Supporting Information

Tin-Containing Silicates: Identification of a Glycolytic Pathway via 3-Deoxyglucosone

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Catalyst Preparation

Sn-, Zr-, Ti and Hf-Beta zeolites via hydrothermal synthesis procedure

Sn-Beta zeolites (Si/Sn = 125) were synthesized by modifying the route described by Valencia *et al*.[1] In a typical synthesis procedure, 30.6 g of tetraethyl orthosilicate (TEOS, Aldrich, 98%) was added to 33.1 g of tetraethylammonium hydroxide (TEAOH, Sigma-Aldrich, 35% in water) under careful stirring, forming a two-phase solution. After stirring (~60 min) one phase is obtained and tin(IV) chloride pentahydrate ($SnCl4·5H_2O$, Aldrich, 98%) dissolved in 2.0 mL of demineralized water was added drop wise. Stirring was maintained for several hours to allow ethanol formed from the hydrolysis of TEOS to evaporate. Finally, 3.1 g hydrofluoric acid (HF, Fluka, 47-51%) in 1.6 g of demineralized water was added to the gel, yielding a solid with the molar composition; $1.0Si:0.005Sn:0.02Cl^-:0.55TEA^+:0.55F^-:7.5H_2O$. All samples were then homogenized and transferred to a Teflon-container placed in a stainless steel autoclave. This was then placed at 140°C for 14 days. The solid was recovered by filtration and washed with demineralized water, followed by drying overnight at 80°C in air. The organic template contained within the material was removed by heating the sample at 2°C/min to 550 °C in static air and maintaining this temperature for 6 h.

Zr-Beta (Si/Zr = 150) and Hf-Beta (Si/Hf = 200) zeolites were prepared by the aforementioned procedure, exchanging the tin source with $ZrOCl_2·8H_2O$ (Sigma-Aldrich, 98 %) or $HfCl_4$ (Aldrich, 98 %), respectively. For Ti-Beta (Si/Ti = 150), tetraethyl orthosilicate (Aldrich) was first dissolved in a mixture of H_2O_2 and water and then used in a similar fashion as the metal source.

Purely siliceous Beta (Si-Beta) was prepared by omitting the addition of tin source and SnO_2-Beta was synthesized using tin oxide (SnO_2, Aldrich, <100 nm) as the tin source.[2]

Sn-Beta (Si/Sn = 125) via post-treatment procedure

Sn-Beta (Si/Sn = 125) was prepared according to a modification of the procedure described by Hammond *et al*.[3] Commercial zeolite Beta (Zeolyst, Si/Al = 12.5, NH_4^+-form) was calcined (550 °C for 6 h) to obtain the H-form and treated with 10 g of concentrated nitric acid (HNO_3, Sigma-Aldrich, ≥65 %) per gram of zeolite Beta powder for 12 h at 80 °C. The resulting solid was filtered, washed with ample water and calcined (550°C for 6 h using a ramp of 2°C/min) to obtain the dealuminated Beta (deAl-Beta). This solid was then impregnated by incipient wetness methodology with a Si/Sn ratio of 125. For this purpose, tin(II) chloride (0.128 g, Sigma-Aldrich, 98 %) was dissolved in water (5.75 mL) and added to the dealuminated Beta (5 g). After the impregnation process, the samples were dried 12 h at 110°C and calcined again (550°C for 6 h).

Sn-MFI (Si/Sn = 400)

Sn-MFI was prepared following a procedure described by Mal *et al*.[4] In a typical synthesis, 5.35 g of ammonium fluoride (Sigma-Aldrich, ≥98 %) was dissolved in 25 g of demineralized water under stirring. A solution of $SnCl_4·5H_2O$ in 10 g of water was then added under rapid stirring, followed by slow addition of a solution of 9.8 g of tetrapropylammonium bromide (Aldrich, 98 %) in 56 g of demineralized water. Finally, 8.6 g of fumed silica (Aldrich) was dissolved. The mixture was then stirred for approx. 3 hours and transferred to a Teflon-lined autoclave and crystallized at 200°C for 6 days. The solid was then recovered by filtration, washed with ample water and dried overnight at 80°C followed by calcination (2°C/min, 550°C, 6 hours dwell time) to obtain the finished material.

Sn-MCM-41 (Si/Sn = 200)

The ordered mesoporous stannosilicate, Sn-MCM-41, was prepared according to the route described by Li *et al*.[5] In a typical synthesis, 26.4 g of tetraethylammonium silicate (TMAS, Aldrich, 15-20 wt% in water, ≥99.99%) was added slowly to a solution of 13.0 g of hexadecyltrimethylammonium bromide (CTABr, Sigma, ≥99.0%) dissolved in 38.0 g of water, and the mixture was allowed to stir for approx. 1 hour. At this point, $SnCl_4·5H_2O$ and hydrochloric acid (HCl, Sigma-Aldrich, min. 37%) in 2.1 g of water was added drop wise to the solution and allowed to stir for 1.5 h. To this solution 12.2 g of TEOS was added and stirred for 3 h, giving a gel composition of; $1.0Si:0.005Sn:0.44CTABr:0.27TMA:0.08Cl^-:46H_2O$. The samples were then transferred to a Teflon-lined container placed in a stainless steel autoclave and placed in a pre-heated oven at 140°C for 15 h. The solid was recovered by filtration and washed with ample water and dried overnight at 80°C. The material was finalized by calcination, heating the sample to 550°C at 2°C/min in static air and maintaining this temperature for 6 h.

Catalyst Characterization

Powder X-ray diffraction (XRD) patterns of the calcined samples were measured on an X'Pert diffractometer (Philips) using Cu-Kα radiation. Surface area and pore volume measurements were performed using multipoint N_2 adsorption/desorption on an Autosorb automatic surface area and pore size analyzer (Quantachrome Instruments). The total surface area of the samples was obtained using the BET method and the micropore volume was calculated by the *t*-plot method using the Autosorb3 software. UV-Vis measurements were done using a DH-2000-BAL balanced deuterium, halogen light source (Ocean Optics). Mesoporous materials were characterized using low angle x-ray diffraction to verify the ordered nature of these materials.

Production of 2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM)

Synthesis and Purification

Post-treated Sn-Beta (3 g), Glucose (12 g, Sigma-Aldrich, >99.0%) and methanol (200 g, Sigma-Aldrich, >99.8%) were added to the Teflon liner of a 1 L autoclave reactor (Autoclave Engineers). The reactor was sealed and heated to 160°C under stirring (450 rpm) for 16 hours. The reaction mixture was then cooled and filtered resulting in the crude reaction mixture. The crude reaction mixture was concentrated under reduced pressure at 40°C. 2.1 g of the concentrate was dissolved in methanol, evaporated onto Celite and purified by flash column chromatography (silica gel 15-40 Mesh, CH_2Cl_2, 20:1 CH_2Cl_2:MeOH) affording 0.30 g of pure THM.

Analysis and Identification

NMR experiments were recorded on a Bruker Ascend 400 spectrometer, ^{1}H -NMR was recorded at 400 MHz and ^{13}C-NMR was recorded at 100 MHz. The chemical shifts are given in ppm relative to the residual solvent signals and the chemical shifts are reported downfield to TMS. HRMS was recorded on an LC-TOF (ES).

^{1}H-NMR (400 MHz, CD_3OD): δ (ppm) 5.93 (dd, *J* = 15.3, 4.3 Hz, 1H), 5.88 (dd, J = 15.3, 4.1 Hz, 1H), 4.69 (d, *J* = 4.1 Hz, 1H), 4.14 (ddd, *J* = 6.7, 4.7, 4.1 Hz, 1H), 3.73 (s, 3H), 3.51 (dd, *J* = 10.9, 4.7 Hz, 1H) 3.45 (dd, *J* = 10.9, 6,7 Hz, 1H). ^{13}C-NMR (100 MHz, CD_3OD) : δ (ppm) 174.6, 133.8, 129.4, 73.4, 72.2, 67.0, 52.6. HRMS (ESI+) *m/z* calculated for $C_7H_{12}O_5$ [M + **Na**]$^+$: 199.0577; found: 199.0572.

Figures

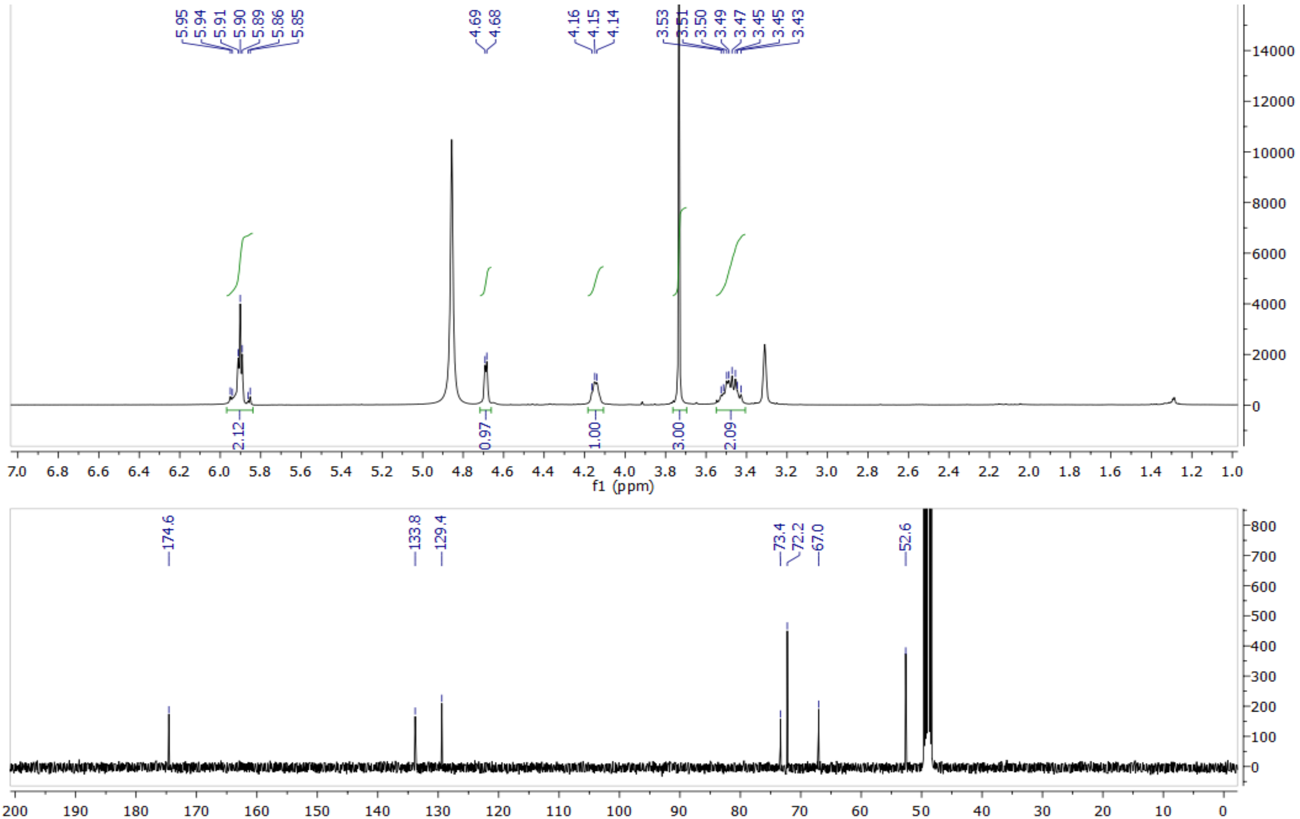

Figure S1: ^{1}H and ^{13}C NMR spectra of purified THM produced by the aforementioned procedure.

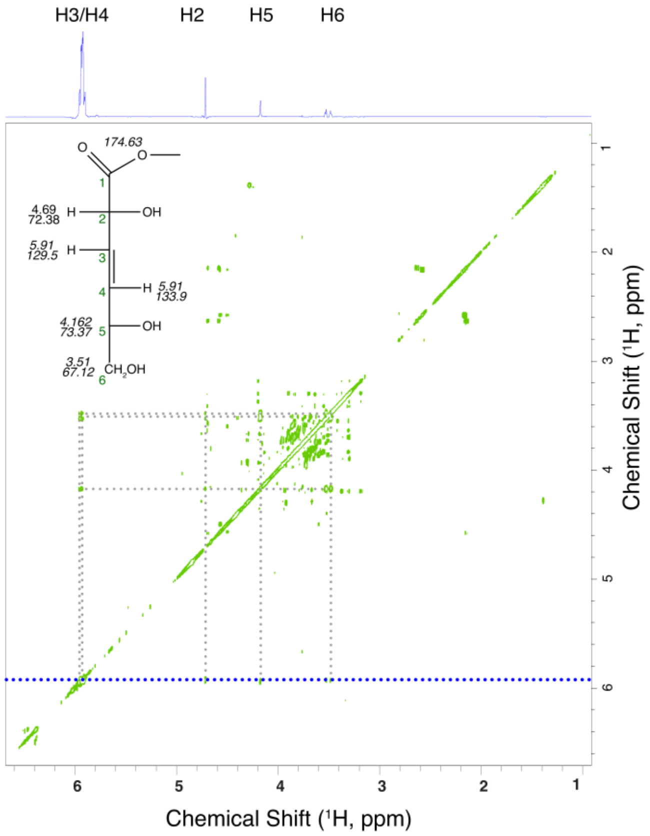

Figure S2: ^{1}H-^{1}H TOCSY correlations between protons of the THM spin system in a reaction mixture produced by Sn-Beta catalyzed glucose conversion in methanol.

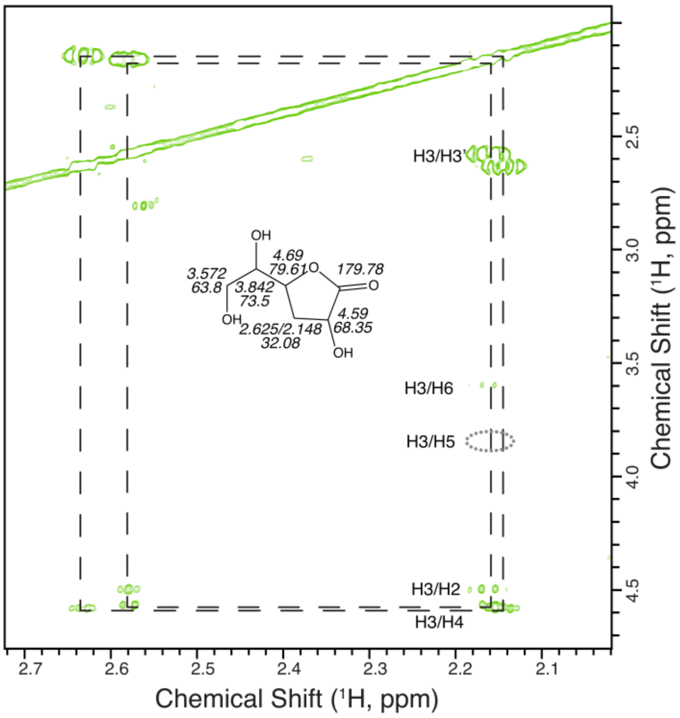

Figure S3: ^{1}H-^{1}H TOCSY correlations from the methylene protons to other protons in the spin systems of 3-deoxy-γ–lactones present in a glucose-derived reaction mixture.

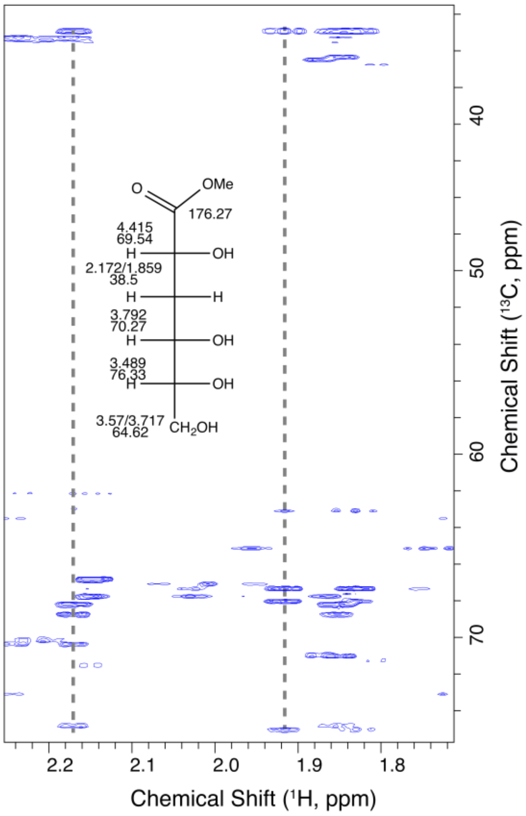

Figure S4: ^{1}H-^{13}C HSQC-TOSCY correlations between the protons and carbons of the DGM spin system in a reaction mixture produced by Sn-Beta catalyzed glucose conversion in methanol,

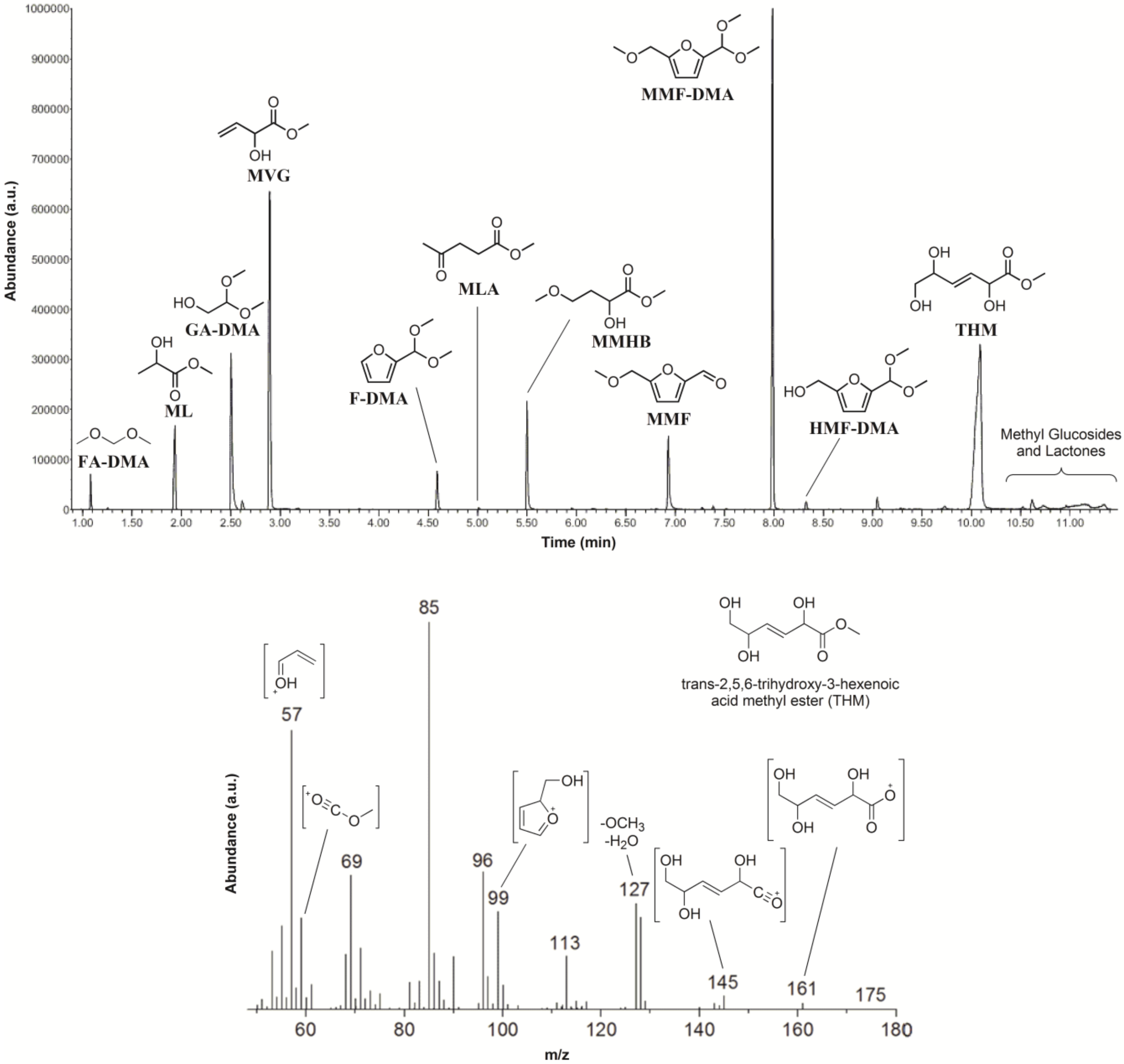

Figure S5: GC-MS analysis of the reaction liquid obtained from the reaction between glucose and alkali-free Sn-Beta at 140°C in methanol showing a) chromatogram and b) the specific fragmentation pattern of trans-2,5,6-trihydroxy-3-hexenoic acid methyl ester taken at 10.062 min.

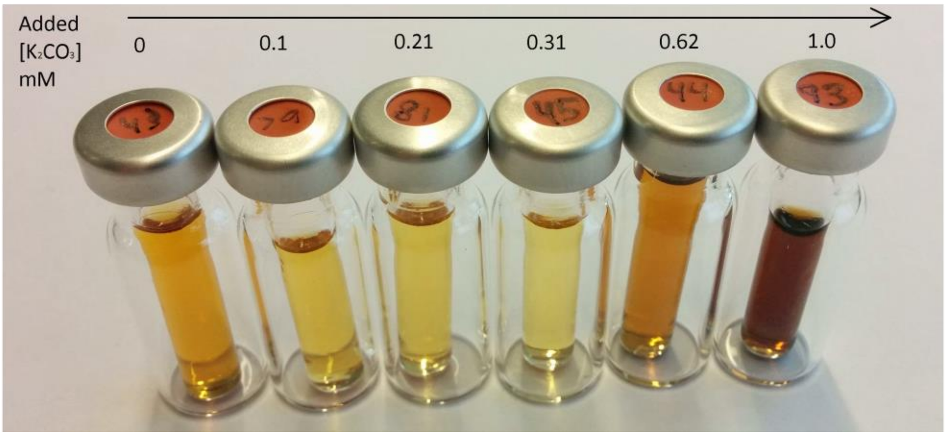

Figure S6: Visual change in color of reaction liquids with increase in K_2CO_3 added to the methanol used as solvent. The vials were prepared using 180 mg Sn-Beta (PT), 360 mg glucose, 4 g of solvent, reacted for 6 hours at 160°C.

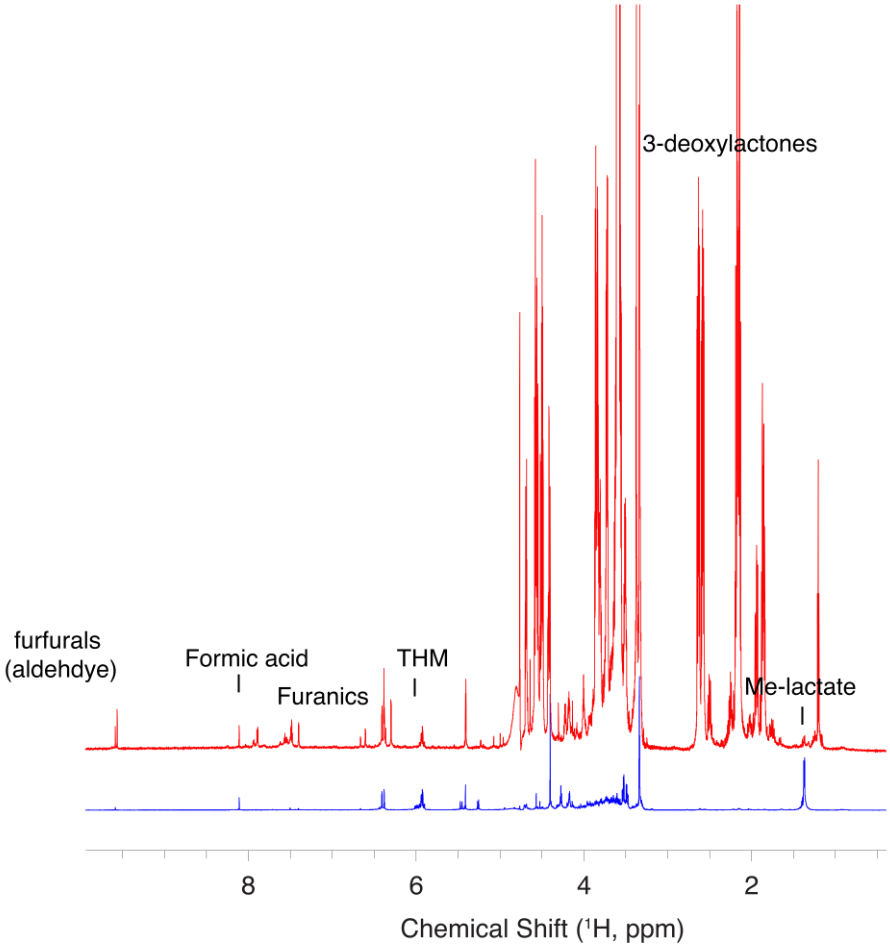

Figure S7: ^{1}H-NMR spectrum of the product mixture formed by reaction of a commercial 3-deoxyglucosone (red) and glucose (blue) substrate with a Sn-Beta catalysis in methanol at 160°C. Spectra are renormalized to identical THM signal amplitude to highlight the higher ratio of furanics/THM using 3-deoxyglucosone as the substrate.

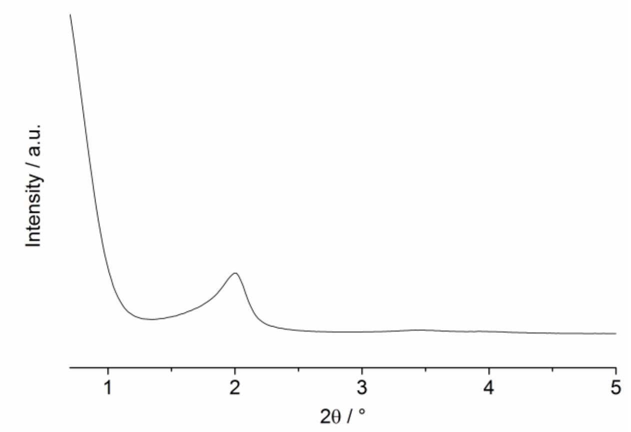

Figure S8: Low angle XRD diffractogram of Sn-MCM-41 (Si/Sn = 200).

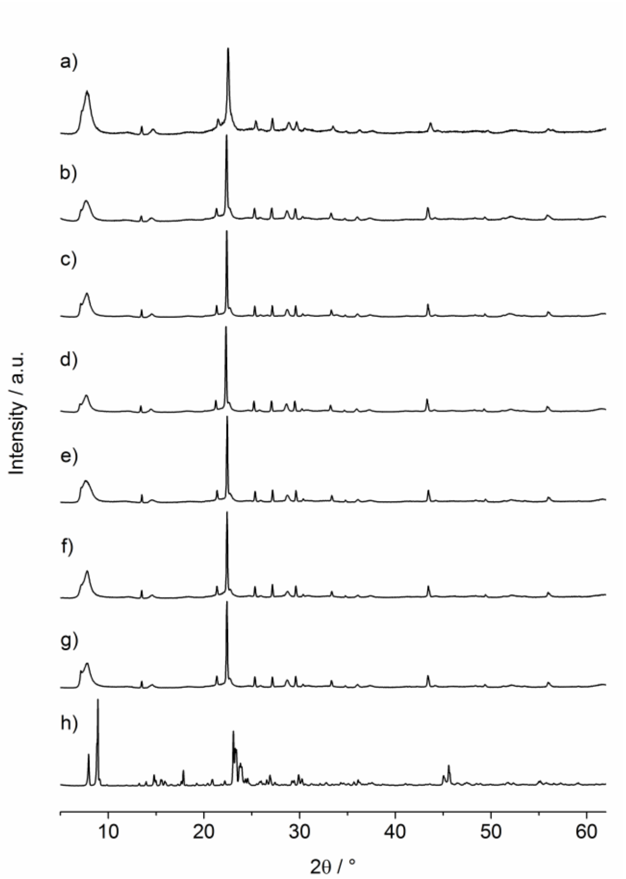

Figure S9: XRD diffractograms of a) Sn-Beta (PT), b) Sn-Beta (HF), c) SnO_2-Beta (HF), d) Si-Beta (HF), e) Zr-Beta (HF), f) Ti-Beta (HF), g) Hf-Beta (HF) and h) Sn-MFI.

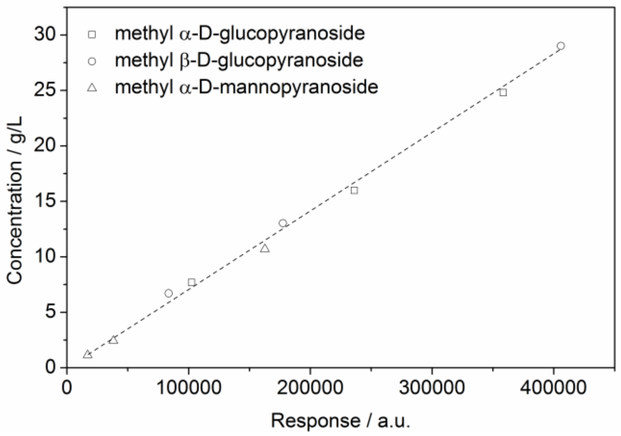

Figure S10: Calibration curve for the three methyl glucosides; methyl α-D-glucopyranoside, methyl β-D-glucopyranoside and methyl α-D-mannopyranoside measured on an an Agilent 1200 series HPLC equipped with a Carbohydrate (Zorbax) column (60 wt% acetonitrile/water, 0.5 mL/min, 30°C).

Tables

Table S1: Conversion of glucose in the presence and absence of alkali using Sn-Beta prepared by the post-treatment method (PT Sn-Beta).

			Retro-aldol pathway					3DG pathway					
Entry	c_{K2CO3} (in methanol)	MG	ML	GA-DMA	MVG	MMHB	ML/'RA products'	HMF	MMF	MLA	F-DMA	DGL	THM
	mM	%	%				%	%					
1	0	16	17	3	6	1	63	0	10	2	<1	6	14
2	0.10	9	26	2	11	2	64	0	7	<1	<1	5	13
3	0.21	9	37	1	15	3	66	0	4	<1	<1	6	11
4	0.31	6	48	1	18	3	70	0	2	<1	<1	3	6
5	0.62	7	49	<1	16	2	72	<1	0	<1	<1	0	3
6	1.03	3	37	<1	14	2	69	2	4	<1	<1	<1	1

Yields (carbon%) of methoxylated sugars (MG), methyl lactate (ML), glycolaldehyde dimethylacetal (GA-DMA), methyl vinylglycolate (MVG), methyl 4-methoxy-2-hydroxybutanoate (MMHB), 5-(hydroxymethyl)furfural (HMF), 5-(methoxymethyl)furfural (MMF), methyl levulinate (MLA), furfural dimethylacetal (F-DMA), 3-deoxy *γ*-lactones (DGL), and trans-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM).
Reaction conditions: 160°C, 360 mg glucose, 4 g solvent, 180 mg Sn-Beta (PT) (Si/Sn = 125), 6 hours, 600 rpm stirring.

Table S2: Standard deviations given in parenthesis at alkali concentrations of 0 and 0.31 mM K_2CO_3/methanol for the conversion of glucose using PT Sn-Beta.

Entry	c_{K2CO3} (in methanol)	MG	ML	GA-DMA	MVG	MMHB	MMF	MLA	THM
	mM	%							
1	0	16(3)	17(1)	2(0.2)	7(1)	1(0.1)	10(1)	2(0.3)	14(1)
2	0.31	6(0.4)	49(2)	1(0.3)	18(1)	3(0.1)	2(1)	<1	6(0.9)

Yields (carbon%) of methoxylated sugars (MG), methyl lactate (ML), glycolaldehyde dimethylacetal (GA-DMA), methyl vinylglycolate (MVG), methyl 4-methoxy-2-hydroxybutanoate (MMHB), 5-(hydroxymethyl)furfural (HMF), 5-(methoxymethyl)furfural (MMF), methyl levulinate (MLA), and trans-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM).
Reaction conditions: 160°C, 360 mg glucose, 4 g solvent, 180 mg Sn-Beta (PT) (Si/Sn = 125), 6 hours, 600 rpm stirring.

Table S3. Conversion of glucose in the presence and absence of alkali using Sn-Beta prepared by the post-treatment method (PT Sn-Beta) for 10-30 mins.

				Retro-aldol pathway					3DG pathway					
Entry	Time	Solvent	MG	ML	GA-DMA	MVG	MMHB	ML/'RA products'	HMF	MMF	MLA	F-DMA	FUR	THM
	min		%	%				%	%					
1	10	Methanol	45	8	2	3	<1	59	2	4	<1	<1	6	7
2	20	Methanol	31	10	3	4	<1	59	1	8	<1	<1	11	10
3	30	Methanol	29	11	3	4	<1	59	1	8	<1	<1	10	11
4	10	0.62 mM K_2CO_3 /methanol	13	39	<1	15	2	69	<1	<1	<1	<1	1	2
5	20	0.62 mM K_2CO_3 /methanol	9	42	<1	16	2	69	<1	<1	<1	<1	1	2
6	30	0.62 mM K_2CO_3 /methanol	8	47	<1	17	2	69	1	<1	<1	<1	1	2

Yields (carbon%) of methoxylated sugars (MG), methyl lactate (ML), glycolaldehyde dimethylacetal (GA-DMA), methyl vinylglycolate (MVG), methyl 4-methoxy-2-hydroxybutanoate (MMHB), 5-(hydroxymethyl)furfural (HMF), 5-(methoxymethyl)furfural (MMF) and furfural dimethylacetal (F-DMA) and the combined furan yield of HMF, MMF, F-DMA and MLA denoted FUR as well as *trans*-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM).
Reaction conditions: 160°C, 360 mg substrate, 4 g methanol, 180 mg catalyst, 600 rpm stirring.

Table S4: Conversion of various methyl glucosides using Sn-Beta (PT) and blank experiments both in the presence of and in the absence of alkali, reacted at 160 °C.

						Retro-aldol pathway				3DG pathway	
Entry	Catalyst	Substrate	Solvent	Unconverted sugars	MG	ML	GA-DMA	MVG	MMHB	FUR	THM
				%		%				%	
1	Sn-Beta (PT)	Methyl *α*-D-glucopyranoside	Methanol	-	85	1	<1	1	<1	<1	<1
2	Sn-Beta (PT)	Methyl *β*-D-glucopyranoside	Methanol	-	82	1	<1	1	<1	<1	<1
3	Sn-Beta (PT)	Methyl *α*-D-mannopyranoside	Methanol	-	97	2	<1	<1	<1	<1	<1
4	-	Glucose	Methanol	78	18	<1	<1	<1	<1	1	<1
5	-	Glucose	0.62 mM K_2CO_3/ methanol	39	34	<1	<1	<1	<1	2	<1

Yields (carbon%) of unconverted sugars, methoxylated sugars (MG), methyl lactate (ML), methyl vinylglycolate (MVG), glycolaldehyde dimethylacetal (GA-DMA), methyl 4-methoxy-2-hydroxybutanoate (MMHB), combined yield of 5-(hydroxymethyl)furfural (HMF), 5-(methoxymethyl)furfural (MMF) and furfural dimethylacetal (F-DMA) denoted FUR and *trans*-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM).
Reaction conditions: 160°C, 360 mg substrate, 4 g methanol, 180 mg catalyst, 6 hours, 600 rpm stirring.

Table S5: Conversion of monosaccharides in the absence of alkali using a selection of Beta-framework and/or tin containing catalysts.

					Retro-aldol pathway				3DG pathway				
Entry	Catalyst	Substrate	Temperature	MG	ML	GA-DMA	MVG	MMHB	HMF	MMF	MLA	F-DMA	THM
			°C	%	%				%				
1	Sn-Beta (PT)	Glucose	120	44	4	1	1	<1	1	9	<1	<1	8
2	Sn-Beta (PT)	Glucose	140	21	10	2	3	1	2	12	<1	<1	12
3	Sn-Beta (PT)	Glucose	160	13	17	3	6	1	<1	10	2	1	14
4	Sn-Beta (PT)	Glucose	180	5	26	2	11	1	<1	7	2	1	8
5	Sn-Beta (PT)	Fructose	160	9	19	2	7	1	<1	11	2	1	18
6	Sn-Beta (PT)	Mannose	160	12	20	2	8	1	<1	10	1	1	15
7	Sn-Beta (PT)	Sorbose	160	13	15	3	9	2	<1	11	2	1	17
8	Sn-Beta (PT)	Galactose	160	26	10	2	6	1	<1	11	2	1	12
9	Sn-Beta (PT)	Tagatose	160	11	11	<1	6	1	<1	14	2	2	9
10	Sn-Beta (PT)	Sucrose	160	10	22	2	8	2	<1	11	1	<1	15
11	Sn-Beta (HF)	Glucose	160	8	24	1	8	1	4	5	<1	<1	16
12	Zr-Beta (HF)	Glucose	160	27	25	5	7	<1	<1	1	<1	<1	2
13	Ti-Beta (HF)	Glucose	160	14	28	3	6	1	2	1	<1	<1	3
14	Hf-Beta (HF)	Glucose	160	35	18	3	5	<1	<1	7	<1	<1	4
15	Al-Beta	Glucose	160	32	<1	<1	<1	<1	<1	2	12	<1	<1
16	deAl-Beta	Glucose	160	86	<1	<1	<1	<1	<1	<1	<1	<1	<1
17	deAl-Beta	Fructose	160	51	<1	<1	<1	<1	<1	12	<1	<1	<1
18	Sn-MCM-41	Glucose	160	16	26	3	5	3	4	7	<1	<1	18
19	Sn-MFI	Glucose	160	40	8	8	4	<1	<1	<1	<1	<1	<1
20	SnO_2-Beta (HF)	Glucose	160	37	1	<1	<1	<1	2	<1	<1	<1	<1
21	Si-Beta (HF)	Glucose	160	46	3	2	1	<1	3	<1	<1	<1	<1

Yields (carbon%) of methoxylated sugars (MG), methyl lactate (ML), methyl vinylglycolate (MVG), glycolaldehyde dimethylacetal (GA-DMA), methyl 4-methoxy-2-hydroxybutanoate (MMHB), combined yield of 5-(hydroxymethyl)furfural (HMF), 5-(methoxymethyl)furfural (MMF) and furfural dimethylacetal (F-DMA) and *trans*-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM) from the conversion of various sugars using a variety of catalysts, different sugars and at different temperatures.
Reaction conditions: 360 mg substrate, 4 g methanol, 180 mg catalyst, 6 hours, 600 rpm stirring.

Table S6. Physical properties of the various catalysts used in the study measured using N_2-adsorption/desorption and from XRD diffraction.

		X-ray diffraction	N_2-adsorption/desorption			
Entry	Catalyst	Primary phase	S_{BET}	$S_{micropore}$[a]	V_{total}	$V_{micropore}$[a]
			m^2/g		mL/g	
1	Sn-Beta (PT)	*BEA	557	373	0.37	0.19
2	Sn-Beta (HF)	*BEA	486	362	0.33	0.19
3	SnO_2-Beta	*BEA	457	365	0.27	0.19
4	Si-Beta	*BEA	465	378	0.27	0.20
5	Zr-Beta (HF)	*BEA	490	391	0.27	0.20
6	Ti-Beta (HF)	*BEA	481	392	0.27	0.20
7	Hf-Beta (HF)	*BEA	541	376	0.32	0.20
8	Sn-MFI	MFI	377	191	0.20	0.09
9	Sn-MCM-41	Mesoporous silica, a = 45 Å[b]	962	-	1.00	-

a. Determined using the *t*-plot method.

b. Determined using low angle x-ray diffraction (0.5-5° 2θ)

Table S7: Conversion of glucose using Zr-Beta (HF) in different concentration of K_2CO_3 in methanol.

					Retro-aldol pathway				3DG pathway	
Entry	Catalyst	Substrate	Solvent	MG	ML	GA-DMA	MVG	MMHB	FUR	THM
				%	%				%	
1	Zr-Beta (HF)	Glucose	Methanol	27	25	5	7	<1	2	2
2	Zr-Beta (HF)	Glucose	0.31 mM K_2CO_3/methanol	15	27	2	10	2	2	1
3	Zr-Beta (HF)	Glucose	0.62 mM K_2CO_3/methanol	12	25	1	10	3	1	1

Yields (carbon%) of unconverted sugars, methoxylated sugars (MG), methyl lactate (ML), glycolaldehyde dimethylacetal (GA-DMA), methyl vinylglycolate (MVG), methyl 4-methoxy-2-hydroxybutanoate (MMHB), combined yield of 5-(hydroxymethyl)furfural (HMF), 5-(methoxymethyl)furfural (MMF) and furfural dimethylacetal (F-DMA) denoted FUR and *trans*-2,5,6-trihydroxy-3-hexenoic acid methyl ester (THM).
Reaction conditions: 160°C, 360 mg substrate, 4 g methanol, 180 mg catalyst, 6 hours, 600 rpm stirring.

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