Electronic Supplementary Information (ESI) Isomorphous Substitution of Gallium into MFI-Framework Zeolite Increases 2,5-Dimethylfuran to Aromatics Selectivity and Suppresses Catalyst Deactivation

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Electronic Supplementary Information

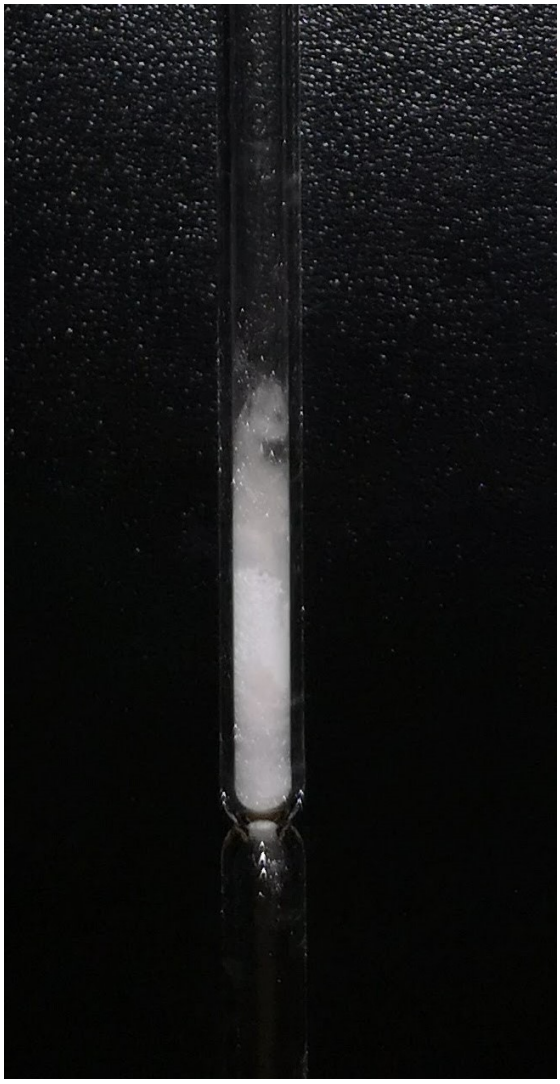

Figure S1: Catalyst powder (300 µm to 355 µm) held between two quartz wool plugs in a quartz tube (ID: 4 mm)

Table S1: Information about the analyzed molecules of the gas stream. The m/z values are those used in the MS analysis. Xe = 12.13 eV (for CO (28), CO_2 (44), O_2 (33), Ar (40)) or Hg = 10.44 eV (rest) as ionizers. Based on a previously described method [3] with additions and adaptions.

Compound	Formula	m/z	IR band /cm^{-1}
Other rings			
2-methylnaphthalene	$C_{11}H_{10}$	142	785.38 – 831.18
Naphthalene	$C_{10}H_8$	128	758.62 – 807.32
Indene	C_9H_8	116	2811.26 – 3176.23
2-methyl-CPO	C_6H_8O	(96), 68	1668.88 – 1809.90
3-methyl-CPO	C_6H_8O	(96), 68	1701.42 – 1811.83
Furans			
2,5-dimethylfuran	C_6H_8O	96, (81)	1168.43 – 1282.69
2,4-dimethylfuran	C_6H_8O	(96), 68	1074.17 – 1174.70
2-methylfuran	C_5H_6O	(81)	1117.57 – 1176.87
BTX			
Benzene	C_6H_6	78	606.51 – 726.80
Toluene	C_7H_8	92	689.44 – 769.95
o-xylene	C_8H_{10}	106	702.45 – 779.59
p-xylene	C_8H_{10}	106	735.32 – 867.92
Olefins			
Ethene	C_2H_4	(28), 27	900.12 – 1000.16
Propene	C_3H_6	42, (41)	900.61 – 1019.69
1,3-butadiene	C_4H_6	(54), 39	822.26 – 977.02
C1			
Methane	CH_4	-	3000.25 – 3176.23
Carbonmonoxide	CO	28	2146.16 – 2159.90
Carbondioxide	CO_2	44	2223.57 – 2280.94
Formaldehyde	CH_2O	(30)	2698.93 – 2822.36
Water	H_2O	18	1416.97 – 1502.31
Ammonia	NH_3	16	903.98 – 977.27

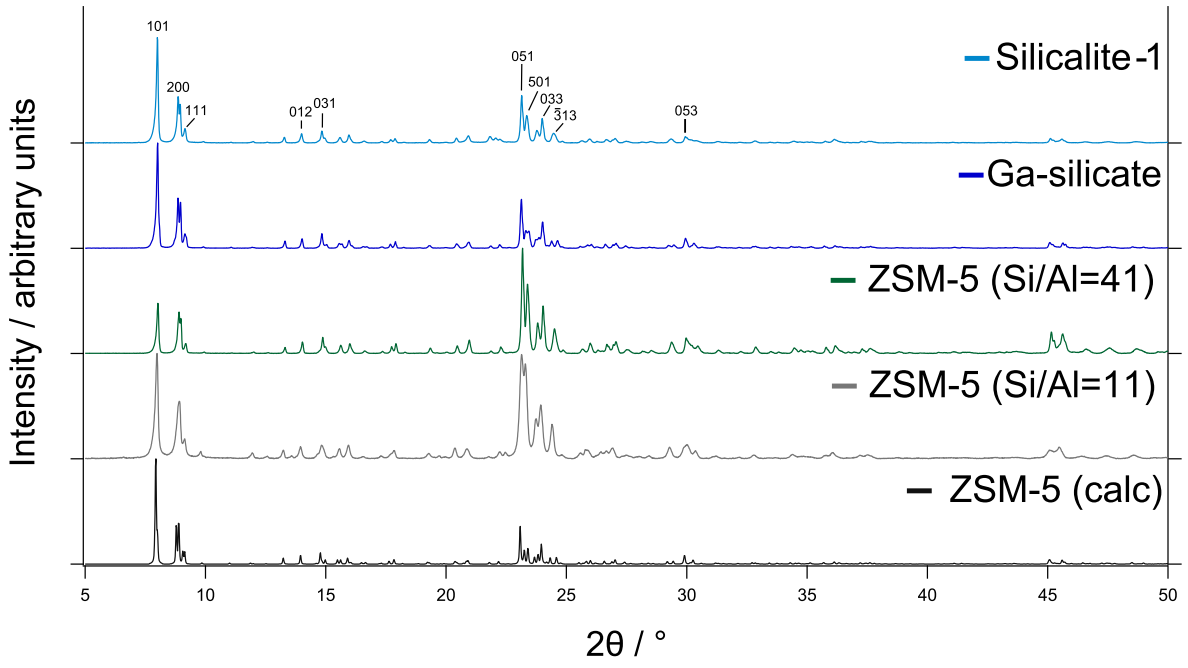

Figure S2: X-Ray diffractogram patterns of the synthesized zeolites. Including a calculated pattern of H-ZSM-5 using crystal data and Pseudo-Voigt for the peak shape.[1, 2]

Table S2: Chemical analyses by XRF. Water content determined by TGA at 200 °C. All other elements are normalized to a total weight percentage of 100. M = Al, Ga.

sample	Si/M	Al	Ga	O	H_2O	Na	S	K	Ti	Fe	Zr	Ca
					/wt%							
Silicalite-1	-	0	0	53.6	0.880	0.313	0	0.101	0	0	0	0
Ga-Silicate	33	0.043	3.23	52.9	0.274	0	0	0	0	0	0	0.013
ZSM-5(41)	41	1.04	0	54.3	3.35	0	0	0	0	0	0	0
ZSM-5(11)	11	3.49	0	56.1	7.15	0	0.011	0	0.020	0.058	0.007	0

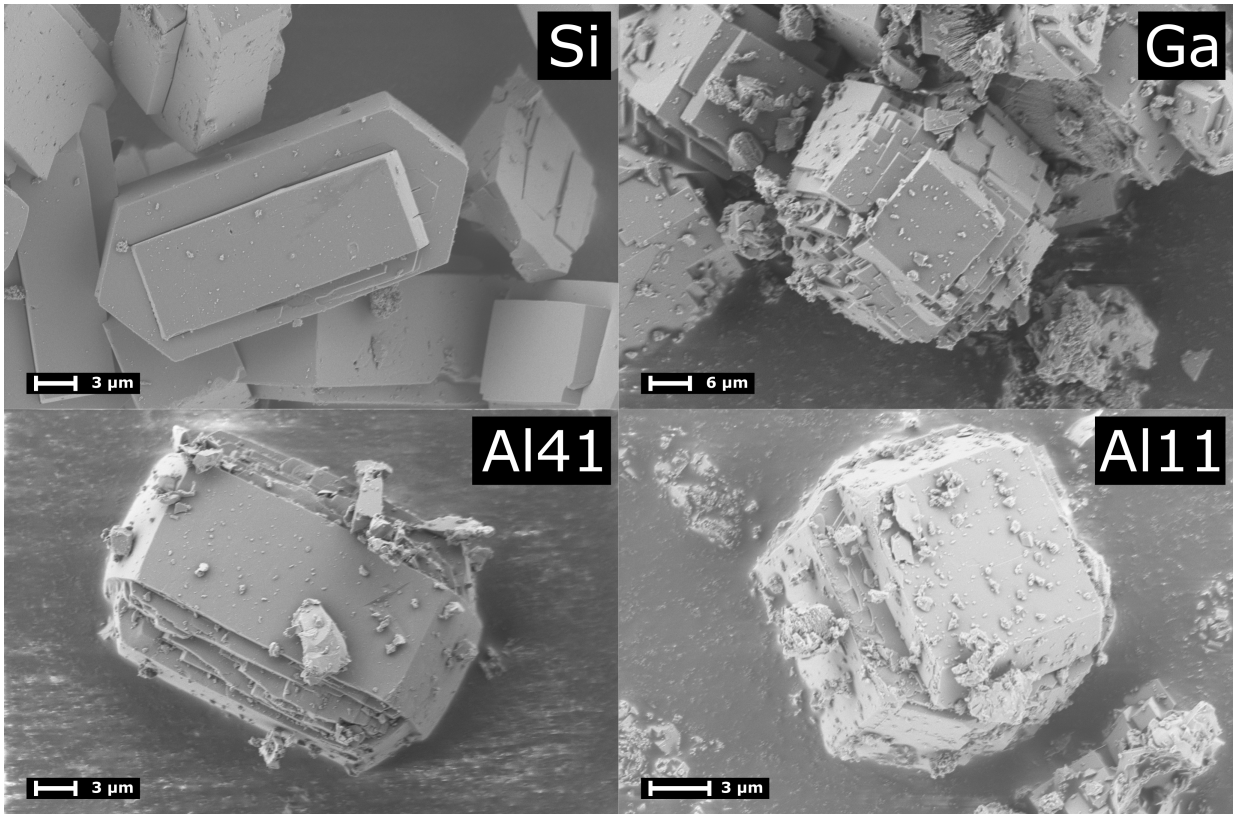

Figure S3: SEM images of Silicalite-1 (top left), Ga-silicate (top right), H-ZSM-5 (Si/Al=41, bottom left), and H-ZSM-5 (Si/Al=11, bottom right). Images were taken with an SE2 detector at an accelerating voltage of 1.5 kV.

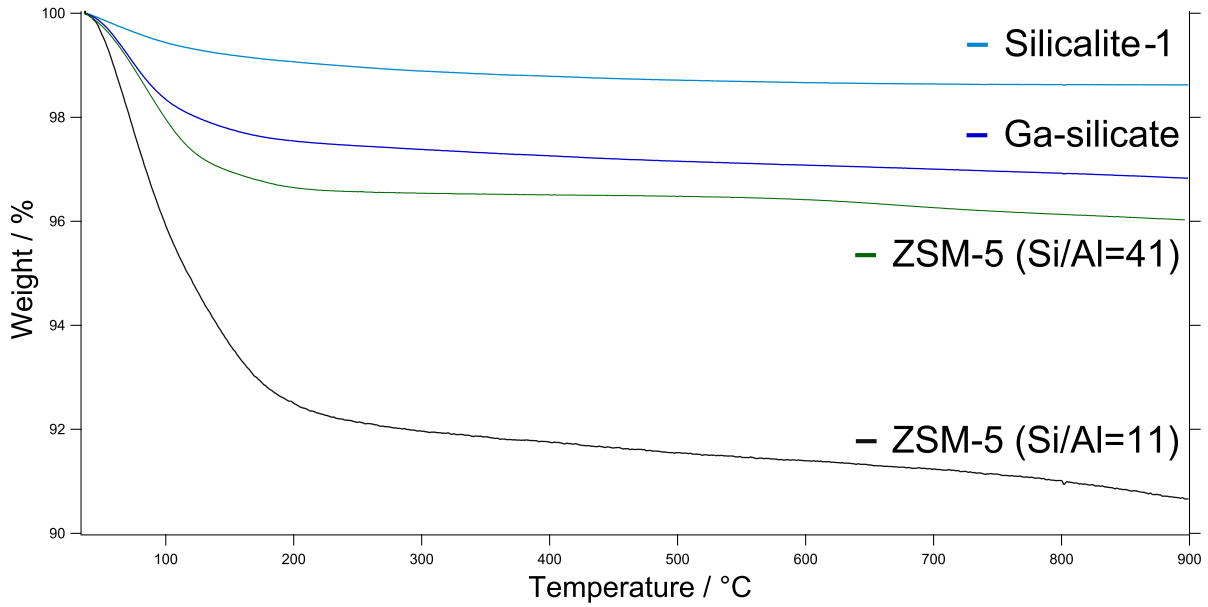

Figure S4: TGA profiles of Silicalite-1, Ga-silicate and ZSM-5 over a temperature range of 30 °C to 900 °C with a heating rate of 10 °C min^{-1}, in 60 mL min^{-1} air flow.

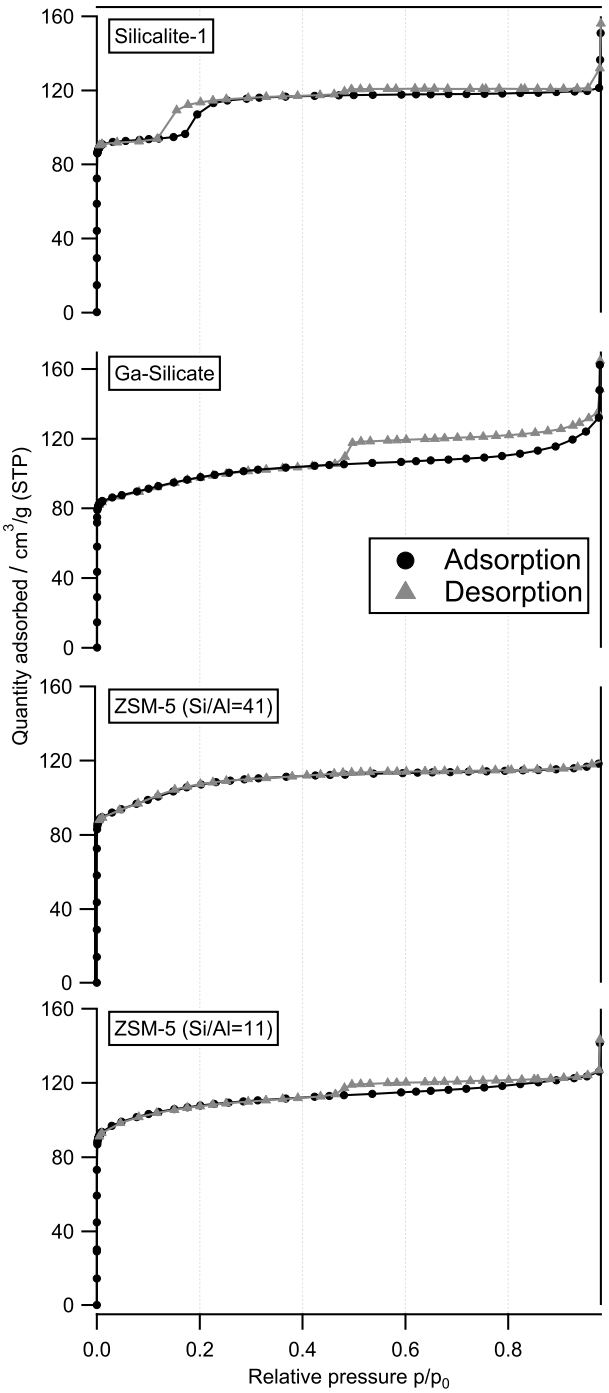

Figure S5: N_2-sorption isotherms at 77K of the catalyst samples. Adsorption: circles; desorption: triangles.

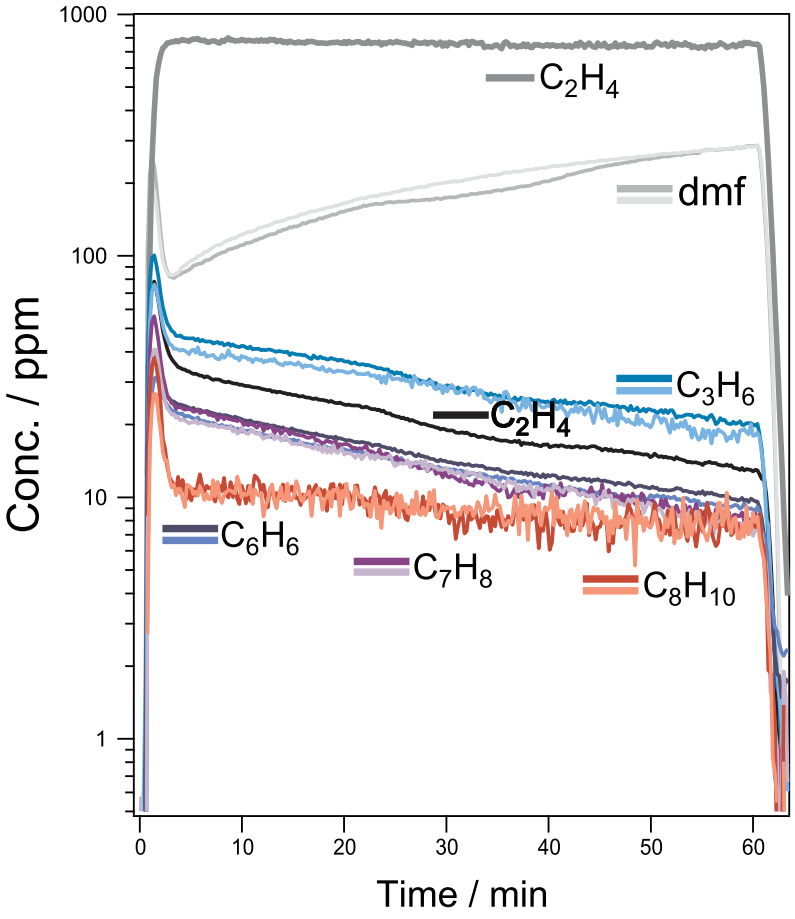

Figure S6: FTIR intensity profiles of ethene (C_2H_4, dark gray), propene (C_3H_6, light blue), toluene (C_7H_8, purple), benzene (C_6H_6, dark blue), xylenes (C_8H_{10}, red), and dimethylfuran (gray) during 60 min step response experiments, once without (dark color) and once with (light color) additional ethene feed (730 ppm). Feed: 800 ppm 2,5-dmf, 400 °C, catalyst: 68.8 mg Ga-silicate.

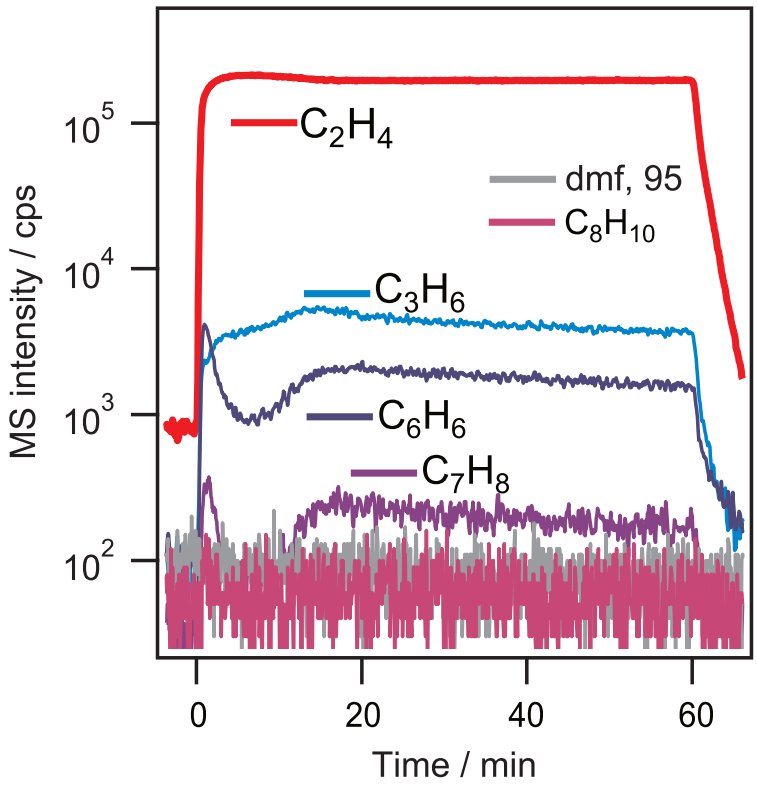

Figure S7: MS intensity profiles of ethene, propene, benzene, toluene, xylenes and dimethylfuran during a 60 min step response experiment of ethene (730 ppm) over 68.8 mg Ga-silicate (500 °C).

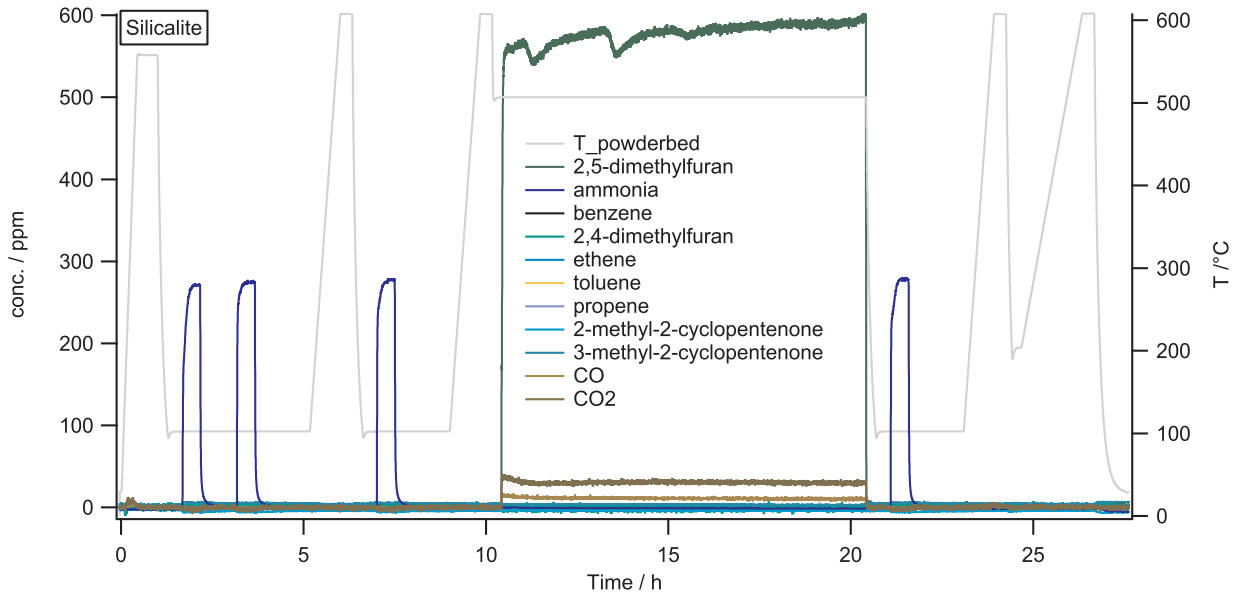

Figure S8: Concentration profiles of the reactant and various products during NH_3-TPD, 10 h step response experiment of 600 ppm 2,5-dimethylfuran and TPO over 60.8 mg Silicalite-1.

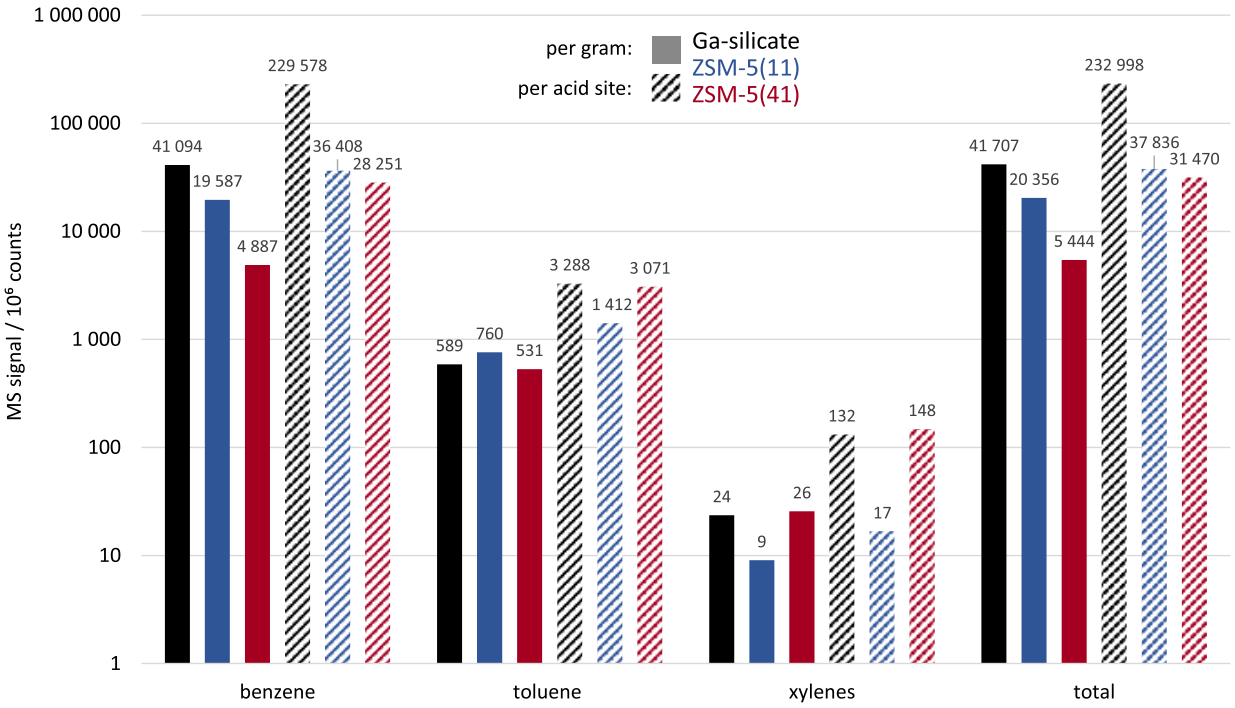

Figure S9: MS intensity signals of benzene, toluene, and xylenes during a 10h catalytic experiment normalized to amount of catalyst per gram (solid fill) and normalized to amount of acid sites (striped fill) for Ga-silicate (black), ZSM-5(11) (blue) and ZSM-5(41) (red) samples. Conditions: after pretreatment in 20% O_2 at 550 °C and NH_3-TPD. Feed: 540 ppm 2,5-dimethylfuran, 500 °C, catalyst: 77.5 mg Ga-silicate, 65.6 mg ZSM-5(11) and 76.0 mg ZSM-5(41).

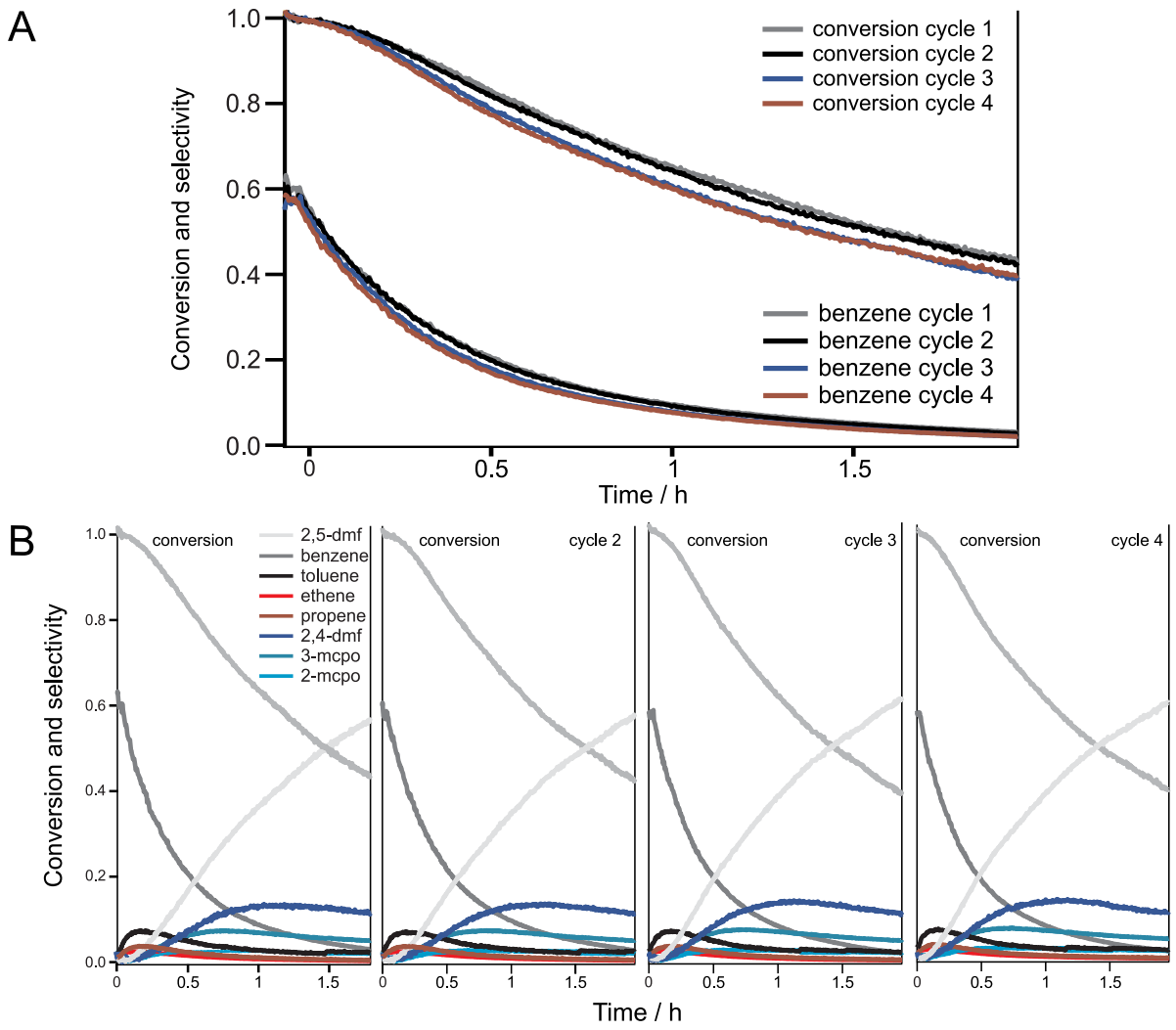

Figure S10: Conversion and selectivity of 2,5-dmf and benzene in Ga-silicate during four 2h cycles of at 500 °C, after an initial 10h experiment (A, top panel). Conversion and selectivity of 2,5-dmf, benzene, toluene, ethene, propene, 2,4-dmf, 3-mcpo, and 2-mcpo during each cycle (B, bottom panels). The catalyst was regenerated between each cycle at 608 °C (10 °C min^{-1}) for 1h in 20 % O_2. Note: the shown selectivities do not account for the carbon loss due to coking.

References

[1] Ch. Baerlocher and L.B. McCusker. *Database of Zeolite Structures*. URL: http://www.iza-structure.org/databases/.

[2] H. van Koningsveld, J. C. Jansen, and H. van Bekkum. "The monoclinic framework structure of zeolite H-ZSM-5. Comparison with the orthorhombic framework of as-synthesized ZSM-5". In: *Zeolites* 10.4 (Apr. 1990), pp. 235–242. ISSN: 0144-2449. DOI: 10.1016/0144-2449(94)90134-1.

[3] Christopher Sauer et al. "On-Line Composition Analysis of Complex Hydrocarbon Streams by Time-Resolved Fourier Transform Infrared Spectroscopy and Ion–Molecule Reaction Mass Spectrometry". In: *Analytical Chemistry* 93.39 (Oct. 2021), pp. 13187–13195. DOI: 10.1021/ACS.ANALCHEM.1C01929. URL: https://pubs.acs.org/doi/full/10.1021/acs.analchem.1c01929.