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**Electronic Supporting Information**

# The dynamic nature of Cu sites in Cu-SSZ-13 and the origin of the seagull NOx conversion profile during $NH_3$-SCR

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**Table S1.** Results of analysis of EXAFS spectra of Cu-0.5 and Cu-1.2 catalysts measured under dry air at 350 °C.

| | **CN (O) / d (Cu-O)** | **CN (Cu) / d (Cu-O-Cu)** | **CN (Al) / d (Cu-O-Al)** | **$\sigma^2$ ($10^{-3}$ Å$^2$)** | **$\delta E_0$ (eV)** | **ρ (%)** |
|---|---|---|---|---|---|---|
| **Cu-0.5 Dry air 350 °C** | 2.4±0.4<br>1.88±0.01 Å | 0.37±0.24<br>2.91±0.05 Å | n.a. | 1.9±1.9 | -6.1±1.8 | 1.7 |
| **Cu-1.2 Dry air 350 °C** | 3.0±0.4<br>1.92±0.01 Å | 1.0±0.5<br>2.96±0.03 Å | n.a. | 8.4±2.4 | -2.8±1.3 | 0.9 |

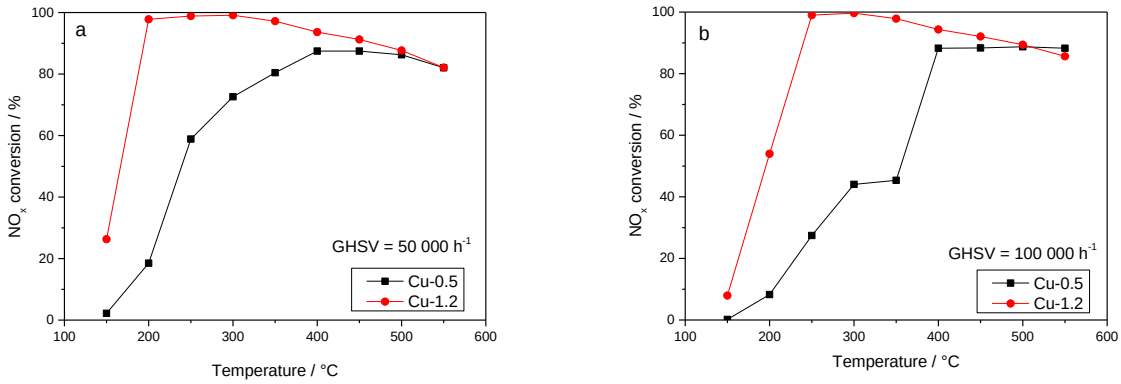


**Figure SI1.** $NO_x$ conversion during $NH_3$-SCR over the tested Cu-zeolites measured in the laboratory plug-flow reactor. Conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10 % $O_2$, 5 % $H_2O$, balance $N_2$, at (a) GHSV 50 000 $h^{-1}$ and (b) GHSV 100 000 $h^{-1}$.

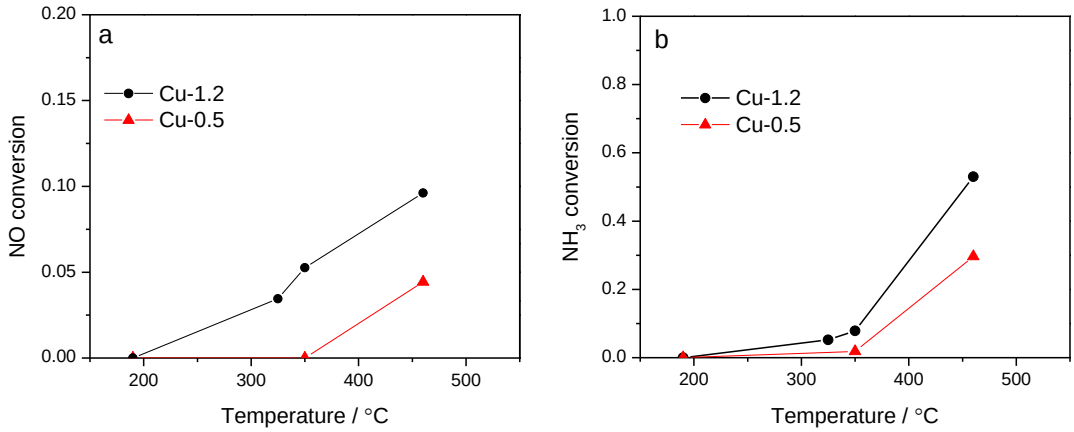


**Figure SI2.** Oxidation of NO (a) and oxidation of $NH_3$ (b) over tested Cu-zeolites measured in the laboratory plug-flow reactor. Conditions: 1000 ppm NO or 1000 ppm $NH_3$, 10 % $O_2$, 5 % $H_2O$, balance $N_2$, GHSV 200 000 $h^{-1}$.

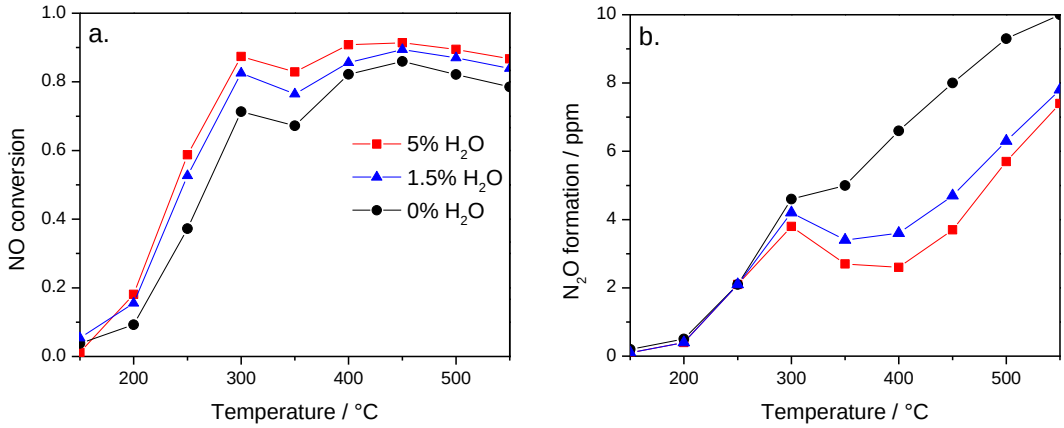


**Figure SI3.** Effect of water vapor concentration on (a) the conversion of NO and (b) formation of $N_2O$ during $NH_3$-SCR over Cu-1.2 catalyst. Conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10 % $O_2$, 0 - 5 % $H_2O$, balance $N_2$, GHSV 200 000 $h^{-1}$.

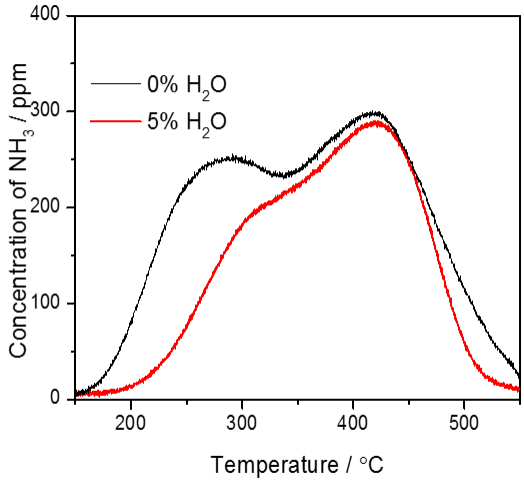


**Figure SI4.** Ammonia TPD after $NH_3$ adsorption at 150 °C on Cu-1.2 followed by He flushing. $NH_3$ was adsorbed from the following feed: 1000 ppm $NH_3$, 0 % (black line) $H_2O$ and 5 % (red line) $H_2O$ ($N_2$ balance). GHSV was kept at 50 000 $h^{-1}$.

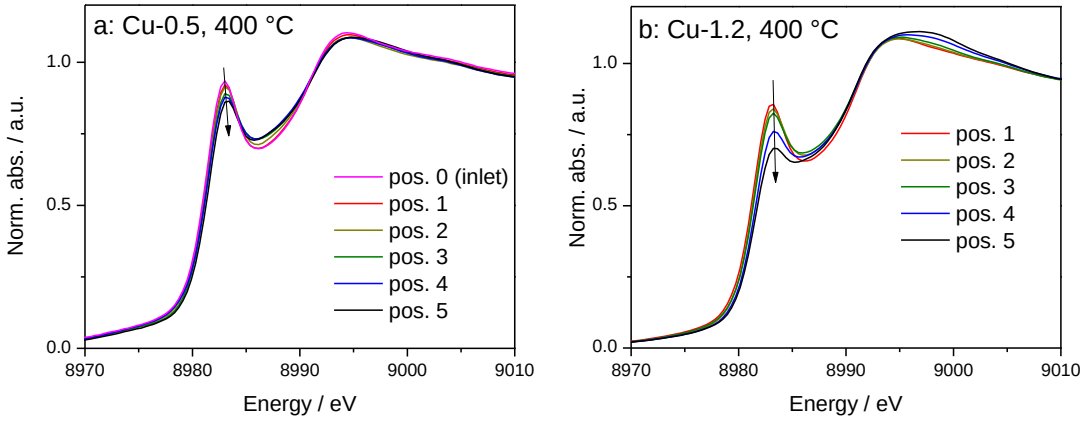


**Figure SI5.** *Operando* XANES spectra of (a) Cu-0.5 and (b) Cu-1.2 measured at 400 °C under SCR feed. The spatially resolved spectra are measured at equidistant points (the first and the last points are at 0.5 mm from the inlet / outlet of the 7 mm long catalyst bed, an additional point is measured for Cu-0.5 at the inlet-most measurable position). Conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10 % $O_2$, 1.5 % $H_2O$, balance He, GHSV 200 000 $h^{-1}$.

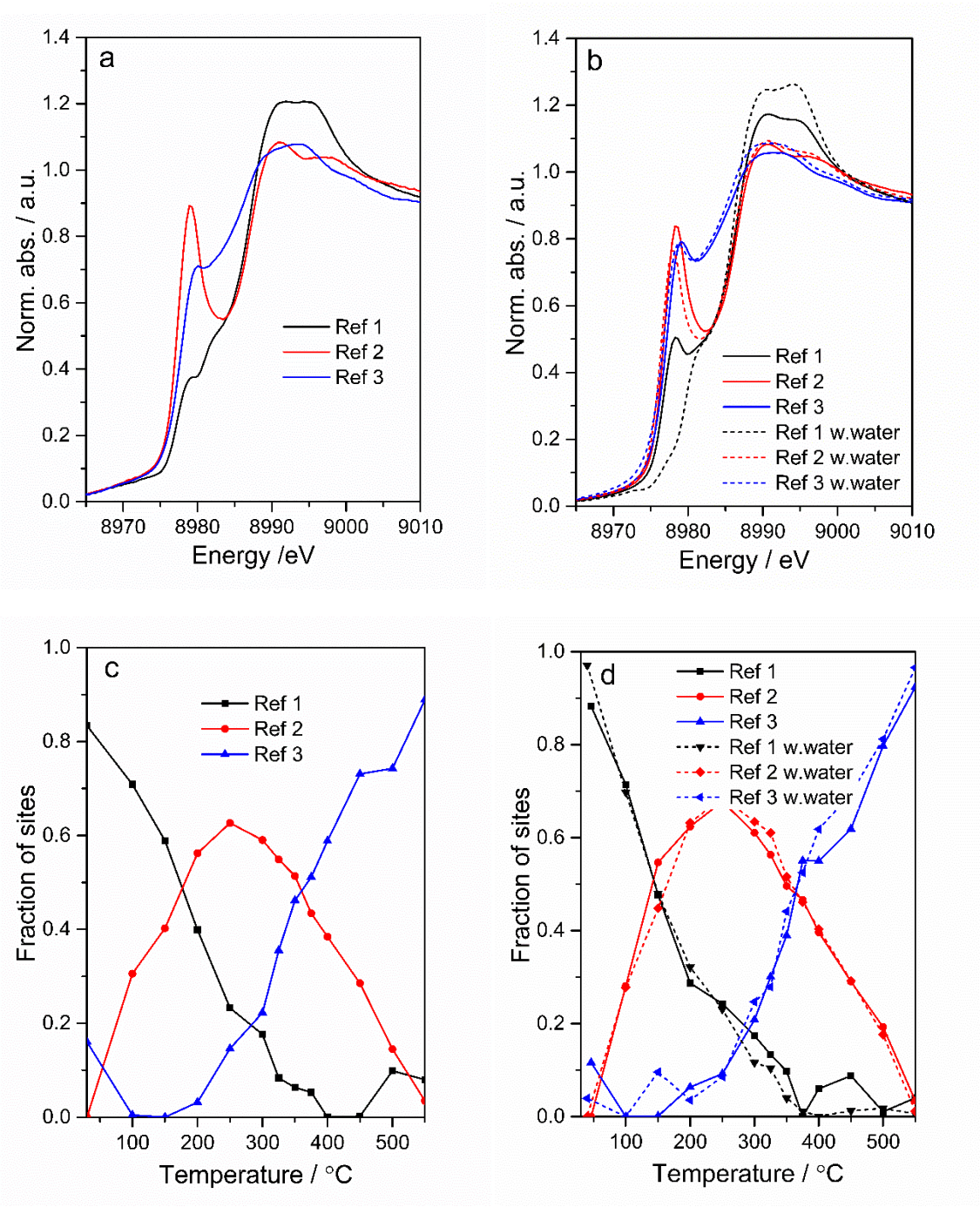


**Figure SI6.** Reference spectra obtained from $NH_3$-TPR of (a) Cu-0.5 and (b) Cu-1.2 using MCR-ALS as well as the concentration profiles for those components during TPR-XANES of (c) Cu-0.5 and (d) Cu-1.2. From the comparison with the large amount of available high-energy resolution XAS spectra of Cu sites in SSZ-13 (Fig. S5), spectrum Ref. 1 can be attributed to a mixture of $Cu^{2+}$ and $Cu^{+}$ sites (when no water is dosed with $NH_3$) or pure $Cu^{2+}$ in the presence of water vapour. Spectral component named Ref. 2 originates from $Cu^{+}$ sites with adsorbed ammonia (a complex with linear geometry), while high-temperature component Ref. 3 shows a spectrum of $Cu^{+}$ sites without direct coordination to ammonia. Thus, conversion from component "Ref. 2" to "Ref. 3" represents desorption of ammonia from reduced $Cu^{+}$ sites.

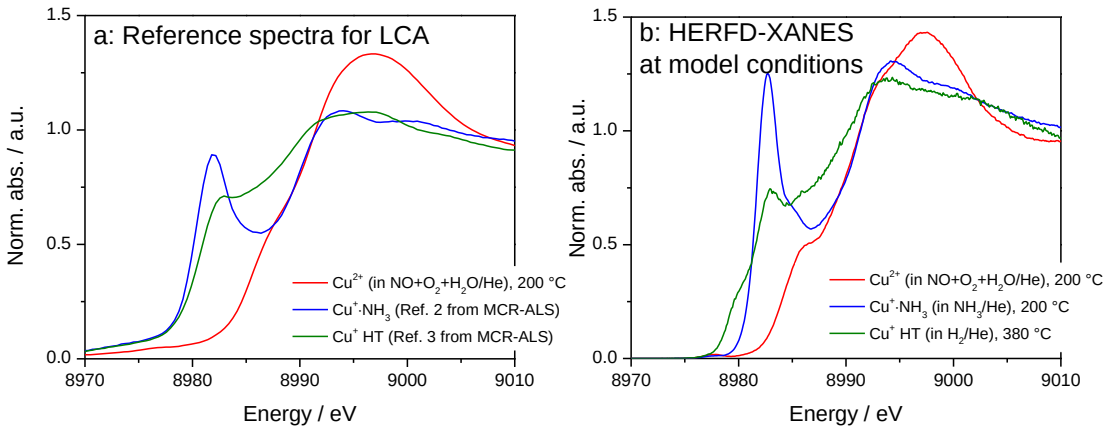


**Figure SI7.** (a) Reference spectra used for linear combination analysis of operando XANES recorded under SCR conditions. (b) Spectra of Cu-1.2 zeolite acquired earlier [15] under model conditions.

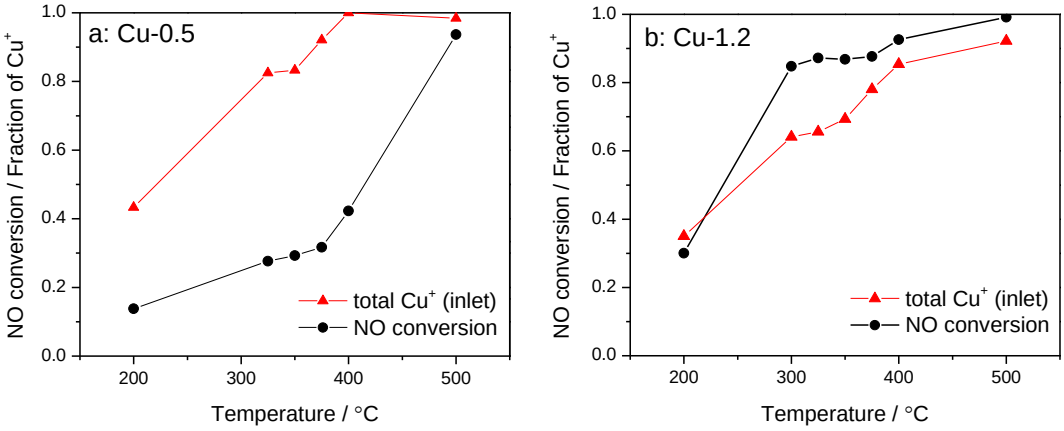


**Figure SI8.** Conversion of NO and total fraction of $Cu^+$ (normalized to all Cu species) obtained by LCA of XANES spectra measured during *operando* XAS studies at SLS. Values reported for (a) Cu-0.5 and (b) Cu-1.2 catalysts. The fraction of $Cu^+$ is reported for inlet of the catalyst bed. The error bars of the LCA are within 10 %. Conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10 % $O_2$, 1.5 % $H_2O$, balance He, GHSV 200 000 $h^{-1}$.

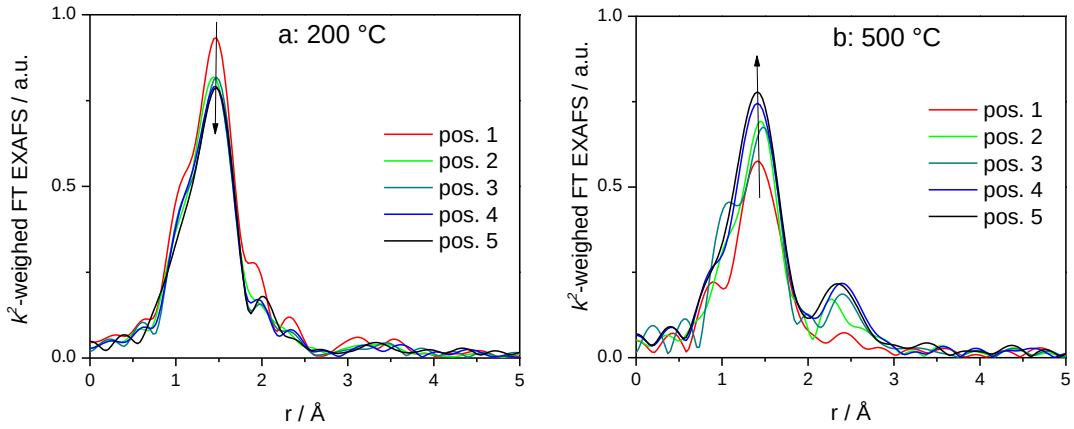


**Figure SI9.** *Operando* FT EXAFS spectra (uncorrected for the phase shift) of Cu-1.2 measured at (a) 200 °C and (b) 500 °C under SCR feed. The spatially resolved spectra are measured at equidistant points (the first and the last points are at 0.5 mm from the inlet / outlet of the 7 mm long catalyst bed. Conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10 % $O_2$, 1.5 % $H_2O$, balance He, GHSV 200 000 $h^{-1}$.

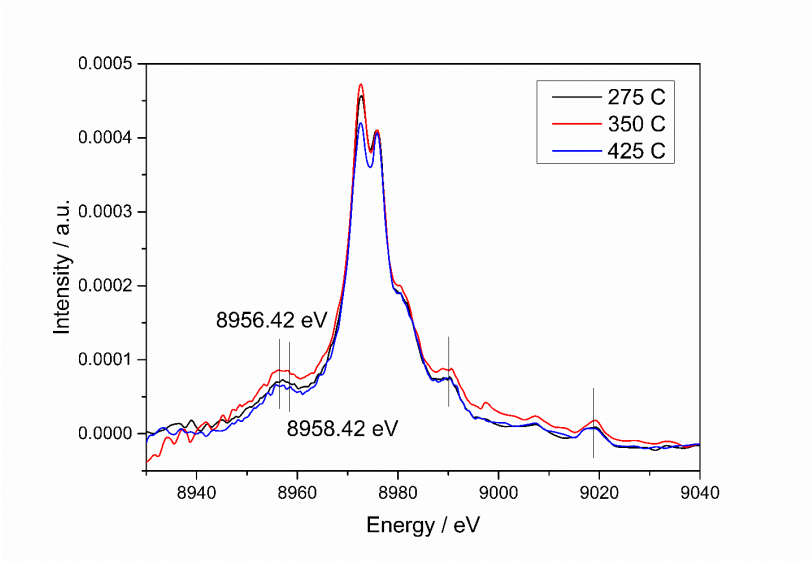


**Figure SI10.** *In situ* vtc-XES measured on Cu-1.2 at 275 °C, 350 °C and 425 °C. Conditions: 1000 ppm NO, 1000 ppm $NH_3$, 10 % $O_2$, 1.5 % $H_2O$, balance He, GHSV 200 000 $h^{-1}$.