Electronic Supplementary Material (ESI) for Green Chemistry.

Sn-Al-USY in glucose valorization to methyl lactate: switching from hydrolytic to retro-aldol activity by alkaline ion exchange.

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Electronic Supporting Information

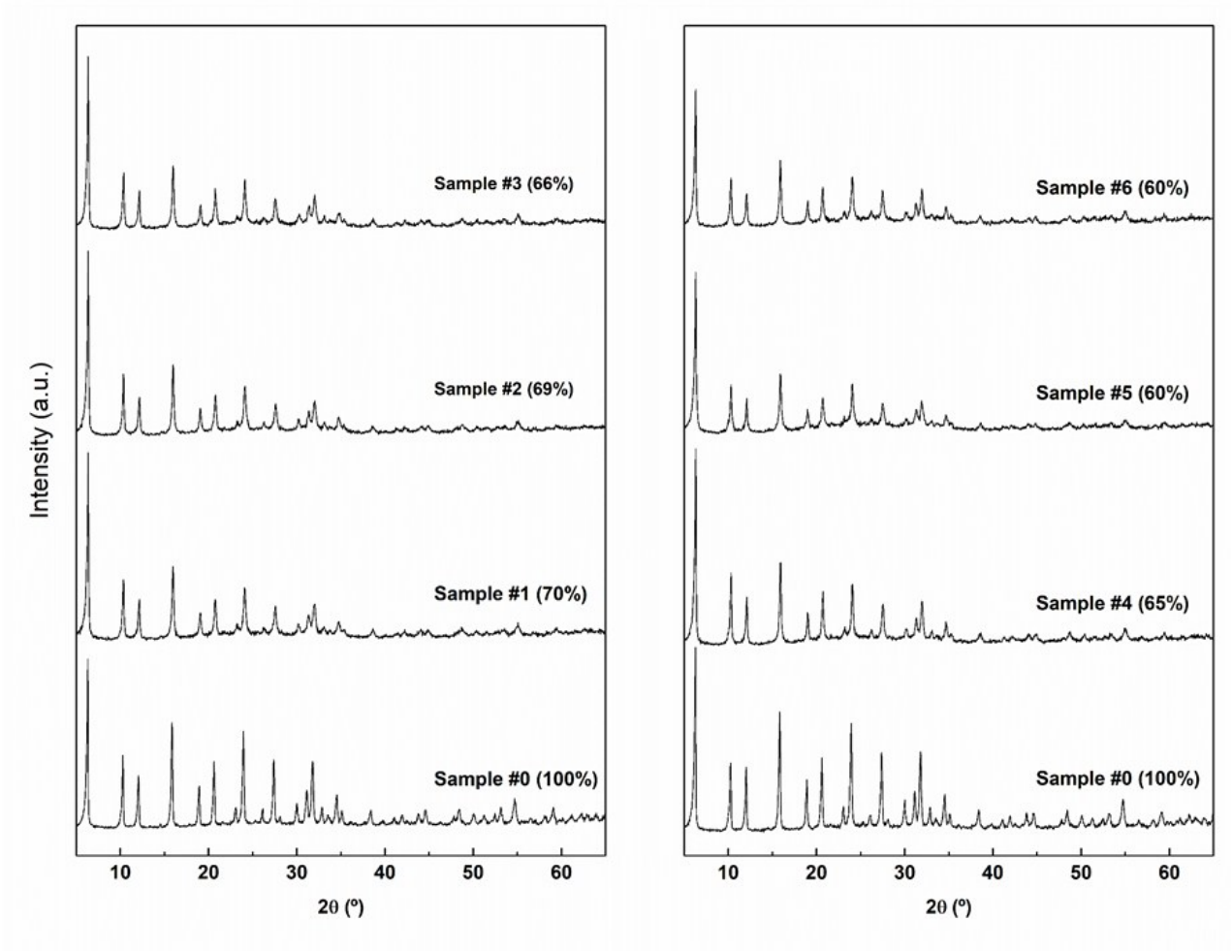


Figure ESI-1. XRD patterns and crystallinity (in brackets) recorded for USY samples (left) dealuminated with different concentrations of HNO_3 and metalated with constant loading of $SnCl_4$ in iPrOH, and (right) dealuminated with 10M HNO_3 and metalated with different loadings of $SnCl_4$ in CH_2Cl_2. Cristallinity has been calculated using commercial USY sample (Sample #0) as reference, assuming 100% crystallinity.

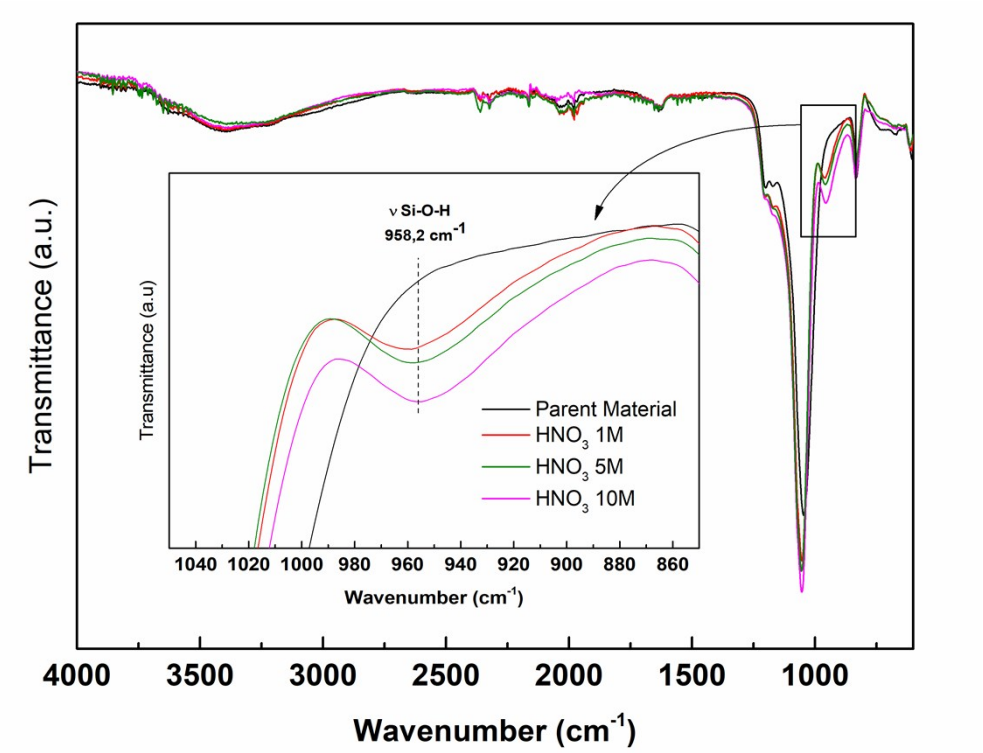


Figure ESI-2. FTIR spectra recorded for USY samples dealuminated with aqueous HNO_3 solutions with different acid concentrations. Inset: detail of the 960 cm^{-1} vibration attributed to Si-OH stretching.

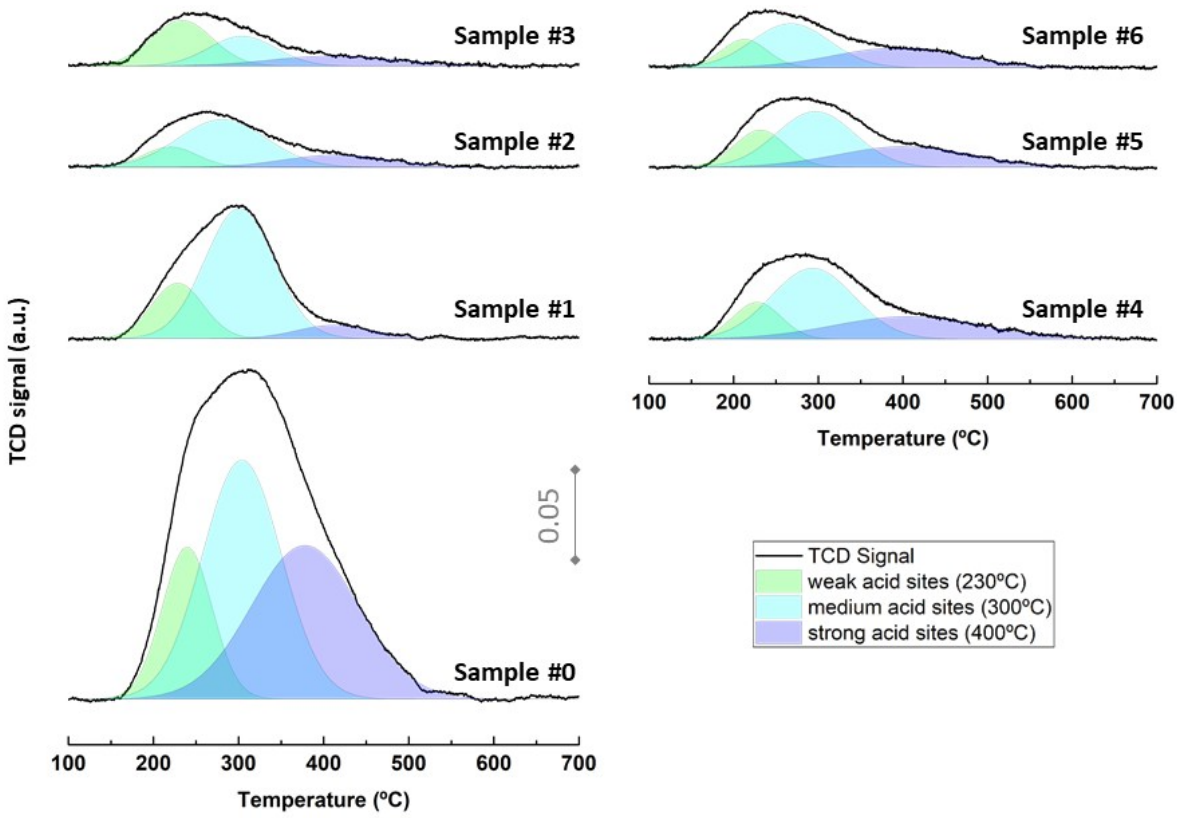


Figure ESI-3. Ammonia TPD profiles recorded for USY parent material and Sn-Al-USY samples prepared by different grafting methods.

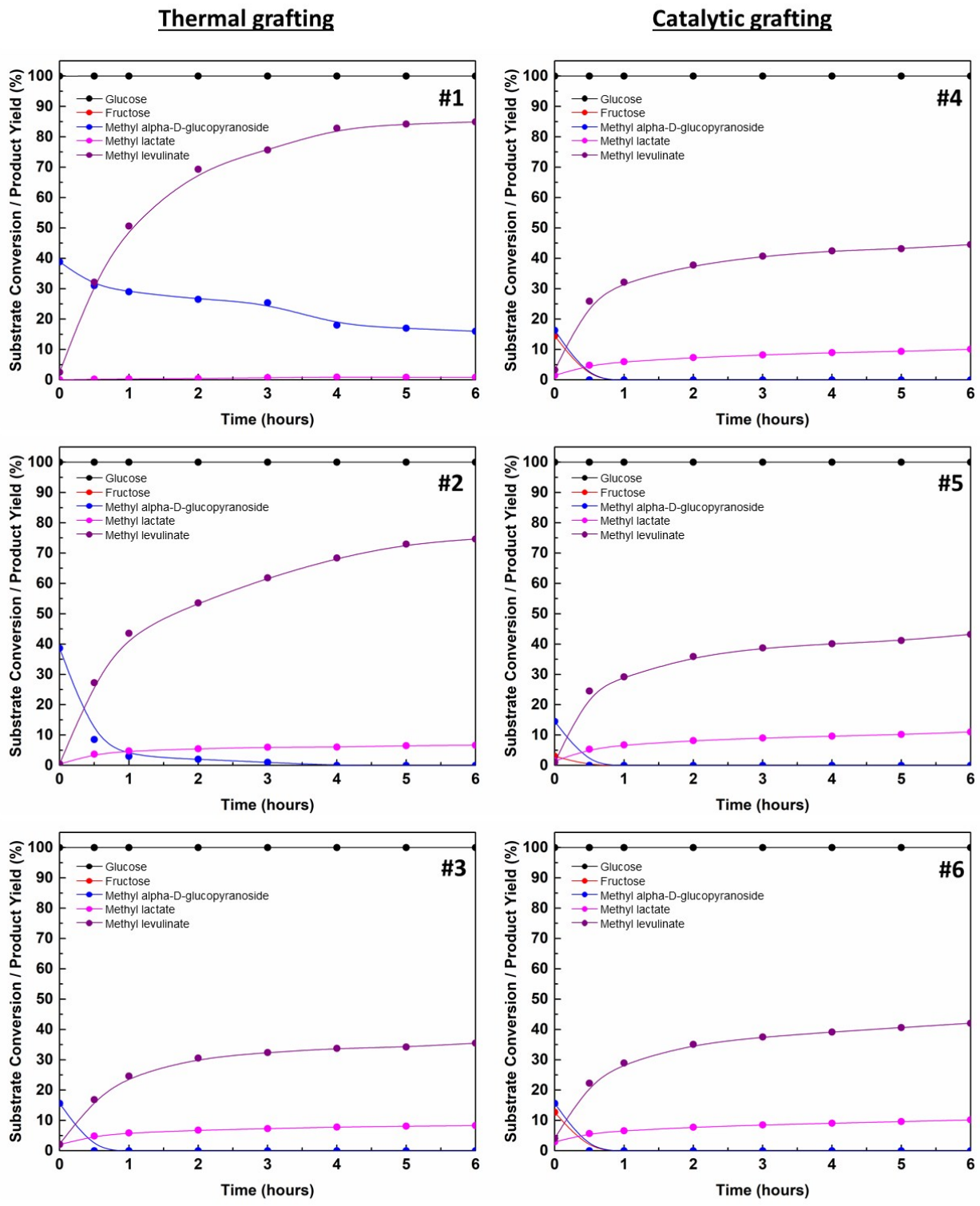


Figure ESI-4. Products yields profiles achieved in the treatment of methanolic solutions of glucose in presence of Al-Sn-USY prepared by different grafting methods. Reaction conditions: temperature: 170ºC; starting glucose concentration: 48 g/L; catalyst loading: 1.0 g; total reaction volume: 100 mL.

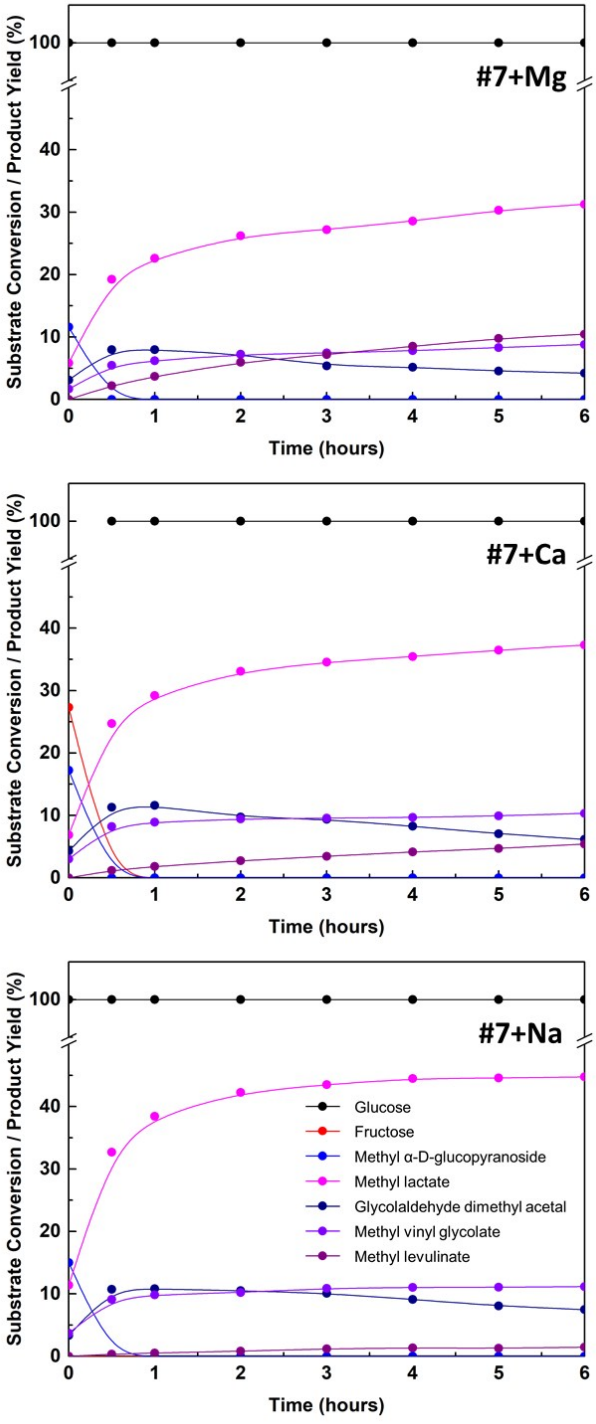


Figure ESI-5. Products yields profiles achieved in the treatment of methanolic solutions of glucose in presence of ion exchanged Al-Sn-USY with magnesium, calcium and sodium chlorides. Reaction conditions: temperature: 170ºC; starting glucose concentration: 48 g/L; catalyst loading: 1.0 g; total reaction volume: 100 mL.

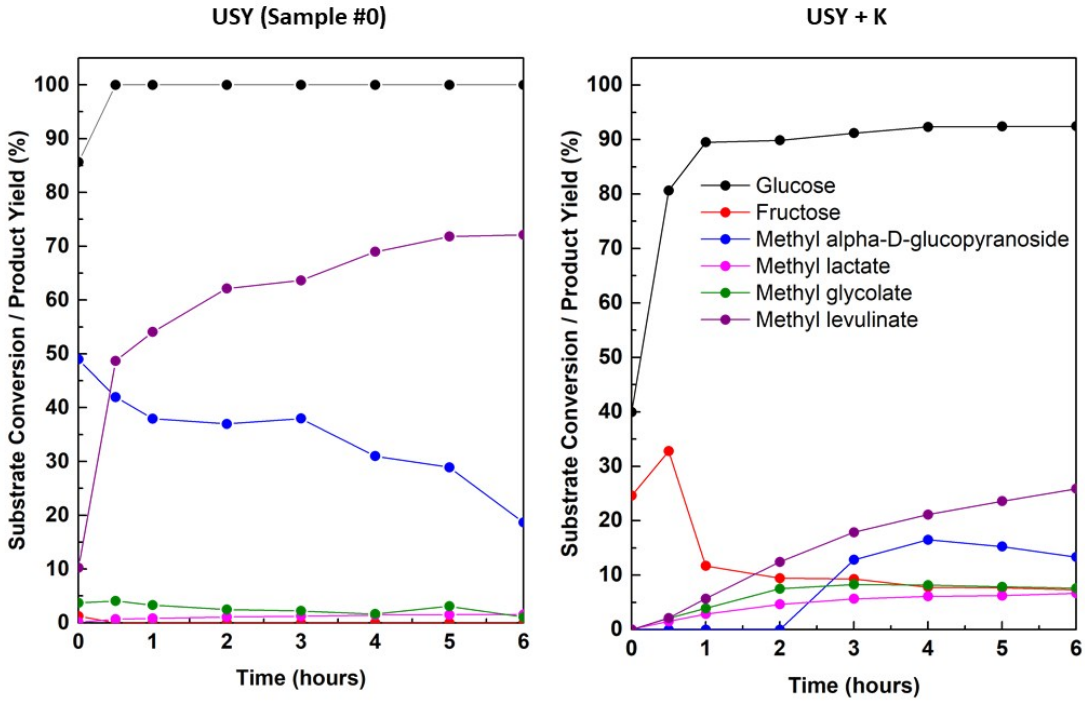


Figure ESI-6. Kinetic profiles achieved in the treatment of methanolic solutions of glucose in presence of sample #0 and K-exchanged sample #0. Reaction conditions: temperature: 170ºC; starting glucose concentration: 48 g/L; catalyst loading: 1.0 g; total reaction volume: 100 mL.

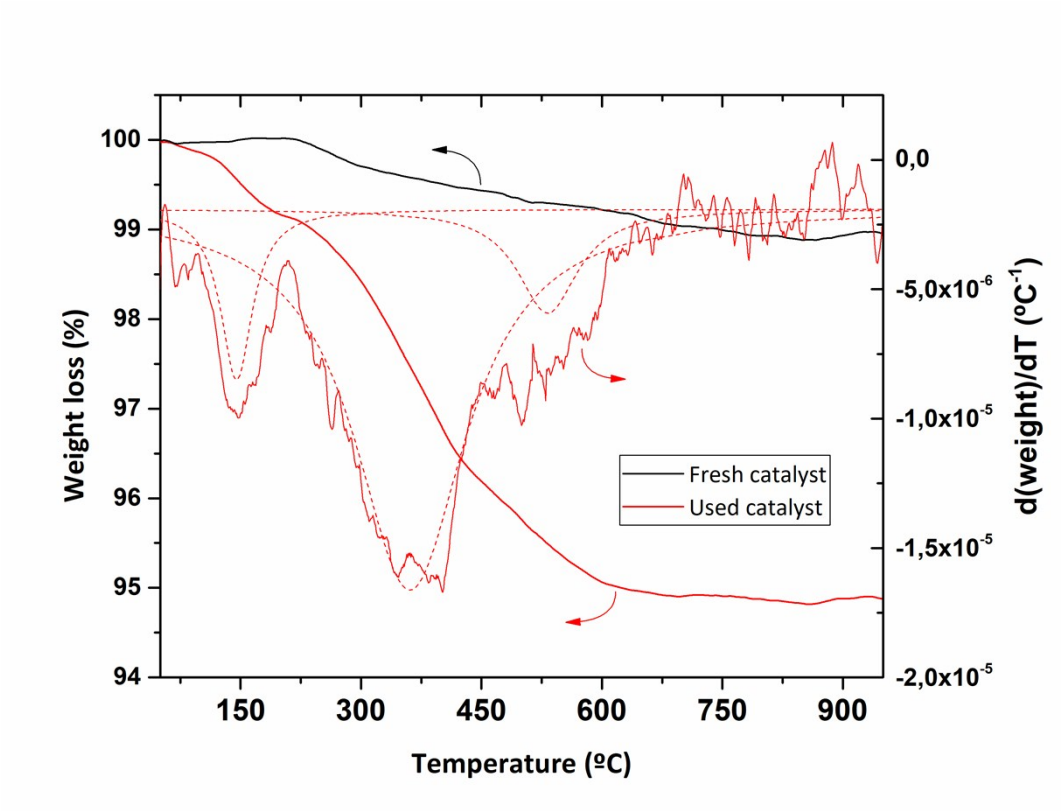
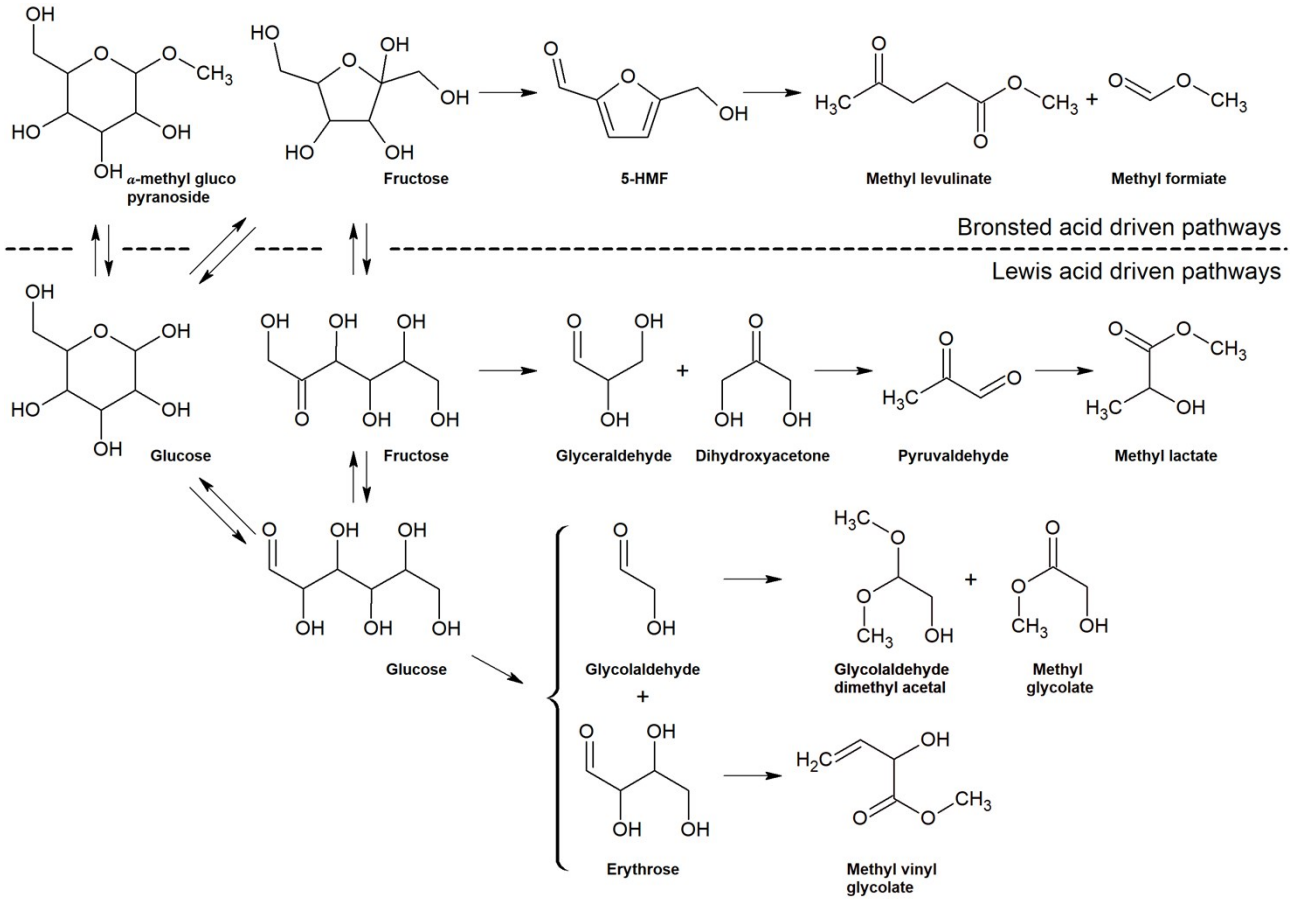


Figure ESI-7. Thermogravimetric analysis (TGA – left axis & DTA – right axis) performed on a fresh (black line) and a used (red line) sample of K-exchanged Sn-Al-USY material (sample #7).



Scheme ESI-1. Reaction pathways promoted by different acid sites in presence of Sn-Al-USY zeolites in methanol media.

Table ESI-1. Physicochemical properties achieved for ion exchanged Sn-Al-USY zeolites with different alkaline and alkaline earth metal chlorides.[a]

#	$MeCl_x$ [b]	Al [c] (wt%)	Sn [d] (wt%)	Me [e] (wt%)	Me/Al [f] (at.)	H^+ [g] (meq/g)	Td_{NH3} [h] (ºC)	B:L [i] (mol)
7	---	0.52	2.41	---	---	0.86	301.5	0.151
7-Mg	$MgCl_2$	0.52	2.62	0.06	0.13	0.91	281.7	0.063
7-Ca	$CaCl_2$	0.51	2.56	0.19	0.25	0.64	275.2	0.071
7-Na	NaCl	0.50	2.55	0.18	0.42	0.50	259.8	0.032
7-K	KCl	0.50	2.37	0.29	0.40	0.40	262.5	0.034

[a] All metal contents were measured by means of ICP-OES; [b] metal chloride used for ion exchange; [c] aluminium content; [d] tin content; [e] alkaline/alkaline earth metal content; [f] alkaline/alkaline earth metal to aluminium atom ratio; [g] acid capacity determined by NH_3 TPD; [h] average ammonia desorption temperature; [h] Brønsted to Lewis acid molar ratio.

Table ESI-2. Products distributions and carbon balances achieved in the treatment of glucose with ion exchanged Sn-Al-USY zeolites with different alkaline and alkaline earth metal chlorides

#	Y_{MGP} [b] (mol%)	Y_{HMF} [c] (mol%)	Y_{MLEV} [d] (mol%)	Y_{MG} [e] (mol%)	Y_{GADMA} [f] (mol%)	Y_{MVG} [g] (mol%)	Y_{MLAC} [h] (mol%)	CB [h] (mol%)
7	0.0	0.1	41.7	2.7	2.2	3.1	10.7	49.3
7-Mg	0.0	0.1	10.5	1.0	4.2	8.8	31.3	50.8
7-Ca	0.0	0.0	5.4	0.6	6.2	10.3	37.3	50.9
7-Na	0.0	0.6	1.4	1.4	7.5	11.2	44.8	57.0
7-K	0.0	0.3	11.1	3.2	8.9	9.2	43.2	63.0

[a] Reaction conditions: temperature: 170°C; starting glucose concentration: 48 g/L; catalyst loading: 1.0 g; total reaction volume: 100 mL. Total conversion was achieved for all the catalysts at 6h. All the product yields have been expressed as mol %; [b] Yield to α-methyl glucopyanoside; [c] Yield to 3-hydroxymethyl furfural; [d] Yield to methyl levulinate; [e] Yield to methyl glycolate; [f] Yield to glycolaldehyde dimethyl acetal; [g] Yield to methyl vinyl glycolate; [h] Yield to methyl lactate; [i] Carbon Balance calculated as the ratio of carbon in glucose quantified as products.