# Supporting Information

# Active Sites and Structure-activity Relationships of Copper-based Catalysts for Carbon Dioxide Hydrogenation to Methanol

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**XRD:**

Rietveld refinements of the diffraction data collected after in situ reduction at 250 $^{o}$C were performed using the PANalytical's X'Pert Highscore Plus software. A silicon standard with neither size nor strain broadening (NIST 640B) was used to determine the instrument contribution to peak broadening. Pattern refinements were carried out multiple times with varying parameters (e.g., excluded regions, multiple crystalline phases, size only, strain only) and the best fits were obtained when both size and strain were refined together. The region from 25° to 35°, that contains peaks from phases which become amorphous, was excluded from refinements and the only refined crystalline component was Cu metal. Based upon these refinements, values for particle size and microstrain were determined from the parameters of the pseudo-Voigt function that was used to model the peak shape, specifically the full width at half maximum (FWHM). This method was applied to a whole pattern and therefore the size and strain were modeled isotropically. Table S1 shows refined and derived parameters determined by Rietveld refinements for all catalysts. R-factors are useful indicators for the quality of the fit of the structural model to the data. In particular, RBragg relates to the refined phase (copper metal) while Rprofile relates to the overall fit of the pattern.[1] The fits are very good when RBragg is between 2-3%.[2] Figure S1 compares the measured XRD data with the patterns simulated by the Rietveld method for the reduced CuZr and CuZnZrGaY catalysts.

**XPS:**

Table S2 summarizes the Cu $2p_{3/2}$ binding and Cu(LMM) kinetic energies for various catalysts. The Cu $2p_{3/2}$ BE of the calcined samples is in the range of 933.2-933.9 eV and decreases to 931.2-931.8 eV after reduction and reaction. On the other hand, the Cu(LMM) KE for the reduced catalysts increases to 919.0-919.9 eV compared to the values of the calcined samples. After exposure to 25% $CO_2/H_2$, the KE of the Cu(LMM) peak remains constant or

increases further by up to 1.0 eV. Our KE values agree well with those reported for $Cu^0$ species on the surface of copper-containing catalysts.[3-6] Alternatively, the modified Auger parameter ($\alpha_{Cu}$ = hν + KE ($Cu_{LMM}$) - KE (Cu $2p_{3/2}$) = KE ($Cu_{LMM}$) + BE (Cu $2p_{3/2}$)) can be employed to differentiate $Cu^0$ (1850.6-1851.6 eV) from $Cu^+$ species (1848.6-1849.5 eV).[7-17] As also displayed in Table S1, the values of the modified Auger parameter for the reduced and post-reaction catalysts are 1850.7-1851.3 eV, which again corresponds to $Cu^0$ species. Figures S2-S6 show corresponding Cu 2p XPS and Cu(LMM) Auger spectra for the other 5 catalysts after being subject to different treatments.

**Table S1. Refined and Derived Parameters Determined by Rietveld Refinements for All Catalysts. Error Values are Shown in the Parentheses**

| | CuZr | CuZn | CuZnZr | CuZnZrGa | CuZnZrY | CuZnZrGaY |
|---|---|---|---|---|---|---|
| Refined Data | | | | | | |
| Zero Shift | -0.058185 (0.004) | -0.097555 (0.02) | -0.071164 (0.01) | -0.104327 (0.02) | -0.103151 (0.02) | -0.088580 (0.02) |
| Coefficient 1 | -3.363675 (0.2) | 5.455194 (0.6) | 0.412694 (0.3) | -0.362171 (0.2) | -0.578397 (0.2) | -0.361045 (0.2) |
| Coefficient 2 | 0.002255 (0.003) | -0.117406 (0.009) | -0.051478 (0.003) | -0.045900 (0.002) | -0.042858 (0.002) | -0.042243 (0.002) |
| Coefficient 3 | 0.000088 (0.00001) | 0.000527 (0.00004) | 0.000285 (0.00002) | 0.000278 (0.00001) | 0.000266 (0.00001) | 0.000260 (0.00001) |
| Cu Profile U | 0.311306 (0.04) | 0.754244 (0.3) | 1.231666 (0.2) | 2.448439 (0.6) | 2.669091 (0.3) | 1.471194 (0.4) |
| Cu Profile W | 0.005184 (0.007) | 0.755899 (0.07) | 0.256203 (0.03) | 0.994333 (0.1) | 0.916010 (0.06) | 0.967175 (0.08) |
| Cu Peak Shape 1 | 1.357388 (0.07) | 0.124648 (0.1) | 0.761176 (0.08) | 0.437901 (0.09) | 0.562507 (0.09) | 0.150716 (0.1) |
| Cu Peak Shape 2 | -0.002469 (0.001) | 0.007487 (0.002) | 0.002529 (0.001) | 0.007797 (0.002) | 0.006625 (0.002) | 0.010514 (0.002) |
| Derived Data | | | | | | |
| Microstrain (%) | 0.206 | 0.588 | 0.366 | 0.313 | 0.491 | 0.264 |
| Crystallite Size (Å) | 27913.4 (bulk) | 190.0 | 176.2 | 126.9 | 92.5 | 90.0 |
| R Bragg (phase) | 4.99 | 2.26 | 3.50 | 3.04 | 1.42 | 1.64 |
| R expected | 4.26192 | 3.94554 | 4.23540 | 4.57201 | 4.61598 | 4.68725 |
| R profile | 4.47743 | 3.31932 | 4.75871 | 4.35663 | 4.45849 | 4.54761 |
| Weighted R profile | 5.95120 | 4.20496 | 6.34797 | 5.46874 | 5.57409 | 5.67595 |
| D-statistics | 0.22211 | 0.75496 | 0.41530 | 0.70363 | 0.71649 | 0.68911 |
| Weighted D-statistics | 0.54512 | 0.91635 | 0.48288 | 0.74227 | 0.74685 | 0.72330 |
| Goodness of Fit | 1.94984 | 1.13582 | 2.24637 | 1.43074 | 1.45821 | 1.46636 |

**Figure S1.** Experimental and simulated XRD patterns of (a) CuZr (b) CuZnZrGaY. The dashed box shows the excluded region from refinements.

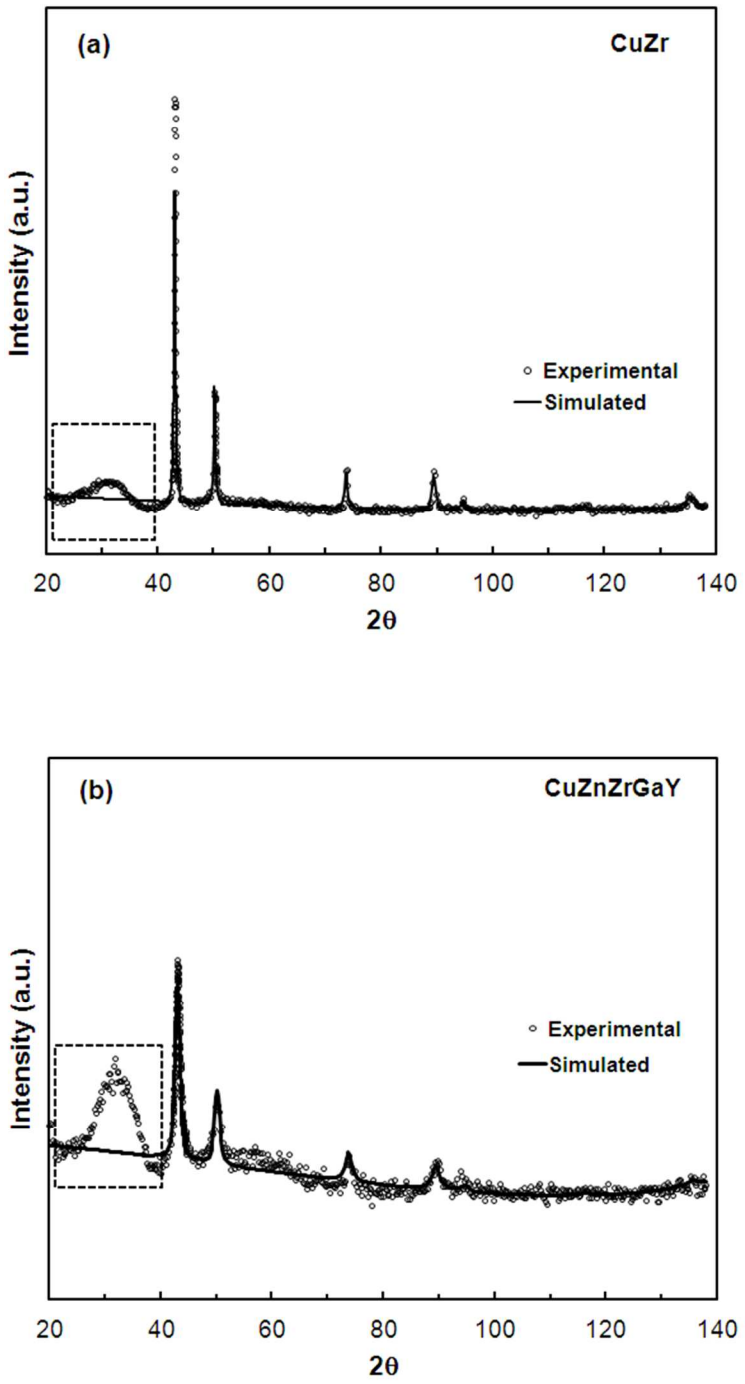


**Table S2. XPS Results for Treated Catalysts**

| Catalyst | Treatment | Cu $2p_{3/2}$ BE (eV) | Cu(LMM) KE (eV) | $\alpha_{Cu}$ (eV) |
|---|---|---|---|---|
| CuZr | Calcination | 933.8 | 917.5 | |
| | Reduction | 931.2 | 919.9 | 1851.1 |
| | Post-reaction | 931.2 | 919.9 | 1851.1 |
| CuZn | Calcination | 933.2 | 917.9 | |
| | Reduction | 931.8 | 919.5 | 1851.3 |
| | Post-reaction | 931.6 | 919.6 | 1851.2 |
| CuZnZr | Calcination | 933.6 | 917.8 | |
| | Reduction | 931.7 | 919.0 | 1850.7 |
| | Post-reaction | 931.7 | 919.6 | 1851.3 |
| CuZnZrGa | Calcination | 933.8 | 917.6 | |
| | Reduction | 931.5 | 919.6 | 1851.1 |
| | Post-reaction | 931.3 | 919.8 | 1851.1 |
| CuZnZrY | Calcination | 933.9 | 917.2 | |
| | Reduction | 931.7 | 919.0 | 1850.7 |
| | Post-reaction | 931.3 | 920.0 | 1851.3 |
| CuZnZrGaY | Calcination | 933.8 | 917.3 | |
| | Reduction | 931.7 | 919.3 | 1851.0 |
| | Post-reaction | 931.4 | 919.6 | 1851.0 |

**Figure S2.** Spectra for the CuZr catalyst after different treatments: (a) Cu 2p XPS (b) Cu(LMM) Auger.

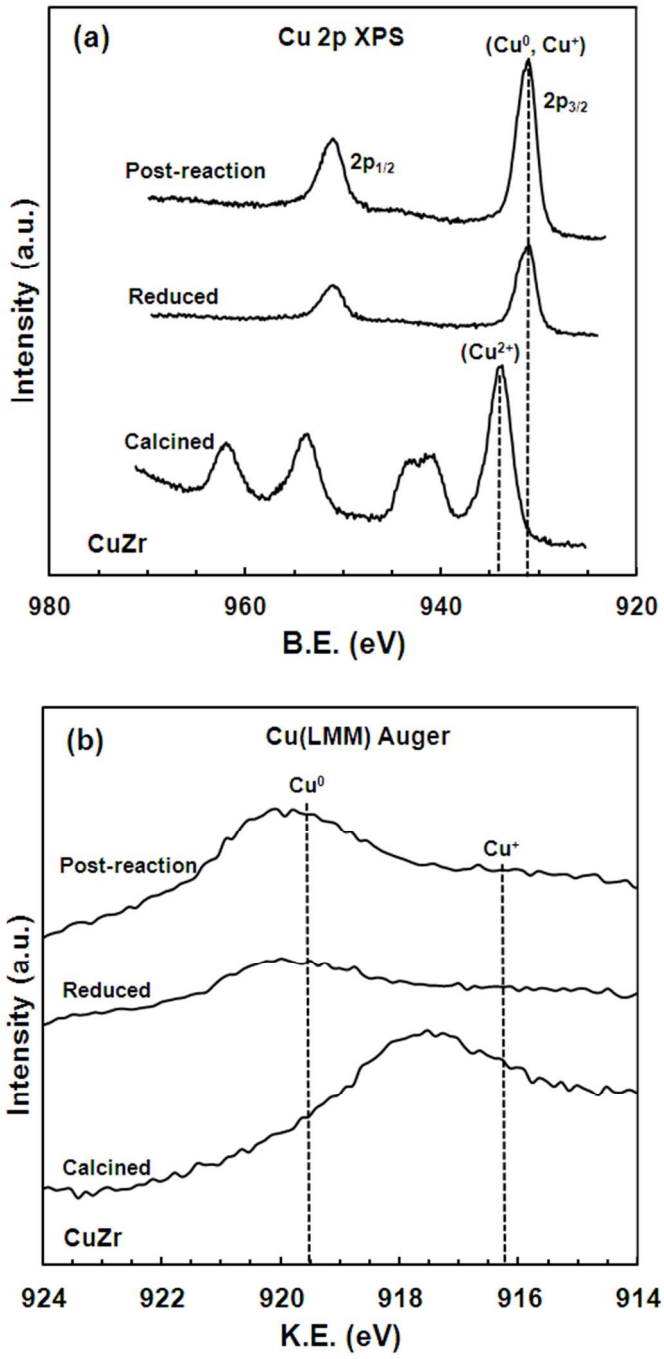


**Figure S3.** Spectra for the CuZn catalyst after different treatments: (a) Cu 2p XPS (b) Cu(LMM) Auger.

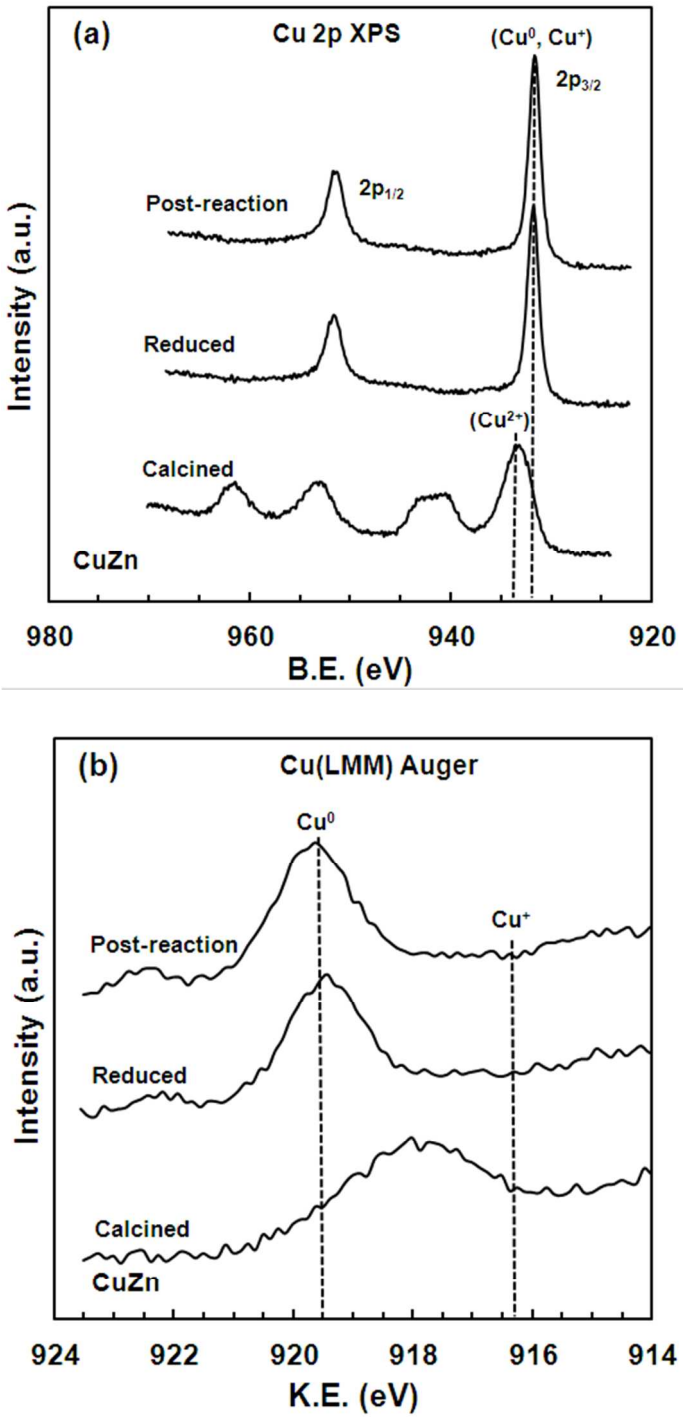


**Figure S4.** Spectra for the CuZnZr catalyst after different treatments: (a) Cu 2p XPS (b) Cu(LMM) Auger.

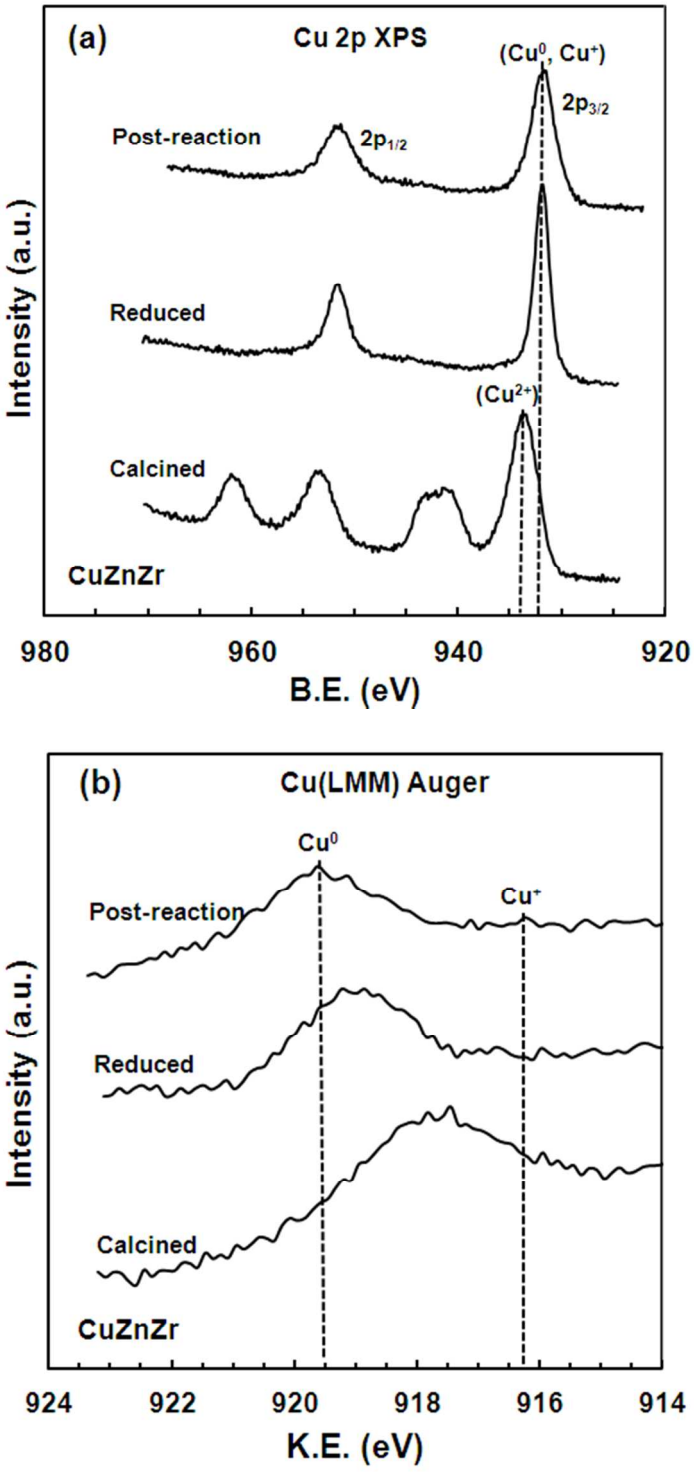


**Figure S5.** Spectra for the CuZnZrGa catalyst after different treatments: (a) Cu 2p XPS (b) Cu(LMM) Auger.

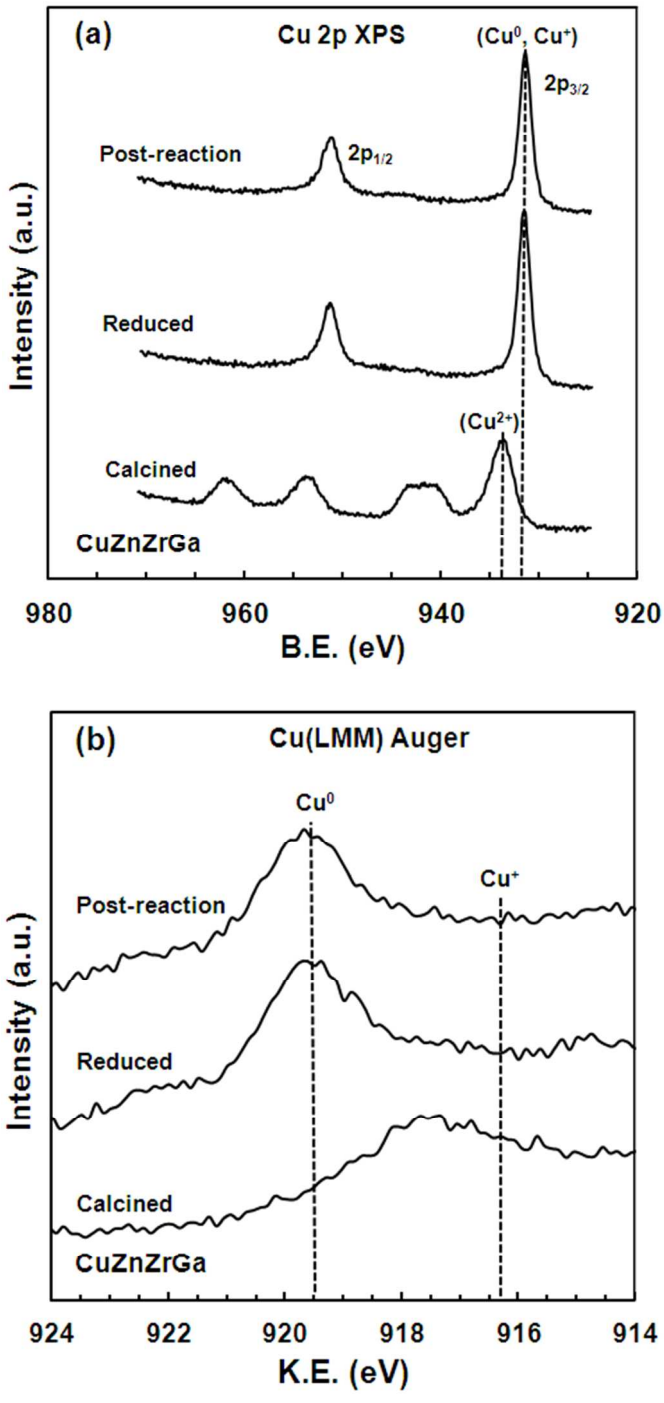
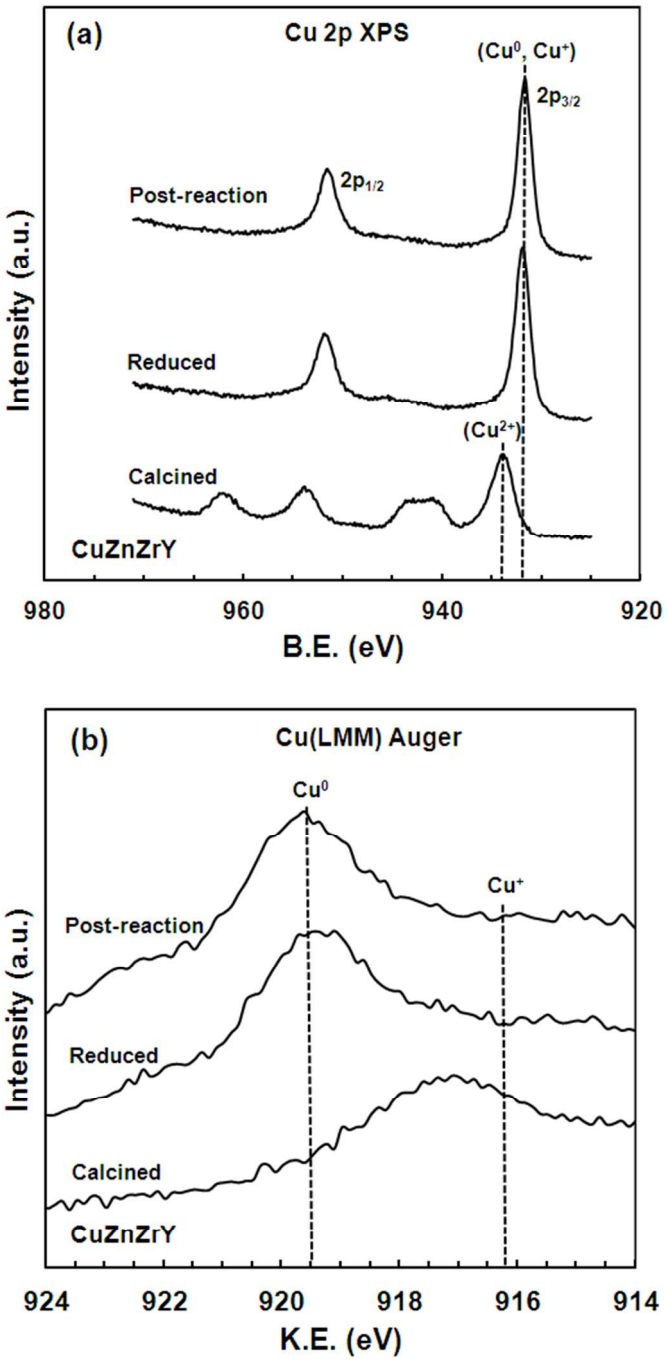


**Figure S6.** Spectra for the CuZnZrY catalyst after different treatments: (a) Cu 2p XPS (b) Cu(LMM) Auger.



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