

Supplementary Information

A Spectroscopic Paradox: The Interaction of Methanol with ZSM-5 at Room Temperature

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Microreactor Experiments

The microreactor set up is a flow reactor, with a bed length of 1 cm and a zeolite weight of 0.5g. Two reactions were carried out, one at room temperature and one at 350 °C (which is the temperature most commonly used for the Methanol-to-Hydrocarbons reaction). The 350 °C reaction behaved like any other MTH reaction with the products ranging from light olefins to methylated aromatics.¹ Figure S1, shows the cumulative concentration of the major products identified and quantified by GC-FID (Shimadzu GC-2014, BP-20 column), as well as the total concentration of the unreacted methanol. The methanol conversion (Figure S2a) also remains high, with the conversion being at 100% until 14 hours after which it starts to slightly drop. On the other hand, methanol at room temperature (Figure S2b) shows no conversion at all, with the conversion staying at 0%, except at the start of the reaction, where the methanol is being absorbed by the zeolite. Unfortunately, with the sampling time required for the GC-FID to sample the outlet stream, there would be no possible way to quantify the uptake of the methanol by the ZSM-5. No other products have been identified on the room temperature reaction.

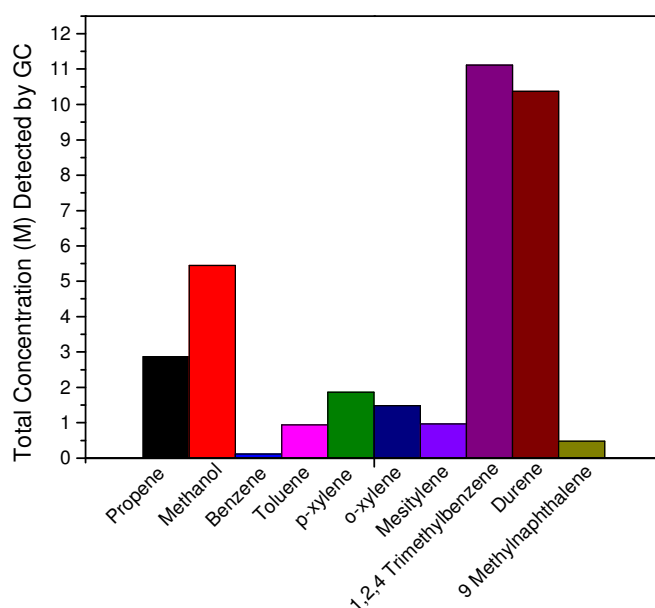


Figure S1: Methanol-to-Hydrocarbons carried out at 350 °C, total concentration of 26 hours of reaction. Cumulative concentration calculated by a GC-FID.

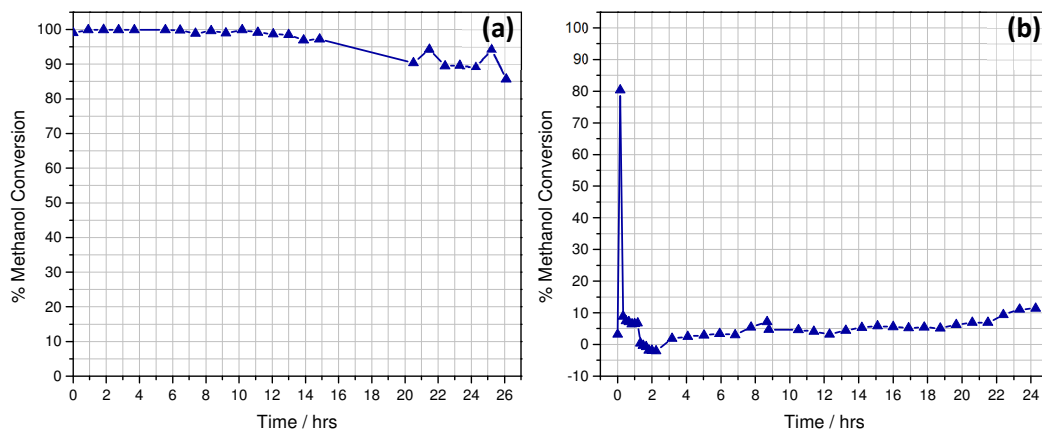


Figure S2: Methanol percentage conversions (a) Methanol-to-Hydrocarbons reaction over ZSM-5 at 350 °C, with 0.02 ml/min methanol in 20 ml/min N₂ (b) Methanol over ZSM-5 at room temperature (30 °C) with 0.02 ml/min methanol in 20 ml/min N₂.

To check whether the spike at near-zero time in Figure S2b was the result of methoxylation or just adsorption of methanol by the zeolite, the room temperature reaction was repeated with the same experimental conditions but for a shorter period of time of 5 hours. A mass spectrometer (EcoCat – portable mass spectrometer), was attached to the reactor outlet to monitor the outlet gases. The methanol uptake is seen clearly over a period of 30 minutes, and no production of water is observed at any point in this reaction, as can be seen in Figure S3.

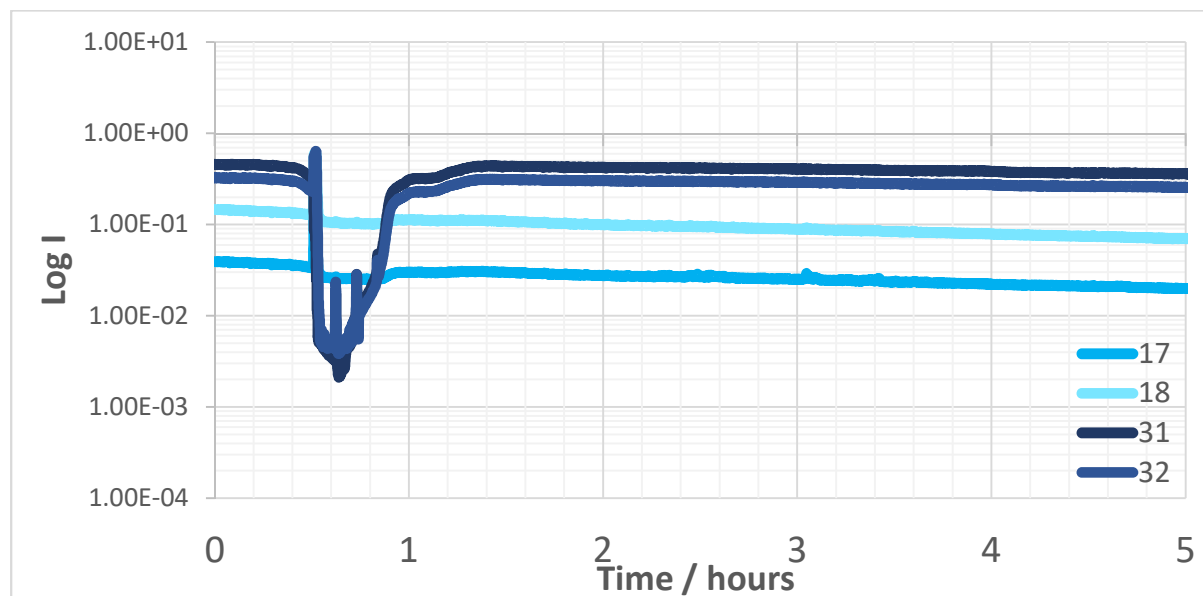


Figure S3: Mass spectrometer profile of outlet gases from the reactor. The large dip in the methanol level at ~0.5 hours occurred when the methanol was switched from the bypass to going through the reactor, i.e. this corresponds to time = 0. The ions at $m/z = 17$ and 18 are used to monitor water and $m/z = 31$ and 32 are used to monitor methanol.

INS Spectrum of Fresh ZSM-5 dried.

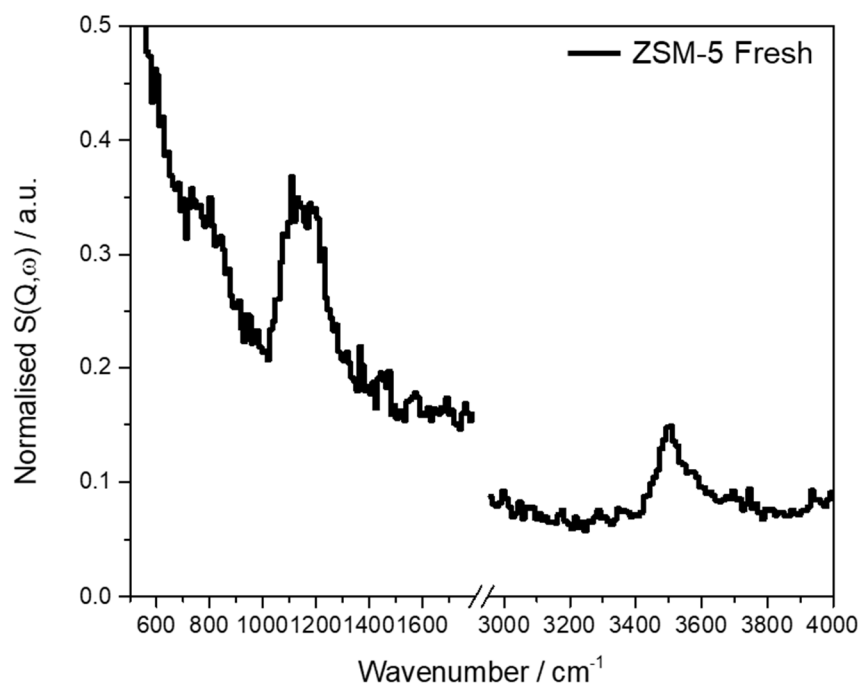


Figure S4: INS Spectrum of fresh ZSM-5 collected using the MAPS spectrometer with the A-chopper package. Region of 500 – 1900 cm^{-1} collected at an incident energy of 2044 cm^{-1} and the region of 3000 – 4000 cm^{-1} collected at an incident energy of 5244 cm^{-1} .

FD-MEOH without zeolite subtraction

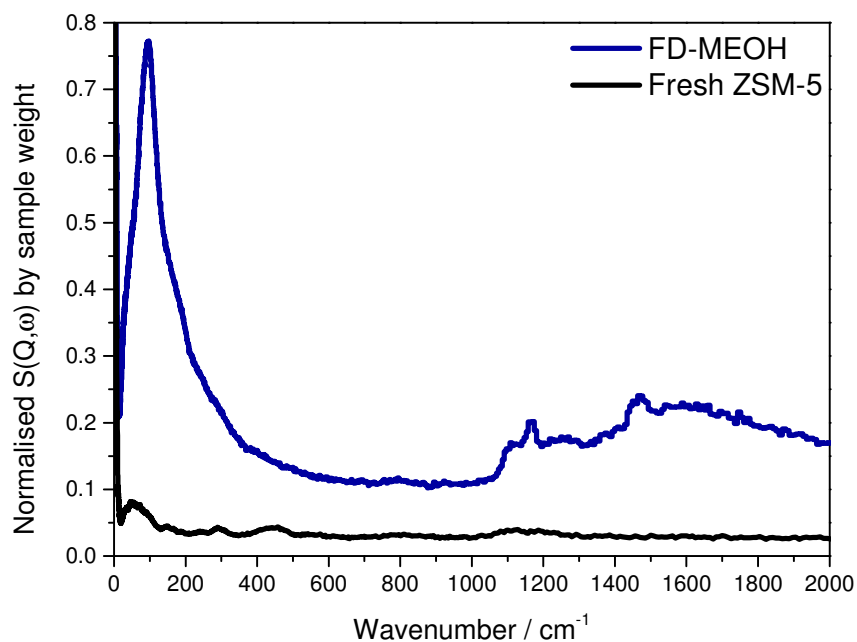


Figure S5: INS Spectrum of FD-MEOH sample shown in Figure 1 without the zeolite subtraction in the main text and fresh ZSM-5. Both samples were collected using the TOSCA instrument and their intensity has been normalised with respect to the sample weight so as to compare them.

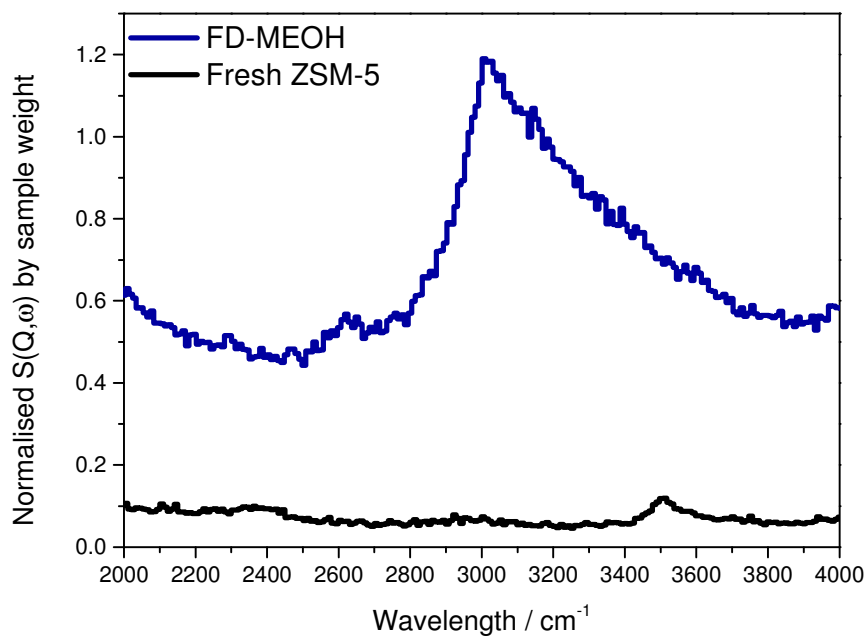


Figure S6: INS Spectrum of FD-MEOH sample shown in Figure 1 without the zeolite subtraction in the main text and fresh ZSM-5. Both samples were collected using the MAPS instrument using the A-chopper package at an incident energy of 5243 cm^{-1} and their intensity has been normalised with respect to the sample weight so as to compare them.

Difference Spectra of Figure 2

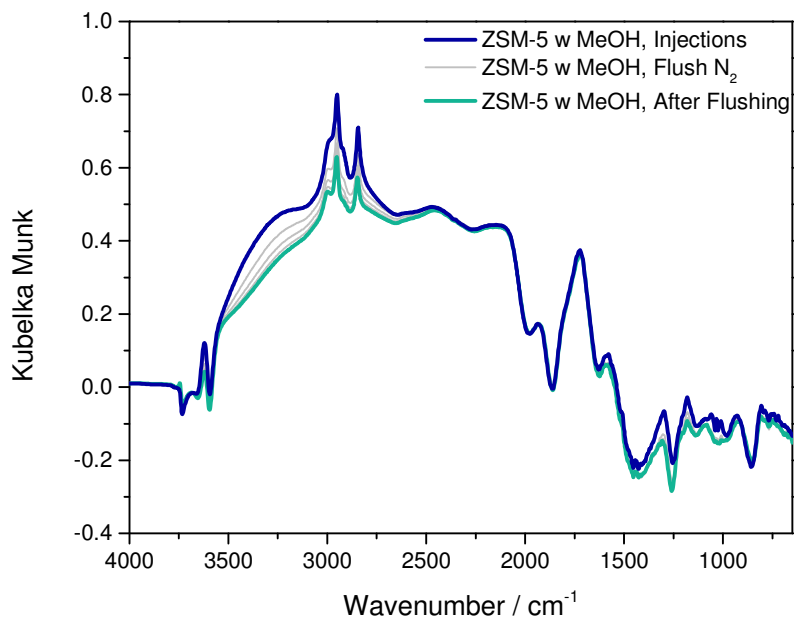


Figure S7: Difference spectra of Figure 2 (main text). Difference spectra made with ZSM-5 as the background.

Difference spectrum comparison with liquid methanol and vapour methanol The difference spectrum of the methanol injection spectrum minus the flushed spectrum after injection from Figure 2 in the main paper is seen in Figure S8. The difference spectrum is compared with the vapour and liquid spectrum of methanol. The liquid methanol spectrum was obtained from the NIST website².

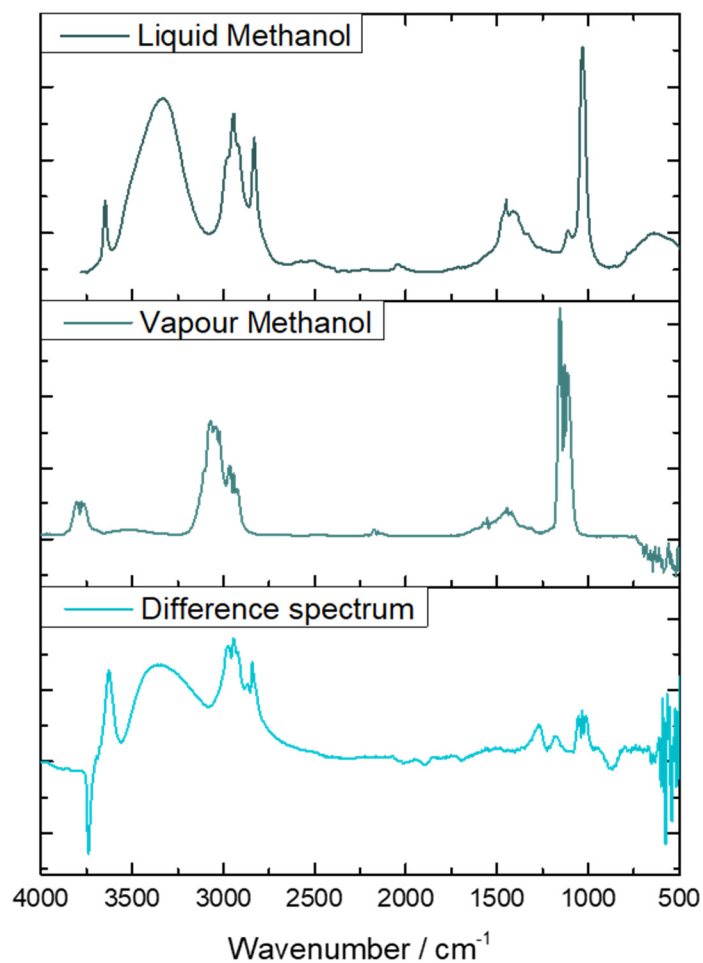


Figure S8: Difference spectrum of the methanol injection spectrum minus the flushed spectrum after injection. Liquid methanol spectrum² and vapour methanol spectrum are used for comparison purposes.

Crude Determination of Extinction Coefficient of OH stretch Vs CH stretch

A crude approximation of the difference in extinction coefficients between the OH stretch and the CH peaks is completed by integrating the area corresponding to each mode. The C-H region is between 3100 cm^{-1} – 2800 cm^{-1} whereas the rest of the intensity is assumed to be due to OH. When comparing the integrated area of the CH region (65.73) with the OH (1265.92), it is seen that OH is 19.26 larger than the CH integrated area.

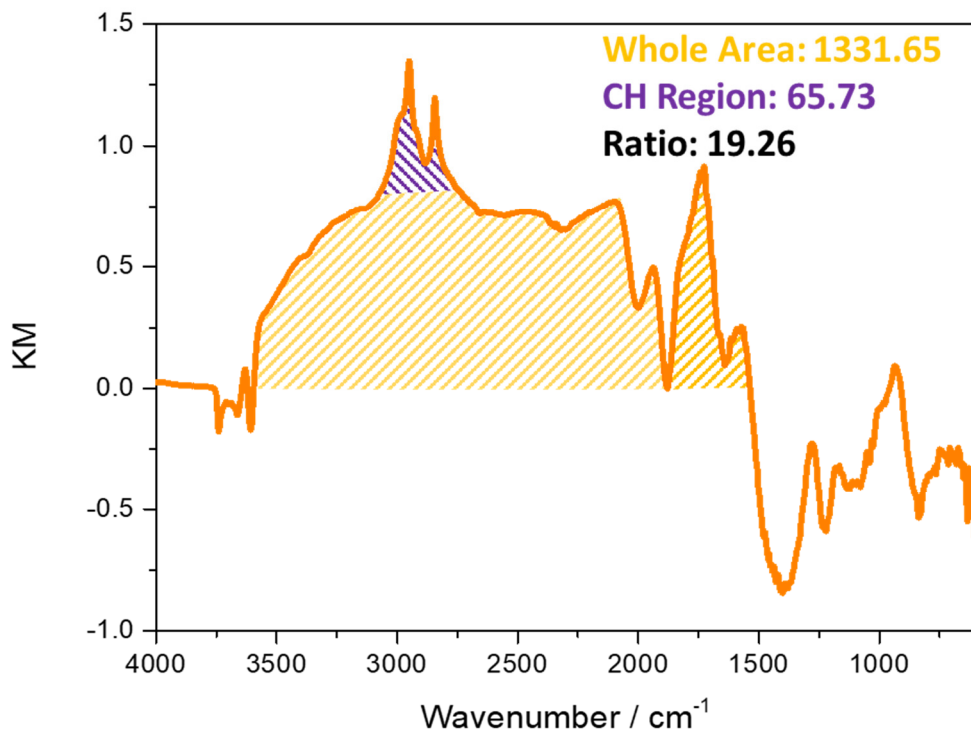


Figure S9: Spectrum of Injection 5, RT, Before Heat on Figure 5 (main text) with the integrated areas used in determining the extinction coefficients shaded in.

Figure 8 Expanded to lower wavenumbers

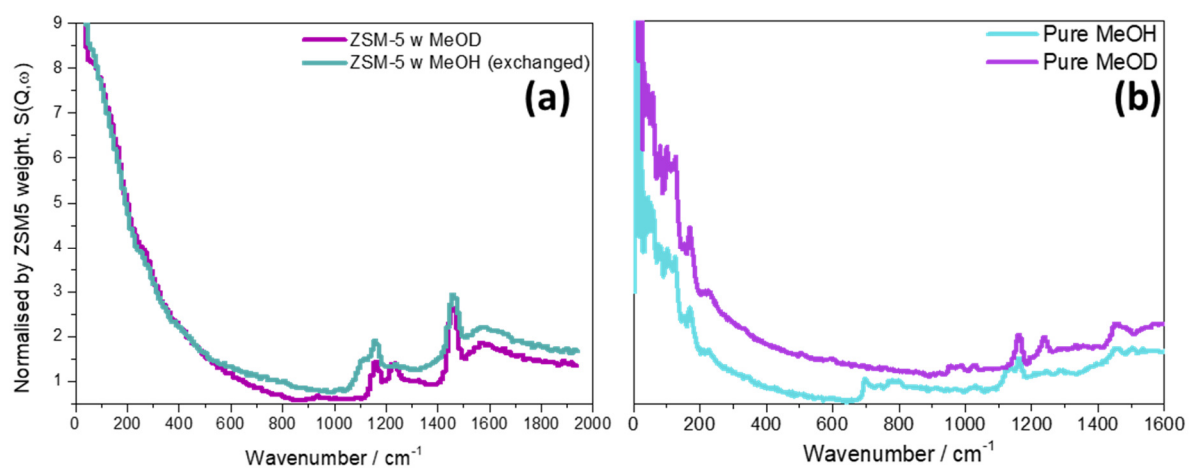


Figure S10: (a) Expanded range spectrum of Figure 8a from 0-2000 cm⁻¹ (b) Expanded range spectrum of Figure 8c in the main manuscript from 0-1600 cm⁻¹

References

- 1 F. L. Bleken, T. V. W. Janssens, S. Svelle and U. Olsbye, *Microporous Mesoporous Mater.*, 2012, **164**, 190–198.
- 2 <https://webbook.nist.gov/cgi/cbook.cgi?ID=C67561&Type=IR-SPEC&Index=2#IR-SPEC>