Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information:

Room temperature methoxylation in zeolite H-ZSM-5: An operando DRIFTS/Mass spectrometric study

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Experimental Section:

Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and mass spectrometer (MS) experiments were conducted on Agilent Cary 600 series spectrometer equipped with Harrick Praying Mantis reaction cell. Spectra were collected at a time resolution of around 20s. The cell outlet was connected to Hiden QGA MS. Highest purity He (grade 6, BOC, UK) was passed through in line zeolite moisture traps to the reaction cell to minimise the moisture content in the He flow. Methanol Conversion (X(%)) is calculated as:

$X(\%) = (C_{inlet} - C_{outlet}) / (C_{inlet}) * 100$

C_{inlet} = inlet methanol concentration

C_{outlet} = outlet methanol concentration

Results and Discussion:

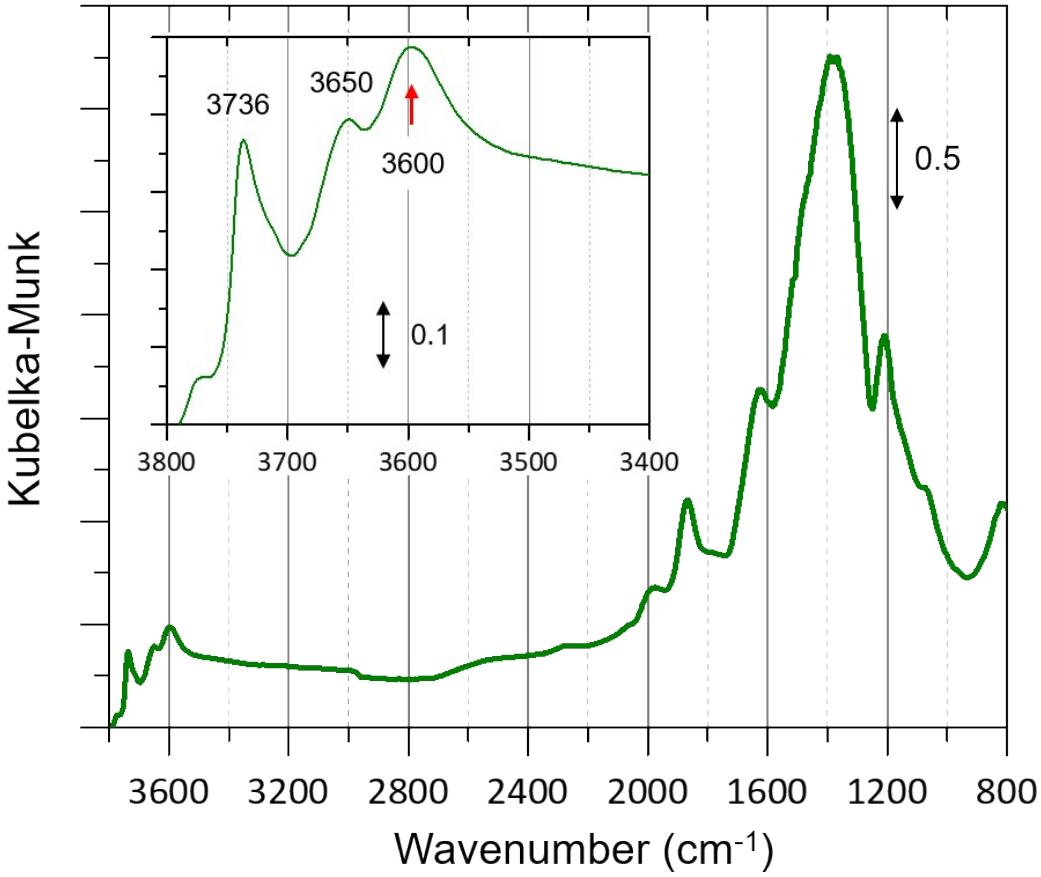

Figure S1. DRIFTS spectrum of H-ZSM-5 at room temperature after dehydration in He flow at 500 ^{o}C for 4 h. Magnified υ(O – H) region is shown in the inset.

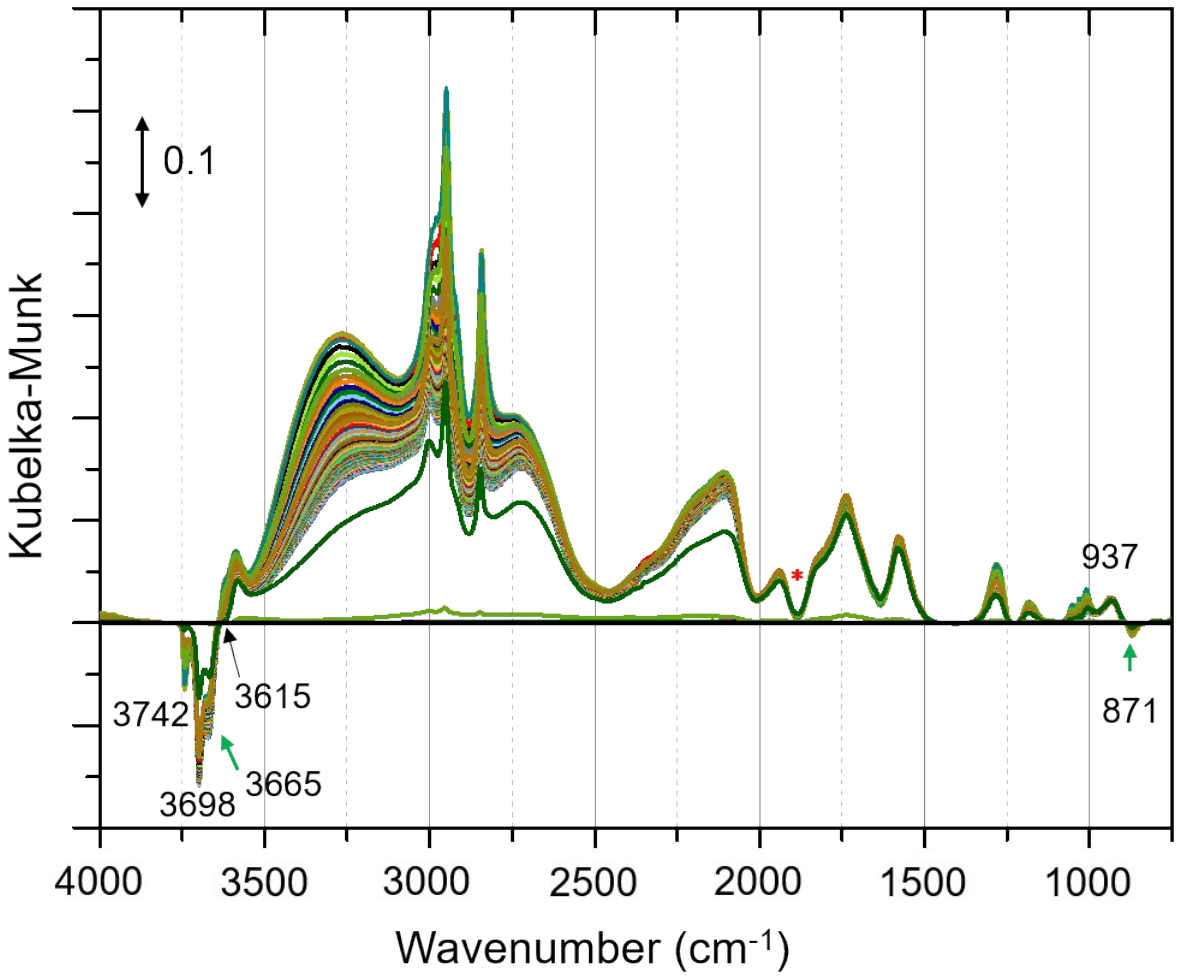

Figure S2. Infrared difference spectra (complete data set) of zeolite ZSM-5 with a methanol pulse of 7 molecules per Brønsted acidic site at room temperature (RT). Artefact arising from the subtraction process is indicated with asterisk[1].

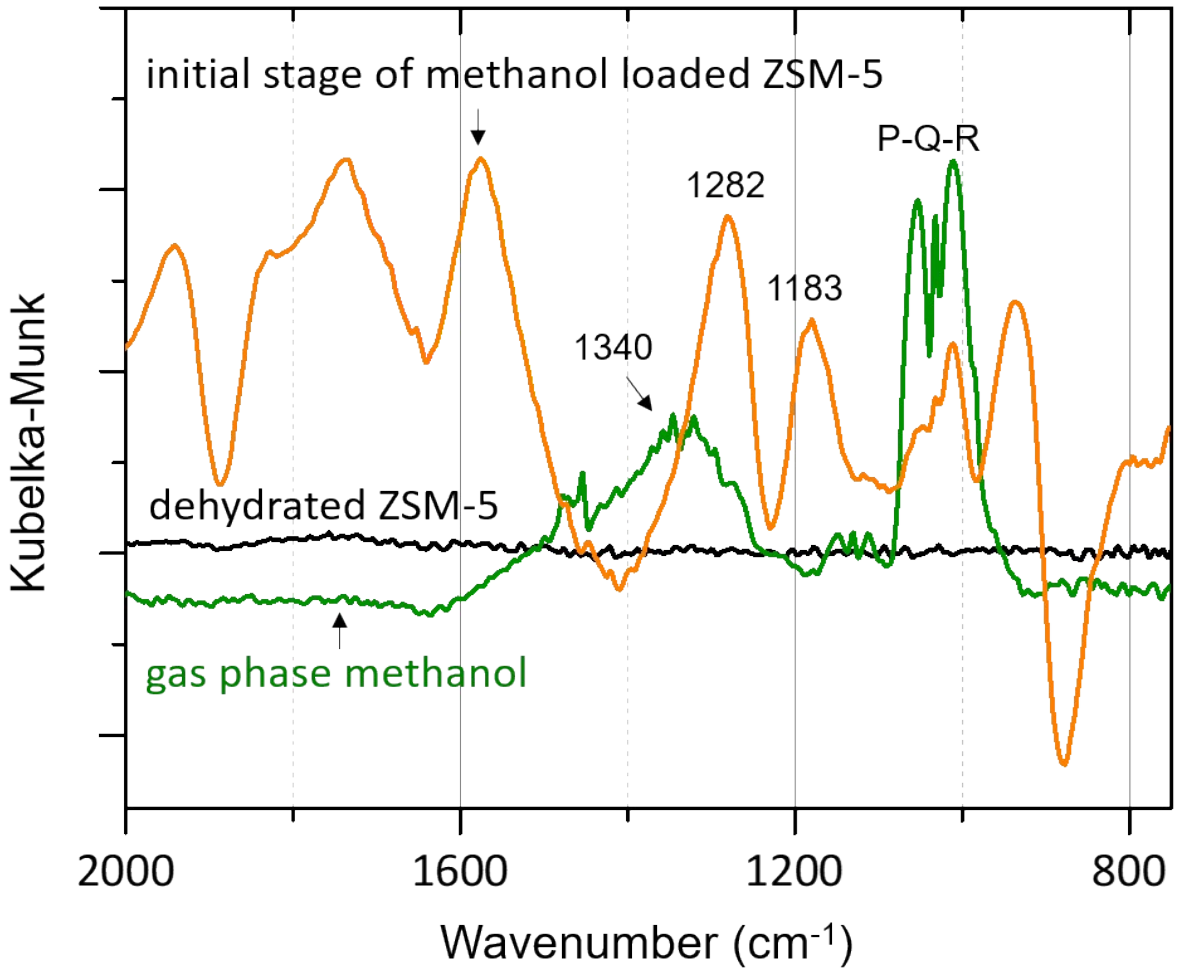

Figure S3. Infrared difference spectra of gas phase methanol as well as dehydrated and methanol-loaded ZSM-5 at RT.

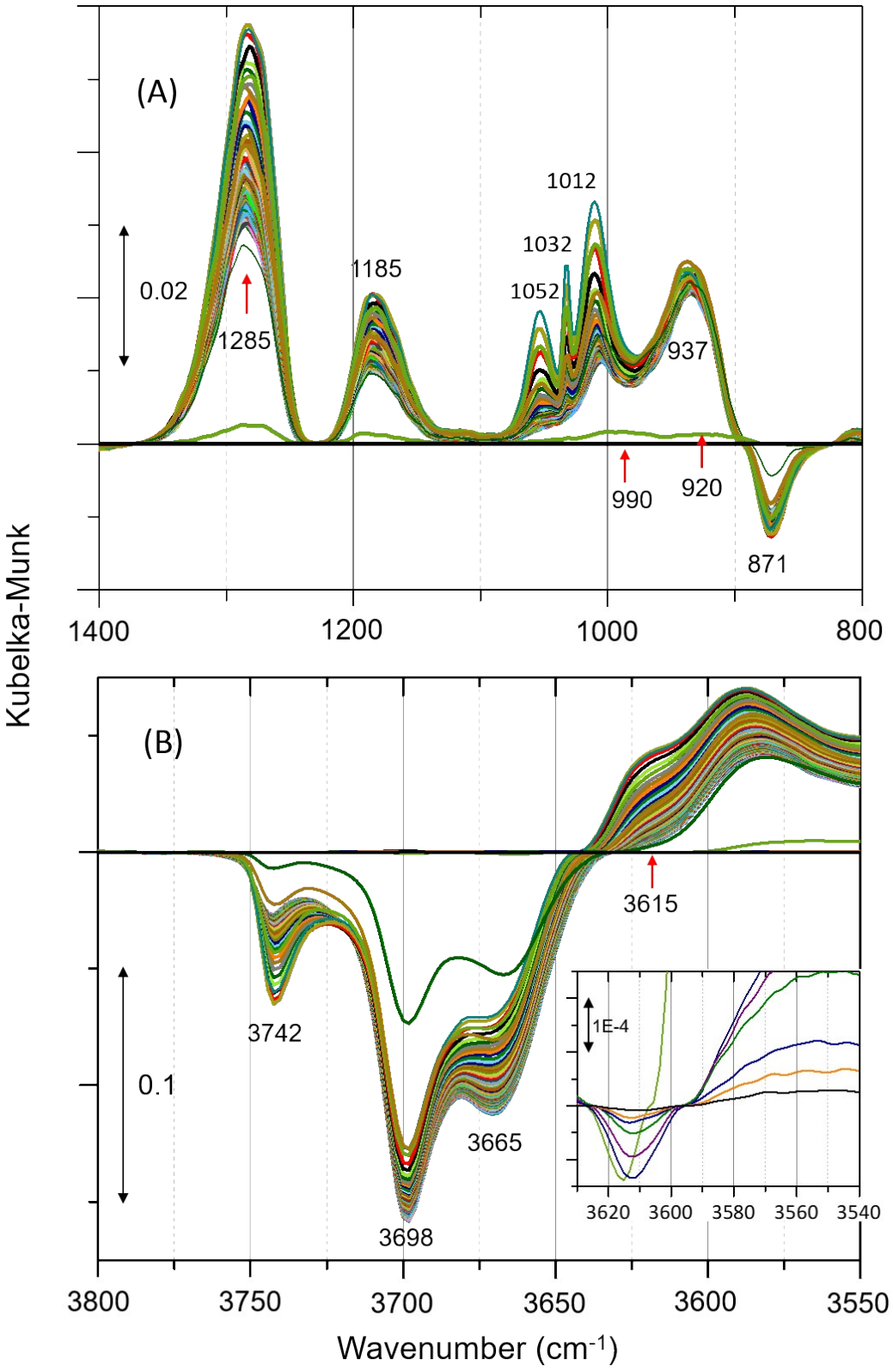

Figure S4. Magnified regions of Figure S2: (A) evolution of methoxy and (B) subsequent consumption of hydroxyls. Inset depicts the consumption of Brønsted acidic hydroxyls at the initial stages of the reaction.

Table S1: The assignment of observed vibrational frequencies in Figures 1, 2, S2 and S3.

Observed vibrational Frequencies	Assignment		Reference
Wavenumbers (cm^{-1})	Vibrational mode	Structure	
871	υ_{SiOSi} -	Si –O– CH_3	1
937	υ_{CO}	C – O	2,3
1135-1190	ρ_{CH3}	Si/Al–O– CH_3 Si –O– CH_3	2,3 This work
2865	υ_{CH}	Si–O– CH_3	4-6
2875	υ_{CH}	Si–O– CH_3	4-6
2967	υ_{CH}	Si/Al–O– CH_3	4-6
2980	υ_{CH}	Si/Al–O– CH_3	4-6
3615	υ_{OH}	Si/Al–O– H	2,3
3665	υ_{OH}	SiOH/Al–O– H	2,3
3698	υ_{OH}	Z–O– H[a]	This work
3742	υ_{OH}	Si–O– H	2,3

[a] A different kind of hydroxyl group

References:

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