

## Supporting information

### *In situ* spectroscopic studies of the water effect on the redox cycle of Cu ions in Cu-SSZ-13 during selective catalytic reduction of NO<sub>x</sub>

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## Experimental

### 1. Zeolite synthesis

SSZ-13 ( $\text{Si}/\text{Al}_2 = 9$ ) was synthesized by hydrothermal synthesis. 0.8 g of NaOH (Sigma Aldrich) and 25 g of  $\text{Na}_2\text{SiO}_3$  (Sigma Aldrich) were dissolved in deionised water (52 mL). After vigorous stirring for 30 min under ambient conditions, 2.5 g of CBV 500 (Zeolyst) and 10.5 g of Trimethyladamantylammonium Hydroxide (TMAdaOH, SACHEM) were added and stirred for 30 min under ambient conditions. The prepared mixture was transferred to a 200 mL Teflon-lined stainless steel autoclave and placed in a forced convection oven at 140 °C for 5 days. The obtained solution was washed with deionised water, dried at 105 °C and calcined at 550 °C for 8 h at a ramp rate of 1 °C /min. Ammonium ion exchange was repeated two times using 1 M ammonium nitrate solution (Sigma Aldrich) at 65 °C to obtain the  $\text{NH}_4^+$  form of SSZ-13. Cu ion was also exchanged by using a conventional ion exchange method.  $\text{NH}_4^+$ -SSZ-13 was added to an aqueous solution of copper nitrate trihydrate precursor (Sigma Aldrich) and stirred at 65 °C for 24 h. The mixture was filtered and dried in a forced convection oven at 105 °C. The dried catalyst was calcined at 550 °C for 4 h and was denoted as Cu-SSZ-13.

### 2. Catalyst characterization

DRIFT spectra were obtained at a spectral resolution of 4  $\text{cm}^{-1}$  using a diffuse reflectance cell (Praying Mantis, Harrick) installed in a Fourier transform infrared (FT-IR) spectrometer (Nicolet 6700, Thermo Fisher Scientific). ICP-AES results were obtained by OPTIMA 8300 (Perkin-Elmer) to measure the amount of copper and aluminum in Cu-SSZ-13.

The micropore volume of Cu-SSZ-13 was measured from Ar adsorption isotherm using a Micromeritics 3Flex Surface and Catalyst Characterization instrument. Typically, 0.02-0.03g of the sample were loaded in the cell and isotherms were obtained at -186 °C after degassing at 120 °C overnight. X-ray diffraction (XRD) patterns were obtained on a Smartlab diffractometer (Rigaku) operated at 40 kV and 30 mA.

Electron paramagnetic resonance (EPR) measurements were conducted on an EMXmicro-9.5/2.7 spectrometer (Bruker) at a microwave power of 0.73 mW and frequency of 9.41 GHz. 10 mg of sample was loaded in a quartz tube (OD= 5 mm; Wilmad). The field was swept by 3000 G in 31 s, and modulated at 100 kHz with 1 G amplitude. Time constant was 1.28 ms.

Time-resolved XAS spectra were measured at 1 Hz at the Cu K-edge (8.9789 keV) in transmission mode using  $\text{N}_2$ -filled ionization chambers at the SuperXAS beamline of the Swiss Light Source. A Cu reference foil was measured simultaneously for energy calibration. Approximately 25 mg of Cu-SSZ-13 were loaded into a custom-built spectroscopic cell fixed between quartz wool plugs, and sealed with 20-  $\mu\text{m}$  graphite windows. This system ensures sufficient X-ray transmission in an airtight environment. The spectra were extracted, normalized, averaged, and post-processed using the ProQEXAFS software. Linear combination fitting (LCF) was performed in the X-ray absorption near edge structure (XANES) region between the energy range of 8935.0 and 9050.0 eV using spectral components that were obtained from multivariate curve resolution (MCR). The analysis was performed under the constraints that the concentrations cannot be negative and that the sum of all the components

should be equal to unity.

### 3. NH<sub>3</sub>-SCR reaction

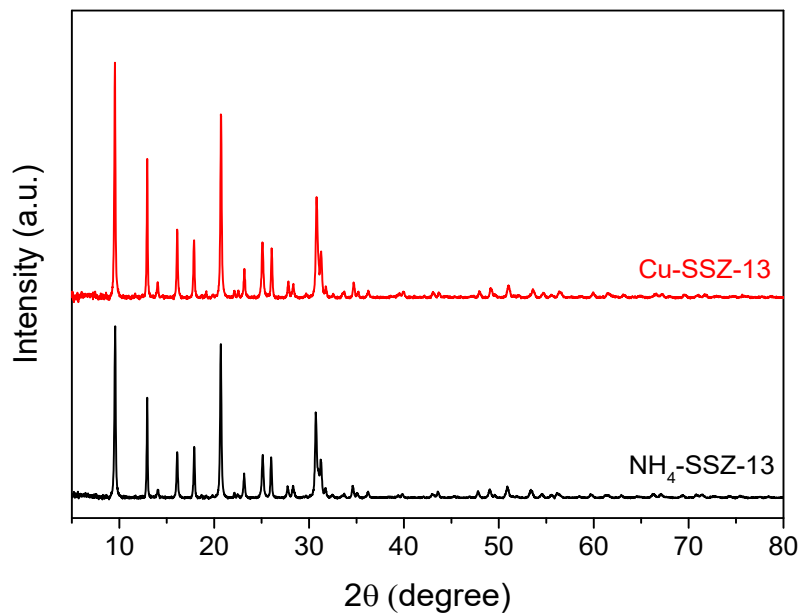
NH<sub>3</sub>-SCR reaction tests were conducted in the temperature range of 130-300 °C in a down-flow 1/4" ID tubular quartz reactor. All catalysts were pelletized and sieved to 300-500 μm particles to prevent pressure drop. Reactant gas consisted of 500 ppm NO (5000 ppm in N<sub>2</sub>, Deokyang Co., Ltd.), 500 ppm NH<sub>3</sub> (5000 ppm in N<sub>2</sub>, Deokyang Co., Ltd.), 10 vol% O<sub>2</sub> (99.995%, Daesung industrial gases Co., Ltd.), 5 vol% H<sub>2</sub>O (deionized, introduced from PURELAB Chorus, ELGA in the wet SCR) and balance N<sub>2</sub> (99.999%, Daesung industrial gases Co., Ltd.). The gas hourly space velocity (GHSV) was 240,000 mL/h·g<sub>cat</sub>. In the case of dry NH<sub>3</sub>-SCR, the catalyst was pretreated at 200 °C in air for a dehydration before the reaction. Concentration of NO<sub>x</sub> was measured with a NO<sub>x</sub> chemiluminescence analyzer (42i High level, Thermo Scientific). Based on the measured concentration data, NO<sub>x</sub> conversion was calculated using the following equation.

$$NO_x \text{ conversion (\%)} = \frac{NO_{xout} - NO_{xin}}{NO_{xin}} \times 100$$

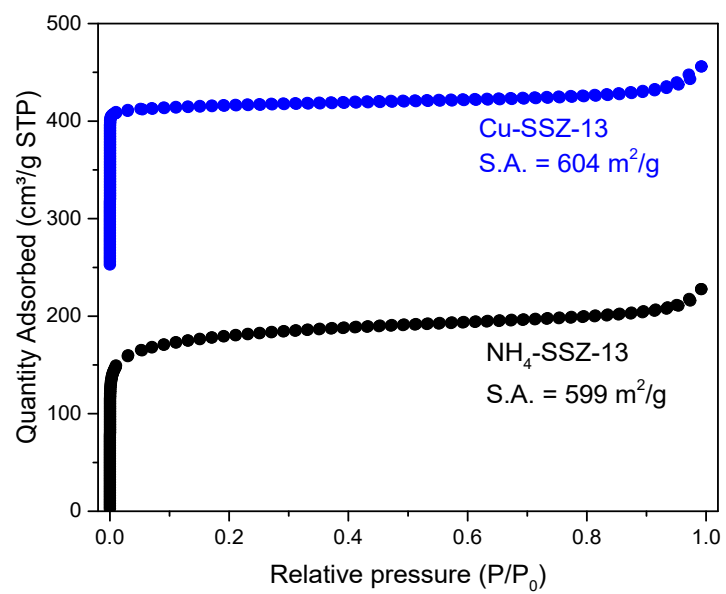
The NO<sub>x</sub> consumption rate in the NH<sub>3</sub>-SCR reaction is calculated using

$$r = \frac{F}{W} (-\ln(1 - X))$$

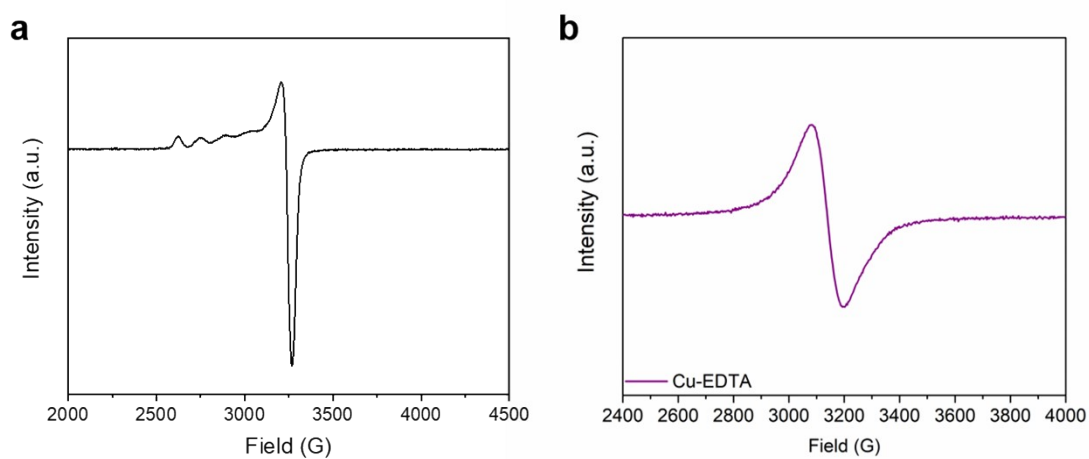
where F is the molar NO<sub>x</sub> feed rate (mol/s), W the catalyst weight (g) and X the NO<sub>x</sub> conversion. The NH<sub>3</sub>-SCR activity is represented by the turnover frequency (TOF) defined as the NO<sub>x</sub> consumption rate per mol of active Cu ions assuming all Cu ions are involved in the reaction. The apparent activation energy of the catalyst was obtained using the Arrhenius equation by plotting 1000/T (K<sup>-1</sup>) vs ln(TOF).



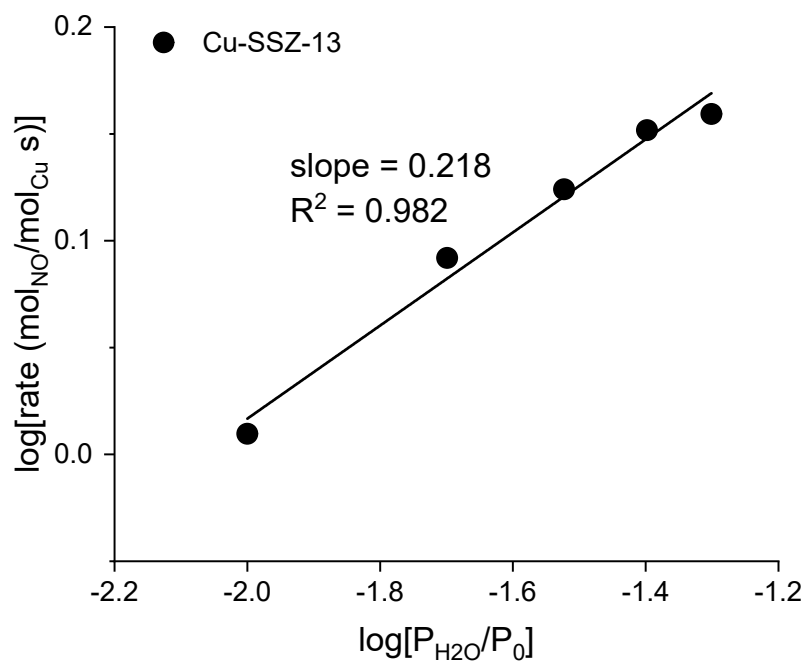
**Figure S1.** The XRD patterns of NH<sub>4</sub>-SSZ-13 and Cu-SSZ-13.



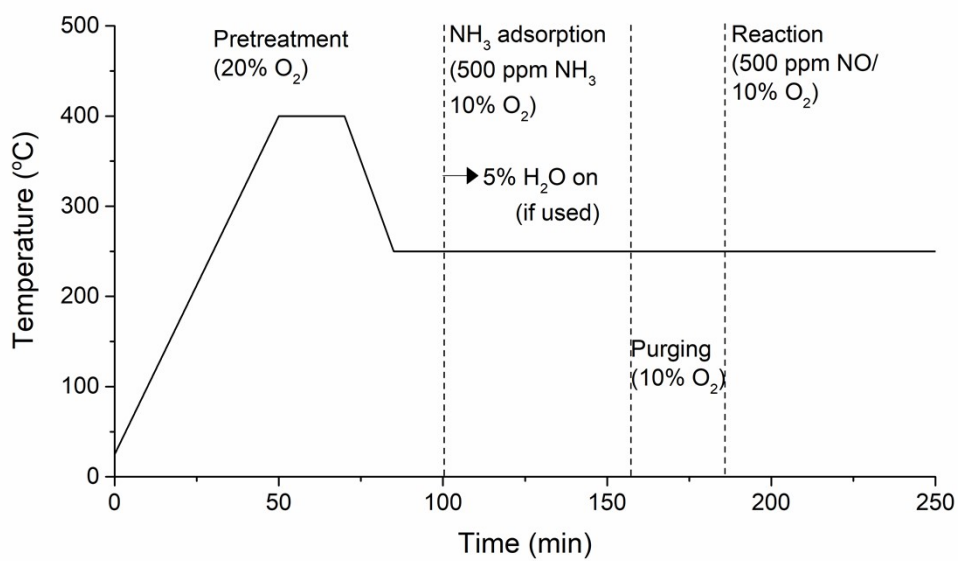
**Figure S2.** Ar adsorption isotherms of NH<sub>4</sub>-SSZ-13 and Cu-SSZ-13.



**Figure S3.** The EPR spectra of (a) Cu-SSZ-13 (b) Cu-EDTA standard solution (0.025M). Quantifying the spectra of Cu-SSZ-13 by the EDTA reference, the amount of Cu ions was measured as 0.89 wt%, which was almost same with the amount of Cu obtained from the ICP-AES result. It indicates that the most of Cu exist as the divalent ionic form.

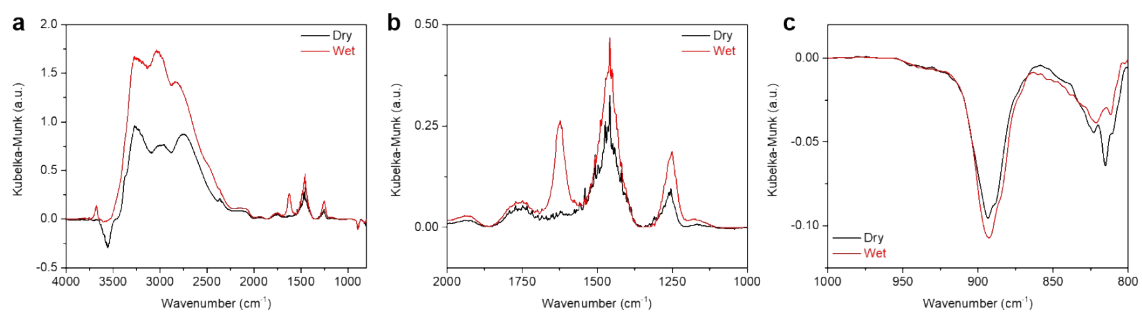


**Figure S4.** Logarithm relationship of H<sub>2</sub>O concentration and NH<sub>3</sub>-SCR activity at 250 °C.

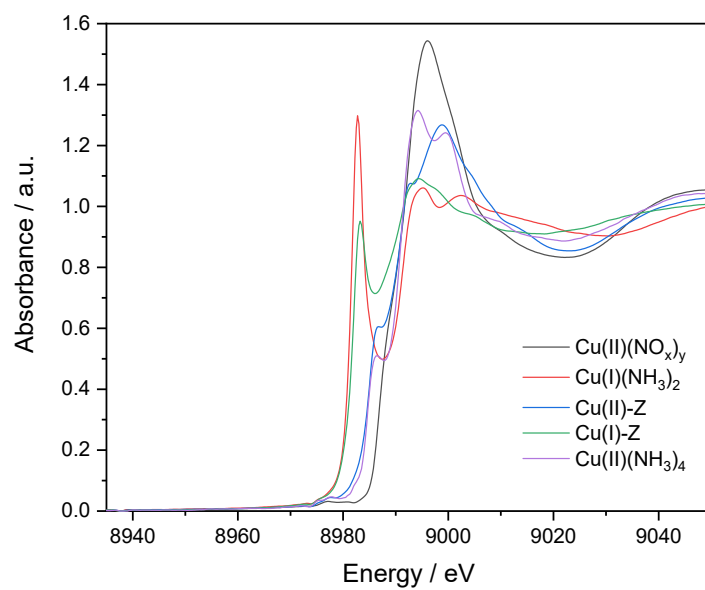


**Figure S5.** Protocol of simulated NH<sub>3</sub>-SCR reaction for DRIFTS and XAS measurements. The carrier gas was N<sub>2</sub> and Ar, respectively.

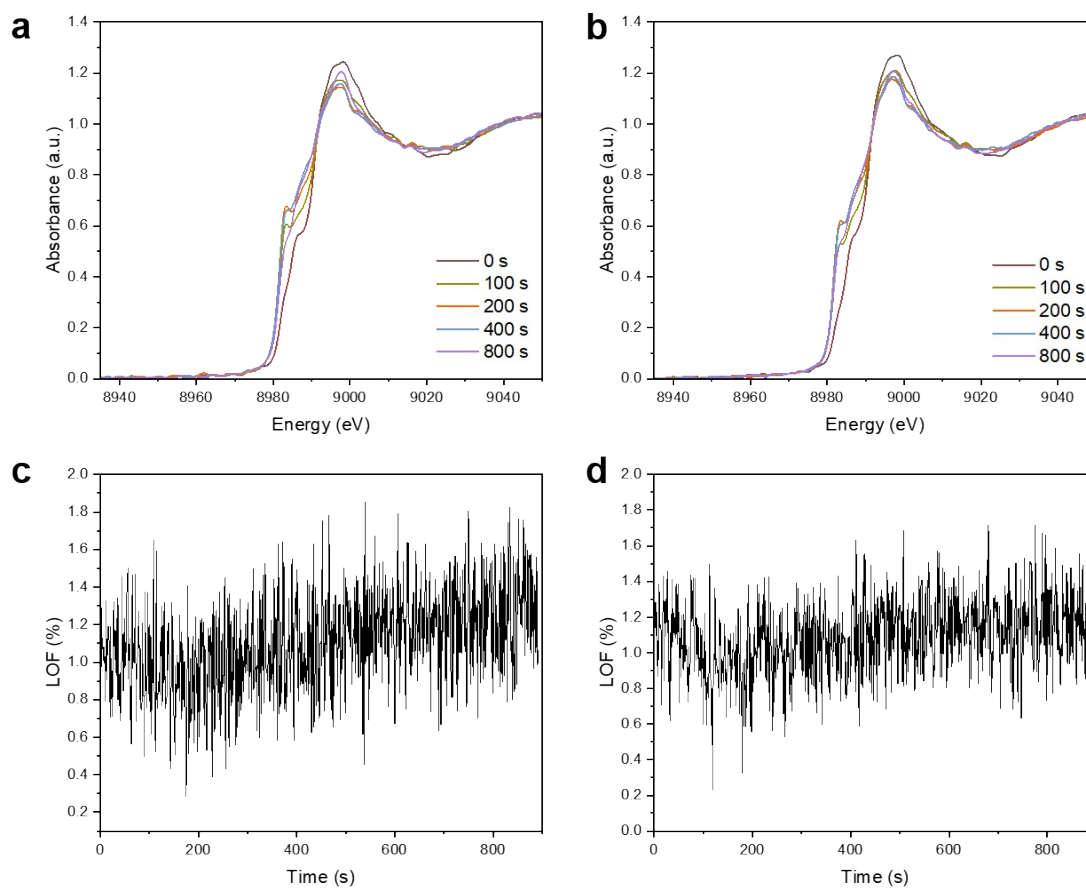




**Figure S6.** Comparison of DRIFT spectra after equilibration with NH<sub>3</sub> under dry and wet conditions. a) Overview; b) N-H deformation region; c) T-O-T region.



**Figure S7.** The XANES spectra of various reference components used for the linear combination fit of time-resolved XAS spectra.



**Figure S8.** XANES evolution of Cu-SSZ-13 and Lack-of-fit (LOF) of the dataset upon NO addition under (a, c) dry and (b, d) wet  $\text{NH}_3$ -SCR conditions, respectively.

**Table S1.** Component of prepared Cu-SSZ-13 catalyst.

	Na (wt%)	Cu (wt%)	Cu/Al (molar ratio)
Cu-SSZ-13	0.05	0.86	0.05