Electronic Supplementary Information:
Isolated Cu$^{2+}$ Ions: Active Sites for Selective Catalytic Reduction of NO

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1) Equations used to calculate NO$_x$ conversion and selectivity to N$_2$O

Following equations were used to calculate the conversion of NO$_x$ ($X_{NO_x}$) and the selectivity to N$_2$O ($S_{N_2O}$).

$$X_{NO_x} = \frac{F_{NO,IN} - (F_{NO,OUT} + F_{NO_2,OUT})}{F_{NO,IN}} \cdot 100\%$$

$$S_{N_2O} = \frac{2 \cdot F_{N_2O,OUT}}{F_{NO,IN}} \cdot 100\%$$

where $F_{IN/OUT}$ is the flow rate of the component in mol/min.

2) Preparation of CuZSM-5 and its performance in NH$_3$-SCR and NO decomposition

CuZSM-5 sample was prepared by ion exchange. First commercial NH$_4$-ZSM-5 (Zeolyst, Si/Al 17) was ion exchanged 3 times at room temperature with NaNO$_3$ (1M) to obtain a Na-form of the zeolite. Thereafter, the sample was ion exchanged twice with Cu(NO$_3$)$_2$ (1M) solution under refluxing conditions for 12 h to obtain a sample containing 2.9 wt-% Cu. The sample was washed with distilled water, dried at 120 °C, and calcined at 550 °C under static air before use.

3) Selectivity to N$_2$O for CuCHA

![Fig. 1 Conversion of NO$_x$ for CuZSM-5 during NO decomposition (filled circles) and NH$_3$-SCR (open triangles). Note that the conversion of NO$_x$ in NO decomposition has been multiplied by 3 for the sake of clarity. The maximum NO decomposition activity was 26% at 500 °C.](image)

![Fig. 2 Selectivity to N$_2$O for CuCHA during NO decomposition (open circles) and during either NH$_3$- (filled circles) or C$_3$H$_6$-SCR (fresh catalyst: open triangles, aged catalyst: filled squares). Feed: 4000 ppm NO during NO decomposition and 1000 ppm NO, 1000 ppm NH$_3$ or C$_3$H$_6$, and 5% O$_2$ during SCR.](image)

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4) EXAFS analysis of the local environment around Cu\textsuperscript{2+}

Full cluster EXAFS simulations were performed on the data for the calcined sample using Model A from reference 1 as a starting basis. Refinements were performed in K-space over the data range 3–10 Å\textsuperscript{-1}. Coordination numbers were fixed whereas the Debye-Waller factors for shells above 3.20 Å were grouped together. Refinements were performed considering only single scattering contributions and were performed in 2 stages. First, contributions < 3.00 Å were refined and subsequently contributions between 3.00 – 4.15 Å. In order to minimise the number of parameters being, contributions from the same atom types at similar distances were also grouped together. Refinement of the data ceased when the R-factor reached a minimum value whilst yielding a chemically reasonable bond distances/angles for the atoms within the structure. The resultant fit to the data is given in Fig. 3 of the ESI with the resultant structural information obtained given below in Table 1. The refined structural model can be found in Fig. 3 of the main text and corresponds well to the proposed model A in the article by Pierloot et al. although we observe two major differences. Firstly model A in the reference predicts 3 unique bond lengths in the first coordination sphere which cannot be resolved by EXAFS. Since therefore the Cu-O distances were refined together unphysically short (1.53 – 1.56 Å) Si-O bond lengths. Secondly and despite this failing, the data are of sufficient quality so as to observe that the contribution from the longer 4th oxygen which makes up the square planar coordination environment is at 3.21 Å and not 2.37 Å thus suggesting that this oxygen and therefore the zeolite framework is not as distorted as predicted.

Table 1. Parameters derived from EXAFS fit for the Cu\textsuperscript{2+} ion within the dsf of the CHA complex

<table>
<thead>
<tr>
<th>Shells</th>
<th>R (Å)</th>
<th>N</th>
<th>2σ (Å\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O</td>
<td>1.93</td>
<td>3</td>
<td>0.013</td>
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<tr>
<td>Cu-Si</td>
<td>2.21</td>
<td>2</td>
<td>0.032</td>
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<tr>
<td>Cu-O</td>
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<td>1</td>
<td>0.029</td>
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<tr>
<td>Cu-Si</td>
<td>3.21</td>
<td>2</td>
<td>0.023</td>
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<tr>
<td>Cu-O</td>
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<td>0.023</td>
</tr>
<tr>
<td>Cu-O</td>
<td>4.01</td>
<td>3</td>
<td>0.033</td>
</tr>
<tr>
<td>Cu-Cu</td>
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<tr>
<td>Cu-Si</td>
<td>4.04</td>
<td>4</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Ef = 3.64 eV, R = 33.04 %

* For refinement purposes the coordination here is set to 1 although this value is likely to be much lower than this.
Fig. 6 Ex situ UV-Vis-NIR spectrum for fresh CuZSM-5 after calcination.

1) References