Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Extended Supplementary Information for:

Overcoming catalyst deactivation during the continuous conversion of sugars to chemicals: maximising the performance of Sn-Beta with a little drop of water

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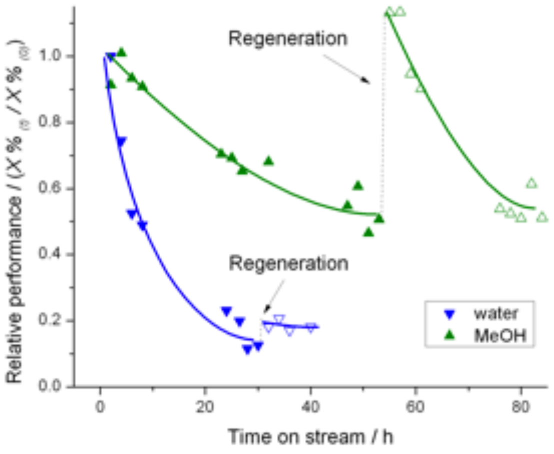

Figure S1. Glucose isomerisation in continuous flow performed in water (blue downward triangles) and in methanol (green triangles) followed by thermal regeneration. Performance in the second cycle *i.e.* following regeneration, is represented by the hollow triangles. Reaction conditions: 110 °C, 1 wt. % of glucose; 30 mg of Sn-Beta and 0.2 mL min^{-1} of flow for the reaction in methanol, and 65 mg of Sn-Beta and 0.1 mL min^{-1} of flow for the reaction in water.

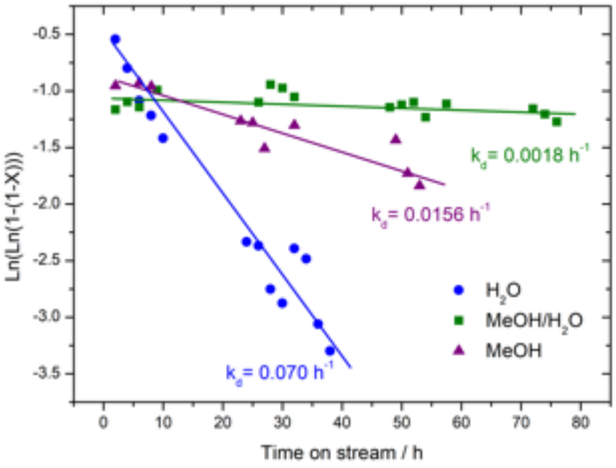

Figure S2. Conversion of glucose vs time on stream plotted in logarithmic form. The deactivation rate (K_d) has been obtained from the slope of the line of best fit.

Reaction conditions: 110 °C, 1 wt. % of glucose; (violet triangles) 30 mg of Sn-Beta and 0.2 mL min^{-1} of flow for the reaction in methanol; (blue circles) 65 mg of Sn-Beta and 0.1 mL min^{-1} of flow for the reaction in water; and (green squares) 30 mg of Sn-Beta and 0.25 mL min^{-1} of flow for the reaction in water/methanol mixture.

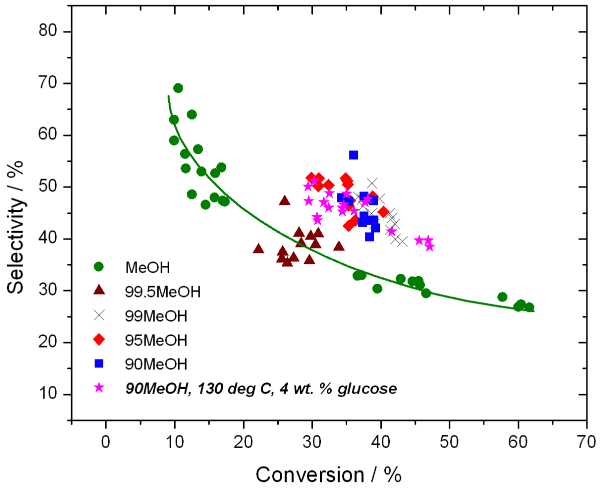

Figure S3. Conversion versus selectivity profile for reaction performed at 130 °C with 4 wt. % glucose solution (pink stars), compared to reactions performed at lower temperatures and lower concentrations of glucose. The methanol fraction is represented by the value prior to MeOH *i.e.* 10:90 H_2O:MeOH is represented by 90MeOH. Unless otherwise stated, reactions were performed at 110 °C at a glucose concentration of 1 wt. % Reaction conditions are fully described in ESI Table S1.

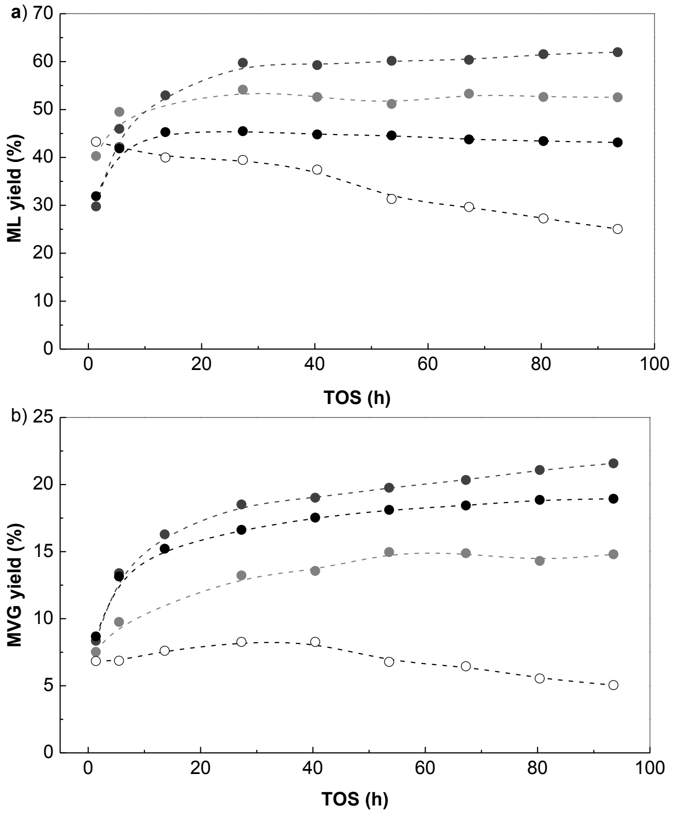

Figure S4. Time on stream data showing the yield of a) methyl lactate and b) methyl vinyl glycolate from fructose using Sn-Beta at 160 °C when adding water to the feed. Legend, 0 wt. % water (*white)*, 1 wt. % water (*light grey*), 2.5 wt. % water (*grey*) and water 5 wt. % (*black*). Reaction conditions are fully described in the experimental section of the primary manuscript.

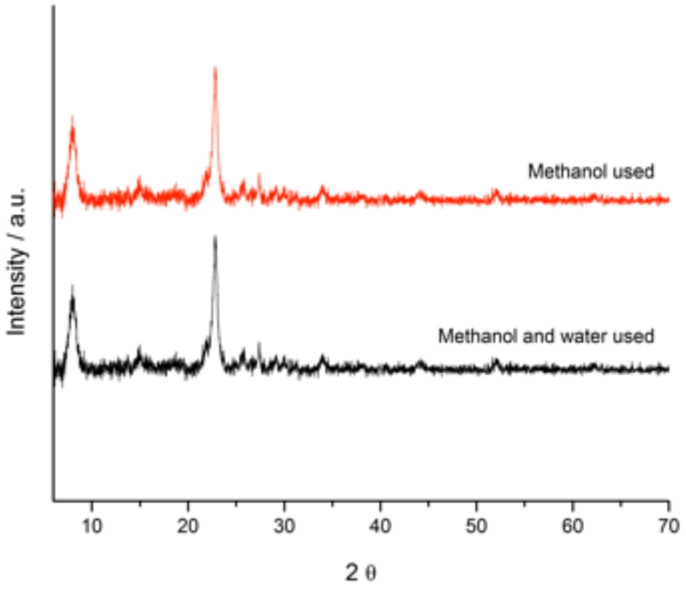

Figure S5. XRD patterns of Sn-Beta samples following reactions in MeOH and 10:90 H_2O:MeOH, after 54 h on stream.

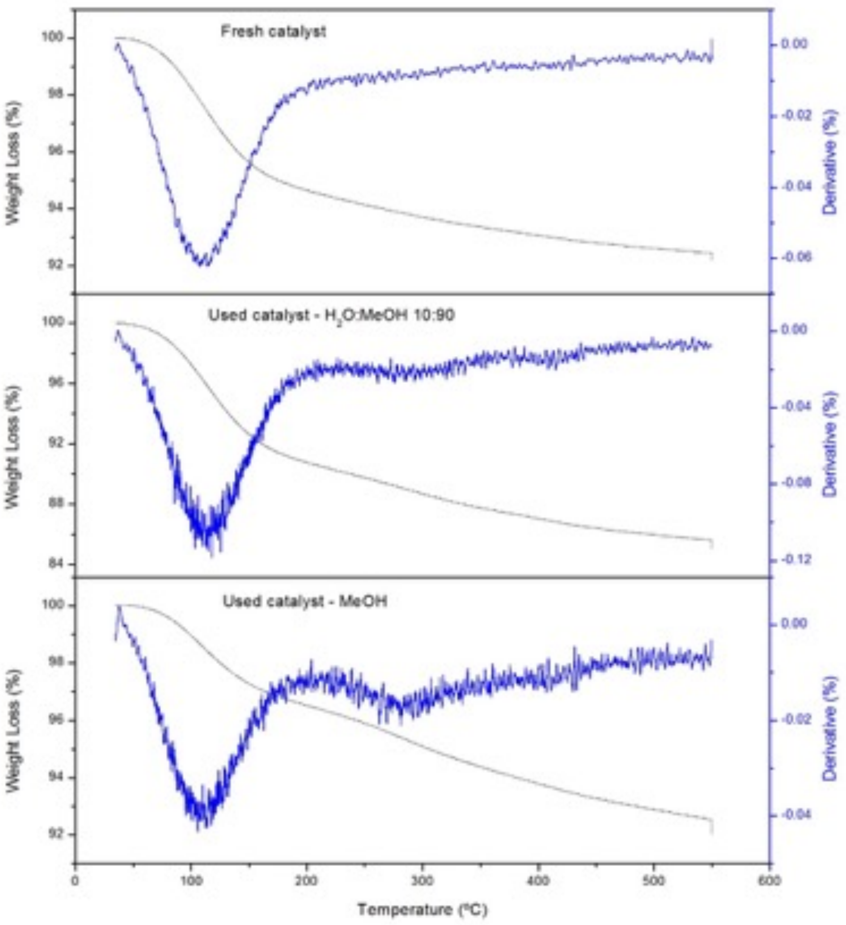

Figure S6. Thermo-gravimetric analysis of the fresh (top), the used in 10:90 H_2O:MeOH (middle) and MeOH (bottom) catalyst. The relative mass loss (black line) and its derivative (blue line) are reported against the temperature.

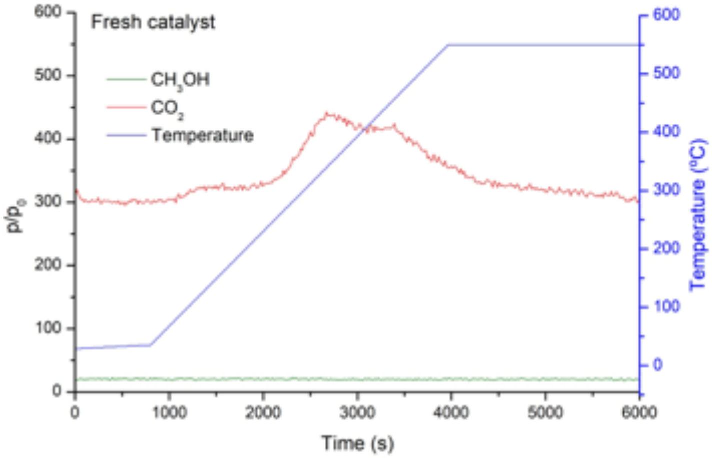

Figure S7. Online composition of the gas evolved from the TPD-MS experiment of the fresh catalyst. The sample was dried at 100 °C overnight prior to analysis to remove most physisorbed species. Air was used as carrier gas at 10 mL min^{-1}. Relative pressure of the gases (left Y axis) and temperature ramp (right Y axis) are displayed in the graphic.

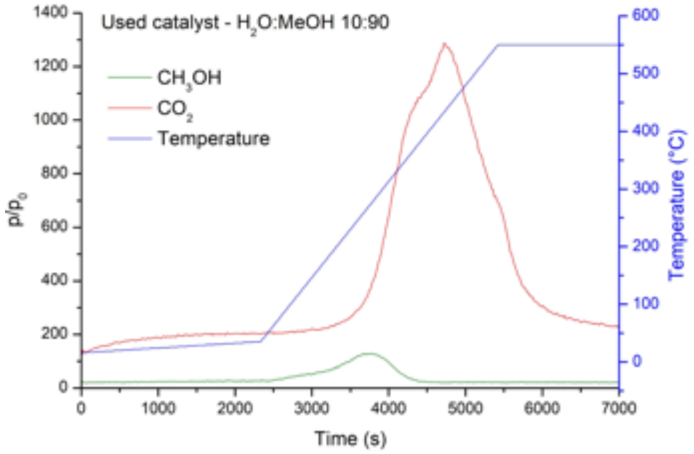

Figure S8. Online composition of the gas evolved from the TPD-MS experiment of the catalyst after 54 h of GI reaction with 10:90 H_2O:MeOH as solvent mixture. Air was used as carrier gas at 10 mL min^{-1}. Relative pressure of the gases (left Y axis) and temperature ramp (right Y axis) are displayed in the graphic.

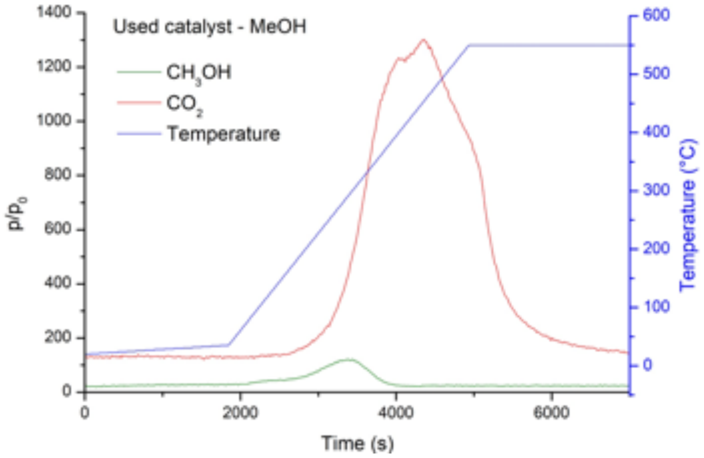

Figure S9. Online composition of the gas evolved from the TPD-MS experiment of the catalyst after 54 h of GI reaction with MeOH as solvent. Air was used as carrier gas at 10 mL min^{-1}. Relative pressure of the gases (left Y axis) and temperature ramp (right Y axis) are displayed in the graphic.

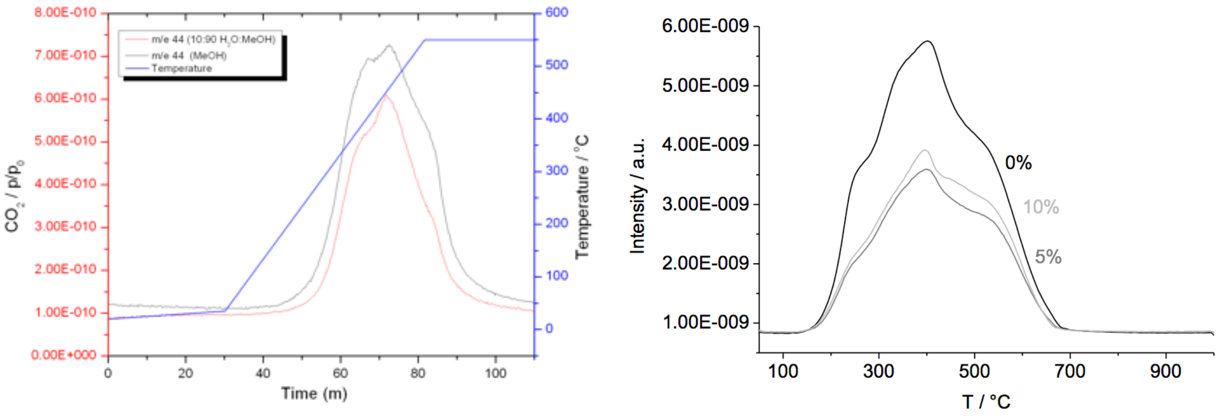

Figure S10. Left: Comparison of the intensity of the m/e = 44 signal from in the effluent from the TPD-MS analysis of Sn-Beta following operation in MeOH (black) and 10:90 H_2O:MeOH (red). Air was used as carrier gas at 10 mL min^{-1}. Relative pressure of the gases (left Y axis) and temperature ramp (right Y axis) are displayed in the graphic. Right: Mass spectrum profile (m/e = 44) obtained following TPD of Sn-Beta samples partially deactivated during the production of methyl lactate at 160 °C in various solvents (water content in wt. % displayed on the figure), as a function of desorption temperature. TPD was performed at 5 °C min^{-1} to 1000 °C with an initial drying step at 125 °C (2 h).

TABLE S1. Experimental parameters relative to the glucose isomerisation reactions performed in the continuous flow system.

Entry	Solvent composition (w/w ratio)	Glucose wt.%	Temperature (°C)	Mass of catalyst (mg)	Flow rate (mL min^{-1})
1	H_2O	1	110	65	0.1
2	H_2O:MeOH (50:50)	1	110	70	0.11
3	H_2O:MeOH (25:75)	1	110	35	0.22
4	H_2O:MeOH (10:90)	1	110	30	0.25
5	H_2O:MeOH (5:95)	1	110	30	0.25
6	H_2O:MeOH (1:99)	1	110	30	0.25
7	H_2O:MeOH (0.5:99.5)	1	110	30	0.25
8	MeOH	1	110	30	0.2
9	H_2O:MeOH (10:90)	1	130	20	0.34
10	H_2O:MeOH (10:90)	4	110	50	0.2
11	H_2O:MeOH (10:90)	4	130	30	0.5

TABLE S2. Conversion and yields of GI in continuous flow after 2 and 24h of time on stream.

Reaction conditions: 110°C, 1 wt. % glucose, 30 mg of Sn-Beta and 0.2 mL min^{-1} of flow for the reaction in methanol or 30mg of Sn-Beta and 0.25 mL min^{-1} of flow for the reaction in water/methanol mixture.

Entry	Conditions	$X_{glucose}$ (mol %)[a]	$Y_{mannose}$ (mol %)[a]	$Y_{fructose}$ (mol %)[a]	$Y_{methyl\ lactate}$ (mol %)[b]
1	110 °C, MeOH, 2 h TOS	31.2	4.4	17.0	1.2
2	110 °C, MeOH, 24 h TOS	13.8	1.3	8.5	0.9
3	110 °C, 10:90 H_2O:MeOH, 2 h TOS	35.5	5.2	23.8	1.1
4	110 °C, 10:90 H_2O:MeOH, 24 h TOS	28.0	5.2	22.2	0.8

[a] Determined by liquid chromatography

[b] Determined by gas chromatography