Electronic Supplementary Information

Supported cobalt catalysts for selective hydrogenation of ethyl levulinate to various chemicals

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Fig. S1 XRD patterns of the as-prepared Co-based catalysts.
Fig. S2 $^1$H NMR spectrum of highly pure EHP obtained over Ru/TiO$_2$ at room temperature without using solvent.

$^1$H NMR (400.13 MHz, D$_2$O) $\delta$ = 4.08-4.02 (m, 2H), $\delta$ = 3.74-3.69 (m, 1H), $\delta$ = 2.36-2.32 (m, 2H), $\delta$=1.66 (m, 2H), $\delta$=1.17-1.13 (t, 3H), $\delta$ = 1.08-1.07 (d, 3H).
Fig. S3 $^{13}$C NMR spectrum of highly pure EHP obtained over Ru/TiO$_2$ at room temperature without using solvent.

$^{13}$C NMR (100.6 MHz, D$_2$O) $\delta = 176.45, 66.81, 61.56, 33.05, 30.47, 21.81, 13.35$. 
Fig. S4 Positive-ion ESI mass spectrum of product obtained over Co/SBA-15 in the hydrogenation of EL.

EHP : ESI-MS m/z: 147.1004 [(M+H)$^+$, C$_7$H$_{15}$O$_3$], m/z: 169.0857 [(M+Na)$^+$, C$_7$H$_{14}$O$_3$Na], Anal. Calcd for C$_7$H$_{14}$O$_3$: 146.1684. The Na$^+$ came from the standard calibration sodium formate of mass spectrometer.
Fig. S5 Magnetic separation of Co/ZrO$_2$ from reaction liquid by an external magnet.
Fig. S6 TEM images and Co particle size distributions of (A) Co/ZrO$_2$ after 1 recycle, (B) Co/ZrO$_2$ after 2 recycles, and (C) Co/ZrO$_2$ after 3 recycles.
Fig. S7 (a) Co 2p, (b) Zr 3d and (c) O 1s XPS spectra of fresh and used Co/ZrO$_2$ catalysts.
Fig. S8 Catalytic results obtained over Co/ZrO$_2$ within first four repeated runs without regeneration

(reaction conditions: 17.4 mmol EL, 15 mL 1,4-dioxane, 140 °C; 4 MPa H$_2$, 1.5 h and 0.1 g Co/ZrO$_2$).
Fig. S9 Negative-ion ESI mass spectrum of the MIBK-extracted organic species occluded in used catalyst.

EHP : ESI-MS m/z: 195.0393 [(M-H)-, C_{10}H_{11}O_{4}], Anal. Calcd for C_{10}H_{12}O_{4}: 196.074. m/z: 293.1839 [(M-H)-, C_{15}H_{17}O_{6}], Anal. Calcd for C_{15}H_{18}O_{6}: 294.111.
Table S1 Catalytic results of Co/ZrO$_2$ and reported heterogeneous catalysts for the hydrogenation of LA and its ester to GVL.

| Catalyst         | Substrate | Reaction conditions         | T[°C] | Conv. [%] | Yield [%] | Productivity a [mol$_{GVL}$ g$_{metal}$⁻¹ h⁻¹] | Ref |
|------------------|-----------|-----------------------------|-------|-----------|-----------|-----------------------------------------------|-----|
| 5% Ru/C          | LA        | 1,4-dioxane, H$_2$ (12 bar) | 130   | 99        | 96        | 1.20                                          | 1   |
| 5% Ru/TiO$_2$    | LA        | ethanol/water, H$_2$ (12 bar) | 130   | 81        | 71        | 0.92                                          | 1   |
| 5% Ru/C          | LA        | solvent-free, H$_2$ (12 bar) | 190   | 100       | 100       | 5.20                                          | 1   |
| 3Pd-10Nb-AC      | EL        | water, H$_2$ (5 bar)        | 100   | 87        | 81        | 0.54                                          | 2   |
| Raney Ni         | EL        | 2-PrOH, Ar                  | r.t.  | -         | 87        | 4.4x10⁻³                                     | 3   |
| Cu-Fe            | LA        | water, H$_2$ (70 bar)       | 200   | 99        | 90        | 0.038                                         | 4   |
| Cu-WO$_3$/ZrO$_2$| LA        | ethanol, H$_2$ (50 bar)     | 200   | 100       | 87        | 0.021                                         | 5   |
| Cu-ZrO$_2$       | ML b      | methanol, H$_2$ (34 bar)    | 200   | 95        | 87        | 0.035                                         | 6   |
| Co               | EL        | solvent free, H$_2$ (33 bar)| 130   | 99        | 94        | 0.022                                         | 7   |
| 4Co/Al$_2$O$_3$  | LA        | 1,4-dioxane, H$_2$ (50 bar) | 180   | 100       | >99       | 0.37                                          | 8   |
| Co/ZrO$_2$       | EL        | 1,4-dioxane, H$_2$ (40 bar) | 190   | 100       | 82.5c    | 1.5                                           | this work |
| Co/ZrO$_2$       | EL        | 1,4-dioxane, H$_2$ (40 bar) | 190   | 100       | 94.3d    | 0.87                                          | this work |

a Calculated from literature data by using the active metal mass in a given catalyst. b ML is methyl levulinate. c The reaction time is 1 h. d The 12th recycle with regeneration of the catalyst by calcining at 550 °C for 2 h in air and reducing 500 °C for 2 h after four recycles (No. 12 in Fig. 4).
References

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