

Electronic Supplementary Information (ESI)
Valorisation of 2,5-dimethylfuran over zeolite catalysts studied
by on-line FTIR-MS gas phase analysis

Christopher Sauer^{‡a}, Anders Lorén^b, Andreas Schaefer^a, and Per-Anders Carlsson^{*a}

^aDepartment of Chemistry and Chemical Engineering, Chalmers University of
Technology, SE-412 96 Gothenburg, Sweden.

^bDepartment of Chemistry and Materials, RISE Research Institutes of Sweden, SE-501
15 Borås, Sweden.

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sauerc@chalmers.se[‡]
per-anders.carlsson@chalmers.se^{*}
phone: +46 (0)31 772 2924
fax: +46 (0)31 160 062

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The ESI contains the flow scheme of the catalytic flow reactor experiments (fig. S1). A schematic description of the catalytic flow reactor can be found in a previous work (SI).[Anal. Chem. 2021, 93, 39, 13187–13195]. The schematic description of the experimental setup during *in situ* IR experiments (DRIFTS) is shown in fig. S2.

Catalyst characterisation for the four samples H-BEA(37), Cu-ZSM-5(22), H-ZSM-5(38) and H-ZSM-5(355) was performed. N_2 -isotherms are shown in fig. S4, X-ray powder diffractograms in fig. S3, chemical analyses by XRF in table S1, NH_3 -TPD in fig. S5. 2,5-dimethylfuran-TPD under oxidative conditions are shown in fig. S6; here the desorbing species are "carbon equivalents" mostly in the form of CO and CO_2 as shown by the continuous lines. The dashed lines include other desorbing species such as small amounts of 2,5-dmf, olefins and btx as described in the online analysis in the main article. Figure S7 shows desorbing species after 2,5-dmf-adsorption in Ar, without the presence of oxygen.

IR spectra of the product stream during online analysis for Cu-ZSM5 SAR(22) and H-ZSM5(355) and its residual (fig. S9) as well as concentration profiles of water, CO and CO_2 (fig. S10) and 2-methylfuran, formaldehyde and methane fig. S11 during the step responses of zeolite exposure to 2,5-dmf are included.

Background subtracted *in situ* IR spectra of during TPD of 2,5-dmf and conversion species from different zeolites are found in figs. S13 to S15.

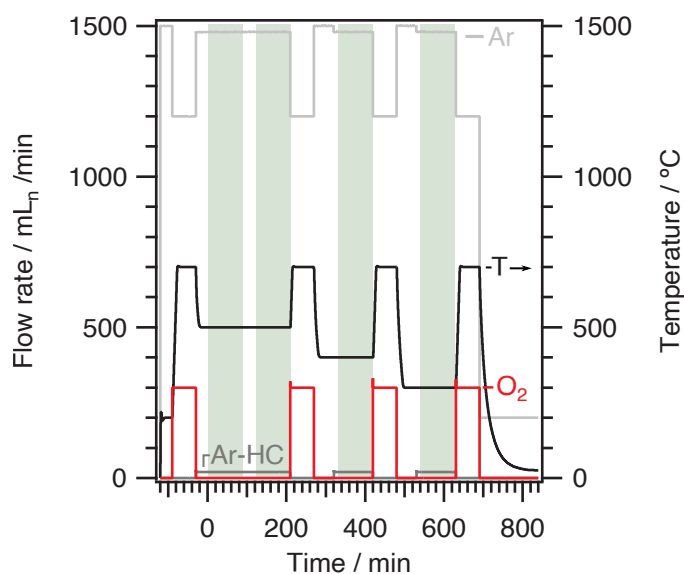


Figure S1: Flowchart of the catalytic experiments. The hydrocarbon stream (HC) of 2,5-dimethylfuran enters the catalytic reactor in 90 min durations as displayed by the solid bars. The gas flow rates are given in mL_n/min at normal conditions.

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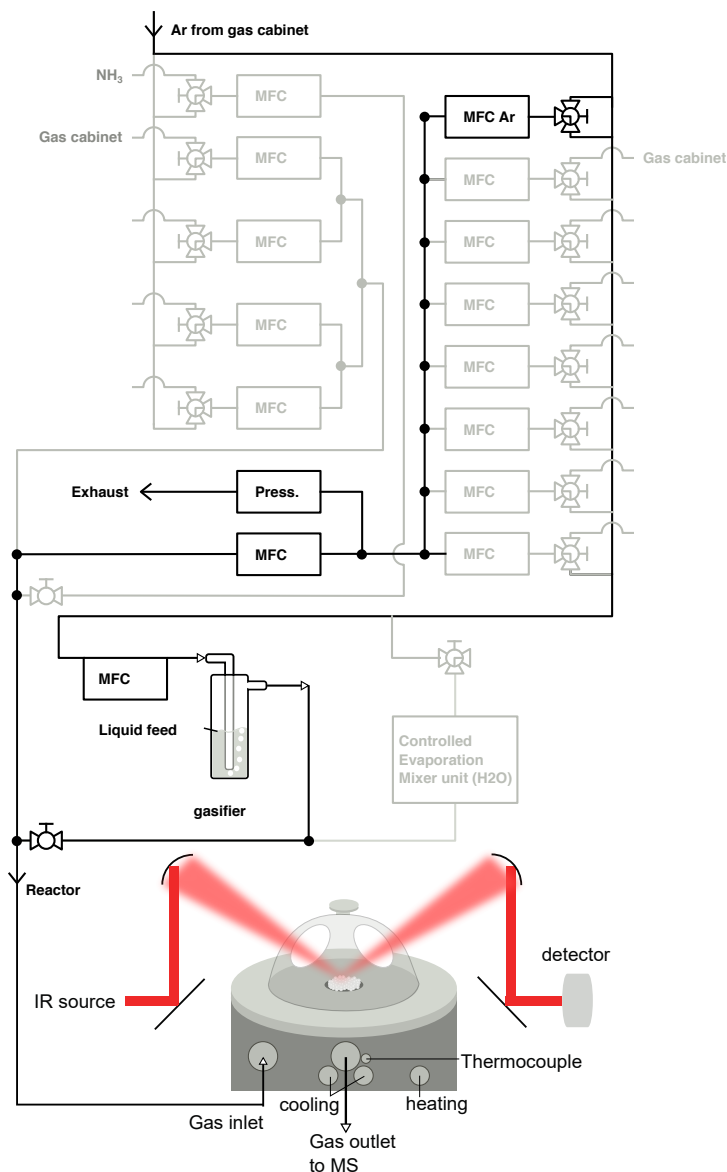


Figure S2: Instrumental setup during DRIFTS experiments. Parts that are greyed out are not used during this work. MFCs control the gas flows to a the reactor cell, which is equipped with a Praying mantis diffuse reflectance accessory and a stainless steel high-temperature reactor cell (Harrick Scientific Products Inc.) with CaF_2 windows, thermocouple, heating and cooling. Its outlet is connected to the MS.

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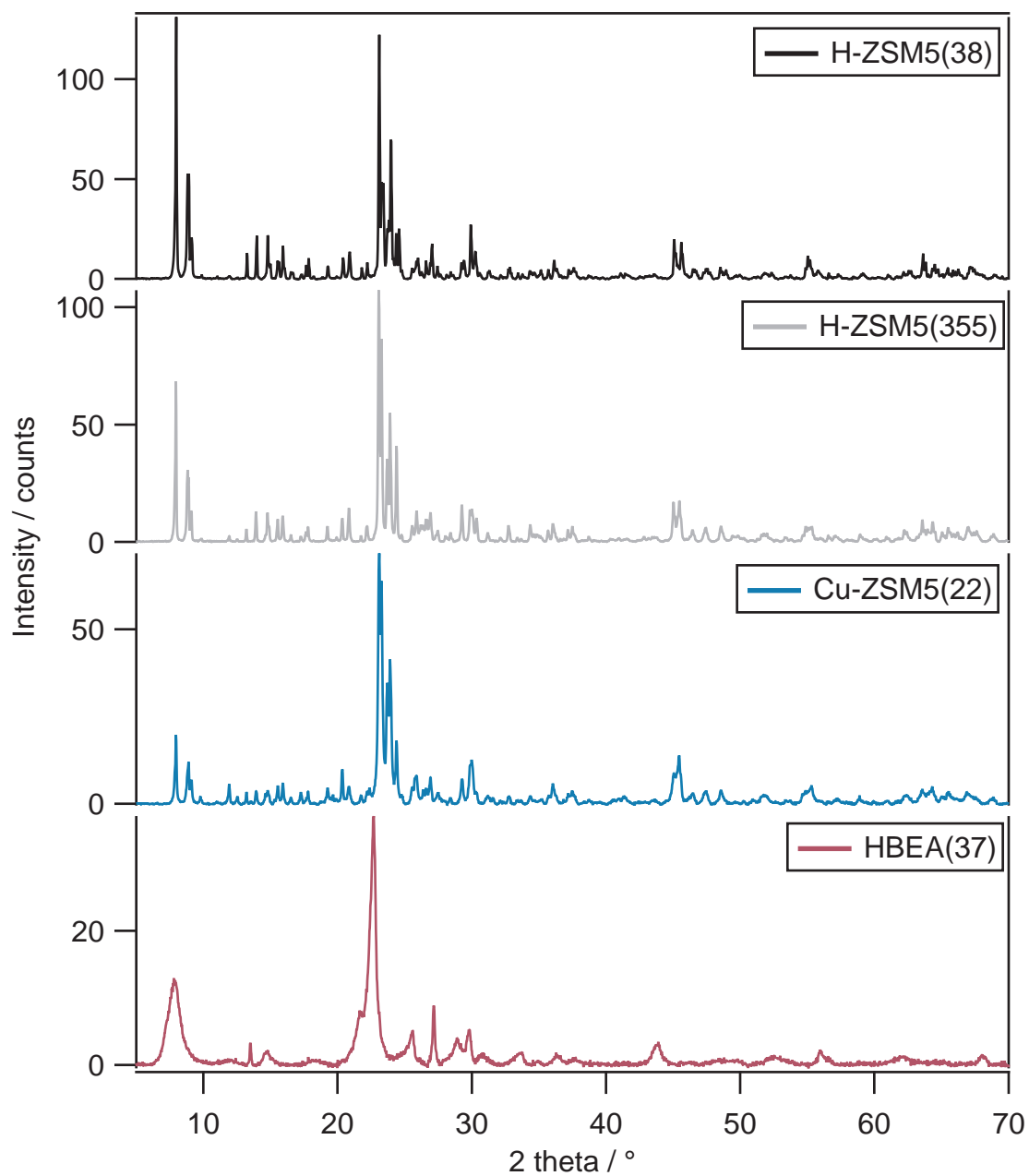


Figure S3: X-ray diffractograms for the four catalytic samples.

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Table S1: Chemical analyses by XRF

sample	SiO ₂ /Al ₂ O ₃	Cu %	Zr	Fe /ppm	Ti	Ca
H-BEA(37)	37	-	250	580		
H-ZSM-5(355)	355	-	123	375	207	236
H-ZSM-5(38)	38	-	158	775	376	
Cu-ZSM-5(22)	22	2.8	74	506	291	

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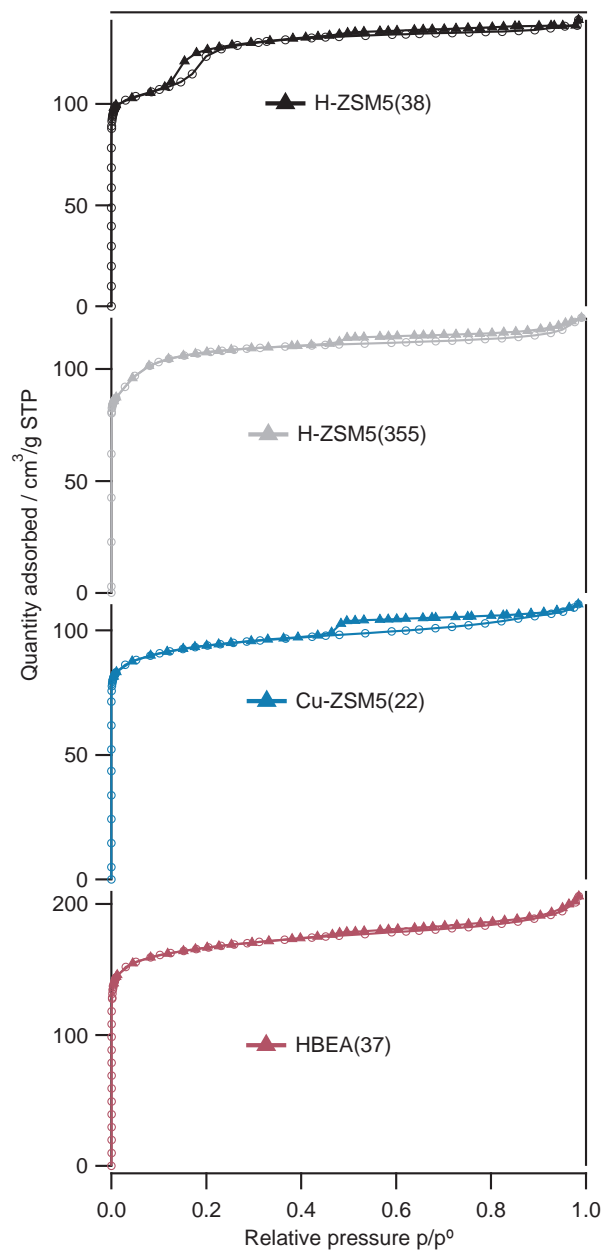


Figure S4: N_2 -sorption isotherms at 77K of the four catalytic samples. Adsorption: circles; desorption: filled triangles.

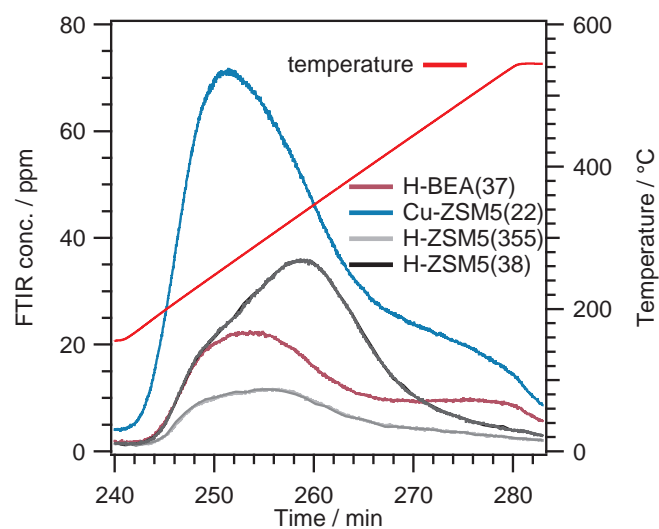


Figure S5: NH_3 -TPD profiles of the four catalytic samples between 150 °C to 550 °C. Conditions: Temperature ramp 10 °C min⁻¹, total flow 1500 mL_n/min, Ar balance.

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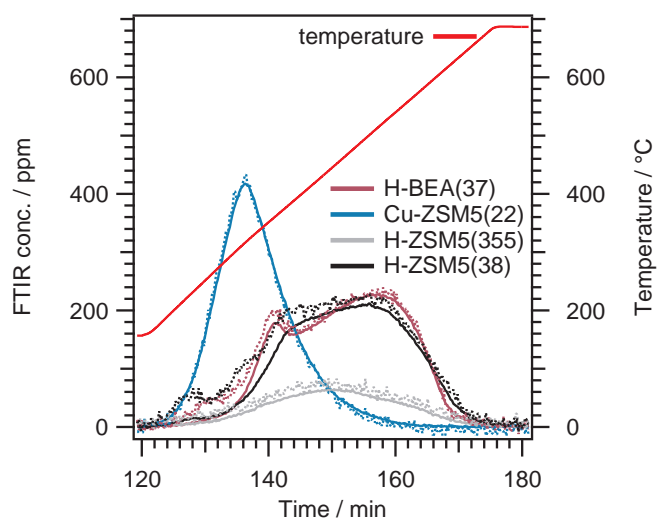


Figure S6: TPD profiles of "carbon equivalents" for the four catalytic samples between 150 °C to 700 °C. Continuous lines show the combined signal of CO and CO₂, while dashed lines show the sum of all detected compounds (as in table 2 of the main article) using the online analysis. Conditions: Temperature ramp 10 °C min⁻¹, total flow 1500 mL_n/min, 20% O₂, Ar balance.

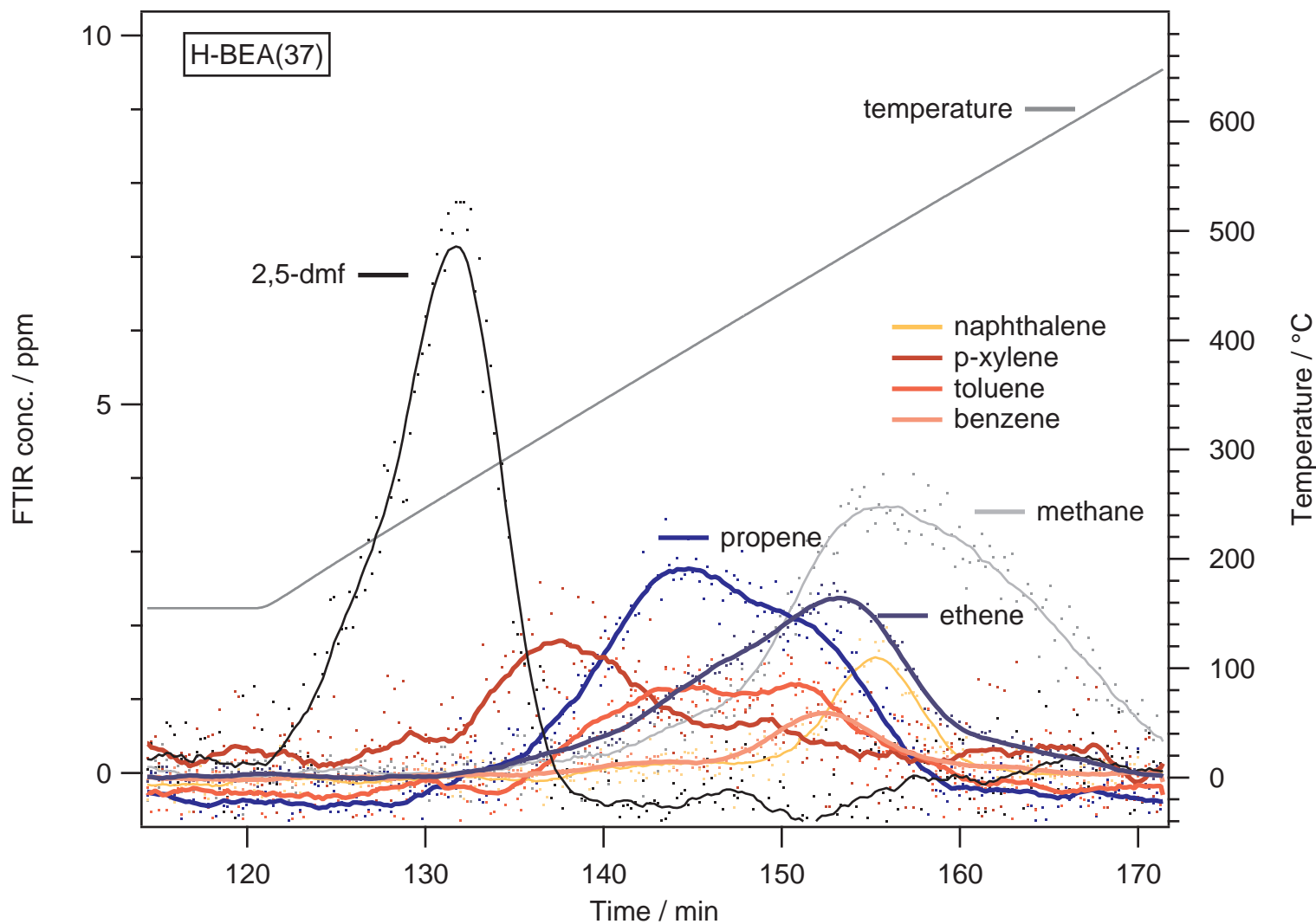


Figure S7: TPD profiles of species for the H-BEA(37) sample between 150 °C to 700 °C. Continuous lines show the smoothed signal, while dots show measured data. Conditions: Temperature ramp 10 °C min⁻¹, total flow 1500 mL_n/min, no O₂, Ar balance.

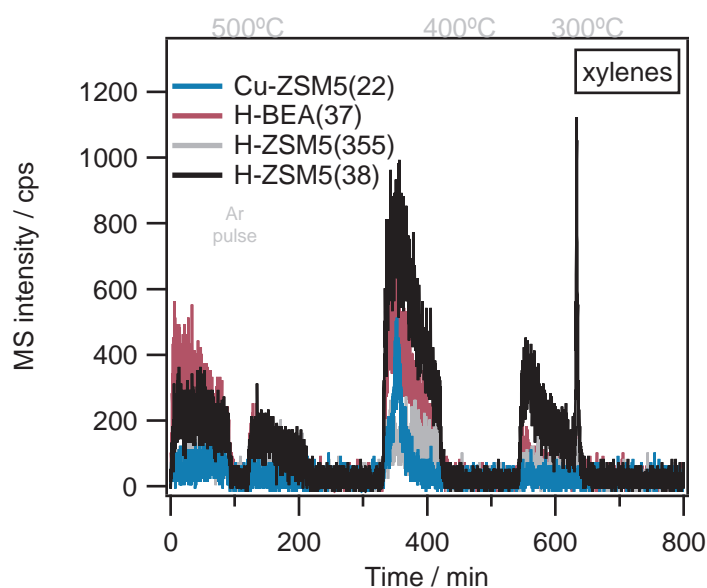


Figure S8: MS signal of xylenes ($m/z = 106$) during 2,5-dmf step response measurements over zeolite catalysts at temperatures 500 °C, 400 °C and 300 °C

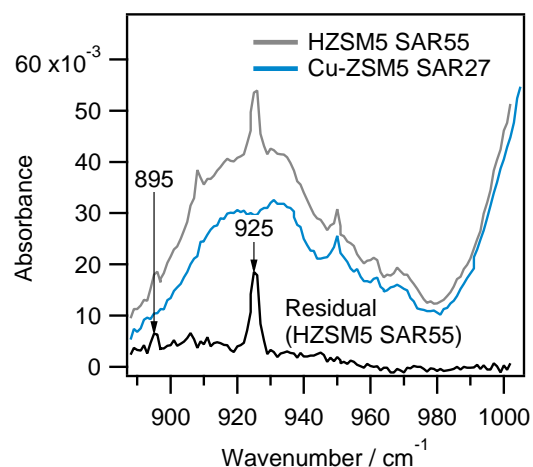


Figure S9: Infrared spectrum of the gaseous product stream during the online analysis for samples H-ZSM-5(355) and Cu-ZSM-5(22). The residual after analysis for H-ZSM-5(355) shows unidentified species with bands at 895 cm^{-1} and 926 cm^{-1} , that are not observed for the Cu-sample.

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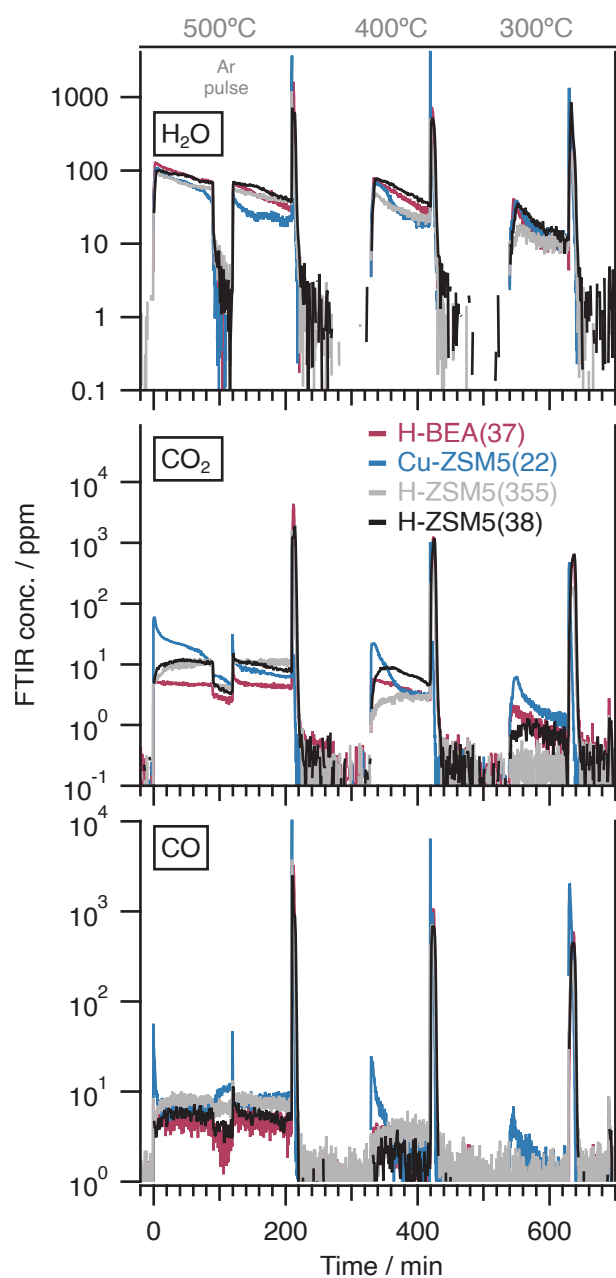


Figure S10: Concentration profiles of water, CO and CO_2 as determined by online FTIR during 2,5-dmf step response measurements over zeolite catalysts at temperatures 500 °C, 400 °C and 300 °C .

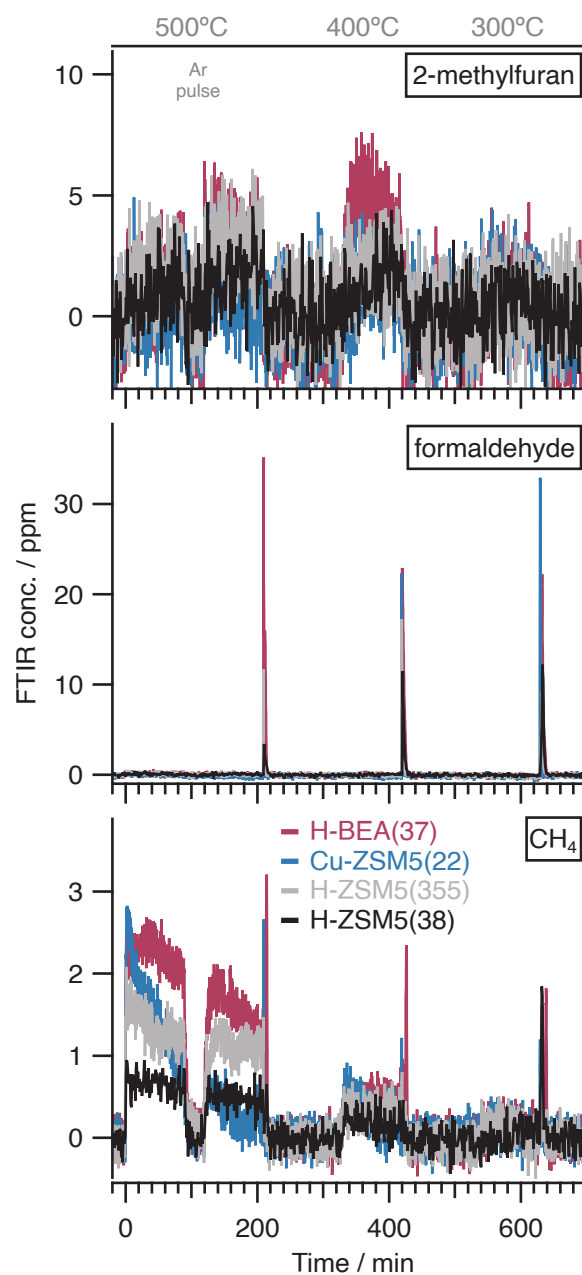


Figure S11: Concentration profiles of 2-methylfuran, formaldehyde and methane as determined by online FTIR during 2,5-dmf step response measurements over zeolite catalysts at temperatures 500 °C, 400 °C and 300 °C .

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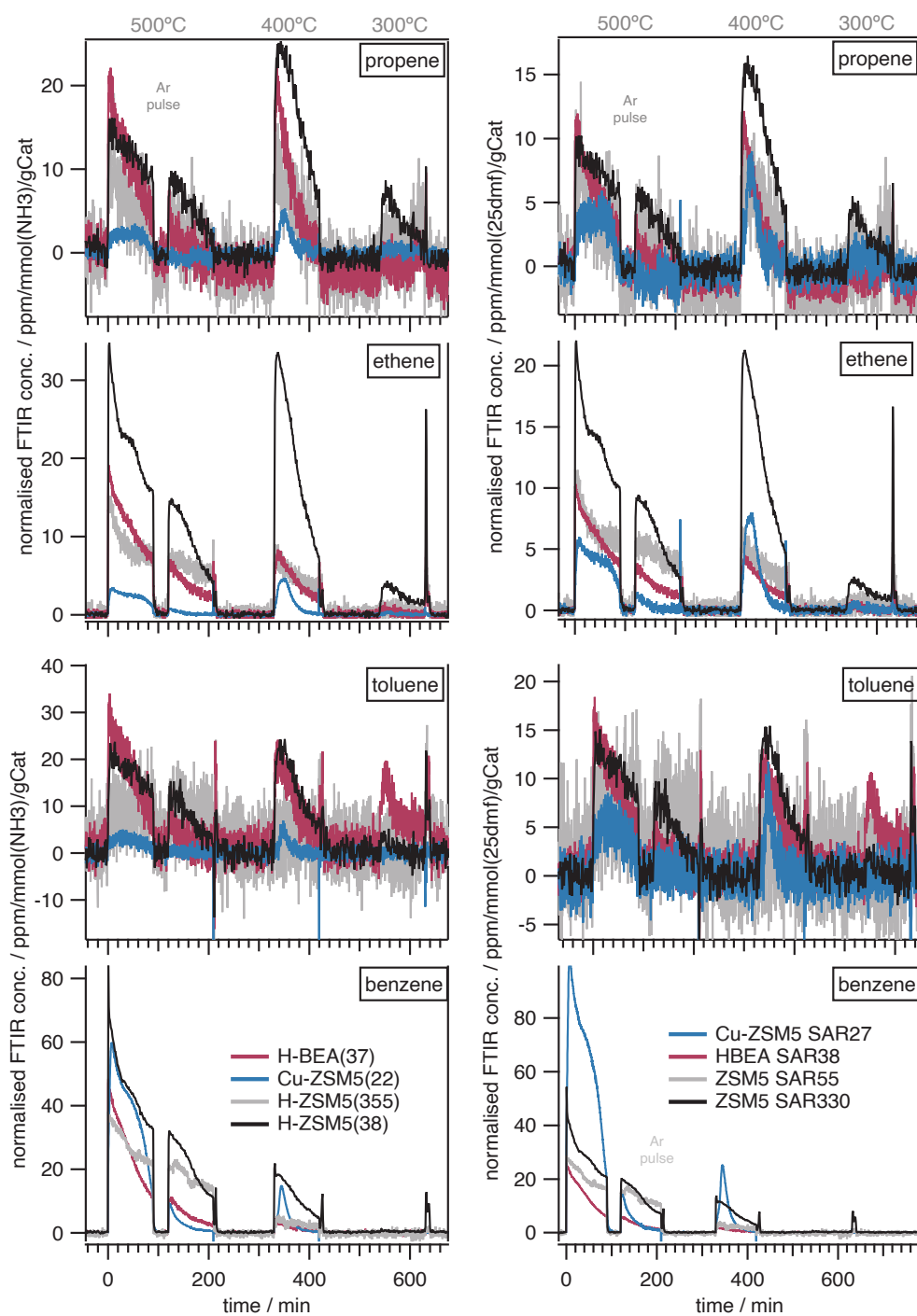


Figure S12: FTIR signal normalised to the amount of acid sites determined by NH₃ (left) and 2,5-dimethylfuran adsorption sites (right) for ethene, propene, toluene and benzene.

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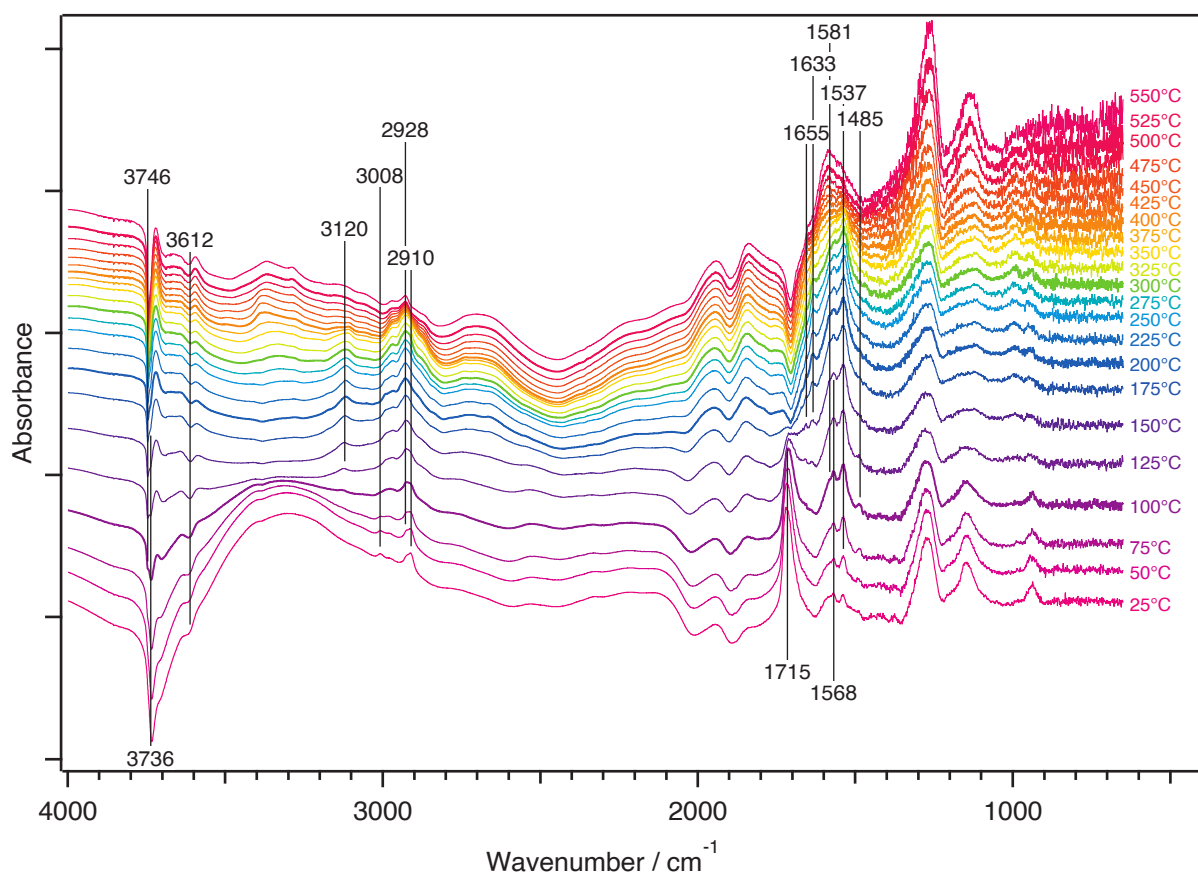


Figure S13: Background subtracted *in situ* IR spectra of TPD of 2,5-dmf and H-BEA(37).

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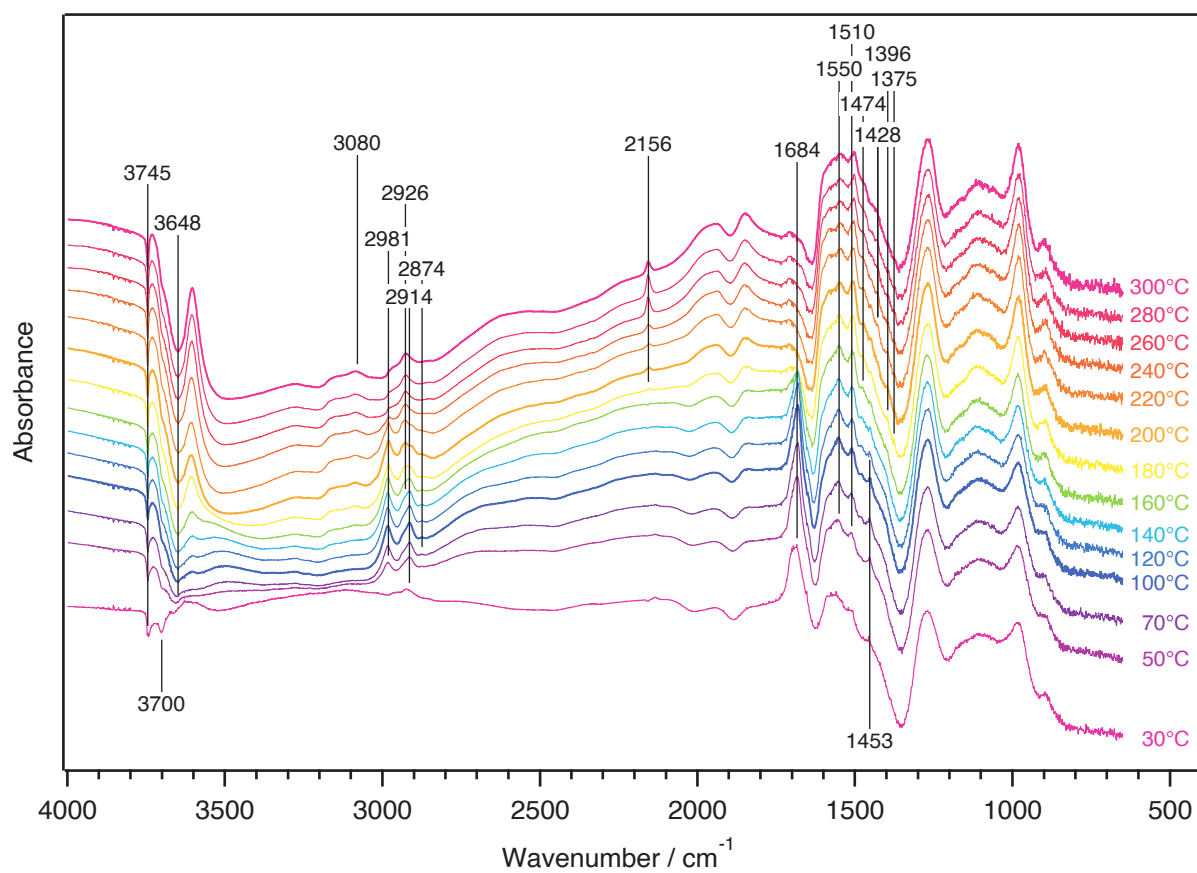


Figure S14: Background subtracted *in situ* IR spectra of TPD of 2,5-dmf and Cu-ZSM-5(22).

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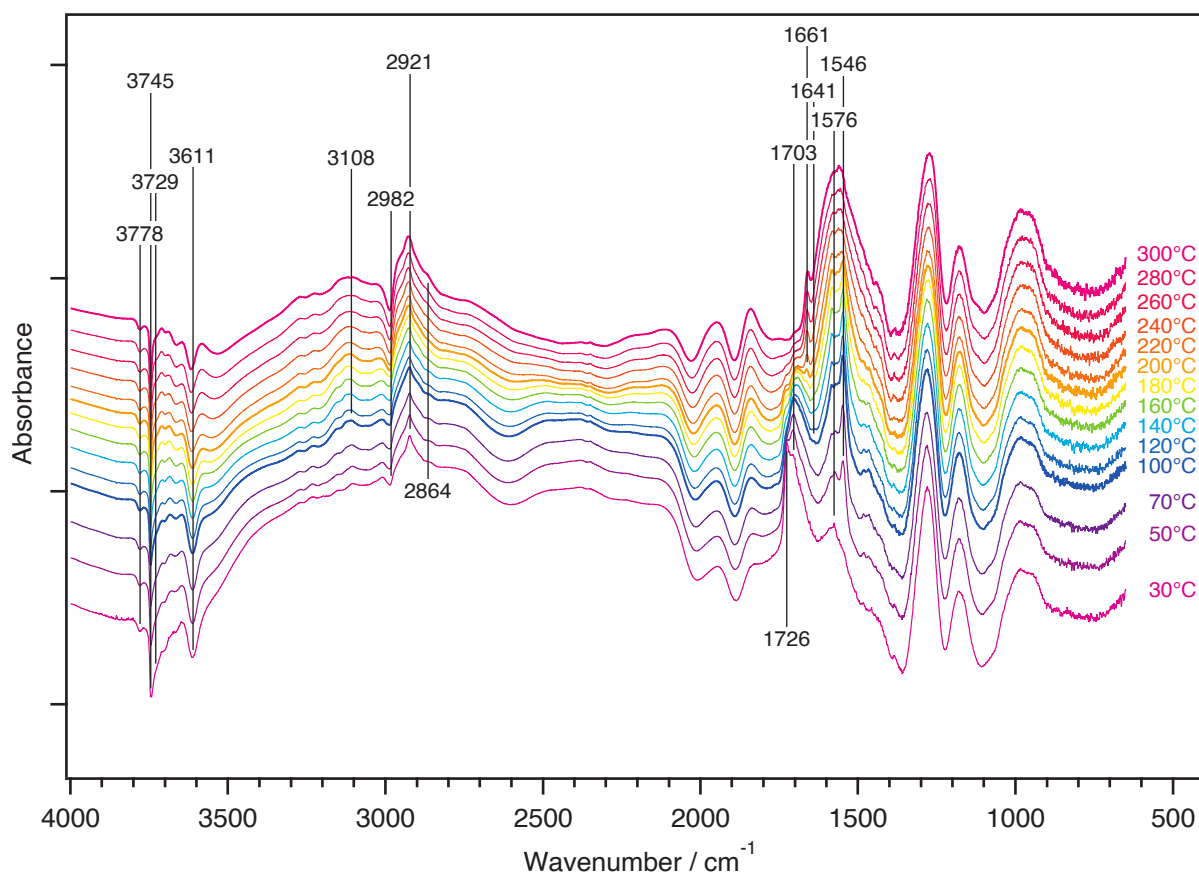


Figure S15: Background subtracted *in situ* IR spectra of TPD of 2,5-dmf and H-ZSM-5(22).