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Supplementary Materials

Oxygen Vacancy-Triggered Performance Enhancement of Toluene Oxidation over Cu Catalysts: A Combined Kinetics and Mechanistic Investigation

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Supporting Tables

Table S1. Structural parameters of Cu foil, Cu/ZrO_2, Cu/ZnO, and Cu/Al_2O_3 catalysts from the EXAFS fitting.

Catalysts	Shell	CN[a]	R (Å)[b]	σ^2 (Å^2)[c]	ΔE_0 (eV)[d]	R factor[e]
Cu foil	Cu-Cu	12	2.54±0.01	0.008±0.001	4.7±0.7	0.012
Cu/ZrO_2	Cu-O	3.9±0.5	1.96±0.01	0.005±0.002	-2.0±1.5	0.015
	Cu-Cu	0.6±1.2	2.57±0.05	0.010±0.017		
Cu/ZnO	Cu-O	0.8±0.6	1.84±0.04	0.002±0.011	2.5±2.5	0.008
	Cu-Cu	5.5±1.3	2.53±0.02	0.006±0.002		
Cu/Al_2O_3	Cu-O	2.4±0.4	1.96±0.02	0.001±0.003	-0.2±1.8	0.020

[a] CN: coordination numbers. [b] R: bond distance. [c] σ^2: Debye-Waller factors. [d] ΔE_0: the inner potential correction. [e] R factor: goodness of fit. S_0^2 was set to 0.864 for Cu, according to the experimental EXAFS fit of Cu foils reference by fixing CN as the known crystallographic value.

Table S2. Assignment of infrared bands appearing in the process of toluene oxidation over the Cu catalysts.

Position (cm^{-1})	**Assignment**
3070, 3032	phenylic υ(C-H) stretching vibration of benzene ring
2945, 2888	asymmetric and symmetric υ(CH-) stretching vibrations of the methylene (C-H_2) group
1958, 1919, 1813, 1721, 1618	asymmetric and symmetric υ(C=O) stretching vibrations of cyclic anhydrides
1597	skeletal υ(C=C) stretching vibrations of the aromatic ring
1530	υ(C=O) stretching vibrations of carboxylate group in benzoate species
1451	υ(C=O) stretching vibrations of benzaldehyde species
1418	υ(C=O) stretching vibrations of carbonate species
1312	CH_2 deformation vibration of benzyl species
1225	υ(CO-) stretching vibrations of phenolate species
1071	υ(CO-) stretching vibrations of alkoxide species

Supporting Figures

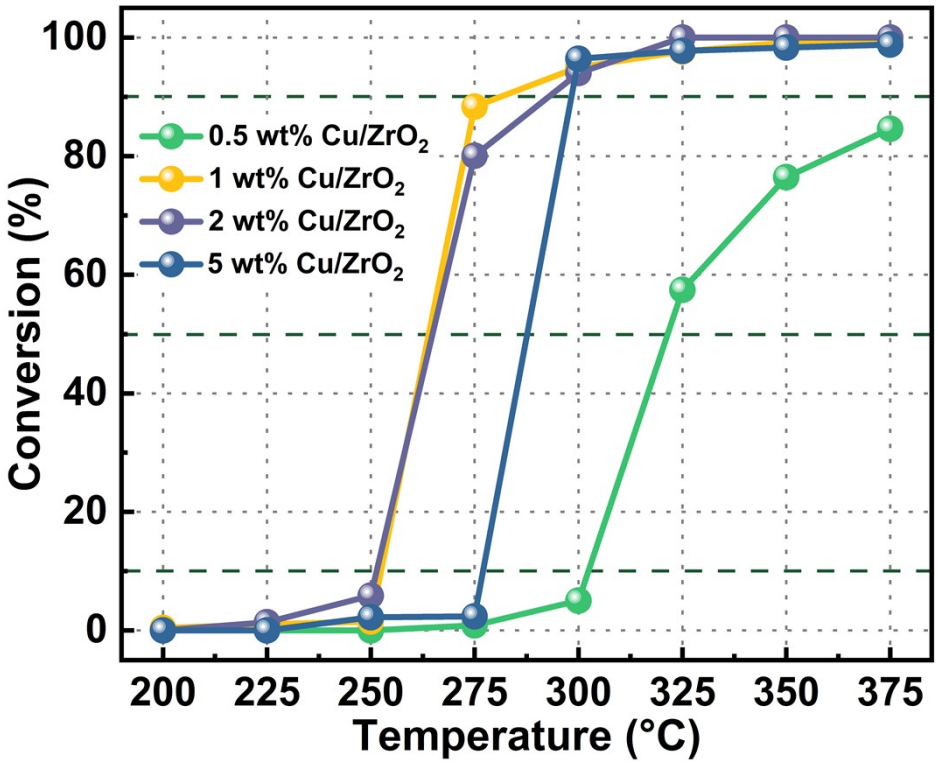

Figure S1. Toluene conversion as a function of reaction temperature over Cu/ZrO_2 catalysts with different Cu loadings.

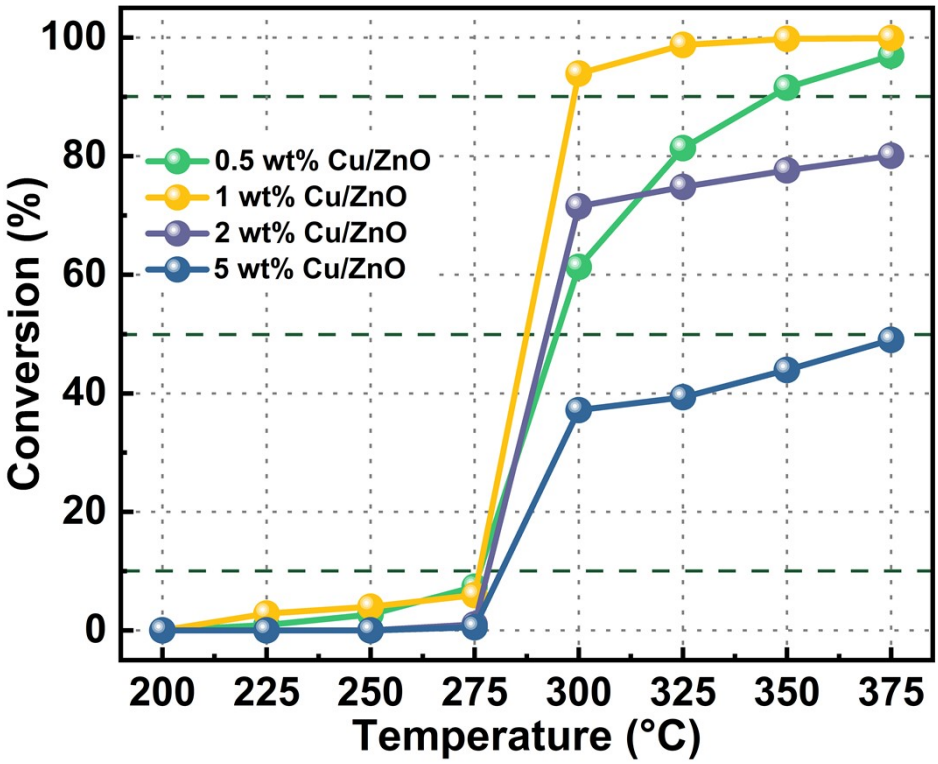

Figure S2. Toluene conversion as a function of reaction temperature over Cu/ZnO catalysts with different Cu loadings.

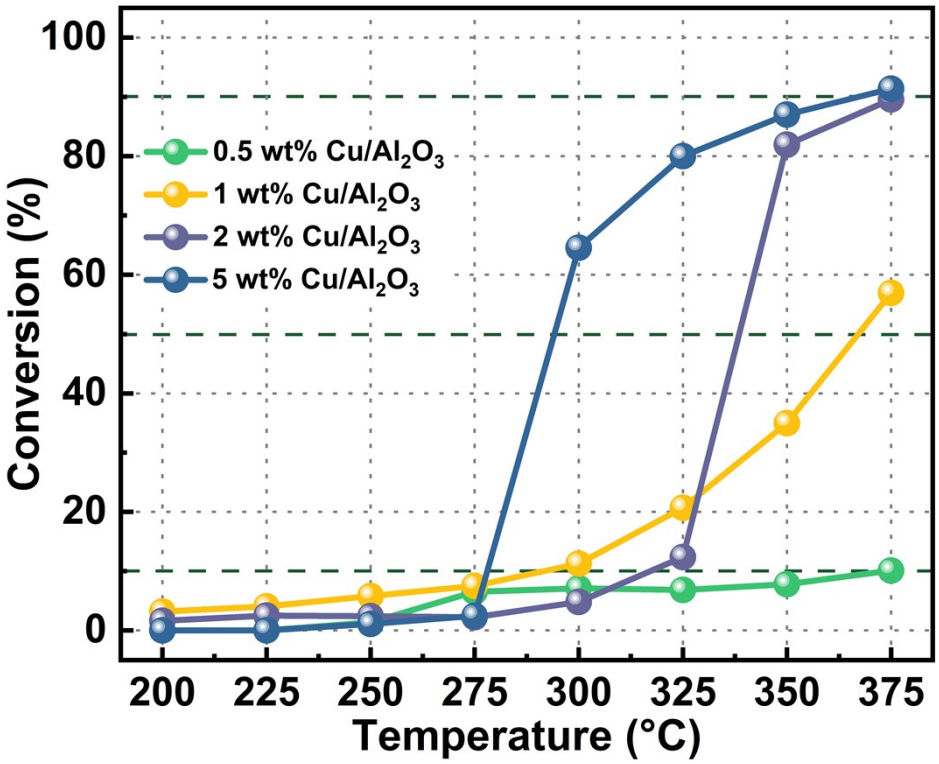

Figure S3. Toluene conversion as a function of reaction temperature over Cu/Al_2O_3 catalysts with different Cu loadings.

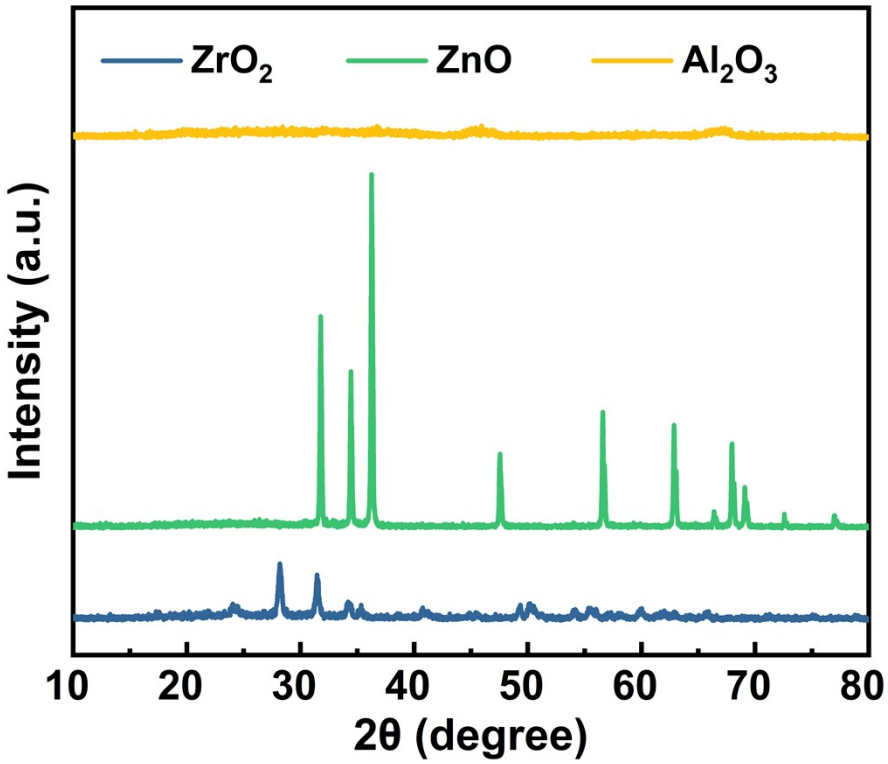

Figure S4. XRD patterns of the ZrO_2, ZnO, and Al_2O_3 supports.

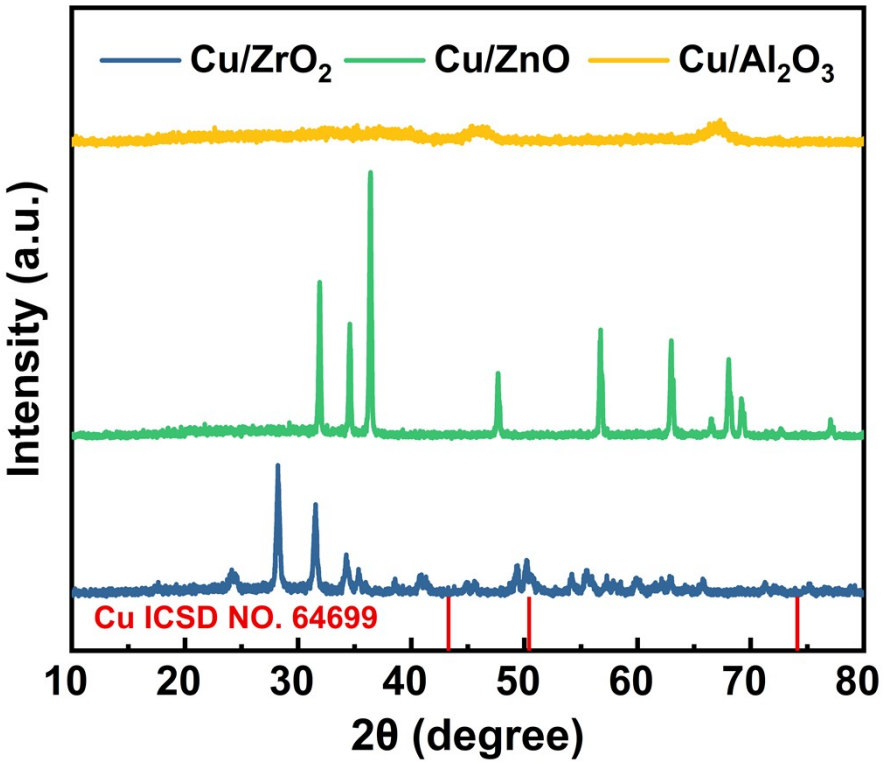

Figure S5. XRD patterns of the Cu/ZrO_2, Cu/ZnO, and Cu/Al_2O_3 catalysts.

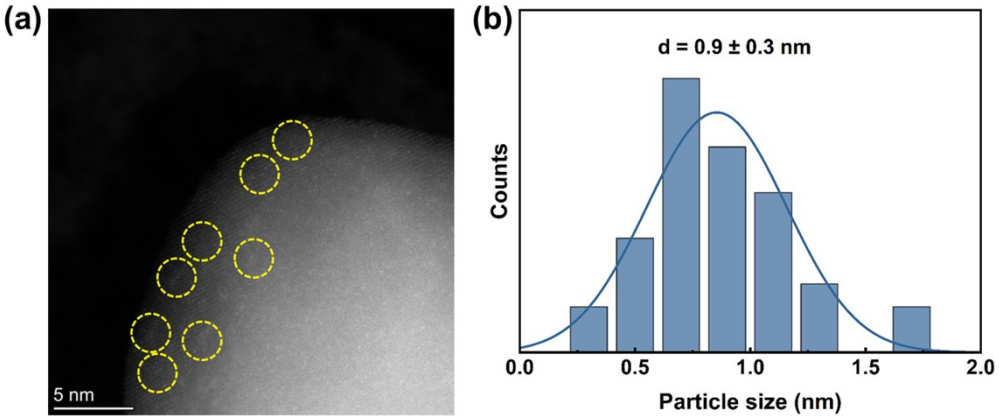

Figure S6. (a) HAADF-STEM images of the Cu/ZrO_2 catalyst and (b) the corresponding histogram of the particle size distributions.

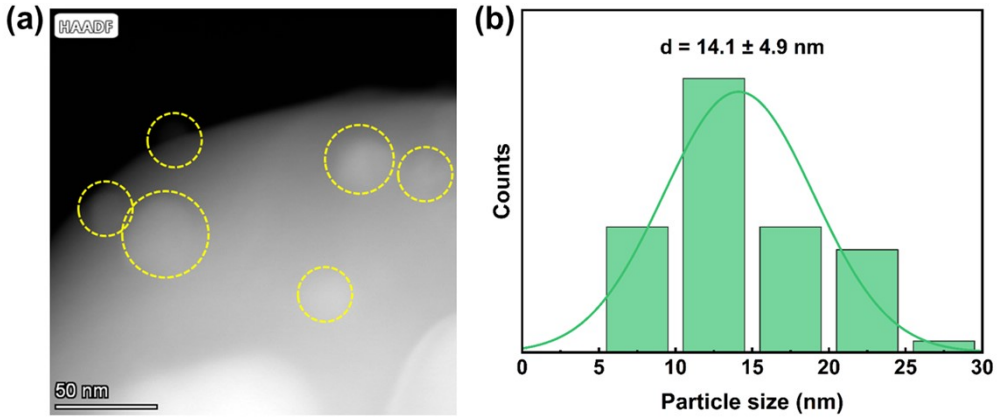

Figure S7. (a) HAADF-STEM images of the Cu/ZnO catalyst and (b) the corresponding histogram of the particle size distributions.

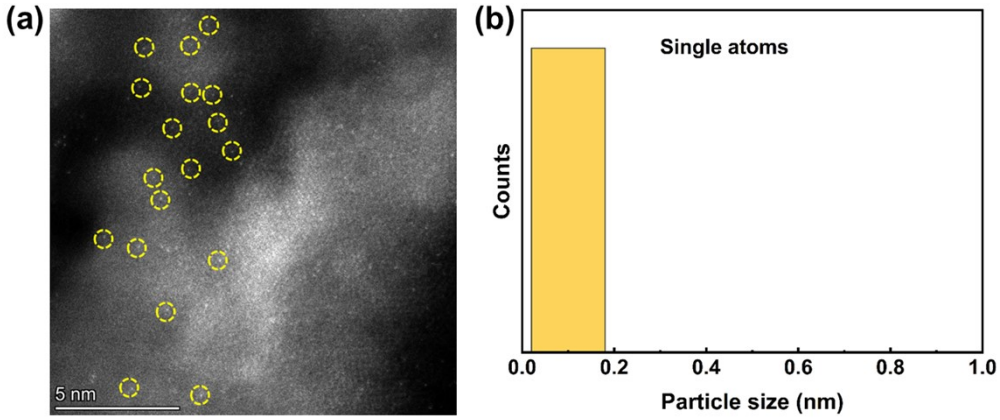

Figure S8. (a) HAADF-STEM images of the Cu/Al_2O_3 catalyst and (b) the corresponding histogram of the particle size distributions.

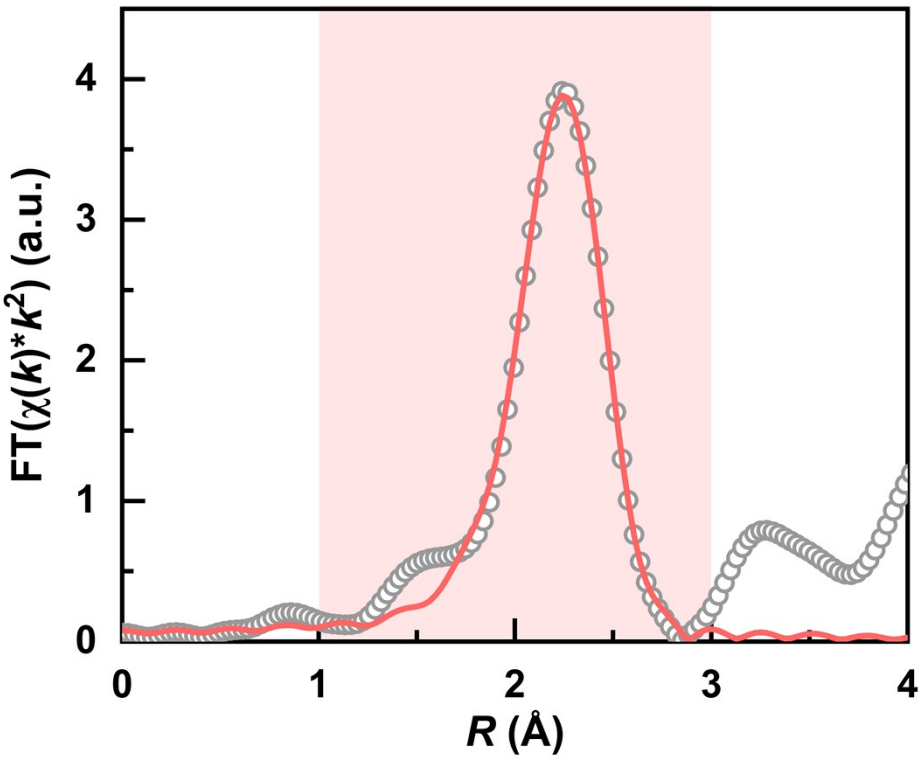

Figure S9. Fourier transforms of the experimental and fitted EXAFS spectra of Cu foil at Cu K-edge.

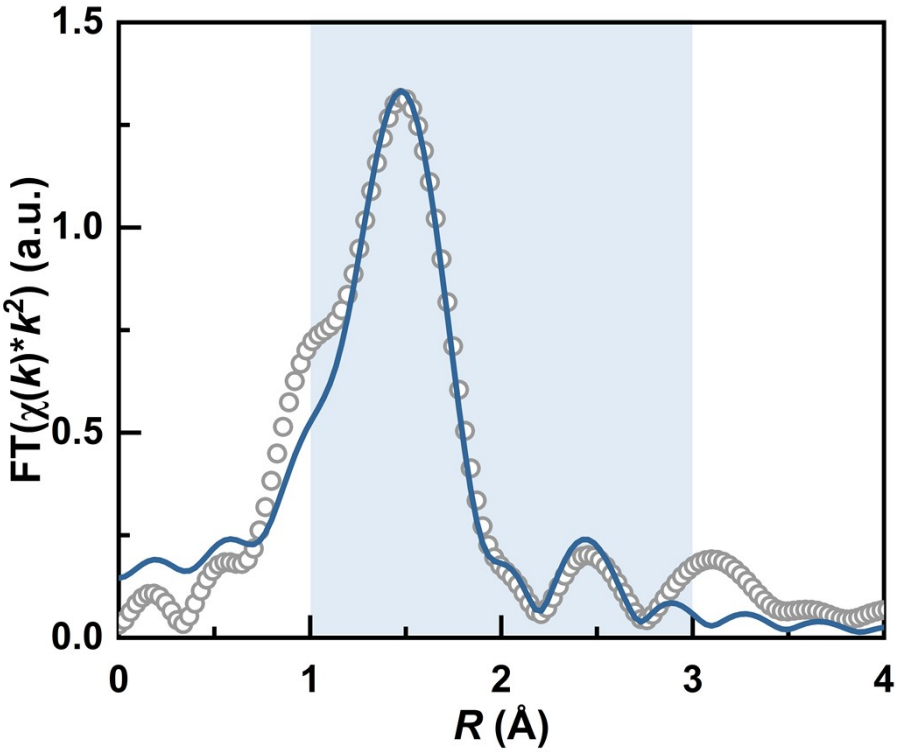

Figure S10. Fourier transforms of the experimental and fitted EXAFS spectra of the Cu/ZrO_2 catalyst at Cu K-edge.

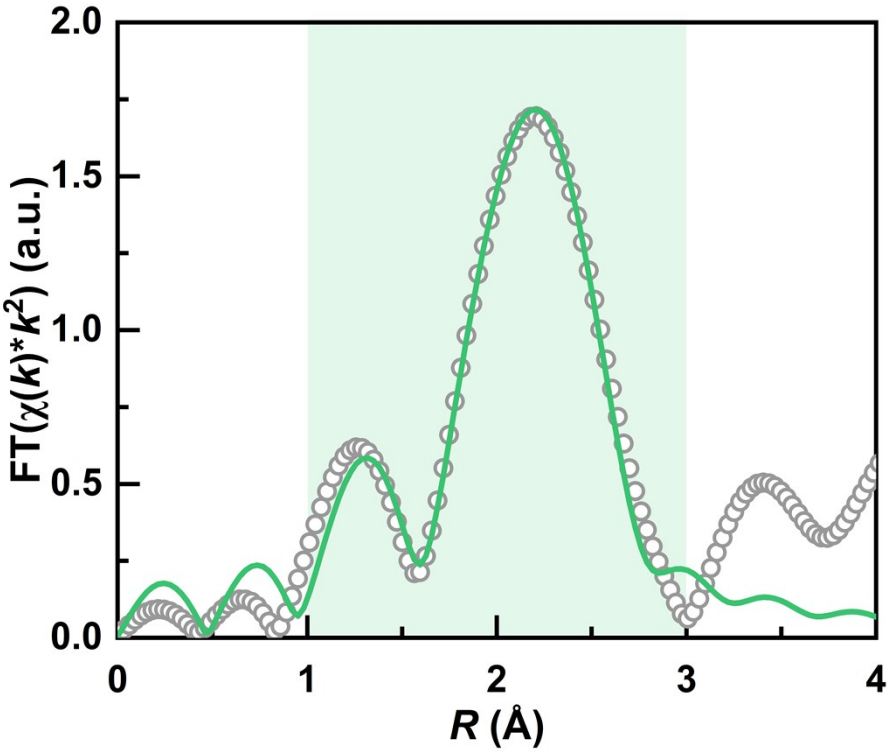

Figure S11. Fourier transforms of the experimental and fitted EXAFS spectra of the Cu/ZnO catalyst at Cu K-edge.

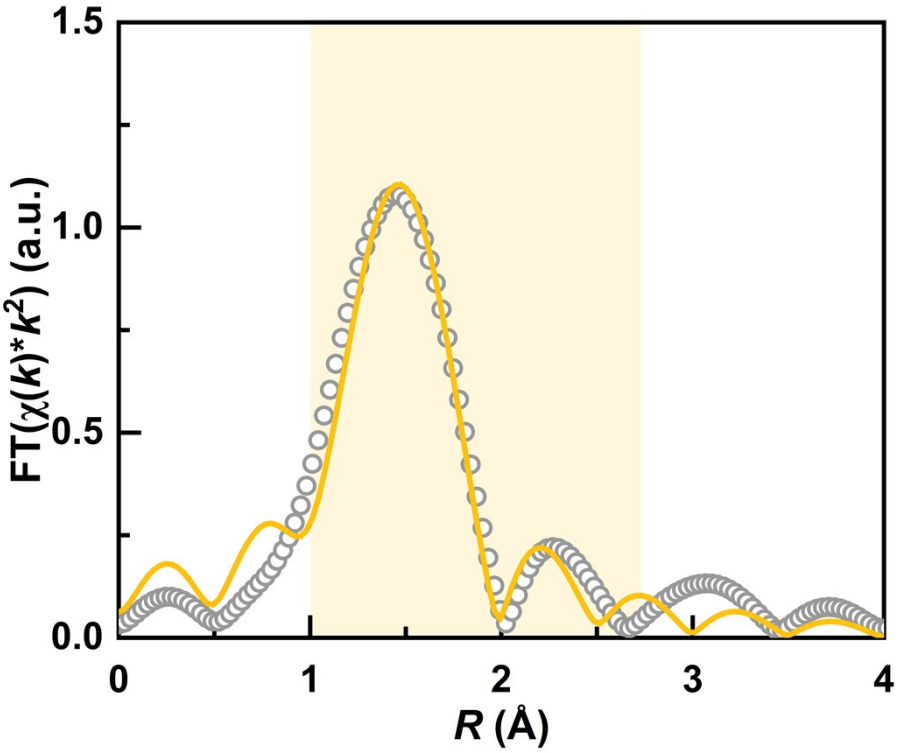

Figure S12. Fourier transforms of the experimental and fitted EXAFS spectra of the Cu/Al_2O_3 catalyst at Cu K-edge.

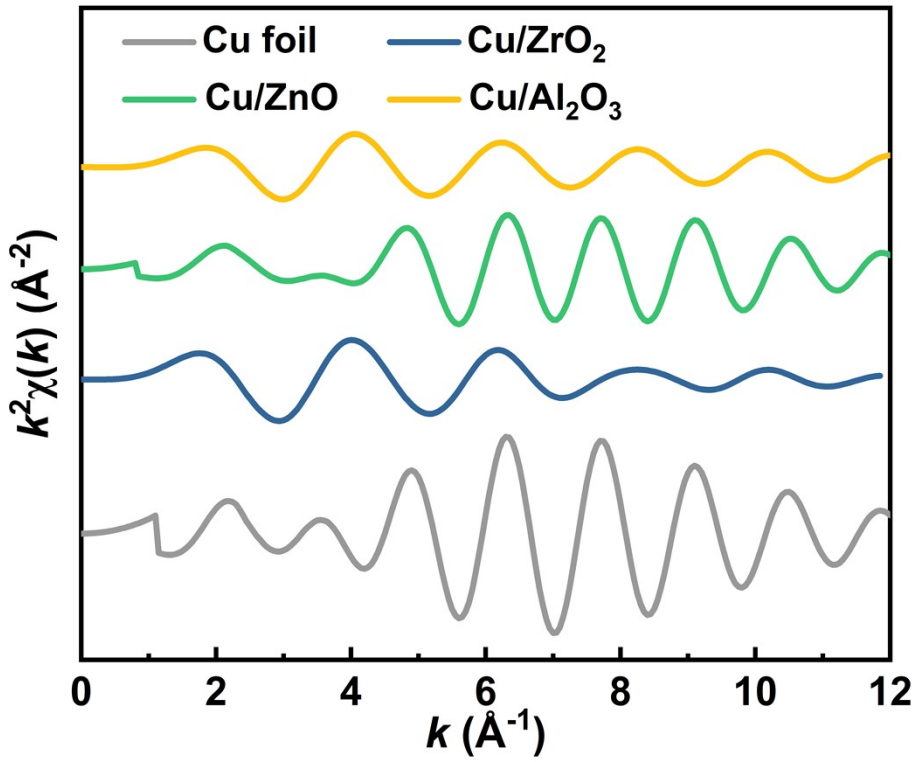

Figure S13. The EXAFS oscillation functions at the Cu K-edge of Cu foil, Cu/ZrO_2, Cu/ZnO, and Cu/Al_2O_3 catalysts.

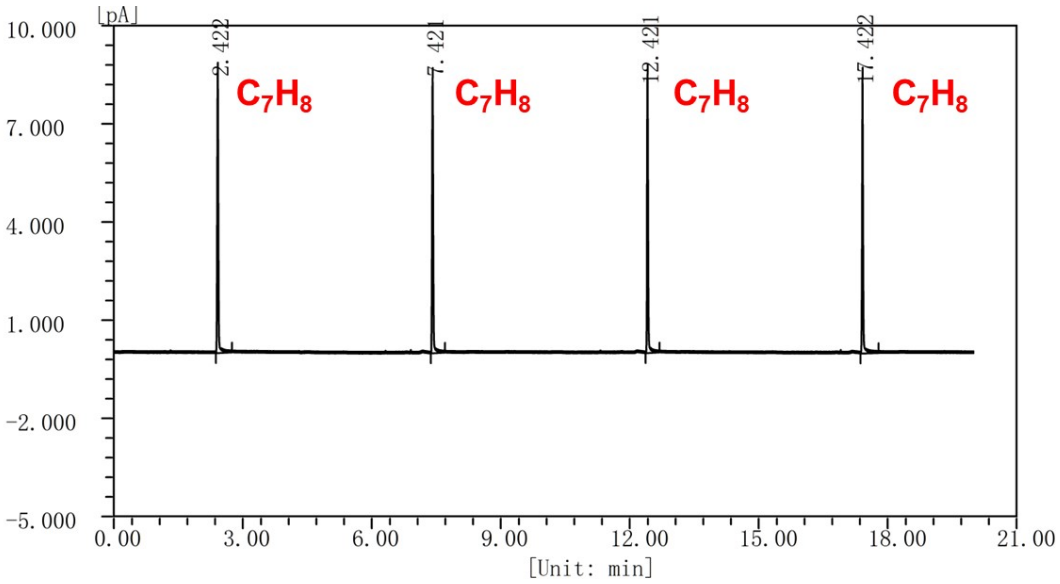

Figure S14. FID spectrogram analysis of toluene oxidation.

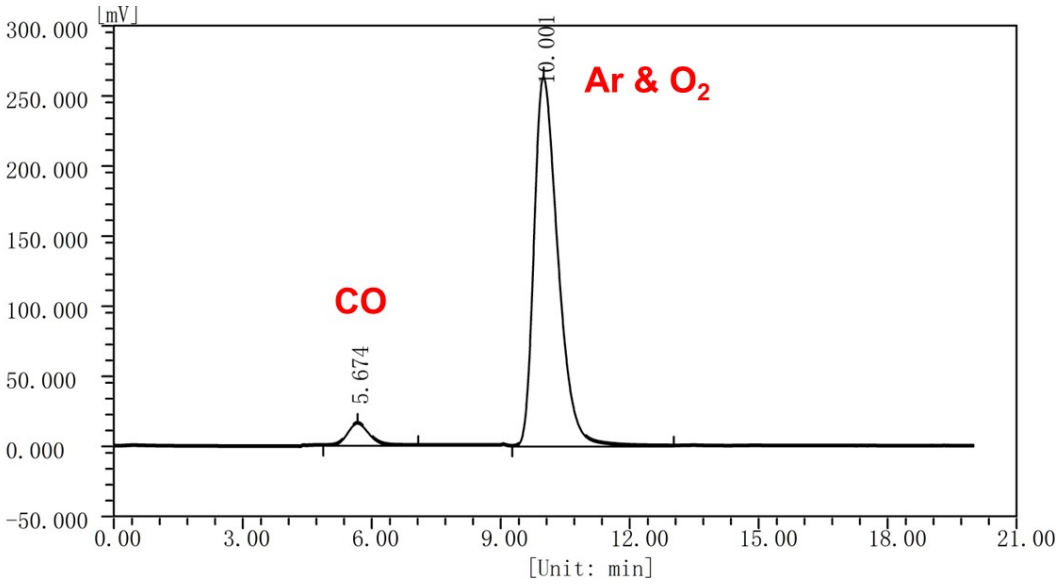

Figure S15. TCD spectrogram analysis of toluene oxidation.

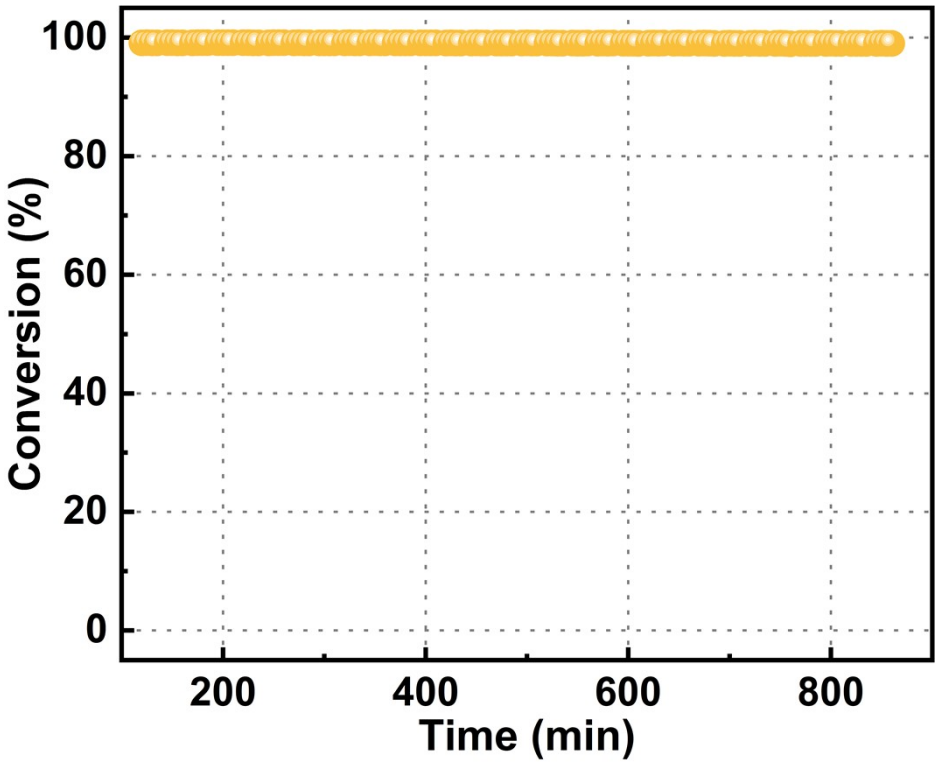

Figure S16. Toluene conversion as a function of reaction time over the Cu/ZrO_2 catalyst at 300 °C.