Electronic supplementary information

Low-temperature catalytic hydrogenation of bio-based furfural and relevant aldehydes using cesium carbonate and hydrosiloxane

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Fig. S2 $^1$H NMR spectra of the siloxane intermediate in hydrogenation of FUR to FFA. Reaction conditions: 0.5 mmol FUR, PhSiH$_3$ (1.47 mmol H), 1 mL DMSO-$d_6$, 16 mg Cs$_2$CO$_3$, 25 ºC, and 6 h.
Fig. S3. $^1$H-$^{13}$C HSQC NMR spectrum of the siloxane intermediate in hydrogenation of FUR to FFA. Reaction conditions: 0.5 mmol FUR, PhSiH$_3$ (1.47 mmol H$^-$), 1 mL DMSO-$d_6$, 16 mg Cs$_2$CO$_3$, 25 °C, and 6 h.

**Table S1** Effect of different hydrosilanes on the hydrogenation of FUR to FFA

| Entry | H-donor                          | Yield (%) | Conversion (%) |
|-------|----------------------------------|-----------|----------------|
| 1     | Et$_3$SiH                        | 0.2       | 0.6            |
| 2     | (MeO)$_3$SiH                     | 5.4       | 10.0           |
| 3     | Me$_3$Si-O-MeSiH-O-SiMe$_3$       | 30.7      | 40.0           |
| 4     | (EtO)$_3$SiH                     | 32.5      | 42.0           |
| 5     | Me$_2$SiH-O-HSiMe$_2$            | 50.7      | 60.0           |
| 6     | Ph$_2$SiH$_2$                    | 88.4      | 90.0           |
| 7     | PhSiH$_3$                        | 99.1      | 99.2           |
| 8     | PMHS                             | 99.5      | 99.5           |

Reaction conditions: 0.5 mmol FUR, 16 mg Cs$_2$CO$_3$, H-donor (1.47 mmol H$^-$), 2 mL DMF, 80 °C, and 6 h.

**Table S2** The recycling study of cesium carbonate-catalyzed reduction of FUR to FFA

| Entry | Time (h) | T (°C) | Catalyst dosage (mg) | Reaction cycle | Yield (%) | Conv. (%) |
|-------|----------|--------|-----------------------|----------------|-----------|-----------|
| 1     | 6        | 80     | 16                    | 1              | 99        | 99        |
| 2     | 6        | 80     | 16                    | 2              | 30.4      | 43.1      |
| 3     | 6        | 25     | 16                    | 1              | 90        | 99        |
| 4     | 6        | 25     | 16                    | 2              | 47        | 48        |

Reaction conditions: 0.5 mmol FUR, PMHS (1.47 mmol H$^-$), 2 mL DMF.
Fig. S4 STEM and elemental mapping profiles of recovered Cs$_2$CO$_3$ catalyst. (A) STEM-HAADF image and elemental mappings of (B) Cs, (C) Si, (D) C and (E) O.

Fig. S5 $^1$H NMR spectra of the formation of formate during hydrosilylation reaction. Reaction conditions (A): PhSiH$_3$ (1.47 mmol H$^-$), 1 mL DMSO-$d_6$, 16 mg Cs$_2$CO$_3$, 25 ºC, and 6 h; Reaction conditions (B): 0.5 mmol FUR, PMHS (1.47 mmol H$^-$), 1 mL DMSO-$d_6$, 16 mg Cs$_2$CO$_3$, 25 ºC, and 6 h.

Fig. S6 The possible structure of pentavalent silicate intermediate in the hydrogenation of FUR to FFA.

Fig. S7 The possible structure of hexavalent silicate intermediate in the hydrogenation of FUR to FFA.
**Fig. S8** $^1$H NMR spectra of the interaction between PMHS and Cs$_2$CO$_3$. Reaction conditions: PMHS (1.47 mmol H$^-$), 1 mL DMSO-$d_6$, 16 mg Cs$_2$CO$_3$, 25 °C, and 6 h.
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Fig. S9 GC-MS spectra of various alcohols obtained from hydrogenation of corresponding aldehyde.

Fig. S10 GC-MS spectrum of dimethoxydiphenylsilane formed in the reaction of Ph₂SiH₂ and MeOH.