Electronic Supplementary Information

Confinement and Surface Sites Control Methanol Adsorbate Stability on MFI Zeolites, SBA-15, and Silica-supported Heteropoly Acid

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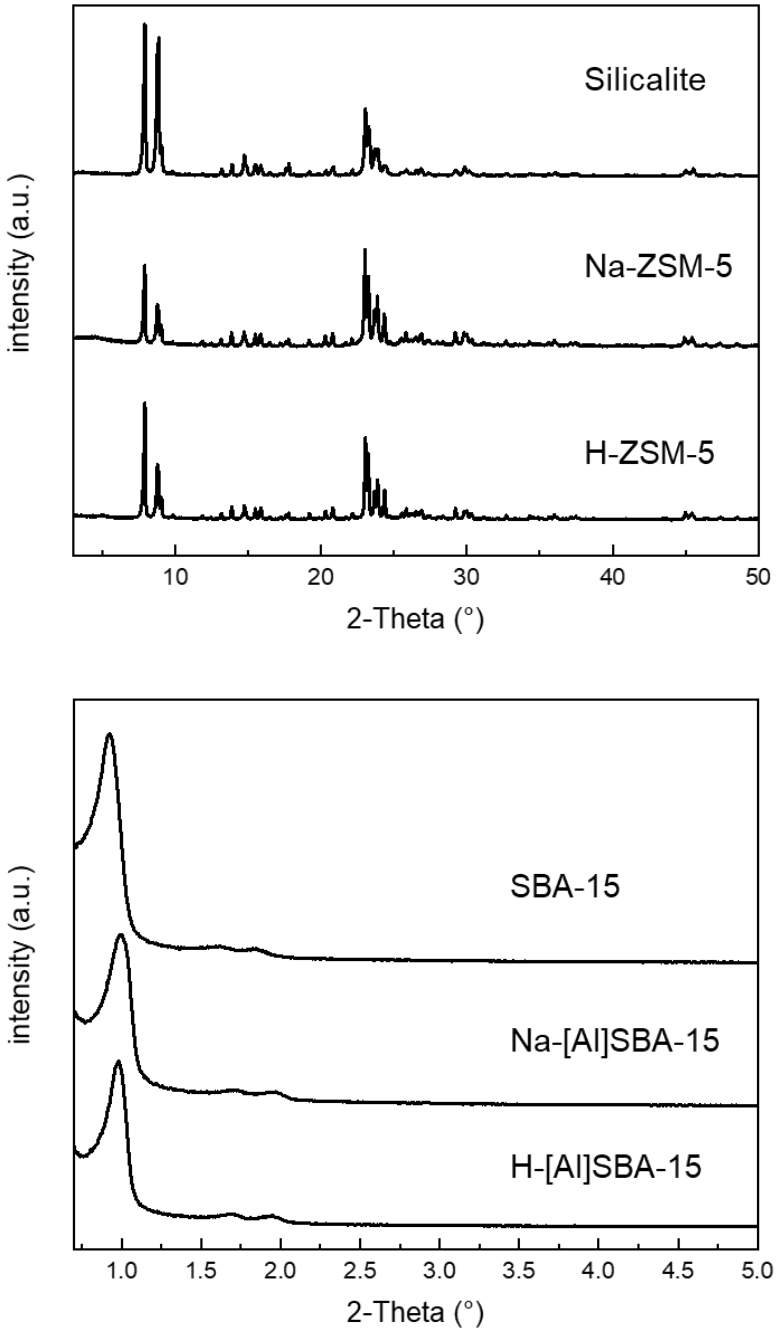

Figure S1: X-ray powder diffraction patterns of the microporous MFI zeolites and small angle X-ray powder diffraction patterns of the mesoporous SBA-15 materials.

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

Material	Si/Al[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	<0.01	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	12.6[c)]	-	0.57	0.34	120	-	0.49	-
Na-STA@A200	12.3[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.

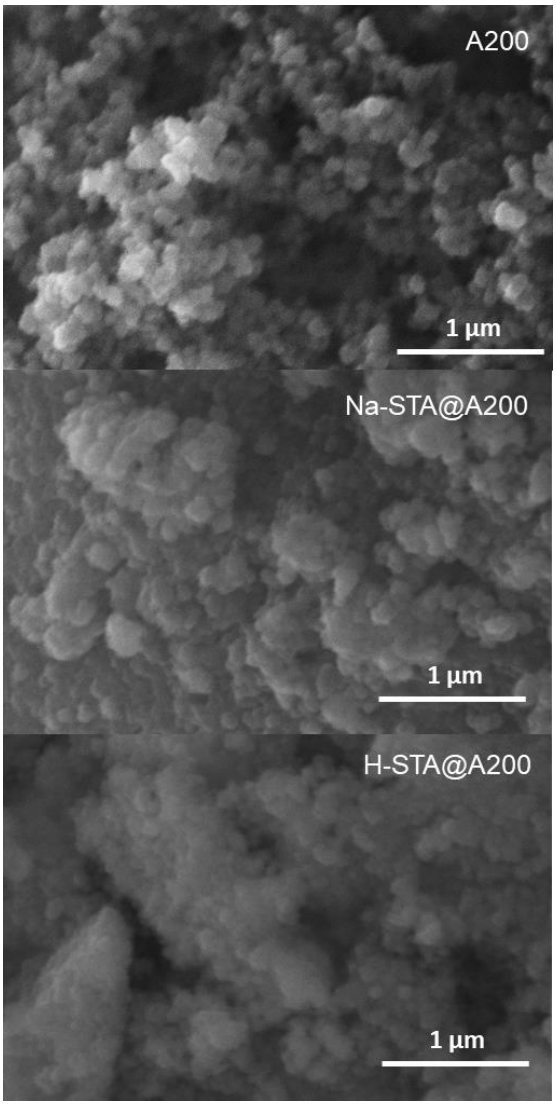

Figure S2: SEM pictures of A200 support and silicotungstic acid (STA) in Na- and H-form supported on A200.

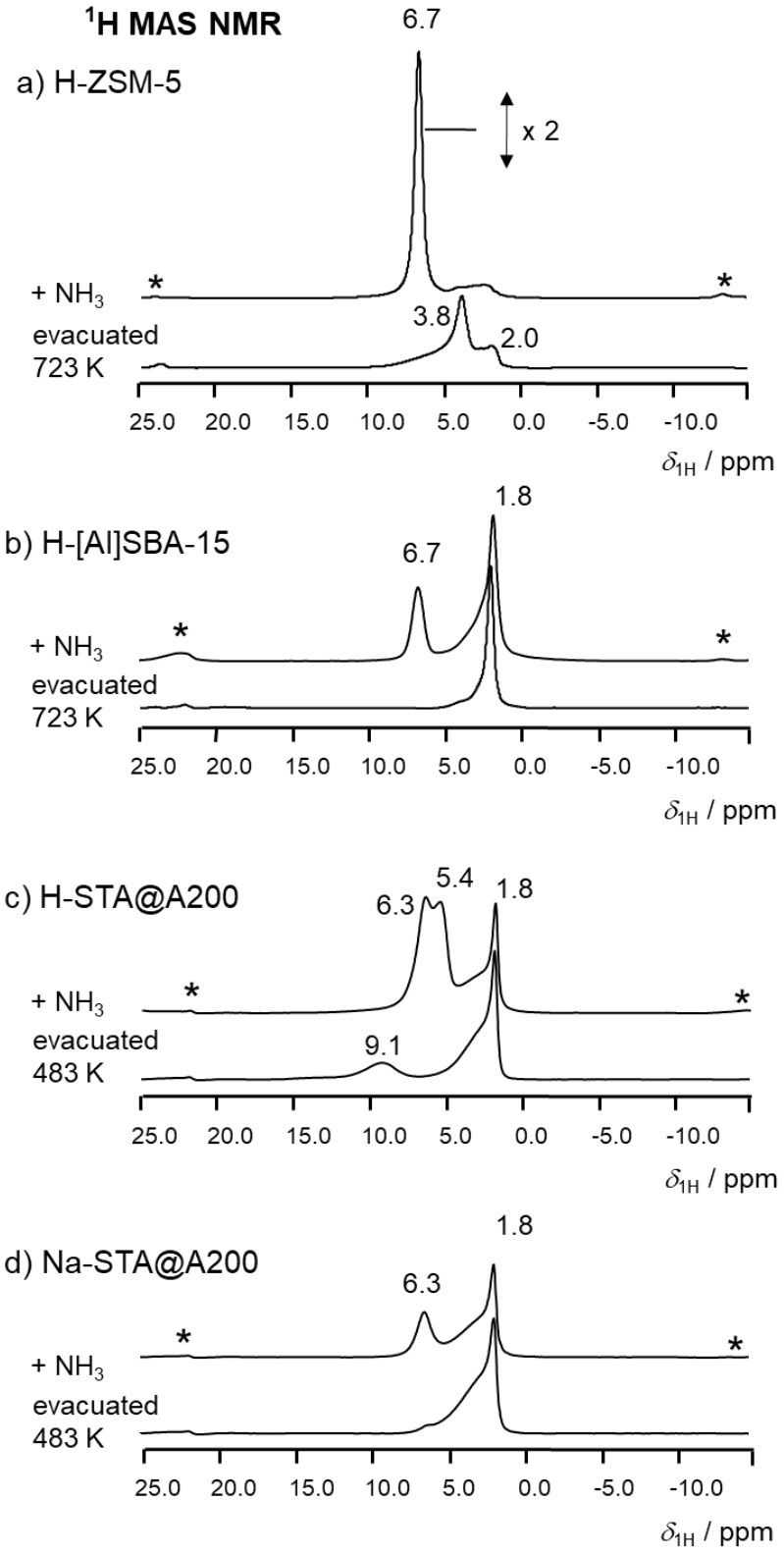

Figure S3: ^{1}H MAS NMR spectra of a) H-ZSM-5, b) H-[Al]SBA-15, c) H-STA@A200 and d) Na-STA@A200 after NH_3 loading and desorb at 453 K for 2 h (top) and in activated state (bottom).

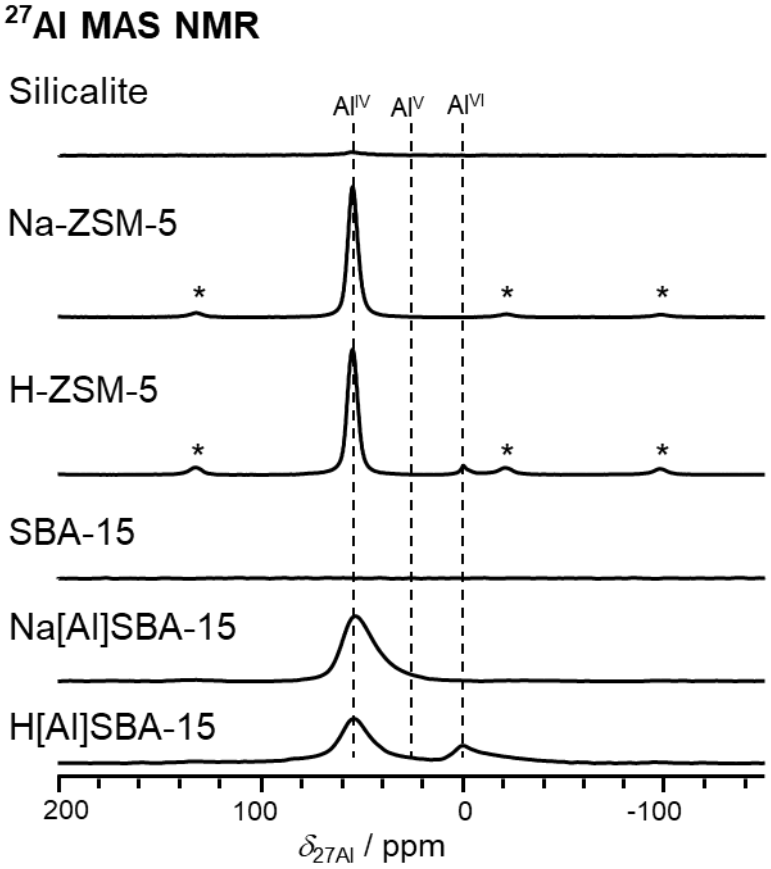

Figure S4: ^{27}Al MAS NMR spectra of the fully hydrated materials under study. The signal assignments are those for aluminum in tetrahedral (Al^{IV}), pentahedral (Al^{V}), and octahedral (Al^{VI}) oxygen coordination.

Methanol Desorption

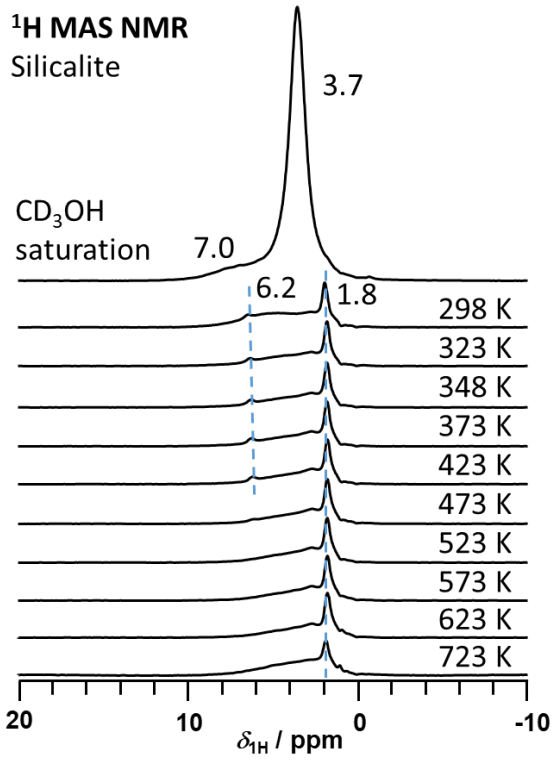

Figure S5: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from Silicalite.

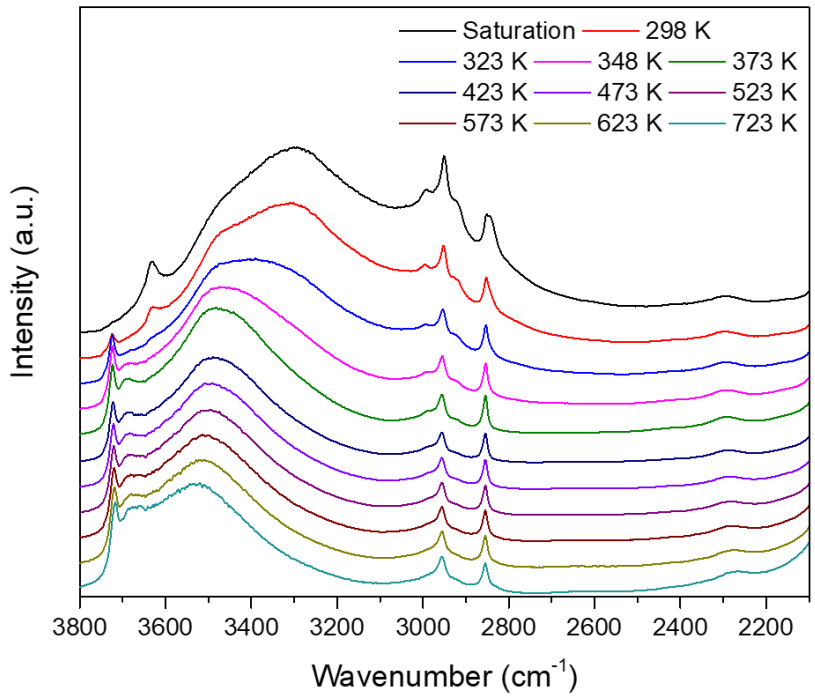

Figure S6: DRIFTS spectra of the stepwise desorption of CH_3OH from Silicalite.

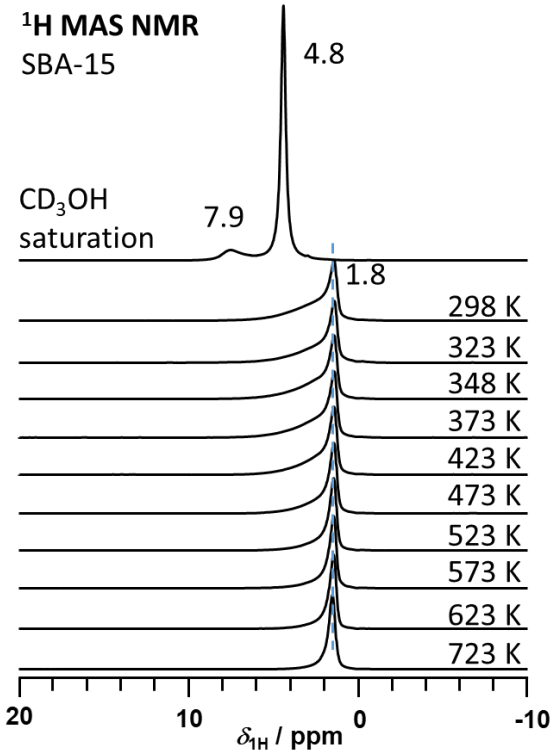

Figure S7: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from SBA-15.

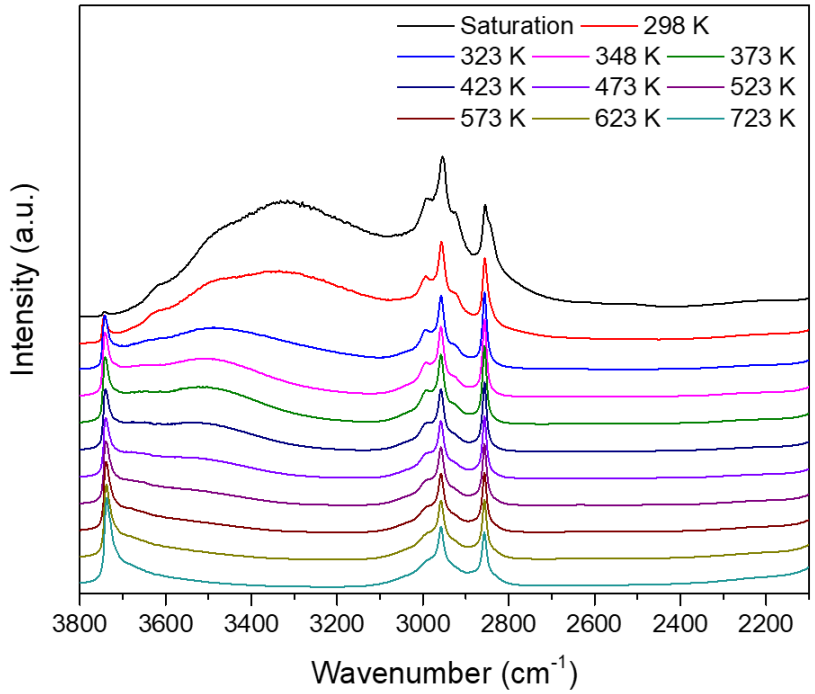

Figure S8: DRIFTS spectra of the stepwise desorption of CH_3OH from SBA-15.

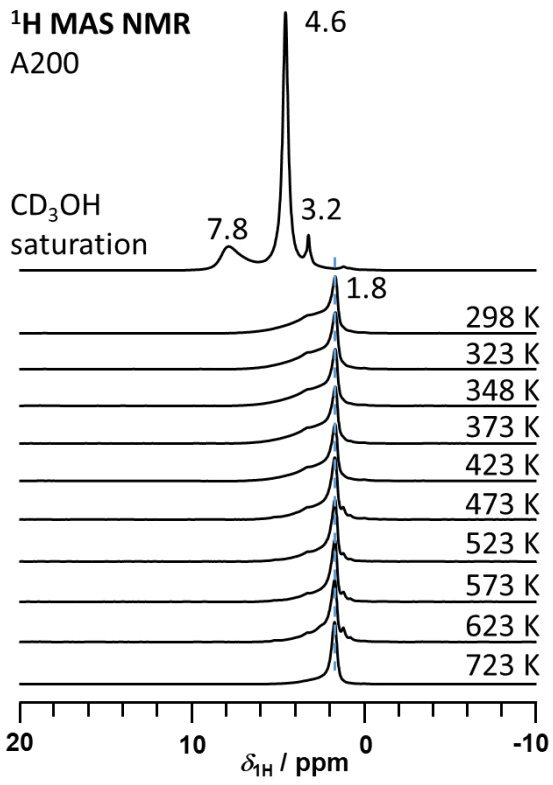

Figure S9: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from A200.

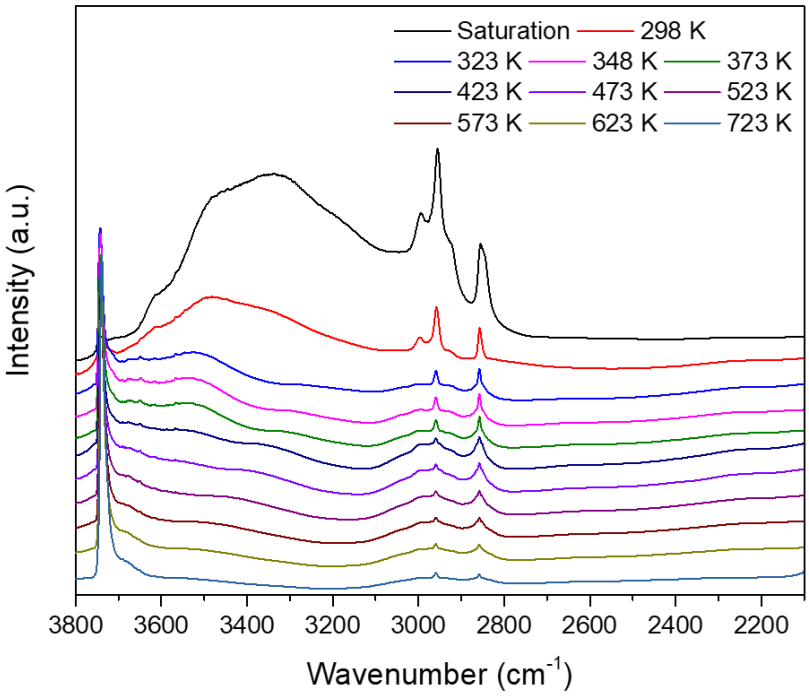

Figure S10: DRIFTS spectra of the stepwise desorption of CD_3OH from A200

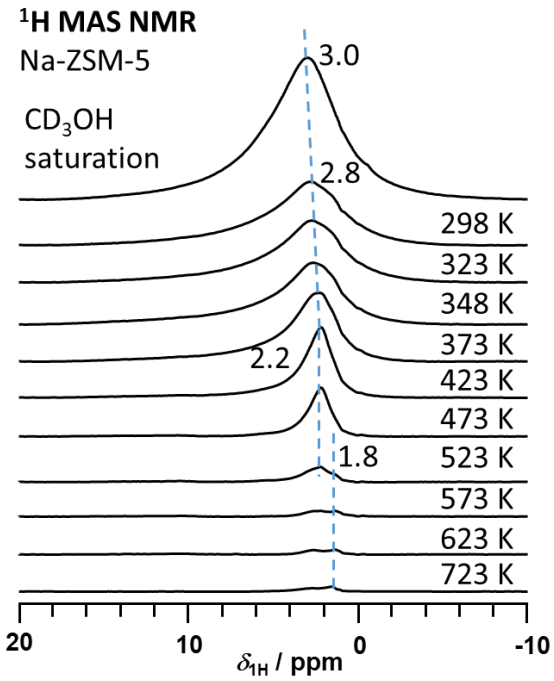

Figure S11: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from Na-ZSM-5.

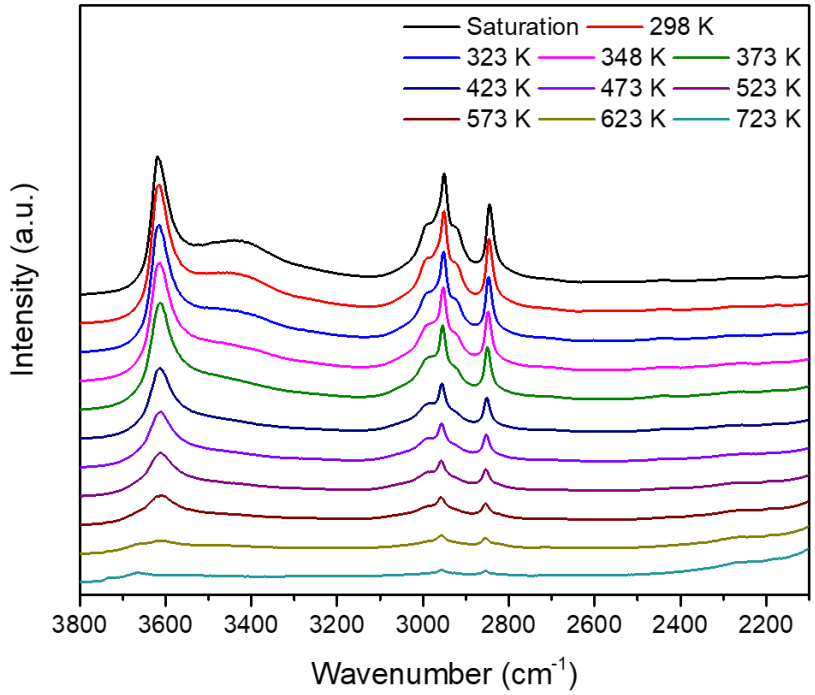

Figure S12: DRIFTS spectra of the stepwise desorption of CH_3OH from Na-ZSM-5.

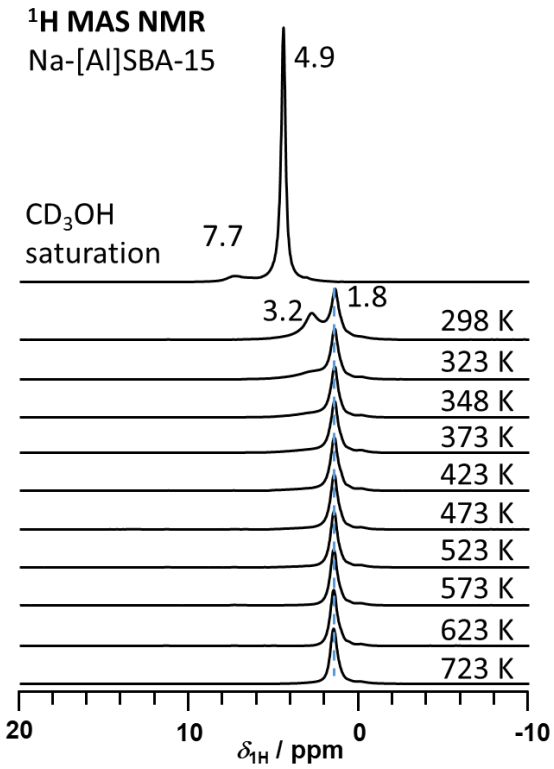

Figure S13: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from Na-[Al]SBA-15.

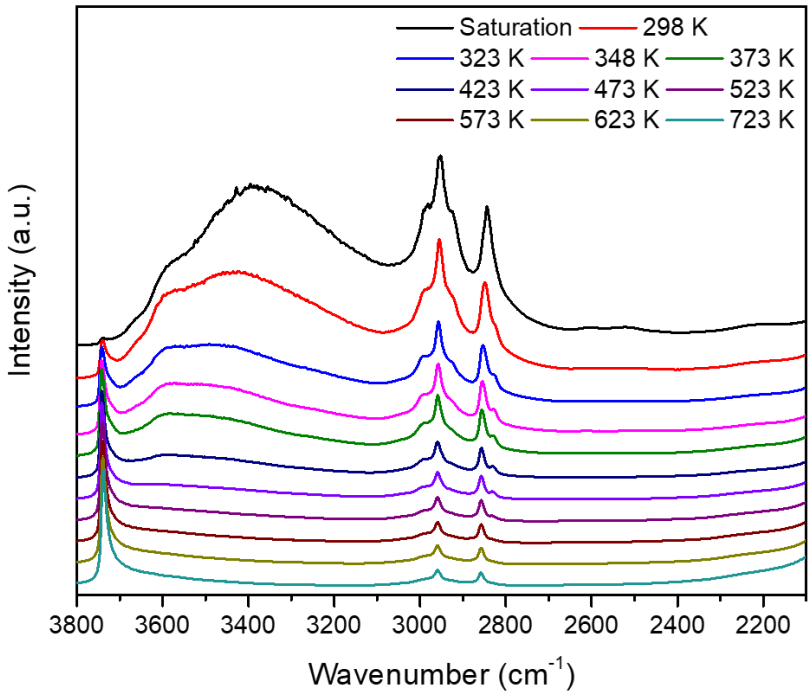

Figure S14: DRIFTS spectra of the stepwise desorption of CH_3OH from Na-[Al]SBA-15.

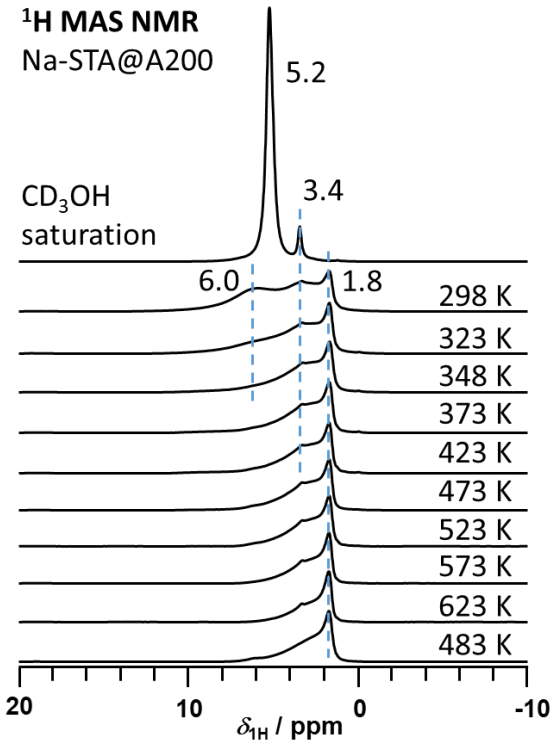

Figure S15: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from Na-STA@A200.

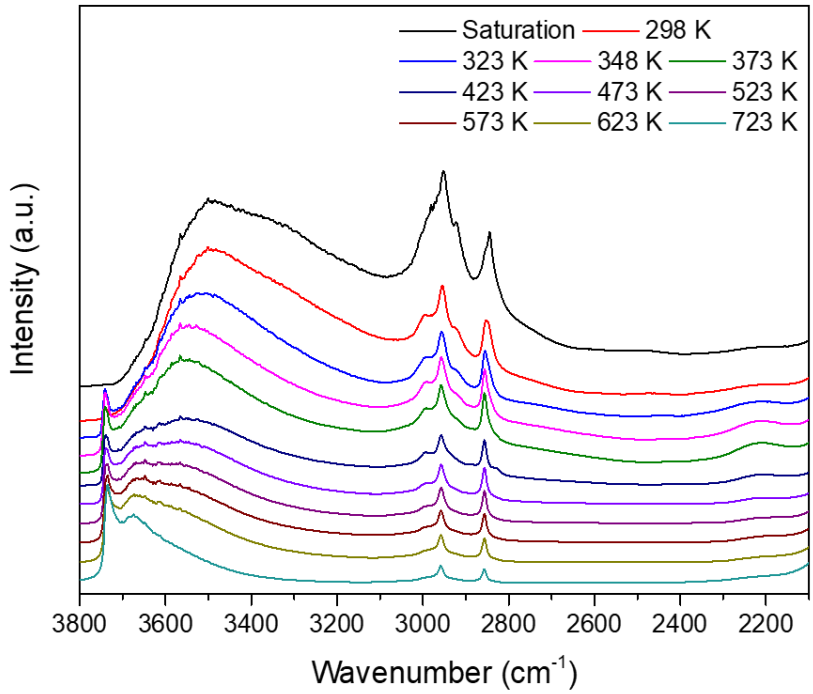

Figure S16: DRIFTS spectra of the stepwise desorption of CH_3OH from Na-STA@A200.

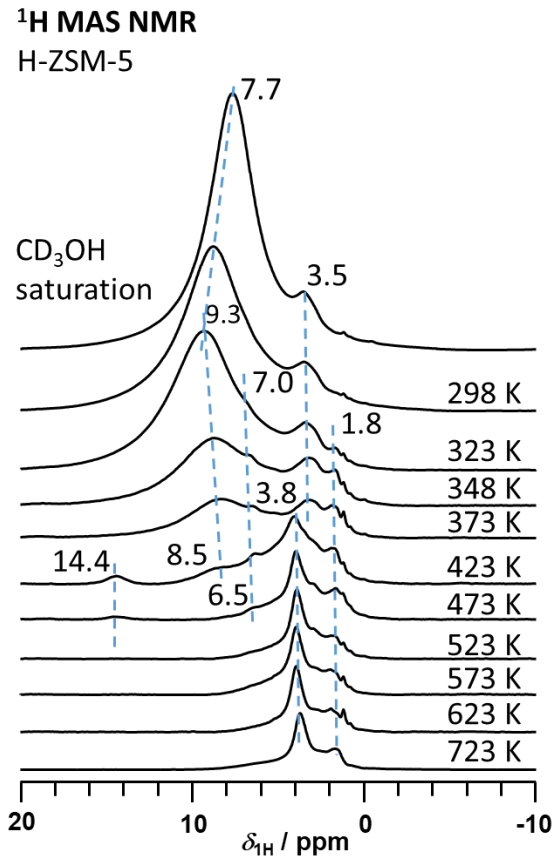

Figure S17: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from H-ZSM-5.

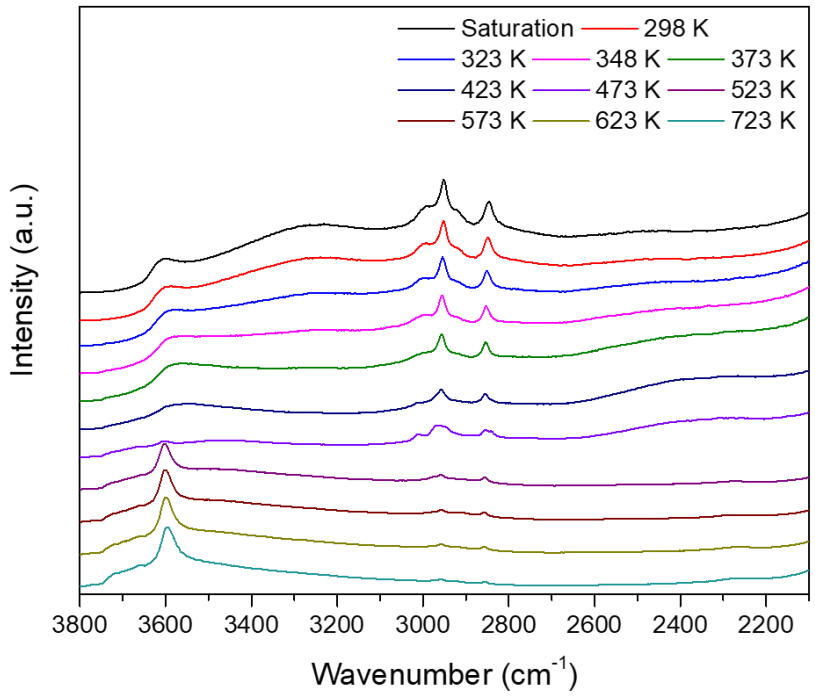

Figure S18: DRIFTS spectra of the stepwise desorption of CH_3OH from H-ZSM-5.

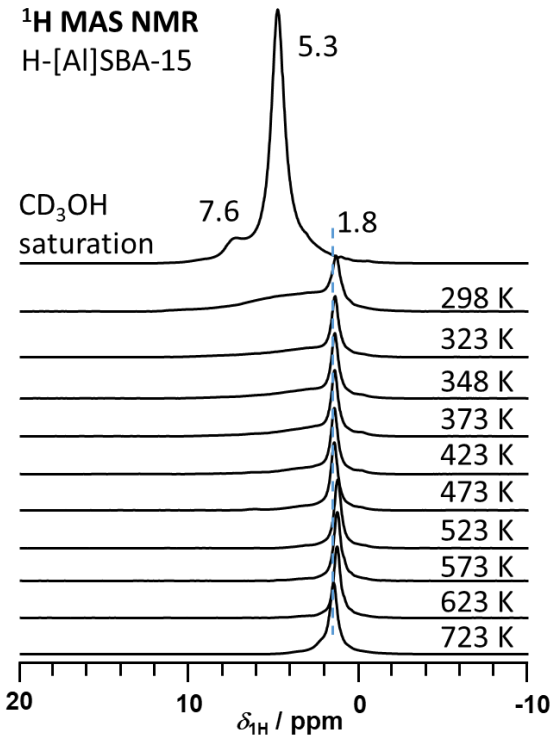

Figure S19: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from H-[Al]SBA-15.

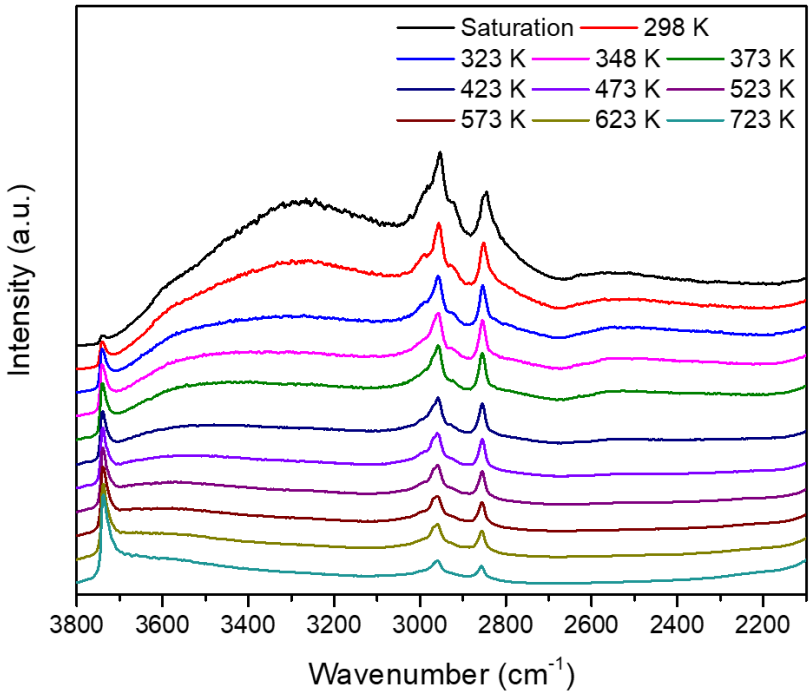

Figure S20: DRIFTS spectra of the stepwise desorption of CH_3OH from H-[Al]SBA-15.

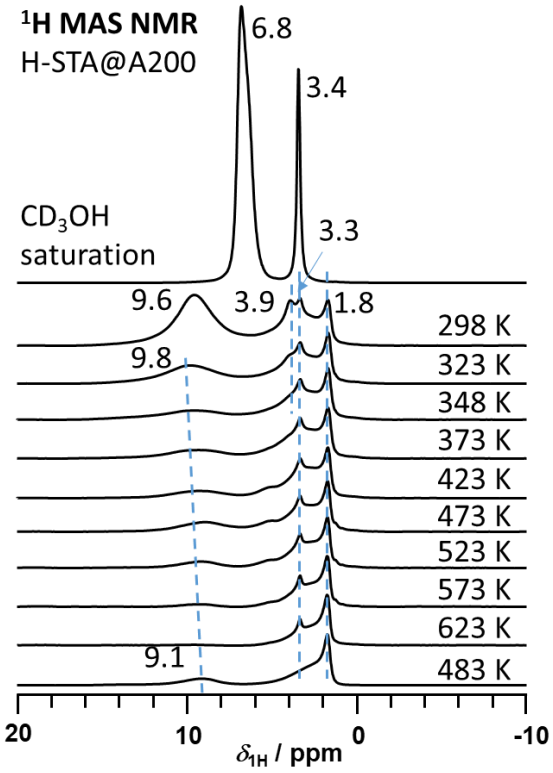

Figure S21: ^{1}H MAS NMR spectra of the stepwise desorption of CD_3OH from H-STA@A200.

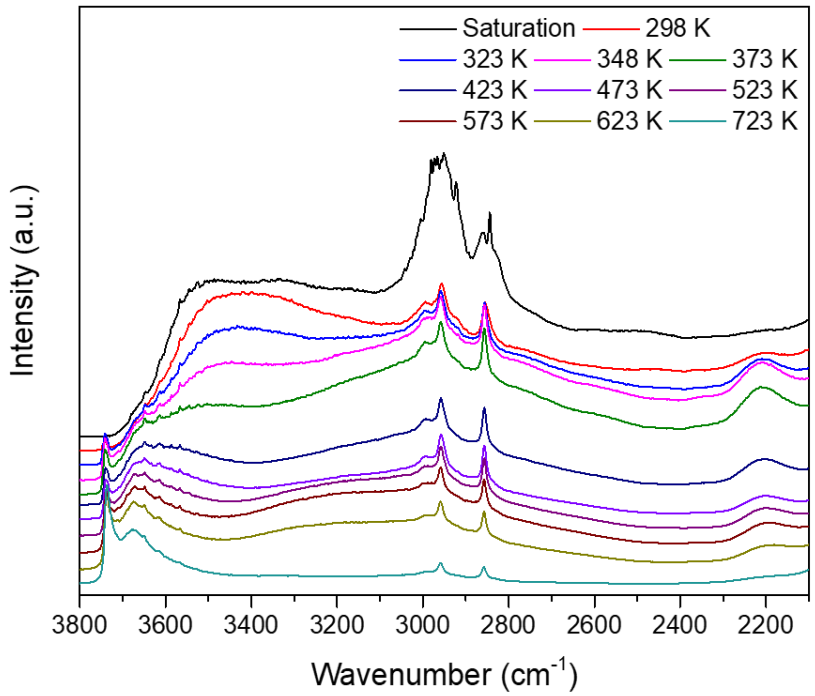

Figure S22: DRIFTS spectra of the stepwise desorption of CH_3OH from H-STA@A200.

Table S2: Quantitative evaluation of ^{1}H MAS NMR spectra during the stepwise desorption of CD_3OH from MFI zeolites.

CD_3OH@	Silicalite		Na-ZSM-5			H-ZSM-5			
Temperature	mmol/g	CD_3OH/ Si(OH)	mmol/g	CD_3OH/ Na^+	CD_3OH/ Si(OH)	mmol/g	CD_3OH/ H^+	CD_3OH/ Si(OH)	CD_3OH/ H^++Si(OH)
loading	2.46	3.7	3.03	5.1	38.9	3.63	7.4	5.3	18.7
298	0.10	0.2	1.68	2.8	21.6	2.13	4.3	3.1	11.0
323	0.08	0.1	1.36	2.3	17.4	1.57	3.2	2.3	8.1
348	0.06	0.1	1.09	1.8	14.0	0.68	1.4	1.0	3.5
373	0.06	0.1	0.88	1.5	11.3	0.41	0.8	0.6	2.1
423	0.04	0.1	0.42	0.7	5.4	0.26(0.06)	0.5(0.2)	0.4(0.1)	1.3(0.4)
473	0.01	0.0	0.18	0.3	2.3	0.07(0.05)	0.2(0.1)	0.1(<0.1)	0.4(0.2)
523	0.01	0.0	0.07	0.1	1.0	0.03(0.02)	0.1(<0.1)	0.1(<0.1)	0.2(0.1)
573	<0.01	0.0	0.05	0.1	0.6	0.02(0.01)	0.0(0.0)	0.0(0.0)	0.1(0.1)
623	<0.01	0.0	0.04	0.1	0.5	<0.01(<0.01)	0.0(0.0)	0.0(0.0)	0.0(0.0)

Values in bracket are the quantities of DME

Table S3: Quantitative evaluation of ^{1}H MAS NMR spectra during the stepwise desorption of CD_3OH from SBA-15 materials.

CD_3OH@	SBA-15		Na-[Al]SBA-15			H-[Al]SBA-15			
Temperature	mmol/g	CD_3OH/ Si(OH)	mmol/g	CD_3OH/ Na^+	CD_3OH /Si(OH)	mmol/g	CD_3OH/ H^+	CD_3OH/ Si(OH)	CD_3OH / H^++Si(OH)
loading	9.89	4.5	8.78	10.2	7.7	5.18	27.3	8.7	6.6
298	1.08	0.5	0.87	1.0	0.8	1.12	5.9	1.9	1.4
323	1.05	0.5	0.45	0.5	0.4	0.62	3.3	1.0	0.8
348	1.02	0.5	0.27	0.3	0.2	0.52	2.7	0.9	0.7
373	1.00	0.5	0.22	0.3	0.2	0.45	2.4	0.8	0.6
423	0.91	0.4	0.17	0.2	0.2	0.30	1.6	0.5	0.4
473	0.66	0.3	0.14	0.2	0.1	0.06	0.3	0.1	0.1
523	0.25	0.1	0.12	0.1	0.1	0.03	0.2	0.1	0.0
573	0.21	0.1	<0.01	0.0	0.0	<0.01	0.0	0.0	0.0
623	<0.01	0.0	<0.01	0.0	0.0	<0.01	0.0	0.0	0.0

Table S4: Quantitative evaluation of ^{1}H MAS NMR spectra during the stepwise desorption of CD_3OH from STA materials.

CD_3OH@	A200		Na-STA@A200			H-STA@A200			
Temperature	mmol/g	CD_3OH/ Si(OH)	mmol/g	CD_3OH / Na^+	CD_3OH/ Si(OH)	mmol/g	CD_3OH / H^+	CD_3OH/ Si(OH)	CD_3OH/ H^++Si(OH)
loading	2.76	7.1	3.60	14.4	5.9	5.29	15.6	9.3	5.8
298	0.48	1.2	0.40	1.6	0.7	0.75	2.2	1.3	0.8
323	0.30	0.8	0.28	1.1	0.5	0.27	0.8	0.5	0.3
348	0.29	0.8	0.12	0.5	0.2	0.09	0.3	0.2	0.1
373	0.28	0.7	0.09	0.4	0.2	0.06	0.2	0.1	0.1
423	0.22	0.6	0.08	0.3	0.1	0.01	0.0	0.0	0.0
473	0.12	0.3	0.05	0.2	0.1	<0.01	0.0	0.0	0.0
523	0.10	0.3	<0.01	0.0	0.0	<0.01	0.0	0.0	0.0
573	0.09	0.2	<0.01	0.0	0.0	<0.01	0.0	0.0	0.0
623	0.06	0.2	<0.01	0.0	0.0	<0.01	0.0	0.0	0.0

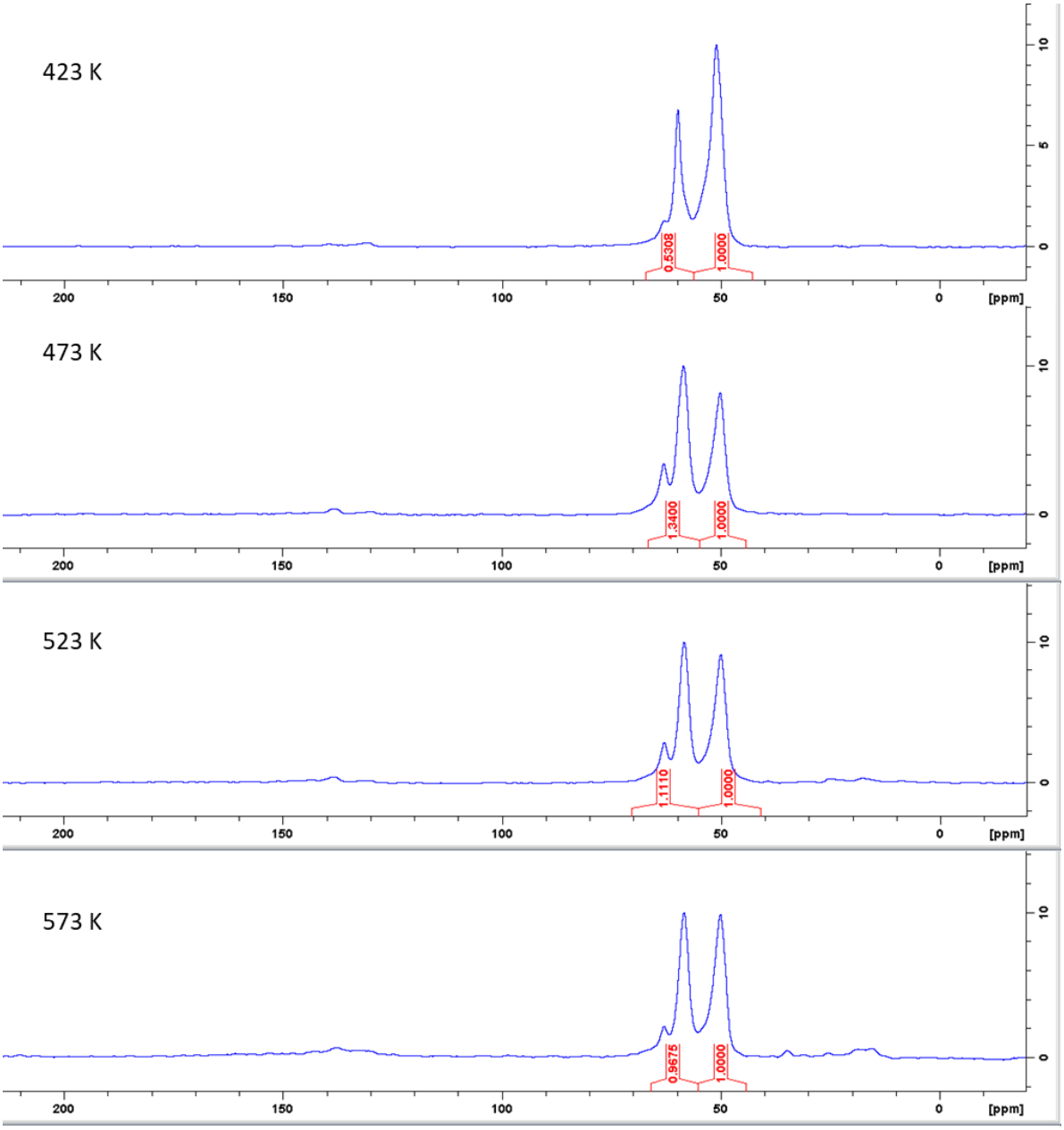

Figure S23: ^{13}C CP MAS NMR spectra of the stepwise desorption of CD_3OH from H-ZSM-5 in the temperature range from 423 K to 573 K to estimate the ratio between methanol and DME. Note that direct excitation measurements and CP measurements are in reasonable agreement (with error <10%).

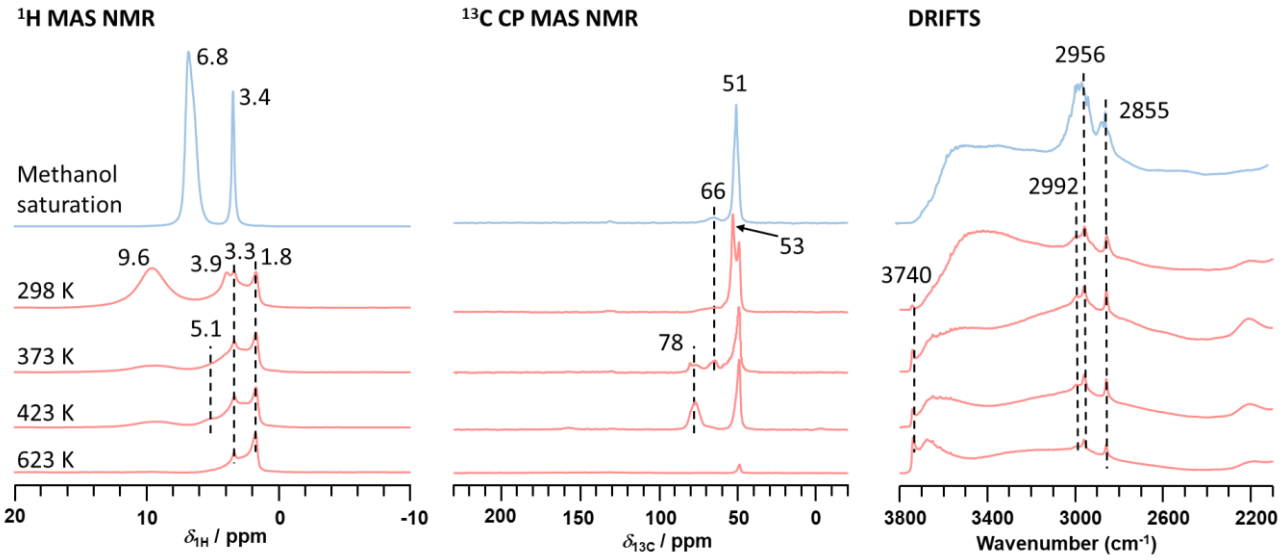

Figure S24:^{1}H and ^{13}C MAS NMR and DRIFTS spectra of stepwise desorption of CD_3OH from H-STA@A200 at chosen temperatures.