

Effect of the Preparation Method on the Catalytic Properties of Copper-containing Zeolite Y Applied for NH₃-SCR-DeNO_x

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1. Experimental

1.1 Catalyst physico-chemical characterization

The XRD patterns were recorded using a HUBER G670 (Rimsting, Germany) diffractometer applying Cu-K α radiation (wavelength: 0.154 nm). The samples were measured with a scanning range of the diffraction angle 2θ between 4 and 90° in intervals of 0.005°. CRYSTAL IMPACT software version 3.6.2.121 was used to analyze the results.

SEM images were carried out using a scanning electron microscope (SEM) LEO Gemini 1530 SEM from Zeiss (Oberkochen, Germany) operated at an acceleration voltage of 5 kV. The samples were gently crushed using a ceramic pestle and mortar. Before taking the images, the samples were placed on carbon conductive tabs. For conductivity, the samples were sputtered with Au. ImageJ software version 1.53t was used to derive the average particle sizes from the SEM images.

Transmission electron microscopy (TEM) was carried out using a JEM-2100Plus instrument from JEOL (Tokyo, Japan) operated at an accelerating voltage of 200 kV. The images were taken with a 4K CMOS camera from TVIPS (Gauting, Germany). The TEM is equipped with a LaB₆ cathode and a high-resolution pole piece to achieve a point resolution in TEM mode of 0.23 nm. The sample preparation was performed by grinding the sample in a mortar and pestle in ethanol, and the dispersed particles were supported on a Ni-TEM grid.

Analysis of Al, Si, Na, and Cu content in the samples was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) on Perkin Elmer, Optima 8000 instrument (Rodgau, Germany). The samples (ca. 100 mg) were dissolved in a mixture of hydrofluoric acid (2 ml, 48 wt.-%, Sigma-Aldrich), nitric acid (2 ml, 69 wt.-%, Sigma-Aldrich), and hydrochloric acid (3 ml, 35 wt.-%, Sigma-Aldrich) with microwave radiation (1 h, 200 °C). Before measurement, HF was removed by microwave radiation (5 min, 200 °C) by complexing with H₃BO₃ (12 ml, 99.99 wt.-%, Sigma-Aldrich).

Solid-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 750 spectrometer (magnetic field 17.6 T, Rheinstetten, Germany) at a frequency of 195.06 MHz for ^{27}Al and 148.69 MHz for ^{29}Si . The ^{27}Al experiments were recorded at a spinning frequency of 12 kHz and a recycle delay of 0.1 s. A $1\ \mu\text{s}$ pulse was used that corresponds to about a 30° pulse angle. ^{29}Si spectra were obtained with direct excitation $2.5\ \mu\text{s}$ 90° pulse, spinning frequency of 7 kHz and a recycle delay of 10 s. Spectra are referenced to 1 M $\text{Al}(\text{NO}_3)_3$ solution and TMS for ^{27}Al and ^{29}Si , respectively.

Hydrogen temperature programmed reduction (TPR- H_2) measurements were carried out by MicrotracBel Corp., BELCAT II (Haan/Duesseldorf, Germany). The samples were pressed and sieved to 100-300 μm . Approximately 0.05 g sample was used for the measurement. For each sample, 20 vol.-% O_2 in Ar was used for pretreatment at 300 $^\circ\text{C}$, and reduction was done with 10 vol.-% H_2 in Ar at total flow rate of 30 ml min^{-1} to 800 $^\circ\text{C}$.

Nitrogen sorption isotherms were recorded at -196 $^\circ\text{C}$ using a MicrotracBEL Corp., BELSORP-miniX (Haan/Duesseldorf, Germany). Before measurement, ca. 100-200 mg of the sample was activated at 250 $^\circ\text{C}$ and 1 Pa. The total pore volume was taken from the point $p/p_0 = 0.99$. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the pore width distribution was obtained using the Barret-Joyner-Halenda (BJH) method. The micropore volume was calculated using the Harkins and Jura model (t-plot analysis).

Diffuse Reflectance (DR) UV-Vis spectra of the samples were recorded at room temperature using a Perkin Elmer Lambda 650S UV-Vis spectrometer (Rodgau, Germany) equipped with a 150 mm integrating sphere using spectralon® (PTFE, reflective value 99%, Rodgau, Germany) as a reference. The experiments were carried out in the wavelength range of 200-900 nm with a step width of 1 nm and a slit width of 2 nm.

X-ray absorption spectroscopy (XAS) measurements were performed at the SuperXAS beamline, Swiss Light Source (SLS) of the Paul Scherrer Institute (Villigen, Switzerland). The

polychromatic beam from the storage ring was collimated by a Si-coated mirror and subsequently monochromatized. The beamline utilizes a fast scanning monochromator (Quick-EXAFS) based upon rapid oscillation of a liquid-cooled Si(111) channel cut crystal with an acquisition rate of 2 Hz (500 milliseconds per spectrum). Cu K-edge XAS spectra of copper-containing zeolites Y were collected in transmission mode using N₂-filled ionization chambers, which were 15 cm long. The materials were prepared as 10 mm diameter pellets, using optimal amounts for transmission measurements homogeneously mixed with cellulose. Cu foil spectra were collected simultaneously for internal energy calibration (edge energy, E₀ = 8979 eV). The resulting raw data were pre-processed using the in-house developed ProQEXAFS software [1]. Standard XAS data reduction steps were performed with Larch software (Open source, version 0.9.65). These include subtraction of pre-edge and post-edge backgrounds, determination of the edge energy, and normalization of the data set to an edge jump of 1.

The continuous-wave electron paramagnetic resonance (CW-EPR) measurements of the samples were carried out with a Bruker EMX micro (X-band, 9.4 GHz) spectrometer equipped with an Oxford Instruments He cryostat ESR 900. The spectrometer was fitted with an ER 4119 HS cylindrical cavity. The microwave power and modulation amplitude were adjusted such that no line shape distortion occurred. Powder samples (ca. 10 mg) were put into a quartz tube with 3.8 mm inner diameter and then sealed to avoid contact with the air. An activation procedure was carried out on all samples at 200 °C for 2 h under vacuum for comparison with the as-synthesized one. The measurement of EPR for hydrated and dehydrated samples was conducted at room temperature and -193 °C, respectively. Simulations of EPR spectra were done using Easyspin MATLAB toolbox.

TPD-NO_x profiles of the samples were recorded with a NO_x analyzer Eco Physics Inc., CLD 70S ECO Physics (Michigan, USA). Before the NO sorption, the sample (100 mg) placed in a fixed-bed flow microreactor (i.d., 6 mm; l., 300 mm) was outgassed in a flow of pure helium (20 ml min⁻¹) at 350 °C for 1 h. Subsequently, the microreactor was cooled down to 100 °C, and

the sample was saturated with 500 ppm of NO in He flow (1 h, 120 ml min⁻¹). Afterward, the sample was purged in a flow of 4 vol.-% of O₂ in He flow until a constant baseline level was reached (1.5 h, 120 ml min⁻¹). For the desorption step, the microreactor temperature was raised to 450 °C with a linear heating rate of 10 °C min⁻¹ in a flow of 4 vol.-% of O₂ in He flow (120 ml min⁻¹).

Prior to IR studies of NO_x thermal desorption studies the catalysts were shaped in the form of thin wafers (6-8 mg cm⁻²), placed in a custom-made quartz cell and thermally treated in a vacuum (10-5 mbar) or oxygen atmosphere for 1 h at 350 °C. After cooling to 100 °C, the catalysts were contacted with NO for 10 min, then gradually evacuated up to 500 °C.

1.2 Catalytic experiments

The catalytic experiments were carried out in a fixed-bed quartz tube reactor (inner diameter: 6 mm, length: 200 mm). For catalytic experiments, a fraction of particle size in the range of 200-400 μm was used. Before each experiment, the catalysts (100 mg) were activated at 350 °C for 1.5 h under a flow of 50 ml min⁻¹ of He and then cooled down to 50 °C. After that, the simulated flue gas, composed of 500 ppm NO, 575 ppm NH₃ and 4 vol.-% O₂ and balance He for a total flow rate (F_{TOT}) of 120 ml min⁻¹, was switched on to pass through the catalyst bed. For selected samples, the catalytic tests were carried out in the presence of water vapor (5 vol.-%). The gas hourly space velocity (GHSV) was determined to be ~30 000 h⁻¹. The reaction was carried out at atmospheric pressure and in a range of temperatures from 50 °C to 450 °C with an interval of 25-50 °C. At each temperature, the reaction was stabilized for 70 min before the quantitative analysis of NO and N₂O concentration. The gas leaving the reactor is washed in a gas-washing bottle filled with concentrated phosphoric acid. The NO_x-converter was used to reduce NO₂ to NO, to measure the total concentration of NO_x. Analysis of the NO and N₂O was performed using a non-dispersive infrared sensor (NDIR) URAS 10E Fa. Hartmann und Braun (Frankfurt a. M., Germany). The conversion of NO ($X(NO)$) was

determined according to $X(\text{NO}) = ([c(\text{NO})_{in} - c(\text{NO})_{out}] / c(\text{NO})_{in}) \times 100\%$, where: $c(\text{NO})_{in}$ and $c(\text{NO})_{out}$ - concentration of NO in the inlet and the outlet gas, respectively. The yield of N_2O ($Y(\text{N}_2\text{O})$) was calculated based on the following equation: $Y(\text{N}_2\text{O}) = (2 * c(\text{N}_2\text{O}) / [c(\text{NO})_{in} + c(\text{NH}_3)_{in}]) \times 100\%$,¹ where: $c(\text{N}_2\text{O})$, $c(\text{NO})_{in}$, $c(\text{NH}_3)_{in}$ - concentration of N_2O in the outlet gas, the concentration of NO and NH_3 in the inlet gas, respectively.

To measure the *in situ* DR UV-Vis in NH_3 -SCR-De NO_x activity of the catalysts, a 100 mg powder sample, (sieve fraction 150-300 μm), was added to a tube quartz micro reactor with an inner diameter of 4 mm. The concentrations of NH_3 , NO, O_2 , and He in the feed were measured with mass-flow controller. We used the same flows of the catalytic measurements described above. Before the measurements, the catalysts were heated to 350 $^\circ\text{C}$ in an atmosphere of He or O_2 for 0.5 h. Then, we cooled to 50 $^\circ\text{C}$, introduced the reaction feed gas, and heated up to 100, 200, 300, 400 and 500 $^\circ\text{C}$ with a rate of 10 $^\circ\text{C min}^{-1}$. In each step, the temperature was kept for 0.5 h, while continuously recording the product gas composition with OmniSTAR GDS320 mass spectrometer. UV-Vis spectra were collected during the whole experiment with AvaSpec-ULS2048CL-EVO equipped with a reflection probe optical fiber. Spectra were acquired every 30 seconds during the reaction.

2. Results and Discussion

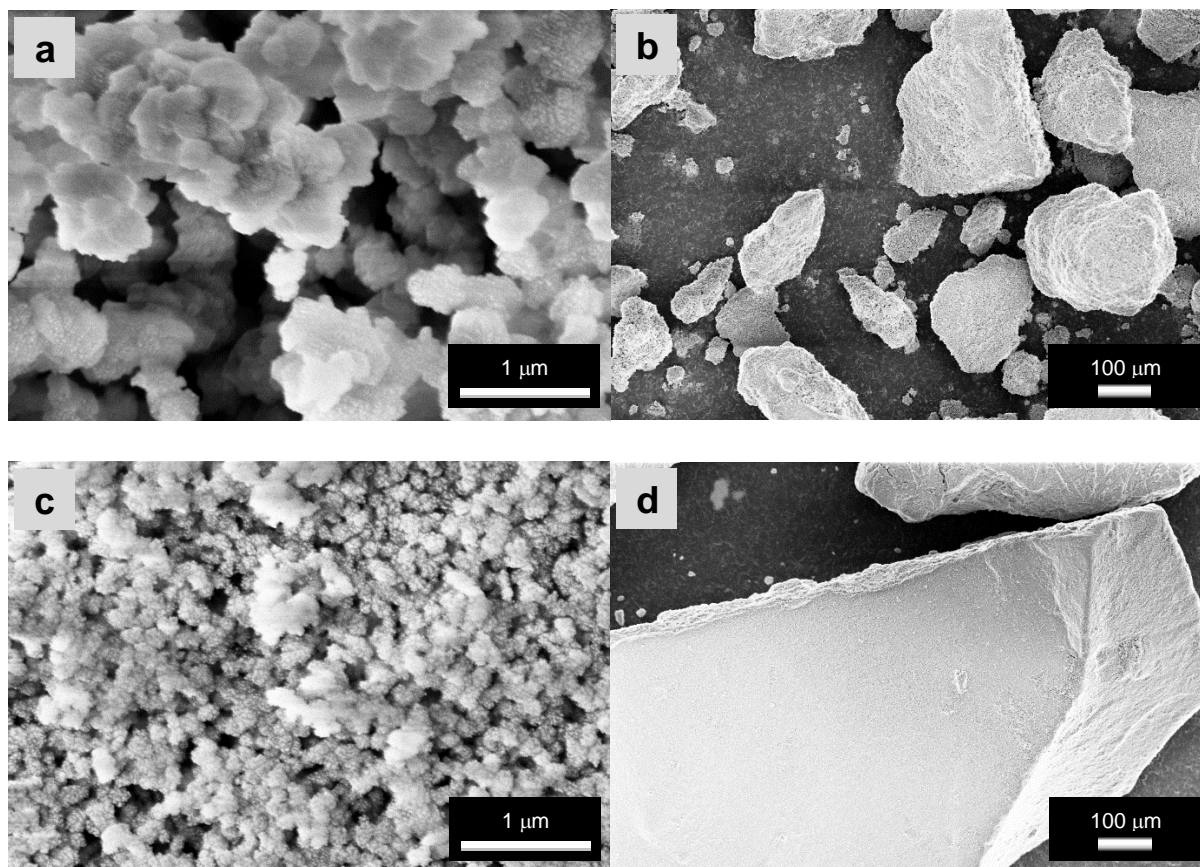


Fig. S11: SEM images of the zeolite Y: a,b) ZY-0h-B and c,d) ZY-24h-B.

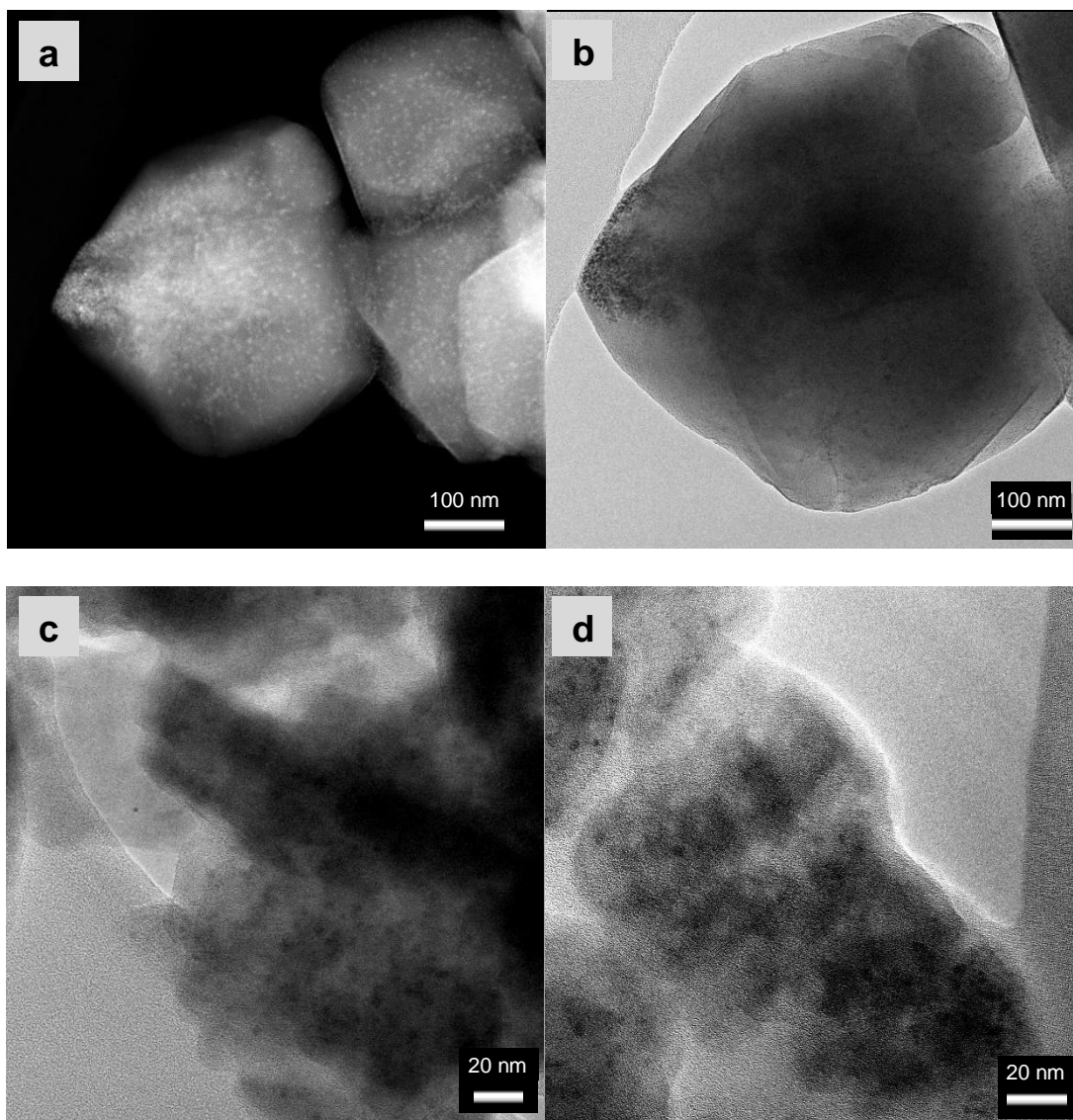


Fig. S12: a) STEM images of CuY-24h-A, b) TEM images of CuY-24h-A, c) TEM images of CuY-0h-B and d) TEM images of CuY-24h-B.

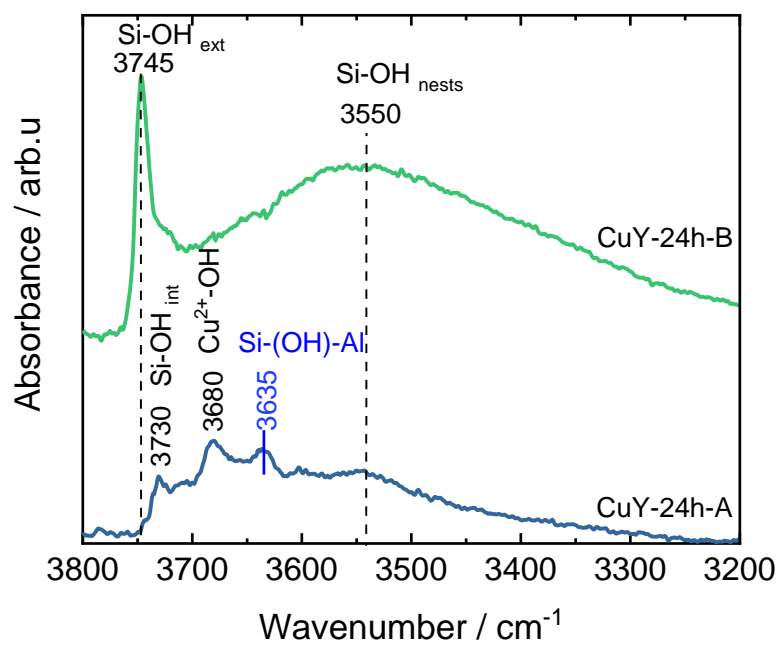


Fig. S13: FT-IR spectra in the hydroxyl groups region of CuY-24h-A and CuY-24h-B; $\text{Si-OH}_{\text{ext}}$ – external Si-OH, $\text{Si-OH}_{\text{int}}$ – isolated internal Si-OH, $\text{Si-OH}_{\text{nests}}$ – nests Si-OH.

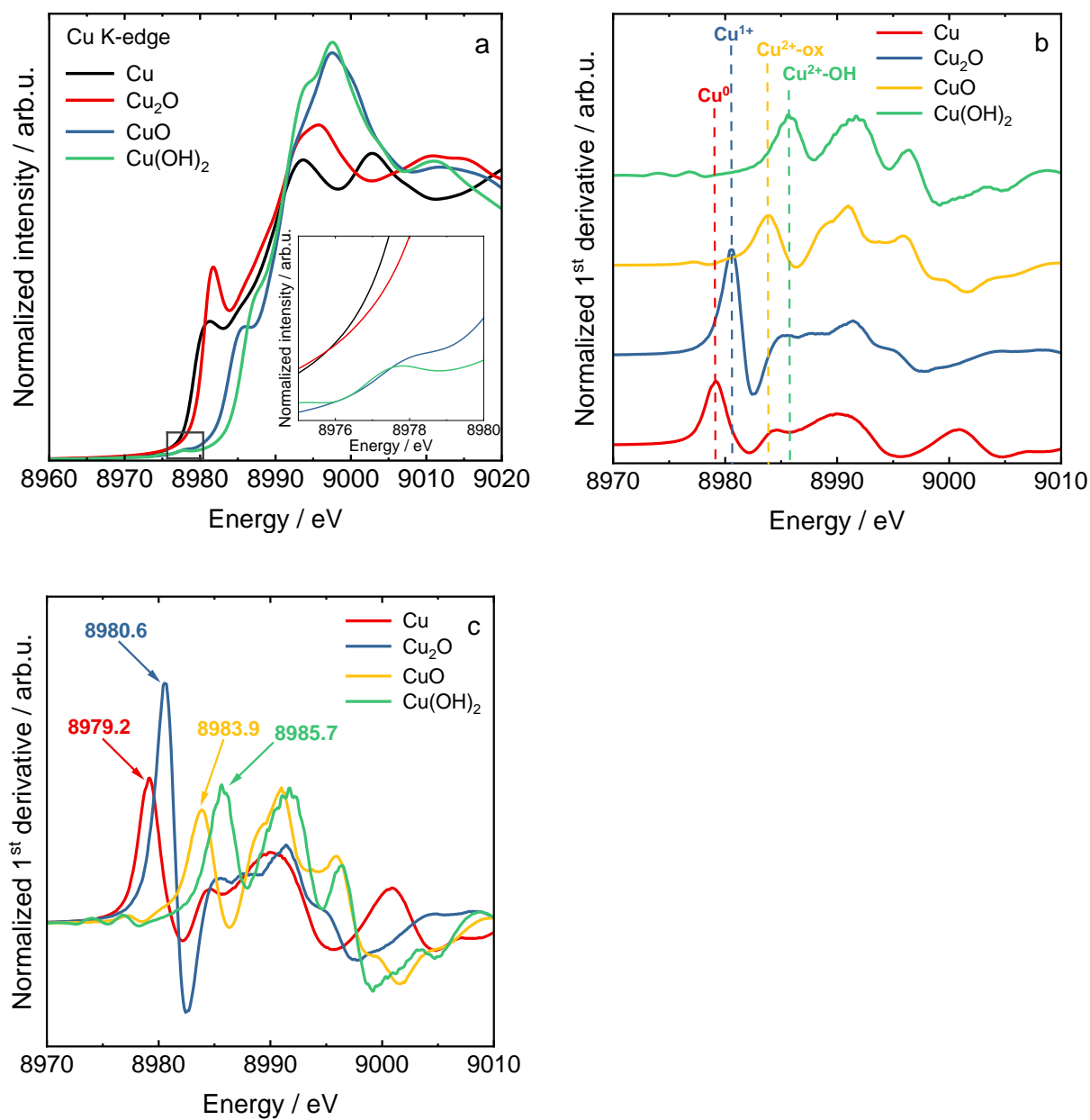


Fig. S14: a) Cu K-edge XANES spectra of Cu reference compounds: Cu foil, Cu₂O, CuO, Cu(OH)₂, with the pre-edge region emphasized in the inset, and b,c) first derivative of spectra with labelled first inflection-point energies.

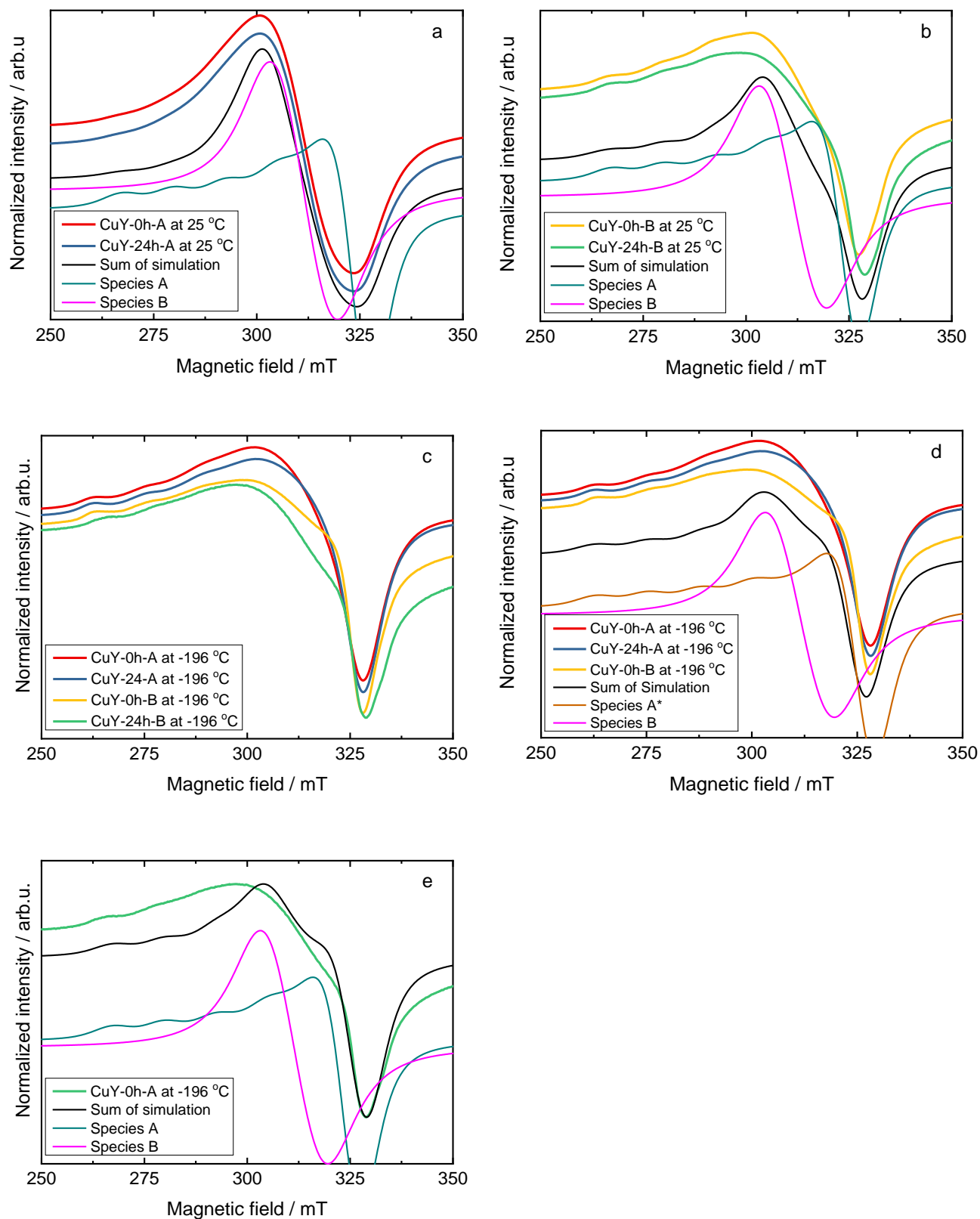


Fig. SI5. Summary of spectral simulations for all hydrated samples at 25 °C and -193 °C. Spectral simulation based on the weighing contribution obtained in Tab. SI1.

Tab. S11. Composition in percentage for different copper species in hydrated materials recorded at 25 °C and -196 °C.

Samples	25 °C			-196 °C		
	A / %	B / %	A* / %	A / %	B / %	A* / %
CuY-0h-A	20	80	0	0	30	70
CuY-24h-A	20	80	0	0	30	70
CuY-0h-B	80	20	0	0	30	70
CuY-24h-B	80	20	0	70	30	0

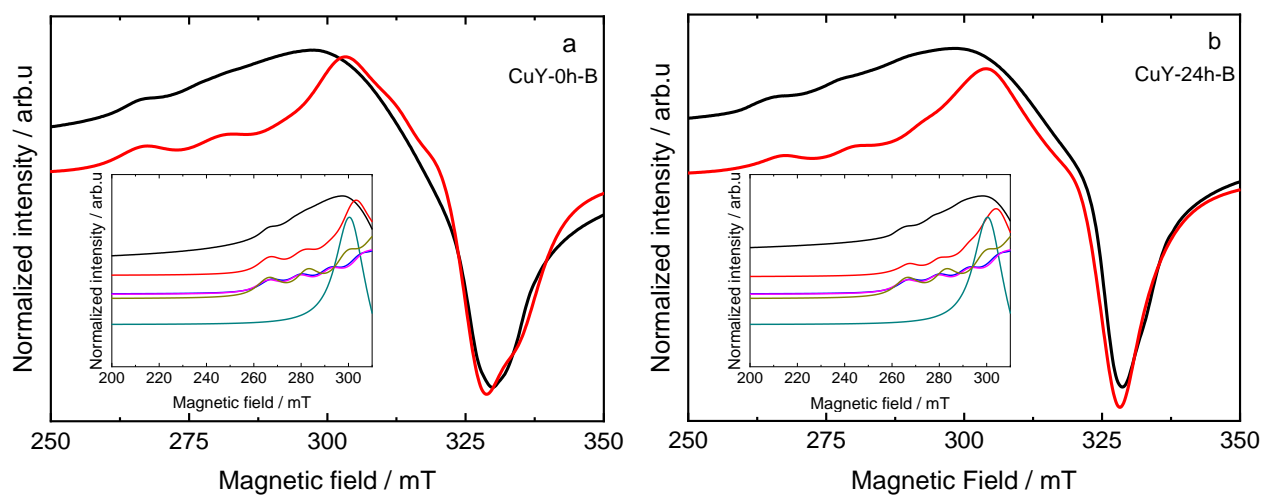


Fig. S16: Spectral simulation of a) CuY-0h-B and b) CuY-24h-B samples recorded at -193 °C (sample activated at 200 °C for 2 h under vacuum). The insets show the contributions of different copper species to the simulations.

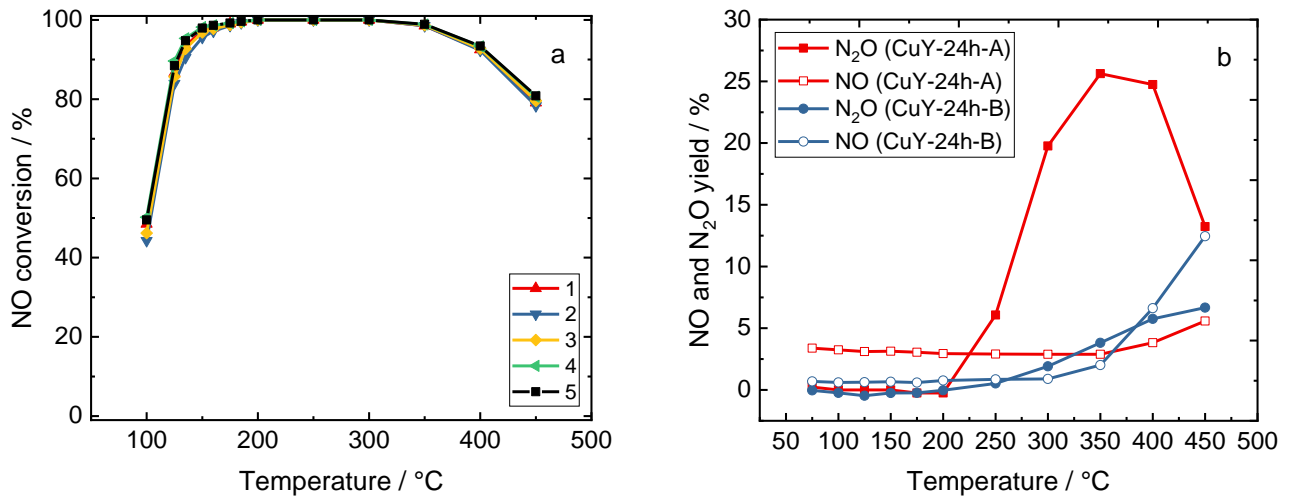


Fig. S17: a) NO conversion during NH₃-SCR-DeNO_x over CuY-24h-A in five consecutive runs, and b) N₂O and NO yield obtained during NH₃-SCO. Reaction conditions: $m_K = 0.2$ g; GHSV = 30,000 h⁻¹, ($c(\text{NO}) = 500$ ppm used in NH₃-SCR-DeNO_x), $c(\text{NH}_3) = 575$ ppm, $c(\text{O}_2) = 4$ vol.-%, He balance, $F_{\text{TOT}} = 120$ ml min⁻¹.

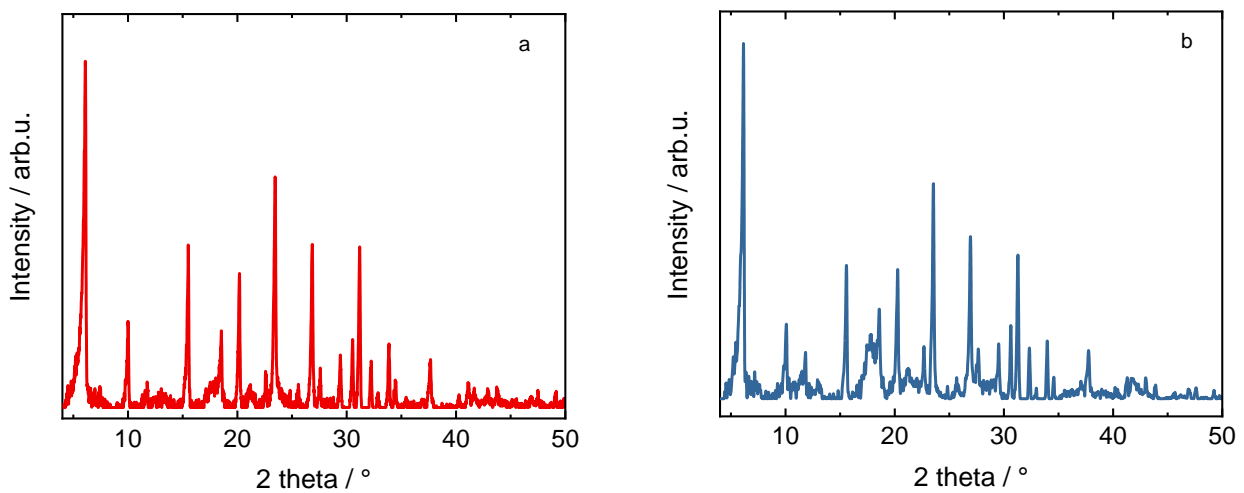


Fig. S18: XRD pattern of CuY-24h-A samples after consecutive five runs in NH₃-SCR-DeNO_x a) without water vapor and b) in the presence of water vapor at 200 °C.

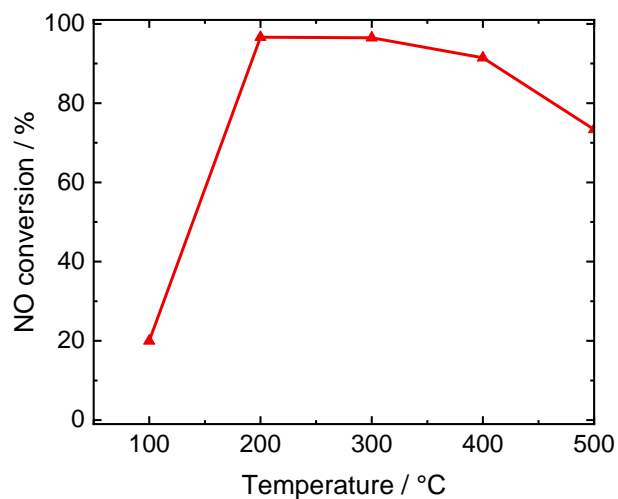


Fig. S19: NO conversion during NH_3 -SCR-De NO_x over CuY-24h-A. Reaction conditions: $m_K = 0.1$ g; GHSV = 30,000 h^{-1} , ($c(\text{NO}) = 500$ ppm used in NH_3 -SCR-De NO_x), $c(\text{NH}_3) = 575$ ppm, $c(\text{O}_2) = 4$ vol.-%, He balance, $F_{\text{TOT}} = 120$ ml min^{-1} .

References

- [1] A.H. Clark, J. Imbao, R. Frahm, M. Nachtegaal, J. Synchrotron Radiat. 27 (2019) 551-557.
- [2] S. Stoll, A. Schweiger, J. Magn. Reson. 178 (2006) 42-55.