Transforming lignosulfonate into versatile acidic carbons: Preparation and catalytic applications

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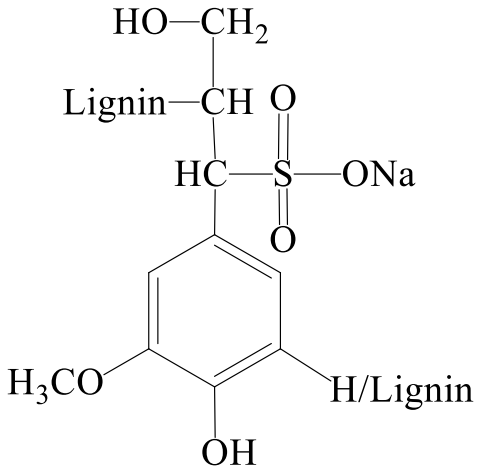
A major obstacle to the progress of research in the field of solid acid catalysis has been the lack of an affordable materials whose acid activity (strength: $H_0 \leq -11$, acid site concentration, H^+ conductivity etc), stability and cost is an par to that of H_2SO_4.

Raw material



Na-Lignosulfonate (LS)

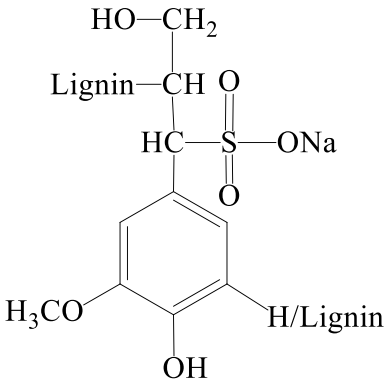
A byproduct from the production of wood pulp using sulfite pulping

Limited market opportunites (as plasticizers, binders and surfactants)

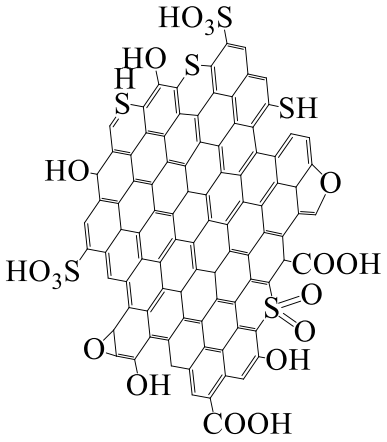
Vanillin is the most successful chemical product derived from LS

Desulfurization is expensive

Can we transform LS into SO_3H containing acid carbon materials ?



Na-Lignosulfonate (LS)



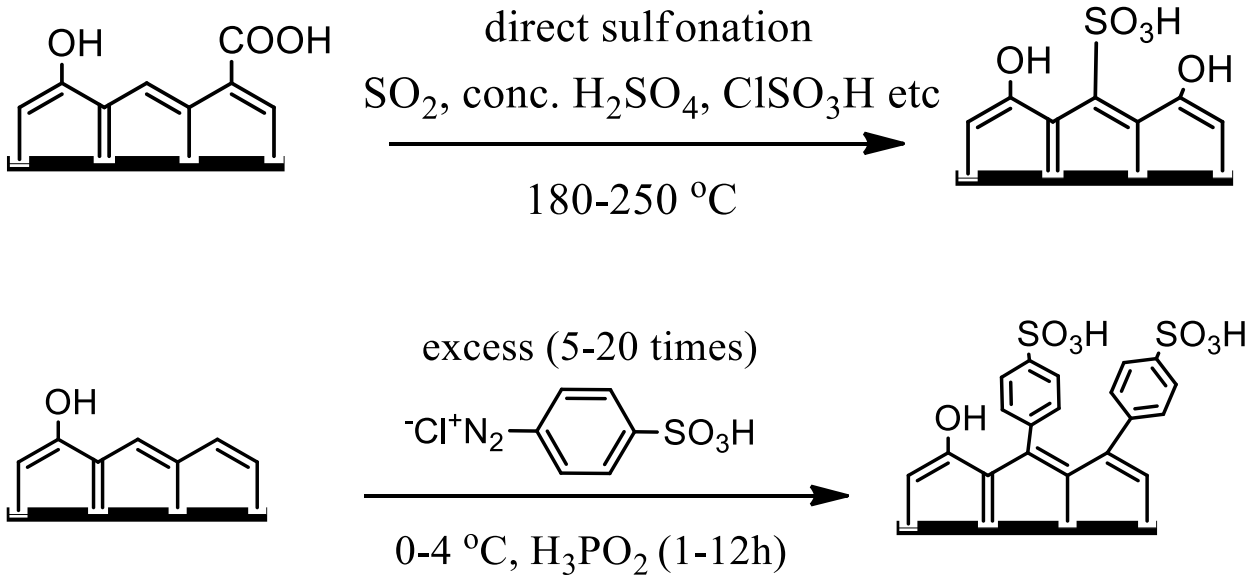
Acidic carbon ($C\text{-}SO_3H$)

A potential substitute to H2SO4, expensive acid resins (e.g Amberlyst 15, 70 etc)

Applications as acid catalyst, proton exchange material and water purification

Nature. 2005 Nov 10;438(7065):178.

L.J. Konwar, New biomass derived carbon catalysts for biomass valorization, ÅAU, ISBN:978-952-12-3396-8



Complicated synthesis and use of large excess of hazardous sulfonating agents

Increasing importance of water tolerant catalysts

biomass streams are typically obtained as dilute aqueous streams

processed in liquid phase reactions

Carbon materials represent potential solution

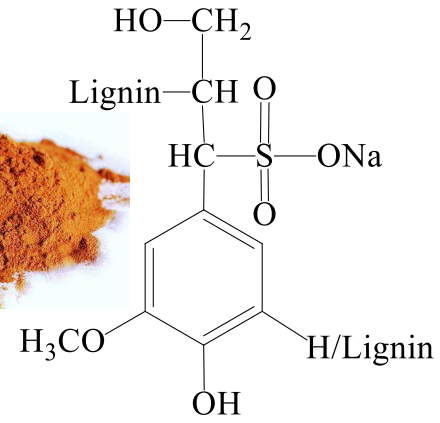
Low cost
Exceptional hydrothermal stability
Chemical inertness

Nature. 2005 Nov 10;438(7065):178.

L.J. Konwar, New biomass derived carbon catalysts for biomass valorization, ÅAU, ISBN:978-952-12-3396-8

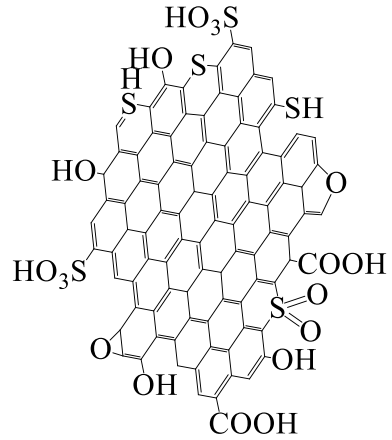
Catal. Sci. Technol., 2014, 4, 2180.

Phenol formaldehyde type condensation rxn followed by H+ excahnge



Na-Lignosulfonate (LS)

Ice-templeting, Mid-pyrolysis and H⁺ exchange with dil. HCl



Highly acidic meso/macroporous carbon (C-SO3H) SO_3H 1-1.8 mmol/g

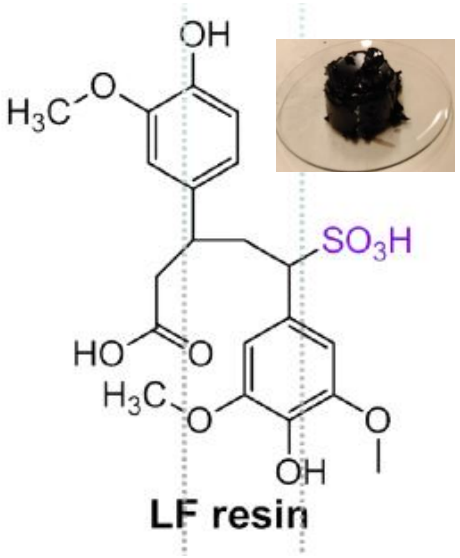
10-40% polystyrene sulfonate (PS) doping during ice-templeting impored porosity and acidity

T_{max} 230 oC

Chemical or physical activation

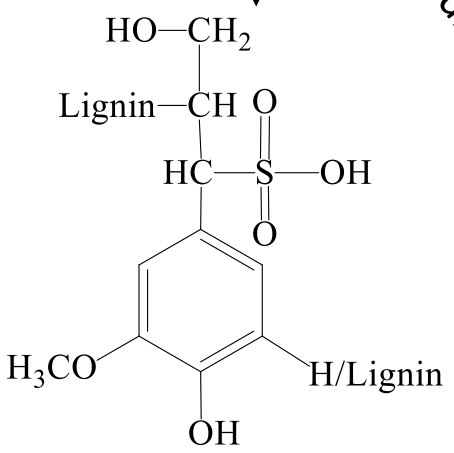
Mid-pyrolysis and H+ exchange with dil. HCl

H^+ excahnge



Non-porous, T_{max} 200 oC

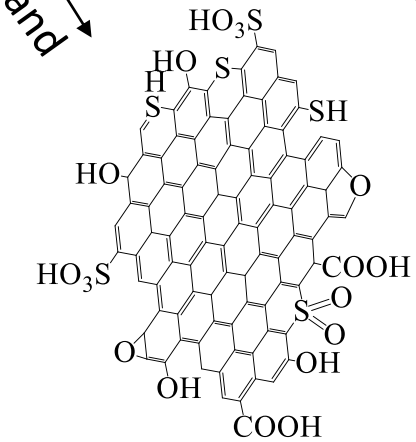
Green Chem., 2015,17, 3644-3652



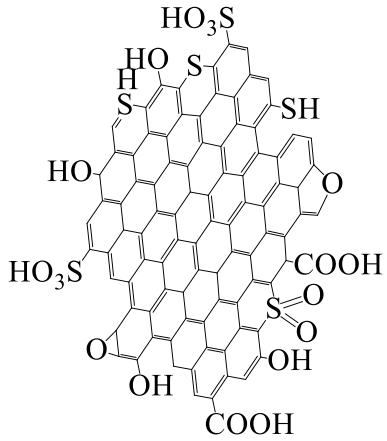
H-Lignosulfonate (LS)

Homogeneous, complicated precipitation/recovery

ACS Sustainable Chem. Eng., 2015, 3 (7), pp 1366–1373



Highly acidic non porous carbon (C-SO_3H) SO_3H 1-1.8 mmol/g



Low acidic meso/microporous carbon (C-SO_3H) SO_3H 0.15-0.5 mmol/g

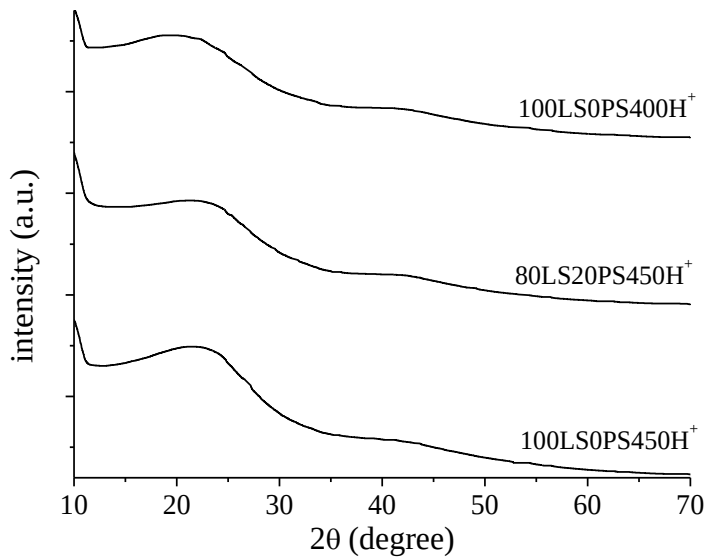
Applied Catalysis B Environmental, 2018, 220, 314-323

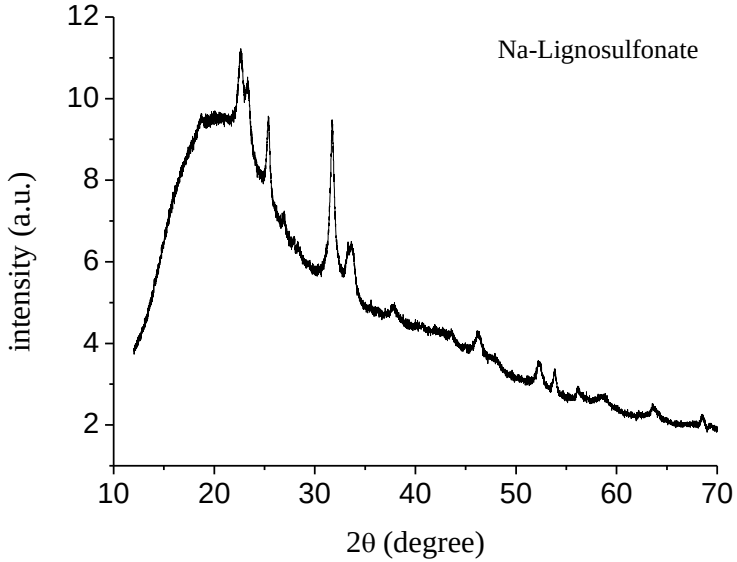
Summary of textural and acidic properties

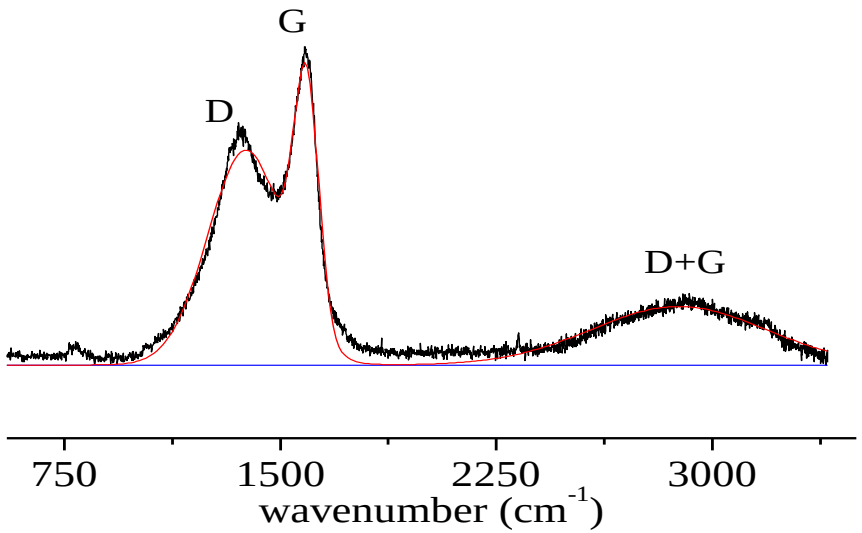
Surface and textural characteristics of the carbon materials obtained from LS/LS-PS monolith 45							
Catalyst	[a] S_{BET}	[b] V_p	[c] D_p	[d] V_{mp}	I_D/I_G	[f] SO_3H	[g] acid density
	(m^2/g)	(cm^3/g)	(nm)	(cm^3/g)		(mmol/g)	($mmolH^+/g$)
LS (Na form)	<1	-	-	-	n.d	2.61	n.d
LS-RES	3	0.023	18.5	0	n.d	2.08	n.d
Amberlyst® 70	**<1**	**-**	**-**	**-**	**n.d**	**2.50**	**2.50**
Amberlite® IR120	<1	-	-	-	n.d	1.80	1.80
100LS0PS350H$^+$	2	0.018	47	0	0.90	1.09	4.2
100LS0PS400H$^+$	6.5	0.019	14	0	0.87	0.84	3.7
100LS0PS400H$^+$#	10	0.043	18	0	n.d	0.58	3.94
100LS0PS450H$^+$	12	0.033	14.3	0.0007	0.84	0.32	2.99
90LS10PS350H$^+$	4	0.019	21	0	n.d	1.24	4.74
90LS10PS450H$^+$	35	0.14	13.3	0.001	0.84	n.d	3.1
80LS20PS350H$^+$	11	0.019	14	0	0.85	n.d	5.0
80LS20PS450H$^+$	**122**	**0.32**	**14.5**	**0.024**	**0.80**	**1.21**	**3.49**
80LS20PS450H$^+$*	95	0.20	12	0.013	n.d	1.18	3.48
60LS20PS450H$^+$	8	0.046	29	0	n.d	1.4	3.75
60LS20PS350H$^+$	4.3	0.03	43	0	n.d	1.56	6.41

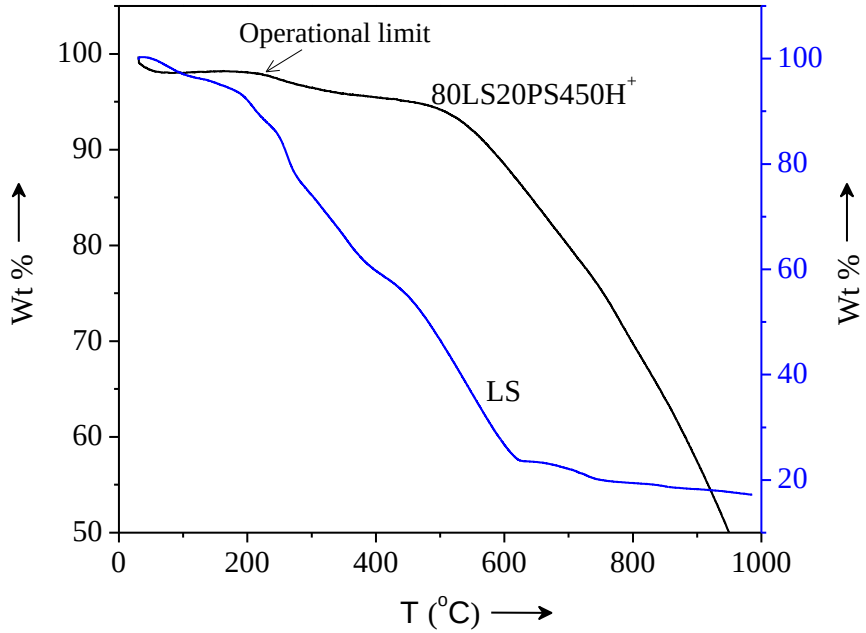
[a] specific surface area, [b] total pore volume at $P/P_0 = 0.95$, [c] average pore diameter, [d] micropore volume, [f] based on XPS/elemental analysis (excluding % of S-H and C=S), [g] total acidity based on titration, # treated with 50% H_2O_2 at 60 °C for 6 h, * After 90 h time on stream

XRD, Raman and TGA

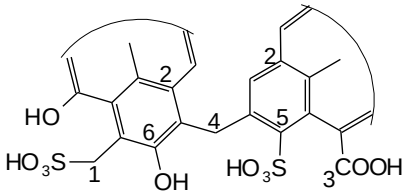


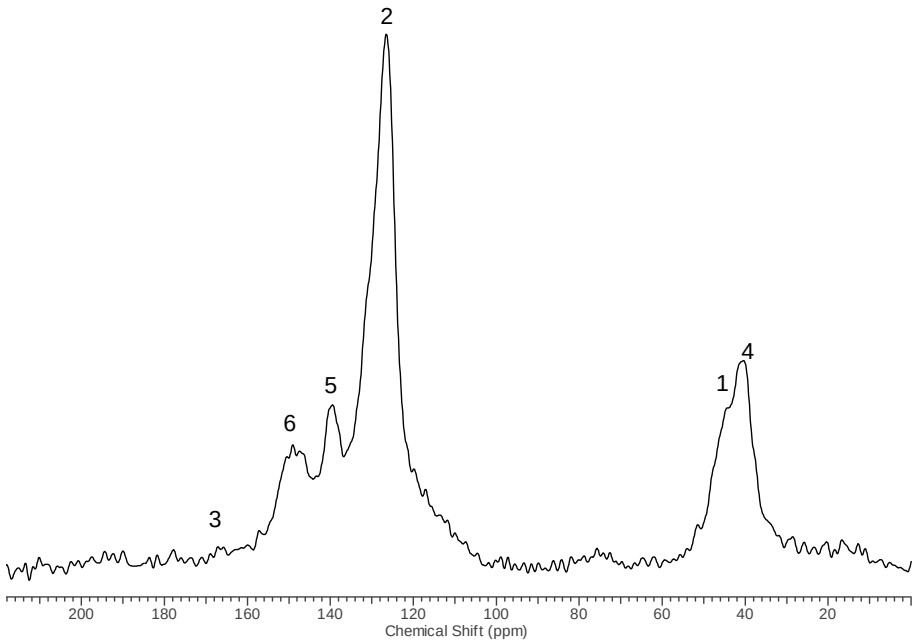


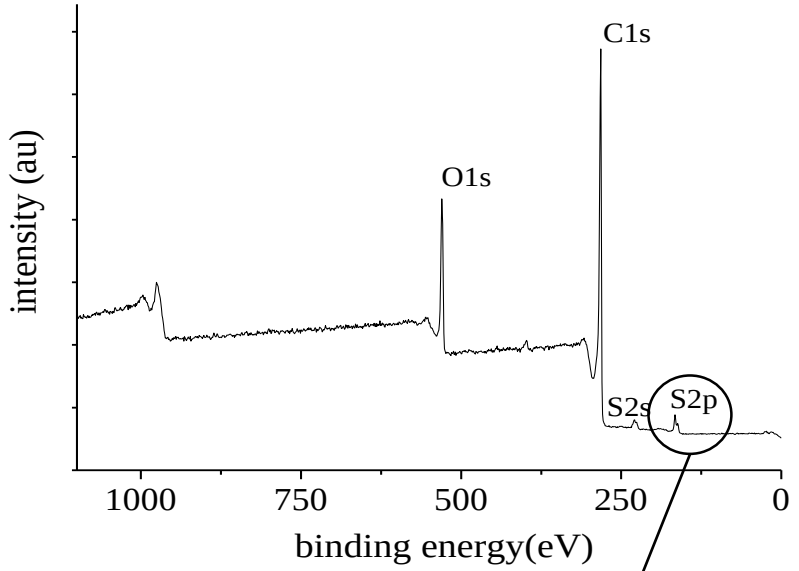


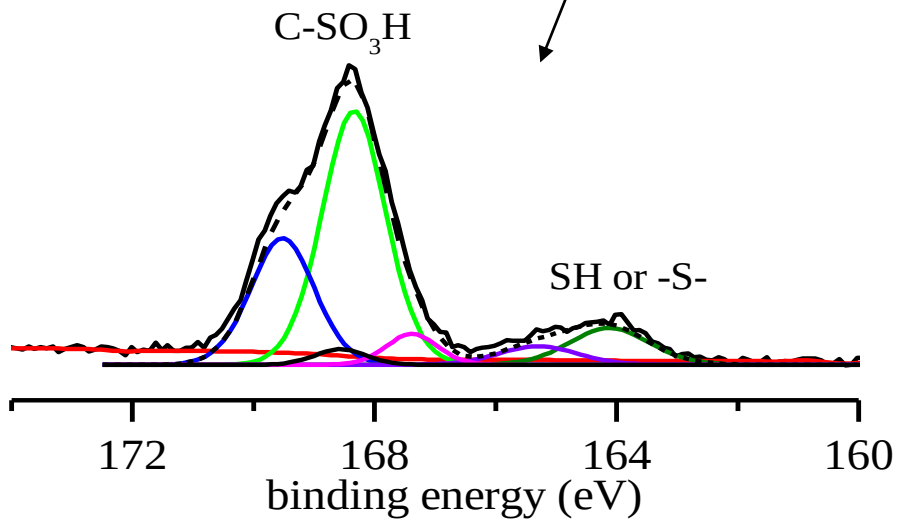


CP/MAS ^{13}C-NMR and XPS



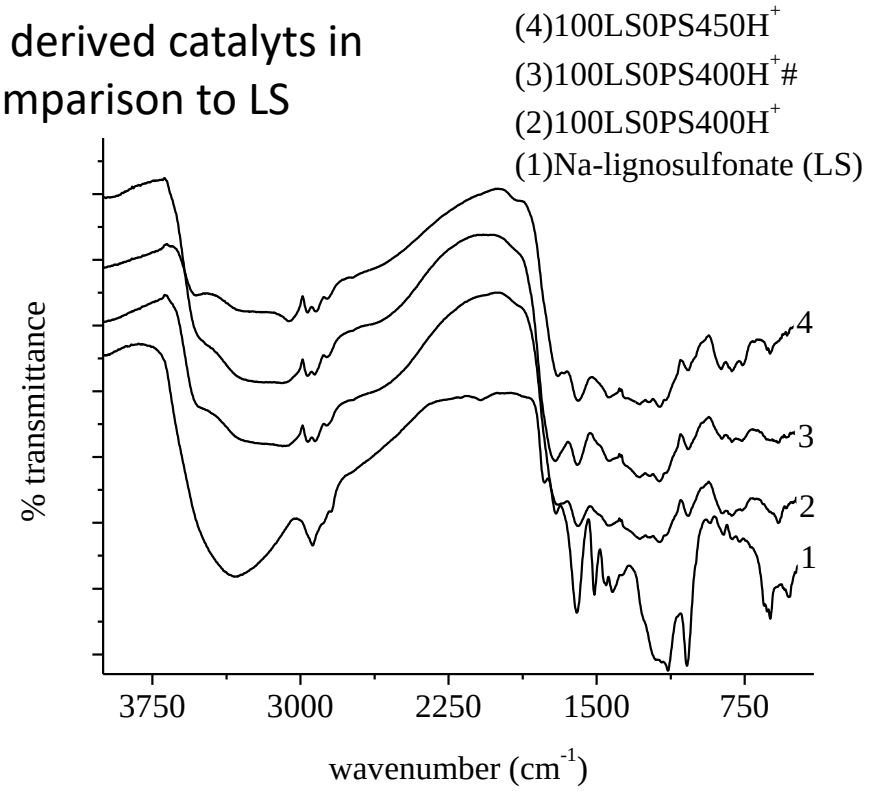




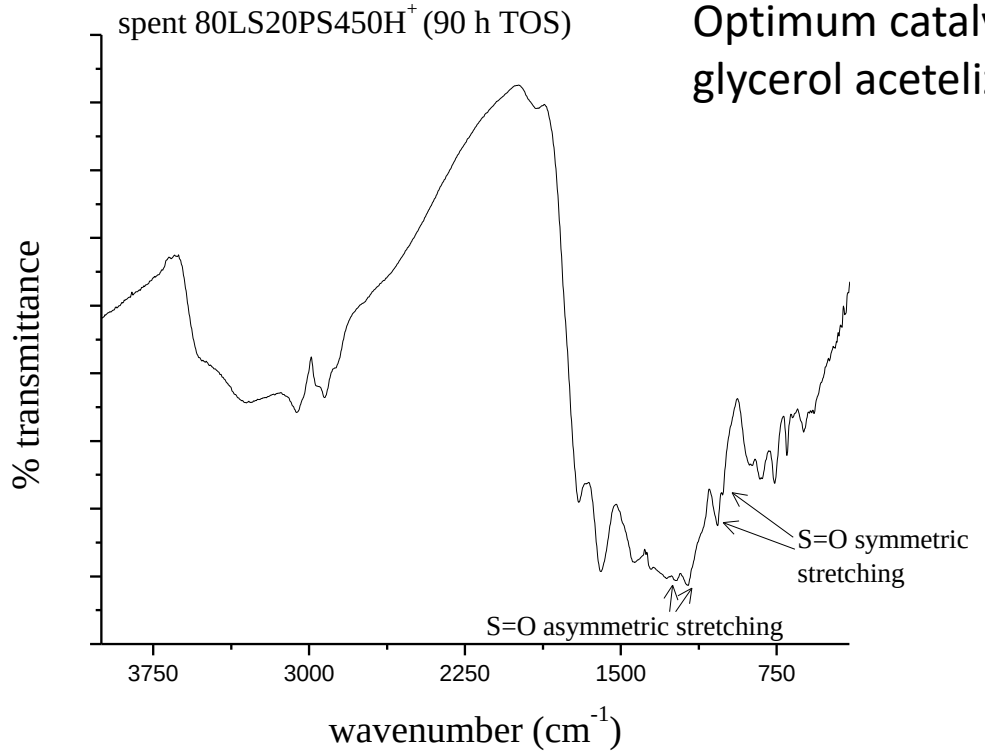


FT-IR patterns

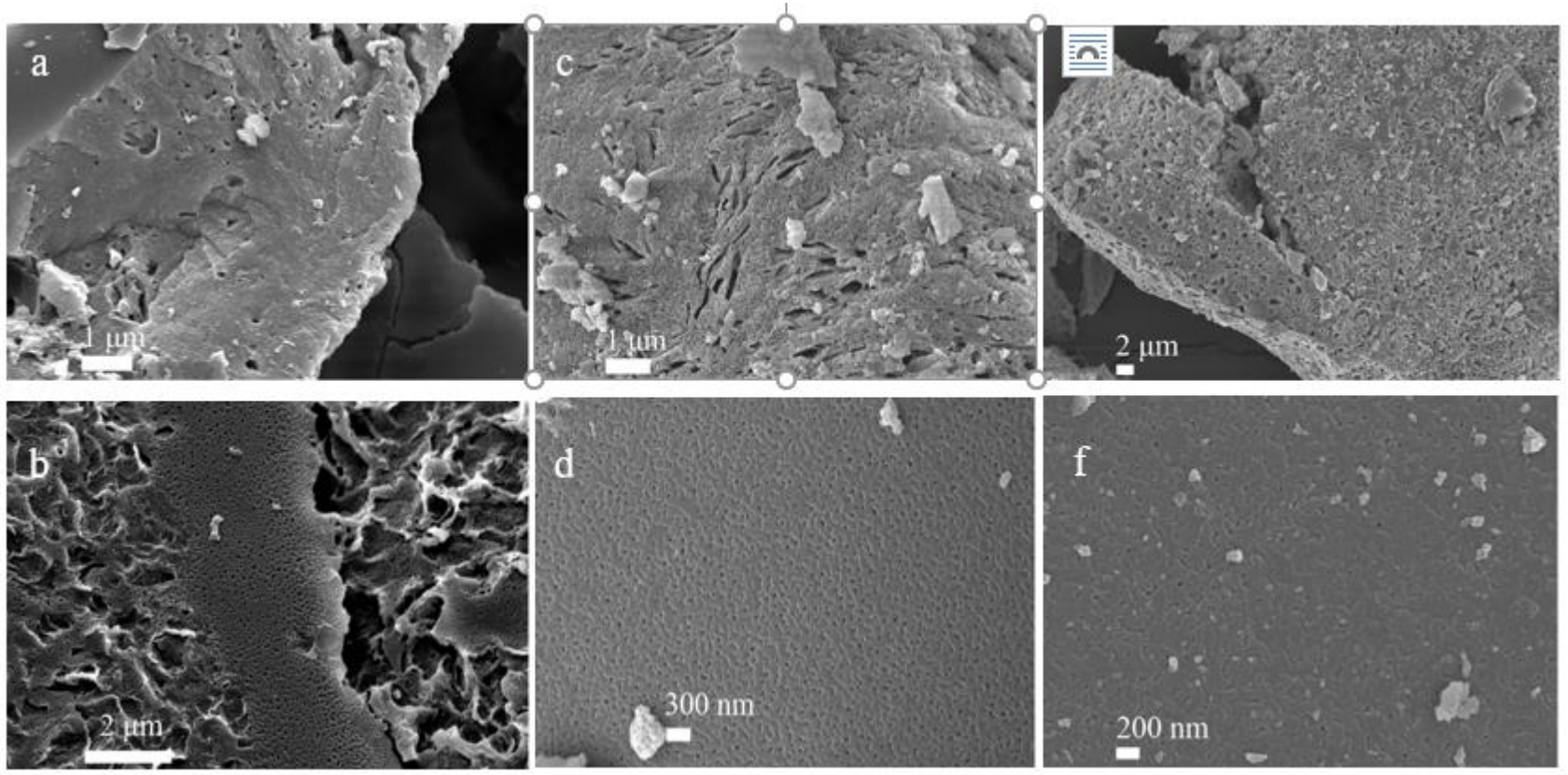
LS derived catalyts in comparison to LS



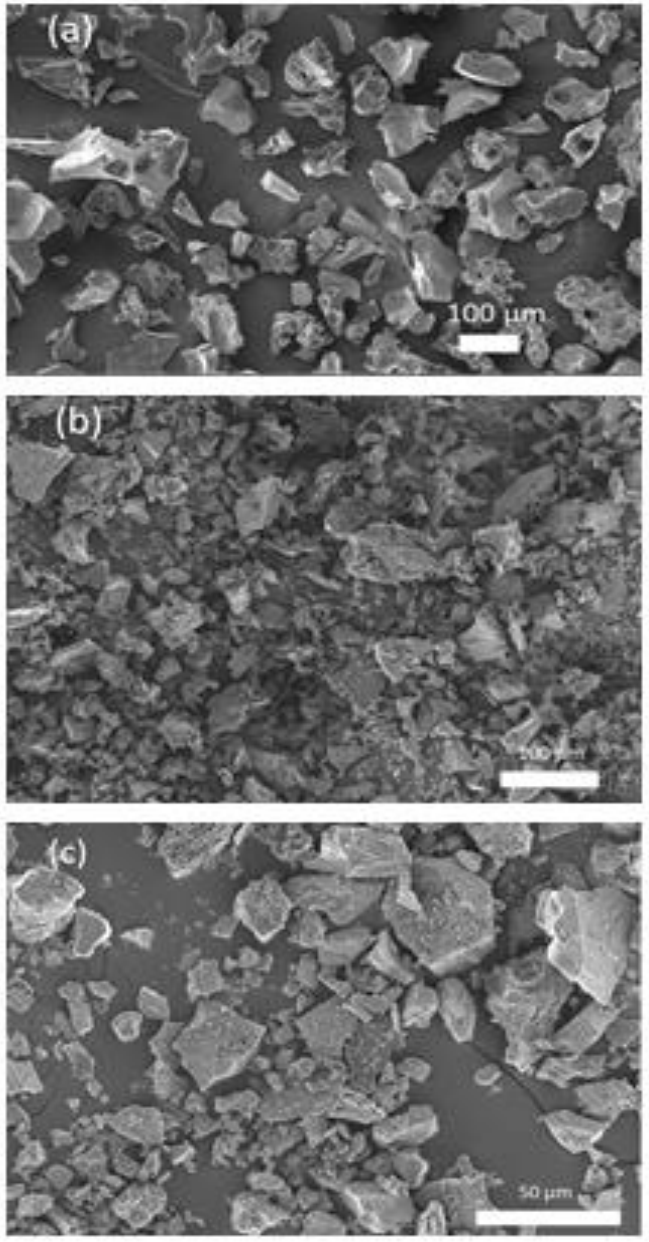
Optimum catalyst upon glycerol acetelization

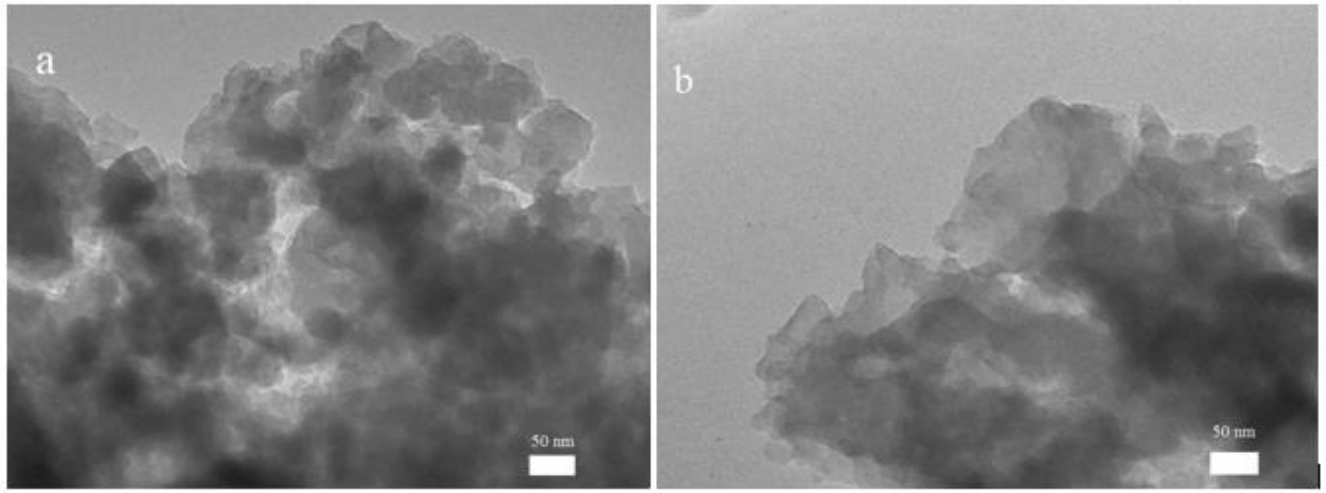


FE-SEM images of representative carbon samples (a) 100LS0PS450H$^+$ (1 µm), (b) 90LS10PS450H$^+$ (2 µm), (c) 80LS20PS450H$^+$ (1 µm), (d) 80LS20PS450H$^+$ (300 nm), (e) 80LS20PS450H$^+$ 90 h after time on stream (2 µm) and (f) 80LS20PS450H$^+$ after 90 h time on stream (200 nm).



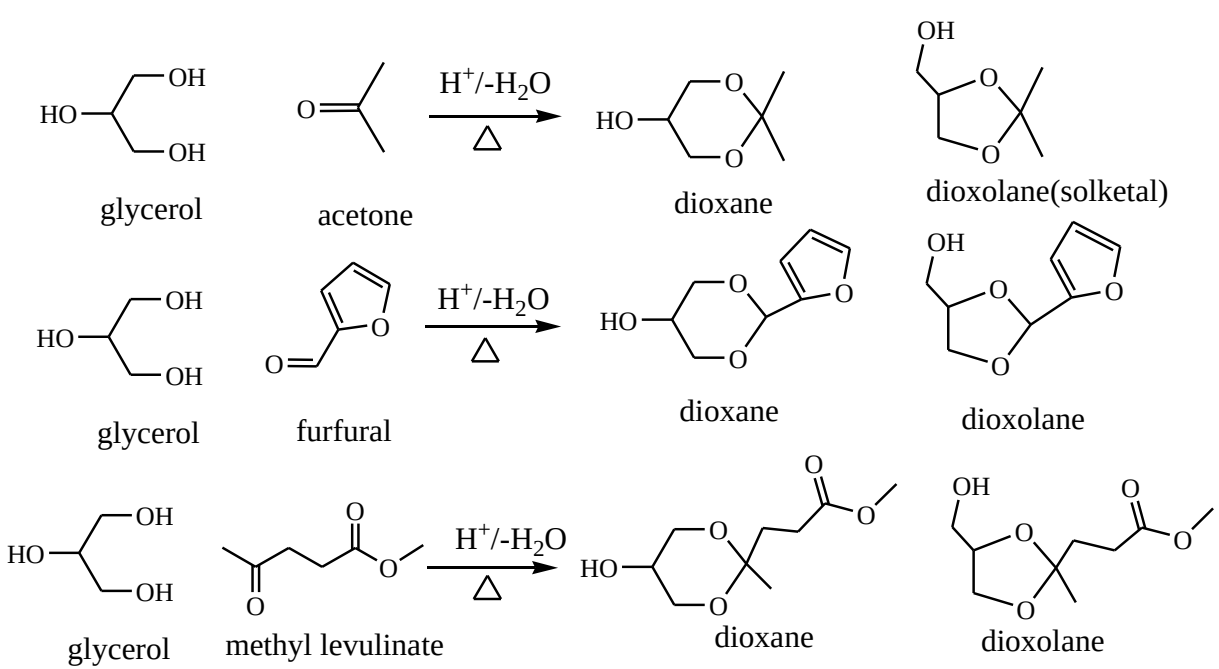
FE-SEM images showing the particles sizes of LS/LS-PS monolith derived acidic catalysts (a) 100LS0PS450H$^+$, (b) 90LS10PS450H$^+$ and (c) 80LS20PS450H$^+$





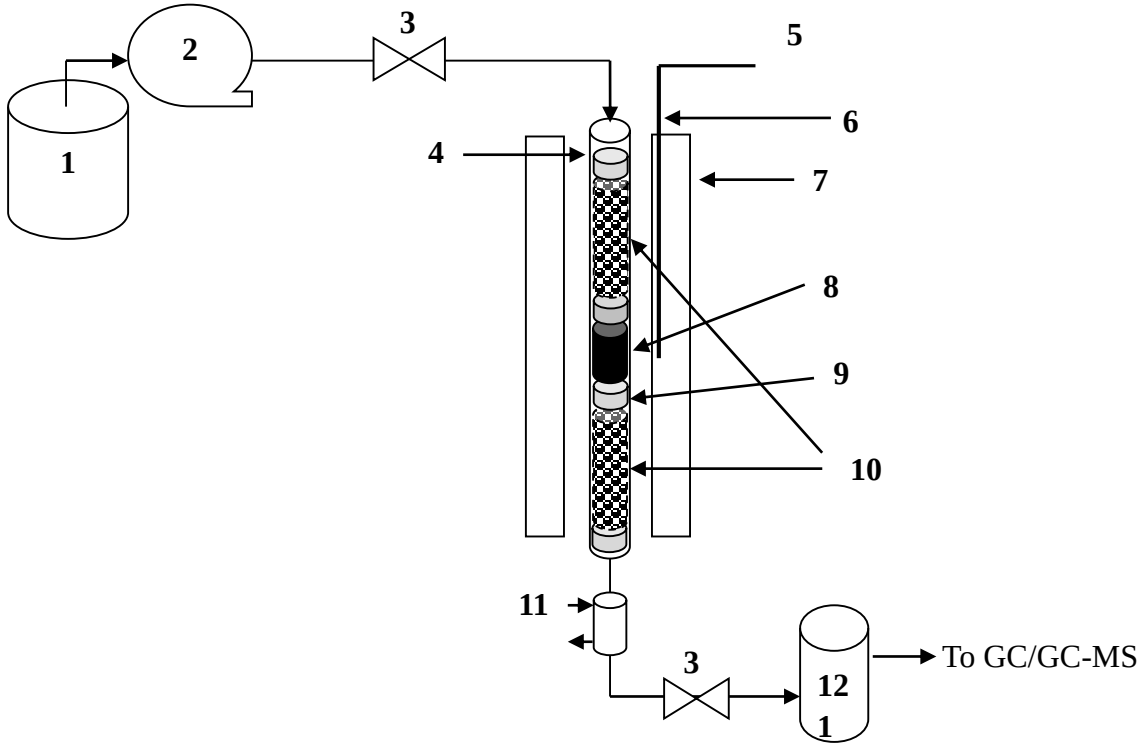
HR-TEM images

Application 1: acetalization of glycerol to bio-additives



Reaction scheme

Experimental set-up for batch experiments

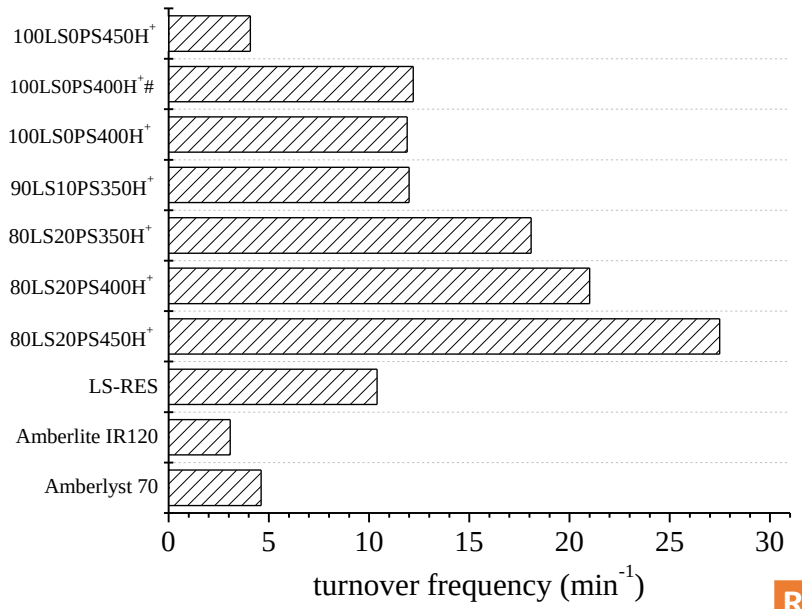


Experimental set-up for continuous acetalization of glycerol to solketal. 1. Feed vessel (glycerol acetone mixture), 2. HPLC pump, 3. On–off valve, 4. Reactor, 5. Temperature controller, 6. Thermocouple, 7. Furnace, 8. Catalyst bed, 9. Quartz wool support, 10. 1 mm glass beads, 11. Cooling jacket, 12. Product collection vessel

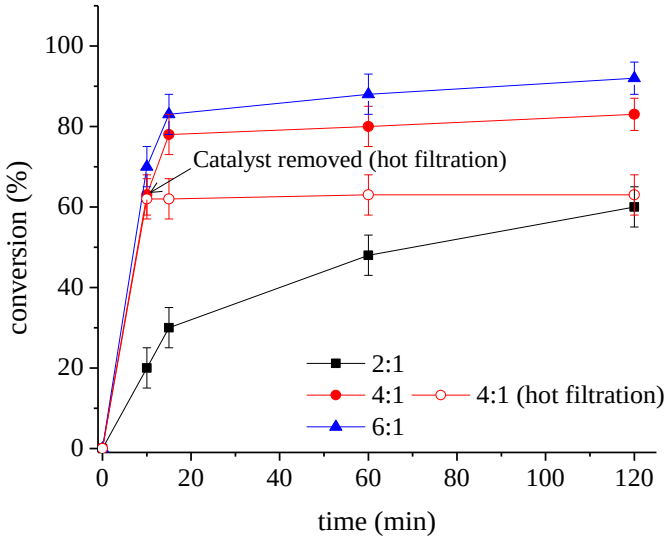
L.J. Konwar, A Samikannu, P. Mäki-Arvela, D. Boström, J-P. Mikkola, **Appl. Catal., B**, 220, 314-323. 2018.

Batch experiment results

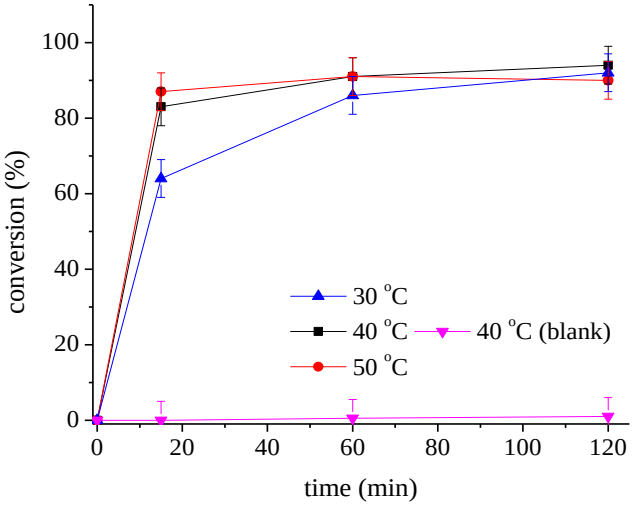
Turnover frequency



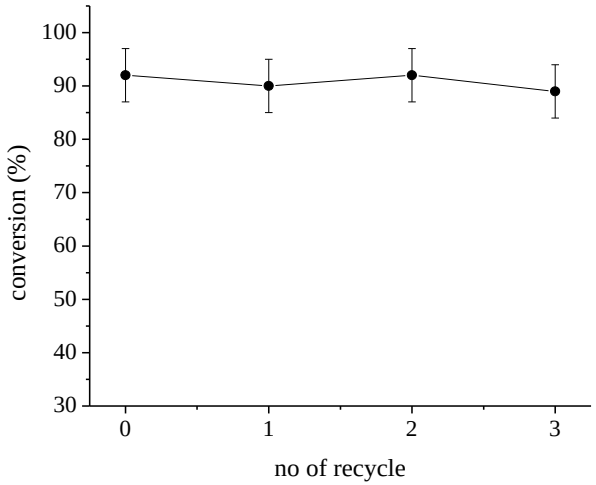
Acetone-glycerol mole ratio



Reaction temperature



reuse



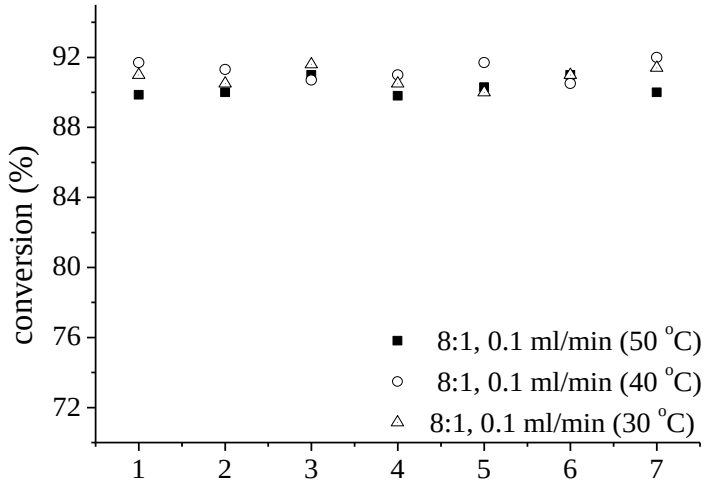
Results of batch catalytic tests conducted upon acetalization of glycerol with furfural and methyl levulinate

Carbonyl compound	Carbonyl compound /glycerol (mole ratio)	Time (min)	Glycerol conversion (%)	Selectiveity (%)	
				dioxolane (5 membered ring)	dioxane (6 membered ring)
Furfural	4*	120	80	52	48
	4	60	100	51	49
	2	60	93	51	49
	1	60	63	51	49
Methyl levulinate	4	60	100	53	47
	2	60	97	53	47
	1	60	67	52	48

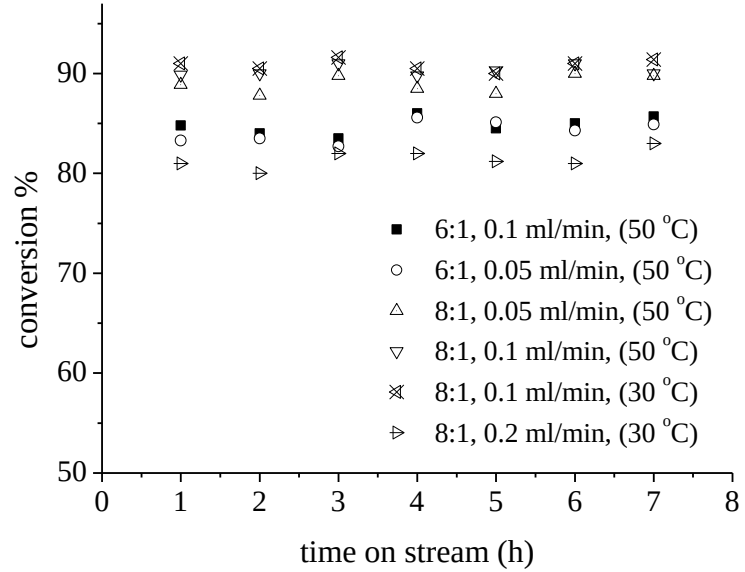
Reaction conditions: 0.5 wt% catalyst, 100 °C with 50 ml/min N_2 flow, 300 rpm stirring rate, *N_2 flow was stopped

Results from continous flow experiments

Reaction temperature

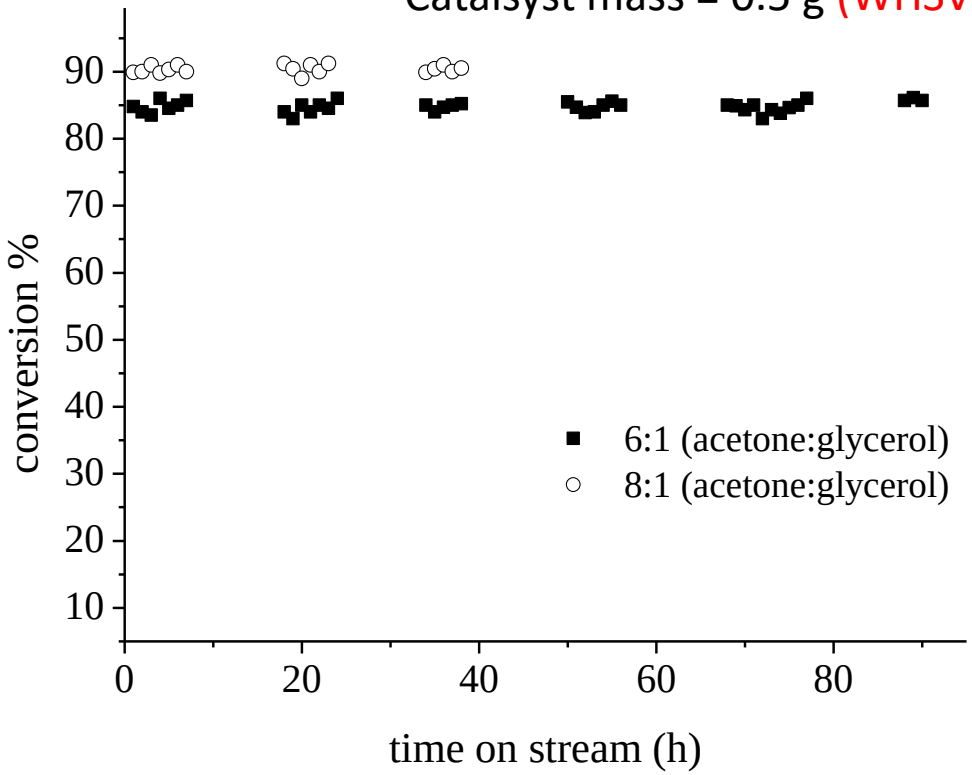


Feed flow rate

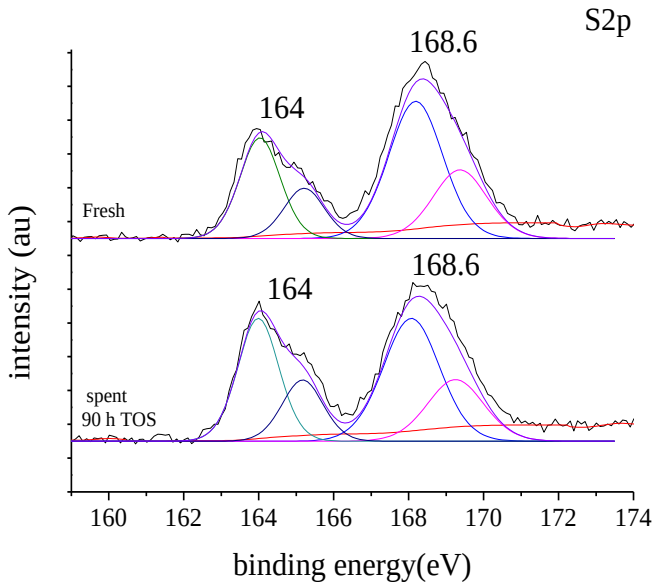


Time on stream

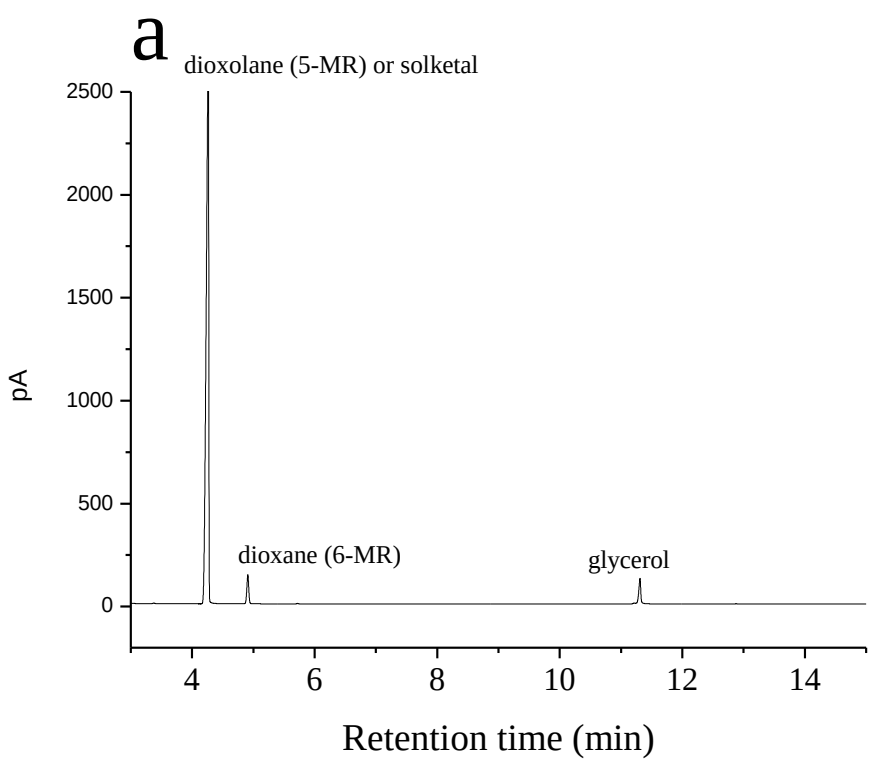
0.1 ml/min mix Feed or 0.0134 g/min glycerol,
Catalsyst mass = 0.5 g (WHSV= 1.6 h^{-1}), 50 °C

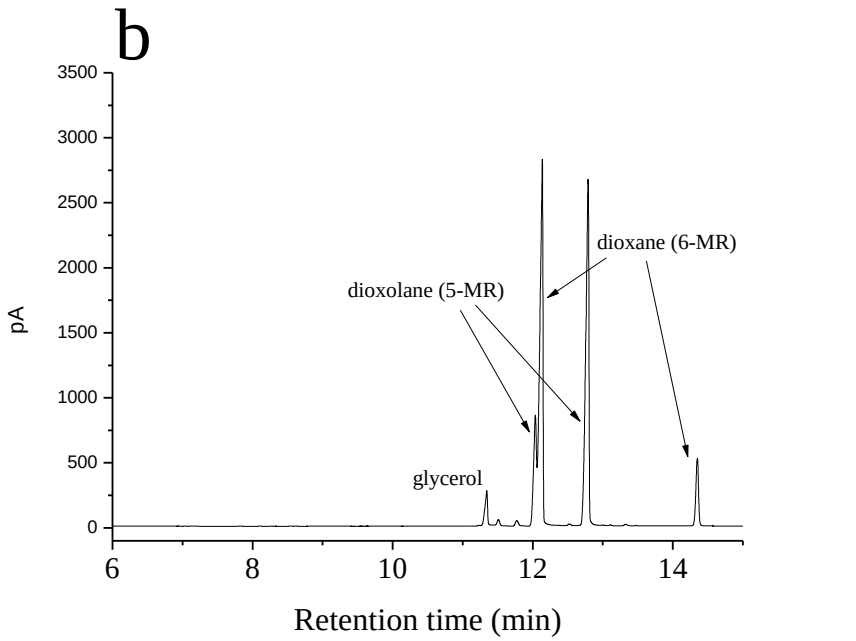


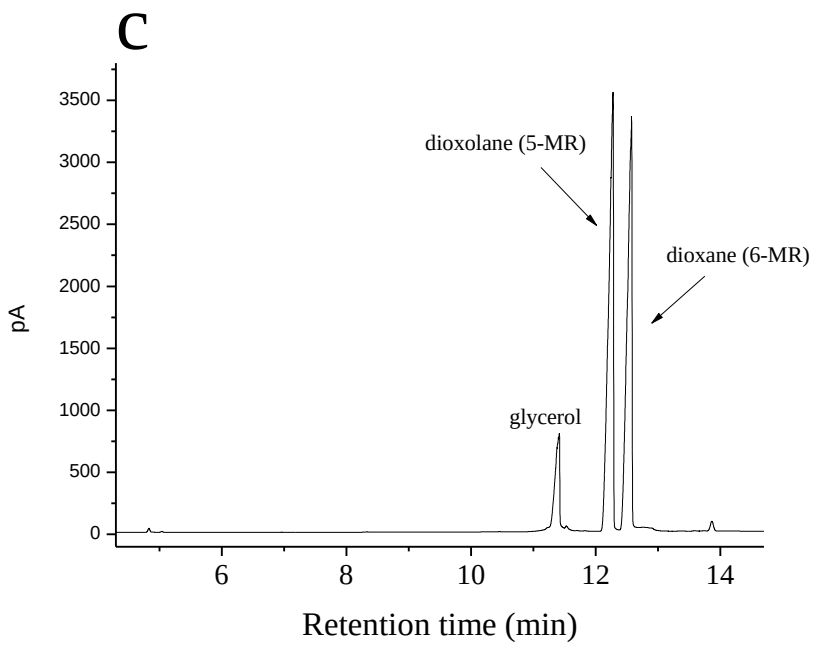
Stability of SO_3H sites



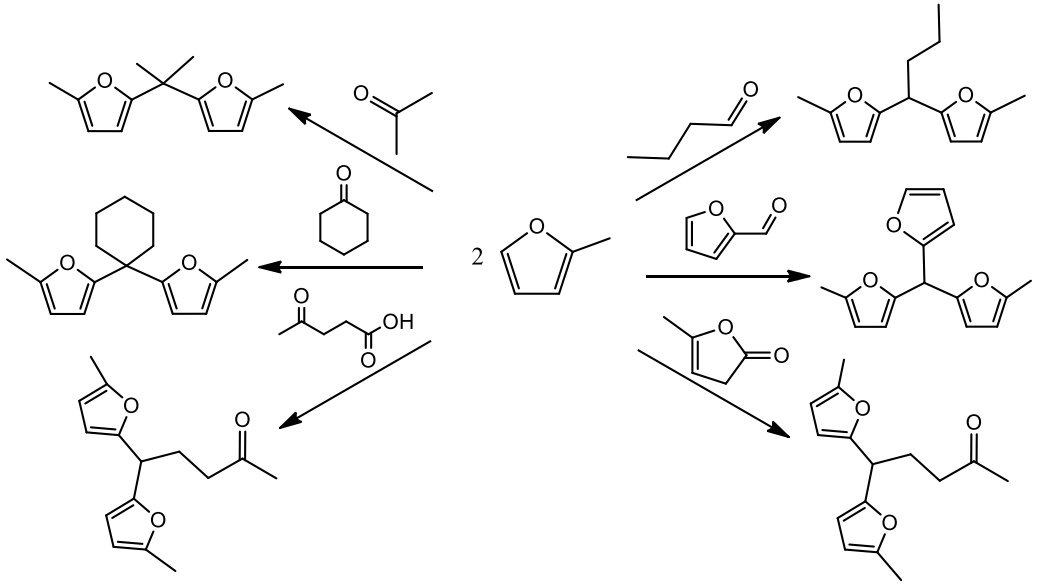
GC-FID chromatograms showing the obtained products upon acetalization of glycerol with (a) acetone, (b) furfural and (c) methyl levulinate





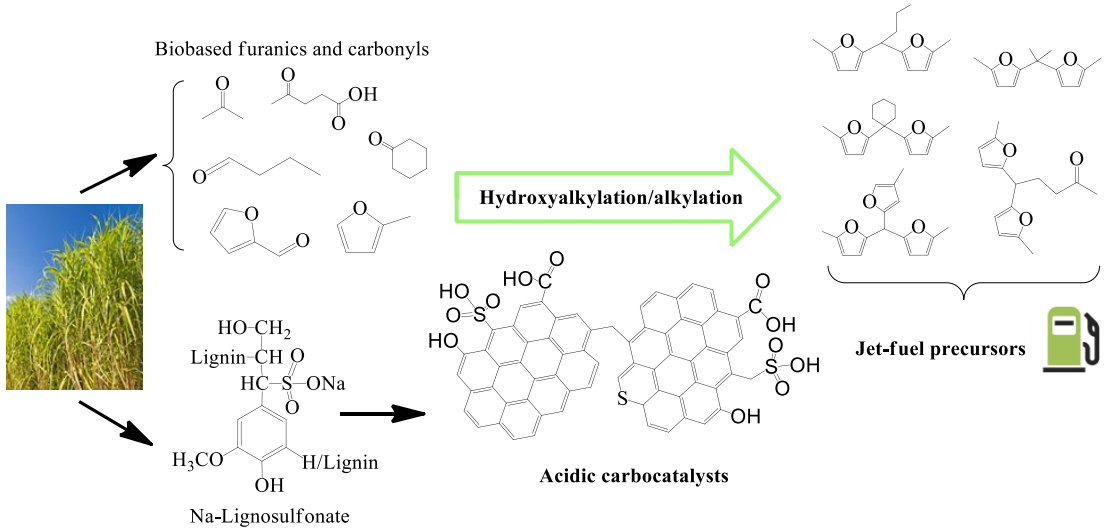


Application 2: C–C coupling of bio-based furanics and carbonyl compounds to liquid hydrocarbon precursors



Reaction scheme for C–C coupling of 2-methylfuran and with bio-based carbonyl compounds via HAA reaction.

Experimental set-up for batch experiments



L.J. Konwar, A. Samikannu, P Mäki-Arvela, J-P Mikkola, **Catal. Sci. Technol**., 8, 2449-2459, 2018.

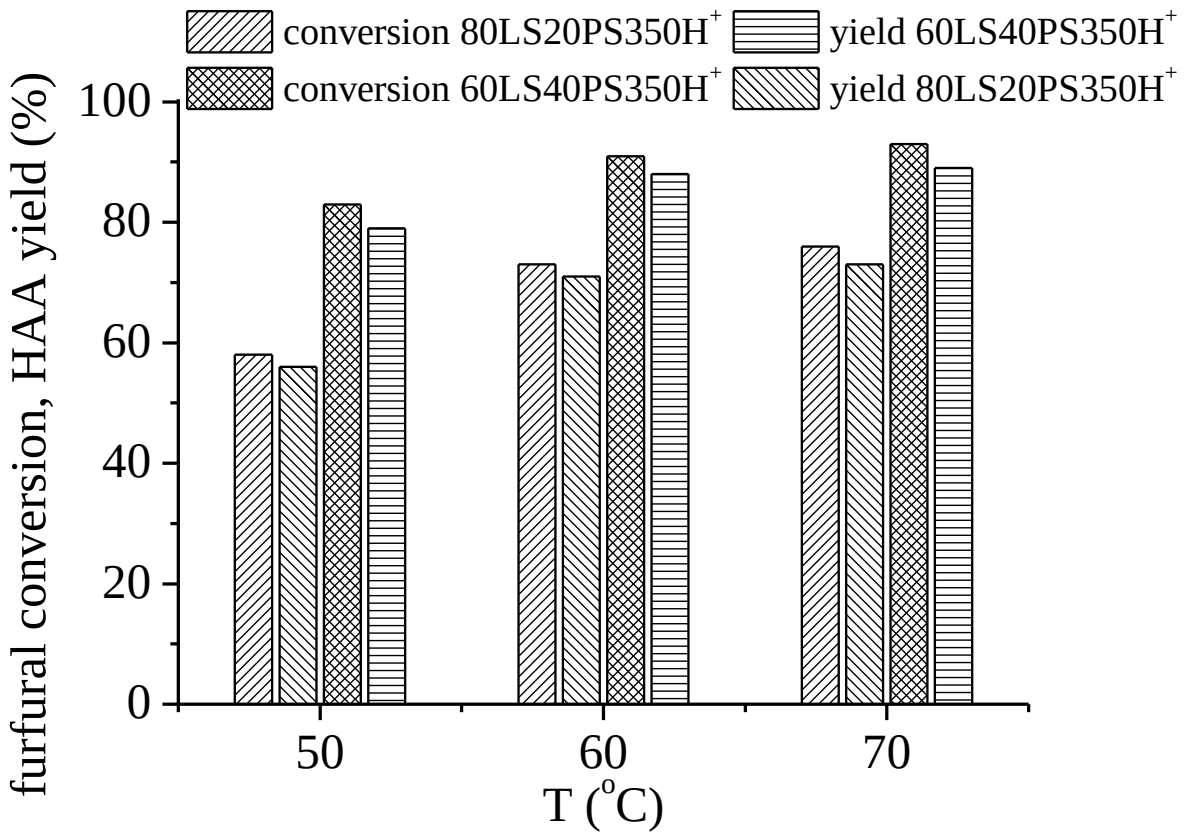
Catalytic activity results upon HAA (hydroxyalkylation/alkylation) of 2-methylfuran with furfural

Catalytic activity of LS derived catalysts in comparison to acidic resins and zeolites				
catalyst	[a] TOF (h^{-1})	time (h)	furfural conversion (%)	HAA product yield (%)
90LS10PS350H$^+$	41	2	52	51
80LS20PS350H$^+$	103	2	73	70
60LS40PS350H$^+$	**185**	**2**	**91**	**88**
80LS20PS450H$^+$	43	4	64	59
60LS40PS450H$^+$	29	4	61	55
LS-RES	23	4	75	73
Amberlyst® 70	59	4	86	83
Amberlite® IR120	7	24	88	84
H-ZSM-5	5.5	24	26	12
p-toluenesulfonic acid	186	2	84	73
Acetic acid	0	24	1	0
Phenol	0	24	1	0
Blank	-	24	2	0

Reaction conditions: 37 mg catalyst, 10.5 mmol 2-methylfuran, 5.25 mmol furfural, 300 rpm stirring rate.

[a] TOF expressed as mmol furfural converted per mmol of acid site per hour.

Temperature effects



Effect of carbonyl compound

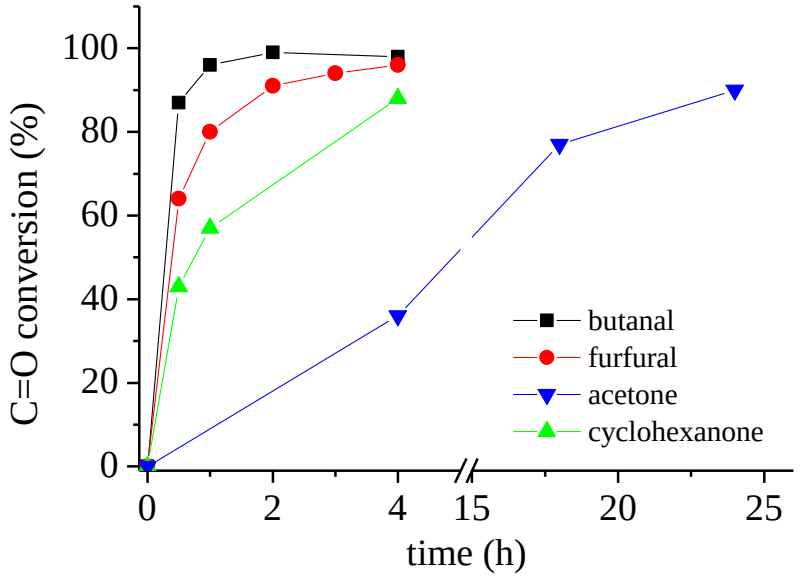
Table 3. Effect of carbonyl compound on the catalytic activity of 60LS40PS350H$^+$ (LS derived catalyst) upon HAA of 2-methylfuran

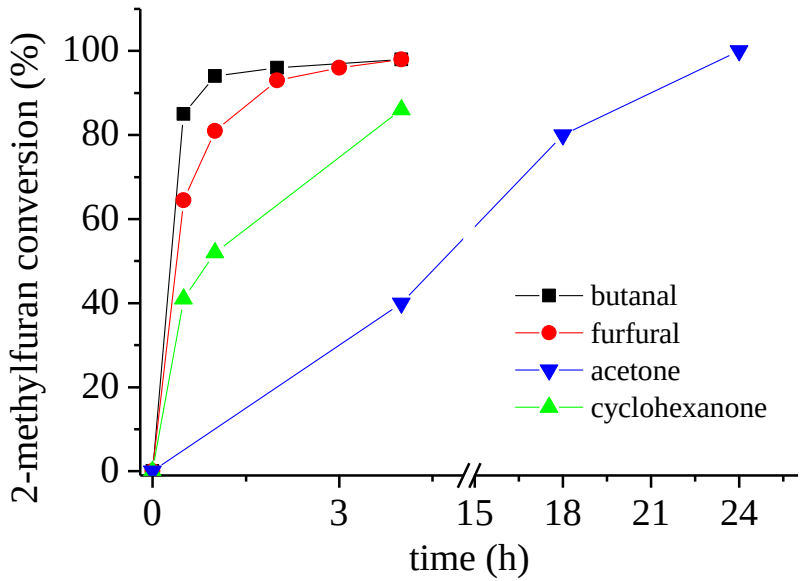
carbonyl compound	[a] TOF (h^{-1})	time (h)	carbonyl conversion (%)	yield (%)			
				HAA product	HA product	2-methylfuran timer	others
butanal	369	2	99	96	0	0	3
furfural	185	4	96	93	0	0	4
acetone	11	24	90	94	0	5	0
cyclohexanone	102	4	88	84	4.5	0	0
α-angelica lactone	7	24	85	57	0	2.3	40
levulinic acid	4.5	24	70	60	0	6	34

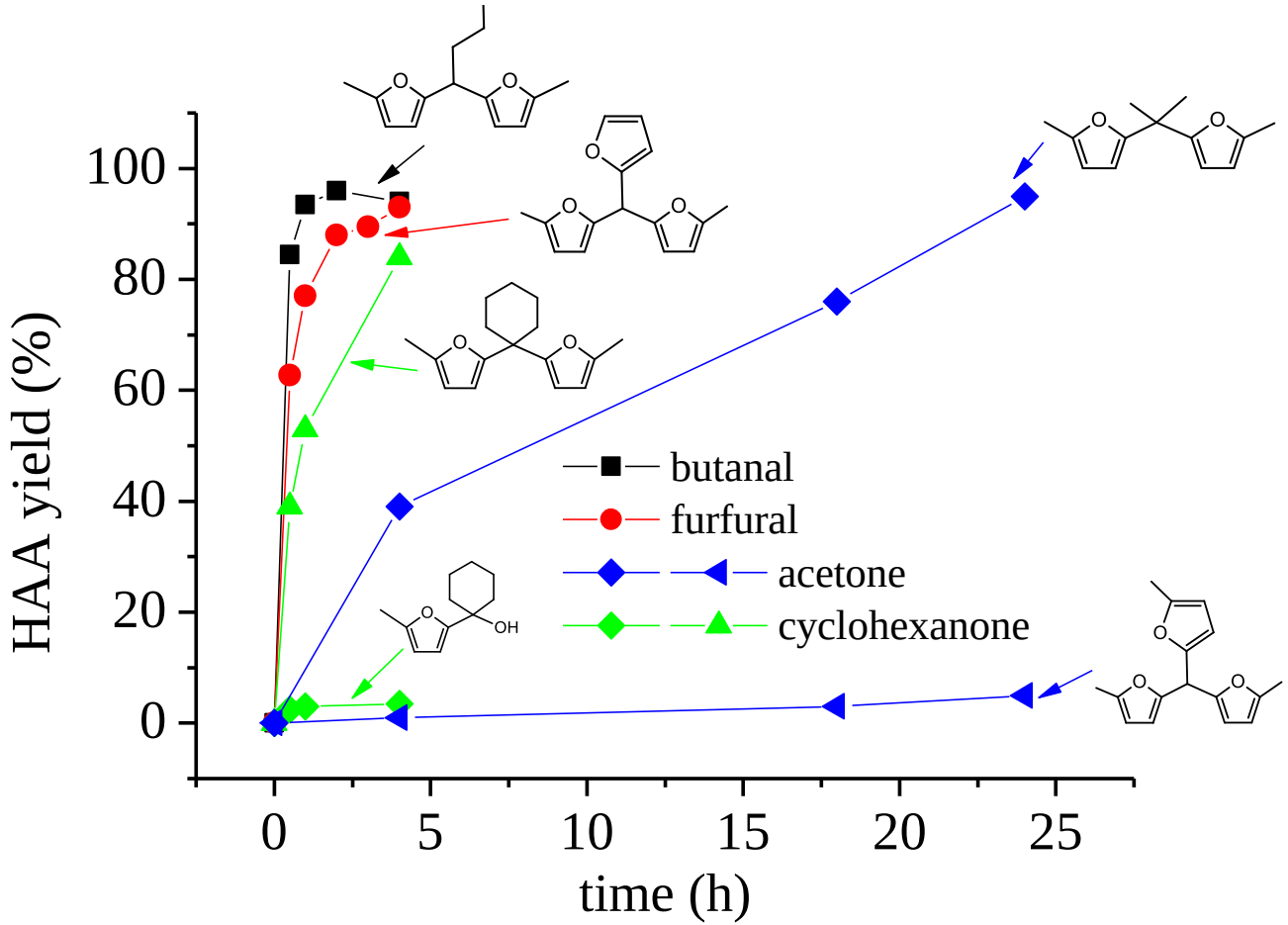
Reaction conditions: 37 mg catalyst, 10.5 mmol 2-methylfuran, 5.25 mmol carbonyl compound, 300 rpm stirring rate.

[a] TOF expressed as mmol carbonyl compound converted per mmol of acid site per hour.

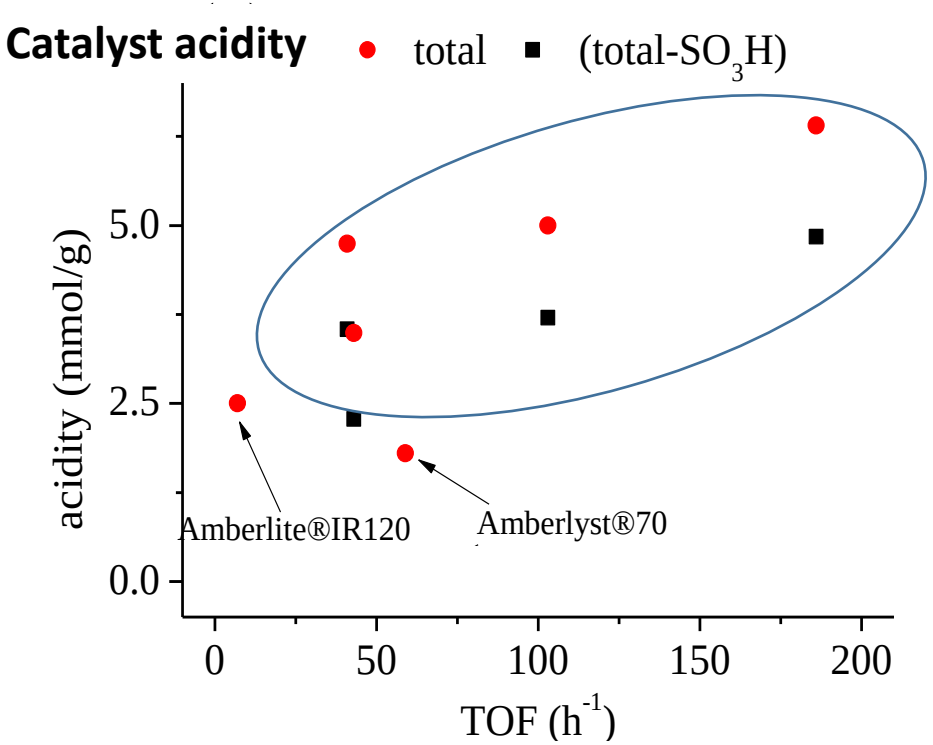
Kinetics of HAA reaction studied over optimum LS catalyst (60LS40PS350H$^+$)

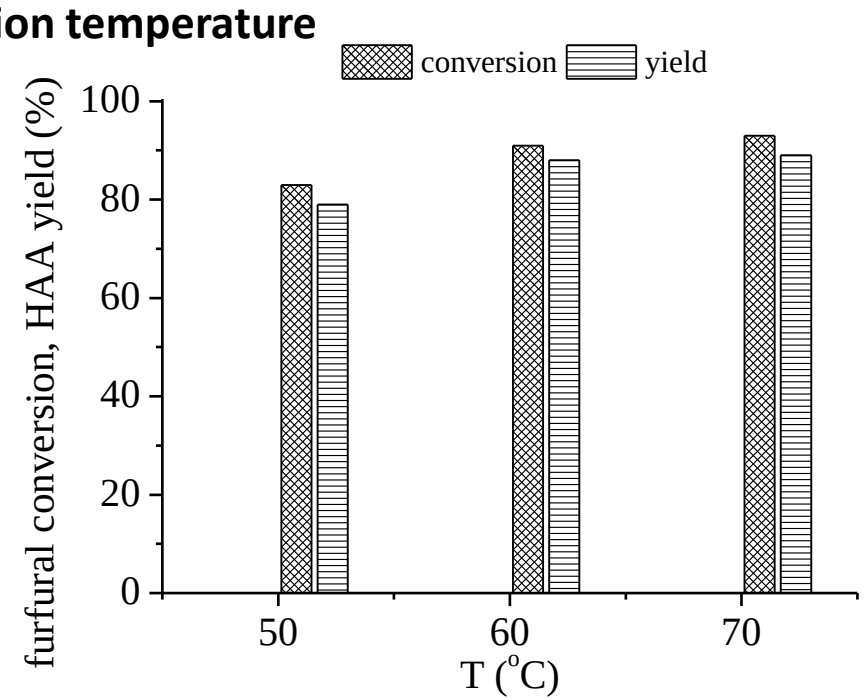


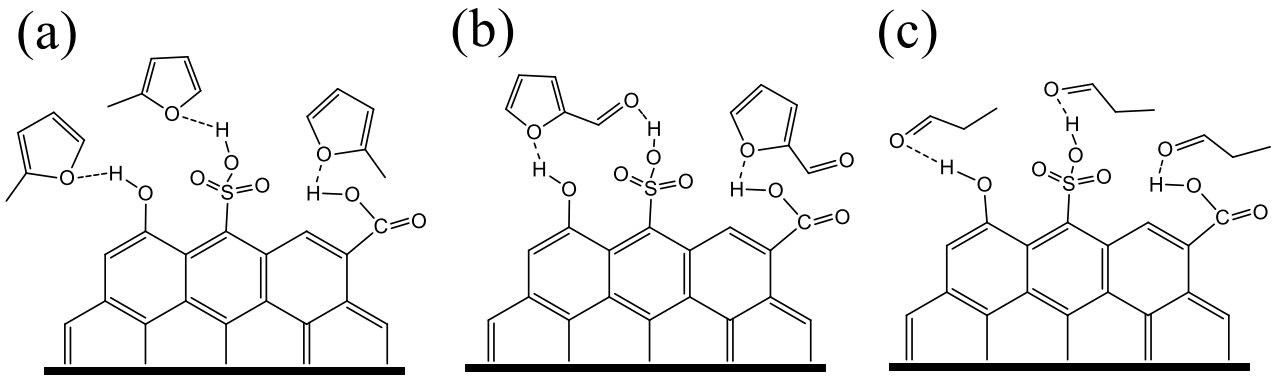




Acidity and temperature effects

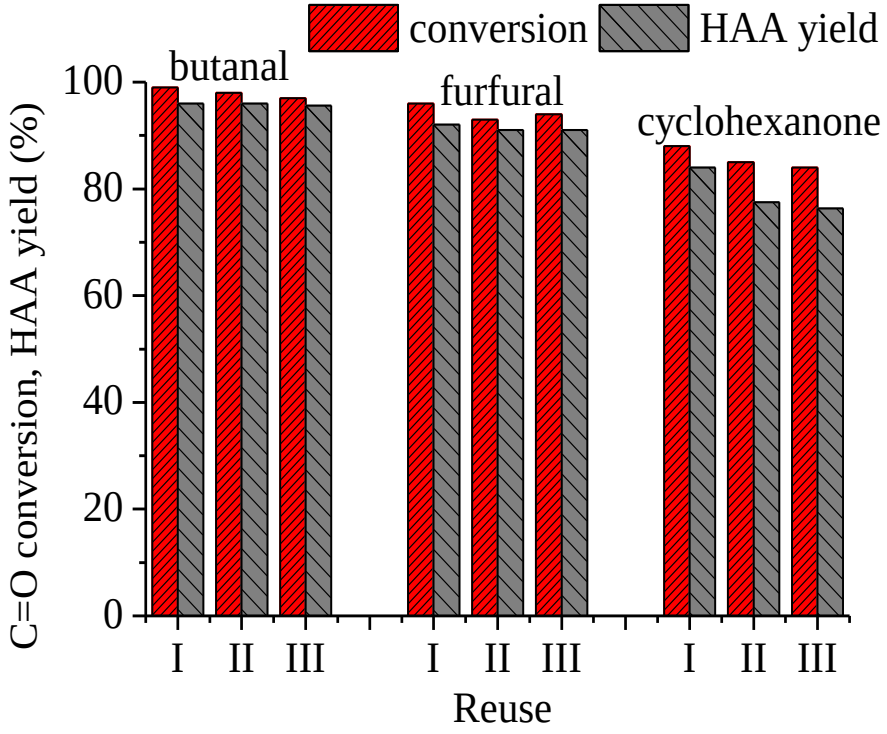


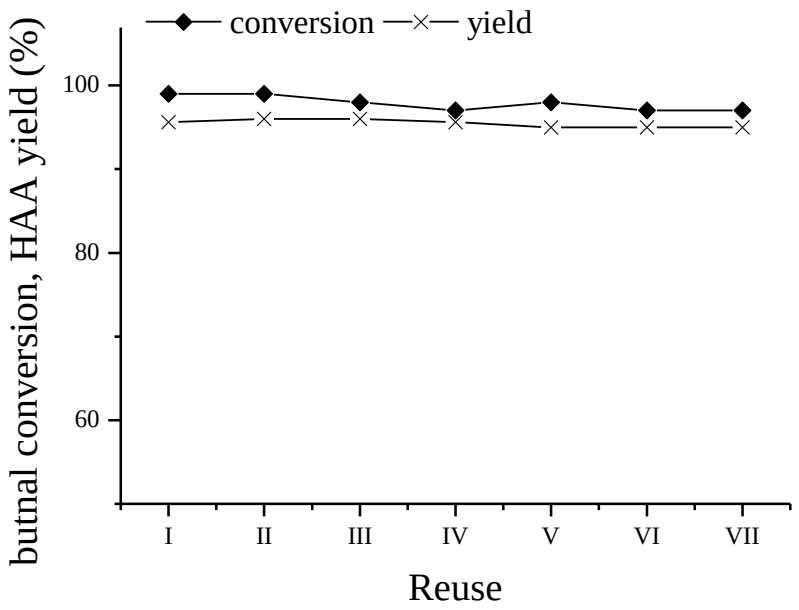


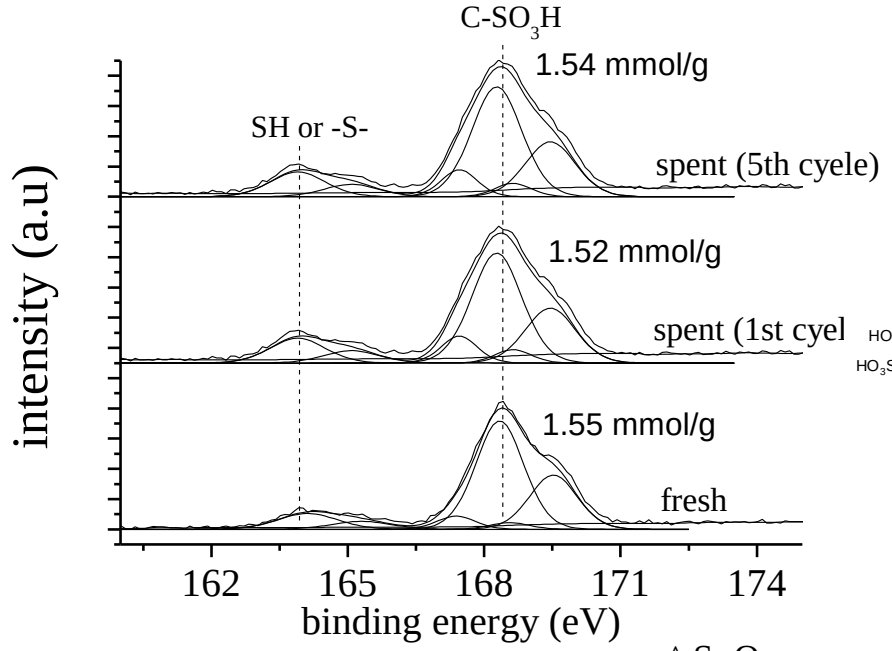


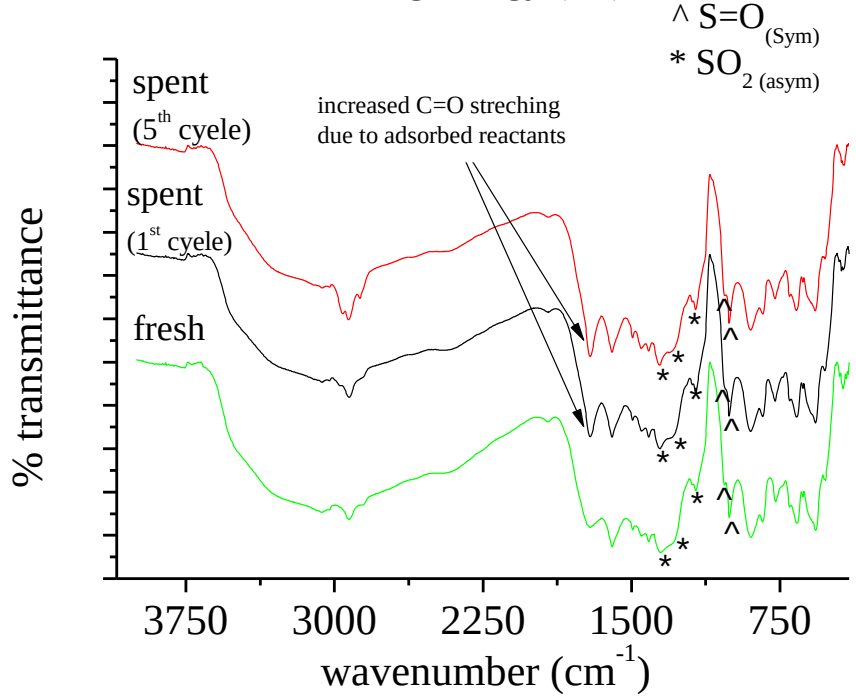
promotional effect hydrophilic surface functional groups upon adsorption of oxygenated reactants through non-covalent interactions

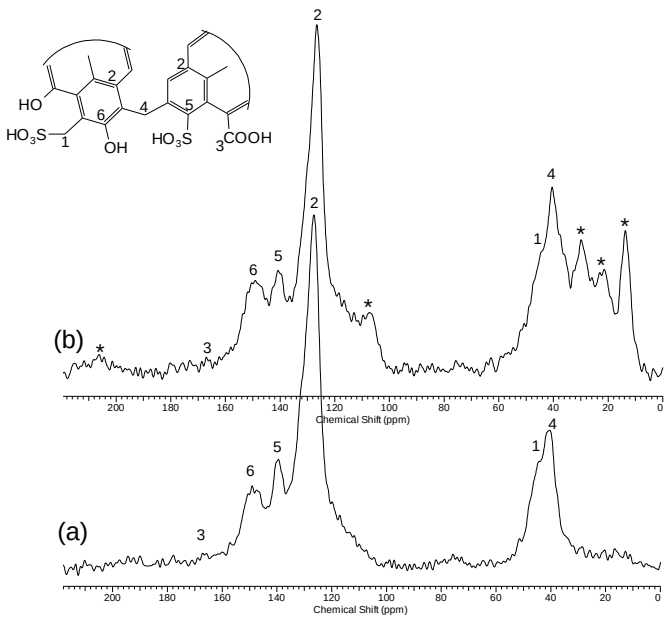
Stability of LS catalyst



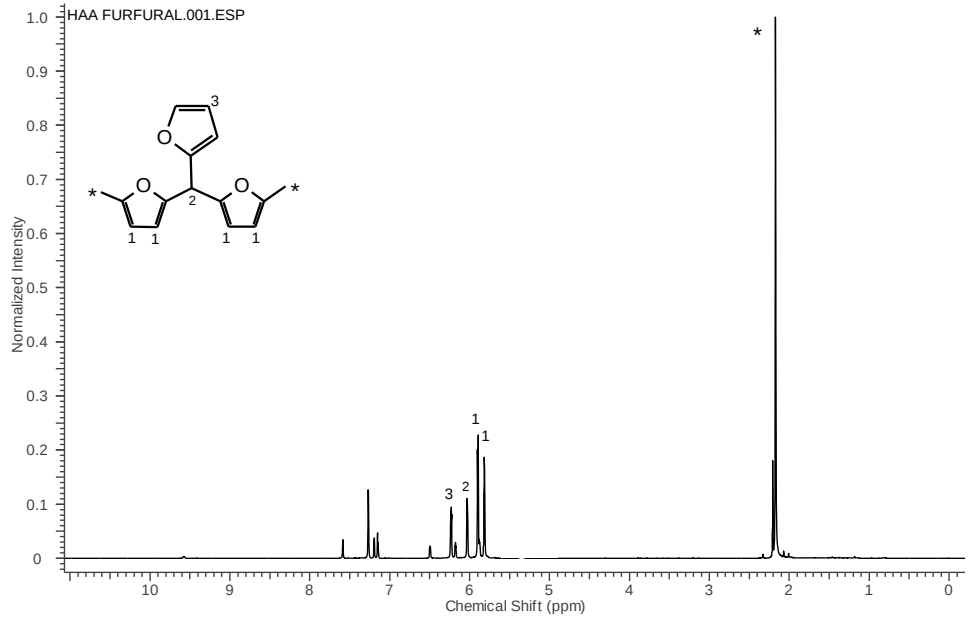


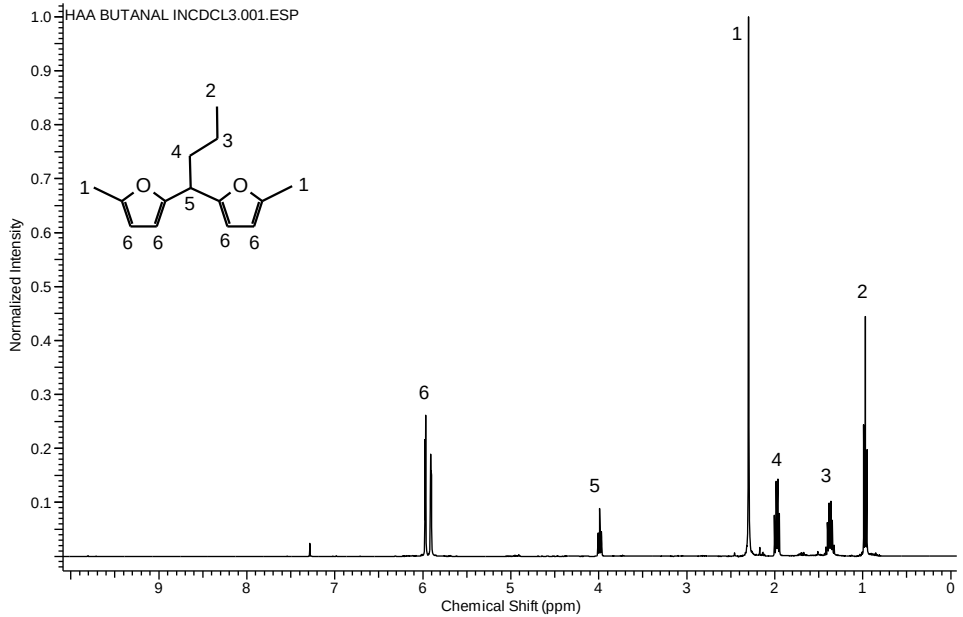






(* denotes adsorbed reactants and products)


HAA FURFURAL.001.ESP
Normalized Intensity
Chemical Shift (ppm)


HAA BUTANAL INCDCL3.001.ESP
Normalized Intensity
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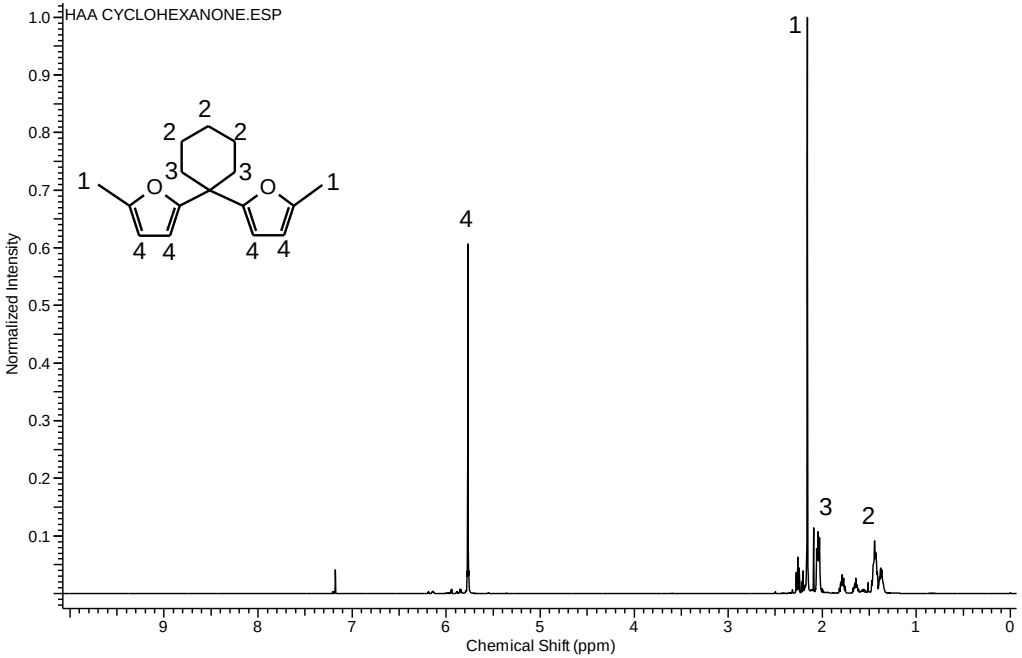
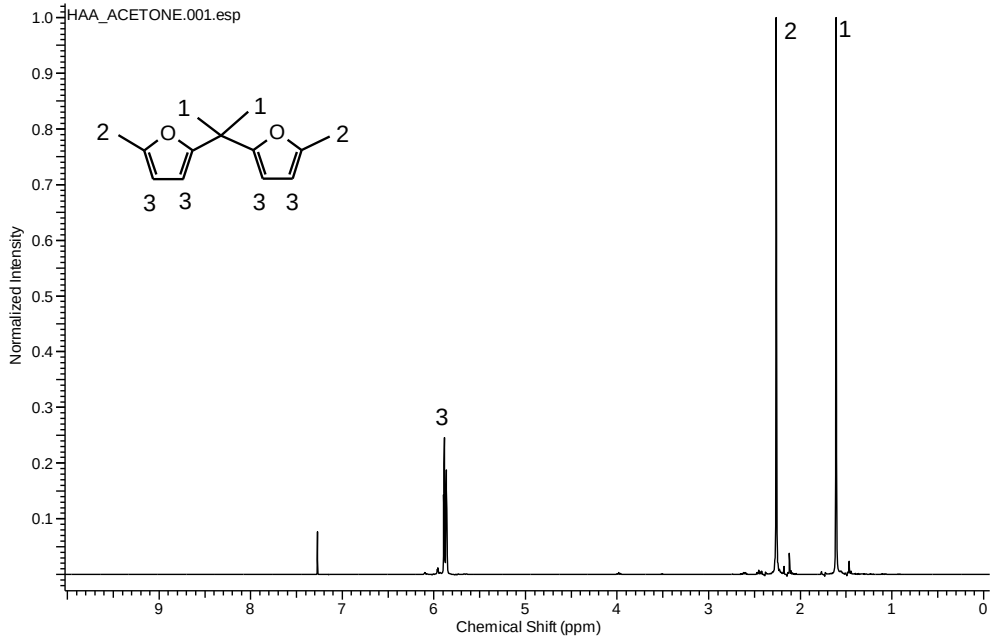
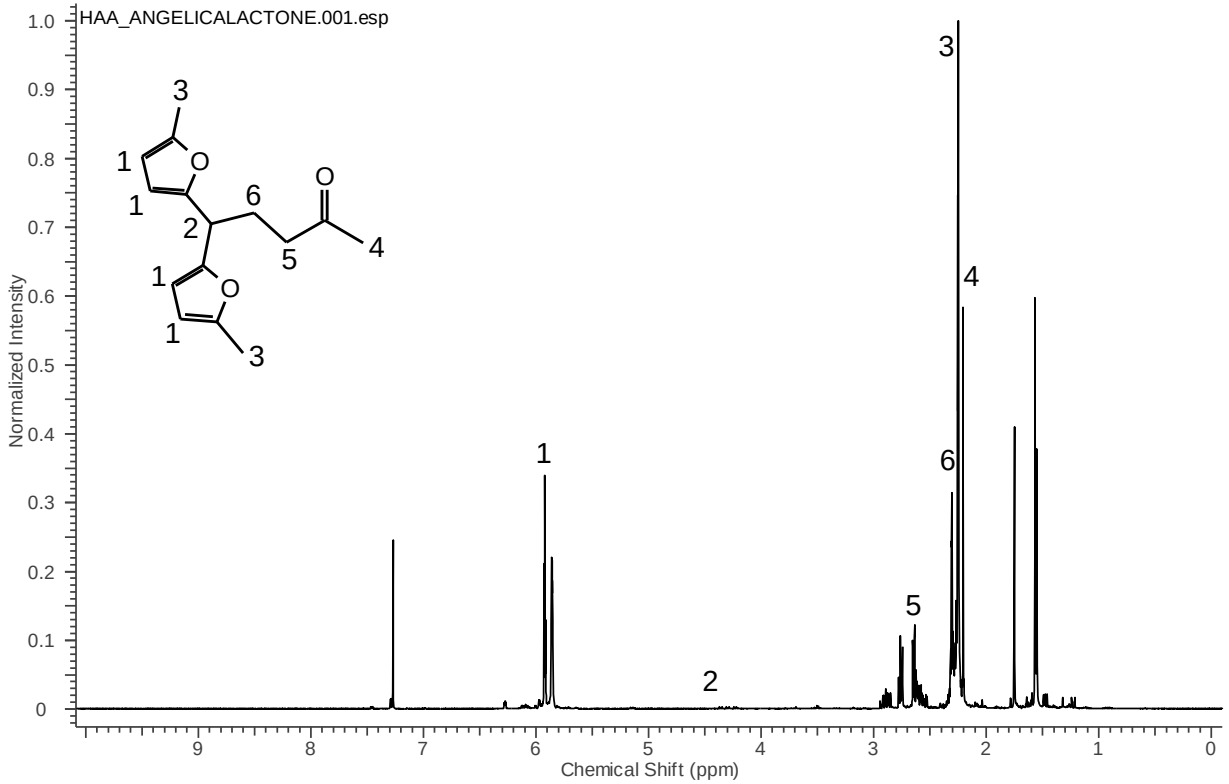
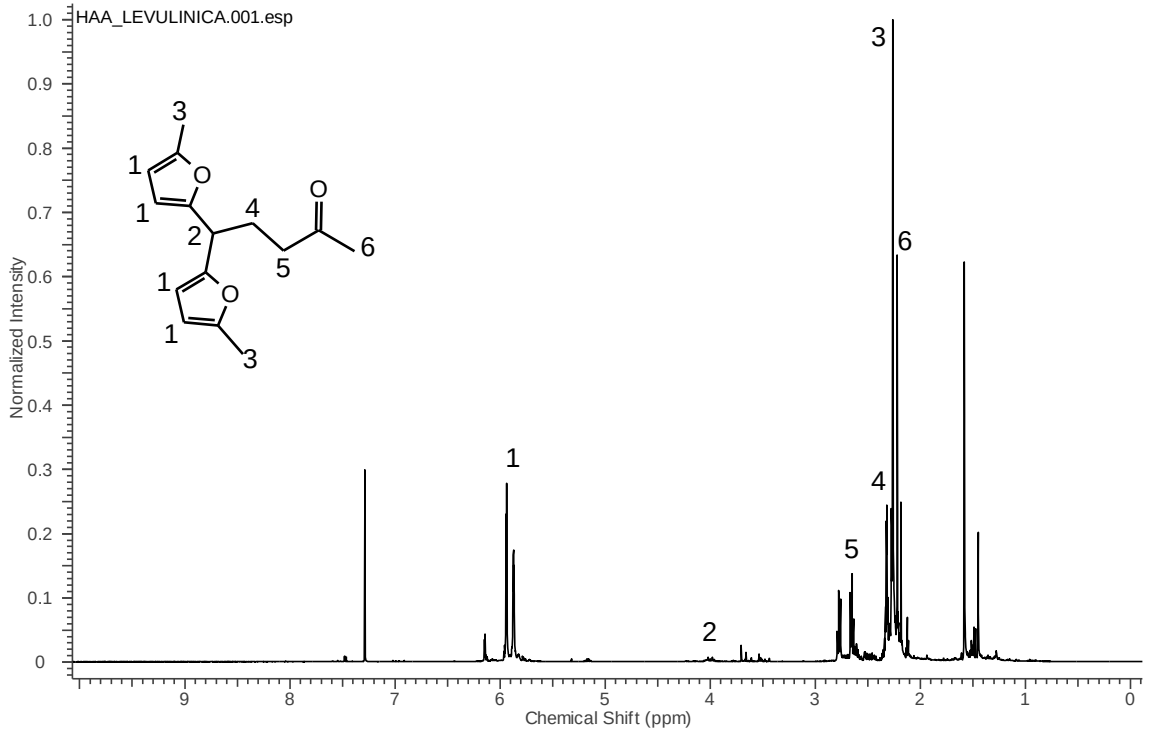

HAA CYCLOHEXANONE.ESP
Normalized Intensity
Chemical Shift (ppm)


HAA_ACETONE.001.esp
Normalized Intensity
Chemical Shift (ppm)

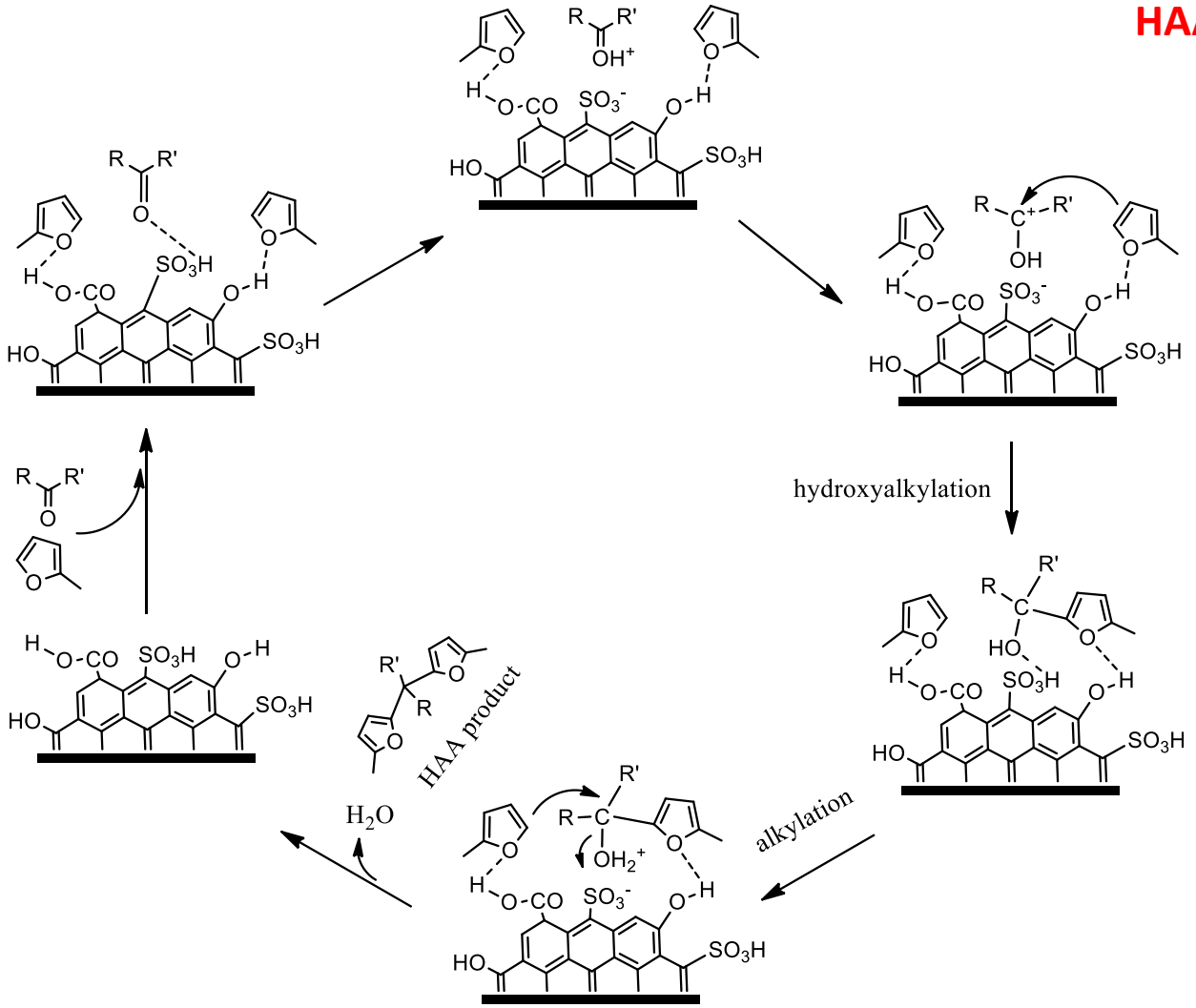
α-angelicalactone HAA



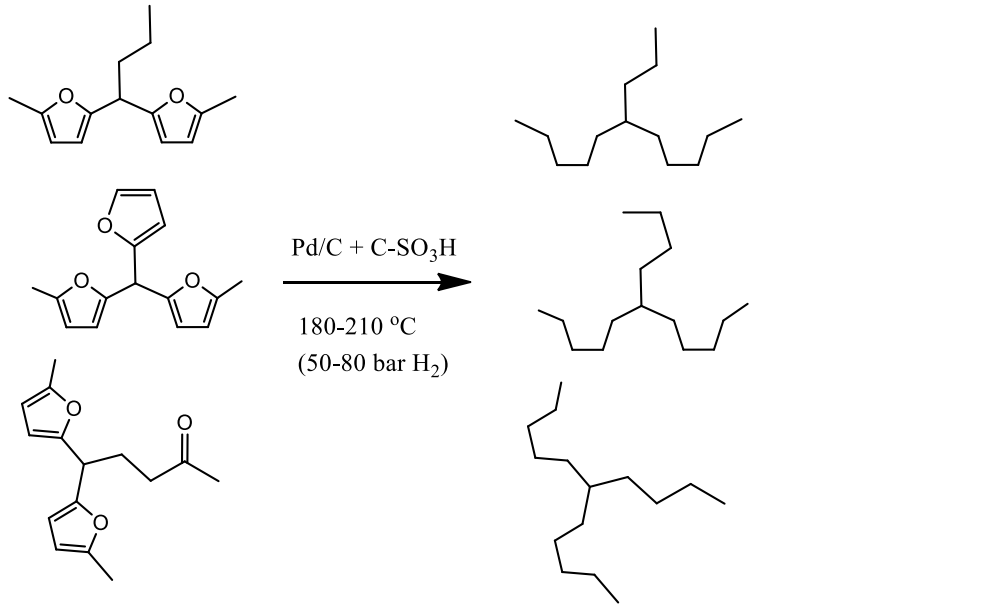
Levulinic acid HAA



Plausible mechanism depicting promotional effects hydrophilic surface functional groups upon HAA of 2-methylfuran with carbonyl compounds over acidic carbons



Solid acid assisted hydrogenation/ Hydrodeoxygenation of HAA products



Conclusions

- LS is a excellent precursor making highly acidic carbon materials
- LS derived material are superior to commercial acidic resins w.r.t porosity, thermal & chemical stability
- Acid site denity and porosity is effected by synthesis conditions

  -sulfonic group density upto 1.6 mmol/g

  -meso/macro porosity can be easily generated
- LS derived materials show expectional potential as solid acid catalysts (outperform acidic zeolites and commercial acidic resins)

  - glycerol valoriation

  - Jet-fuel precursors synthesis

  - dehyration of carbohydrates (results not shown)

Acknowledgements

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storaenso

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lignin (will be tried soon)

NMR for Life
SWEDISH NMR CENTRE

UCEM
Umeå Core Facility
Electron Microscopy

Åbo Akademi

Process Chemistry Centre