

Electronic Supplementary Information

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

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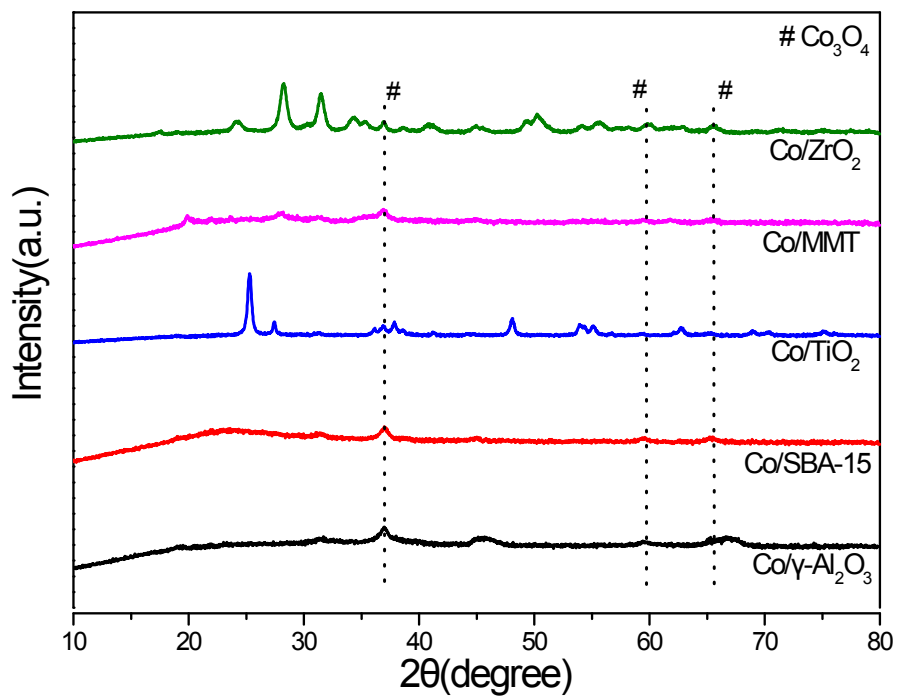


Fig. S1 XRD patterns of the as-prepared Co-based catalysts.

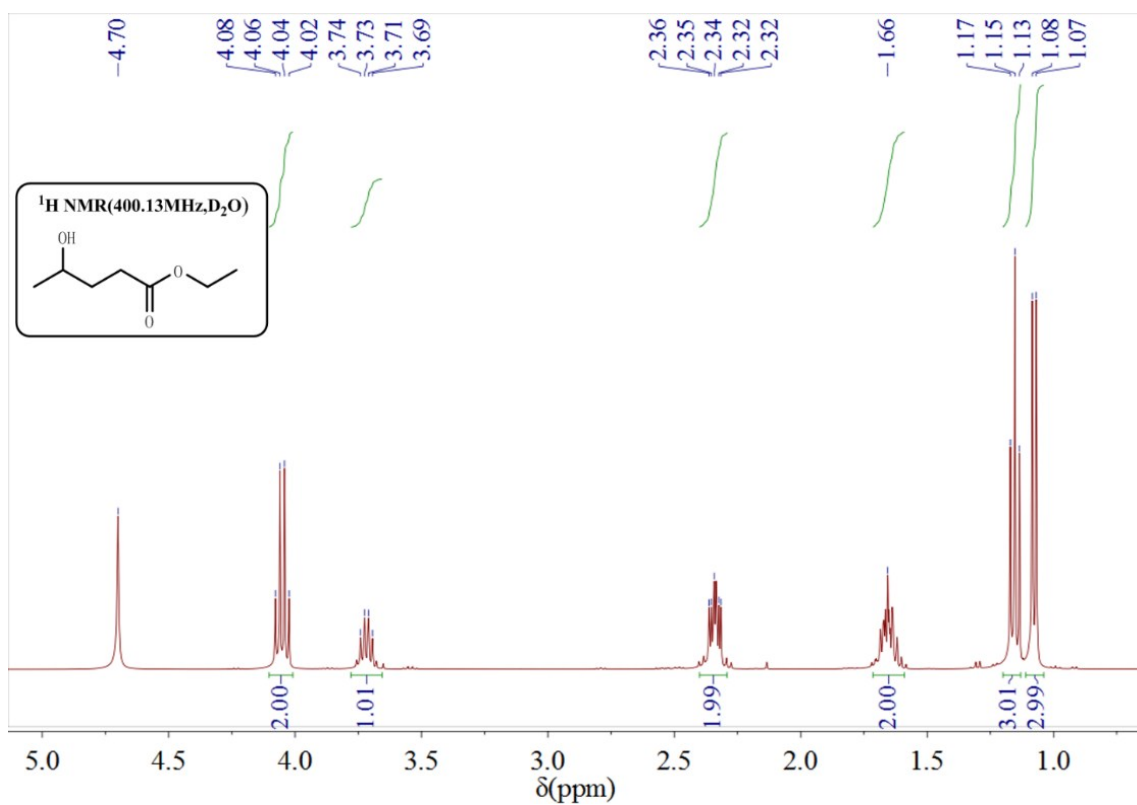


Fig. S2 ¹H NMR spectrum of highly pure EHP obtained over Ru/TiO₂ at room temperature without using solvent.

¹H NMR (400.13 MHz, D₂O) $\delta = 4.08-4.02$ (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).

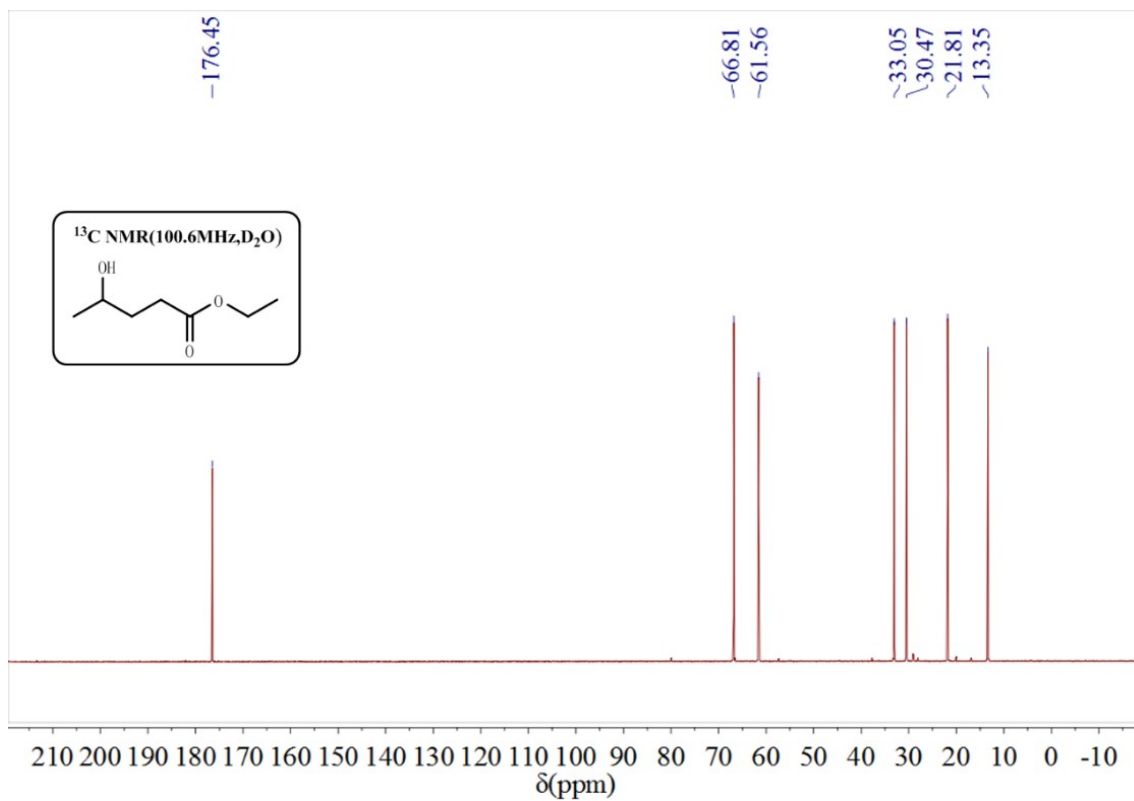


Fig. S3 ¹³C NMR spectrum of highly pure EHP obtained over Ru/TiO₂ at room temperature without using solvent.

¹³C NMR (100.6 MHz, D₂O) δ = 176.45, 66.81, 61.56, 33.05, 30.47, 21.81, 13.35.

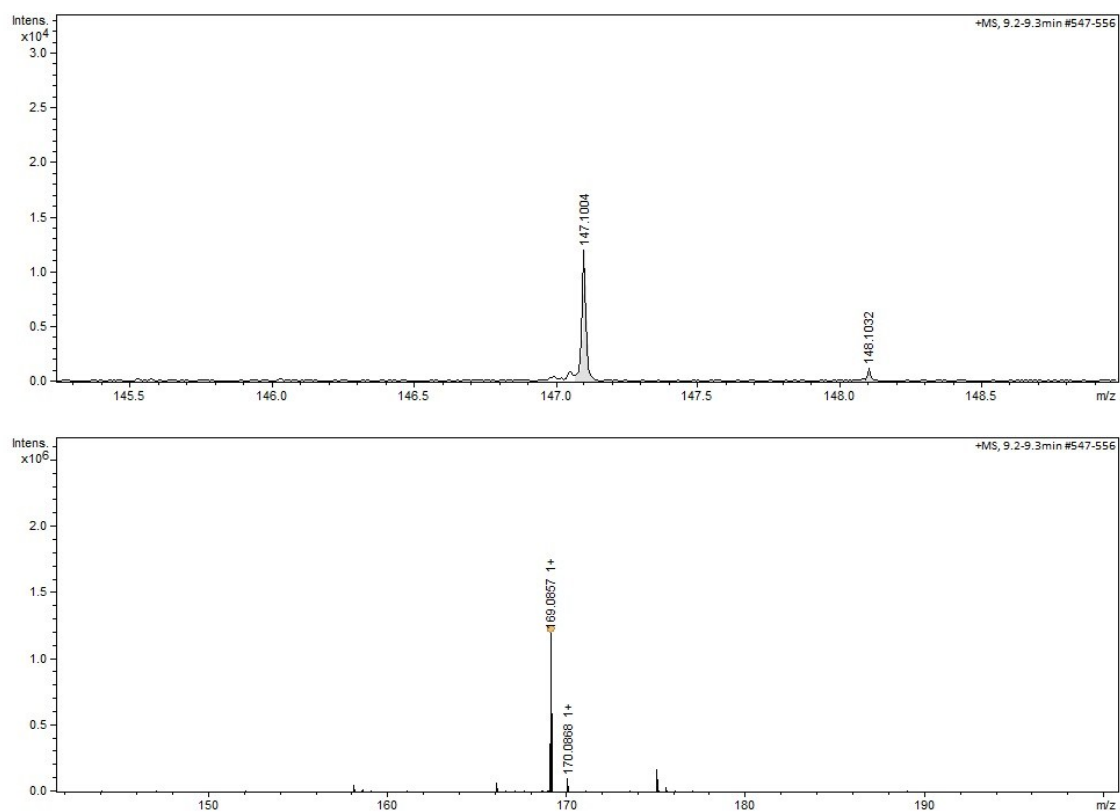


Fig. S4 Positive-ion ESI mass spectrum of product obtained over Co/SBA-15 in the hydrogenation of EL.

EHP : ESI-MS m/z : 147.1004 $[(M+H)^+]$, $C_7H_{15}O_3$, m/z : 169.0857 $[(M+Na)^+]$, $C_7H_{14}O_3Na$, Anal.

Calcd for $C_7H_{14}O_3$: 146.1684. The Na^+ came from the standard calibration sodium formate of mass spectrometer.

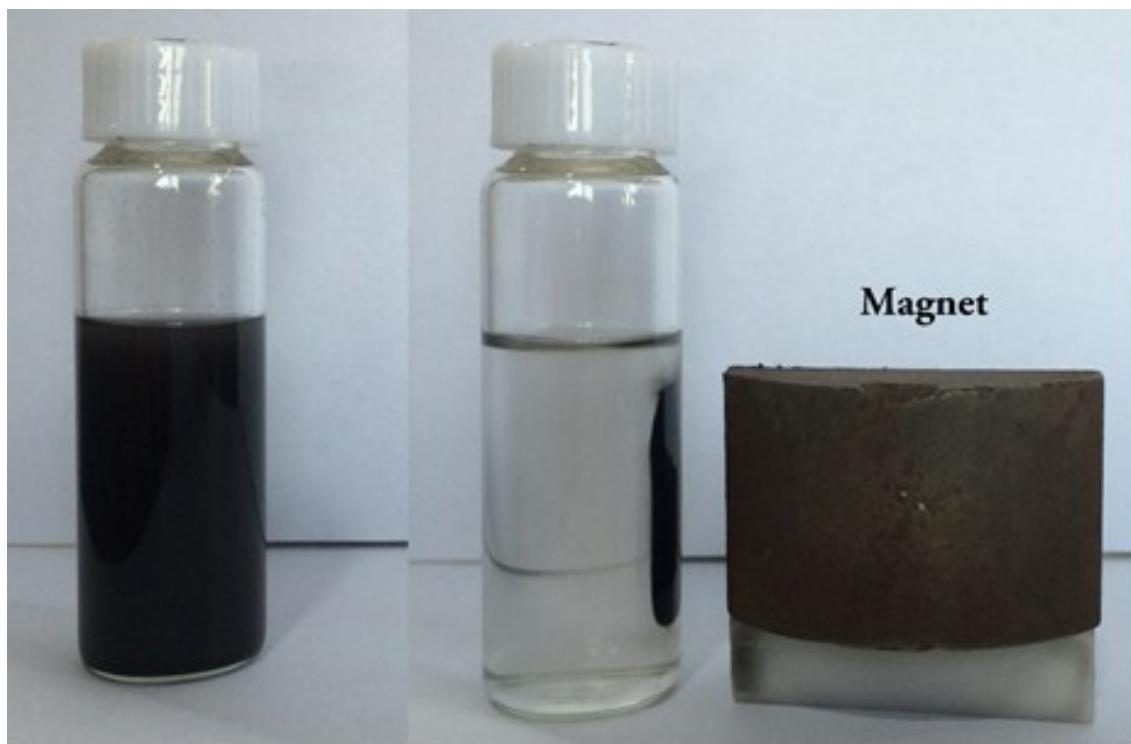


Fig. S5 Magnetic separation of Co/ZrO₂ from reaction liquid by an external magnet.

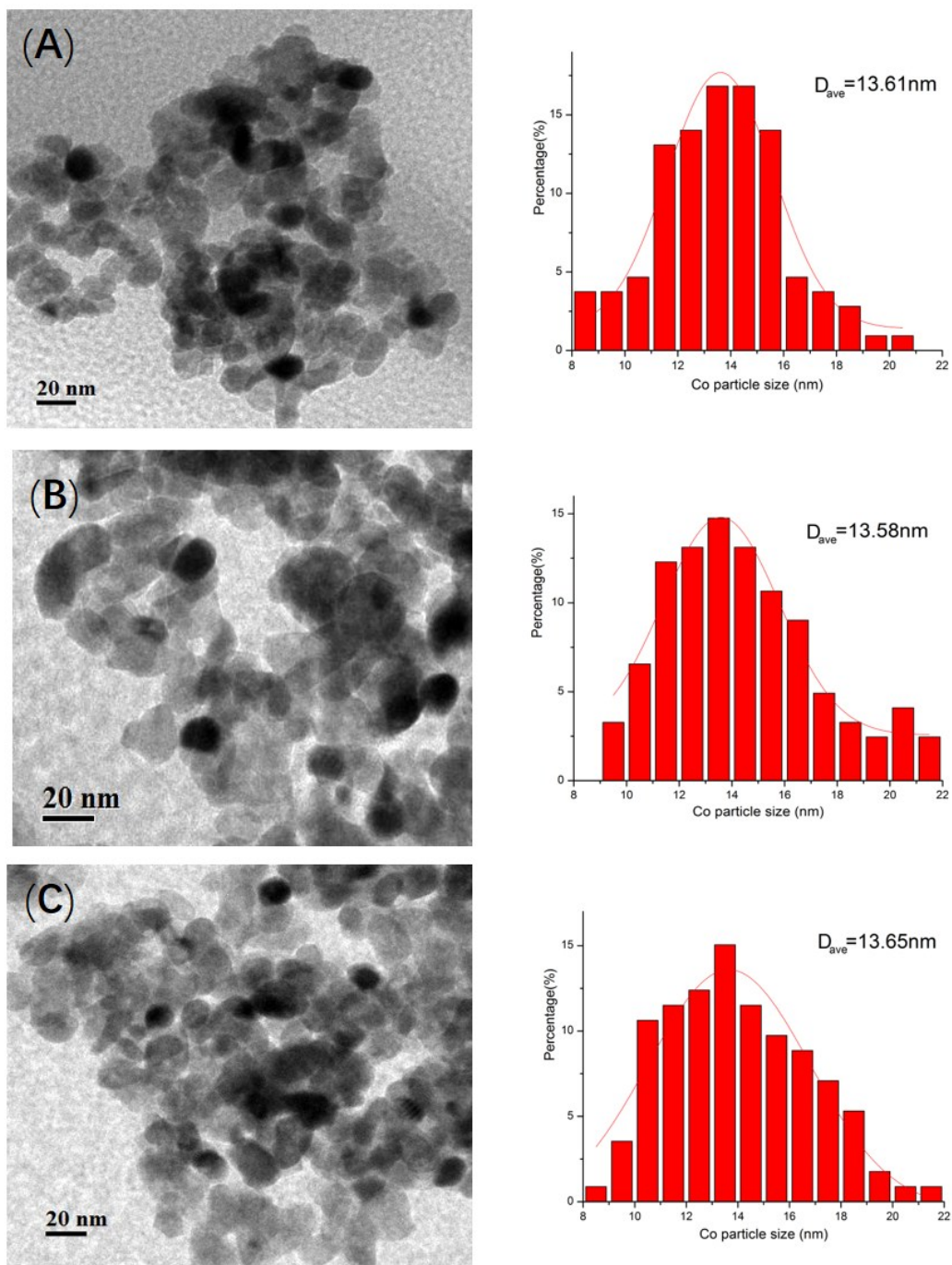


Fig. S6 TEM images and Co particle size distributions of (A) Co/ZrO₂ after 1 recycle, (B) Co/ZrO₂ after 2 recycles, and (C) Co/ZrO₂ after 3 recycles.

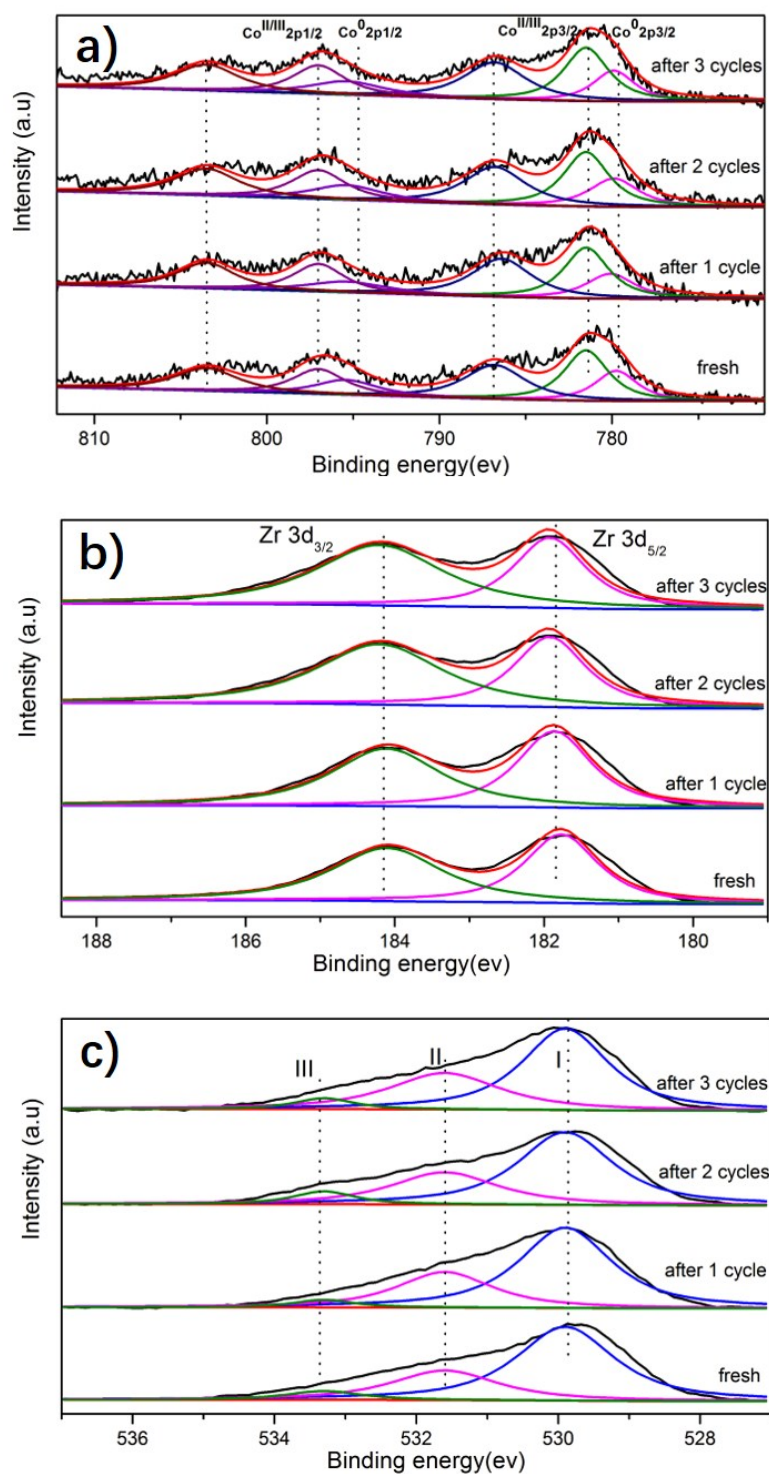


Fig. S7 (a) Co 2p, (b) Zr 3d and (c) O 1s XPS spectra of fresh and used Co/ZrO₂ catalysts.

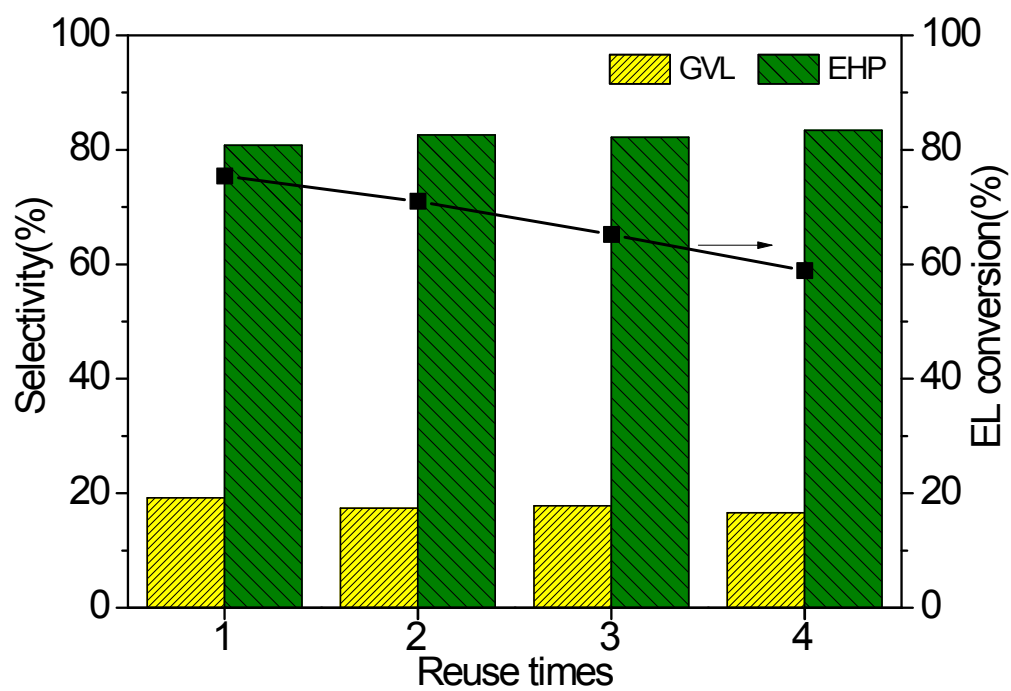


Fig. S8 Catalytic results obtained over Co/ZrO₂ within first four repeated runs without regeneration

(reaction conditions: 17.4 mmol EL, 15 mL 1,4-dioxane, 140 °C; 4 MPa H₂, 1.5 h and 0.1 g Co/ZrO₂).

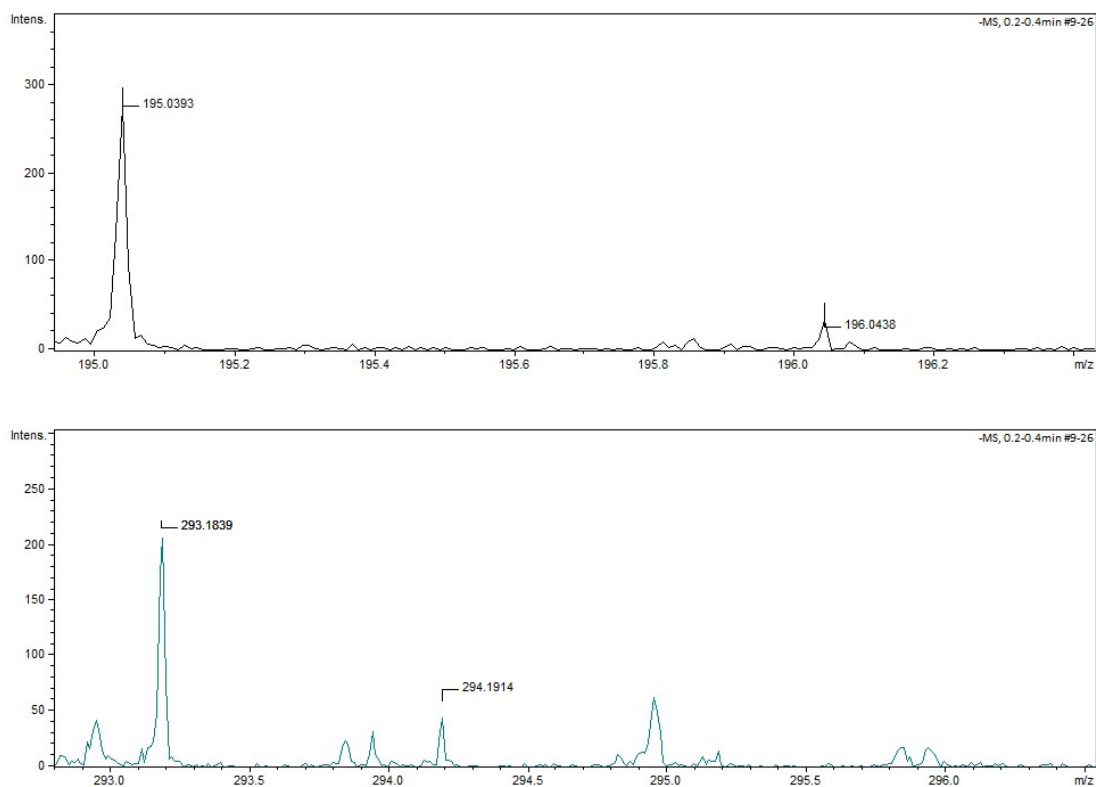


Fig. S9 Negative-ion ESI mass spectrum of the MIBK-extracted organic species occluded in used catalyst.

EHP : ESI-MS m/z: 195.0393 [(M-H)⁻, C₁₀H₁₁O₄], Anal. Calcd for C₁₀H₁₂O₄: 196.074. m/z: 293.1839

[(M-H)⁻, C₁₅H₁₇O₆], Anal. Calcd for C₁₅H₁₈O₆: 294.111.

Table S1 Catalytic results of Co/ZrO₂ 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	4.4×10 ⁻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	82.5 ^c	1.5	this work
Co/ZrO ₂	EL	1,4-dioxane, H ₂ (40 bar)	190	100	94.3 ^d	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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