adsorption branch.

Water Desorption

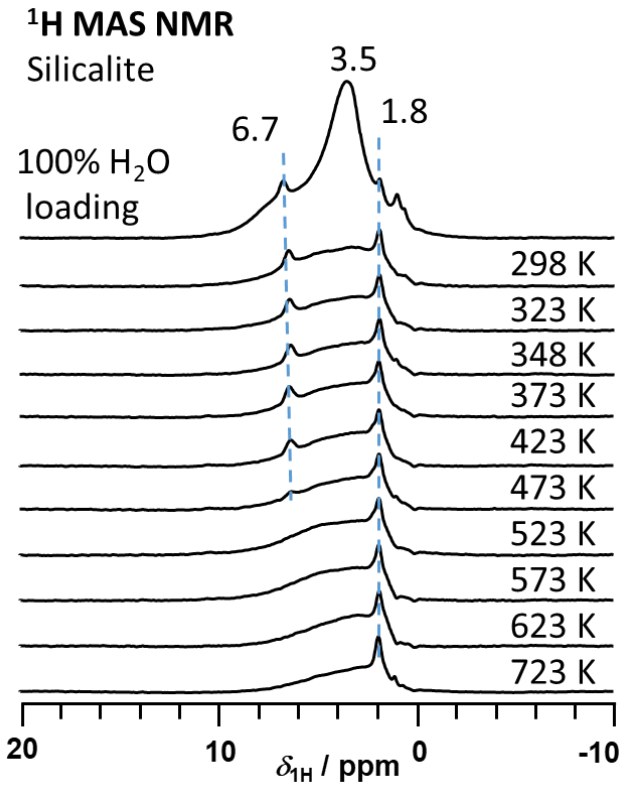

Figure S2: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from Silicalite.

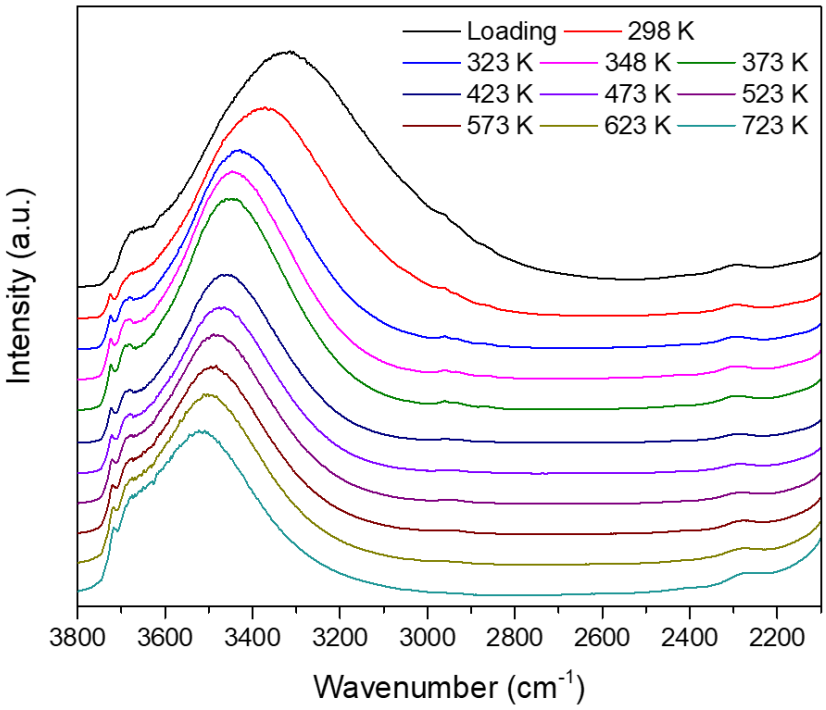

Figure S3: DRIFTS spectra of the stepwise desorption of H_2O from Silicalite.

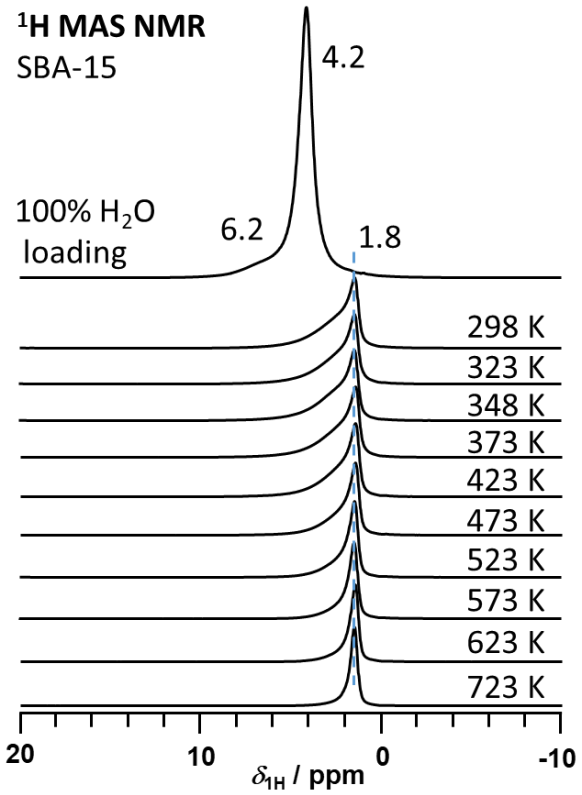

Figure S4: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from SBA-15.

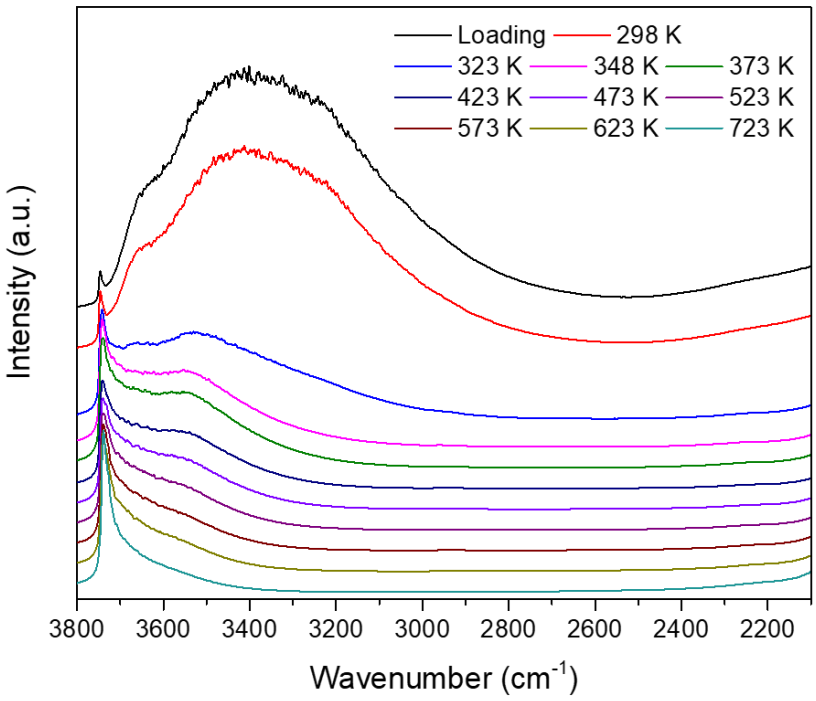

Figure S5: DRIFTS spectra of the stepwise desorption of H_2O from SBA-15.

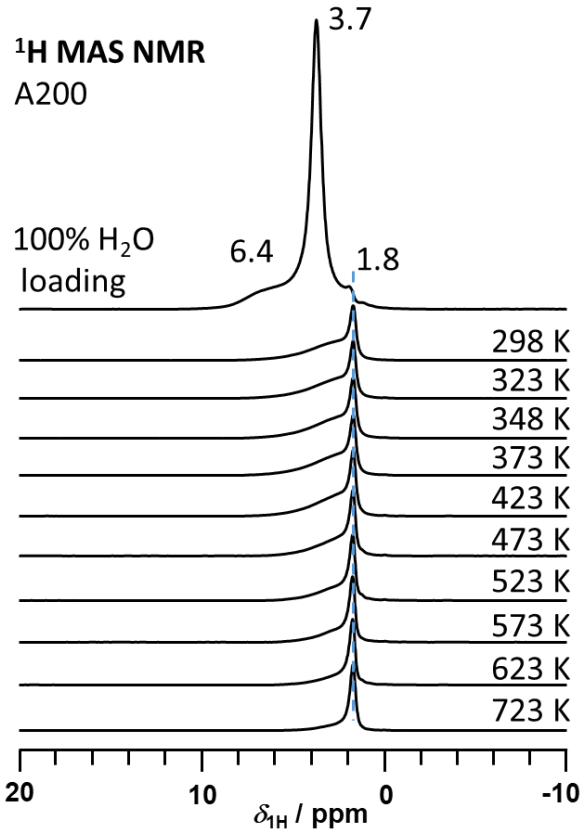

Figure S6: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from A200.

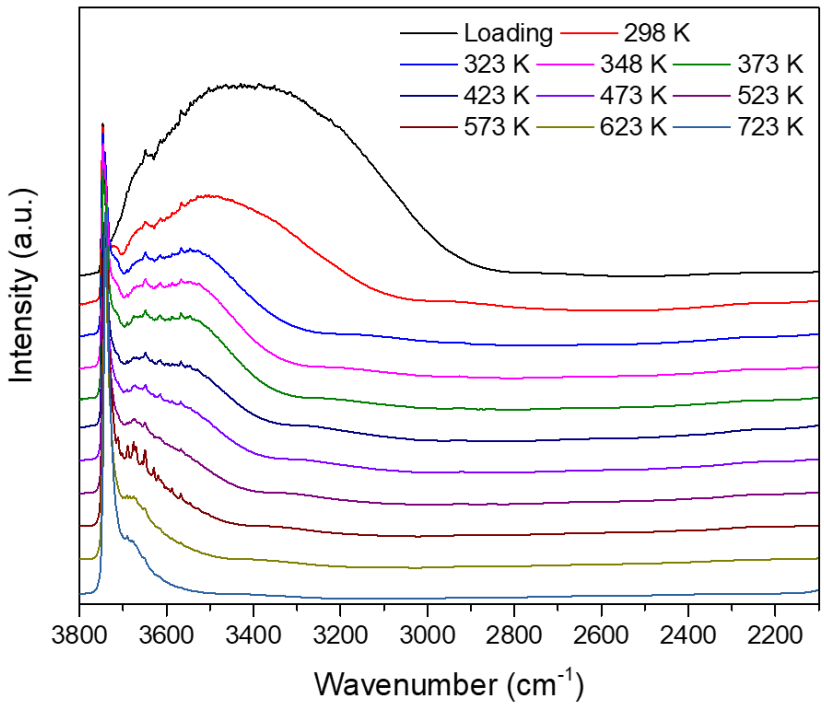

Figure S7: DRIFTS spectra of the stepwise desorption of H_2O from A200.

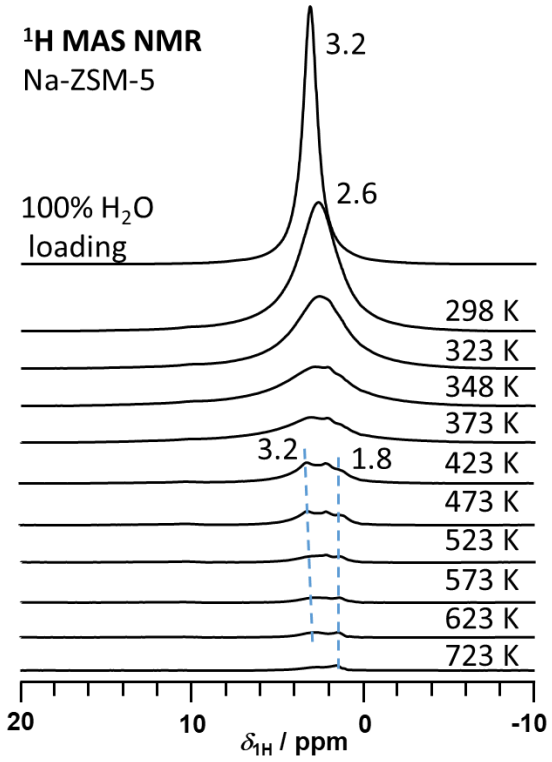

Figure S8: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from Na-ZSM-5.

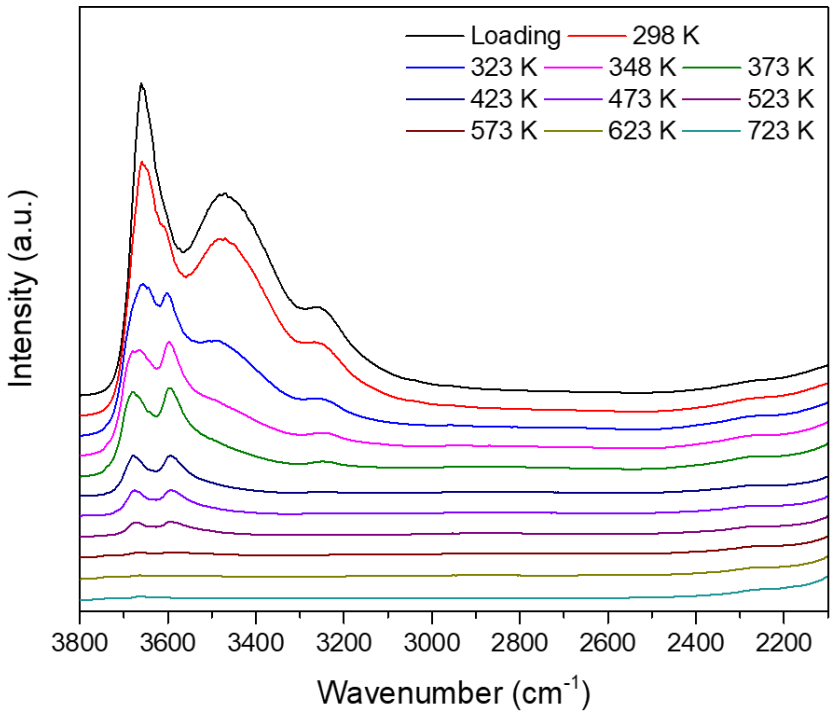

Figure S9: DRIFTS spectra of the stepwise desorption of H_2O from Na-ZSM-5.

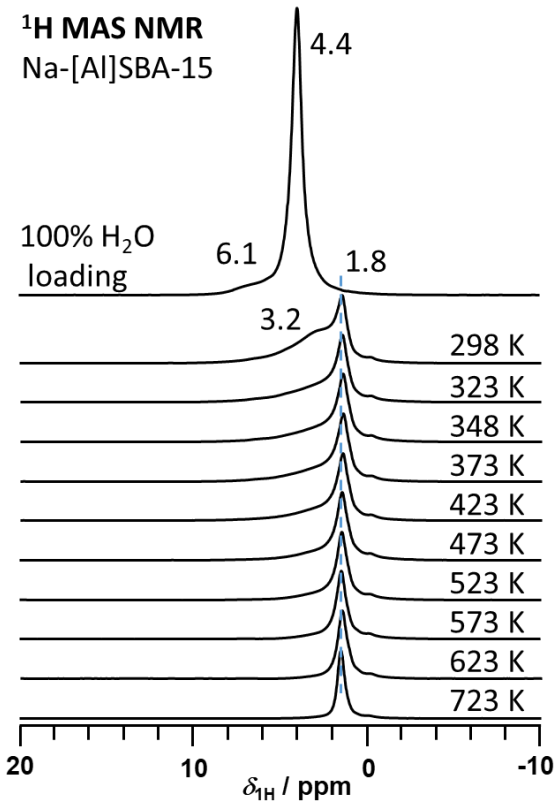

Figure S10: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from Na-[Al]SBA-15.

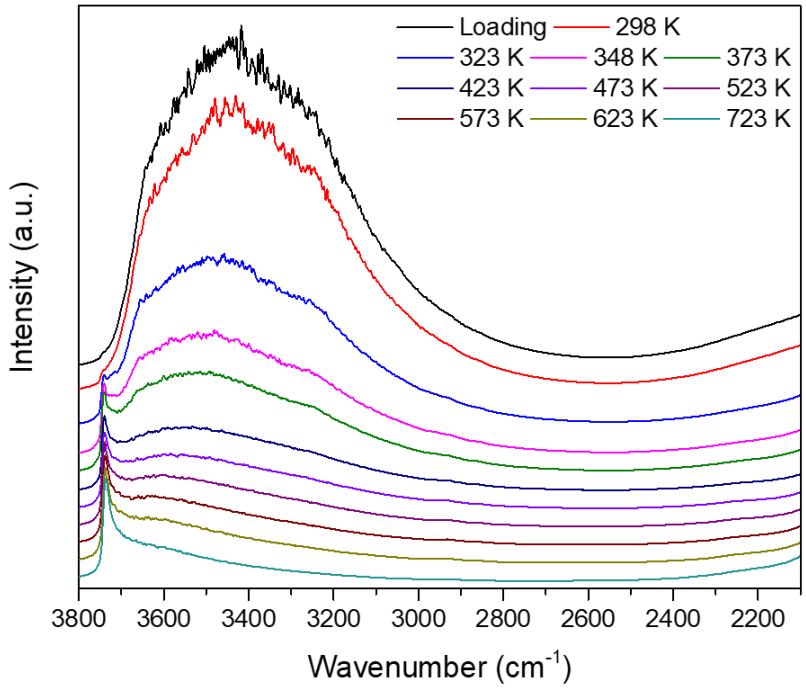

Figure S11: DRIFTS spectra of the stepwise desorption of H_2O from Na-[Al]SBA-15.

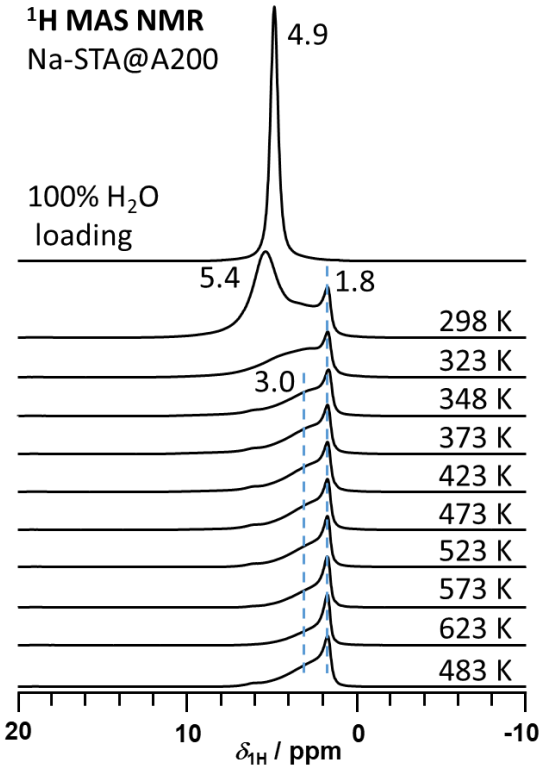

Figure S12: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from Na-STA@A200.

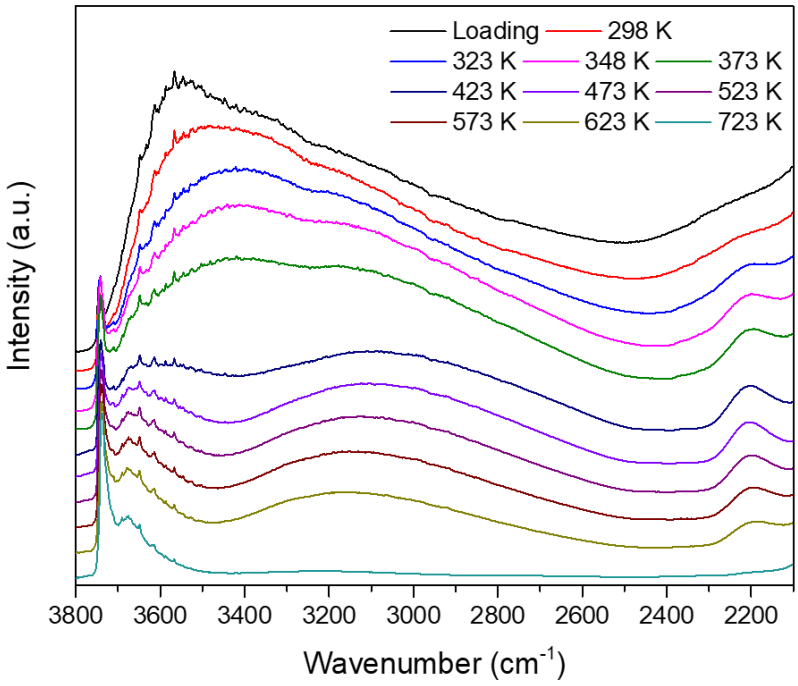

Figure S13: DRIFTS spectra of the stepwise desorption of H_2O from Na-STA@A200.

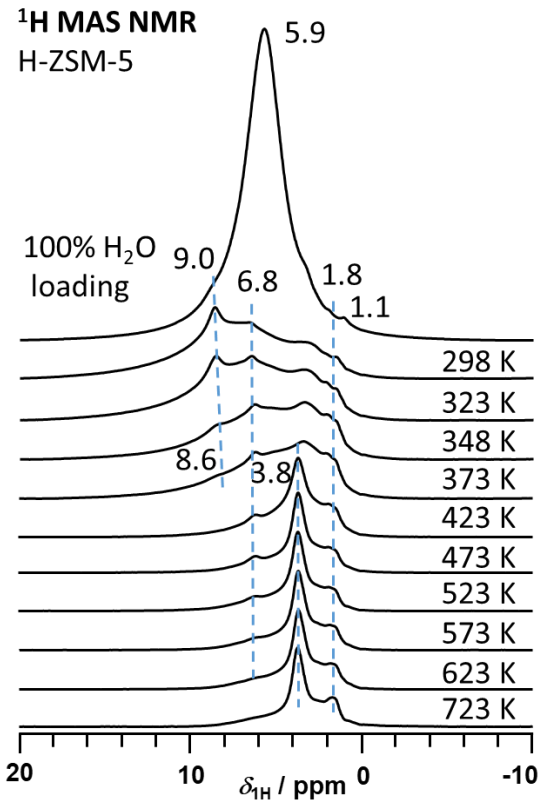

Figure S14: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from H-ZSM-5.

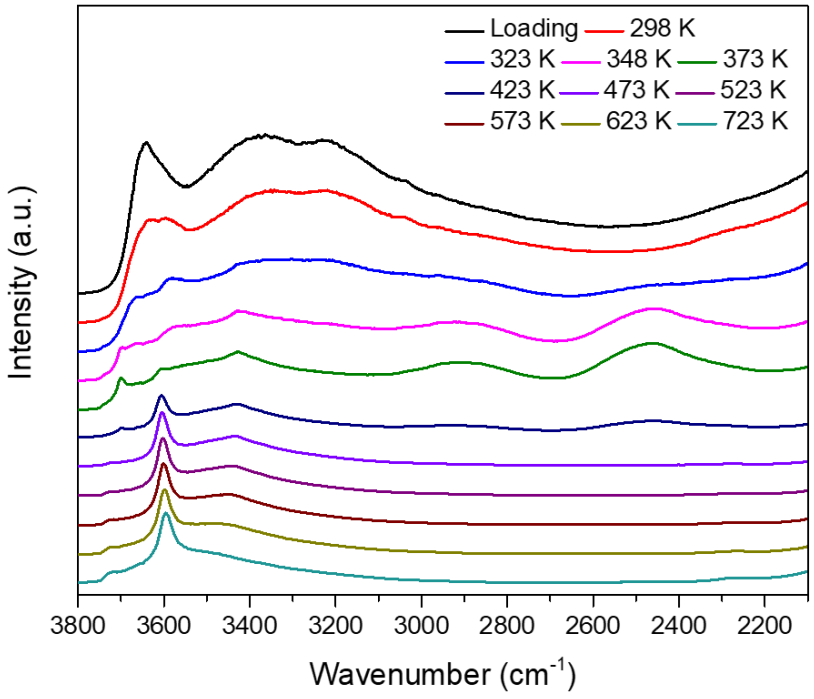

Figure S15: DRIFTS spectra of the stepwise desorption of H_2O from H-ZSM-5.

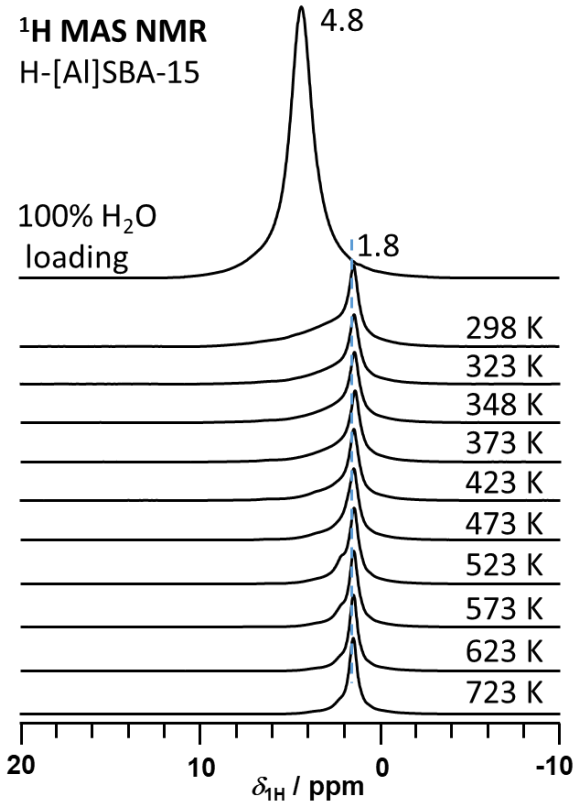

Figure S16: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from H-[Al]SBA-15.

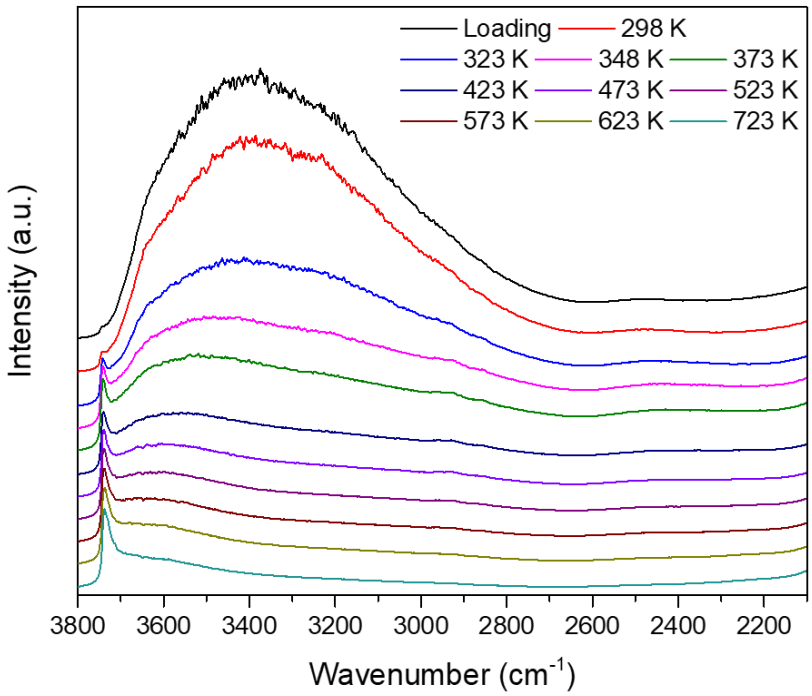

Figure S17: DRIFTS spectra of the stepwise desorption of H_2O from H-[Al]SBA-15.

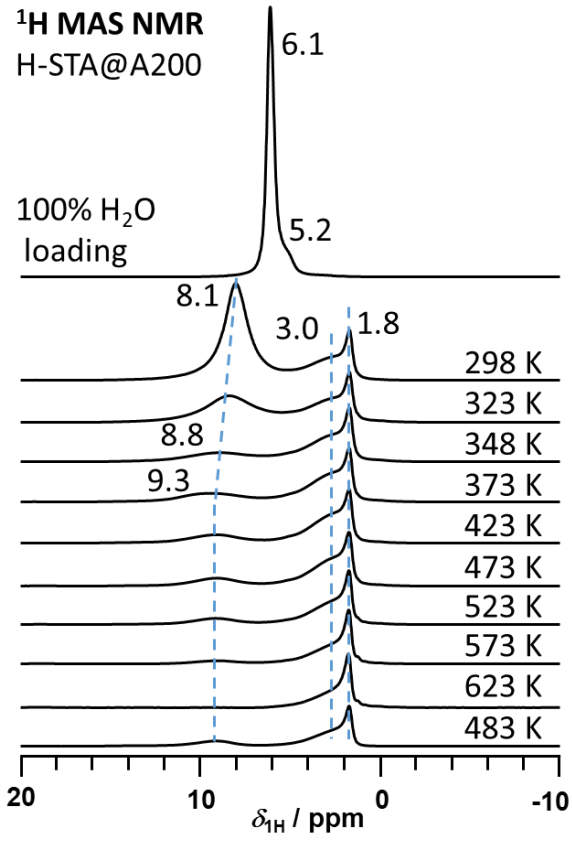

Figure S18: ^{1}H MAS NMR spectra of the stepwise desorption of H_2O from H-STA@A200.

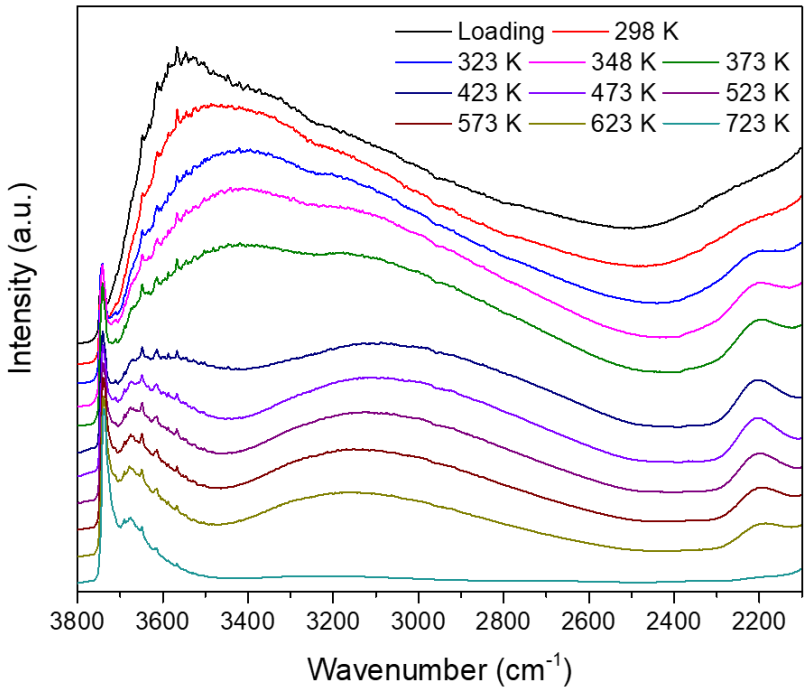

Figure S19: DRIFTS spectra of the stepwise desorption of H_2O from H-STA@A200.

Table S2: Quantitative evaluation of ^{1}H MAS NMR spectra during the stepwise desorption of H_2O from MFI zeolites.

H_2O@	Silicalite		Na-ZSM-5			H-ZSM-5			
Temperature	mmol/g	H_2O/ Si(OH)	mmol/g	H_2O/ Na^+	H_2O/ Si(OH)	mmol/g	H_2O/ H^+	H_2O/ Si(OH)	H_2O/ H^++Si(OH)
Loading	0.54	0.8	3.95	6.6	50.6	3.78	7.7	19.5	5.5
298	0.15	0.2	1.12	1.9	14.4	0.69	1.4	3.6	1.0
323	0.11	0.2	0.77	1.3	9.9	0.56	1.1	2.9	0.8
348	0.07	0.1	0.51	0.8	6.5	0.38	0.8	2.0	0.6
373	0.06	0.1	0.35	0.6	4.5	0.29	0.6	1.5	0.4
423	0.06	0.1	0.19	0.3	2.4	0.19	0.4	1.0	0.3
473	0.05	0.1	0.08	0.1	1.1	0.18	0.4	0.9	0.3
523	0.05	0.1	0.02	<0.1	0.2	0.15	0.3	0.8	0.2
573	0.05	0.1	<0.01	<0.1	0.1	0.13	0.3	0.7	0.2
623	<0.01	<0.1	<0.01	<0.1	0.0	0.11	0.2	0.6	0.2

Table S3: Quantitative evaluation of ^{1}H MAS NMR spectra during the stepwise desorption of H_2O from SBA-15 materials.

H_2O @	SBA-15		Na-[Al]SBA-15			H-[Al]SBA-15			
Temperature	mmol/g	H_2O/ Si(OH)	mmol/g	H_2O/ Na^+	H_2O/ Si(OH)	mmol/g	H_2O/ H^+	H_2O/ Si(OH)	H_2O/ H^++Si(OH)
loading	8.98	4.1	7.33	8.5	6.4	6.18	32.5	10.4	7.9
298	1.38	0.6	1.16	1.3	1.0	0.94	4.9	1.6	1.2
323	1.35	0.6	0.78	0.9	0.7	0.82	4.3	1.4	1.1
348	1.28	0.6	0.73	0.8	0.6	0.81	4.3	1.4	1.0
373	1.27	0.6	0.70	0.8	0.6	0.77	4.0	1.3	1.0
423	1.21	0.6	0.50	0.6	0.4	0.67	3.5	1.1	0.9
473	0.83	0.4	0.29	0.3	0.3	0.67	3.5	1.1	0.9
523	0.50	0.2	0.21	0.2	0.2	0.60	3.1	1.0	0.8
573	0.24	0.1	0.17	0.2	0.1	0.50	2.6	0.8	0.6
623	0.19	0.1	0.01	<0.1	0.0	0.39	2.0	0.7	0.5

Table S4: Quantitative evaluation of ^{1}H MAS NMR spectra during the stepwise desorption of H_2O from STA materials.

H_2O @	A200		Na-STA@A200			H-STA@A200			
Temperature	mmol/g	H_2O/ Si(OH)	mmol/g	H_2O /Na^+	H_2O/ Si(OH)	mmol/g	H_2O/ H^+	H_2O/ Si(OH)	H_2O/ H^++Si(OH)
loading	0.92	2.4	2.90	11.6	4.8	3.48	10.2	6.1	3.8
298	0.32	0.8	0.81	3.2	1.3	0.60	1.8	1.1	0.7
323	0.26	0.7	0.37	1.5	0.6	0.27	0.8	0.5	0.3
348	0.22	0.6	0.24	1.0	0.4	0.13	0.4	0.2	0.1
373	0.20	0.5	0.21	0.9	0.3	0.13	0.4	0.2	0.1
423	0.20	0.5	0.19	0.8	0.3	0.09	0.3	0.2	0.1
473	0.14	0.4	0.16	0.6	0.3	<0.01	<0.1	0.0	0.0
523	0.14	0.4	0.08	0.3	0.1	0.0	0.0	0.0	0.0
573	0.10	0.2	0.02	0.1	0.0	0.0	0.0	0.0	0.0
623	0.08	0.2	<0.01	0.0	0.0	0.0	0.0	0.0	0.0