Electronic Supporting Information

The dynamic nature of Cu sites in Cu-SSZ-13 and the origin of the seagull NOx conversion profile during NH3-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.

<table>
<thead>
<tr>
<th></th>
<th>CN (O) / d (Cu-O)</th>
<th>CN (Cu) / d (Cu-O-Cu)</th>
<th>CN (Al) / d (Cu-O-Al)</th>
<th>σ² (Å²)</th>
<th>δE₀ (eV)</th>
<th>ρ (%)</th>
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</thead>
<tbody>
<tr>
<td>Cu-0.5 Dry air 350 °C</td>
<td>2.4±0.4</td>
<td>0.37±0.24</td>
<td>n.a.</td>
<td>1.9±1.9</td>
<td>-6.1±1.8</td>
<td>1.7</td>
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<tr>
<td></td>
<td>1.88±0.01 Å</td>
<td>2.91±0.05 Å</td>
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<tr>
<td>Cu-1.2 Dry air 350 °C</td>
<td>3.0±0.4</td>
<td>1.0±0.5</td>
<td>n.a.</td>
<td>8.4±2.4</td>
<td>-2.8±1.3</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>1.92±0.01 Å</td>
<td>2.96±0.03 Å</td>
<td></td>
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</tbody>
</table>

Figure SI1. NOx conversion during NH3-SCR over the tested Cu-zeolites measured in the laboratory plug-flow reactor. Conditions: 1000 ppm NO, 1000 ppm NH3, 10 % O2, 5 % H2O, balance N2, 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$_2$O, 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$_2$O during NH$_3$-SCR over Cu-1.2 catalyst. Conditions: 1000 ppm NO, 1000 ppm NH$_3$, 10 % O$_2$, 0 - 5 % H$_2$O, balance N$_2$, GHSV 200 000 h$^{-1}$. 
Figure S14. 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$_2$O and 5 % (red line) H$_2$O (N$_2$ balance). GHSV was kept at 50 000 h$^{-1}$.

Figure S15. 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$_2$O, 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\(_2\)O, 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 NH₃, 10 % O₂, 1.5 % H₂O, 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 NH₃, 10 % O₂, 1.5 % H₂O, balance He, GHSV 200 000 h⁻¹.