Supporting Information:

Thermal Regeneration of Sn-Containing Silicates and Consequences for Biomass Upgrading: From Regeneration to Pre-activation

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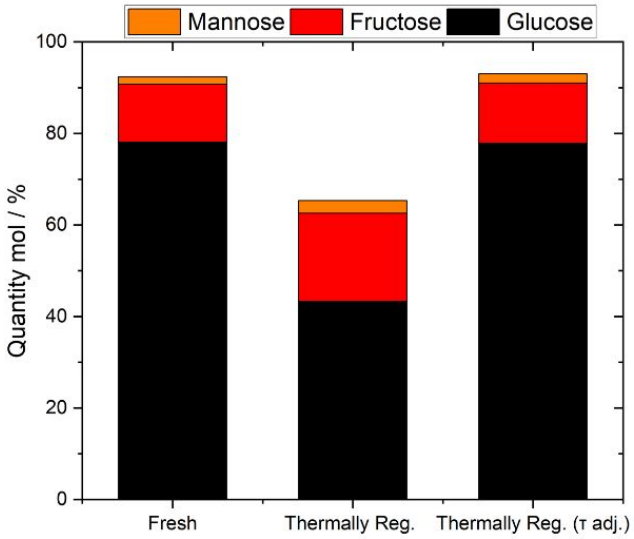

Figure S1. Carbon balance for continuous glucose isomerisation carried out by fresh 10Sn-Beta, thermally regenerated 10Sn-Beta, and thermally regenerated Sn-Beta at an adjusted contact time to have the same level of conversion of the fresh Sn-Beta sample. The reaction effluent was measured at 0.5 h of time on stream. Conditions: 1 wt. % glucose in methanol, 0.75 mL min^{-1} (or 1.5 mL min^{-1} for the adjusted contact time experiment with thermally regenerated Sn-Beta), 0.1 g catalyst, 110 °C.

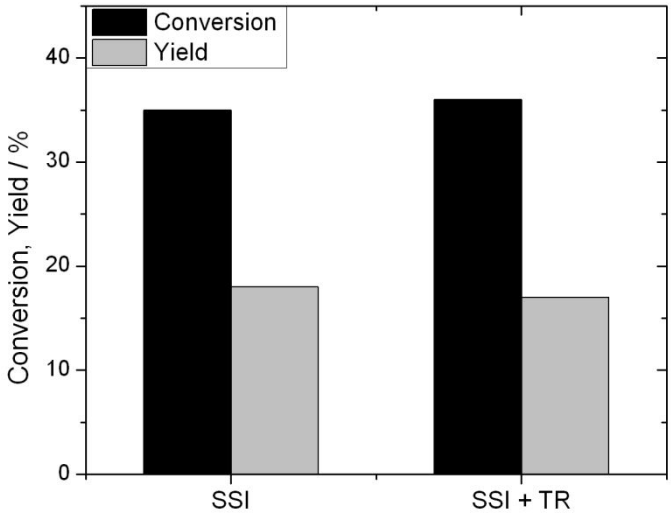

Figure S2. Catalytic activity of 10Sn-Beta for glucose isomerisation at 110 °C after conventional solid state incorporation (the heat treatment procedure of which involves heating to 550 °C for 3 h in N_2, followed by 3 h in air) (labelled SSI), or solid state incorporation followed by an additional thermal treatment at the conditions of thermal regeneration (550 °C, 3 h, air) (labelled SSI + TR). Conditions: 1 wt. % glucose in methanol, 0.75 mL min^{-1}, 0.1 g catalyst, 110 °C.

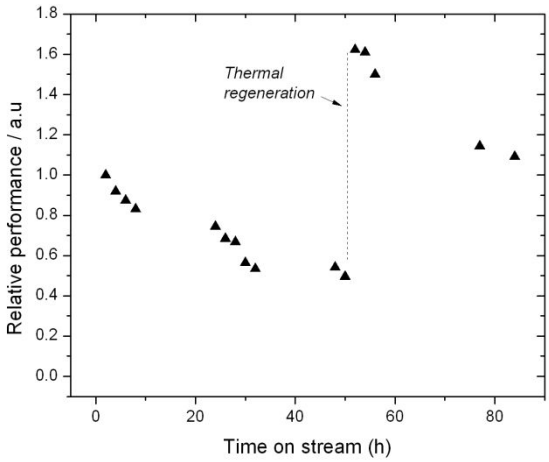

Figure S3. (Left) Relative performance of 2Sn-Beta for glucose isomerisation at 110 °C in MeOH prior to and following thermal regeneration. Reaction conditions: 1 wt. % glucose in methanol, 0.8 mL min^{-1}, 0.1 g catalyst, 110 °C.

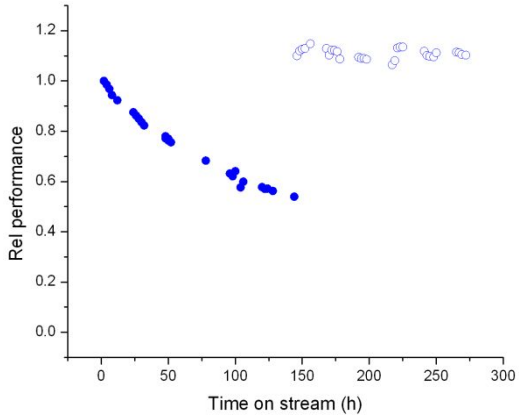

Figure S4. (Left) Relative performance of 2Sn-Beta for the catalytic transfer hydrogenation of furfural as fresh catalyst (cycle 1, filled circles) and following thermal regeneration (empty circles). Reaction conditions: 0.2 M furfural in 2-butanol, flow rate 0.07 mL min^{-1}, 100 °C, 0.2 g 2Sn-Beta. Thermal regeneration performed at 550 °C for 3h in air.

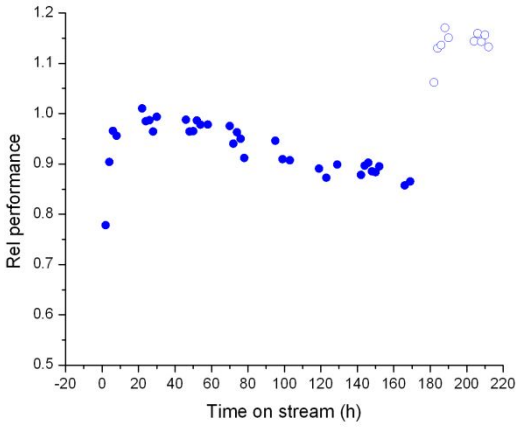

Figure S5. (Left) Relative performance of 2Sn-Beta for the Baeyer-Villiger oxidation of cyclohexanone as fresh catalyst (cycle 1, filled circles) and following thermal regeneration (empty circles). Reaction conditions: 0.33 M cyclohexanone in 1,4-dioxane, 0.08 mL min^{-1}, 100 °C, 0.4 g 2Sn-Beta. Thermal regeneration performed at 550 °C for 3h in air.

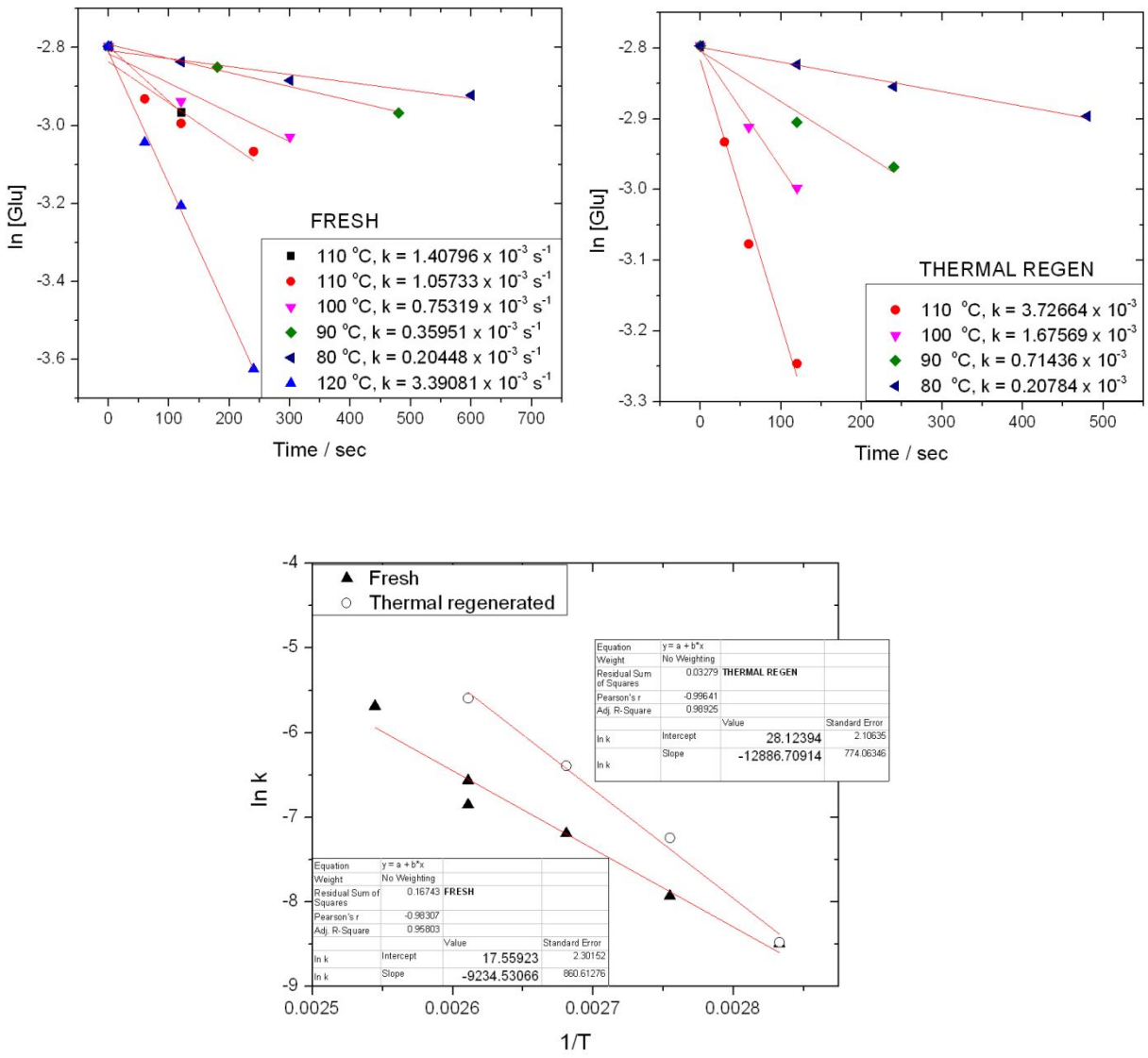

Figure S6. (Top Left) Rate plots determined for fresh 10Sn-Beta between 80-120 °C. (Top Right) Rate plots determined for 10Sn-Beta after thermal regeneration between 80-110 °C. Kinetic rate constants determined for each experiment are provided in the insets. (Bottom) Resulting Arrhenius plots for fresh 10Sn-Beta and 10Sn-Beta following thermal regeneration. Glucose isomerisation reactions performed between 80-120 °C in pressurised Ace tubes at the following conditions: 1 wt. % glucose in methanol, reaction solution 4 g, temperature 80-120 °C, 0.027g catalyst.

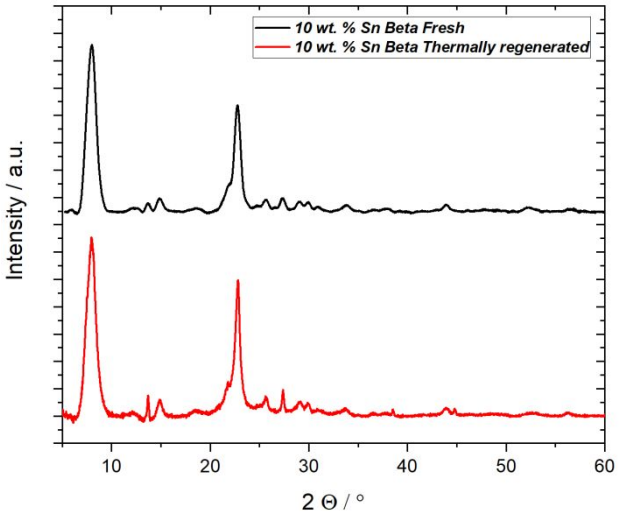

Figure S7. X-Ray diffraction analysis for 10Sn-Beta prior to (Fresh, top) and following thermal regeneration (bottom) after continuous glucose isomerisation in methanol at 110°C and thermal regeneration performed at 550 °C for 3h in air.

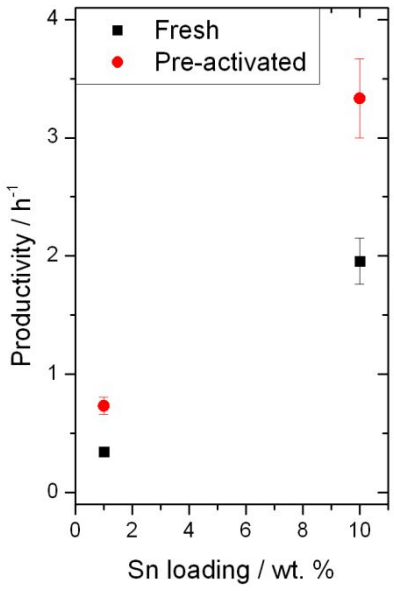

Figure S8. Productivity values achieved by various Sn-Beta catalysts of different Sn loadings during batch operation, prior to (black squares) and following (red circles) pre-activation in methanol at 110 °C for 0.5 h at a flow of 1.5 mL min^{-1} and thermal treatment performed at 550 °C for 3h in air. Experimental conditions described in SI Table S6.

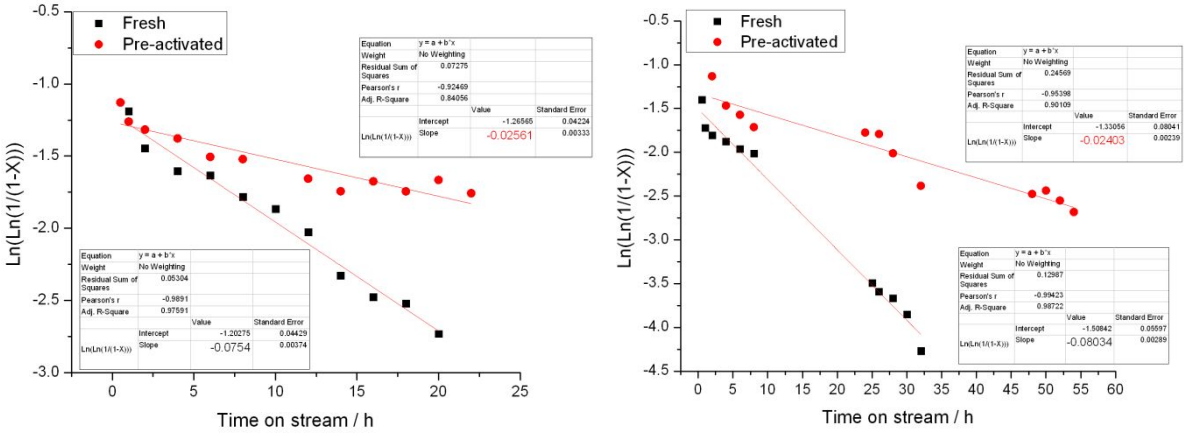

Figure S9. Levenspiel plots for 1Sn-Beta (Left) and 10Sn-Beta (right), prior to (black squares) and following (red circles) pre-activation in methanol at 110 °C for 0.5 h. All experiments performed with a 1 wt. % glucose in methanol solution, 0.1 g catalyst, 110 °C. Flow rates as follows: 1Sn-Beta Fresh = 0.6 mL min^{-1}; 1Sn-Beta Pre-activated = 1.0 mL min^{-1}; 10Sn-Beta Fresh = 1.0 mL min^{-1}; 10Sn-Beta Pre-activated = 1.5 mL min^{-1}.

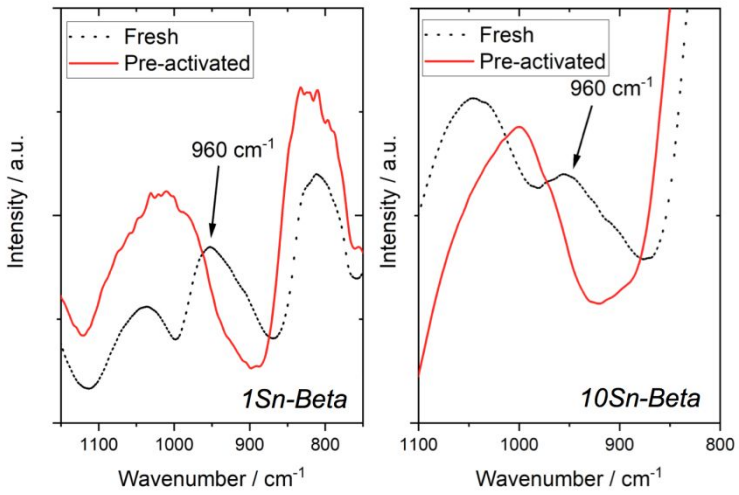

Figure S10. Magnification on DRIFT spectra of 1- and 10Sn-Beta catalysts, in both fresh and pre-activated states, emphasising the 960 cm^{-1} vibration prior to and following pre-activation in methanol at 110 °C for 0.5 h.

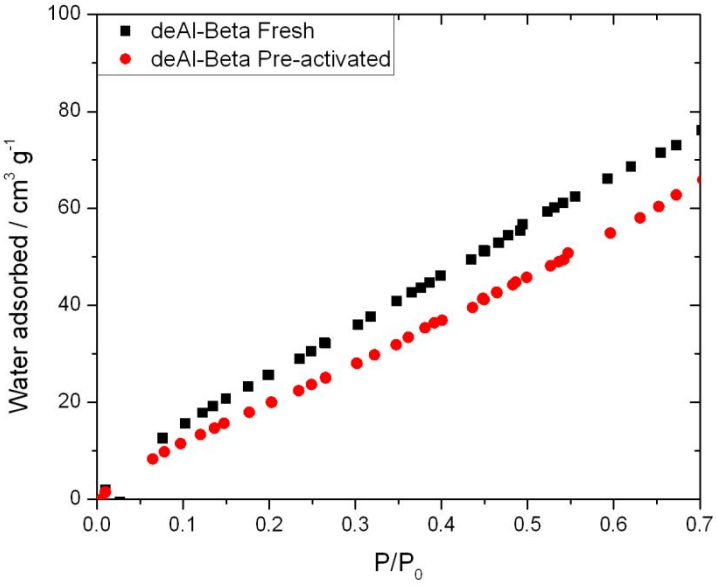

Figure S11. Vapour isotherm of dealuminated beta prior to (black squares) and following (red circles) pre-activation. At P/P_0 values of 0.2, the quantity of water adsorbed by the sample decreased from 26.3 cm^3 g^{-1} to 19.0 cm^3 g^{-1}, indicating approximately 30 % increase in hydrophobicity following pre-activation.

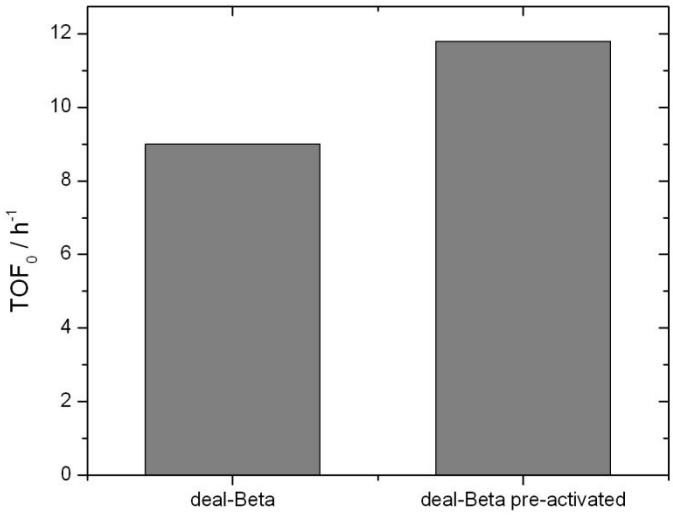

Figure S12. Catalytic performance of 10Sn-Beta depending on whether the dealuminated precursor material was untreated (deal-Beta) or pre-activated in a flow of MeOH (deAl-Beta pre-activated) prior to incorporation of Sn. Pre-activation performed in a flow of methanol at 110 °C for 0.5 h, prior to calcination at 550 °C. Reaction conditions for all experiments: 1 wt. % glucose in methanol, 1.5 mL min^{-1}, 0.1 g catalyst, 110 °C.

Table S1. Experimental conditions related to the initial regeneration study of 10Sn-Beta during continuous glucose isomerisation in methanol. Thermal regeneration performed at 550 °C for 3h in air. Washing regeneration performed at 0.75 mL min^{-1} for 20h with MeOH:H_2O (90:10 w/w). (Experimental conditions related to Figure 1).

Description	Feed	Temperature (°C)	Mass (g)	Flow (mL min^{-1})	X_{Glu} (%)	Y_{Fru} (%)
10Sn-Beta Fresh	1wt. % glucose in methanol	110	0.1	0.75	35	18
10Sn-Beta after 1st Thermal Reg.	1wt. % glucose in methanol	110	0.1	0.75	53	21
10Sn-Beta after 2nd Thermal Reg.	1wt. % glucose in methanol	110	0.1	0.75	52	20

Table S2. Experimental conditions related to alternating regeneration study for 10Sn-Beta during continuous glucose isomerisation in methanol. Thermal regeneration performed at 550 °C for 3h in air. Washing regeneration performed at 0.75 mL min^{-1} for 20h with MeOH:H_2O (90:10 w/w). (Experimental conditions related to Figure 2)

Description	Feed	Temperature (°C)	Mass (g)	Flow (mL min^{-1})	X_{Glu} (%)	Y_{Fru} (%)
10Sn-Beta Fresh	1wt. % glucose in methanol	110	0.1	0.75	35	18
10Sn-Beta 1st Thermal Reg.	1wt. % glucose in methanol	110	0.1	0.75	52	22
10Sn-Beta 1st Washing Reg.	1wt. % glucose in methanol	110	0.1	0.75	20	12
10Sn-Beta 2nd Thermal Reg.	1wt. % glucose in methanol	110	0.1	0.75	50	21

Table S3. Experimental conditions related to contact time online profile of 10Sn-Beta for continuous glucose isomerisation in methanol. Thermal regeneration performed at 550 °C for 3h in air. (Experimental conditions related to Figure 3, Right).

Description	Feed	Temperature (°C)	Mass (g)	Flow (mL min^{-1})
10Sn-Beta Fresh	1wt. % glucose in methanol	110	0.25	0.2
10Sn-Beta Fresh	1wt. % glucose in methanol	110	0.25	0.37
10Sn-Beta Fresh	1wt. % glucose in methanol	110	0.25	0.75
10Sn-Beta Fresh	1wt. % glucose in methanol	110	0.25	1.5
10Sn-Beta Fresh Thermal Reg.	1wt. % glucose in methanol	110	0.25	0.37
10Sn-Beta Fresh Thermal Reg.	1wt. % glucose in methanol	110	0.25	0.75
10Sn-Beta Fresh Thermal Reg.	1wt. % glucose in methanol	110	0.25	1.5

Table S4. Parameters for ^{119}Sn CPMG MAS NMR analysis of various Sn-Beta samples employed in this study. CP and DE Spectra were normalised for publication in Figure 4.

Entry	Analysis	t1 (s)	Scan Number
1	Direct Excitation	2	24000
2	Cross Polarisation	1	14000
3	Direct Excitation	135	512

Table S5. Kinetic diameter and extent of pre-activation of the solvents investigated during pre-activation studies.

Solvents	Kinetic diameter (nm)[1,2]	Extent of pre-activation
MeOH	0.38	2
EtOH	0.43	1.56
2-PrOH	0.47	1
BuOH	0.5	0.95
Acetone	0.47	0.87
cyclohexane	0.51	1.25
1,4-dioxane	0.7	1.373

Table S6. Experimental conditions for different loadings of Sn-Beta employed in continuous glucose isomerisation in methanol. Pre-activation performed by treatment in MeOH at 110°C at a flow of 1.5 mL min^{-1} for 0.5 h, followed by thermal treatment performed at 550 °C for 3h in air. (Experimental conditions related to Figure 6 and Figure 7, Left).

Description	Feed	Temperature (°C)	Mass (g)	Flow (mL min^{-1})	X_{Glu} (%)	Y_{Fru} (%)
0.5Sn Beta	1wt. % glucose in methanol	110	0.1	0.3	41	16
1Sn-Beta	1wt. % glucose in methanol	110	0.1	0.6	34	13
2Sn-Beta	1wt. % glucose in methanol	110	0.1	0.8	38	16
10Sn-Beta	1wt. % glucose in methanol	110	0.1	0.9	37	16
0.5Sn Beta Pre-activated	1wt. % glucose in methanol	110	0.1	0.5	46	18
1Sn-Beta Pre-activated	1wt. % glucose in methanol	110	0.1	1	36	12
2Sn-Beta Pre-activated	1wt. % glucose in methanol	110	0.1	1.2	45	18
10Sn-Beta Pre-activated	1wt. % glucose in methanol	110	0.1	1.5	47	18

Table S7. Experimental conditions for different loadings of Sn-Beta employed for batch glucose isomerisation in methanol. Pre-activation performed by treatment in MeOH at 110°C at a flow of 1.5 mL min^{-1} and thermal treatment performed at 550 °C for 3h in air. 4 g of reaction solution was employed in each batch experiment. (Experimental conditions related to SI Figure S8 and Figure 7, Right).

Description	Reaction solution	Time (min)	Temperature (°C)	Mass (g)	X_{Glu} (%)	Y_{Fru} (%)	Productivity (h^{-1})
1Sn-Beta	1wt. % glucose in methanol	5	110	0.09	6.5	3.6	0.35
10Sn-Beta	1wt. % glucose in methanol	5	110	0.027	11	8.2	1.96
1Sn-Beta Pre-activated	1wt. % glucose in methanol	4	110	0.09	11	6.8	0.73
10Sn-Beta Pre-activated	1wt. % glucose in methanol	4	110	0.027	15	6.9	3.33

References

(1) Bettens, B.; Dekeyzer, S.; Van Der Bruggen, B.; Degrève, J.; Vandecasteele, C. Transport of Pure Components in Pervaporation through a Microporous Silica Membrane. *J. Phys. Chem. B* **2005**, *109* (11), 5216–5222.

(2) Bowen, T. C.; Li, S.; Noble, R. D.; Falconer, J. L. Driving Force for Pervaporation through Zeolite Membranes. *J. Memb. Sci.* **2003**, *225* (1–2), 165–176.