

Supporting information

Efficient One-Pot Tandem Catalysis of Glucose into 1,1,2-Trimethoxyethane over W-Beta Catalyst

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1. Experimental Section

1.1 Catalyst synthesis and characterization

All chemicals were purchased from the major commercial suppliers: the zeolite beta with $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ was purchased from Nankai University Catalyst Co., Ltd, ammonium metatungstate (AMT, Macklin, AR), tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Macklin, AR), HNO_3 (65.0 wt % in water, Macklin), fructose (99.0%, Macklin, AR), glucose (99.0%, Macklin, AR), mannose (99.0%, Macklin, AR), 1,1,2-trimethoxyethane (> 98.0%, Macklin, AR), glycolaldehyde dimethyl acetal (GADMA, 98%, Alfa Aesar, AR), glycolaldehyde dimer ($\geq 94\%$, Aldrich, AR), methyl lactate (98%, Sinopharm, AR), and methyl vinyl glycolate (98%, Sinopharm, AR), and other reagents were purchased from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China). All the commercial chemicals were used as received.

For the Synthesis of deAl-Beta catalysat, commercial Beta zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ was calcinated at 550 °C for 6 h before usage to remove the template and adsorbed impurities. deAl-Beta, short for dealuminated Beta zeolite, was prepared by stirring commercial Beta in a 13.0 mol/L aqueous nitric acid solution at 100 °C for 20 h. Afterwards the power was washed with water until the PH was neutral and dried at 100 °C overnight.

For the synthesis of Sn-Beta, 3.0 g of the deAl-Beta solid power was finely ground with appropriate amount of tin source ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) in the mortar for 1 h. Afterward, the solids were calcined under air (550 °C, 5 °C min^{-1} , 6 h). The synthesized catalysts were denoted as x wt% Sn-Beta, where x denotes the content of tin in catalyst.

For the synthesis of W-Beta, the weighted tungsten source (AMT) was added to water (50 ml) and stirred heavily at room temperature until AMT was completely dissolved, afterward, 5.0 g deAl-Beta was added into the solution and the slurry was kept stirring for 3 h. Then the solid mixtures were obtained by vaporization the water solvent at 90 °C under stirring and dried overnight in the oven at 100 °C. The white power was subsequently calcined under air (550 °C, 5 °C min^{-1} , 6 h). The synthesized catalysts were denoted as x wt% W-Beta, where x denotes the content of tungsten in catalyst.

For the synthesis of WO_3 , AMT was directly obtained by calcining under air (550 °C, 5 °C min^{-1} , 6 h).

The X-ray powder diffraction (XRD) patterns of the support and synthesized catalysts were measured by a Rigaku Ultima IVX-ray diffractometer (40 kV, 40 mA) using Cu-Ka radiation at a scanning rate of 2° min^{-1}

¹. The specific surface area, micropore area and pore size distribution of the samples were determined by N₂-adsorption and desorption using a Micromeritics ASAP 2420 equipment. UV-Vis absorption spectra were recorded on a Shimadzu UV-2700 spectrophotometer in the range of 200-800 nm, with BaSO₄ as the background. For the recording of the Fourier-transform infrared (FT-IR) spectra, the catalysts were mixed with KBr with a mass ratio of 1: 50 as test samples and outgassed at 150°C for 30 min to exclude the influence of water. Then all the samples were recorded on a Nicolet iS50 FTIR spectrometer with a MCT detector (resolution 2 cm⁻¹, 64 scans). All spectra were taken with KBr as background. X-ray photoelectron spectrometry (XPS) was used to analyze the oxidation states and proximal environment of tungsten species in different tungsten-based catalysts on a K-Alpha spectrometer (Thermo Fisher Scientific) with an Al Ka emission source. The H₂-temperature-programmed reduction (H₂-TPR) was conducted using an Auto Chem II 2920 chemisorption analyzer (Micromeritics, USA). Samples of 50 mg were first purged with Helium at a flow rate of 60 ml/min at 80°C for 1 h and then cooled down to 50 °C. H₂-TPR was then conducted under 5% H₂/Ar at a flow rate of 50 cm³/min by raising the temperature from 50 to 800°C at a rate of 10 °C /min. FT-IR spectra of pyridine adsorption (Py-IR) was performed with a spectral resolution of 4 cm⁻¹ on a Nicolet Nexus 670 FT-IR spectrometer. In a home-made vacuum infrared cell with CaF₂ windows, a self-supporting wafer of the sample (about 10 mg) was initially dried under vacuum at 350 °C for 1 h, then cooled down to 50 °C and saturated with about 25 mbar of pyridine vapor at 50 °C for 10 min and then evacuated again for 30 min to fully remove the physisorbed pyridine. Finally, the evacuated sample containing chemisorbed pyridine was heated to 100, 200 and 350 °C for 30 min, with a heating rate of 10 °C /min, and the IR spectra were recorded in situ at these temperatures. The amounts of acid sites were determined from the integral intensity of characteristic bands (1450 cm⁻¹ for Lewis acid sites, and 1540 cm⁻¹ for Brønsted acid sites) using the molar extinction coefficients of Emeis. The concentrations of tin and tungsten in the heteroatom zeolites and filtrate were measured by the Inductively coupled plasma-atomic emission spectrometry (ICP-AES) on Perkin Elmer Optima 3000. The concentrations of Silicon and aluminum in the zeolites were measured by the x-ray fluorescence (XRF) analysis by x-ray fluorescence XRF (Bruker S4 PIONEER). The NH₃-TPD spectra were conducted on Auto Chem. II2920 equipment (Micromeritics, USA). For NH₃-TPD, 100 mg of sample was placed into a U-shaped quartz tube and heated from 50 °C to 200 °C at a ramping rate of 10 °C /min in an Argon atmosphere and then cooled to 50 °C in NH₃ gas for 20 min, afterwards, heated from 50 to 800 °C at a ramping rate of 10 °C/min in an Argon atmosphere to desorb NH₃. The data were recorded from 50

to 800 °C with a ramping rate of 10 °C/min, and simultaneously monitored by a thermal conductivity detector (TCD).

1.2 Catalytic evaluation and product analysis

The catalytic conversion of stock (glucose, fructose, mannose, glycolaldehyde, and erythrose) was carried out in a stainless-steel autoclave (Parr, 100 ml) and 30 ml solvent was added with an initial N₂ pressure of 4 MPa, and 0.25 h was needed to warm up from room temperature to 200 °C. Generally, a mixture of stock, solid acid catalyst, and solvent were loaded into the sealed autoclave with a stirring speed of 570 rpm. After the reaction, the autoclave was cooled with ice bath and the collected liquid solution was filtered through 0.45 µm pore-size filters prior to analysis.

The main products in the resultant solution were identified based on the standard compounds by GC-FID (Shimadzu, 2010 Plus) and their structures were further confirmed by GC-MS (Agilent 7890 GC with Agilent 5975C inert MSD) in the same analysis condition: Column type (HP-5, 30 m, 0.25 mm inner diameter), 40 °C for 3 min, increased from 40 to 120 °C at 2 °C/min and held for 2 min, then increased from 120 to 250 °C at 10 °C/min, final temperature 250 °C for 1 min. The carbohydrates (including glucose, fructose, mannose, glycolaldehyde, and erythrose) were quantified by HPLC (Shimadzu LC-20AD, Aminex HPX-87H ion exclusion column: 300 mm × 7.8 mm, column temperature: 50 °C, mobile phase: 0.005 M aqueous H₂SO₄ with a flow rate of 0.65 mL/min) with a differential refraction detector (RID-10A). Yields of 1-methoxyacetone, methyl glycolate, methyl lactate, 1,1-dimethoxyacetone, GADMA, 1,1,2-trimethoxyethane, methyl vinylglycolate, and 1,1,2,2-tetramethoxyethane were obtained from GC analysis based on a calibration curve from commercial samples of the compounds. The two compounds 2-hydroxy-2-methylpropanoic acid and 3,3-dimethoxy-2-butanone are not commercially available and they were identified by GC-MS and yields were calculated by using calibration data of the Methyl vinyl glycolate while assuming similar carbon response factors.

The conversion of carbohydrates (glucose, fructose, mannose, glycolaldehyde, and erythrose) was calculated based on the following equation:

$$\text{Conversion} = (\text{moles of initial reactant} - \text{moles of reactant in the resultant}) \div (\text{moles of initial reactant}) \times 100\%.$$

The yield of products was calculated based on carbon via the equations:

Yield = (moles of carbon in the product) ÷ (moles of carbon in the reactant) × 100%.

2. Additional table and figures

Table S1. Examples of different catalysts for the conversion of glucose to C₂-based products in the literature

Catalyst	T, °C	Reactant	Device and atmosphere	Target Molecule	Molecule structure	Conversion, %	Yield, %	Ref.
Sn-Beta	160	Glucose	Batch, N ₂	GADMA		>99.0	0.5	1
Ti-Beta	160	Glucose	Batch, N ₂	GADMA		>99.0	2.5	1
Zr-Beta	160	Glucose	Batch, N ₂	GADMA		>99.0	5.5	1
MoO ₃	190	Glucose	Batch, N ₂	GADMA		53.9	16.3	2
MoO ₃	190	Mannose	Batch, N ₂	GADMA		86.5	43.4	2
H ₂ MoO ₄	220	Glucose	Batch, N ₂	2-methyl-3-acetylfuran		100	22.0	3
W/Beta	245	Cellulose	Batch, H ₂	ethylene glycol		90.0	4.1	4
Ni-W/Beta	245	Cellulose	Batch, H ₂	ethylene glycol		100	45.3	4
Ni-W/Beta	245	Glucose	Batch, H ₂	ethylene glycol		100	51.0	4
WO ₃ -ZrO ₂ + Ru/C	215	Cellulose	Batch, H ₂	ethylene glycol		90.0	58.8	5
WO ₃ -ZrO ₂	215	Cellulose	Batch, H ₂	ethylene glycol		90.0	0	5
H ₃ PMo ₁₂ O ₄₀	175	Glucose	Batch, O ₂	glycolic acid		76.8	23.1	6
Mo/Pt/WO _x	245	Glucose	Batch, H ₂	ethanol		100	36.4	7
MoO ₃ +Au/TiO ₂	120	Glucose	Batch, O ₂	Methyl glycolate		56.9	20.7	8

Table S2. Physicochemical properties of the synthesized catalysts

Samples	tungsten content (mg·g ⁻¹)	S _{BET} (m ² ·g ⁻¹)	Micropore area (m ² ·g ⁻¹)	Micropore volume (mL·g ⁻¹)	Mesopore volume (mL·g ⁻¹)	Brønsted/Lewis site density (mmol·g ⁻¹) ^a
0.75 wt% Sn-Beta	0	580.9	444.5	0.177	0.326	0.025/0.017
0.5 wt% W-beta	0.562	564.3	421.7	0.170	0.367	0.016/0.010
1.0 wt% W-beta	1.052	552.0	436.9	0.174	0.329	0.006/0.020
2.0 wt% W-beta	2.011	526.0	408.6	0.163	0.311	0.021/0.021
4.0 wt% W-beta	3.982	515.1	390.0	0.160	0.320	0.021/0.032
8.0 wt% W-beta	8.073	509.1	402.8	0.159	0.366	0.034/0.040

Notes: Brønsted/Lewis site density (mmol·g⁻¹) was calculated from the corresponding peak areas of Py-IR spectra obtained at 350 °C.

Table S3. X-ray fluorescence (XRF) analysis of commercial Beta and deAl-Beta zeolites

Samples	Si/Al ratio
Commercial Beta	24.7
deAl-Beta	>1500

Table S4. W4f Binding energy for different catalysts and the corresponding ratio of W⁶⁺ to W⁵⁺

Samples	W ⁶⁺ (4f5/2)	W ⁶⁺ (4f7/2)	W ⁵⁺ (4f5/2)	W ⁵⁺ (4f7/2)	(W ⁶⁺ / W ⁵⁺) ^a
WO ₃	37.79	35.69	36.9	34.8	13.69
8.0 wt% W-Beta	39.23	37.13	38.23	36.13	1.14
4.0 wt% W-Beta	39.23	37.13	38.15	36.05	0.63
2.0 wt% W-Beta	39.1	37	38.1	36	0.61
1.0 wt% W-Beta	39.34	37.24	38.17	36.07	0.50
0.5 wt% W-Beta ^b	---	---	---	---	---

Notes: ^aW⁶⁺/ W⁵⁺ ratio was calculated by the deconvolution areas of W⁶⁺ and W⁵⁺. ^bThe tungsten signal is too weak for the deconvolution in 0.5 wt% W-Beta catalyst.

Table S5. Detail product distributions under different reaction conditions in methanol phase

Catalyst	Reactant	Time, h	A	B	C	D	E	F	G	H	I	J	K
deAl-Beta	Glucose	1	0.5	0.8	0.2	4.7	0.6	5.0	8.7	0.8	0.7	0.9	68.0
deAl-Beta	Glucose	4	0.3	3.2	3.4	12.7	3.4	3.7	25.7	3.0	0.1	0.6	92.5
0.5 wt% W-Beta	Glucose	1	1.4	1.6	1.7	3.3	4.0	7.5	33.6	1.3	0	2.8	90.9
0.5 wt% W-Beta	Glucose	2	0.7	2.3	7.0	4.6	5.2	0.1	45.7	7.1	1.3	2.6	96.7
0.5 wt% W-Beta	Glucose	3	0.1	2.4	3.5	4.7	6.2	1.4	53.8	2.8	1.5	3.6	98.8
0.5 wt% W-Beta	Glucose	4	0	2.8	4.1	5.3	6.0	1.8	54.2	1.7	2.2	3.4	99.6
1.0 wt% W-Beta	Glucose	1	0.3	0.7	1.1	2.3	1.1	11.4	20.5	0.7	0	1.1	92.8
1.0 wt% W-Beta	Glucose	4	0.2	1.6	10.5	8.1	2.2	1.9	51.2	1.6	0.2	2.6	99.4
2.0 wt% W-Beta	Glucose	1	1.1	0.3	0.9	1.4	1.0	18.4	13.5	0.5	0.2	0.9	89.7
2.0 wt% W-Beta	Glucose	4	0.7	1.1	8.4	5.3	3.8	17.3	31.6	3.9	0.1	3.4	98.1
4.0 wt% W-Beta	Glucose	1	2.2	0.3	2.4	1.8	1.0	17.4	3.1	1.2	0.8	0.5	93.0
4.0 wt% W-Beta	Glucose	4	0.2	0.5	5.6	4.4	1.2	22.9	13.4	2.2	1.2	2.5	97.0
8.0 wt% W-Beta	Glucose	1	3.4	0.2	2.9	2.3	1.3	18.4	1.1	0.4	0.9	0.2	89.8
8.0 wt% W-Beta	Glucose	4	1.2	1.4	3.1	3.9	2.0	22.6	2.0	1.8	0.0	0.7	95.0
0.5 wt% W-Beta	Fructose	4	4.7	2.1	5.4	22.5	1.1	1.3	9.3	4.2	2.7	2.8	99.4
0.5 wt% W-Beta	Erythrose	4	0	1.0	2.0	3.7	1.3	0.8	21.1	3.1	0.3	0.4	100
0.5 wt% W-Beta	Mannose	4	0.3	1.9	5.1	4.9	7.2	1.8	55.2	1.6	2.0	4.0	100
0.5 wt% W-Beta	Glycolaldehyde	4	0	0	0	0	0	0	89.6	0	0	0	100
0.5 wt% W-Beta	Cellulose	4	0	0	0	0	0.1	0	0.1	0.0	0.0	0.0	38.2 ^a
0.75 wt% Sn-Beta	Glucose	4	0	0	0	32.7	0	0	6.2	16.0	0	0	100
No catalyst	Glucose	4	2.0	0	1.3	6.2	0	7.7	0	0.9	0	0	55.2
WO ₃	Glucose	4	0.4	0	0.2	0.8	0	19.1	4.6	0.7	0.4	2.9	93.2

Notes: A-J represent the yield percentage of different products: (A) 1-Methoxyacetone, (B) Methylglycolate, (C) 2-Hydroxy-2-methylpropanoic acid, (D) Methyl lactate, (E) 1,1-Dimethoxyacetone, (F) GADMA, (G) 1,1,2-Trimethoxyethane, (H) Methyl vinyl glycolate, (I) 3,3-Dimethoxy-2-butanone, and (J) 1,1,2,2-Tetramethoxyethane individually; (K) represents the conversion percentage of reactant. ^a The conversion of cellulose was calculated from the weight loss of the solid reactant.

Reaction conditions: 200 °C, 30.0 ml methanol, 10 g/L reactant, 4 MPa N₂, 570 rpm; weight (reactant) : weight (heteroatom)=100 : 1 for W-Beta and Sn-Beta, 0.3 g for deAl-Beta, 0.1g for WO₃.

Table S6. Detail product distributions under different reaction conditions in water phase

Catalyst	T, °C	Reactant	A	B	C	D	E	F
0.5 wt% W-Beta	140	Fructose	9.2	-	0	6.2	4.2	100
0.5 wt% W-Beta	100	Glucose	-	0	0	0	0	0
0.5 wt% W-Beta	140	Glucose	-	0	10.7	0	9.2	63.4
0.5 wt% W-Beta	200	Glucose	-	0	0	0	7.2	91.1
0.75 wt% Sn-Beta	100	Glucose	-	42.0	0	8.4	0	50.5
0.75 wt% Sn-Beta	140	Glucose	-	0	0	58.8	0	100
0.75 wt% Sn-Beta	200	Glucose	-	0	0	60.1	0	100

Notes: (A-J) represent the yield of different products: (A) glucose, (B) fructose, (C) mannose, (D) lactic acid, and (E) glycolaldehyde; (F) represents the conversion percentage of reactant.

Reaction conditions: 30.0 ml water, 10 g/L reactant, weight (reactant): weight (heteroatom)=100: 1 for W-Beta and Sn-Beta, 1.0 h, 4 MPa N₂, 570 rpm.

Table S7. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis of the liquid after each recycle and the fifth-used 0.5 wt% W-Beta catalyst

Samples	W content/initial W content, %
1 st resultant Liquid	2.1
2 nd resultant Liquid	1.2
3 rd resultant Liquid	1.0
4 th resultant Liquid	0.6
5 th resultant Liquid	0.4
5 th used catalyst	94.7

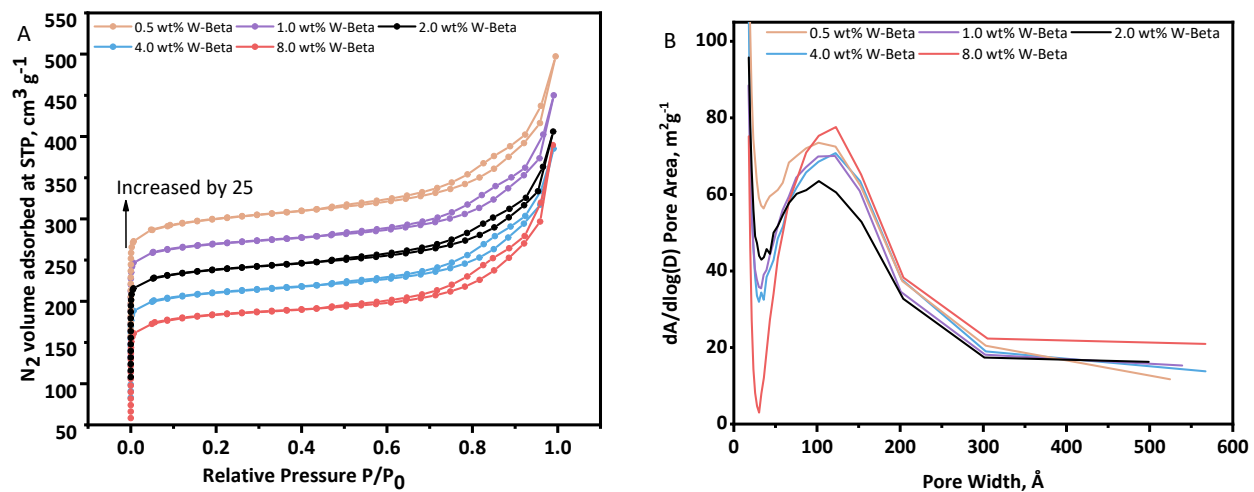


Figure S1. (A) N₂ adsorption-desorption isotherms and (B) the corresponding mesopore size distributions of W-Beta catalysts.

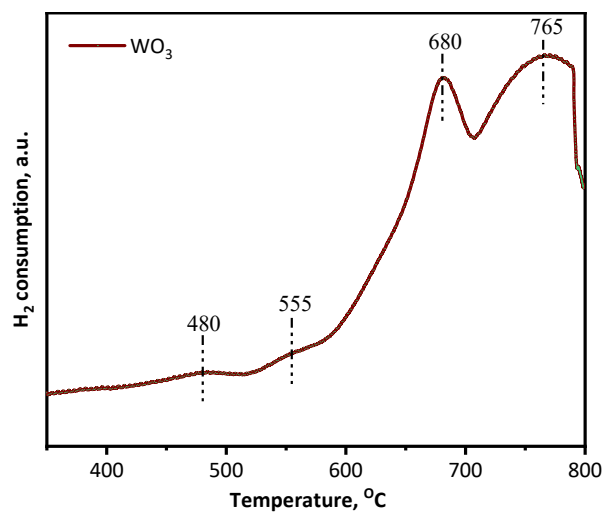


Figure S2. H₂-TPR profile of the bulk WO₃.

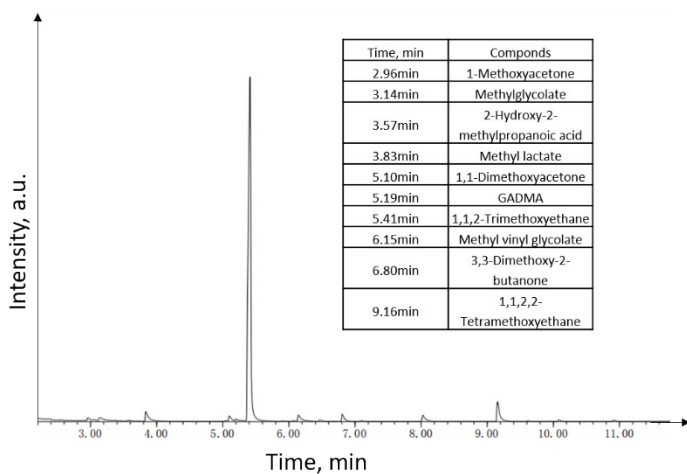


Figure S3. GC-MS analysis of the products using 0.5 wt% W-Beta catalyst.

Reaction conditions: 200 °C, 30.0 ml methanol, 10 g/L glucose, 0.6 g 0.5 wt% W-Beta, 4.0 h, 4 MPa N₂, 570 rpm.

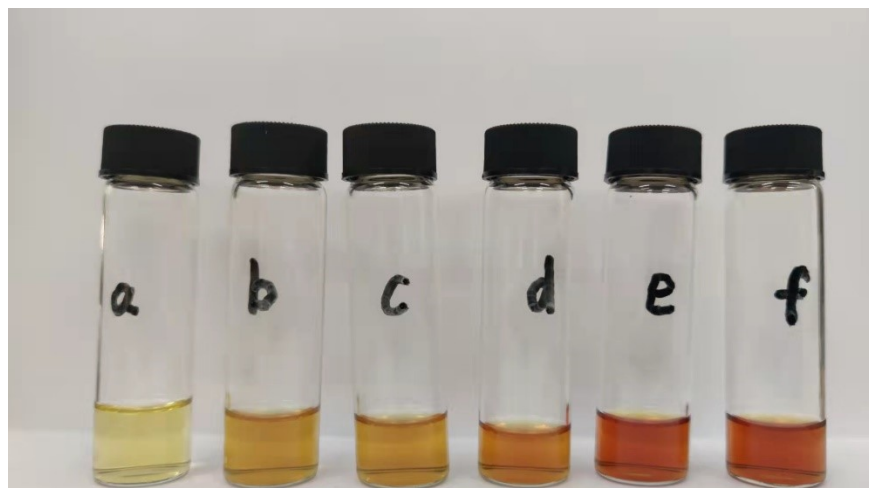


Figure S4. Liquid products from glucose in methanol using deAl-Beta and different W-Beta catalysts.

Notes: (a) for deAl-Beta catalyst, and (b-f) for 0.5, 1.0, 2.0, 4.0, 8.0 wt% W-Beta catalysts.

Reaction conditions: 200 °C, 30.0 ml methanol, 10 g/L reactant, weight (reactant) : weight (W)=100 : 1 for W-Beta and 0.3 g for deAl-Beta, 4.0 h, 4 MPa N₂, 570 rpm.

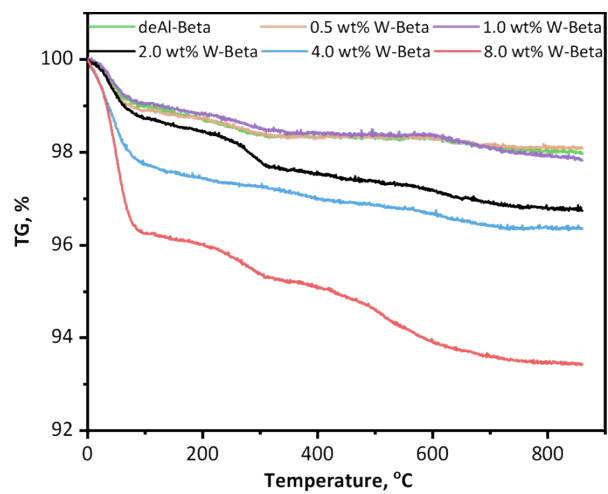


Figure S5. TG profiles of different W-Beta catalysts after a single use.

Notes: The amount of humins on the catalyst surface was calculated by the weight loss from 150 to 850 °C.

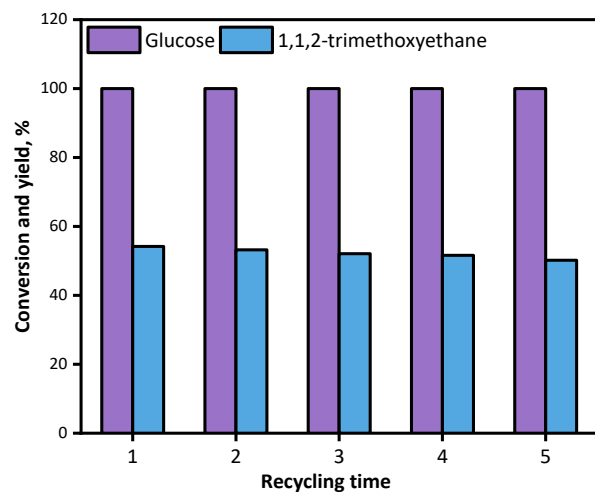


Figure S6. Catalytic recycling results for 0.5 wt% W-Beta catalyst.

Reaction conditions: 200 °C, 30.0 ml methanol, 10 g/L glucose, 0.6 g 0.5 wt% W-Beta catalyst, 4.0 h, 4 MPa N₂, 570 rpm.

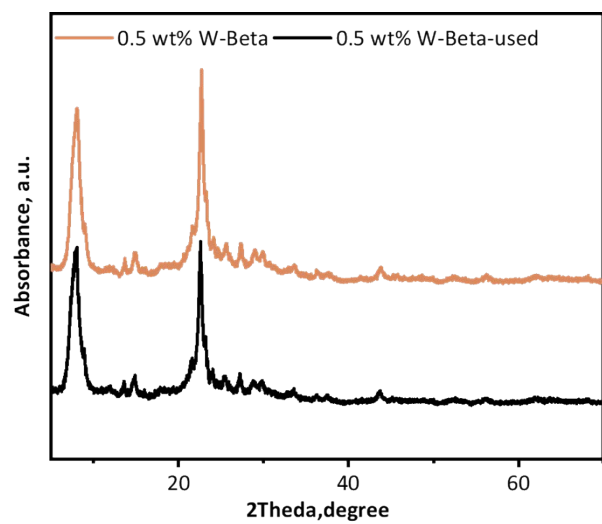


Figure S7. XRD patterns of the fresh, fifth-used 0.5 wt% W-Beta catalyst.

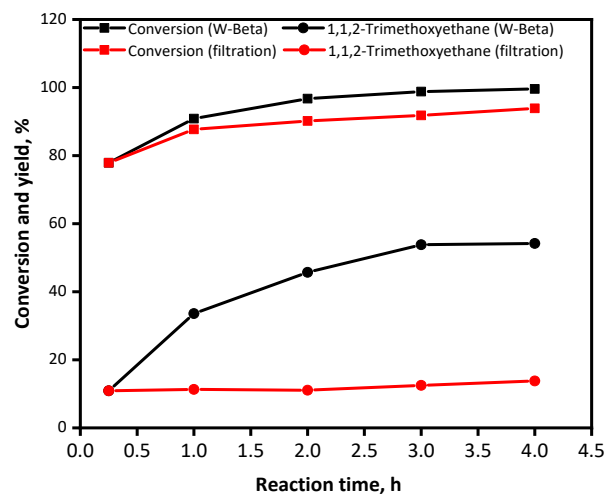


Figure S8. Dependence of glucose conversion and 1,1,2-trimethoxyethane yield on reaction time over 0.5 wt% W-Beta catalyst and filtrate after 0.25 h.

Reaction conditions: 200 °C, 30.0 ml methanol, 10 g/L glucose, 0.6 g 0.5 wt% W-Beta catalyst or filtration, 4.0 h, 4 MPa N₂, 570 rpm.

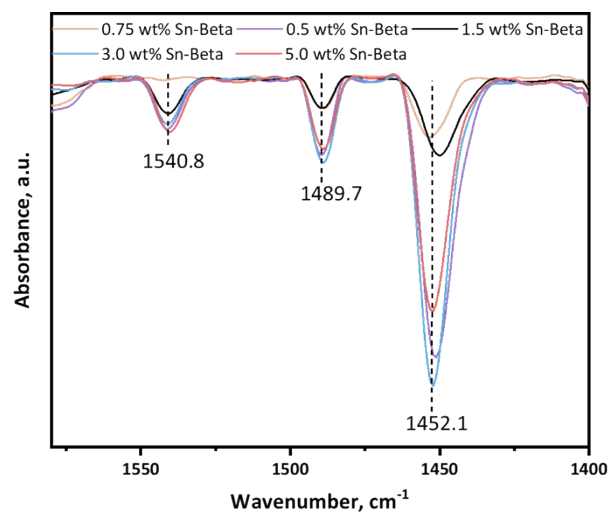


Figure S9. Py-IR spectra of different Sn-Beta catalysts at 350 °C.

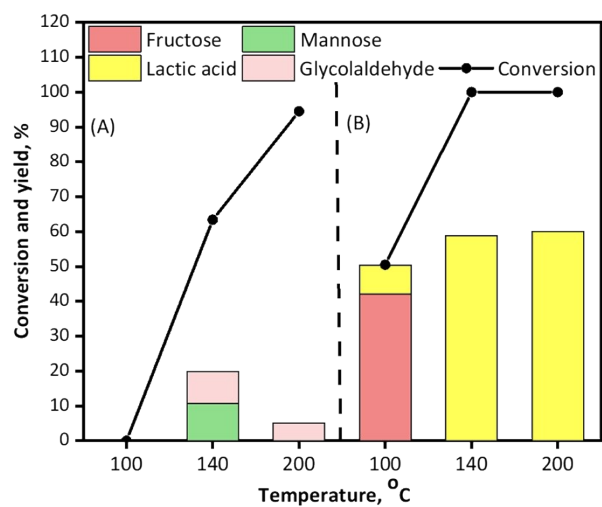


Figure S10. Glucose conversion in water under different temperatures using (A) 0.5 wt% W-Beta and (B) 0.75 wt% Sn-Beta as catalysts.

Reaction conditions: 30.0 ml water, 10 g/L glucose, weight (glucose) : weight (heteroatom)=100 : 1 for W-Beta and Sn-Beta, 1.0 h, 4 MPa N₂, 570 rpm.

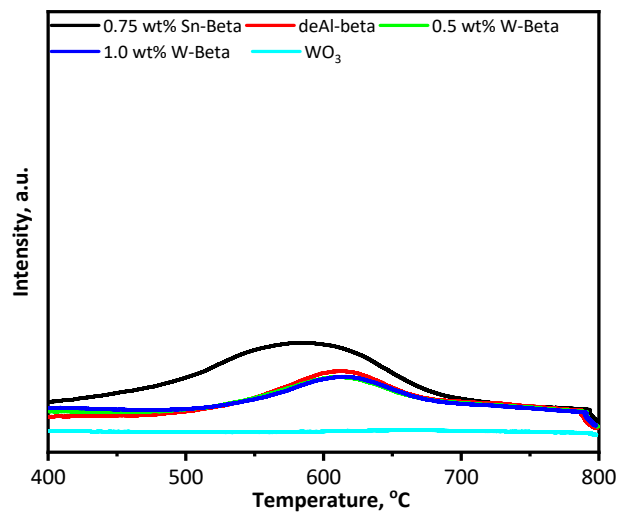


Figure S11. NH₃-TPD profiles of different catalysts from 400 to 800 °C.

3. List of additional references

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