Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

EFFECTS OF CRYSTAL SIZE ON METHANOL TO HYDROCARBON CONVERSION OVER SINGLE CRYSTALS OF ZSM-5 STUDIED BY SYNCHROTRON INFRARED MICROSPECTROSCOPY

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S1 Characterisation

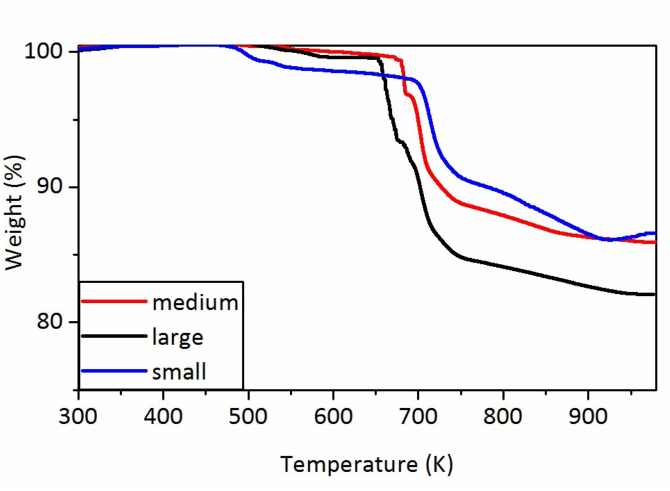

Fig. S1. Thermogravimetric (TGA) analysis of the ‘as-prepared’ ZSM-5 crystals.

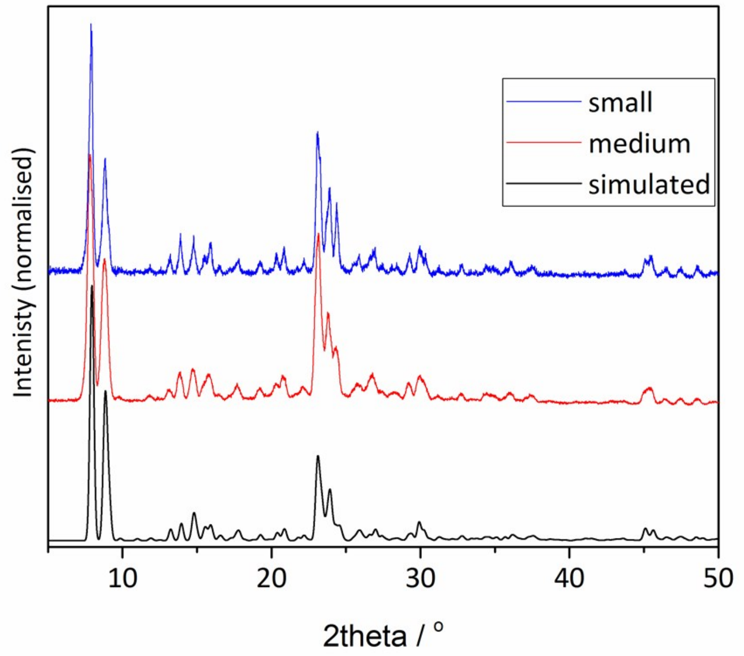

Fig. S2. Capillary XRD data of a calcined *medium* and *small* HZSM-5 crystal compared to the simulated pattern of HZSM-5 (Atlas structural data).

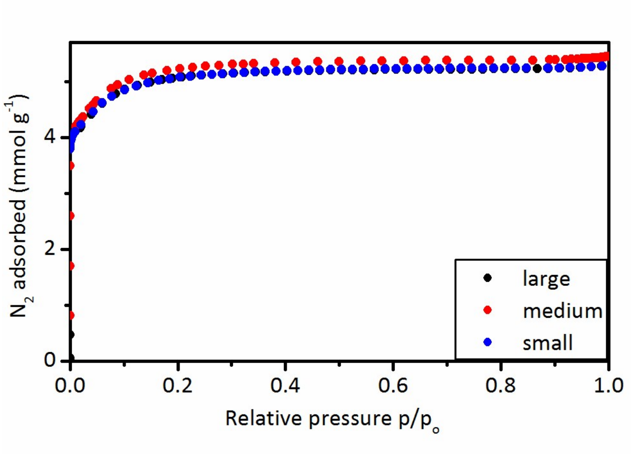

Fig. S3. Nitrogen physisorption on calcined HZSM-5 crystals at 77 K.

Table S1 CHN analysis of the three crystal sizes in their 'as-prepared' form.

wt.%	*Large*	*Medium*	*Small*
C	8.9	9.0	8.2
H	1.7	1.7	1.6
N	1.1	1.1	1.2
C/N	8.1	8.2	6.8

Table S2: Thermodesorption of ammonia (NH_3-TPD) with a gradual temperature increase from 383 K to 1073 K (10 K min^{-1}).

Sample ID	Total $NH_{3,des}$ / ±0.1 mmol g^{-1}	Concentration of strong acid sites [a] / ±0.1 mmol g^{-1}	HTP /°C
Small	1.2	0.8	390
Medium	1.5	0.8	420
Large	1.3	0.9	430

[a] Estimated from the area of the high-temperature peak.

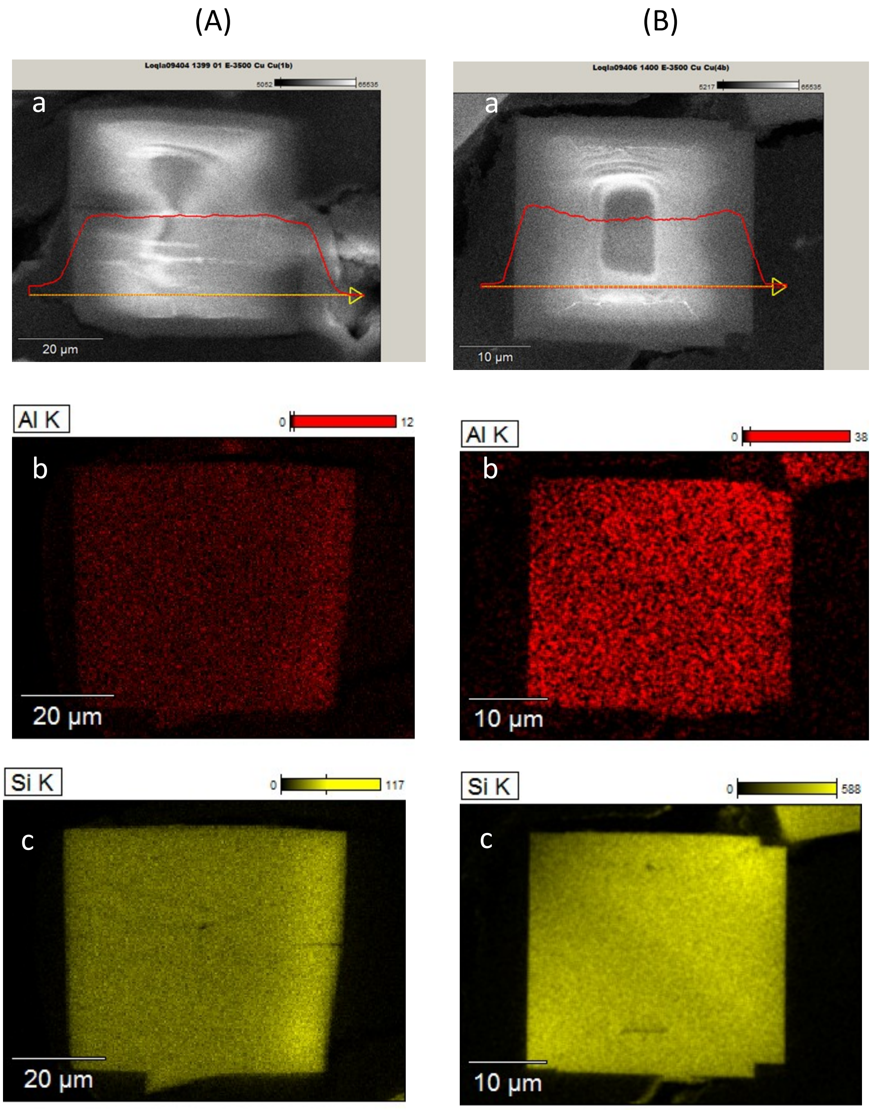

Fig. S4. Electron microprobe analysis across a cleaved HZSM-5 crystal (A) *medium* and (B) *small* where (a) red line follows the quantity of Al across the inner core of the crystal; (b) Al and (c) Si compositional maps across the cleaved HZSM-5 crystal are also shown.

S2 IR spectra of activated zeolite crystals.

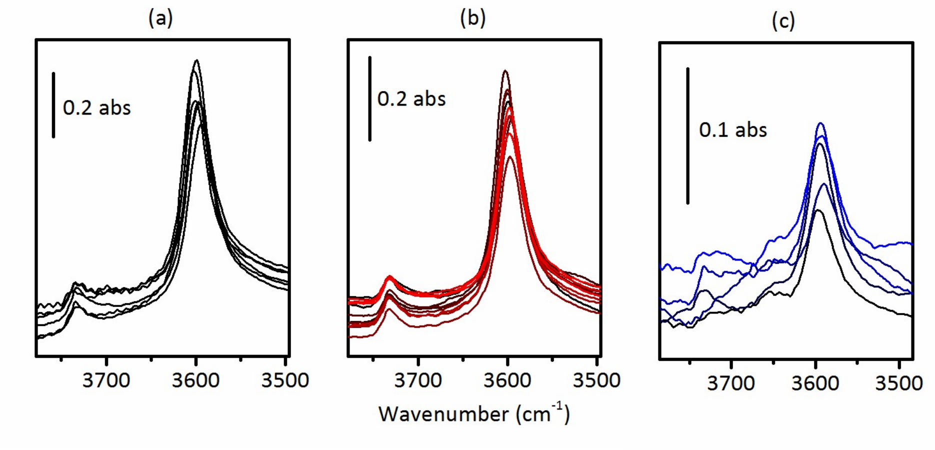

Fig. S5. Uniformity of OH bands (a) *large*; (b) *medium* and (c) *small* crystals. Spectra were measured from different crystals in each batch and different orientations of crystals.

S3 Methanol pulses

At 523 K, methanol is reacting over the acid site of HZSM-5 to form surface methoxy species (SMS) which then methylate further methanol molecules to form dimethylether. What is observed is the transformation of the initially hydrogen bonded methanol to dimethylether with an immediate loss of the Brønsted acid ν(OH) band at 3600 cm^{-1} and appearance of broad ABC triplet and the 'Evans window' (Fig. S6).

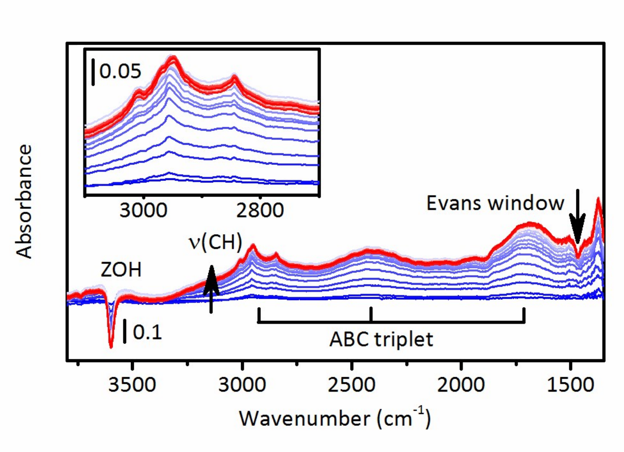

Fig. S6. Formation of H-bonded DME on *medium* HZSM-5 crystal at 523 K following injection of an 8 µL pulse of methanol. Infrared difference spectra during the first 60 s, at 2 s intervals (the colour change from blue to red is made after ~30 s).

The so-called ABC triplet has been extensively discussed in the literature[1,2] and arises from Fermi resonance between the ν(OH) modes of the zeolite hydroxyl groups hydrogen bonded to methanol/dimethylether and overtones of the corresponding OH deformation modes. The mass spectral analysis of the gas phase products during this experiment shows immediate formation of dimethylether with m/z = 45 (the initial apparent growth and decline of m/z = 41 signal is due to an ion source fragment of dimethylether (Fig. S7a). In the trailing edge of each pulse, dimethylether is desorbed from the crystals and the Brønsted acid ν(OH) band at 3600 cm^{-1} is partial recovered (Fig. S7b). By the time the third methanol pulse is injected, very little hydrogen bonded dimethylether remains adsorbed on the crystal (Fig. S7c). In the ν(CH) region the four bands of adsorbed bonded dimethylether (red trace in Fig. S7c), are progressively reduced in intensity and the 2980 cm^{-1} of SMS becomes increasingly evident as the dimethylether bands are reduced (orange trace in Fig. S7c). At around 1040 s, a small burst of propene is detected in the gas phase (Fig. S7a) and the zeolite hydroxyl groups are further recovered (Fig. S7b) due to the loss of bound SMS (2980, 2870 cm^{-1}), and new bands appear in the CH stretching region (Fig. S7c), which we assign to oligomeric cations (2960, 2870 cm^{-1}). Also, we note that no carbonyl bands are observed during the reaction of methoxy groups in the low frequency region (Fig. S7c).

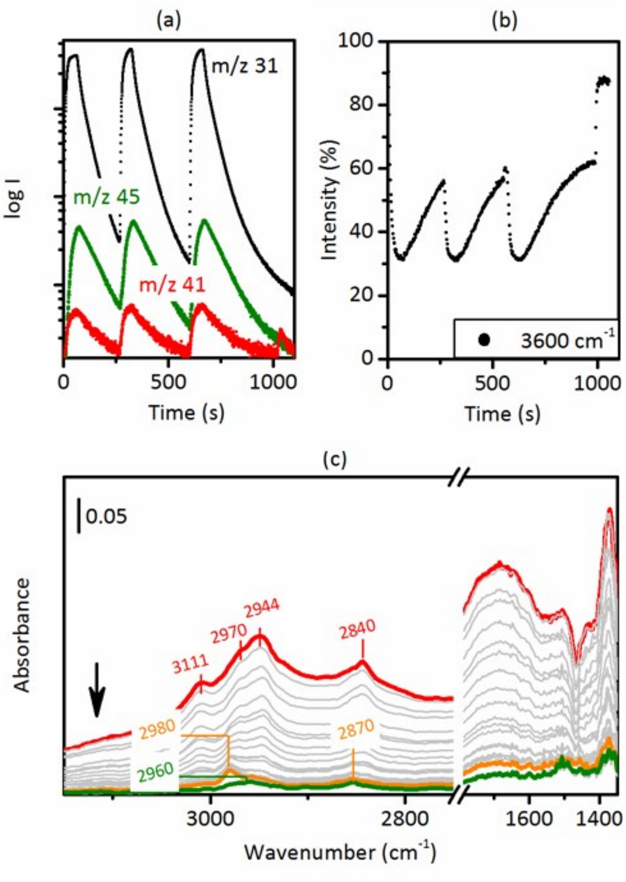

Fig.S7. (a) Mass spectral traces recorded during three 8 µL pulses of methanol into a N_2 flow of 100 mL min^{-1} over *medium* crystal of HZSM-5 at 523 K; (b) Time course of the zeolite hydroxyl ν(OH) 3600 cm^{-1} band intensity relative to an activated crystal recorded at 2 s intervals during these experiments and (c) difference IR spectra in the CH region.

The burst of propene, observed in the trailing edge of the third methanol pulse over the *medium* HZSM-5 crystal at 523 K, is explained by the deprotonation of methoxy groups to form olefins via ‘carbene-like’ species[3] and does not arise from reaction of dimethylether with methoxy groups. Once alkenes are generated from methoxy groups directly, they can either escape the zeolite as gaseous products or oligomerise on the acid site as evident by the new band at 2960 cm^{-1}. The oligomeric species formed in

HZSM-5 are not stable on the acid site of the zeolite and over time the oligomeric hydrocarbons cracks back down to alkenes. Some of the oligomer can also cyclise on the acid site of the zeolite to form cyclopentenyl cations. In all crystal sizes studied, oligomeric hydrocarbon species are observed immediately after the loss of methoxy groups at the end of the induction period.

References

1. Zecchina, A.; Bordiga, S.; Spoto, G.; Scarano, D.; Spono, G.; Geo-baldo, F. IR Spectroscopy of Neutral and Ionic Hydrogen Bonded Complexes from Interaction of CH_3OH, C_2H_5OH, $(CH_3)_2O$, $(C_2H_5)_2O$ and C_4H_8O with H-Y, HZSM-5 and Hmordenite: Comparison with Analogous Adducts Formed on the H-Nafion Superacidic Membrane. *J. Chem. Soc. Farad. Trans.* 1996, **92**, 4863-4875.
2. Bordiga, S.; Lamberti, C.; Bonino, F.; Travert, A.; Thibault-Starzyk, F. Probing Zeolites by Vibrational Spectroscopy, *Chem. Soc. Rev*. 2015, **44**, 7262-7341.
3. I. B. Minova, S. K. Matam, A. Greenaway, C. R. A. Catlow, M. D. Frogley, G. Cinque, P. A. Wright and R. F. Howe, Elementary Steps in the Formation of Hydrocarbons from Surface Methoxy Groups in HZSM-5 Seen by Synchrotron Infrared Microspectroscopy, *ACS Catal.,* 2019, **9**, 6564–6570.