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Supporting Information

Integrated Cascade Process for the Catalytic Conversion of 5-Hydroxymethylfurfural to Furanic and TetrahydrofuranicDiethers as Potential Biofuels

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Integrated cascade process for the catalytic conversion of 5-hydroxymethylfurfural (HMF) to furanic and tetrahydrofuranic diethers as potential bio-fuels

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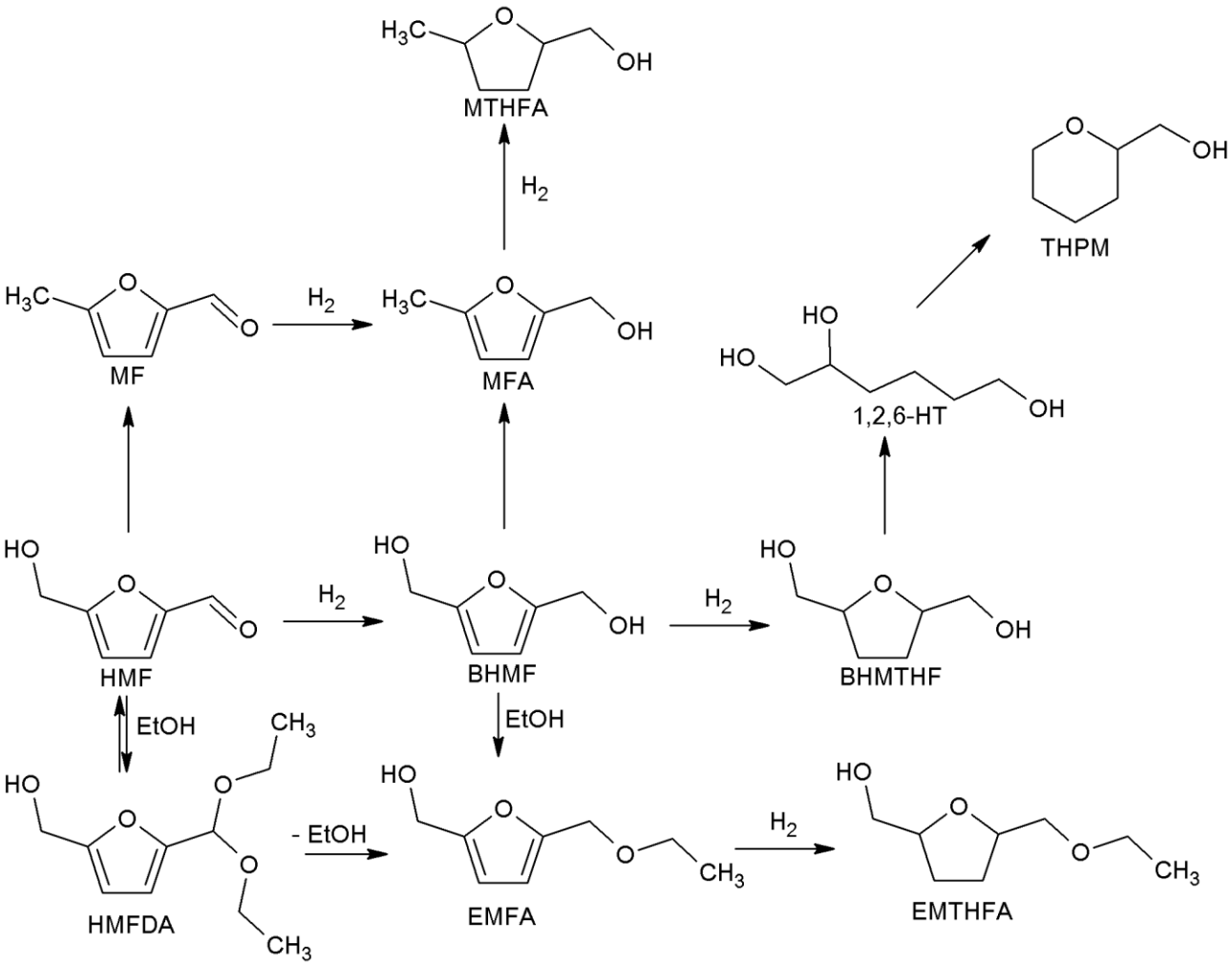
Table S1. Overview of the literature on the pure HMF etherification to EMF carried out in ethanol compared under the same reaction conditions with different catalytic systems.

Test	[HMF] (wt%)	Catalyst	T (°C)	t (h)	HMF[a] Conversion (mol%)	EMF[b] Yield (mol%)	EL[c] Yield (mol%)	Ref.
S1	7.4	H_2SO_4	100	12	100	54	n.a. [d]	1
S2	7.4	*p*-toluene sulfonic acid	100	12	100	61	n.a. [d]	1
S3	7.4	Graphene oxide	100	12	96	92	n.a. [d]	1
S4	3.1	*p*-toluene sulfonic acid	110	0.5	100	83	17	2
S5	3.1	Amberlyst-15	110	0.5	85	71	7	2
S6	3.1	PDVTA-SO_3H[e]	110	0.5	100	88	12	2
S7	10.5	H_2SO_4	140	5	100	3	96	3
S8	10.5	Amberlyst-15	140	5	100	0	99	3
S9	10.5	Z-SBA-15[f]	140	5	100	76	23	3
S10	1.3	ZSM-5	140	6	84	56	n.a.[d]	4
S11	1.3	AT(0.50)-OT[g]	140	6	97	90	n.a.[d]	4
S12	3.3	Nafion NR50	180	3	96	52	27	5
S13	3.3	Ni_2P/SiO_2	180	3	97	65	18	5
S14	2.5	Amberlyst-15	160	2.5	84	64	20	6
S15	2.5	β-zeolite (BEA-25)	160	2.5	66	63	3	6

[a] HMF = 5-hydroxymethylfurfural; [b] EMF = 5-ethoxymethylfurfural; [c] EL = ethyl levulinate; [d] n.a. = not available; [e] Sulfonated copolymer divenylbenzene-triallylamine; [f] ZrO_2 dispersed on the SBA-15 support; [g] ZSM-5 subjected to an alkaline treatment (AT) with NaOH at 0.50 M followed by an oxalic acid treatment (OT)



Scheme S1. Different pathways in the hydrogenation of HMF in ethanol

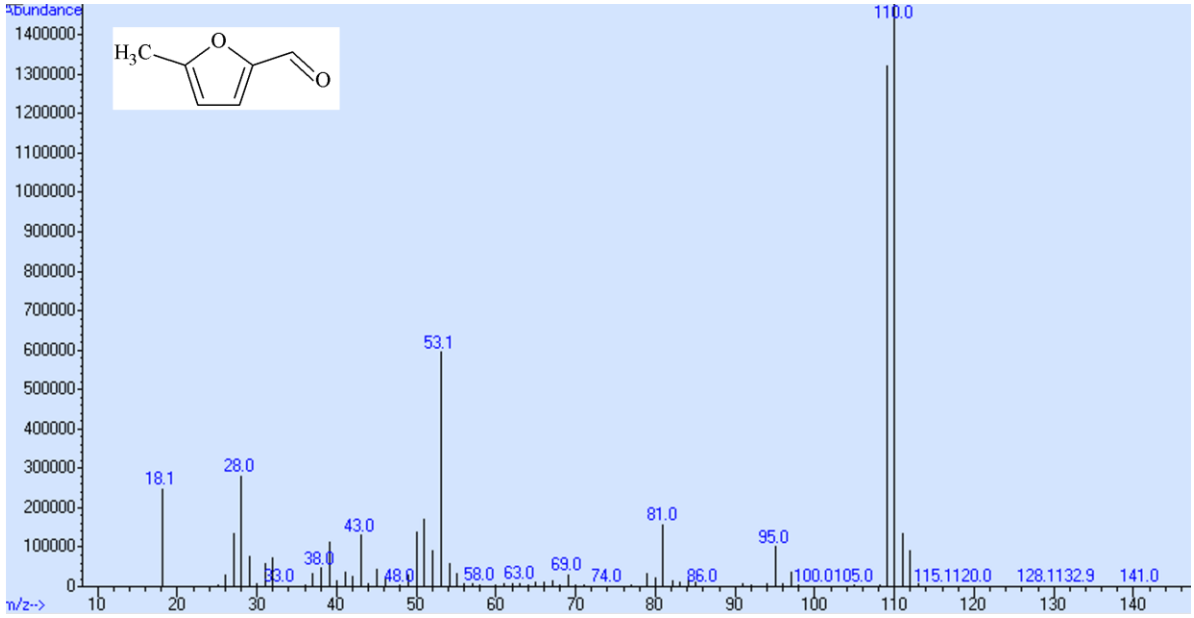


Figure S1. Mass spectrum of 5-methylfurfural (MF), identified by the comparison with library pattern (Wiley Registry 10th Edition).

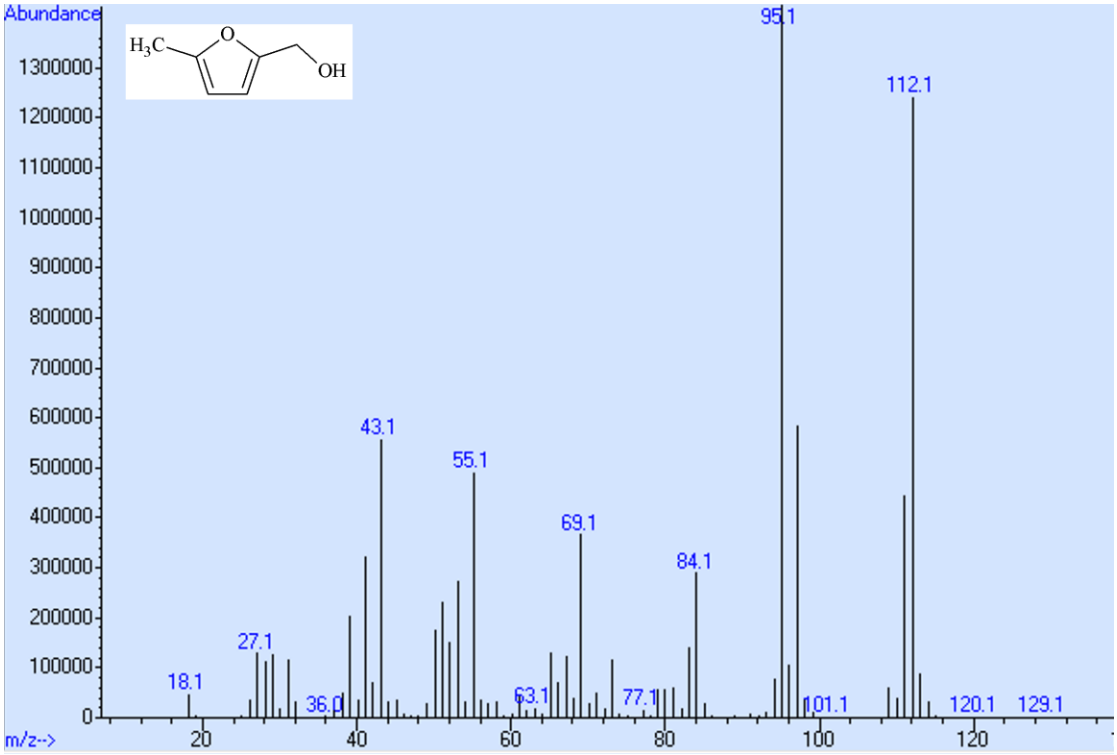


Figure S2. Mass spectrum of 5-methylfurfurylalcohol (MFA) identified by the comparison with library pattern (Wiley Registry 10th Edition).

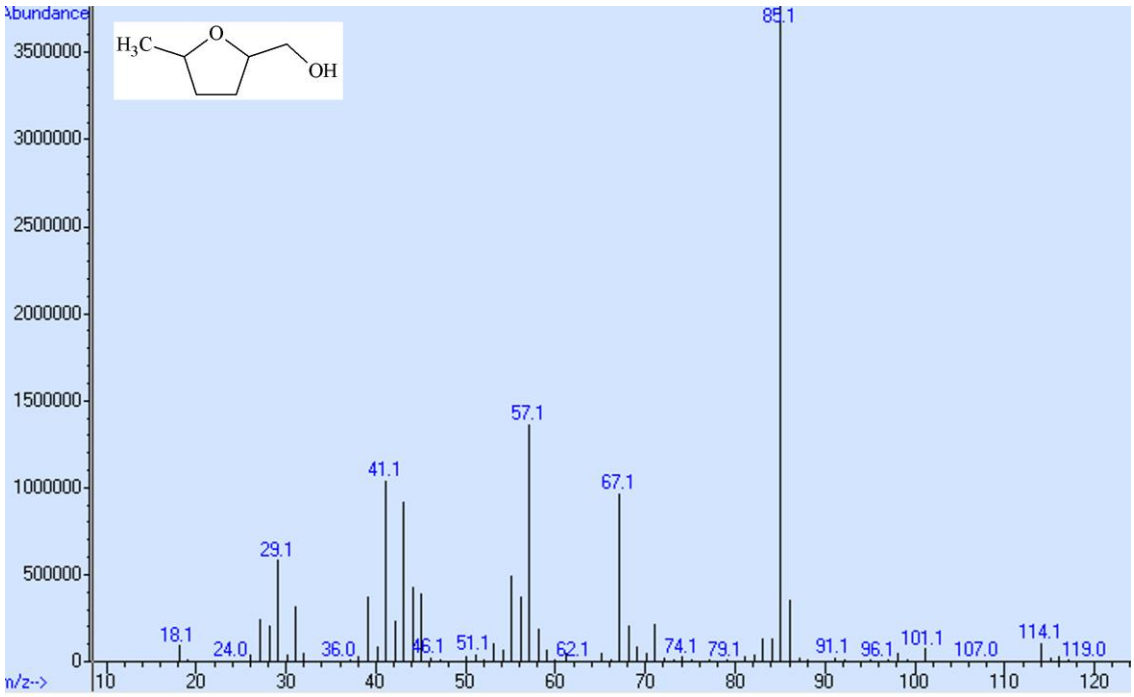


Figure S3. Mass spectrum of 5-methyltetrahydrofurfurylalcohol (MTHFA) identified by the comparison with library pattern (Wiley Registry 10th Edition).

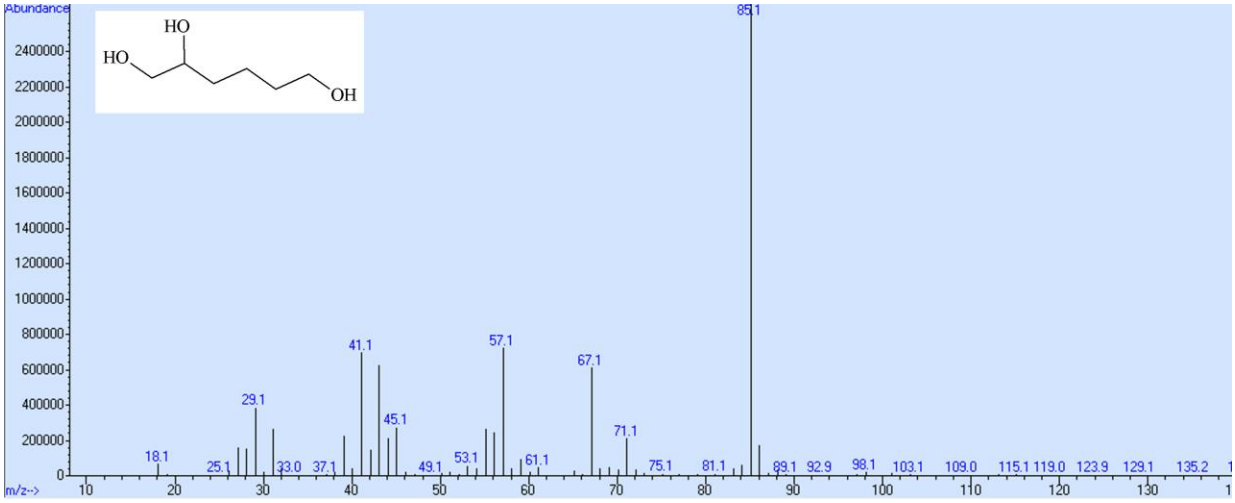


Figure S4. Mass spectrum of 1,2,6-hexanetriol (1,2,6-HT) identified by the comparison with library pattern (Wiley Registry 10th Edition).

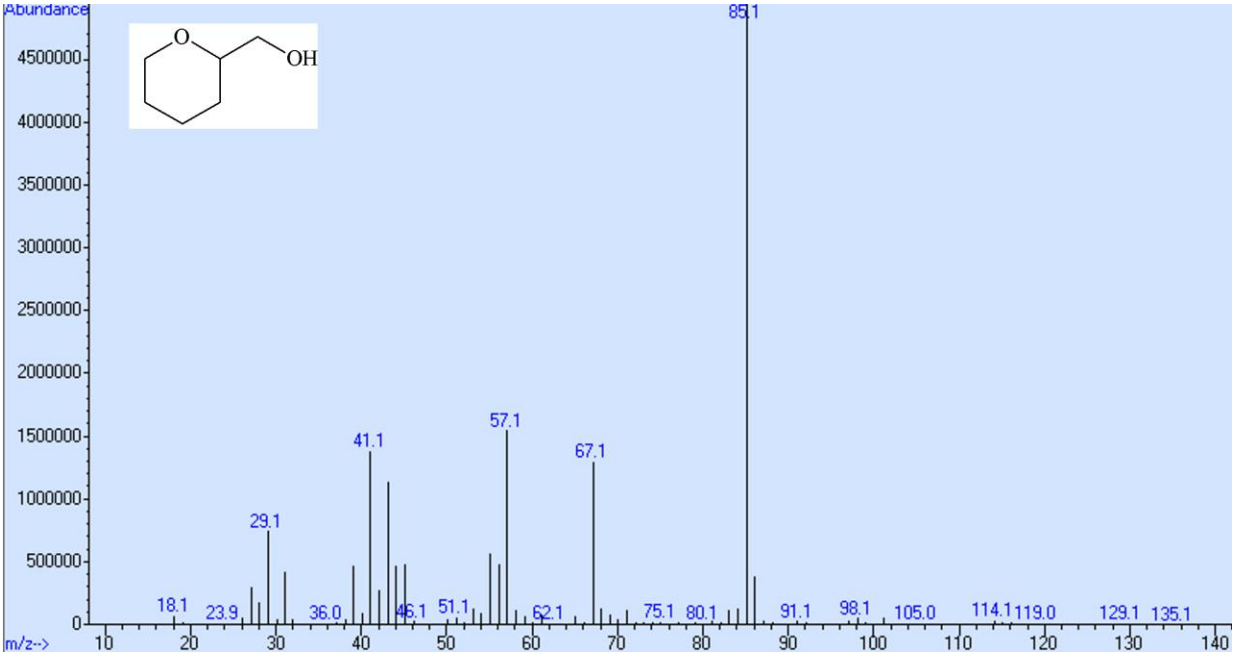


Figure S5. Mass spectrum of tetrahydropyran-2-methanol (THPM) identified by the comparison with library pattern (Wiley Registry 10th Edition).

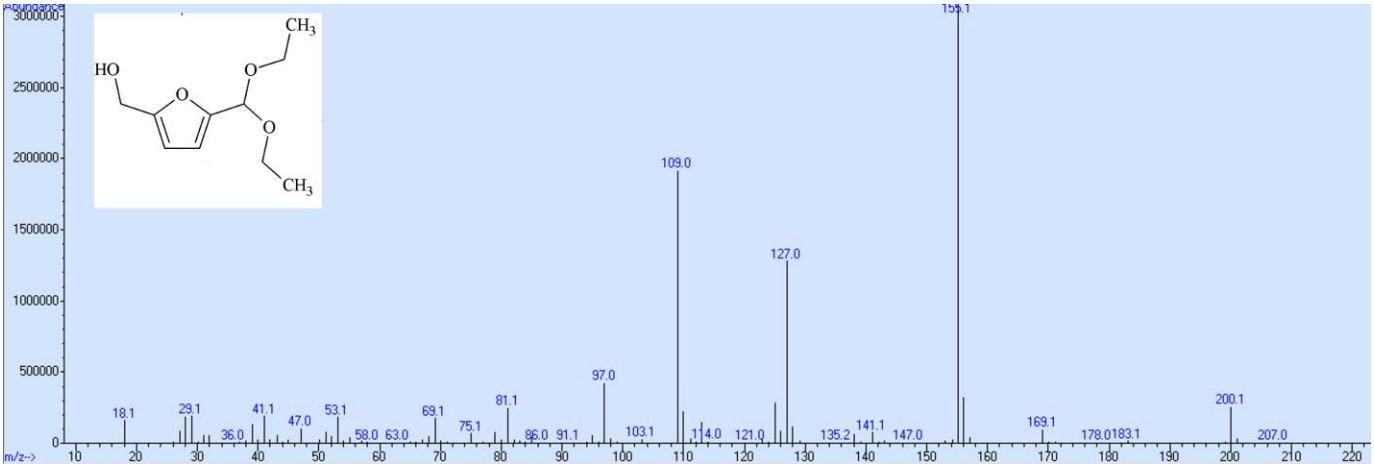


Figure S6. Mass spectrum of 5-(hydroxymethyl)-furfural diethyl acetal (HMFDA) identified by the comparison with literature (main m/z values: 109, 127, 155, 200).[7]

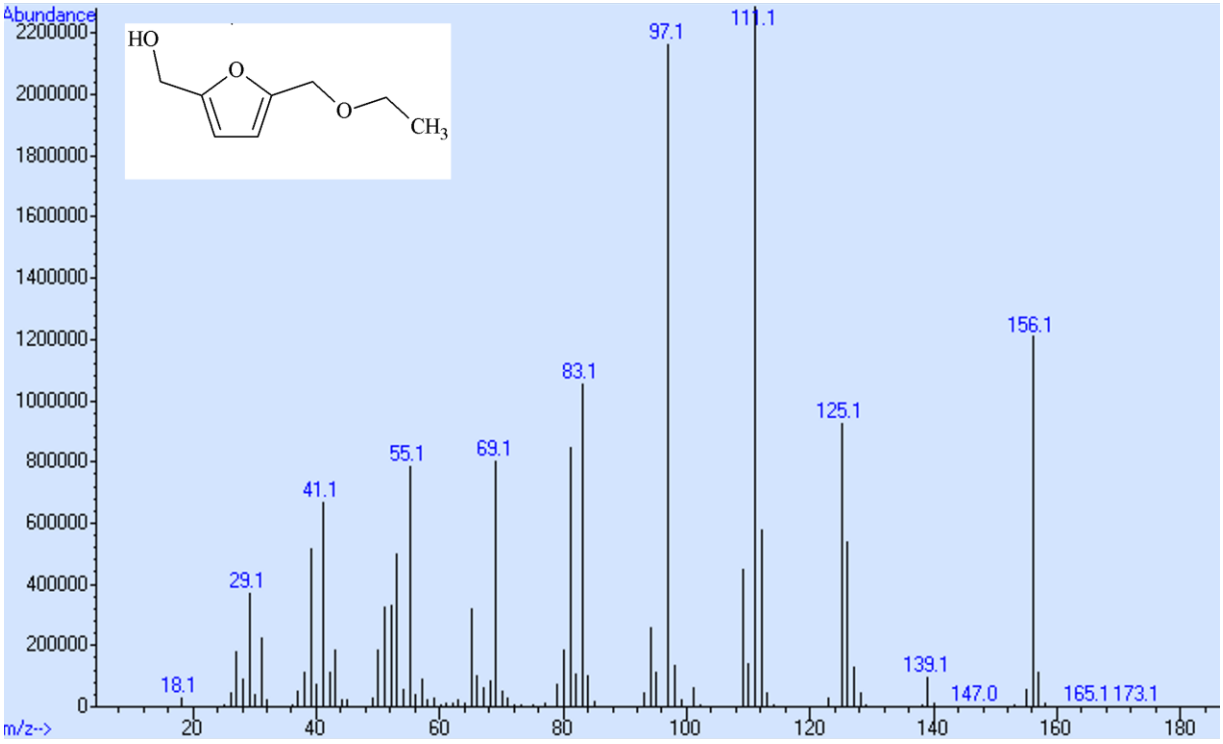


Figure S7. Mass spectrum of 5-(ethoxymethyl)furfuryl alcohol (EMFA) identified by the comparison with literature (main m/z values: 29, 41, 55, 83, 97, 111, 125, 165).[7]

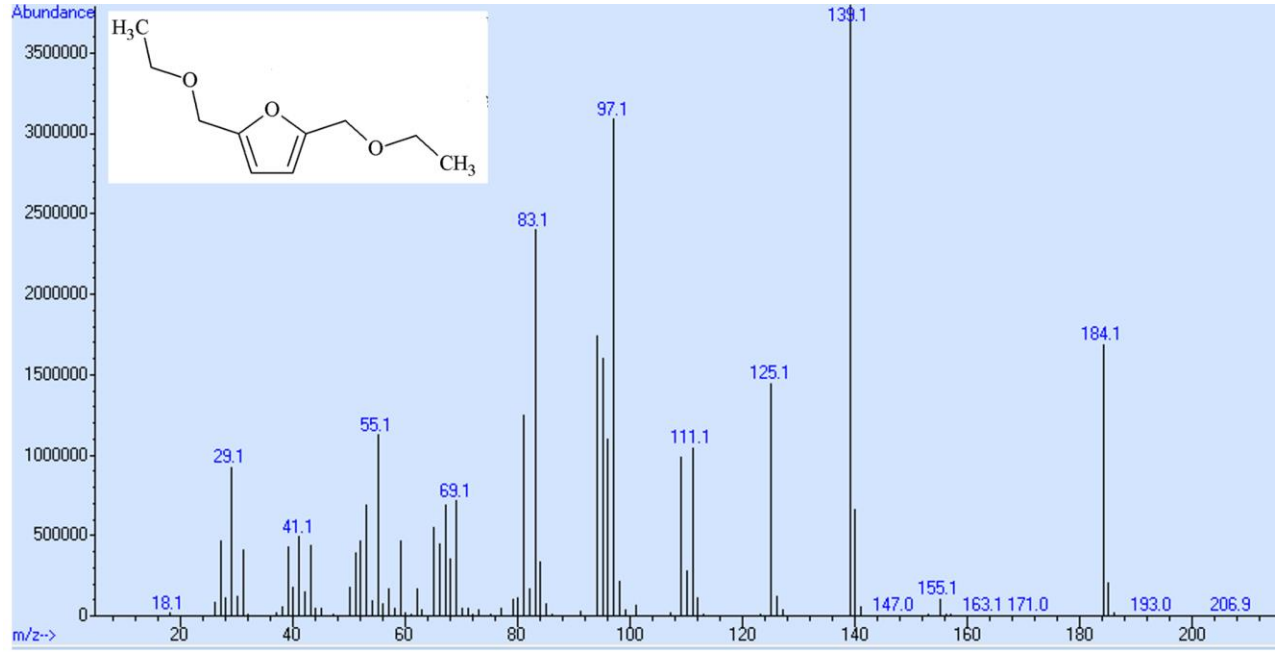


Figure S8. Mass spectrum of 2,5-bis(ethoxymethyl)furan (BEMF) identified by the comparison with literature (main m/z values: 29, 55, 83, 97, 111, 125, 139, 155, 184).[7]

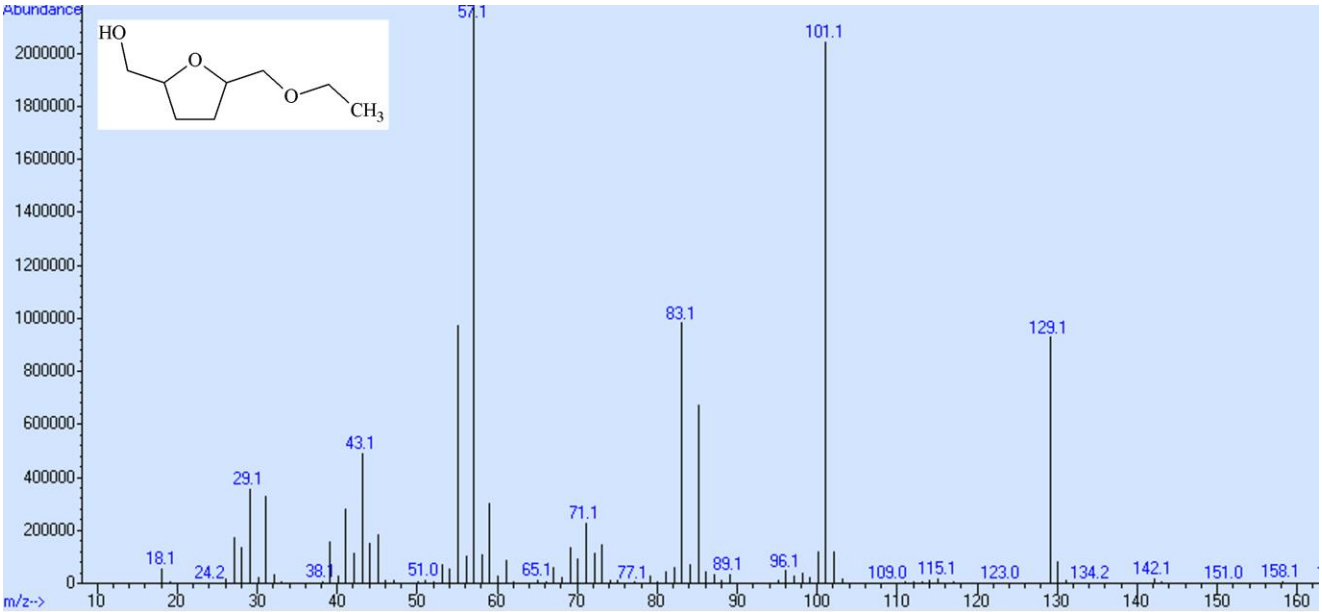


Figure S9. Mass spectrum of 5-(ethoxymethyl)tetrahydrofurfuryl alcohol (EMTHFA) identified by the comparison with literature (main m/z values: 29, 43, 57, 83, 101, 129).[8]

Table S2. Carbon balance values of the reactions reported in Figures 1–3. Reaction conditions: [HMF] = 30 g L^{-1}; Ru/HMF = 1 wt%.

Run	T (°C)	P H_2 (bar)	Carbon Balance (mol%) [a]							
			Time (min)							
			15	30	60	90	120	180	240	300
1	100	50	93.2	97.6	93.0	85.6	86.7	90.4	89.7	86.5
2	80	50	83.1	81.8	82.2	86.5	89.4	92.1	87.0	89.4
3	50	50	96.5	97.3	89.6	93.9	89.1	84.8	86.6	88.6
4	100	60	89.1	92.0	90.5	88.0	87.0	86.3	85.5	85.3
5	100	20	74.6	81.3	93.5	92.4	84.0	80.3	78.4	76.8
6	80	60	83.9	85.9	82.1	88.2	88.7	89.1	89.1	87.2
7	80	20	75.9	75.0	78.4	82.2	83.9	89.4	90.7	85.1
8	100	10	75.9	71.6	72.1	73.4	78.0	74.0	73.2	68.8
9	100	70	92.5	93.9	93.1	90.6	89.2	88.3	88.2	85.3

[a] Carbon Balance = $[(mol_{unconverted\ HMF} + mol_{BHMF} + mol_{BHMTHF})/mol_{starting\ HMF}] \times 100$

Calculations of internal diffusion limitations through the Weisz-Prater criterion

The Weisz-Prater parameter was calculated using the equation 1 (Eq.S1) and the internal diffusion can be considered negligible when N_{W-P} is lower than 0.3:

$$N_{W-P} = \frac{-R_{exp} \cdot r_p^2}{C_s \cdot D_{eff}} \qquad \text{Eq.S1}$$

In the Eq. S1:

- R_{exp} is the experimentally observed reaction rate (mol m^{-3}_{cat} s^{-1}): it was determined by the ratio between the rate of HMF conversion at the beginning of the reaction and the volume of the employed catalyst, estimated by using the amount of catalyst (0.3 g) and its bulk density,

provided by the supplier and equal to 750 kg m^{-3};

- r_p is the radius of catalyst particle (m): according to the supplier information, the particle size distribution is the following one:

  d_{10} = 5 μm (10% of all particles are characterized by a diameter smaller than 5 μm)

  d_{50}= 25 μm (50% of all particles are characterized by a diameter smaller than 25 μm)

  d_{90} = 75 μm (90% of all particles are characterized by a diameter smaller than 75 μm)

  We can suppose the mean value for the particle diameter between 75 and 25 μm, thus an average radius of 2.5×10^{-5} m was considered.

- C_s is the concentration of the component at the catalyst surface (mol m^{-3}): we supposed that the concentration of HMF on the particle surface was equal to that in the bulk of the solution;

- D_{eff} is the effective diffusion coefficient of the component (m^2 s^{-1}): the diffusion coefficient of HMF in water was estimated trough the Wilke-Chang equation (Eq.S2):[10,11]

$$D_{AB} = \frac{7.4 \cdot 10^{-8} \cdot T \cdot (f_B \cdot M_B)^{0.5}}{V_{bA}^{0.6} \cdot m} \qquad \text{Eq.S2}$$

  Where the symbols with subscript A are referred to the solute (HMF), whereas those with subscript B to the solvent (ethanol):

  - D_{AB} is the diffusivity of HMF in ethanol solution, cm^2 s^{-1};

  - M_B is the molecular weight of ethanol, g mol^{-1};

  - T is the temperature, K;

  - μ is the viscosity of ethanol at 100 °C, cP;

  - V_{bA} is the HMF molar volume at its normal boiling point, cm^3 mol^{-1}. It was calculated according to the generalized correlation proposed by Maloka regarding the liquid molar volume at the normal boiling point;[12]

  - ϕ_B is the association factor of ethanol;[10]

The effective diffusion coefficient (D_{eff}) was considered as 10% of the diffusion coefficient,

according to the Wilke-Chang equation.[10,11]

In Table S3 are reported the parameters adopted for the calculation of the Weisz-Prater criterion:

Table S3. Parameters for calculating the Weisz-Prater criterion for the reaction carried out at 100 °C and 50 bar.

Parameter	Description	Value
R_{exp}	experimentally observed reaction rate	24.7 mol m^{-3} s^{-1}
r_p	radius of catalyst particle	2.5×10^{-5} m
C_s	concentration of the component at the catalyst surface	238 mol m^{-3}
T	temperature	373 K
ϕ_B	association factor of ethanol	1.5
M_B	molecular weight of ethanol	46.07 g mol^{-1}
V_{bA}	HMF molar volume at its normal boiling point	119.7 cm^3 mol^{-1}
μ	viscosity of ethanol at 100 °C	0.01104 cP

From the calculation $N_{W\text{-}P}$ was equal to 0.005, which was strongly lower than 0.3, thus we can infer that the internal mass transfer limitation is negligible in the investigated reaction.

Calculations of external diffusion limitations through the Mears criterion

The Mears parameter was calculated using the equation S3 (Eq.S3) and the external diffusion can be considered negligible when C_M is lower than 0.15:

$$C_M = \frac{-R_{exp} \cdot r_p \cdot n}{k_c \cdot C_{AS}} \qquad \text{Eq.S3}$$

In the Eq.S3:

- R_{exp} is the experimentally observed reaction rate (mol m^{-3}_{cat} s^{-1}): it was determined as reported previously;

- r_p is the radius of catalyst particle (m): it was 2.5×10^{-5} m, as previously reported;
- n is the reaction order of HMF;
- C_{AS} is the concentration of HMF in the solution (mol m^{-3});
- k_c is the mass transfer coefficient for HMF-ethanol (m s^{-1}): it was calculated according to Eq.S4:

$$k_c = \frac{Sh \cdot D_{AB}}{d_p} \quad \text{Eq.S4}$$

where D_{AB} is the diffusion coefficient of HMF in ethanol at 373 K (1.185×10^{-7} m^2 s^{-1}), d_p is the catalyst particle diameter (5×10^{-5} m) and Sh is the Sherwood number, which is calculated according to Eq.S5:[13]

$$Sh = 2 + 0.6 \cdot Re^{0.5} \cdot Sc^{1/3} \quad \text{Eq. S5}$$

where Re is the Reynolds number and Sc is the Schmidt number, which are defined according to Eq. S6 and S7, respectively:

$$Re = \frac{N \cdot D^2 \cdot r}{m} \quad \text{Eq.S6}$$

where N is the rotational speed of the stirrer (1000 rpm/60 s = 16.67 s^{-1}), D is the stirrer diameter (3.5×10^{-2} m), ρ is the density of ethanol at 373 K (713 kg m^{-3}), μ is the dynamic viscosity of ethanol at 373 K (11.04×10^{-6} kg m^{-1} s^{-1}).

$$Sc = \frac{V}{D_{AB}} \quad \text{Eq.S7}$$

where V is the kinetic viscosity of ethanol at 373 K (7.27×10^{-6} m^2 s^{-1}) and D_{AB} is the diffusion coefficient of HMF in ethanol at 373 K (1.185×10^{-7} m^2 s^{-1}).

In Table S4 are reported the parameters adopted for the calculation of the Mears criterion:

Table S4. Parameters for calculating the Mears criterion for the reaction carried out at 100 °C and 50 bar.

Parameter	Description	Value
R_{exp}	experimentally observed reaction rate	24.7 mol m^{-3} s^{-1}
r_p	radius of catalyst particle	2.5×10^{-5} m
n	reaction order of HMF	1
C_{AS}	concentration of HMF in the solution	238 mol m^{-3}
D_{AB}	diffusion coefficient of HMF in ethanol at 373K	1.185×10^{-7} m^2 s^{-1}
N	rotational speed of the stirrer	16.67 s^{-1}
D	diameter of the stirrer	3.5×10^{-2} m
ρ	density of ethanol at 373K	713 kg m^{-3}
μ	dynamic viscosity of ethanol at 373 K	11.04×10^{-6} kg m^{-1} s^{-1}
V	kinetic viscosity of ethanol at 373 K	7.27×10^{-6} m^2 s^{-1}

From the calculation C_M was equal to 4.02×10^{-7}, which was strongly lower than 0.15, thus we can infer that the external mass transfer limitation is negligible in the investigated reaction.

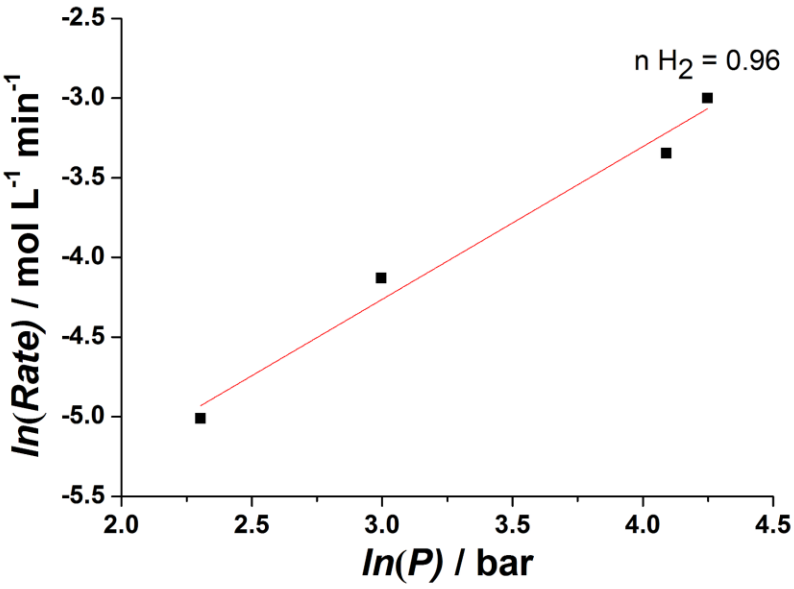


Figure S10. Hydrogen reaction order in the hydrogenation of HMF carried out at 100°C.

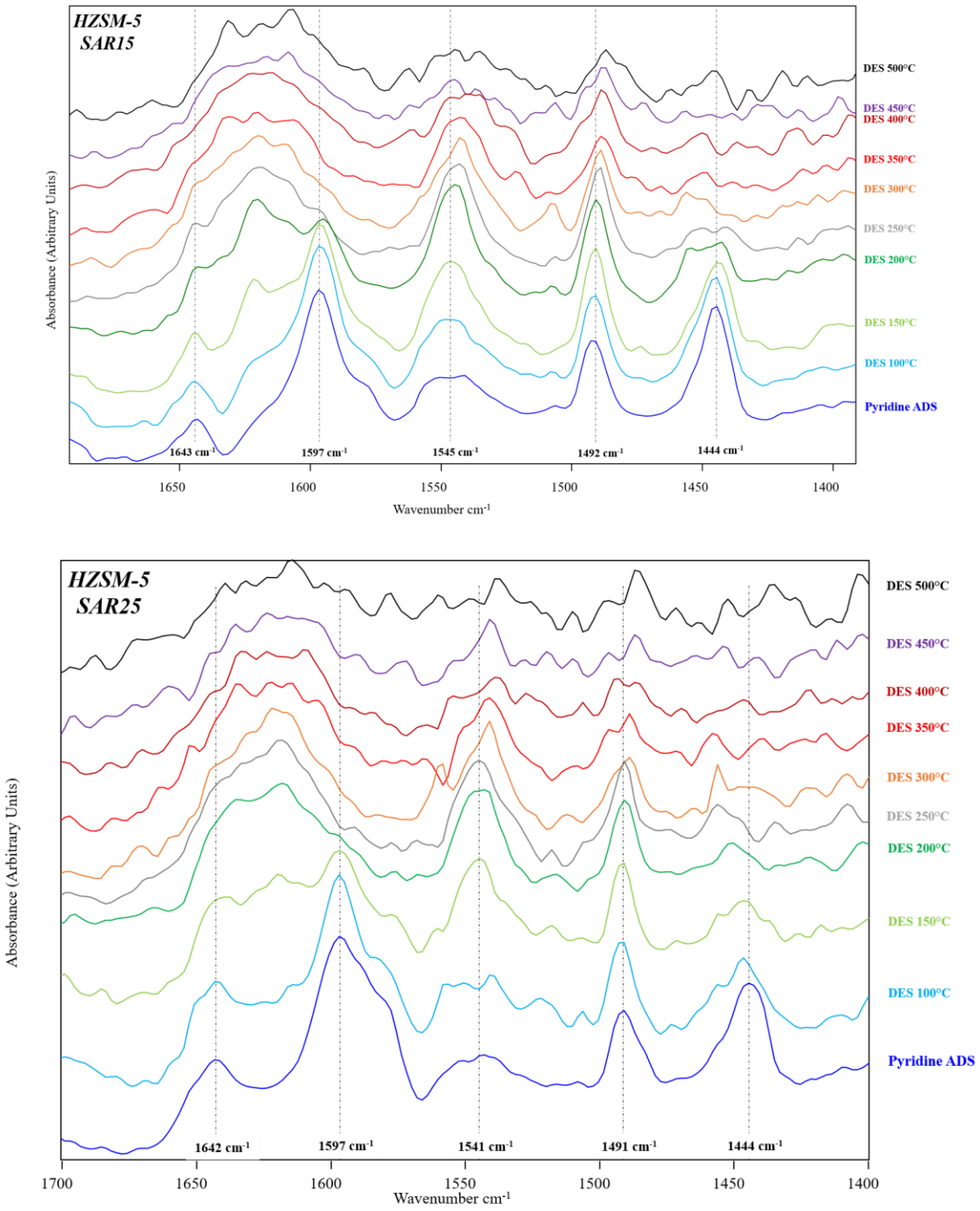
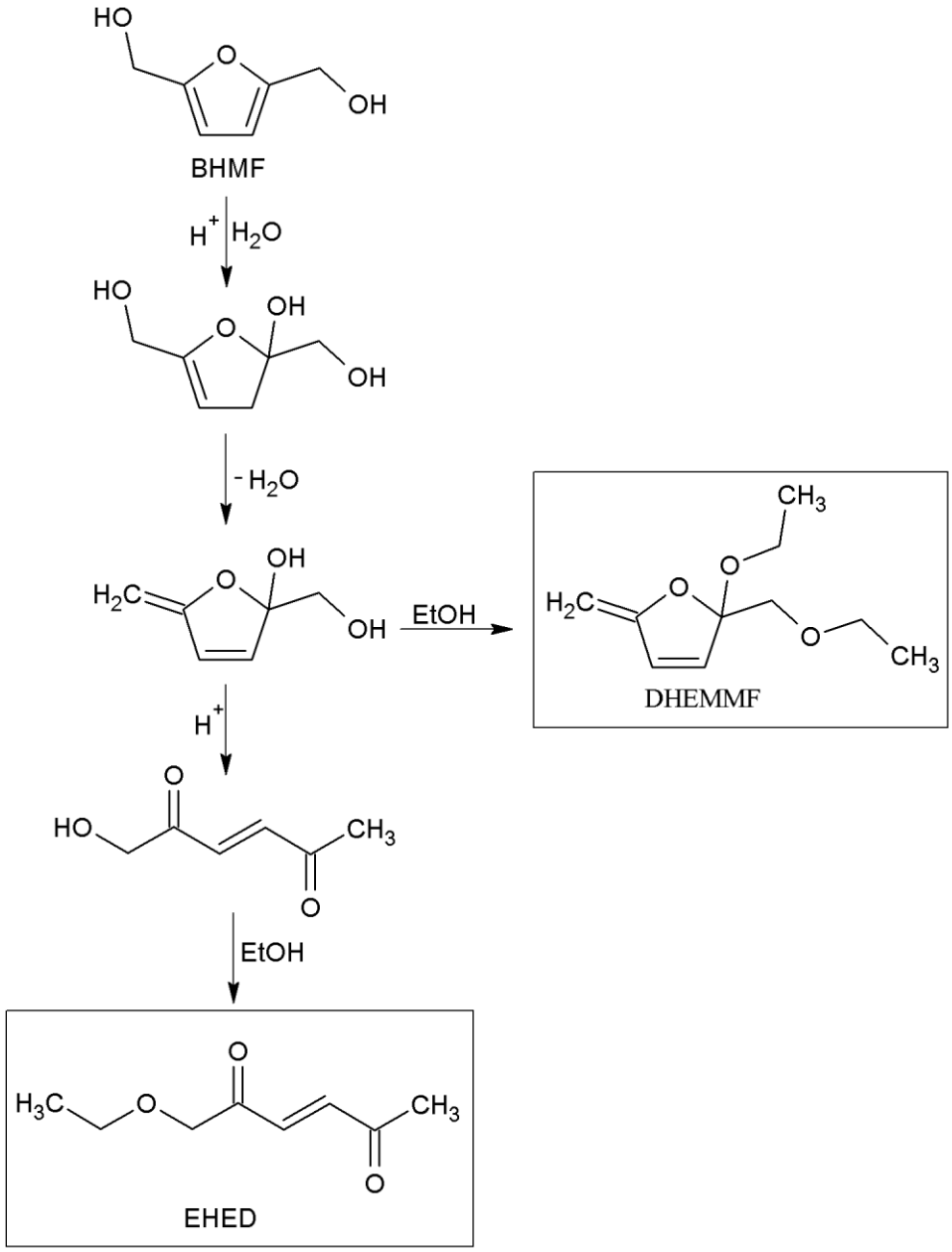


Figure S11. DRIFTS spectra recorded at increasing temperature after pyridine adsorption over HZSM-5 Si/Al=15 (top) and Si/Al=25 (bottom) at 50 °C.



Scheme S2. Possible patwhays of by-products formation in the etherification of pure BHMF.

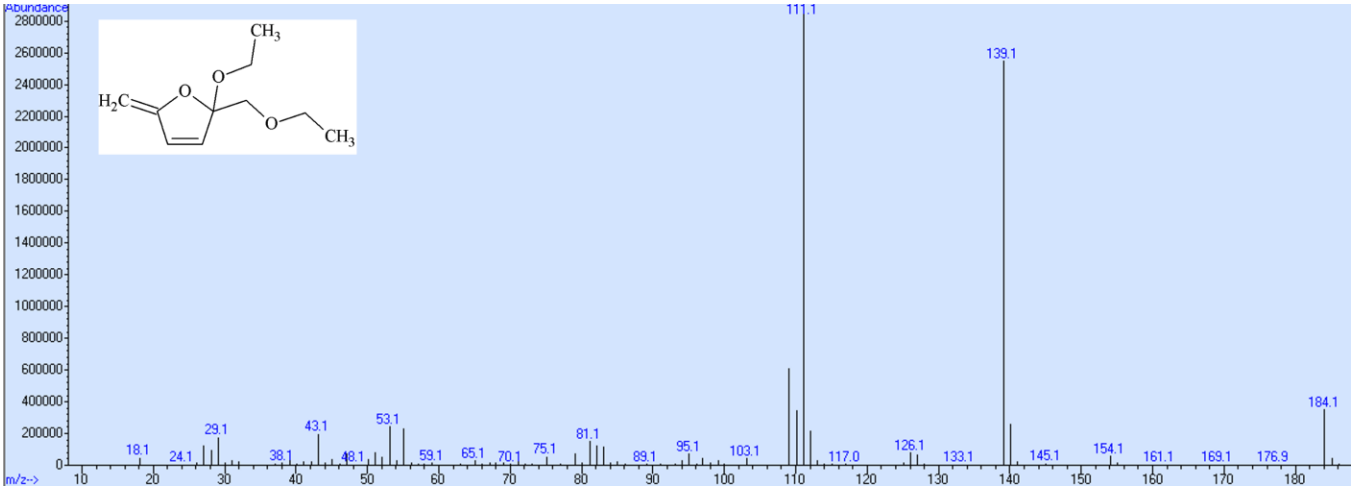


Figure S12. Mass spectrum of 2,5-dihydro-2-ethoxy-2-(ethoxymethyl)-5-methylenefuran (DHEMMF) identified by the comparison with literature (adapted from the fragmentation of the respective methanol ether).[9]

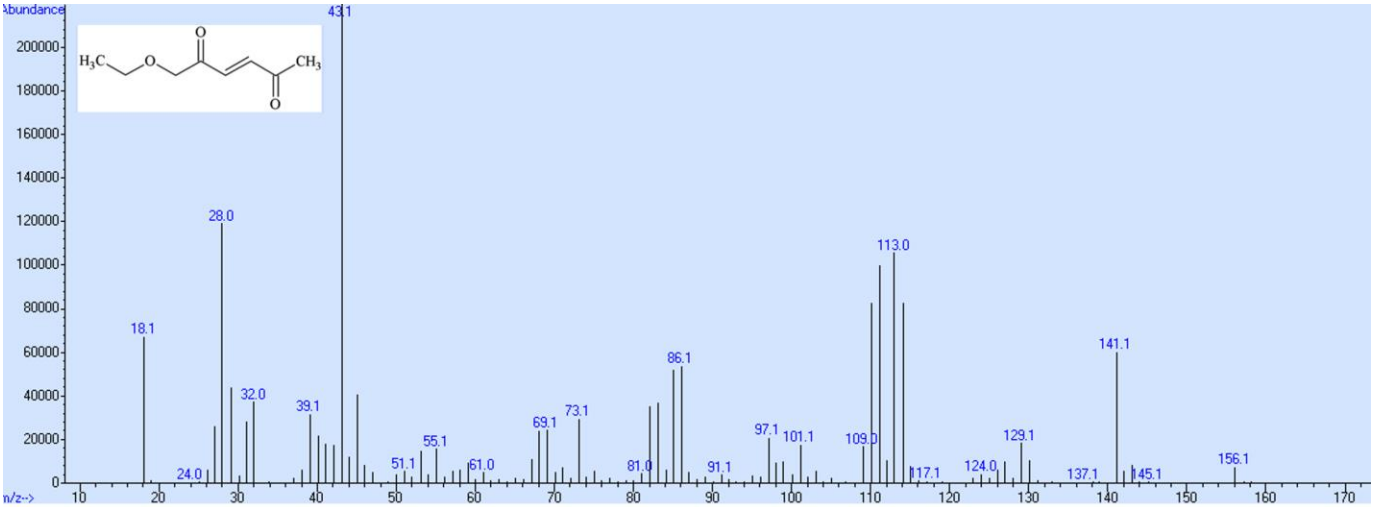


Figure S13. Mass spectrum of 1-ethoxy-3-hexene-2,5-dione (EHED) identified by the comparison with literature (main m/z values: 43, 55, 73, 113).[7]

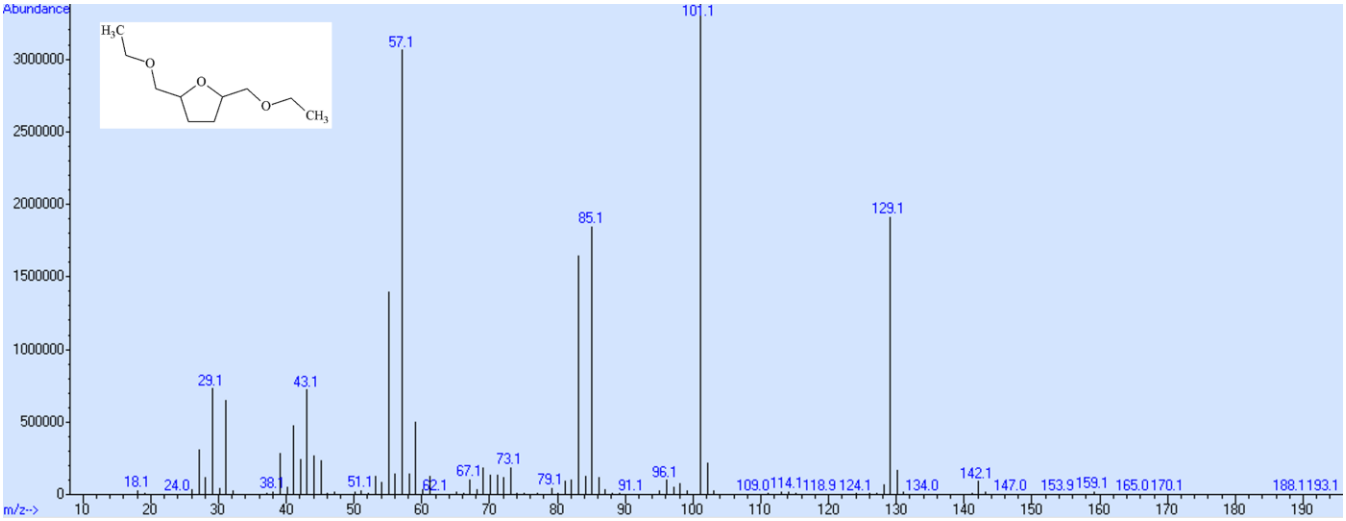


Figure S14. Mass spectrum of 2,5-bis(ethoxymethyl)tetrahydrofuran (BEMTHF)

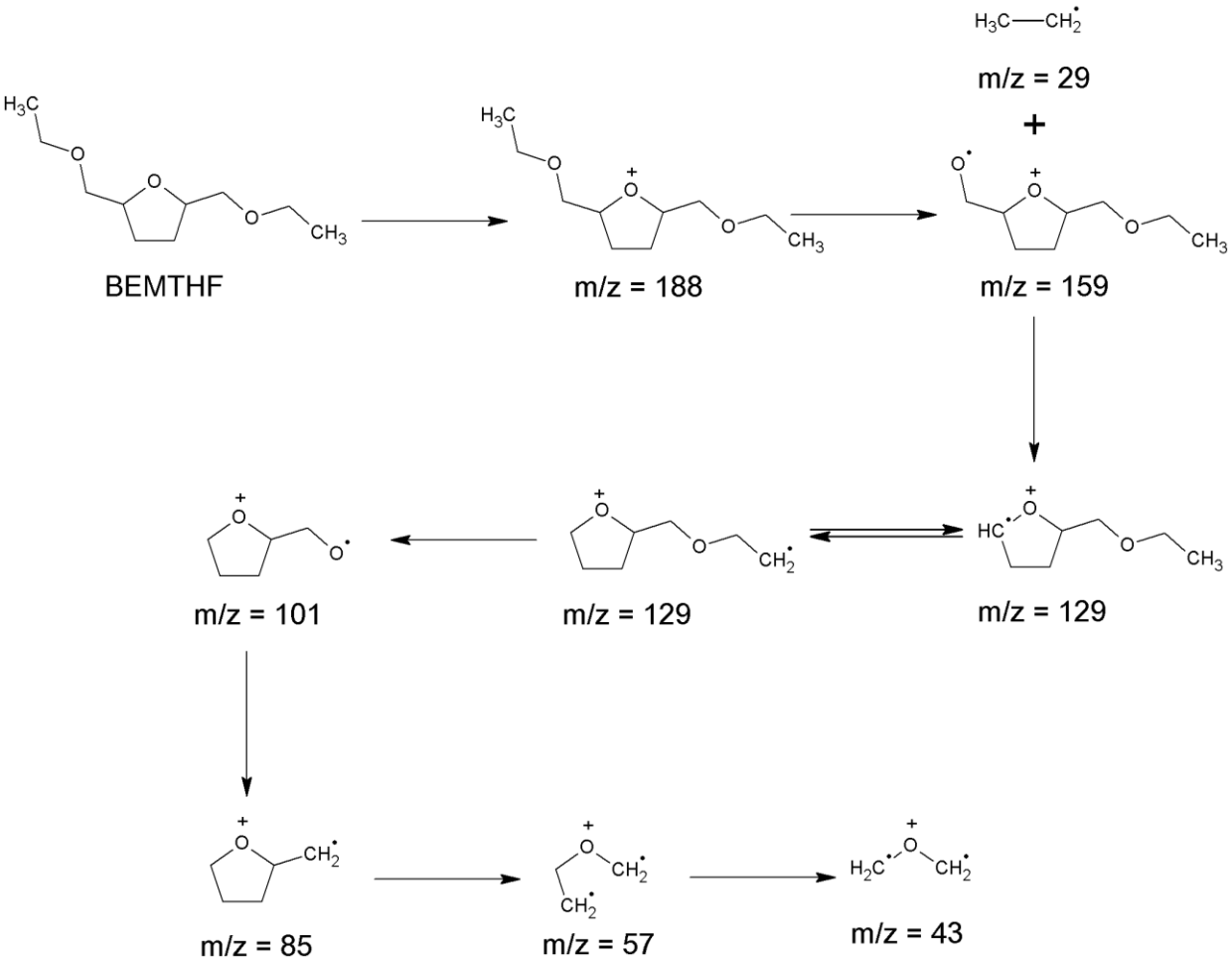


Figure S15. Proposed fragmentation of 2,5-bis(ethoxymethyl)tetrahydrofuran (BEMTHF) in the mass spectrometer

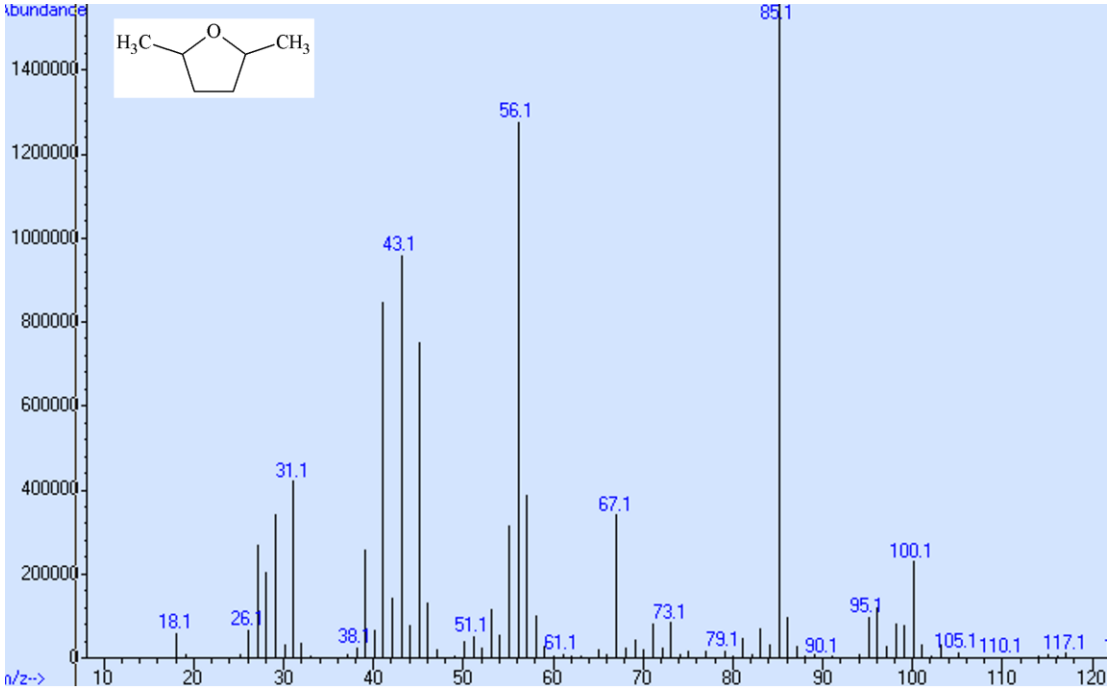


Figure S16. Mass spectrum of 2,5-dimethyltetrahydrofuran (DMTHF) identified by the comparison with library pattern (Wiley Registry 10th Edition).

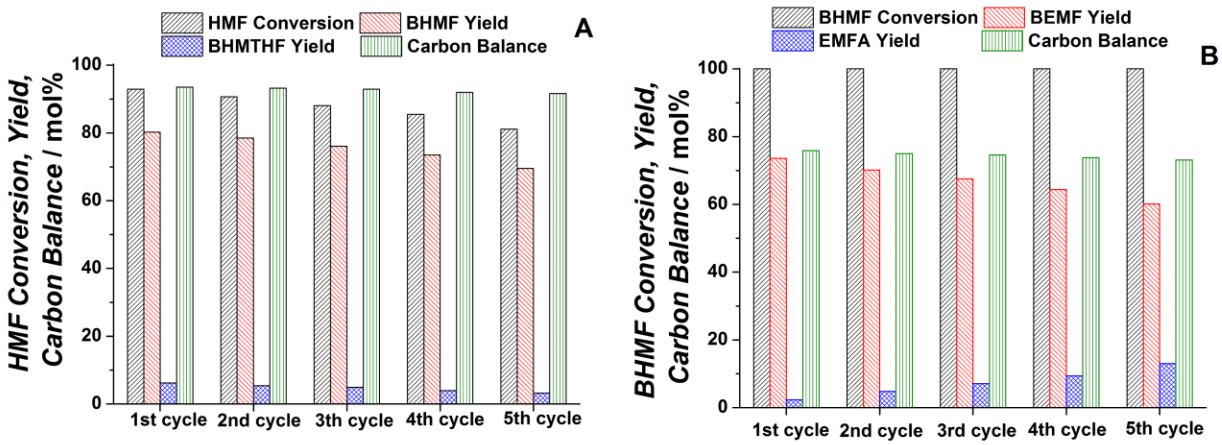


Figure S17. Recyclability tests of: A) 5 wt% Ru/C employed in the optimised hydrogenation of HMF to BHMF (Ru/HMF ratio = 1 wt%, [HMF] = 3.7 wt% 100 °C, 20 bar, 60 min); B) HZSM-5 (Si/Al = 25) employed in the optimised etherification of BHMF to BEMF ($mol_{BHMF}/mol_{total\ acid\ sites}$ = 8.3, [BHMF] = 3.0 wt%, 80 °C, 2h).

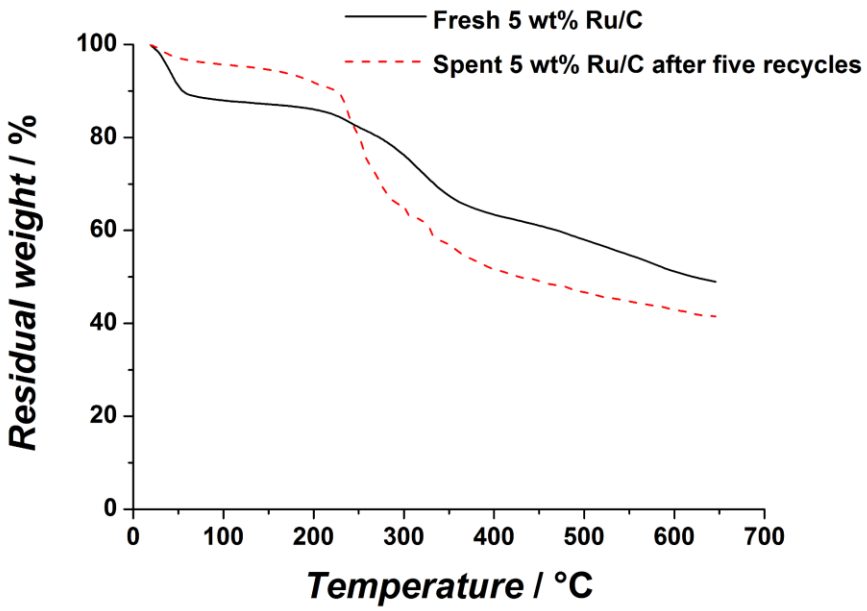


Figure S18. TGA of fresh 5 wt% Ru/C and spent 5 wt% Ru/C recovered at the end of the fifth recycle run (Reaction conditions: Ru/HMF ratio = 1 wt%, [HMF] = 3.7 wt% 100 °C, 20 bar, 60 min).

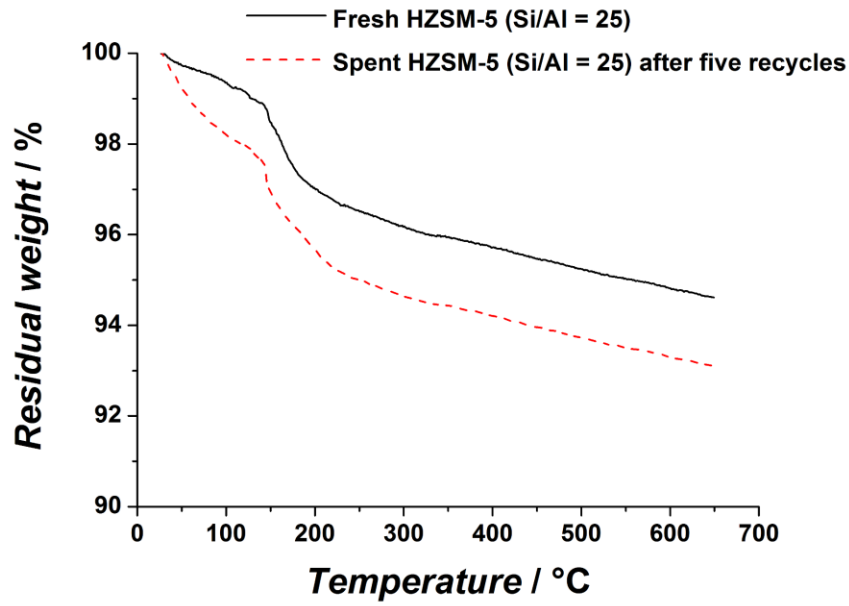


Figure S19. TGA of fresh zeolite HZSM-5 (Si/Al = 25) and spent zeolite HZSM-5 (Si/Al = 25) recovered at the end of the fifth recycle run (Reaction conditions: $mol_{BHMF}/mol_{total\ acidity}$ = 8.3, [BHMF] = 3.0 wt%, 80 °C, 2h).

References

[1] H. Wang, T. Deng, Y. Wang, X. Cui, Y. Qi, X. mu, X. Hou, Y. Zhu, *Green Chem*. **2013**, *15*, 2379–2383.

[2] Y. Xiang, S. Wen, Y. Tian, K. Zhao, D. Guo, F. Cheng, Q. Xu, X. Liu, D. Yin, *RSC Adv*. **2021**, *11*, 3585–3595

[3] P. Lanzafame, D.M. Temi, S. Perathoner, G. Centi, A. Macario, A. Aloise, G. Giordano, *Catal. Today* **2011**, *175*, 435–441

[4] D. Hu, H. Hualei, H. Jin, P. Zhang, Y. Hu, S. Ying, X. Li, Y. Yang, J. Zhang, L. Wang, *Appl. Catal. A, Gen*. **2020**, *590*, 117338–117344;

[5] M. Shin, J. Kim, Y. Suh, *Appl. Catal. A, Gen*. **2020**, *603*, 117763–117772.

[6] M.C. Allen, A.J. Hofman, T. Liu, M.S. Webber, D. Hibbitts, T.J. Schwartz, *ACS Catal*. **2020**, *10*, 6771–6785.

[7] H. Hu, T. Xue, Z. Zhang, J. Gan, L. Chen, J. Zhang, F. Qu, W. Cai, L. Wang, *ChemCatChem*, **2021**, *13*, 3461–3469

[8] X. Hu, S. Kadarwati, Y. Song, C. Li, *RSC Adv*. **2016**, *6*, 4647–4656

[9] W. Fang, H. Hu, Z. Ma, L. Wang, Y. Zhang, *Catalysts*, **2018**, *8*, 383–392

[10] C.R. Wilke, P. Chang, *AIChe J*. **1955** *1*, 264–270.

[11] R. Sitaraman, S.H. Ibrahim, N.R. Kuloor, *J. Chem. Eng. Data* **1963** *8* 198–201.

[12] I.E. Maloka, *Pet. Sci. Technol*. **2005** *23*, 133–136.

[13] S.A. Zavrrazhnov, A.L. Esipovich, S.Y. Zlobin, A.S. Belousov, A.V. Vorotyntsev, *Catalysts* **2019**, *9*, 231–251