Supporting Information

Solvent basicity controlled deformylation for the formation of furfural from glucose and fructose

Miyuki Asakawa,1,2 Abhijit Shrotri,1* Hirokazu Kobayashi,1 Atsushi Fukuoka1*

1Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.

2Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.
Figure S1: Comparison of initial furfural yield in the presence and absence of \( \text{H}_3\text{PO}_4 \) catalyst. Reaction condition: Fructose 0.22 mmol, 5 mL sulfolane with or without \( \text{H}_3\text{PO}_4 \) (1.5 mM), 160 °C.

Figure S2: \( \text{N}_2 \) adsorption isotherms (a) and \( \text{NH}_3 \) TPD spectra (b) for SBA-15 support and Sn/SBA-15 catalyst.
Figure S3: TEM images of Sn/SBA-15 catalyst containing 1 wt.% Sn. Tin nanoparticles were not visible even at high magnification.
**Figure S4:** $^{13}$C NMR of product mixture at different reaction time using $^{13}$C-1 labelled glucose. Reaction condition: $^{13}$C-1 labelled glucose 0.22 mmol, Sn/SBA-15 catalyst 20 mg, 5 mL sulfolane, 160 °C.
Figure S5: $^{13}$C NMR of product mixture at different reaction time using $^{13}$C-6 labelled glucose. Reaction condition: $^{13}$C-6 labelled glucose 0.22 mmol, Sn/SBA-15 catalyst 20 mg, 5 mL sulfolane, 160 °C. Inset of 5 min spectrum shows peaks for fructose, levoglucosan and anhydroglucofuranose. Inset of 30 min spectrum shows a peak for formaldehyde at 84.1 ppm.
Figure S6: $^1$H NMR (a) and $^{13}$C NMR (b) of product obtained after work up of reaction mixture. 60 mg product was dissolved in 1 mL of D$_2$O containing 5 mg mL$^{-1}$ of sodium trimethylsilylpropanesulfonate (DSS) as reference and internal standard.

NMR Resonances:

Furfural: $^1$H NMR (D$_2$O) $\delta$ 9.48 (s, 1H, HCO), $\delta$ 7.91 (s, 1H, HCO), $\delta$ 7.56 (d, 1H, CH), $\delta$ 6.76 (m, 1H, CH). $^{13}$C NMR (D$_2$O) $\delta$ 183.4, 154.8, 152.9, 128.6, 116.0

Sulfolane: $^1$H NMR (D$_2$O) $\delta$ 3.17 (m, 4H, CH$_2$SO$_2$), $\delta$ 2.25 (m, 4H, CH$_2$). $^{13}$C NMR (D$_2$O) $\delta$ 53.7, 25.0

Unidentified: $^1$H NMR (D$_2$O) $\delta$ 5.48 (s). $^{13}$C NMR (D$_2$O) $\delta$ 56.6