

SUPPORTING INFORMATION

Insights into the Preparation of Copper Catalysts Supported on LDH-Derived Mixed Oxides for Ethanol Dehydrogenation

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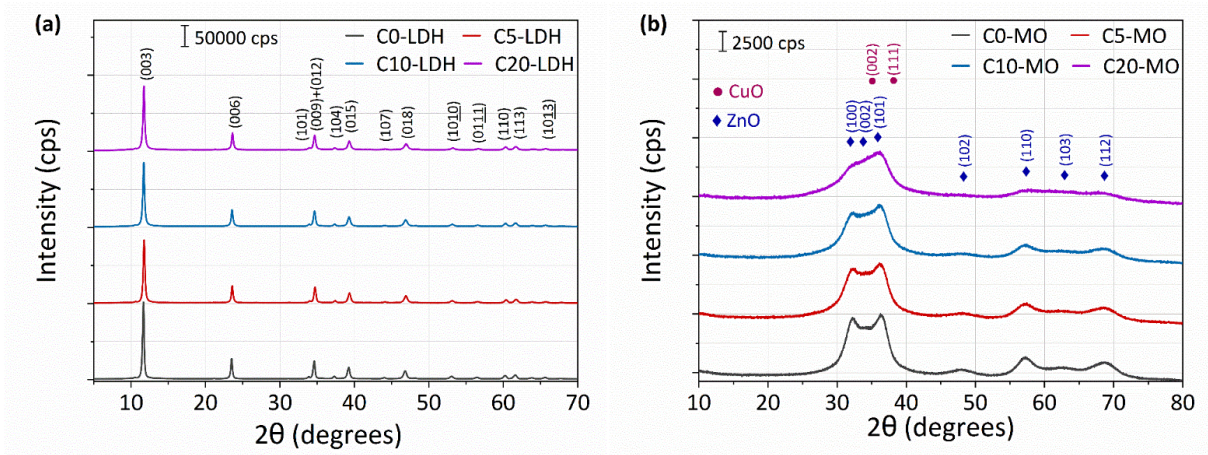


Figure S1. XRD patterns of (a) the as-prepared LDH samples and (b) the thermally decomposed LDH samples (MO), with different copper contents.

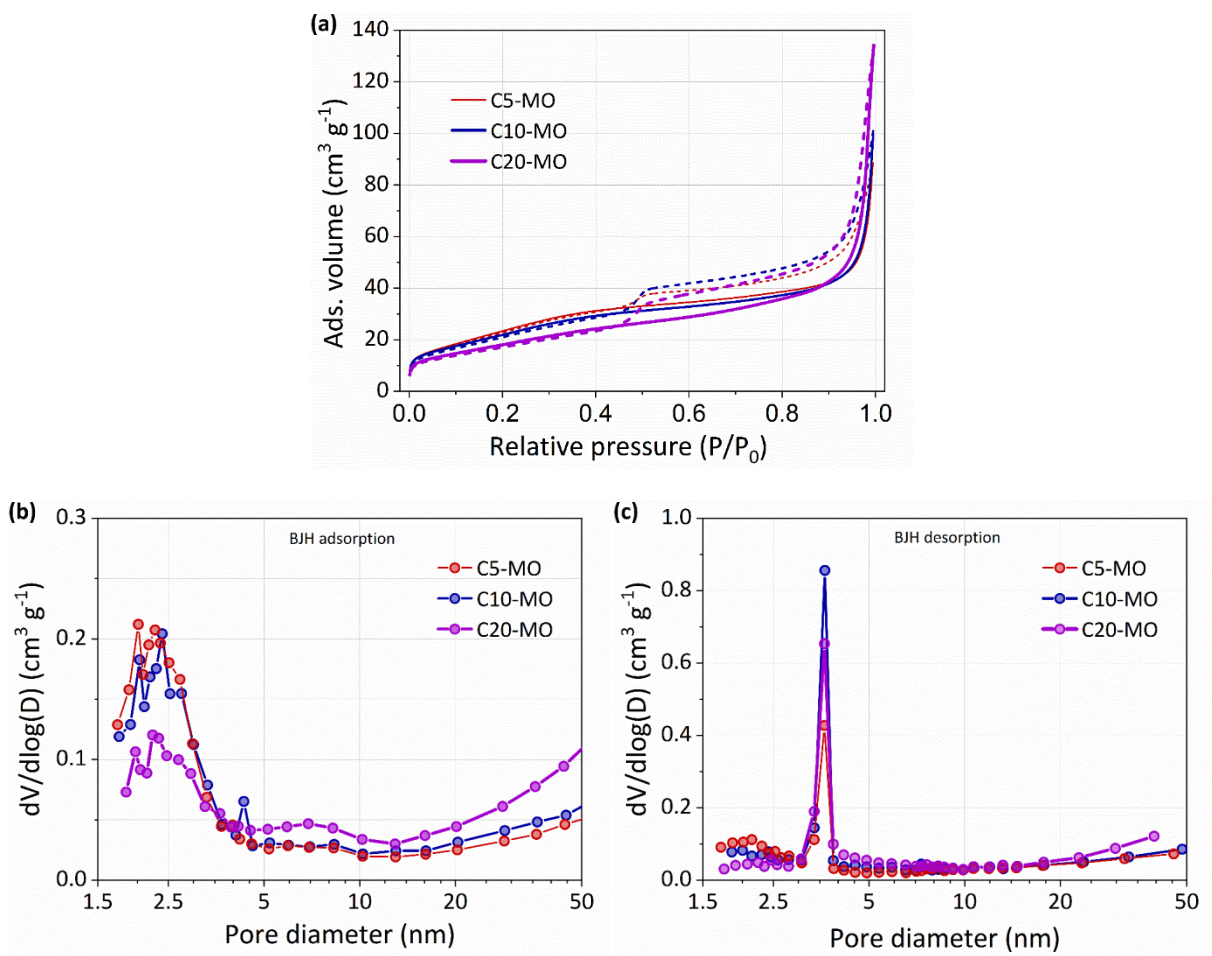


Figure S2. (a) N₂ adsorption-desorption isotherms of the thermally decomposed LDH samples (MO), and pore size distributions determined by the BJH method from (b) adsorption and (c) desorption isotherms.

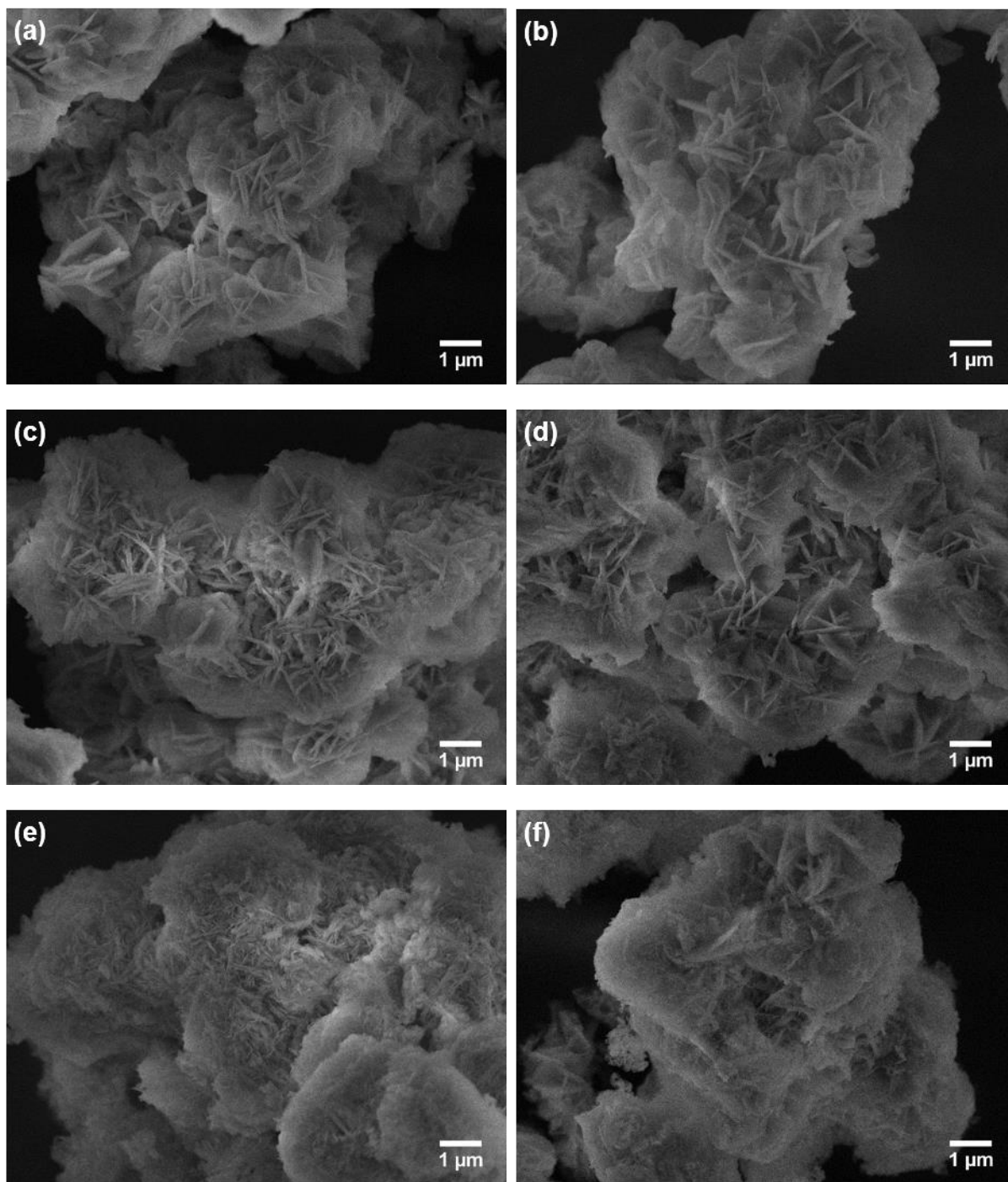


Figure S3. SEM micrographs of the as-prepared LDH and thermally decomposed LDH MO samples with different copper contents: (a) C5-HDL, (b) C5-MO, (c) C10-HDL, (d) C10-MO, (e) C20-HDL, and (f) C20-MO.

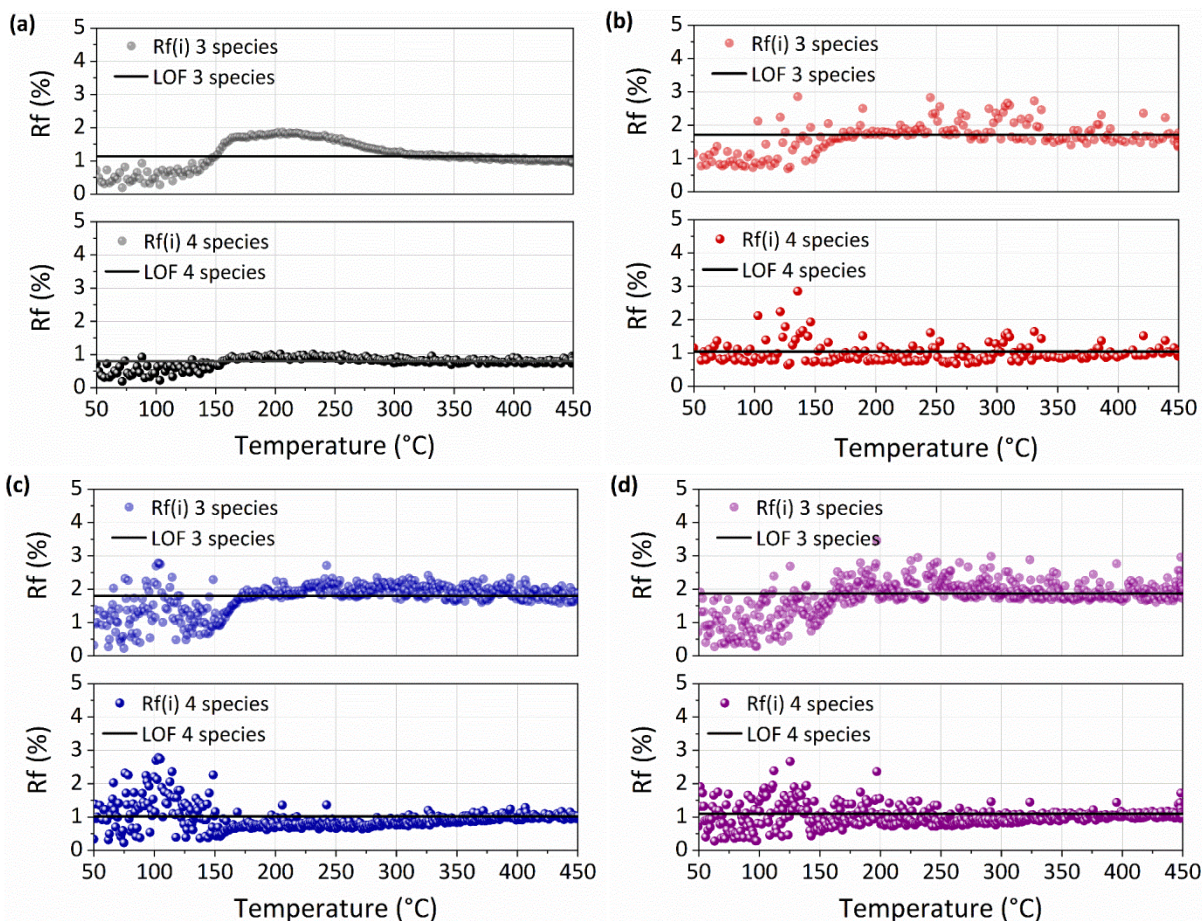


Figure S4. R_f factor and LOF (lack of fit) values obtained by MCR-ALS analysis of the Zn K-edge data measured during thermal decomposition of the LDH in air. The minimizations are compared using 3 and 4 Zn-based species for (a) C0-LDH, (b) C5-LDH, (c) C10-LDH, and (d) C20-LDH.

LOF (%) was defined according to the equation S1:

$$\text{LOF (\%)} = 100 \sqrt{\frac{\sum_{ij} e_{ij}^2}{\sum_{ij} d_{ij}^2}} \quad (\text{S1})$$

where, d_{ij} is an element of the experimental matrix D (i^{th} spectrum at the energy value j) and e_{ij} is the related residual value obtained from the difference between D and the rebuilt data over the 3 or 4 components from the $C.S^T$ matrix product obtained by MCR-ALS. The values of e_{ij} were

calculated as follows: $e_{ij} = d_{ij} - \sum_{k=1}^n C_{ik} \cdot S_{kj}^T$, where C_{ik} is an element of C, S_{kj} is an element of S, and the sub-index k is related to the index of the component isolated by MCR-ALS.

The R-factor ($R_f(i)$, %) is the LOF calculated for each spectrum, using the following equation:

$$R_f^{(i)}(\%) = 100 \sqrt{\frac{\sum_j e_{ij}^2}{\sum_j d_{ij}^2}} \quad (\text{S2})$$

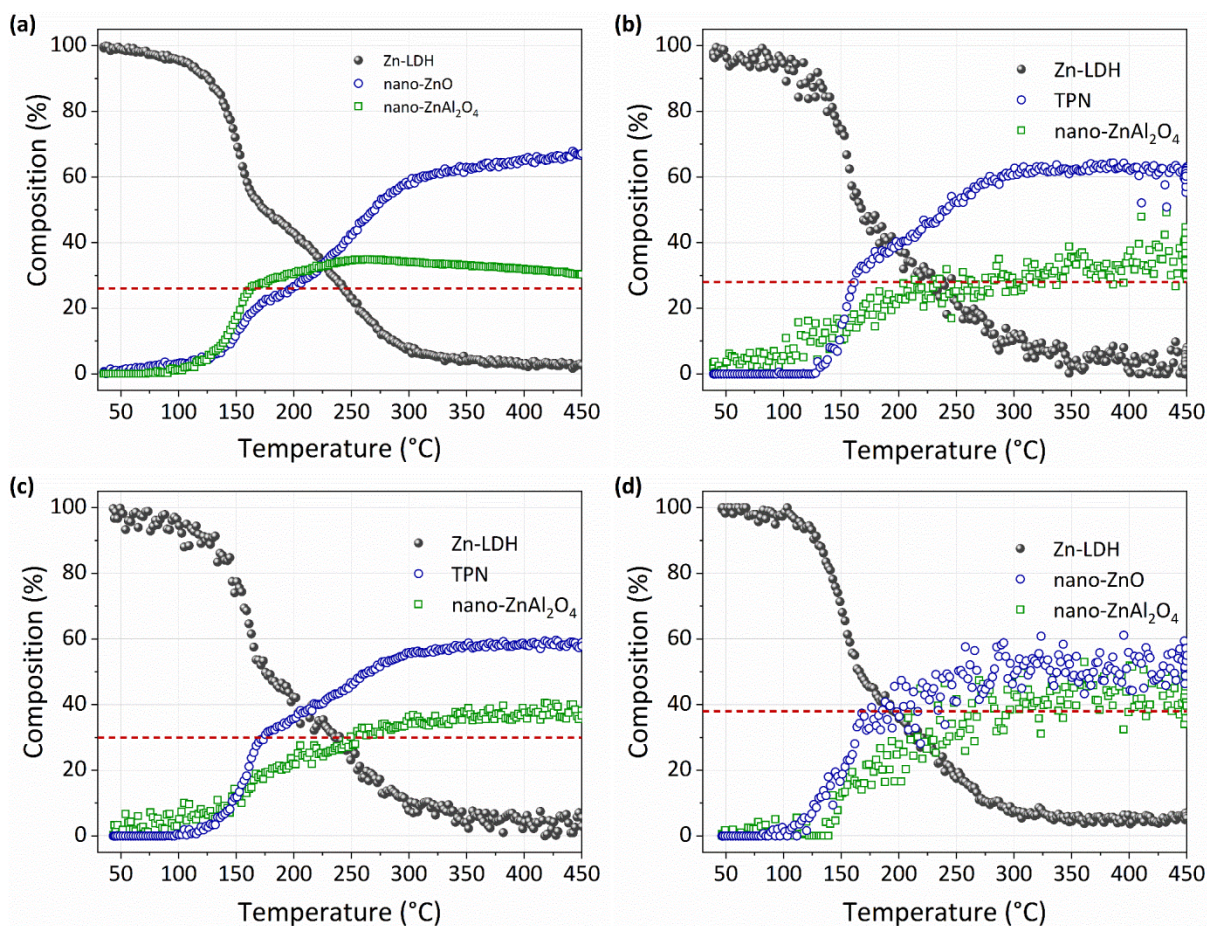


Figure S5. Concentration profiles of Zn-based species during thermal decomposition, in air, of (a) C0-LDH, (b) C5-LDH, (c) C10-LDH, and (d) C20-LDH, obtained by MCR-ALS analysis of the Zn K-edge data, considering only 3 species. The red lines indicate the maximum ZnAl₂O₄ concentrations permitted according to the LDH stoichiometry.

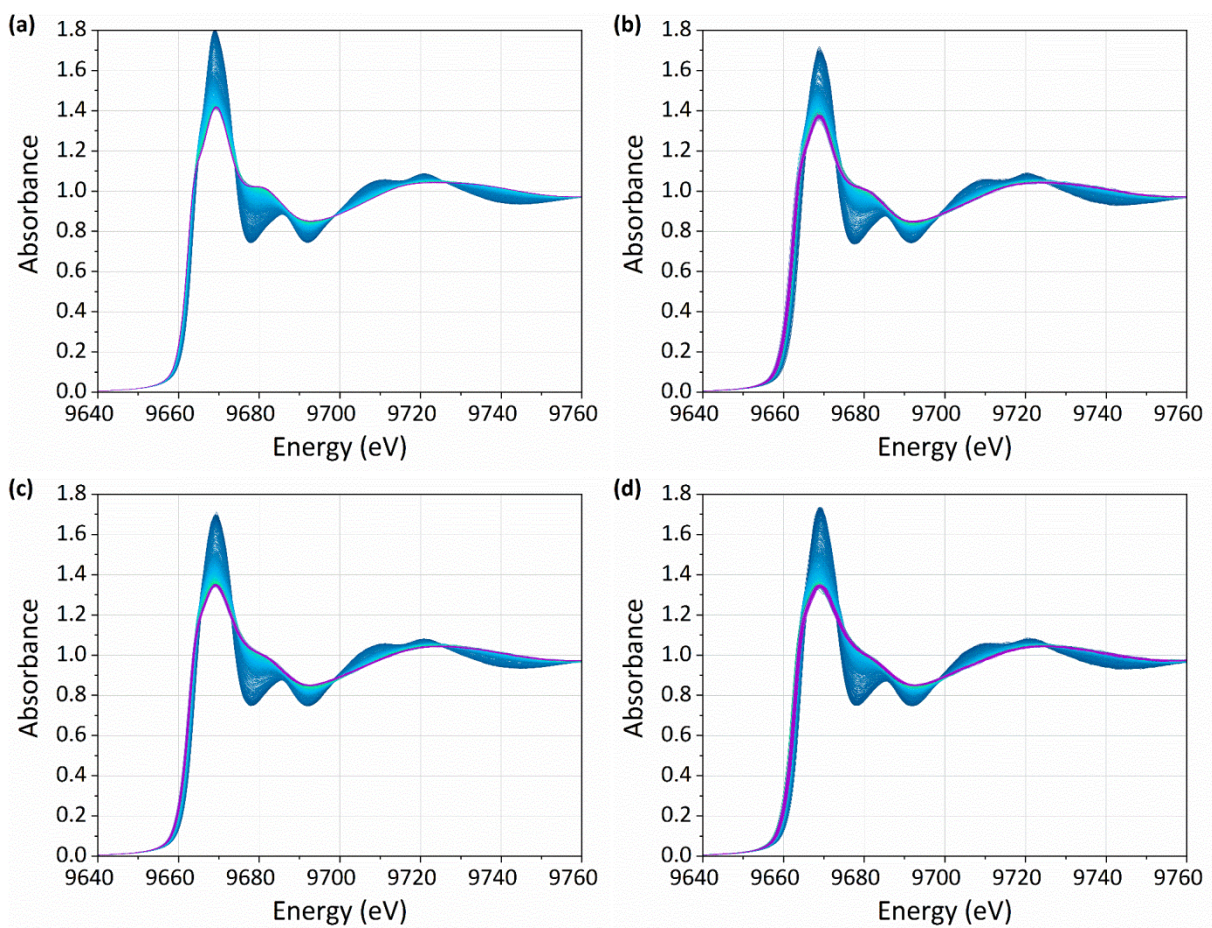


Figure S6. XANES spectra datasets at the Zn K-edge for the thermal decomposition, in air, of (a) C0-LDH, (b) C5-LDH, (c) C10-LDH, and (d) C20-LDH.

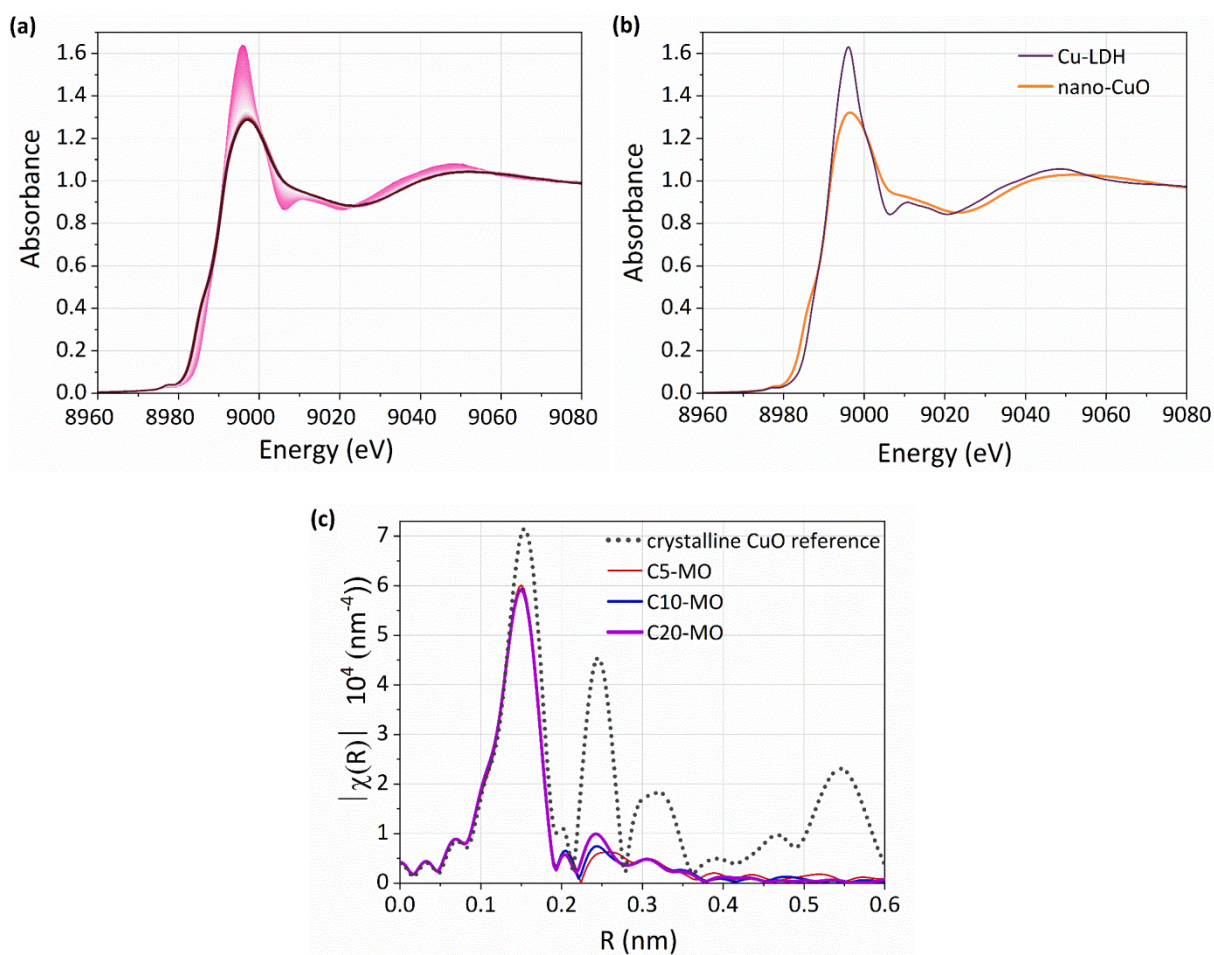


Figure S7. (a) XANES spectra dataset at the Cu K-edge for the thermal decomposition of C20-LDH in air; (b) XANES spectra obtained from the MCR-ALS analysis; and (c) FT of the EXAFS spectra for all the MO samples, in R space, compared to the crystalline CuO reference.

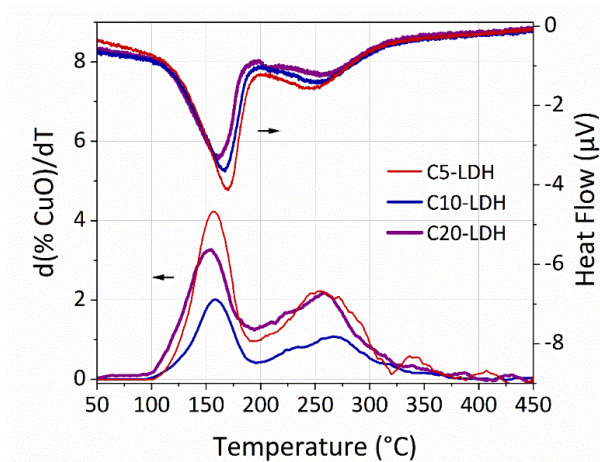


Figure S8. First derivative of the CuO composition, as a function of temperature, calculated from the MCR-ALS analysis (Fig. 4 in the main text), together with the DSC analysis, obtained during thermal decomposition of the LDH samples in air.

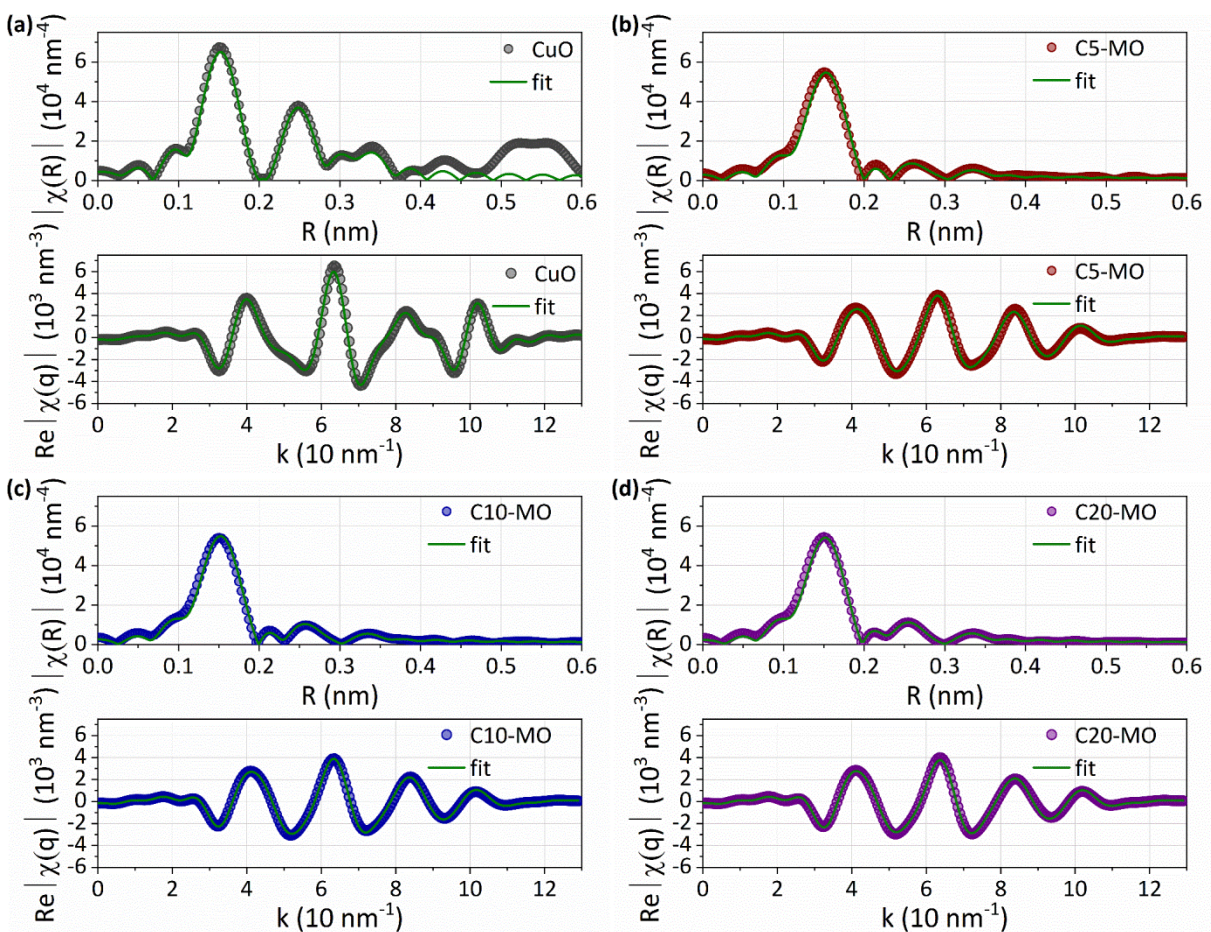


Figure S9. EXAFS fittings in R and k spaces of the spectra recorded for (a) the CuO reference and the thermally decomposed LDH samples (b) C5-MO, (c) C10-MO, and (d) C20-MO, measured at 40 °C.

Table S1. Structural parameters of copper oxides calculated from the EXAFS fittings for the CuO reference and the MO samples ($S_0^2 = 0.72$).

Sample	N	R (nm)	σ^2 (10^{-2} nm ²)	Rf
CuO	4 O	0.197	0.00416	0.0039
	2 O	0.282	0.00416	
	4 Cu	0.294	0.00612	
	4 Cu	0.312	0.00612	
	2 Cu	0.326	0.00612	
	2 Cu	0.342	0.00612	
C5-MO	4.0 ± 0.2 O	0.197	0.00558	0.0086
	2.4 ± 0.8 O	0.300	0.01610	
	4.2 ± 2.0 Cu	0.344	0.02563	
C10-MO	4.0 ± 0.1 O	0.196	0.00586	0.0063
	2.2 ± 0.8 O	0.295	0.01663	
	4.0 ± 1.6 Cu	0.343	0.02488	
C20-MO	4.0 ± 0.1 O	0.196	0.00583	0.0065
	2.3 ± 0.7 O	0.291	0.01623	
	4.3 ± 1.5 Cu	0.341	0.02555	

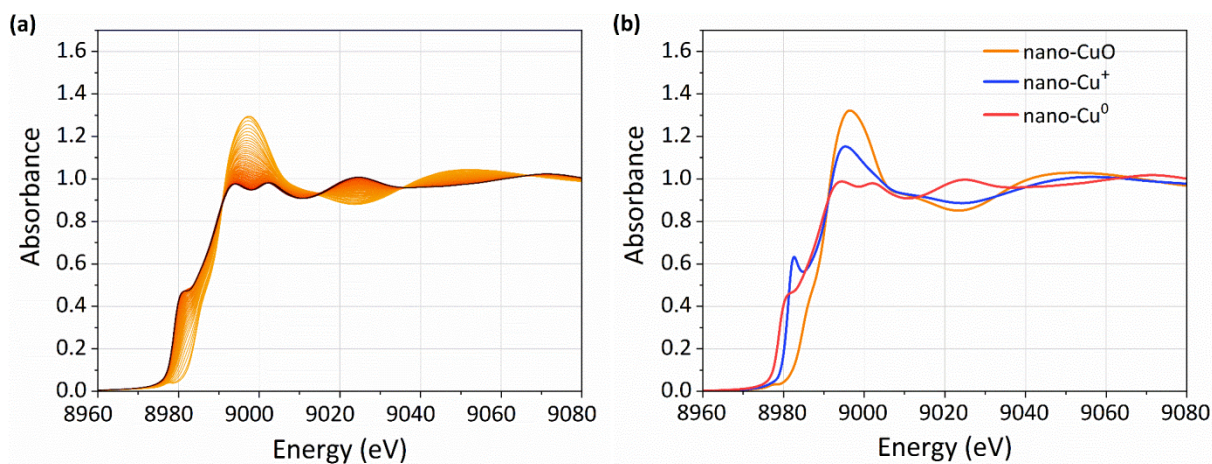


Figure S10. (a) XANES spectra dataset at the Cu K-edge for C20-MO activation in a 5% H_2/He atmosphere. (b) XANES spectra obtained from the MCR-ALS analysis.

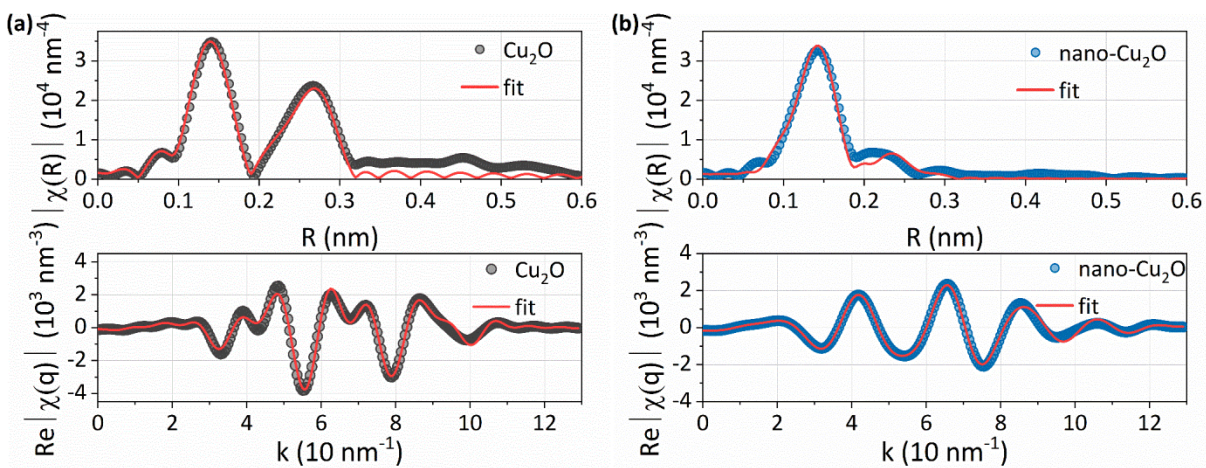


Figure S11. EXAFS fittings in R and k spaces for (a) the Cu_2O reference and (b) the nano- Cu_2O species, obtained using the MCR-ALS method.

Table S2. Structural parameters of copper oxides, calculated from the EXAFS fittings for the Cu₂O reference and nano-Cu₂O species, obtained using the MCR-ALS method ($S_0^2 = 0.72$).

Sample	N	R (nm)	σ^2 (10^{-2} nm ²)	Rf
Cu ₂ O	2 O	0.185	0.00407	0.02091
	12 Cu	0.303	0.02343	
nano-Cu ₂ O	2.7 ± 0.1 O	0.189	0.00646	0.00759
	2.9 ± 0.8 Cu	0.281	0.02857	

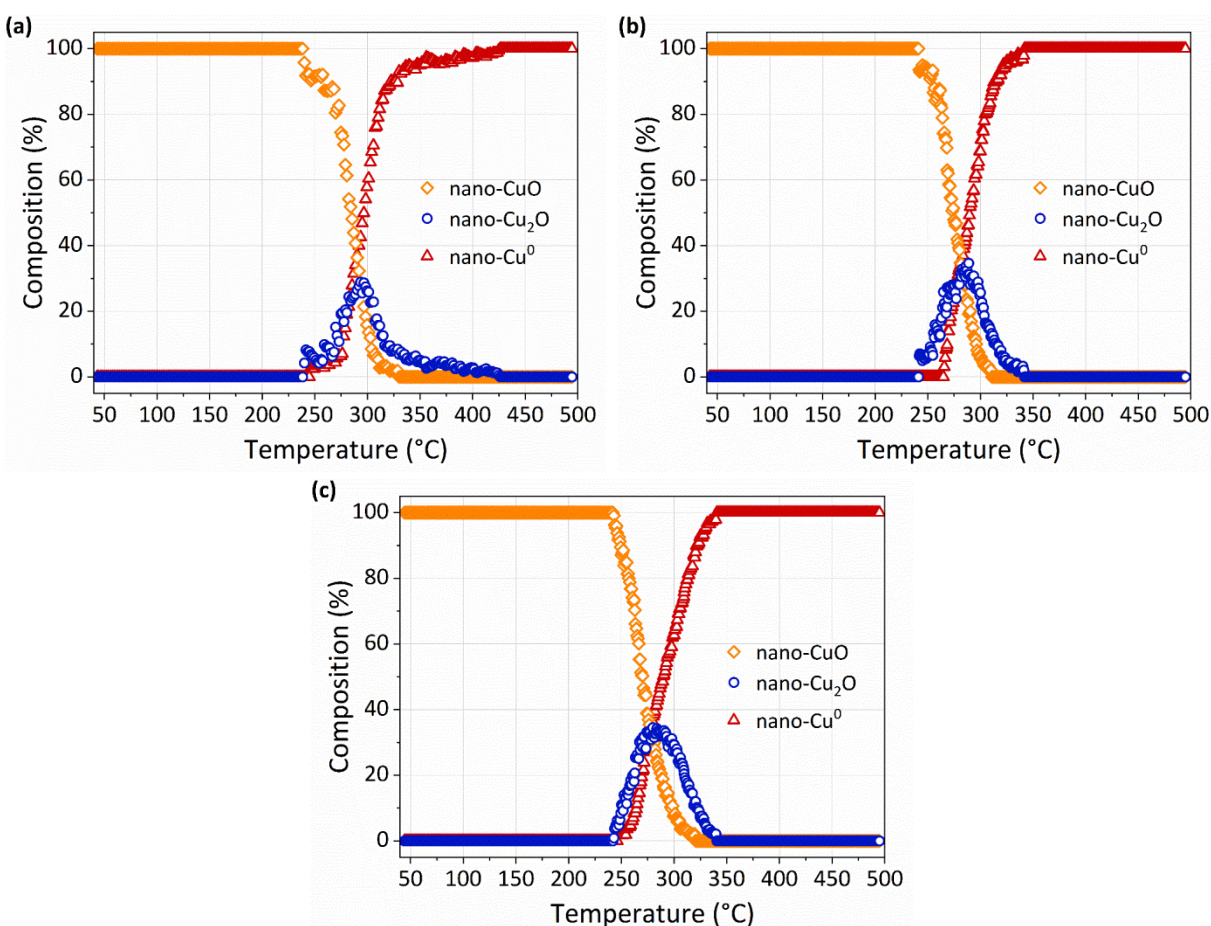


Figure S12. Concentration profiles of copper species determined by MCR-ALS analysis of the quick-EXAFS data recorded during TPR (5% H₂/He) for the thermally decomposed LDH samples: (a) C5-MO, (b) C10-MO, and (c) C20-MO.

Table S3. Parameters determined using the JMA model for the speciation of Cu⁰ during isothermal activation of the thermally decomposed LDH samples in 5% H₂/He.

Sample	n	Nucleation rate, Γ (min ⁻¹)	R ²
C5-MO	0.987	0.534	0.999
C10-MO	1.13	0.468	0.999
C20-MO	1.41	0.486	0.999

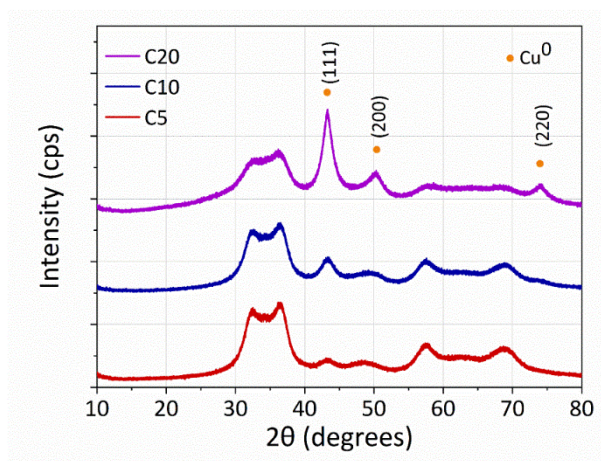


Figure S13. XRD patterns of the activated catalysts with different copper contents.

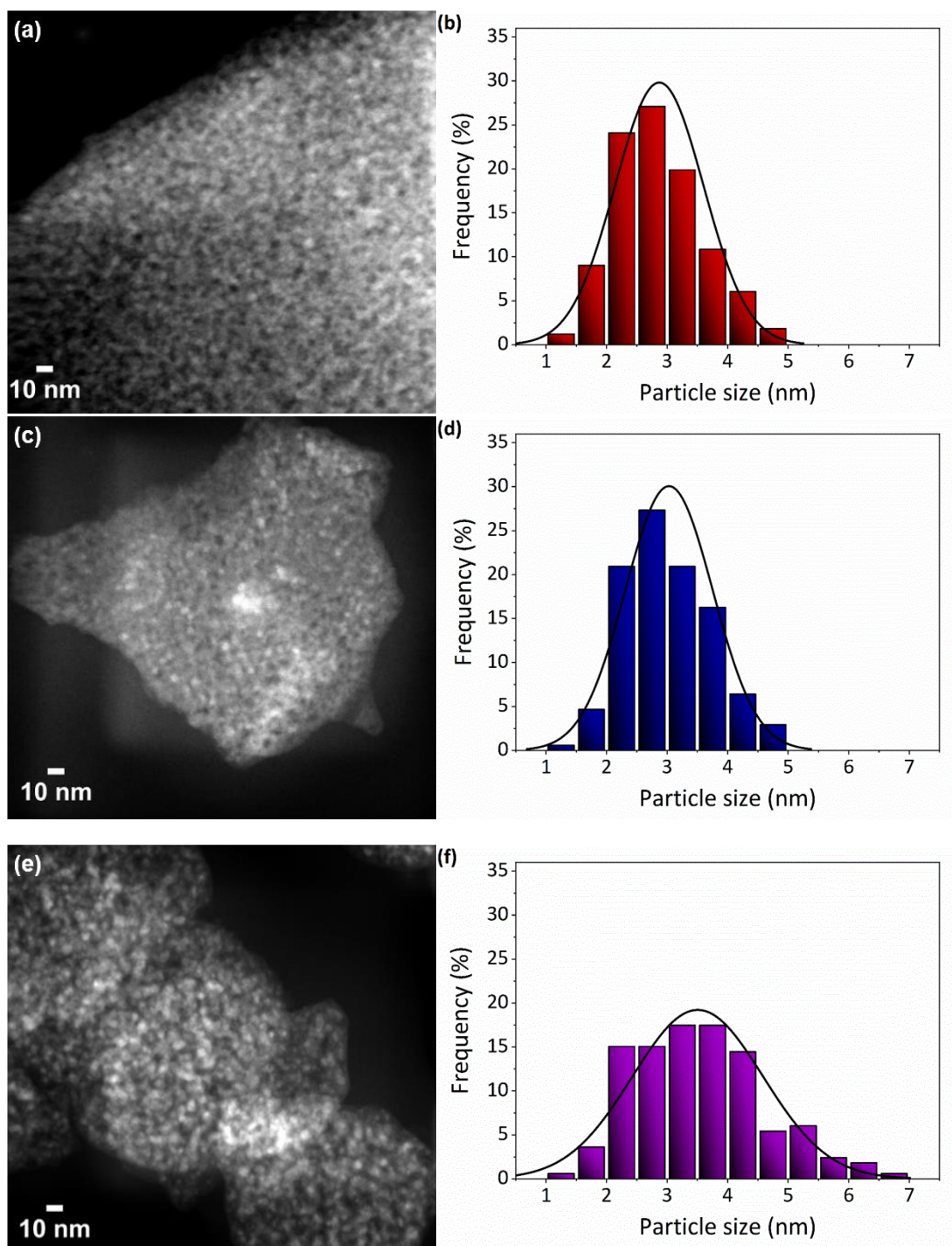


Figure S14. HAADF-STEM micrographs of the thermally decomposed LDH samples with different copper contents, activated in 5% H₂/He: (a) C5-MO, (c) C10-MO, and (e) C20-MO. The corresponding particle size histograms for (b) C5, (d) C10, and (f) C20 were obtained by measuring the diameter of at least 160 particles for each sample.

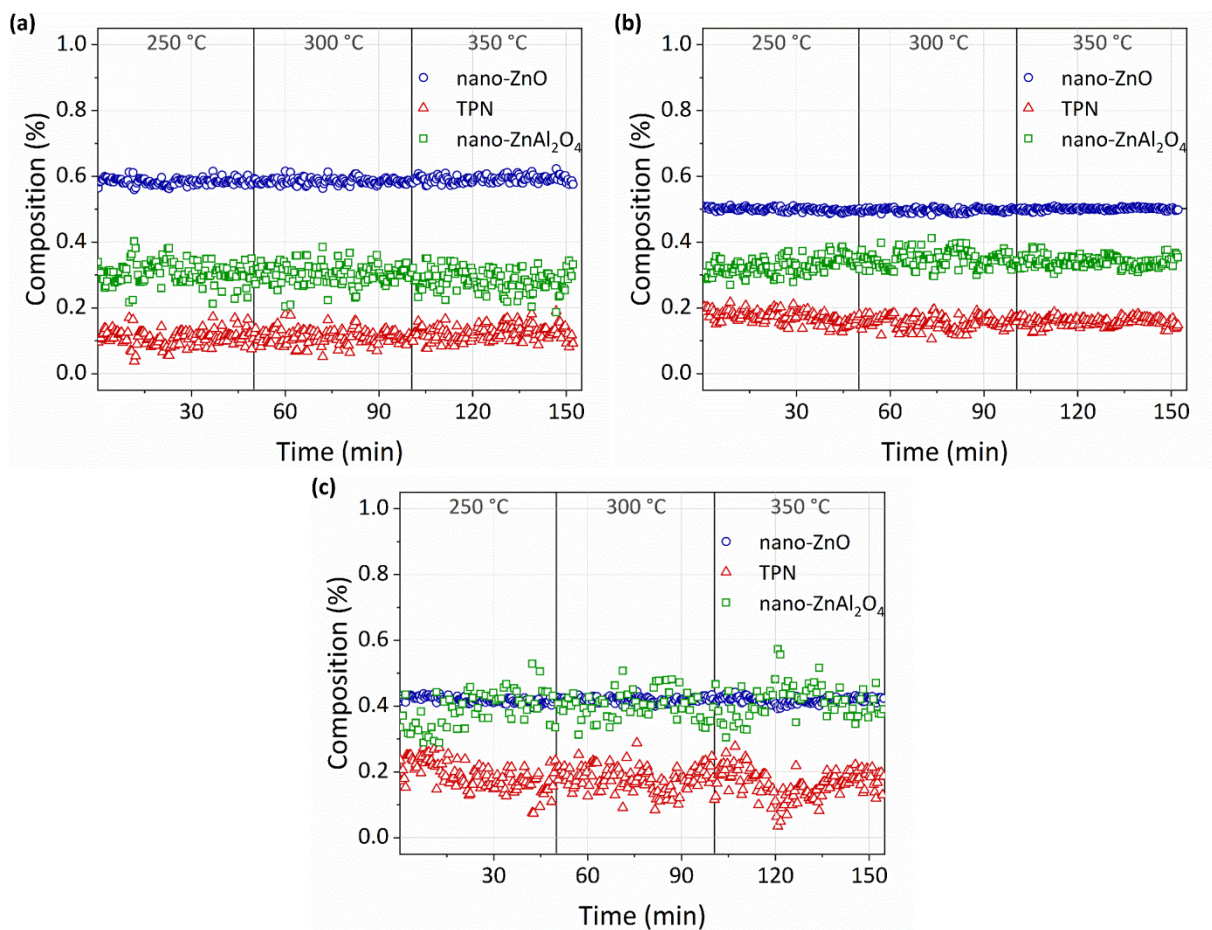


Figure S15. Concentration profiles of Zn-based species during the EDR at different temperatures for (a) C5-MO, (b) C10-MO, and (c) C20-MO, obtained using MCR-ALS analysis of the Zn K-edge data.

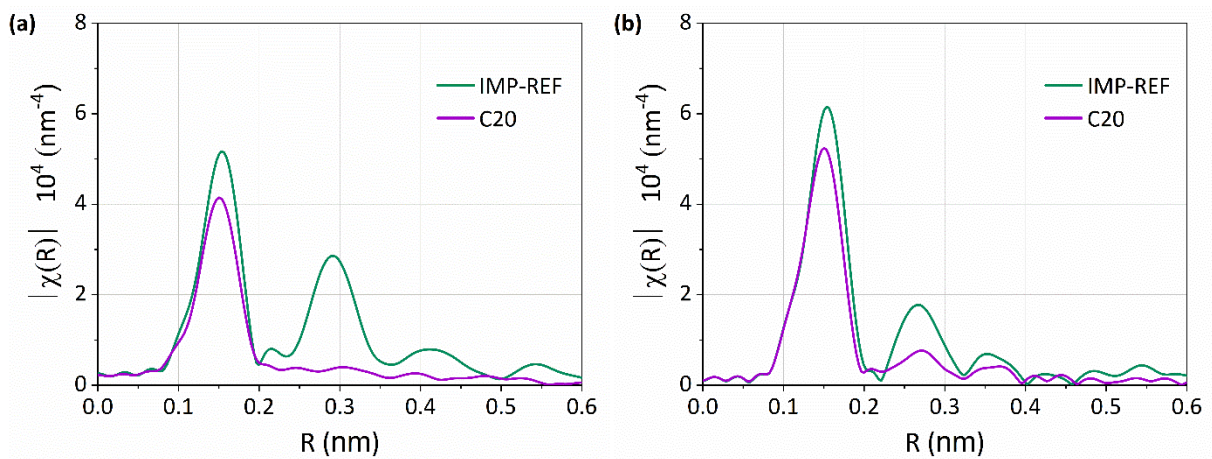


Figure S16. Fourier transforms of the EXAFS spectra at (a) the Zn K-edge and (b) the Cu K-edge for samples IMP-REF and C20-MO at 450 °C.

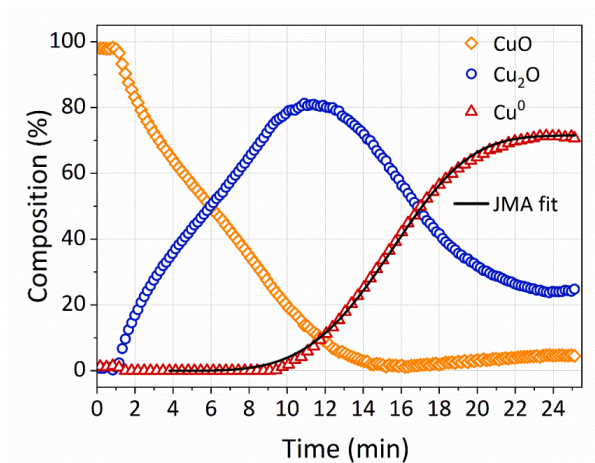


Figure S17. Evolution of copper species composition during isothermal activation of the IMP-REF catalyst at 350 °C, obtained using MCR-ALS analysis of quick-XAS measurements. The continuous line represents the JMA model fit of nano-Cu⁰ evolution.

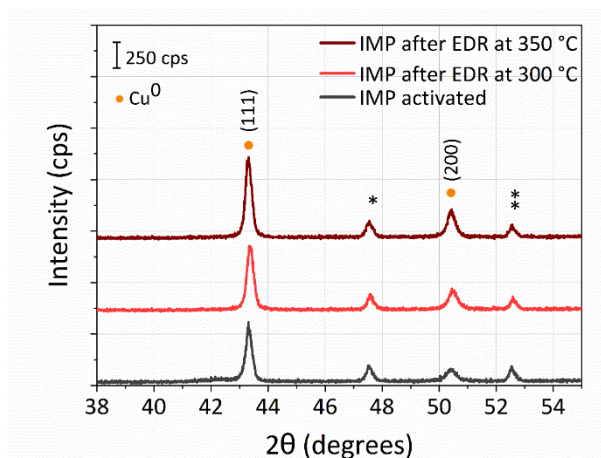


Figure S18. XRD patterns of the IMP-REF catalyst, before and after 6 h of reaction at 300 and 350 °C. Peaks marked as * and ** are related to the ZnO and Al₂O₃ phases, respectively. The average crystallite size of Cu⁰ increased from 18.7 nm (before EDR) to 19.1 and 20.9 nm after EDR at 300 and 350 °C, respectively.