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_2O

Following equations were used to calculate the conversion of NO_x (X_{NO_x}) and the selectivity to N_2O (S_{N_2O}).

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

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

where $F_{i,IN/OUT}$ 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.

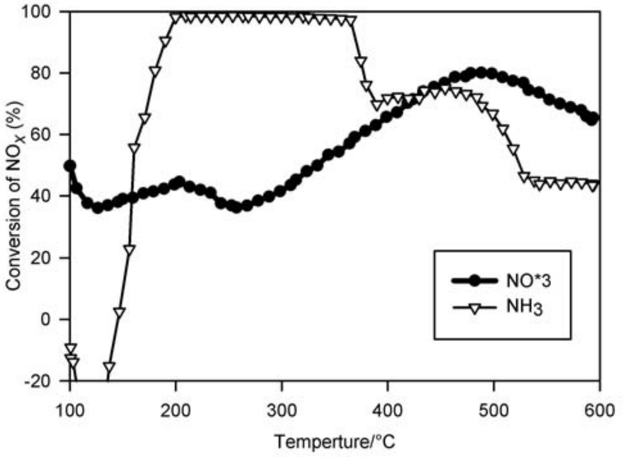

Fig. 1 Conversion of NO_x for CuZSM-5 during NO decomposition (filled circles) and NH_3-SCR (open triangles). Note that the conversion of NO_x in NO decomposition has been multiplied by 3 for the sake of clarity. The maximum NO decomposition activity was 26% at 500 °C.

3) Selectivity to N_2O for CuCHA

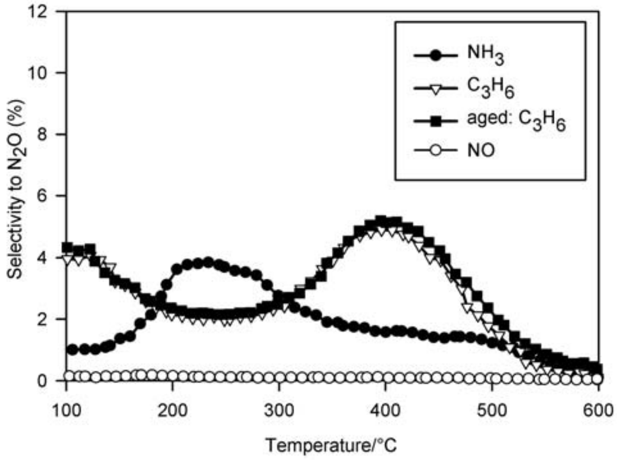

Fig. 2 Selectivity to N_2O for CuCHA during NO decomposition (open circles) and during either NH_3- (filled circles) or C_3H_6.-SCR (fresh catalyst: open triangles, aged catalyst: filled squares). Feed: 4000 ppm NO during NO decomposition and 1000 ppm NO, 1000 ppm NH_3 or C_3H_6, and 5% O_2 during SCR.

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4) EXAFS analysis of the local environment around Cu^{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 $Å^{-1}$. 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 correponds 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. b) 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^{2+} ion within the d6r of the CHA complex

Shells	**R (Å)**	**N**	**$2\sigma^2(Å^2)$**
Cu-O	1.93	3	0.013
Cu-Si	2.21	2	0.032
Cu-O	3.13	1	0.029
Cu-Si	3.21	2	0.023
Cu-O	3.33	2	0.023
Cu-O	4.01	3	0.033
Cu-Cu	3.78	1*	0.022
Cu-Si	4.04	4	0.033

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.

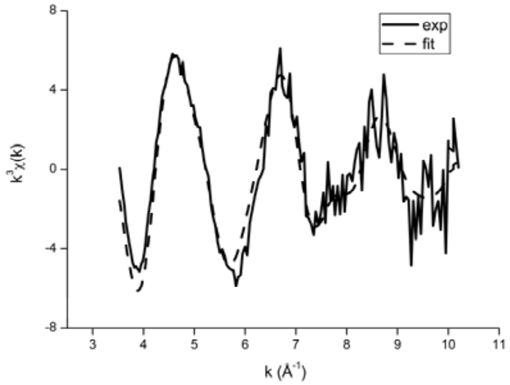

Fig. 3. EXAFS data fitted in K-space corresponding to the FT data shown in Fig. 2 of the manuscript.

5) XANES for CuCHA

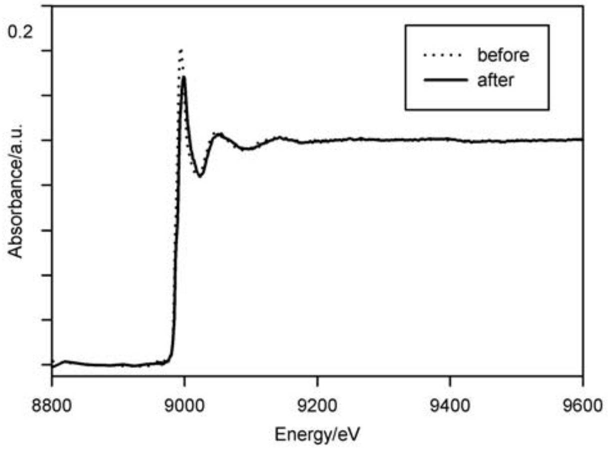

Fig. 4 K-edge XANES for CuCHA before (dotted line) and after (solid line) calcination at 500 °C.

6) Ex situ UV-Vis-NIR spectra for CuCHA, parent CHA, and CuZSM-5

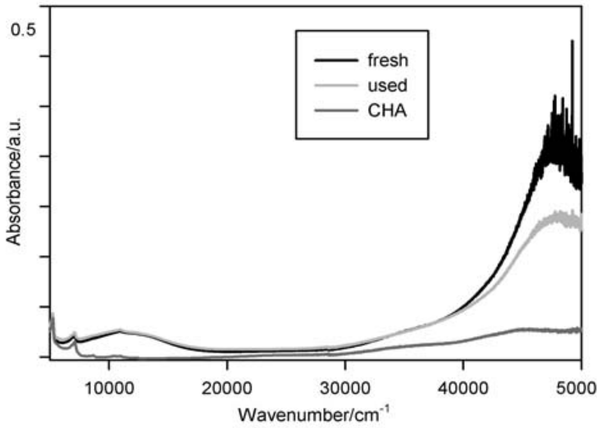

Fig. 5 Ex situ UV-Vis-NIR spectra for fresh and aged CuCHA and parent CHA.

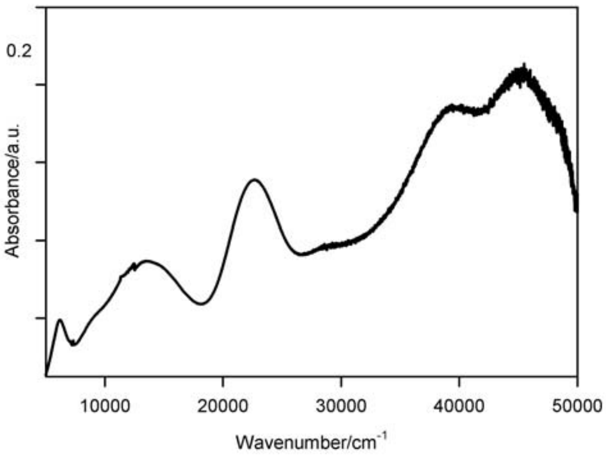

Fig. 6 Ex situ UV-Vis-NIR spectrum for fresh CuZSM-5 after calcination.

7) References

1. K. Pierloot, A. Delabie, M. H. Groothaert, R. A. Schoonheydt, *Phys. Chem. Chem. Phys*. 2001, **3**, 2174.