

Supporting Information

Increasing the activity of the Cu/CuAl₂O₄/Al₂O₃ catalyst for the RWGS through preserving the Cu²⁺ ions

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Methods and Experiments

Catalyst Preparation:

The catalysts were prepared using the wet impregnation method. For the catalyst with the protective silica layer, the impregnation was followed by an aqueous phase silica layer deposition. Typically, γ -alumina (Merck) was impregnated with 1 wt% Cu using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (ABCR) in an aqueous solution as the precursor. The details of the impregnation method can be found elsewhere.¹ For the silica layer deposition, 1 g of the supported γ - Al_2O_3 was dispersed in a mixture of 40 mL methanol, 1 mL H_2O and 0.04 mL NH_3 (25 wt%). The supported γ - Al_2O_3 suspension was stirred and refluxed while keeping the solution at 55 °C. Then 1.1 mL of tetramethyl orthosilicate was injected into the refluxed suspension at a rate of 0.5 mL·h⁻¹ using a KDS 100 legacy syringe pump. 1 h after the injection was completed, the powder was separated by centrifugation (5 min, 4500 rpm). The powder was then washed twice by re-dispersing it with ethanol and then removing the liquid using centrifugation. The washing step was subsequently repeated with water. Finally, the product was dried in a vacuum oven at 45 °C for 8 h. Calcination was done at 900 °C for 6 h. Subsequently, the silica layer was removed by treatment with an NaOH solution to free the Cu on the surface. Typically, 1 g of catalyst was treated with 50 mL 1M solution of NaOH for 1 h at room temperature. The catalyst was then separated by centrifugation and washed multiple times to ensure no Na was retained on the catalyst surface. The NaOH solution was tested for the potential presence of Al using ICP-OES. A control sample (clean 1M NaOH solution) and the main sample (in which the catalyst was treated) were compared. No Al was found in both the pure NaOH solution and the main sample, confirming that Al was not leached from the catalyst.

Catalyst activity test:

For the catalytic tests, 100 mg of catalyst were placed between two quartz wool plugs in a fixed-bed quartz reactor. The catalysts were first activated under Ar flow at 300 °C for 30 min. The temperature was then ramped up to 450 °C. The gas flow was switched to the feed gas stream after the desired temperature was reached. The reactor was working at atmospheric pressure for all catalytic tests. During the reaction, a 70 mL·min⁻¹ flow of Ar, CO_2 and H_2 (Ar: CO_2 : H_2 = 50:5:15) was used, and the product stream was monitored using an online MATRIX-MG01 FTIR spectrometer (Bruker) equipped with OPUS-GA software and a 10 cm gas cell heated at 120 °C.

Catalyst Characterization:

The Brunauer-Emmett-Teller (BET) surface, Barrett-Joyner-Halenda (BJH) mesoporous and DFT microporous volumes were calculated from N_2 -physisorption measurements on a Micromeritics 3Flex apparatus at liquid nitrogen temperature between 10⁻⁵ and 0.99 relative N_2 pressure. Samples (ca. 100 mg)

were dried at 120 °C (temperature reached with a ramp of 2 °C·min⁻¹) under vacuum (< 10⁻³ mbar) for 4 h and a leak test was performed prior to analysis.

Temperature Programmed Reduction (TPR) was performed on a Micromeritics Autochem 2920 II instrument. Typically, the sample (ca. 100 mg) was loaded into a U-shaped cell and dried for 30 min under He flow (50 mL·min⁻¹) at 150 °C (5 °C·min⁻¹). After cooling down to 100 °C, the flow was switched to a 10:90 (volumetric ratio) H₂:Ar mixture and the temperature was ramped to 800 °C (with a 10 °C·min⁻¹ ramp). During this process, H₂ consumption was monitored using a calibrated thermal conductivity detector.

Elemental analyses by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) were performed at the EPFL Central Environmental Laboratory on an ICPE-9000 Multi-type Shimadzu instrument. From these measurements, the copper weight percentages of the samples were measured, which are presented in Table S1.

High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) was conducted on a FEI Talos with 200 kV acceleration voltage in the Z contrast mode. Samples were dispersed in ethanol and placed on a carbon coated grid. Energy-Dispersive X-ray Spectroscopy (EDXS) analysis was performed using Bruker Esprit software. For the particle size distribution, 20 images were taken and about 100 particles were investigated. ImageJ software was used to analyse the particle size distribution.

X-ray diffraction data were collected in Bragg Brentano geometry on a D8 Bruker Discover diffractometer equipped with a non-monochromated Cu-source and a LynxEye XE detector.

X-ray photoelectron (XP) spectra were acquired using a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany). Measurements were done using a monochromatic X-ray source of 24.8 W power and a beam diameter of 100 µm. The spherical capacitor analyzer was set to the take-off angle of 45° relative to the sample surface.

The EPR measurements were performed at room temperature using a Bruker EleXsys E500 Xband EPR spectrometer, equipped with a high-Q cylindrical cavity, Model ER 4122 SHQE (from Bruker BioSpin GmbH, Germany).

The TPSR tests were conducted in the same setup as the catalytic activity tests. For the test without pre-reduction, the catalyst was activated at 300 °C under 50 mL·min⁻¹ flow of Ar. The temperature was then set to 100 °C and the gas flow was switched to the same gas composition as the catalytic test. The temperature was then ramped up at 10 °C·min⁻¹ to 400 °C. For the test with pre-reduction, the same

procedure was used except for the activation process. In this case, the catalyst was reduced under 20% H₂/Ar flow at 450 °C for 30 min.

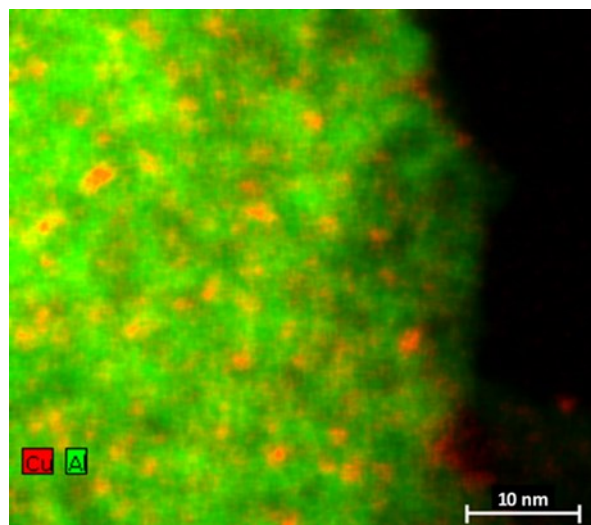


Figure S1. STEM EDXS image of the CuAl-900 catalyst.

Table S1. Comparison of catalyst selectivities and initial CO₂ conversion rates.

Catalysts	Temperature (K)	Selectivity (%)	Rate ($\cdot 10^{-5}$ mol CO ₂ ·g _{cat} ⁻¹ ·s ⁻¹)	Rate/metal loading ($\cdot 10^{-5}$ mol CO ₂ ·g _{metal} ⁻¹ ·s ⁻¹)	Ref.
CuAlSi-900	723	100	0.3	27.6	this work
Pd-Fe/SiO₂	723	97.2	0.3	2.6	2
Cu-Fe/SiO₂	873	NA	3.7	35.4	3
Cu/ZnO/Al₂O₃	873	~100	7.6	18.1	4
PtCo/TiO₂	573	99	0.6	17.8	5
CuAl₂O₄	873	100	0.5	1.5	4
Au/TiO₂	673	100	0.3	25.9	6
Au/Al₂O₃	673	100	0.1	8.1	6
CuO/CeO₂	673	100	0.5	2.4	7

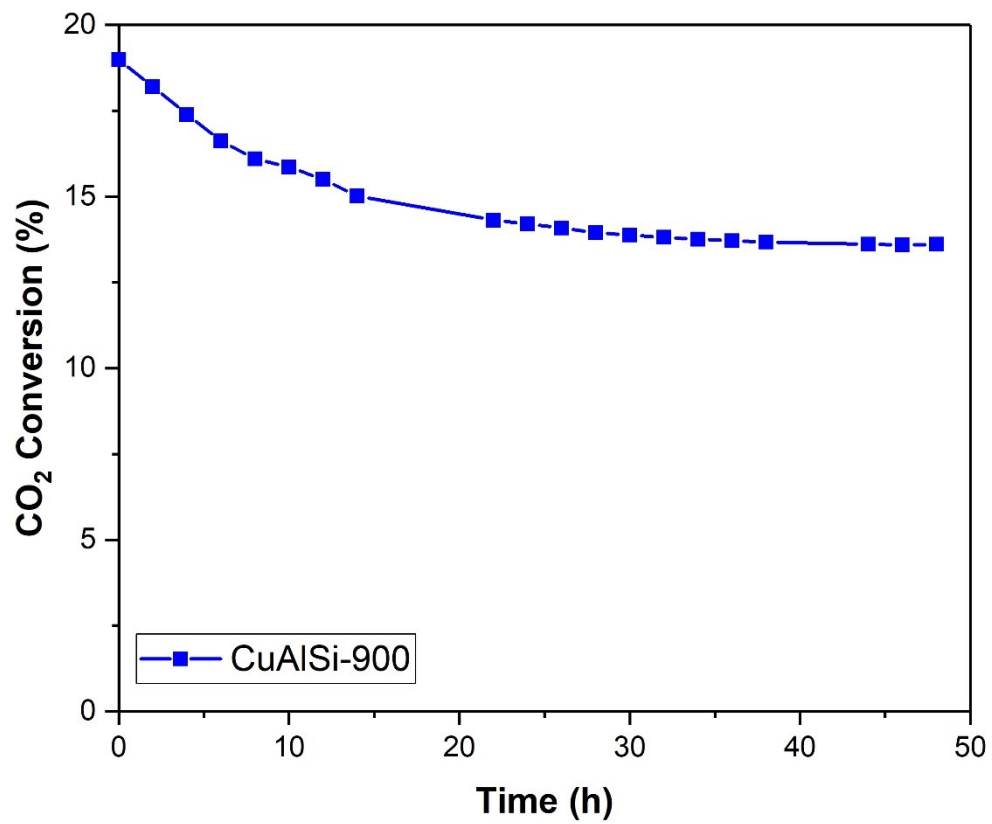


Figure S2. Stability test for CuAlSi-900 catalyst. T = 450 °C, P = 1atm, catalyst = 0.1 g.

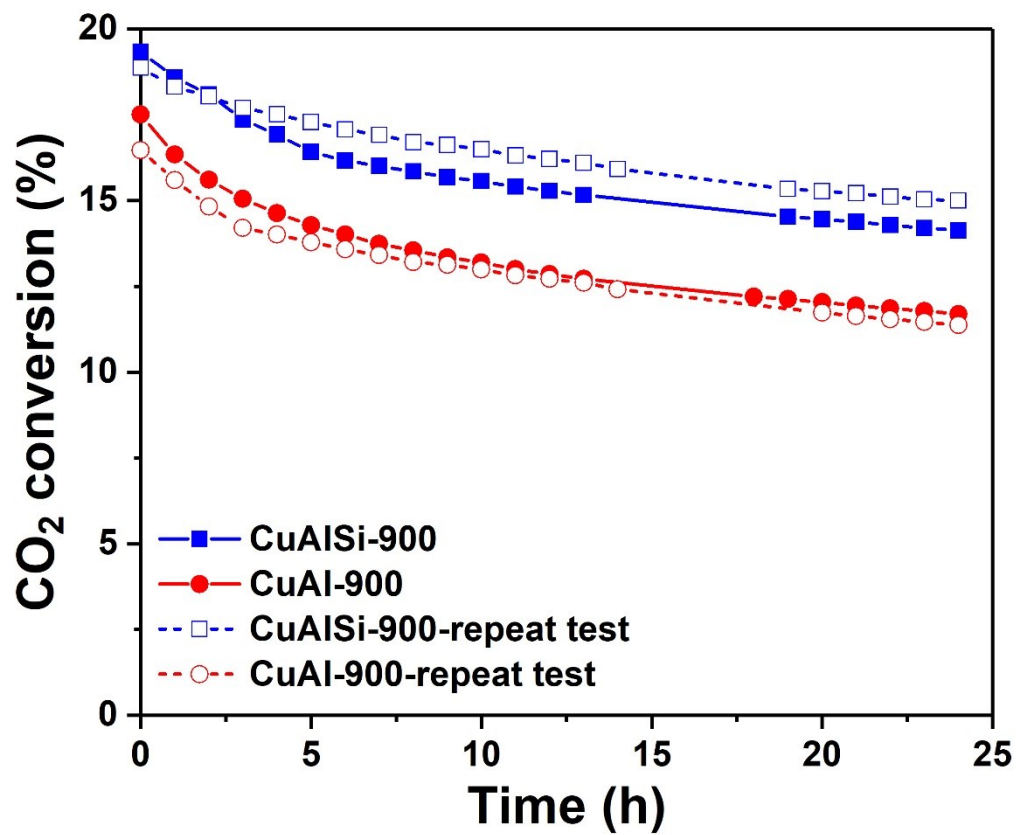


Figure S3. Reproducibility of the activity test for CuAl-900 and CuAlSi-900 catalysts.

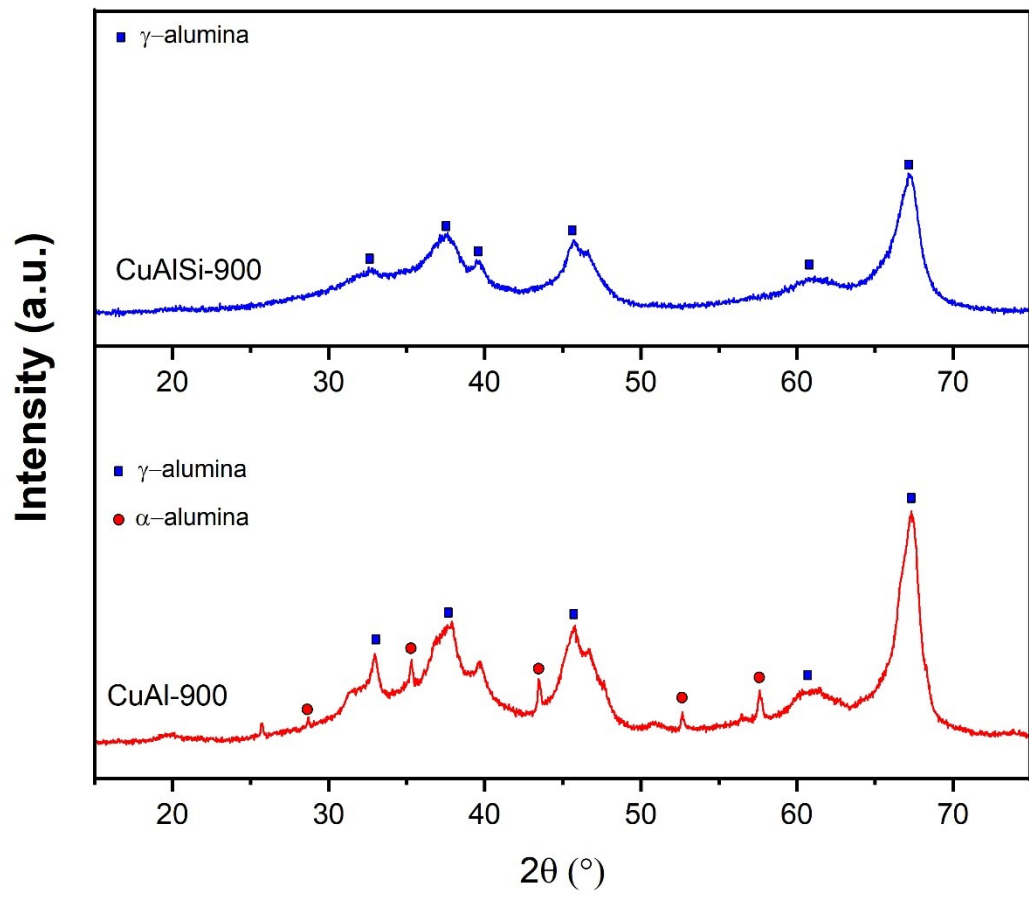


Figure S4. XRD patterns for CuAl-900 and CuAlSi-900 catalysts.

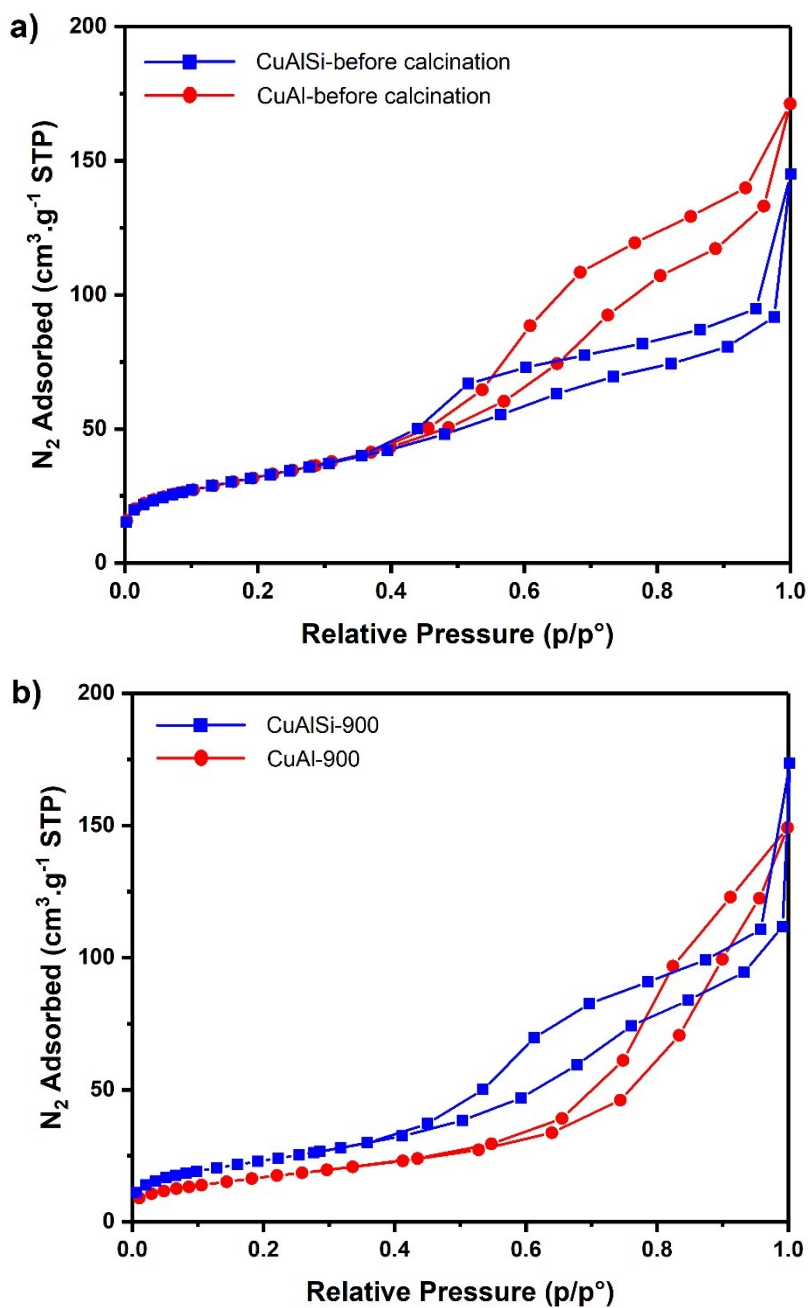


Figure S5. Isotherms of the CuAl and CuAlSi catalysts a) before and b) after calcination.

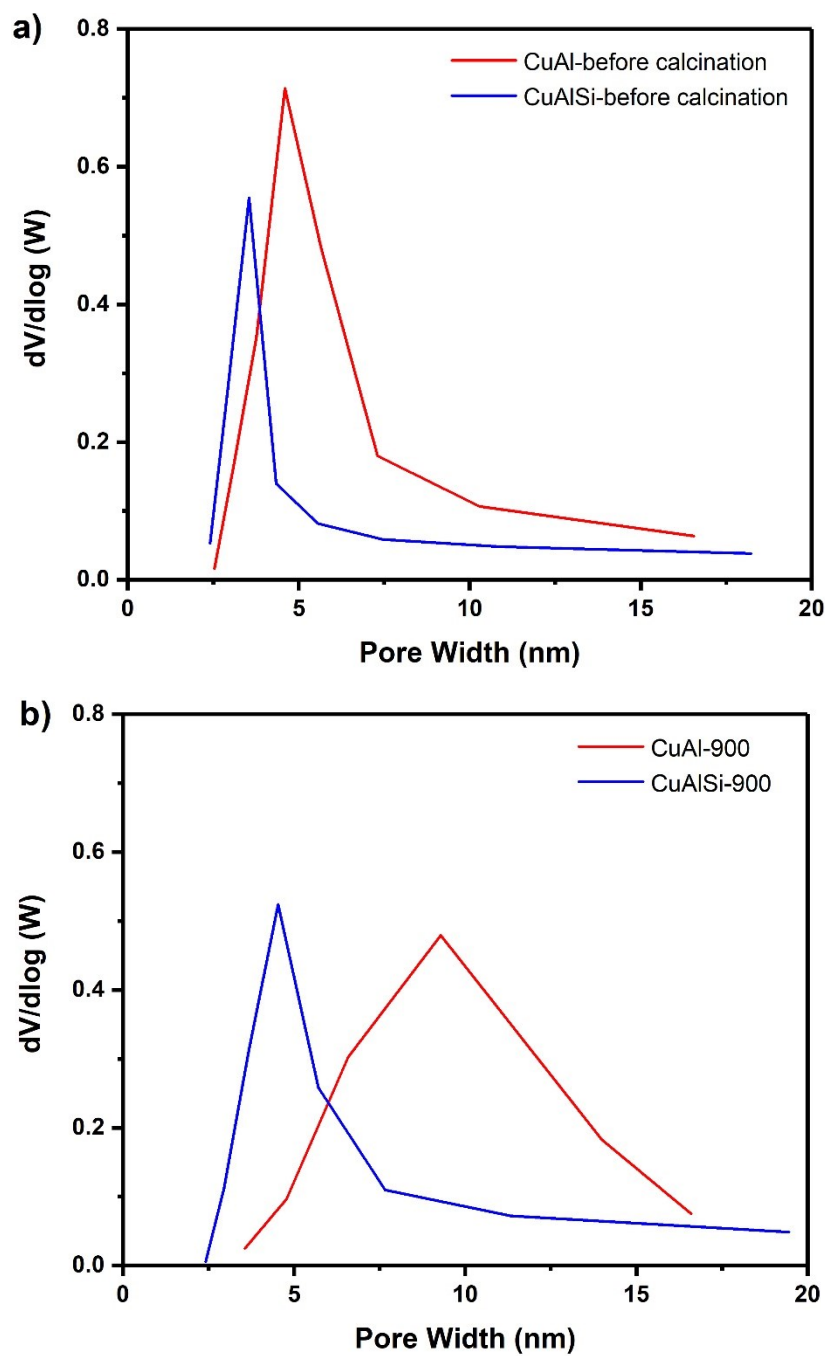


Figure S6. Pore size distribution for CuAl-900 and CuAlSi-900 a) before and b) after calcination.

Table S2. Catalyst characterization data.

Catalysts	S _{BET} before calcination (m ² ·g ⁻¹)	S _{BET} after calcination (m ² ·g ⁻¹)	V _p before calcination (mL·g ⁻¹)	V _p after calcination (mL·g ⁻¹)	Cu (wt%) ^a	Surface Cu/Al ratio ^b
CuAl-900	116	63	0.22	0.19	1.6	0.012
CuAlSi-900	115	85	0.13	0.17	1.5	0.012

^a Measured by ICP-OES.

^b Measured by XPS.

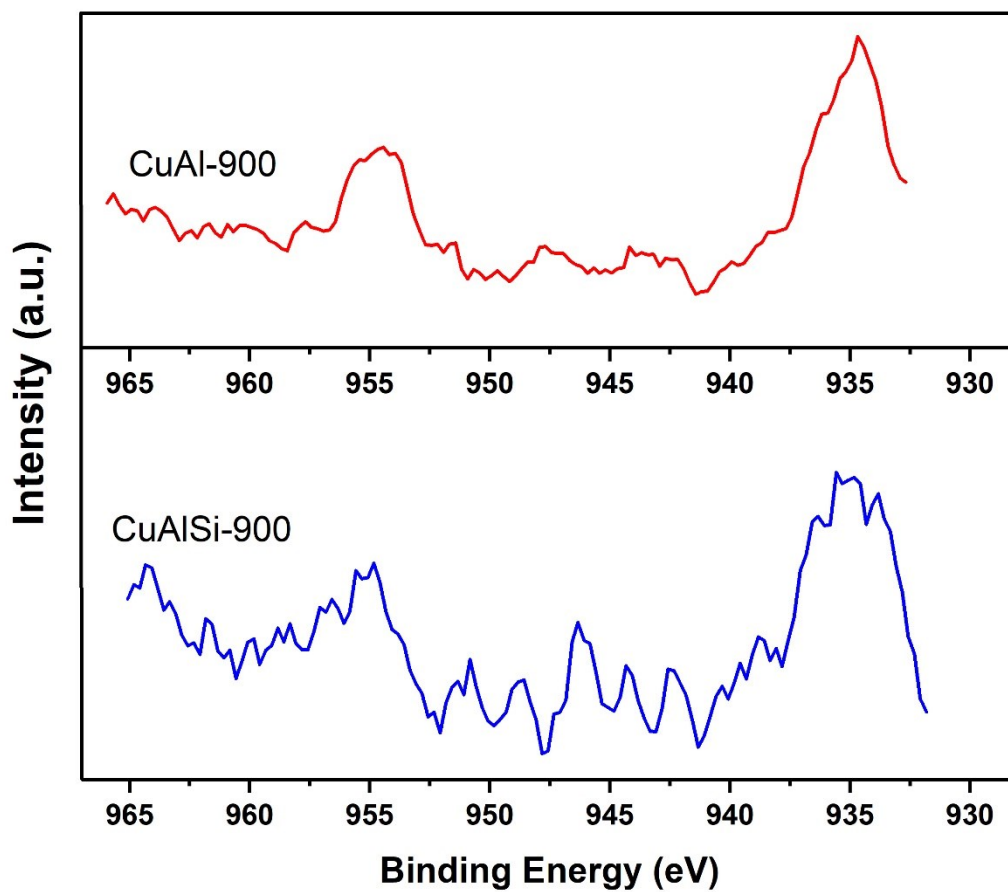


Figure S7. XP spectra for CuAl-900 and CuAlSi-900 catalysts.

References

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