Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information to

Catalytic conversion of furanic compounds over Ga-modified ZSM-5 zeolites as a route to biomass-derived aromatics

Evgeny A. Uslamin,[1] Nikolay Kosinov,[1], Evgeny A. Pidko[1, †,]* and Emiel J.M. Hensen[1,]*

[1] Schuit Institute of Catalysis, Laboratory of Inorganic Materials Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

[†]Current address: Inorganic Systems Engineering group, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands

Corresponding author: E.J.M.H. (e.j.m.hensen@tue.nl); E.A.P. (e.a.pidko@tudelft.nl)

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Characterization of the catalysts

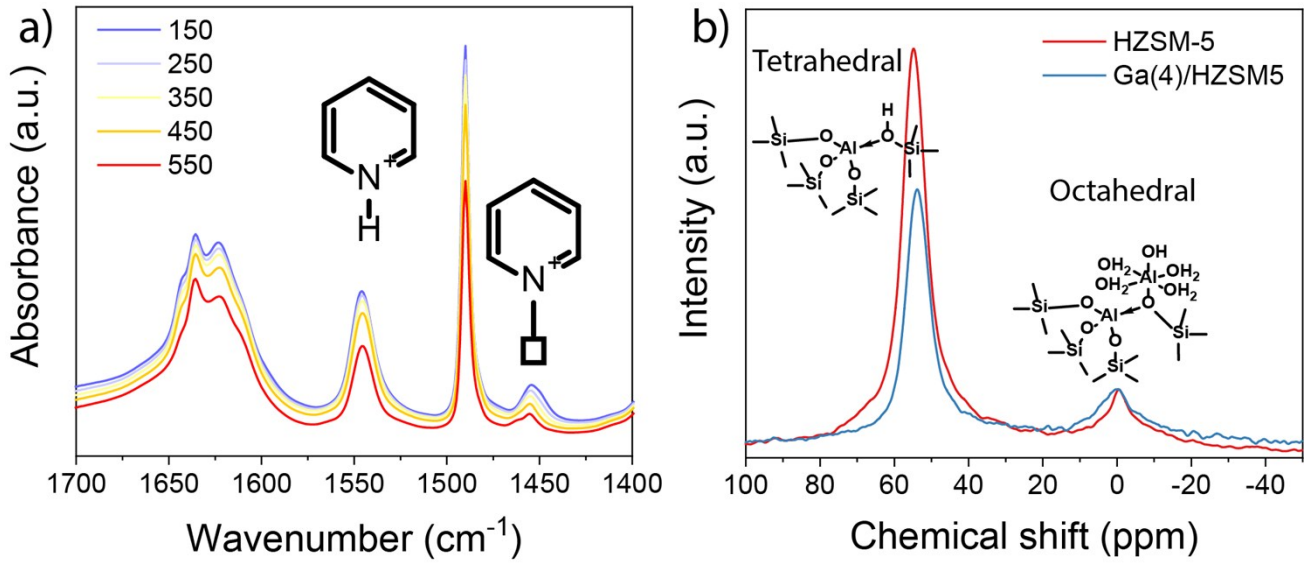

Figure S1. Acidic properties of starting HZSM-5 material: a) FTIR spectrum of pyridine adsorbed on HZSM-5 showing characteristic PyH^+ and PyLAS bands b) ^{27}Al MAS NMR spectra showing two shifts corresponding to tetrahedral and octahedral Al species.

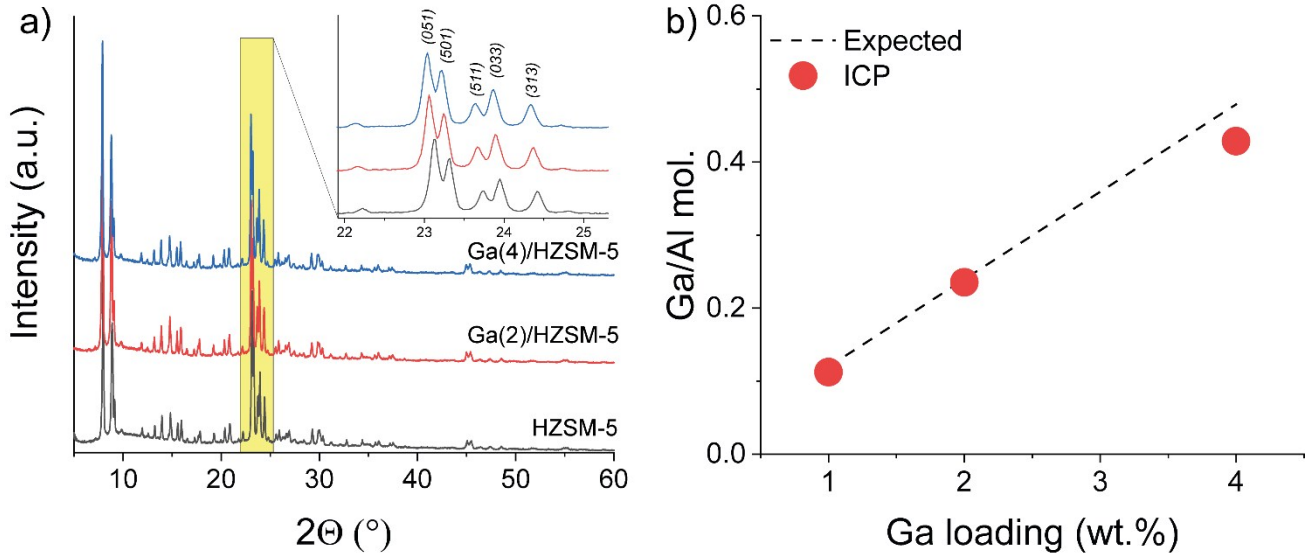

Figure S2. XRD crystallinity and chemical composition of Ga(x)/HZSM-5 samples: a) XRD patterns; b) content of Ga measured by ICP as compared with theoretical loading (dashed line)

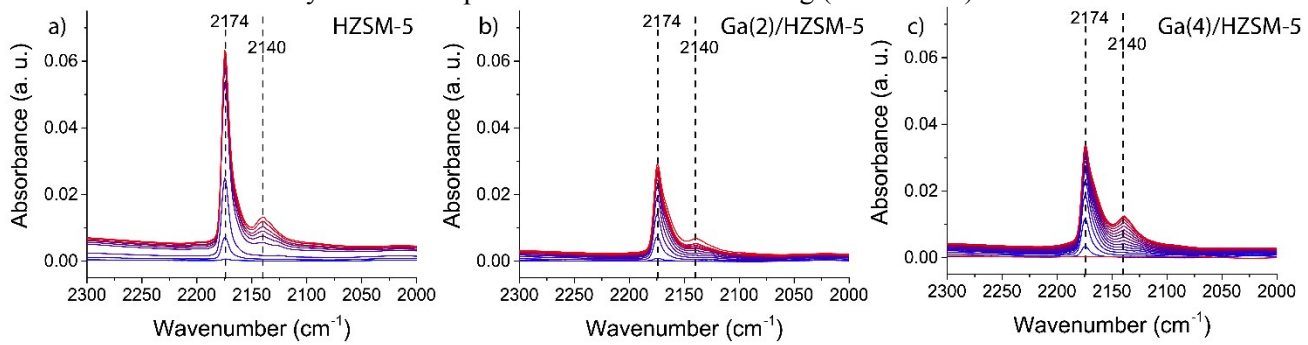

Figure S3. CO stretching region of FTIR spectrum of a) parent HZSM-5; b) Ga(2)/HZSM-5; c) Ga(4)/HZSM-5 under sequential dosing of CO at T = 77 K.

Catalytic measurements

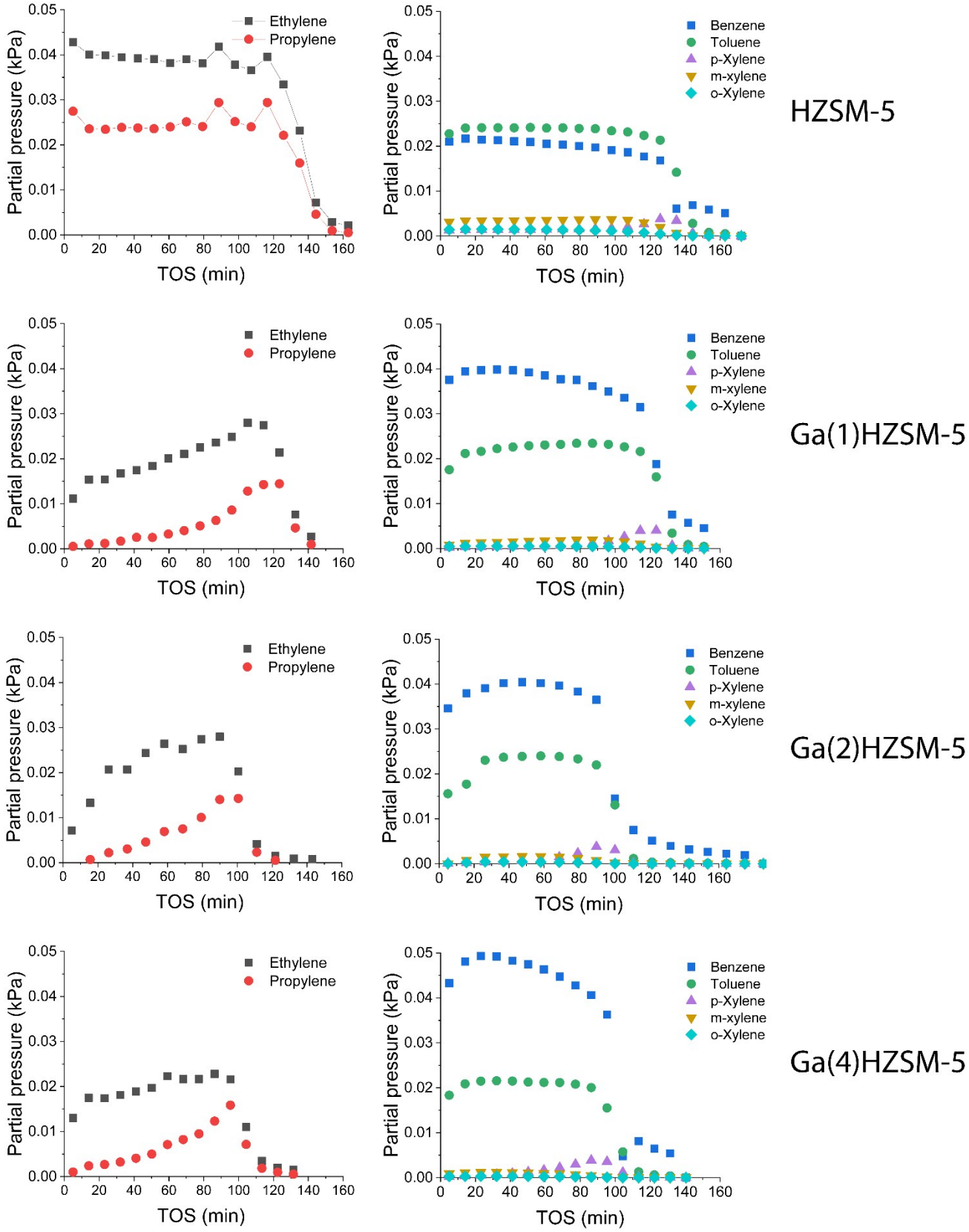

Figure S4. Evolution of the main reaction products including light hydrocarbons (left column) and aromatics (right column) during conversion of 2,5-dMF over HZSM-5 and Ga(x)/HZSM-5 catalysts.

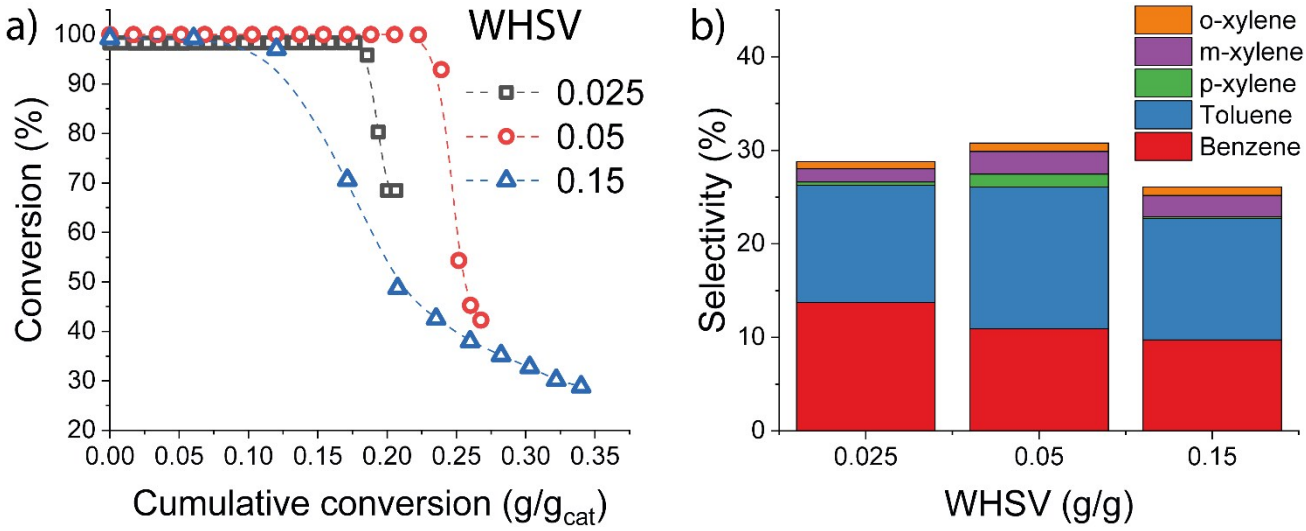

Figure S5. a) Conversion of 2,5-dMF on HZSM-5 catalyst as function of cumulative amount of 2,5-dMF converted. b) Distribution of BTX in the aromatization reaction of 2,5-dMF with different WHSV over HZSM-5 catalysts. Conditions: reaction temperature 450 °C; p(2,5-dMF) 0.2 kPa; atmospheric pressure; carrier – 100 mL/min Ar.

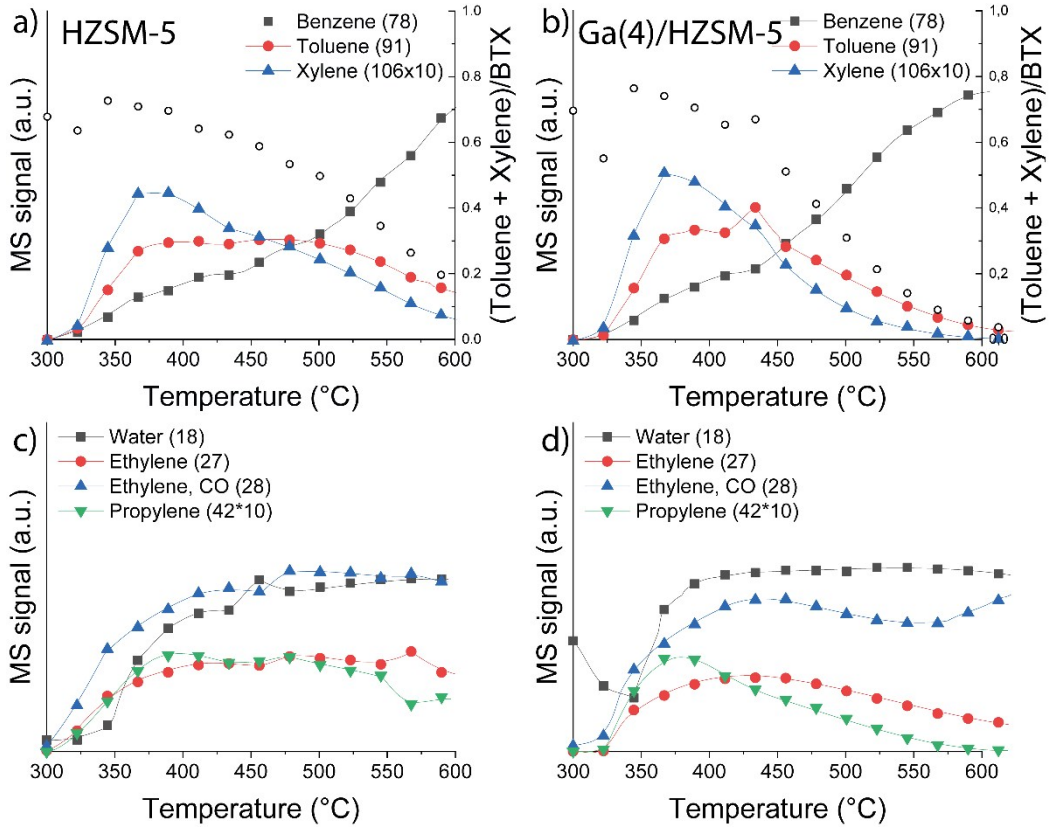

Figure S6. Evaluation of selected MS signals during TPR of 2,5-dMF over the parent ZSM-5 (a,c) and 4%Ga samples (b,d). The absolute MS signal was normalized by Ar signal (m/z = 40). Conditions: ramp rate 5 °C/min; p(2,5-dMF) = 0.2 kPa; atmospheric pressure; carrier – 100 mL/min Ar.

Table S1. Cumulative conversion and the product distribution in the furanics aromatization reaction on zeolites. Conditions: reactor temperature 450 °C; p(2,5-dMF) 0.2 kPa; atmospheric pressure; carrier – 100 ml/min Ar.

Substrate		**Furan**	**Furan**	**2-mF**	**2-mF**	**2,5-dMF**	**2,5-dMF**	**2,5-dMF**	**2,5-dMF**
Catalyst		H*	Ga(4)	H	Ga(4)	H	Ga(1)	Ga(2)	Ga(4)
Converted, mmol		1.1	0.7	1.0	0.9	1.0	1.1	0.8	0.8
H_2O, mmol		0.36	0.27	0.90	0.75	1.03	0.97	0.94	0.82
Carbon based selectivity, %									
1	Light h.c.	9.6	10.8	20.0	9.2	14.3	5.6	6.3	6.0
	Aromatics	39.7	49.8	45.2	54.9	46.7	45.3	51.4	52.7
	BTX	22.8	31.3	27.8	32.8	30.8	33.0	38.6	39.6
	Coke	32.1	14.6	24.4	24.4	37.3	44.6	39.0	38.6
	CO	11.3	13.7	8.3	5.2	1.4	1.3	1.9	1.2
	CO_2	6.5	8.3	2.4	3.8	0.5	0.6	0.7	0.6
2	Methane	0.1	0.1	0.0	0.3	0.0	0.2	0.3	0.2
	Ethylene	4.0	4.8	10.7	4.6	7.1	3.5	4.1	3.7
	Ethane	0.0	0.0	0.1	0.1	0.0	0.1	0.1	0.0
	Propylene	5.3	5.5	8.6	3.9	6.9	1.5	1.7	1.9
	Propane	0.2	0.3	0.6	0.2	0.3	0.3	0.1	0.2
3	Benzene	10.3	17.2	8.9	16.0	10.9	18.0	23.0	24.5
	Toluene	10.2	12.5	12.9	13.5	15.2	12.8	13.6	13.0
	Ethylbenzene	0.1	0.2	0.2	0.4	0.2	0.1	0.1	0.2
	p-Xylene	0.7	0.9	1.8	1.8	1.4	0.9	1.0	1.3
	m-xylene	1.2	0.6	3.1	1.2	2.4	1.0	0.9	0.6
	o-Xylene	0.4	0.1	1.1	0.3	0.9	0.3	0.2	0.2
	Propylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Alkylbenzenes	0.1	0.1	0.2	0.3	0.3	0.1	0.1	0.1
	1,3,5-trimethyl benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Styrene	0.2	0.6	0.1	0.5	0.1	0.1	0.1	0.1
	Indane	0.9	0.1	1.6	0.3	1.0	0.3	0.2	0.4
	Indanes	0.2	0.0	0.4	0.1	0.9	0.1	0.1	0.1
	Indene	3.3	5.3	2.4	4.8	2.0	1.7	1.9	2.1
	Indenes	0.9	0.5	1.4	1.4	1.6	0.6	0.6	0.8
	Tetralin	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
4	Benzofuran	1.3	2.6	0.1	0.1	0.1	0.0	0.0	0.0
5	Naphthalene	8.0	9.2	5.5	9.3	3.0	4.6	5.1	4.5
	Methyl-naphthalene	2.5	2.1	4.0	4.3	3.4	3.0	3.1	3.3
	Naphthalenes	0.8	0.4	1.5	0.7	3.3	1.6	1.4	1.5

1 – Grouped main products; 2 – light hydrocarbons; 3 – 1 benzene ring aromatic products; 4 – oxygen-containing aromatics; 5 – heavier aromatics (naphthalenes).

*HZSM-5

Furanics adsorbed on zeolites

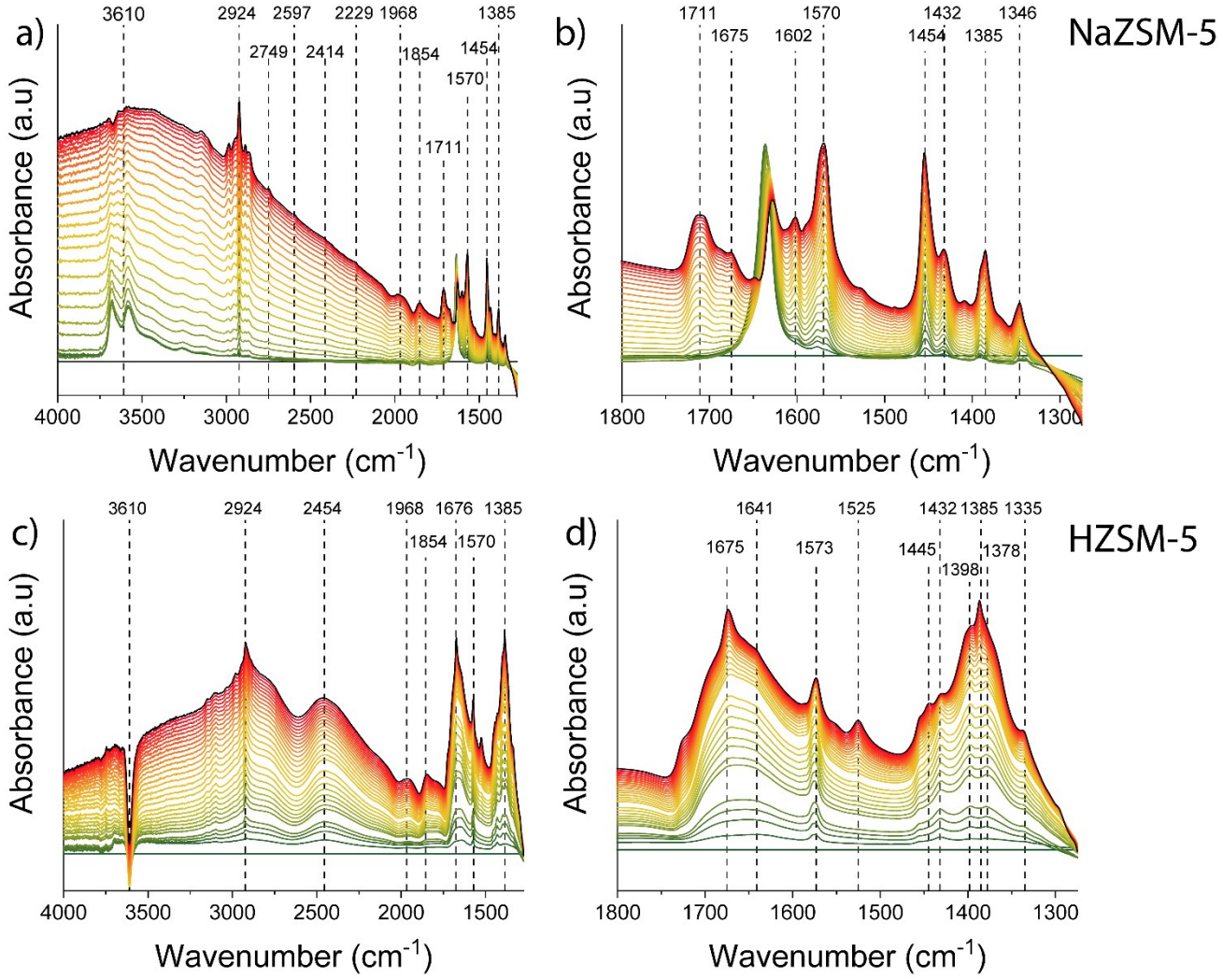

Figure S7. FTIR spectra of 2,5-dimethylfuran adsorbed on NaZSM-5 (a, b) and on HZSM-5 (c, d) at 50 °C. Shown are the whole spectra (a, c) and zoomed 1800 – 1250 cm^{-1} region.

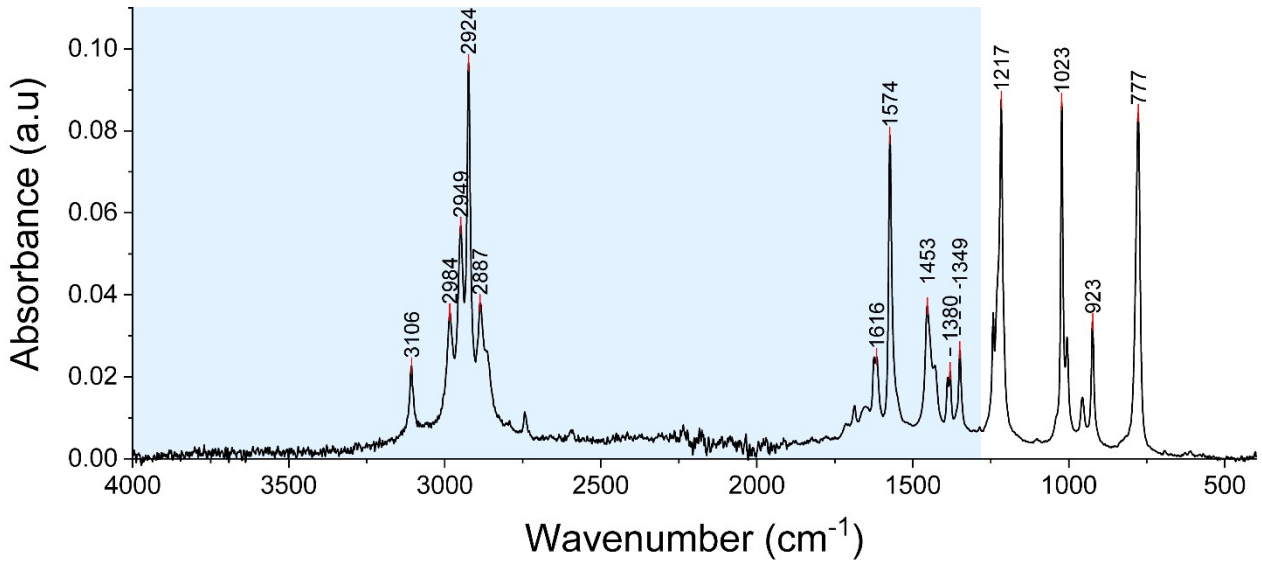

Figure S8. ATR FTIR spectrum of pure 2,5-dimethylfuran in the liquid phase. Highlighted is a region studied.

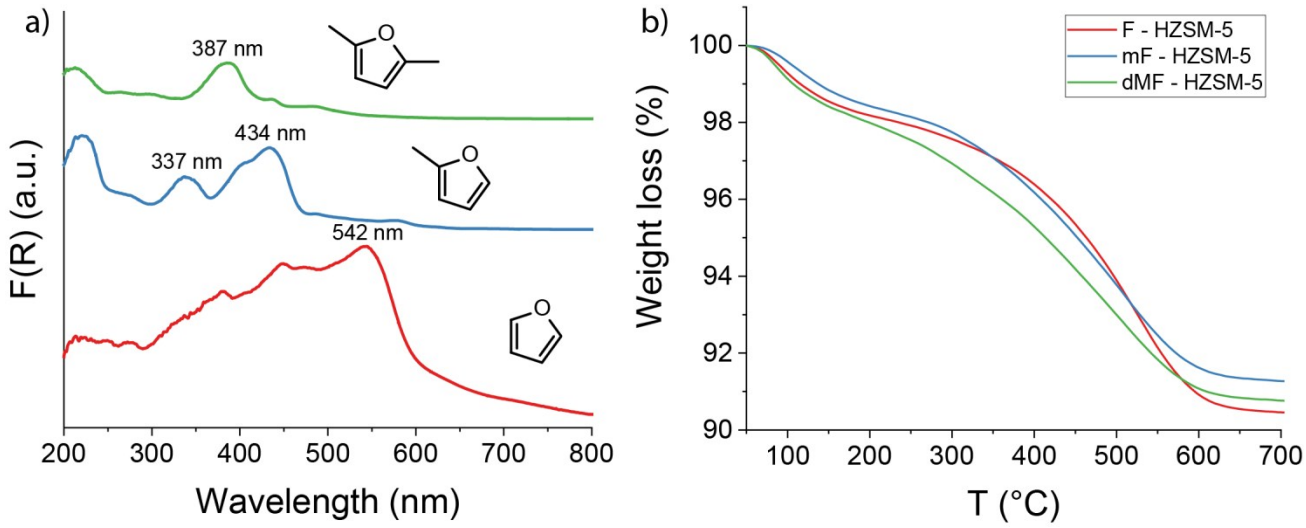

Figure S9. (a) KM transformed UV-vis spectra of furanics adsorbed on HZSM-5 at room temperature; (b) TGA profiles of furanics adsorbed at RT on HZSM-5.

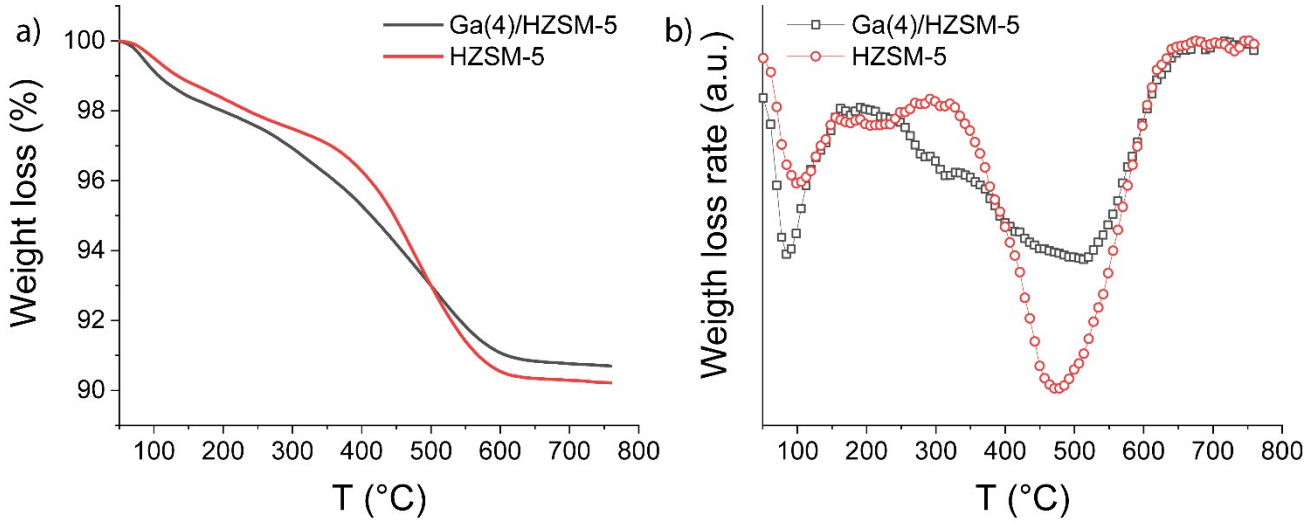

Figure S10. TGA (a) and DTGA (b) profiles of 2,5-dimethylfuran adsorbed at RT on HZSM-5 and Ga(4)/HZSM-5.