Supporting Information

Efficient and switchable production of bio-diol/triol chemicals from 5-hydroxymethylfurfural

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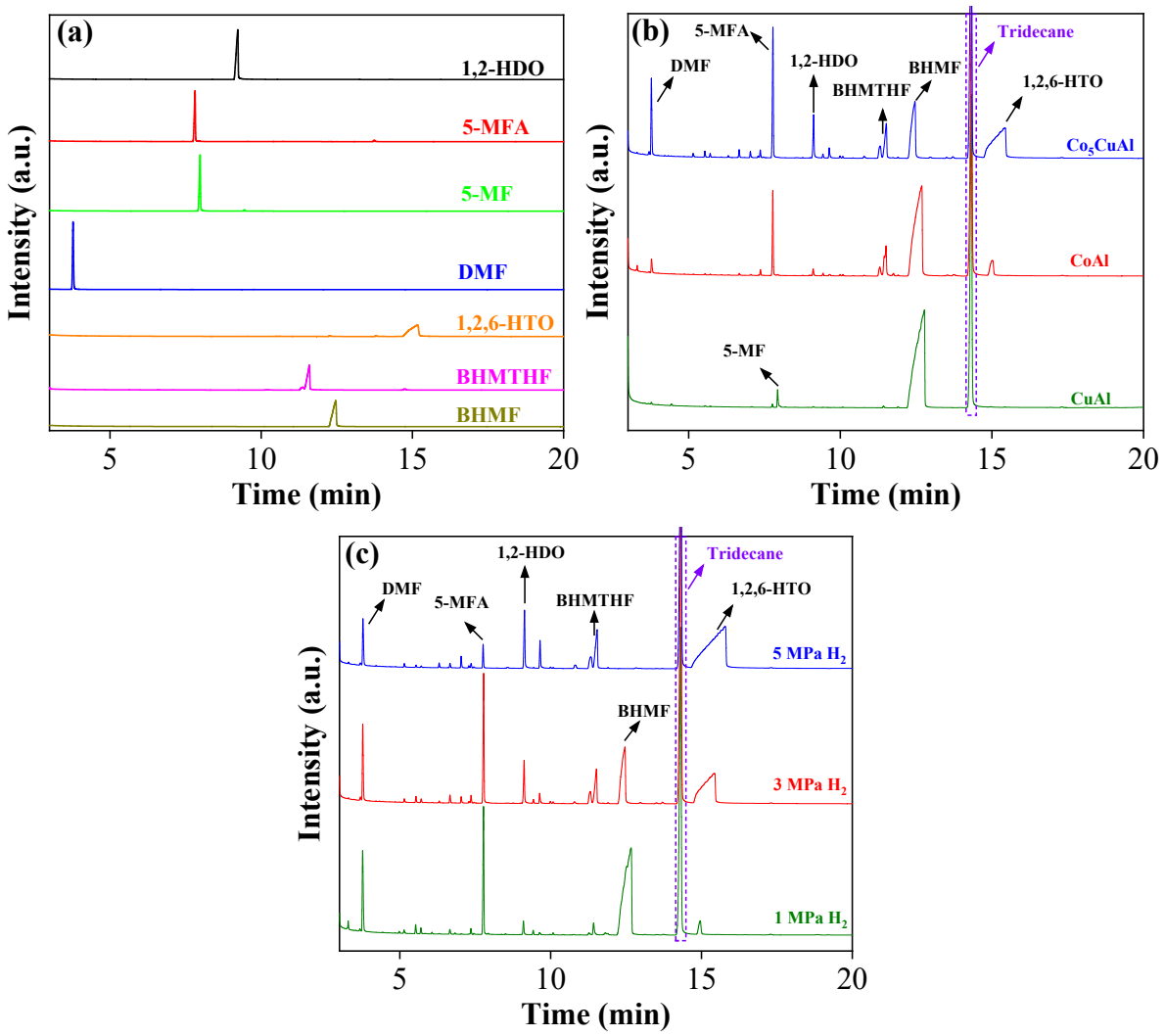


Figure S1. a) Standard samples' Peak identification using GC-MS. GC patterns of the samples under different conditions: **b)** 30 mg catalyst, 10 mL methanol, 1 mmol HMF, 120 °C, 3 h, 3 MPa H_2 **c)** 30 mg Co_5CuAl, 10 mL methanol, 1 mmol HMF, 120 °C, 3 h

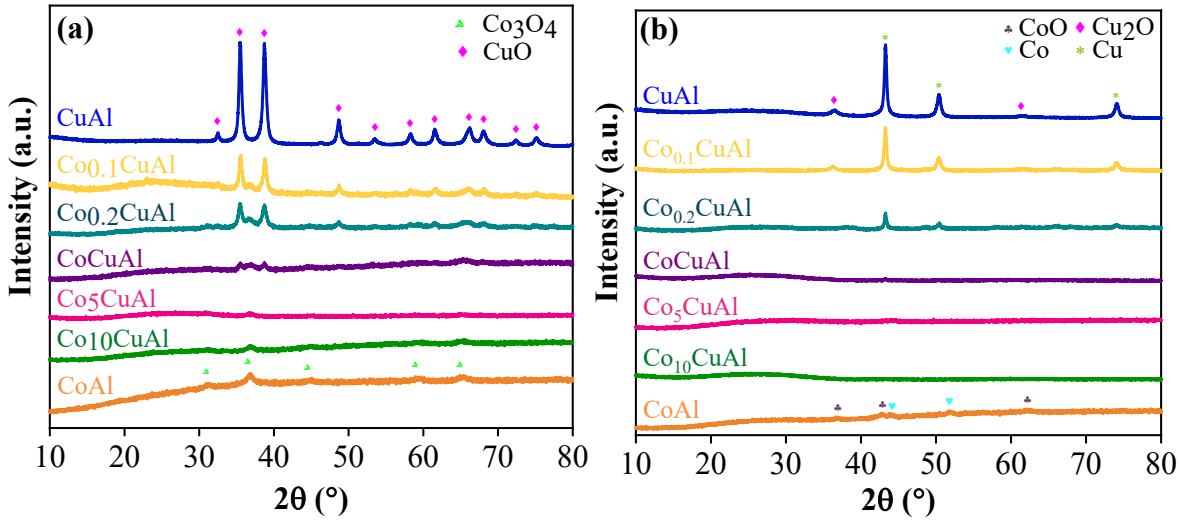


Figure S2. XRD patterns of LDOs catalysts **(a)** before reduction, and **(b)** after reduction.

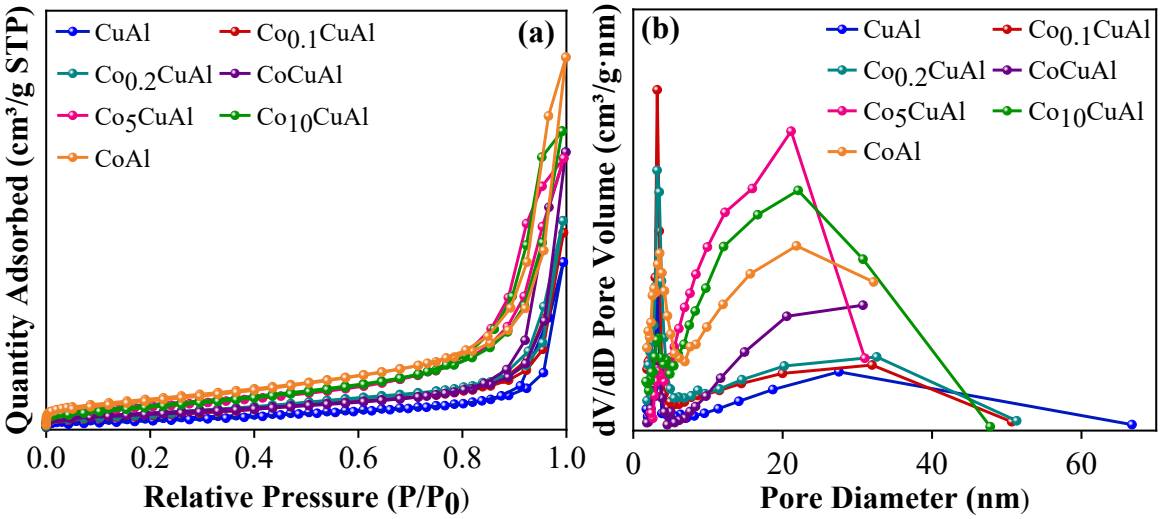


Figure S3. (a) N_2 adsorption/desorption isotherm and **(b)** pore size distribution of reduced LDOs catalysts.

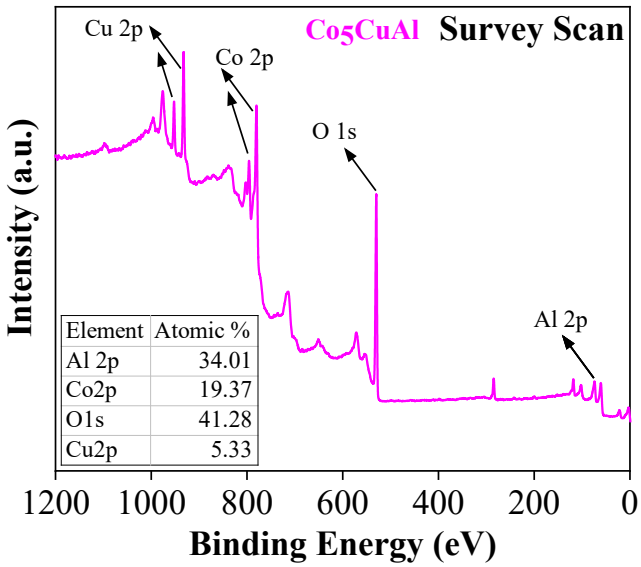


Figure S4. XPS survey and the atomic percentages of elements in the reduced Co_5CuAl catalyst.

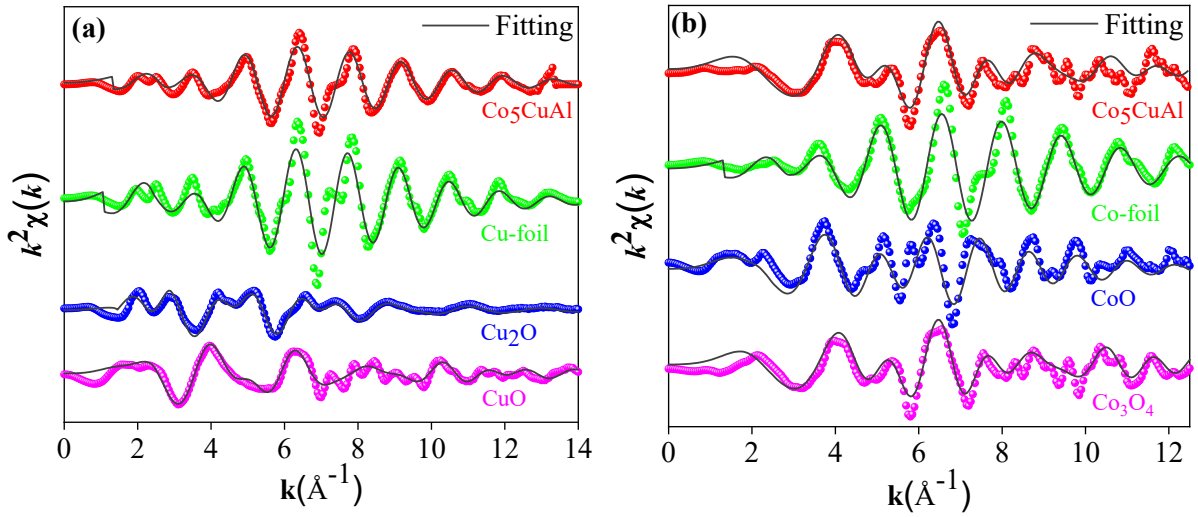


Figure S5. K space-fitting curves of Co_5CuAl and reference **(a)** Cu species **(b)** Co species.

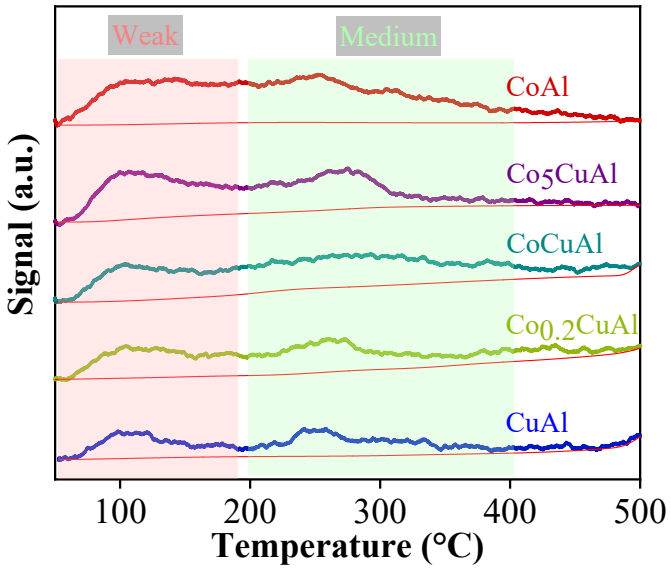


Figure S6. NH_3-TPD patterns of reduced LDOs catalysts.

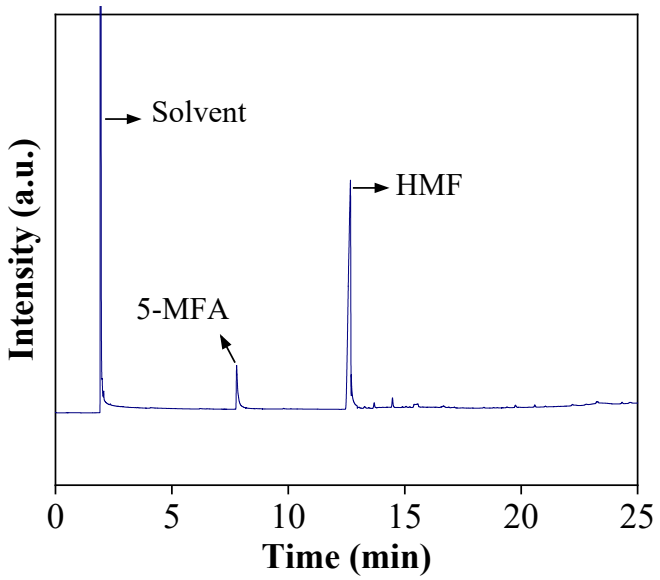


Figure S7. The GC pattern obtained for the sample under 3 MPa N_2 at 120°C for 3 h reaction.

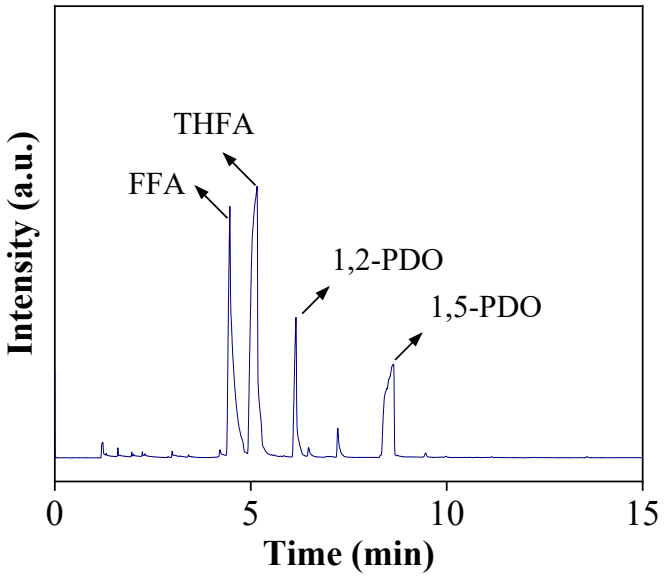


Figure S8. The GC pattern obtained for the sample under following reaction conditions: 1 mmol FF, 30 mg Co_5CuAl, 10 mL methanol, 3 h, 120°C, 5 MPa.

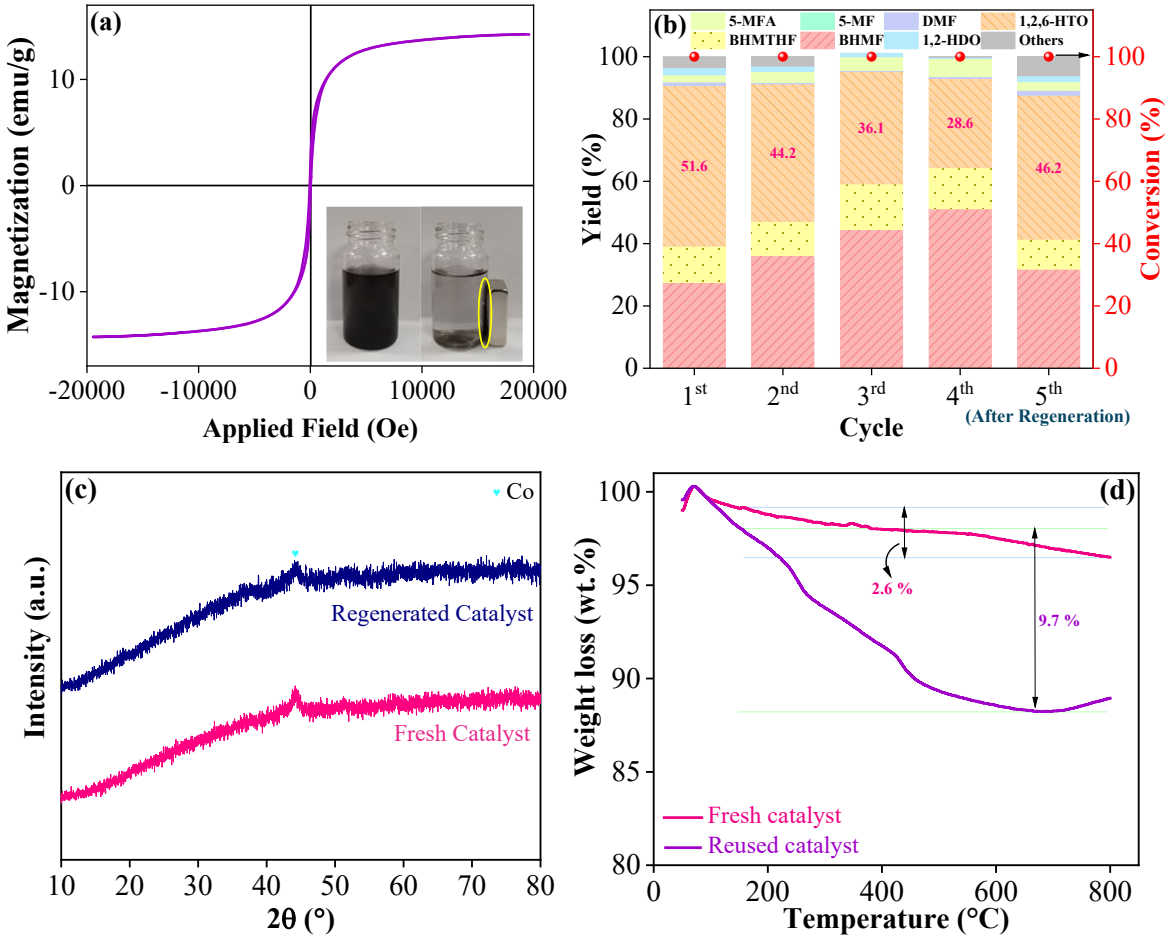


Figure S9. (a) VSM magnetization curve **(b)** Performance of the Co_5CuAl during five consecutive runs. Reaction conditions: 30 mg of Co_5CuAl, 10 mL methanol, 1 mmol HMF, 1 h, 120 °C, 4 MPa. **(c)** XRD patterns of the fresh and regenerated Co_5CuAl catalyst. **(d)** TGA analysis of fresh and spent catalysts.

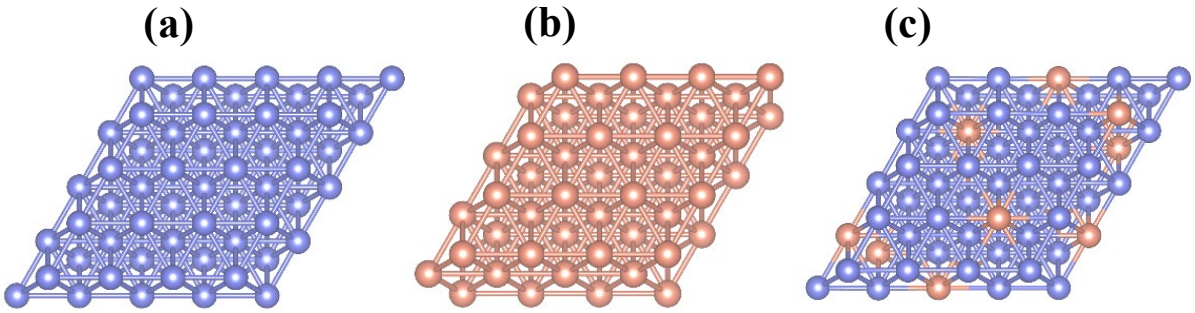


Figure S10. Constructed surfaces of **a)** Co(111), **b)** Cu(111), and **c)** CoCu(111) for the performed DFT computational calculations (Top-view).

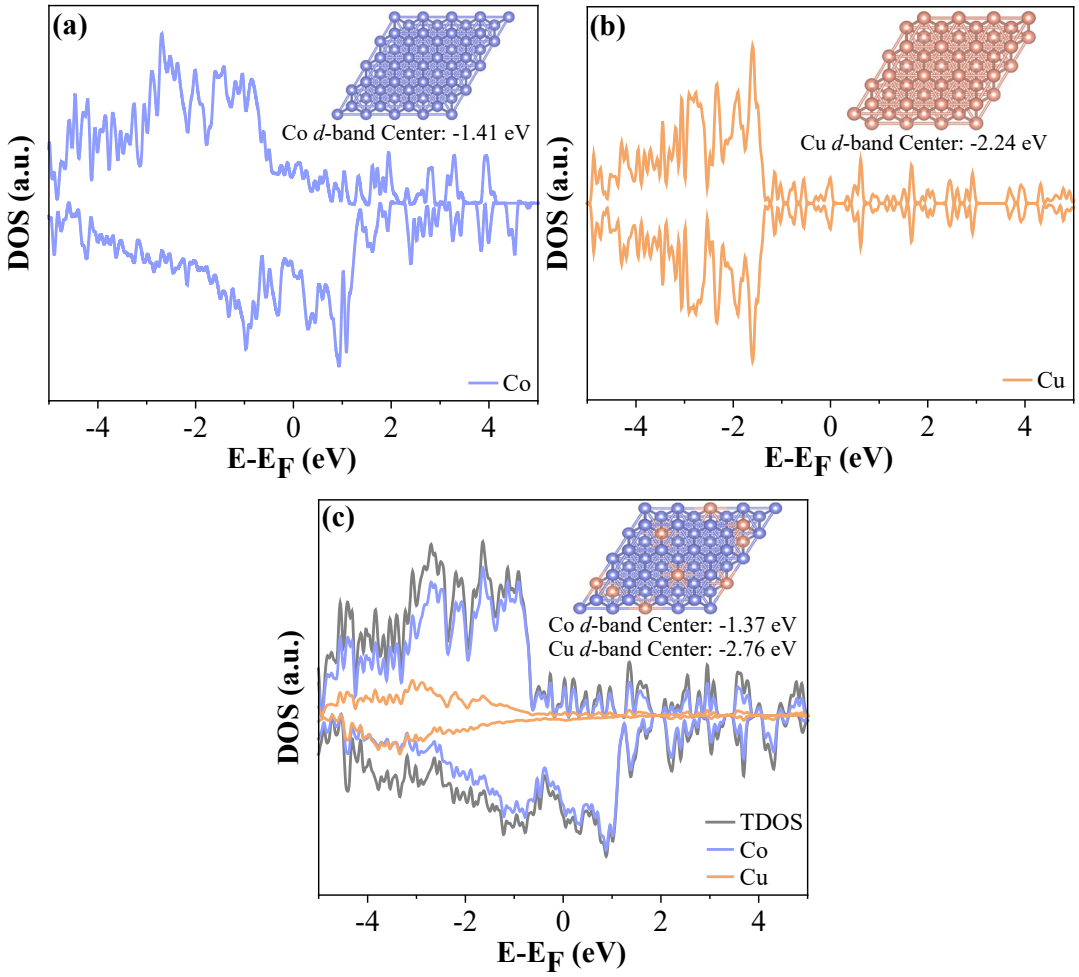
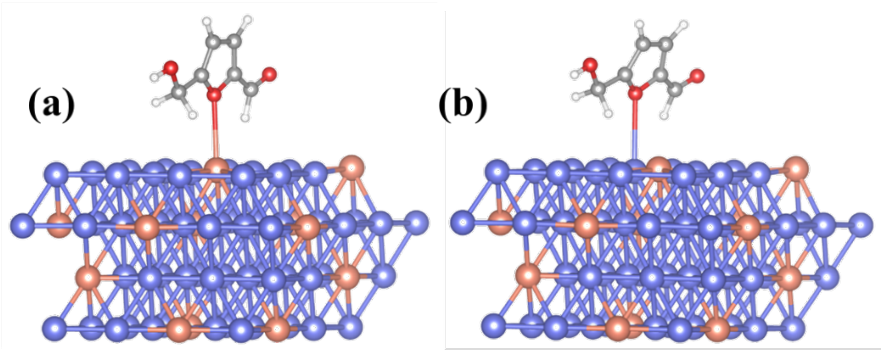


Figure S11. Calculated *d*-band center value for **(a)** Co(111) **(b)** Cu(111) and **(c)** CoCu(111) surfaces.



$E_{Ads.}$ = -1.45 $E_{Ads.}$ = -1.47

Figure S12. Adsorption energies of HMF *via* its furan ring on the **(a)** Cu of CoCu(111) and **(b)** Co of CoCu(111) surface. (Side-view; blue= Co; orange= Cu)

Table S1. Textual properties of reduced LDO catalysts.

Catalyst	Total surface area (m^2/g)	Total pores volume (cm^3/g)	Average pores size (nm)	Cu* (nm)	Co* (nm)	CoO* (nm)
CuAl	57	0.36	23.3	26.3	-	-
$Co_{0.1}$CuAl	70	0.39	18.4	24.6	-	-
$Co_{0.2}$CuAl	89	0.41	15.1	21.8	-	-
Co_{1}CuAl	97	0.46	17.4	19.2	-	-
Co_{5}CuAl	117	0.51	13.8	-	-	-
Co_{10}CuAl	122	0.57	15.6	-	-	-
CoAl	151	0.65	16.2	-	18.8	17.6

***** Measured by Scherrer equation

Table S2. EXAFS fitting parameters at the Cu K-edge for various samples（S_0^2=0.90 from Cu-foil）

	shell	CN*	R(Å)†	σ^c(Å^2)‡	ΔE_0(eV)♦	R factor
Cu-foil	Cu-Cu	12	2.54±0.01	0.0088	4.5±0.5	0.0027
	Cu-O	2	1.85±0.01	0.0031		
Cu_2O	Cu-Cu	12	3.02±0.01	0.0220	7.7±0.8	0.0086
	Cu-O	6	3.53±0.04	0.0211		
	Cu-O	4	1.95±0.01	0.0040		
	Cu-O	2	2.74±0.04	0.0108		
CuO	Cu-Cu	4	2.89±0.01	0.0049	-0.2±0.9	0.0078
	Cu-Cu	4	3.05±0.01	0.0040		
	Cu-Cu	2	3.17±0.01	0.0031		
Co_5CuAl	Cu-Co	6.5±0.2	2.53±0.01	0.0075	6.8±1.0	0.0120

***** Coordination numbers; † Bond distance; ‡ Debye-Waller factors; ♦ Inner potential correction. CN±20%; R ± 1%; σ^2 ± 20%.

Table S3. EXAFS fitting parameters at the Co K-edge for various samples（S_0^2=0.76 from Co-foil）

	shell	CN*	R(Å)†	σ^c(Å^2)‡	ΔE_0(eV)♦	R factor
Co-foil	Co-Co	12	2.49±0.01	0.0063	6.9±0.3	0.0008
CoO	Co-O	6	2.12±0.02	0.0125	-3.1±0.7	0.0066
	Co-Co	12	3.00±0.01	0.0088		
Co_3O_4	Co-O	5.3	1.91±0.02	0.0034	-6.3±0.5	0.0044
	Co-Co1	4	2.85±0.01	0.0035		
	Co-Co2	8	3.36±0.02	0.0064		
Co_5CuAl	Co-O	5.1±0.5	1.87±0.01	0.0041	-10.8±2.5	0.0163
	Co-Cu	1.0±0.2	2.51±0.01	0.0140		
	Co-Co1	3.4±0.6	2.83±0.02	0.0050		
	Co-Co2	8.4±1.2	3.32±0.02	0.0086		

***** Coordination numbers; † Bond distance; ‡ Debye-Waller factors; ♦ Inner potential correction. CN±20%; R ± 1%; σ^2 ± 20%.

Table S4. Chemical properties of different catalysts.

Samples	Acidity (mmol NH_3/g)		
	Weak	**Medium**	**Total**
CuAl	0.12	0.14	0.26
$Co_{0.2}$CuAl	0.17	0.16	0.33
CoCuAl	0.18	0.26	0.44
Co_5CuAl	0.30	0.30	0.60
CoAl	0.31	0.43	0.74

Table S5. ICP results of the fresh and regenerated Co_5CuAl catalyst.

Catalyst	Co (wt.%)	Cu (wt.%)	Al (wt.%)
Fresh	52.7	12.2	9.7
Regenerated	51.9	11.3	9.5