

Supplementary Information

Engineering Metal-Support Interactions of Ceria Supported Cobalt Catalysts for Durable Hydrogenation of Levulinic Acid to γ - Valerolactone

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Table S1. Results of BET surface areas.

	BET surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore Size (nm)
CeO ₂	2.9	0.014	19.2
0.5CoCe	5.7	0.020	14.2
1CoCe	4.6	0.017	14.8
5CoCe	3.7	0.020	21.8

Table S2 The percentage of cobalt species calculated from Co 2p XPS.

Sample	Co ⁰ (%)	Co ²⁺ (%)	Co ³⁺ (%)	Co ³⁺ (%)	Ov (%)
0.5CoCe	5.0	61.3	33.7	25.7	27.3
1CoCe	6.0	69.0	25.0	28.7	29.7
5CoCe	7.6	55.7	36.7	27.3	20.7
CeO ₂				18.7	19.8

Table S3. Co loadings and H₂ consumption from H₂ TPR profiles.

	^a Co loadings (wt%)	^b Total H ₂ consumption of each catalyst (mmol/g)	H ₂ consumption per Co (mmol/g)
0.5CoCe	0.50	0.15	30.0
1CoCe	0.89	0.40	43.0
5CoCe	5.06	0.62	12.0

^aCo loadings are determined by ICP.

^bTotal H₂ consumption is calculated based on the area from 100 °C to 450 °C in the TPR profiles.

Table S4. LA hydrogenation by bare CeO₂.

Conversion (%)	EL selectivity (%)	GVL selectivity (%)
3.8	100	0

Reaction conditions: catalyst 50 mg, LA 4.3 mmol, 180°C, 3 MPa H₂, 20 min.

Table S5. Recently reported non-precious catalysts for LA to GVL.

Sample	Reaction conditions	TOF (mol/mol _C /h)	Ref.
30%Ni/O-clay450N	140°C, 3 MPa H ₂ , 1,4-Dioxane	1.73	[1]
Cu/NC300@NMSSs	140°C, 3 MPa H ₂ , methanol	11.51	[2]
Cu/NC@SBA-15-1.0	140°C, 3 MPa H ₂ , methanol	5.42	[3]
Co NPs/SAs-NC@HNC-1	180°C, 4.5 MPa H ₂ , H ₂ O	731	[4]
1CoCe	140°C, 3 MPa H ₂ , EtOH	21.8	This work
1CoCe	180°C, 3 MPa H ₂ , EtOH	194.6	This work

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[2] F. Lan, H. Zhang, C. Zhao, Y. Shu, Q. Guan, W. Li, Copper clusters encapsulated in carbonaceous mesoporous silica nanospheres for the valorization of biomass-derived molecules, *ACS Catal.* 12 (2022) 5711-5725.

[3] F. Lan, J. Aarons, Y. Shu, X. Zhou, H. Jiao, H. Wang, Q. Guan, W. Li, Anchoring strategy for highly active copper nanoclusters in hydrogenation of renewable biomass-derived compounds, *Appl. Catal. B Environ.* 299 (2021) 120651.

[4] S. Shao, Z. Ding, C. Shang, S. Zhang, Y. Ke, G. Zhu, Yang, Yolk-shell Co catalysts with controlled nanoparticle/single-atom ratio for aqueous levulinic acid hydrogenation to γ -valerolactone, *Chem. Eng. J.* 450 (2022) 138153.

Table S6. Co loadings of fresh and spent for cobalt catalysts.

	Fresh (wt%)	Spent (wt%)
0.5CoCe	0.50	0.28
1CoCe	0.89	0.88
5CoCe	5.06	2.27

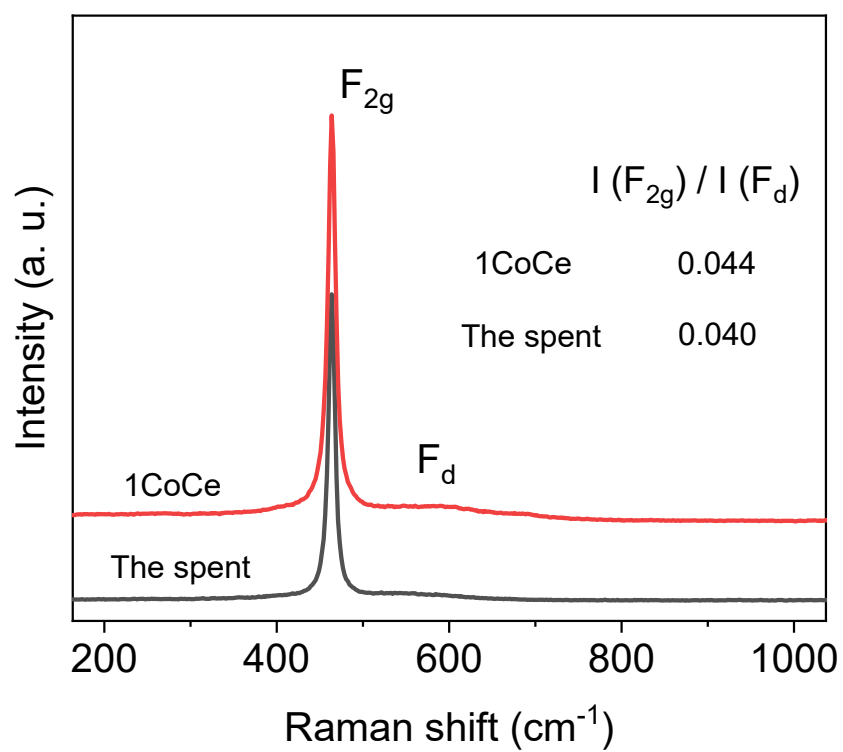


Figure S1. Comparison of Raman of 1CoCe and the spent (from fixed bed).