Supporting Information

Glucose isomerization in Dioxane/Water with Sn- β catalyst: improved catalyst stability and use for HMF production

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Experimental Section

Materials: Glucose, fructose, mannose, sucrose, maltose, trehalose, cellobiose, Hydroxymethylfurfural(HMF) and Amberlyst-131 were purchased from Sigma-Aldrich. Dioxane was purchased from Merck Millipore and difructose anhydride (III) was purchased from Wako Chemicals USA, Inc.

Sn- β was synthesized according to a literature method.^[51] First, 30.612 g of tetraethyl orthosilicate (98%, Sigma-Aldrich) was mixed with 33 g of tetraethylammonium hydroxide solution (TEAOH, 35 wt %, SACHEM) and stirred for 1 hour. A clear solution of 0.412 g of SnCl₄·5H₂O (98 %, Sigma-Aldrich) in 2.75 g of water was added into the above mixture and stirred overnight to fully evaporate the ethanol. Then 3.143g of hydrofluoric acid (HF 48-51 wt % in H₂O, Sigma-Aldrich) was added under stirring followed by adding a dealuminated β seeds suspension (0.36 g dealuminated β seeds in 1.75 g H₂O). After manually mixing for 5 min, the final gel with a chemical composition 1.0SiO₂:0.54TEAOH:10.6H₂O:0.54HF:0.008SnO₂ was transferred to autoclaves and hydrothermally treated in a rotation oven at 413 K for 21 days. The product was separated and fully washed by filtration followed by drying at 343 K overnight. After calcination at 873 K in the static air for 6 hours, final product was obtained.

Catalytic reactions: All reactions were carried out in stirred 20-mL thick-walled glass reactors (VWR) sealed with crimp tops (PTFE/silicone septa, Sigma-Aldrich). In a typical reaction (one-pot synthesis of HMF from glucose), 0.05 g of glucose, 4.7 g of dioxane, 0.25 g of ultrapure water, 0.02 g of Sn- β and 0.04 g of Amberlyst-131 catalysts were added into the reactor and sealed. The reactor was placed in a temperature-controlled oil bath at 90 °C for a certain period of time. After quenching the reactor in an ice bath, 4 g of ultrapure water was added and then the sample was taken and filtered for analysis. All the reactants and products were analyzed by high performance liquid chromatography (HPLC) using a refractive index detector with a Bio-Rad Aminex HPX87C (300 x 7.8 mm) column (Phenomenex). The mobile phase was ultrapure water (pH=7) and the column temperature was 80 °C.

Catalysts were separated from the reaction solution by centrifugation. Sn- β was washed with water between each run for glucose isomerization and dried in a convection oven at 70 °C

overnight. Amberlyst-131 was washed with water and Sn- β was calcined at 550 °C for 10 hrs between each run for the one-pot synthesis of HMF from glucose.

Characterization: FTIR spectra were recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer. Self-supporting wafer was pressed and sealed in a heatable quartz vacuum cell with removable KBr windows. The cell was evacuated under dynamic vacuum, heated to 250 °C, and then held there overnight to pre-treat sample. IR spectra were then collected (2 cm⁻¹ resolution, 64 scans) for the sample wafer and the data analysis was performed using Omnic software. Thermogravimetric analysis (TGA) was performed using a ShimadzuTGA-50 analyzer. Analysis was carried out by heating about 7 mg of the samples in air flow (100 mL/min) from room temperature to 600 °C at a heating ramp rate of 5 °C/min.



Scheme S1. Schematic representation of series of reactions.



Figure S1. XRD patterns of fresh Sn- β (a); Sn- β used three times in dioxane/water (5 wt% water) solvent (b); and Sn- β used three times in pure water (c).



Figure S2. SEM images of fresh Sn- β (Si/Sn=111) (a and b); Sn- β used three times in dioxane/water (5 wt% water) solvent (Si/Sn=114) (c and d); and Sn- β used three times in pure water (Si/Sn=117) (e and f).



Figure S3. Results of the recycling tests for production of HMF from glucose on Sn- β and Amberlyst-131. (Reaction conditions: 50 mg glucose, 4.7 g dioxane, 0.25 g water, 20 mg Sn- β , 40 mg Amberlyst-131, 90 °C, 6 h.)

| Water content/% | Conversion/% | Product dis | TOF/h ⁻¹ | | |
|-----------------|--------------|-------------|---------------------|----|--|
| | | Fructose | Mannose | | |
| 0 | 1.8 | 1.3 | - | 8 | |
| 2.5 | 15.9 | 12.5 | 1.3 | 66 | |
| 5 | 13.4 | 9.9 | 1 | 56 | |
| 7.5 | 8.8 | 5.9 | 0.6 | 37 | |
| 10 | 5.5 | 3.4 | 0.4 | 23 | |
| 100 | 3 | 2.9 | - | 12 | |

Table S1. Glucose isomerization on Sn- β in different solvents mixture.

Reaction conditions: 50 mg glucose, 4.95 g solvent, 20 mg Sn- β (Si/Sn=125), 90 °C, 15 min.

| Solvents | Salt | T/ºC | Catalyst(s) | HMF | Ref. |
|-----------------------------------------------------|------|------|------------------------------------------------|---------|-----------|
| | | | | yield/% | |
| Ionic Liquids | - | 100 | CrCl ₂ | 70 | S2 |
| N,N-dimethylacetamide | - | 100 | CrBr ₃ /LiBr | 80 | S3 |
| THF(66) ^a /water | NaCl | 180 | Sn-Beta, HCl | 56.9 | S4 |
| SBP(108) ^a /water | NaCl | 170 | AICI ₃ | 61.9 | S5 |
| GVL(207) ^a /water | NaCl | 170 | AICI ₃ | 61.6 | S6 |
| GHL(215) ^a /water | - | 170 | AICI ₃ | 58.5 | S6 |
| THF(66) ^a /water | - | 130 | Sn-Beta, Amberlyst-70 | 63 | S6 |
| MTHF(63) ^a /water | - | 180 | TiO ₂ -containing carbonaceous acid | 60 | S7 |
| | | | catalyst | | |
| MIBK(117) ^a /water | - | 150 | large-pore mesoporous tin | 50 | S8 |
| | | | phosphate | | |
| 1-Butanol(117.7) ^a /water | - | 175 | Phosphated TiO ₂ | 81 | S9 |
| DMSO(189) ^a /THF(66) ^a | - | 160 | Sn-Mont ^b | 53.5 | S10 |
| DMSO(189) ^a /THF(66) ^a /water | - | 180 | H-Beta | 42.9 | S11 |
| Dioxane(101) ^a /water | - | 220 | H ₃ PO ₄ , pyridine | 46 | S12 |
| Dioxane(101) ^a /water | - | 90 | Sn-Beta, Amberlyst-131 | | This work |

Table S2. Conversion of glucose to HMF in different solvents mixture.

THF: Tetrahydrofuran; SBP: *sec*-butylphenol; GVL: γ-valerolactone; GHL: γ-hexalactone; MTHF: methyltetrahydrofuran; MIBK: Methyl isobutyl ketone; DMSO: Dimethyl sulfoxide. a: boiling point of the organic solvent; b: Sn-Montmorillonite

| Feed | Catalyst | Solvent | T/⁰C | HMF yield/% | Ref. |
|------------|-----------------------------|------------------|------|-------------|-----------|
| Sucrose | Ionic Liquids | DMSO | 160 | 68.7 | S13 |
| Cellobiose | Ionic Liquids | DMSO | 160 | 24.7 | S13 |
| Sucrose | CrCl ₂ /HCl | Ionic Liquids | 120 | 82 | S14 |
| Sucrose | ZnCl ₂ /HCl | Ionic Liquids | 120 | 68.4 | S14 |
| Sucrose | CrCl ₂ | Choline chloride | 100 | 42 | S15 |
| Sucrose | SnCl ₄ | Ionic Liquids | 100 | 65 | S16 |
| Cellobiose | SnCl ₄ | Ionic Liquids | 100 | 57 | S16 |
| Maltose | Sn-β/Amberlyst-131 | Dioxane/water | 90 | 56 | This work |
| Trehalose | Sn-β/Amberlyst-131 | Dioxane/water | 90 | 56 | This work |
| Cellobiose | Sn-β/Amberlyst-131 | Dioxane/water | 90 | 56 | This work |
| Sucrose | Sn- <i>β</i> /Amberlyst-131 | Dioxane/water | 90 | 60 | This work |

Table S3. Comparison of disaccharides conversion to HMF.

Reference:

- [S1] Corma. A;, Nemeth. L. T.; Renz. M.; Valencia. S., Nature 2002, 412, 423.
- [S2] Zhao, H. B.; Holladay, J. E.; Brown, H.; Zhang, Z. C. Science 2007, 316, 1597.
- [S3] Binder, J. B.; Raines, R. T. J. Am. Chem. Soc. 2009, 131, 1979.
- [S4] Nikolla, E.; Roman-Leshkov, Y.; Moliner, M.; Davis, M. E. ACS Catal. 2011, 1, 408.
- [S5] Pagan-Torres, Y. J.; Wang, T. F.; Gallo, J. M. R.; Shanks, B. H.; Dumesic, J. A. ACS Catal.

2012, 2, 930.

- [S6] Gallo, J. M. R.; Alonso, D. M.; Mellmer, M. A.; Dumesic, J. A. Green Chem. 2013, 15, 85.
- [S7] Mazzotta, M. G.; Gupta, D.; Saha, B.; Patra, A. K.; Bhaumik, A.; Abu-Omar, M. M.
- ChemSusChem 2014, 7, 2342.
- [S8] Dutta, A.; Gupta, D.; Patra, A. K.; Saha, B.; Bhaumik, A. ChemSusChem 2014, 7, 925.
- [S9] Atanda, L.; Mukundan, S.; Shrotri, A.; Ma, Q.; Beltramini, J. ChemCatChem 2015, 7, 781.
- [S10] Wang, J. J.; Ren, J. W.; Liu, X. H.; Xi, J. X.; Xia, Q. N.; Zu, Y. H.; Lu, G. Z.; Wang, Y. Q.
- Green Chem. 2012, 14, 2506.
- [S11] Otomo, R.; Tatsumi, T.; Yokoi, T. Catal. Sci. Technol. 2015, 5, 4001.
- [S12] Mednick, M. L. J. Org. Chem. 1962, 27, 398.
- [S13] Qu, Y. S.; Li, L.; Wei, Q. Y.; Huang, C. P.; Oleskowicz-Popiel, P.; Xu, J. Sci. Rep. 2016, 6.
- [S14] Chun, J. A.; Lee, J. W.; Yi, Y. B.; Hong, S. S.; Chung, C. H. Korean J. Chem. Eng. 2010, 27, 930.
- [S15] Ilgen, F.; Ott, D.; Kralisch, D.; Reil, C.; Palmberger, A.; Konig, B. *Green Chem.* 2009, *11*, 1948.
- [S16] Hu, S. Q.; Zhang, Z. F.; Song, J. L.; Zhou, Y. X.; Han, B. X. Green Chem. 2009, 11, 1746.