SUPPORTING INFORMATION

Effects of Dioxygen Pressure on Rates of NO\textsubscript{x} Selective Catalytic Reduction with NH\textsubscript{3} on Cu-CHA Zeolites

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Section S.1. Characterization data of H-CHA zeolite samples

Figure S1. X-Ray diffraction pattern of a representative parent H-CHA (Si/Al = 15) sample prepared using methods reported in Paolucci et al. [1]

Figure S2. Ar adsorption isotherm (87 K) on a representative parent H-CHA (Si/Al = 15) sample prepared using methods reported in Paolucci et al. [1]
Section S.2. Characterization of Cu-CHA zeolites with varying Cu ion density

Cu-CHA samples with varying spatial density of isolated Cu sites (present either as Cu$^{II}$ at paired framework Al or as [Cu$^{II}$OH]$^{+}$ at isolated framework Al) were studied here, as in our previous study [1]. These samples are denoted Cu-CHA-X, where X refers to the volumetric Cu density (atoms Cu per 1000 Å$^3$). Relevant structural and site characterization of these samples are provided in Table S1, including bulk elemental analysis, the number of Cu$^{II}$ and [Cu$^{II}$OH]$^{+}$ sites (per Al), the concentration of Cu ions per crystallite volume, and the mean Cu-Cu distance. Additional Cu site characterization (ex situ X-ray absorption and UV-Visible spectra) can be found in our previous study [2].

Table S1. Characterization data of oxidized Cu$^{II}$ forms of Cu-CHA-X samples (X = Cu volumetric density per 1000 Å$^3$). Elemental analysis, number of H$^+$ sites titrated by NH$_3$ on H-CHA and Cu-CHA samples, number of isolated Cu$^{II}$ and [Cu$^{II}$OH]$^{+}$ sites, concentration of Cu ions per crystallite volume, and the mean Cu-Cu distance. Characterization data originally reported in our prior study [2].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of H$^+$ sites</th>
<th>Number of Cu sites</th>
<th>Cu / 1000 Å$^3$</th>
<th>Mean Cu-Cu distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$^+$/Al (H-form)$^a$</td>
<td>H$^+$/Al (Cu-form)</td>
<td>Cu/Al</td>
<td>Cu$^{II}$/Al$^b$</td>
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<tr>
<td>Cu-CHA-0.078</td>
<td>0.98</td>
<td>0.81</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu-CHA-0.084</td>
<td>0.98</td>
<td>-</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>Cu-CHA-0.10</td>
<td>0.98</td>
<td>0.80</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu-CHA-0.17</td>
<td>0.98</td>
<td>0.70</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu-CHA-0.23</td>
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<td>0.64</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>Cu-CHA-0.29</td>
<td>1.00</td>
<td>0.61</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu-CHA-0.31</td>
<td>0.98</td>
<td>0.58</td>
<td>0.33</td>
<td>0.09</td>
</tr>
<tr>
<td>Cu-CHA-0.35</td>
<td>0.98</td>
<td>0.51</td>
<td>0.37</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$^a$ Different parent samples of H-CHA (Si/Al = 15), from replicate syntheses, were used to prepare the Cu-form samples.

$^b$ Determined from a site balance considering total Cu/Al, the number of H$^+$ titrated on H-form and Cu-form samples, and the 2:1 and 1:1 H$^+$.Cu exchange stoichiometry expected for Cu$^{II}$ and Cu$^{II}$OH, respectively.
Section S.3. Methods used to measure and calculate NO SCR rates by correcting for contributions of “fast” SCR reactions from NO₂

All reported NO SCR rates were corrected for contributions from the “fast” SCR reaction due to background NO₂, which is present as an impurity in NO cylinders and is formed by gas-phase NO oxidation. A blank reactor tube was loaded with 0.070 g SiO₂ to measure background NO₂ formation rates at fixed NO pressure (0.03 kPa) at 473 K, but with varying O₂ pressures (0.5–60 kPa O₂) and total gas flow rates (1.0–2.5 L min⁻¹ at ambient temperature and pressure) (Fig. S3a). The gas-phase NO₂ concentration in the reactor outlet was linearly proportional to O₂ pressure ($P_{O_2}$) and inversely proportional to gas flow rate $F$ (i.e., proportional to gas residence time), with a constant of proportionality $k$, as shown in Figure S3a and as described by Equation (S1); the non-zero y-intercept $b$ reflects NO₂ present as impurity levels in the NO cylinder.

$$[NO_2, \text{background}] = b + k\left(\frac{P_{O_2}}{F}\right)\left(\frac{P_{NO}}{0.03 \text{ kPa NO}}\right)^2$$  \hspace{1cm} (S1)

NO₂ formation rates that show a first-order dependence on O₂ pressure and second-order dependence on NO pressure are consistent with gas-phase NO oxidation kinetics [3]. Background NO₂ formation rates indeed showed a nearly second-order dependence in NO pressure (0.015–0.060 kPa) (Fig. S3b). In order to correct for background NO₂ formation for experiments in which the NO pressure was varied from 0.03 kPa, such as when NO reaction orders were measured, Equation S1 also accounts for the second-order dependence of NO₂ formation rates on NO pressure. For these experiments, the y-intercept ($b$) of Figure S3a was also adjusted based on measurements of NO₂ concentration at 0 kPa O₂ and different NO pressures. Given that the background NO₂ concentration depends on the reactant source (e.g., NO₂ impurities in the NO cylinder) and reactor size and hydrodynamics (e.g., internal volumes of the reactor and gas lines, gas mixing patterns, gas residence time), the NO₂ background
concentration must be independently measured for each reactor system and NO cylinder used to measure SCR rates.

**Figure S3.** NO$_2$ concentration in reactor outlet of blank reactor experiments (SiO$_2$ only). (a) Variation of residence times and O$_2$ pressures. Dotted line represents regression of the data to Eq. (S1) (reaction conditions: 0.030 kPa NO, 0.030 kPa NH$_3$, 1–60 kPa O$_2$, 7 kPa CO$_2$, 1 kPa H$_2$O and balance N$_2$, 1.0–2.5 L min$^{-1}$ total gas flow rate). (b) Variation of NO pressure. Linear fits were used to calculate NO reaction orders (reaction conditions: 0.015–0.060 kPa NO, 0.030 kPa NH$_3$, 10 (■) or 60 kPa (▲) O$_2$, 7 kPa CO$_2$, 1 kPa H$_2$O and balance N$_2$, 2.0 L min$^{-1}$ total gas flow rate).

In experiments with Cu-CHA catalysts, the NO$_2$ consumed over the catalyst bed was calculated as the difference between NO$_2$ formed in the blank reactor and NO$_2$ measured in the outlet of the reactor in each experiment (Equation S2).

$$NO_2\text{ consumed} = NO_2,\text{ background} - NO_2,\text{ reactor outlet} \quad (S2)$$

NO$_2$ consumption is assumed to occur through a “fast” SCR pathway, which consumes an equimolar amount of NO:

$$4\text{ NH}_3 + 2\text{ NO} + 2\text{ NO}_2 \rightarrow 4\text{ N}_2 + 6\text{ H}_2\text{O} \quad (S3)$$

To calculate the rate of “standard” NO SCR, NO$_2$ consumption was subtracted from the total NO consumption:

$$NO_2\text{ consumed, standard SCR} = NO\text{ consumed} - NO_2\text{ consumed} \quad (S4)$$
The ratio of “NO$_2$ consumed” to “NO consumed” is shown as a function of O$_2$ pressure for a representative sample (Cu-CHA-0.23) in Figure S4. For this sample, the magnitude of the “fast SCR correction” is 5-10% of the total NO consumption across all measured O$_2$ pressures.

**Figure S4.** Ratio of “NO$_2$ consumed” to “NO consumed” as a function of O$_2$ pressure for Cu-CHA-0.23 (reaction conditions: 0.030 kPa NO, 0.030 kPa NH$_3$, 1–60 kPa O$_2$, 7 kPa CO$_2$, 1kPa H$_2$O and balance N$_2$).

For each Cu-CHA zeolite sample, SCR rates (473 K) at twenty O$_2$ pressures between 1–60 kPa were measured in random order, holding the concentration of other gases fixed (1 kPa H$_2$O, 7 kPa CO$_2$, 0.030 kPa NO, 0.030 kPa NH$_3$, balance N$_2$) while maintaining differential conversion. Figure S5 shows SCR rates as a function of varying O$_2$ pressure measured on Cu-CHA-0.23 in two different flow reactor systems of different internal volumes; the agreement between these measurements validates the methods described here to measure and calculate NO SCR rates.
Figure S5. NO SCR rates (per Cu, 473 K) as a function of O₂ pressure in two separate reactor units for Cu-CHA-0.23 (reaction conditions: 0.030 kPa NO, 0.030 kPa NH₃, 1–60 kPa O₂, 7 kPa CO₂, 1 kPa H₂O and balance N₂). In order to account for background NO₂ formation in each reactor unit, the values of $k$ and $b$ in Equation S1 were measured independently for each system: Reactor Unit A (black diamonds), $k = 210.9$ (ppm mL min⁻¹ kPa⁻¹); $b = 0.73$ ppm. Reactor Unit B (grey squares), $k = 129.6$ (ppm mL min⁻¹ kPa⁻¹); $b = 1.6$ ppm.
Section S.4. Assessment of potential corruption of measured rates by transport phenomena

In order to assess the extent to which external transport phenomena influenced measured SCR rates, the gas hourly space velocity was varied from 1.13–2.26 ($10^6$ hr$^{-1}$) by varying total gas flow rates (1–2 L min$^{-1}$ at ambient temperature and pressure) for Cu-CHA-0.084 at different O$_2$ pressures (1, 10, 30, and 60 kPa O$_2$). SCR rates were invariant with space velocity at all O$_2$ pressures (Figure S6), indicating that measured rates were uncorrupted by external transport processes, and confirming the absence of bed-scale gradients in concentration or temperature. The invariance of measured NO SCR rates with gas flow rate also shows that measured reaction rates are not influenced by changes to the gas-phase NO$_2$ concentration at the front of the catalyst bed.

Figure S6. NO SCR rates (per Cu, 473 K) for Cu-CHA-0.084 as a function of gas hourly space velocity (reaction conditions: 0.030 kPa NO, 0.030 kPa NH$_3$, 1/10/30/60 kPa O$_2$, 7 kPa CO$_2$, 1 kPa H$_2$O and balance N$_2$).

The Weisz-Prater criterion (Equation S5) was used to estimate whether intracrystalline mass transport limitations affected measured rate data, and was calculated separately for O$_2$, NO, and NH$_3$, according to the following equation [4]:

$$N_{WP} = \frac{r_{obs} r_p^2}{(C_s D_{eff})}$$  \hspace{1cm} (S5)
where \( r_{obs} \) is the reaction rate per volume, \( r_p \) is the crystallite radius and taken as half (0.75 \( \mu \)m) of the crystallite length (1.5 \( \mu \)m) measured from SEM images of H-form CHA zeolites reported in our prior study [5], and \( C_s \) is the reactant concentration at the crystallite surface and taken as the bulk fluid concentration in the absence of external transport limitations. The final parameter in Equation (S5) is \( D_{eff} \), or the effective diffusivity of each molecule within zeolite crystallites, and were estimated according to:

(i) \( \text{O}_2 \): As an order-of-magnitude estimate, \( D_{eff} \) was taken as the diffusivity of \( \text{O}_2 \) in Zeolite 5A (LTA, containing 8-membered rings) at 303 K (1.2* 10^{-7} \text{ m}^2 \text{ s}^{-1}) [6], scaled to the reaction temperature of 473 K using Chapman-Enskog theory (2.3 x 10^{-7} \text{ m}^2 \text{ s}^{-1}):

\[
D_{eff,T_2} = D_{eff,T_1} (T_2/T_1)^{3/2}
\]

(S6)

At the most severe condition (Cu-CHA-0.37, 1 kPa \( \text{O}_2 \)), \( N_{WP,O_2} \sim 2 \times 10^{-5} \ll 1 \), verifying the absence of significant intracrystalline \( \text{O}_2 \) transport limitations.

(ii) \( \text{NO} \): The diffusivity of NO in LTA was not found in the literature; thus, as an order-of-magnitude estimate, \( D_{eff} \) was taken as the diffusivity of \( \text{N}_2 \) in Zeolite 5A (LTA, containing 8-membered rings) at 303 K (6.8* 10^{-8} \text{ m}^2 \text{ s}^{-1}) [6], scaled to the reaction temperature of 473 K using Chapman-Enskog theory (1.3 x 10^{-7} \text{ m}^2 \text{ s}^{-1} ) according to Equation (S6). At the most severe condition (Cu-CHA-0.37, 60 kPa \( \text{O}_2 \)), \( N_{WP,NO} \sim 6 \times 10^{-3} \ll 1 \), verifying the absence of significant intracrystalline NO transport limitations.

(iii) \( \text{NH}_3 \): \( D_{eff} \) was set equal to the reported diffusivity of saturated \( \text{NH}_3 \) in Cu-CHA at 473 K (1.2* 10^{-9} \text{ m}^2 \text{ s}^{-1}), which was measured using quasielastic neutron scattering on a 3 wt% Cu-CHA sample (Si/Al = 17) exposed to 80 kPa \( \text{NH}_3 \) [7]. \( N_{WP,\text{NH}_3} \) is plotted as a function of Cu density and \( \text{O}_2 \) pressure in Figure S7. \( N_{WP,\text{NH}_3} < 1 \) at all conditions, suggesting the absence of
severe intracrystalline NH$_3$ transport limitations. These conservative estimates of N$_{WP, \text{NH}_3}$ become $> 0.1$ at higher Cu densities and O$_2$ pressures, however, indicating that NH$_3$ diffusion might affect rates measured under certain conditions.

**Figure S7.** Estimated Weisz-Prater number for NH$_3$ as a function of O$_2$ pressure and Cu density for Cu-CHA-X samples. 1 kPa (triangles), 10 kPa (circles) and 60 kPa O$_2$ (squares) (reaction conditions: 0.030 kPa NO, 0.030 kPa NH$_3$, 1/10/60 kPa O$_2$, 7 kPa CO$_2$, 3 kPa H$_2$O and balance N$_2$ at 473 K).
Section S.5. Measurement of apparent reaction orders on Cu-CHA samples in low and high O₂ pressure limits

The data in Figure 2b (main text) are plotted in a log-log scale in Figure S8 to better visualize the quality of the fit between the measured data and the rate model (Eq. (3)).

Figure S8. Steady-state SCR rates (per Cu) as a function of O₂ pressure plotted using logarithmic scales on Cu-CHA-X samples (light-to-dark shading as X increases). Dashed lines represent regression of the data to Eq. (3).

With increasing O₂ pressure (1–60 kPa), apparent NO orders increase systematically from 0.2 to 0.8, while apparent NH₃ orders remain essentially invariant near a value of -0.5 (Table S2).

Table S2. SCR kinetic parameters measured on Cu-CHA samples at 1, 10, and 60 kPa O₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 kPa O₂</th>
<th>10 kPa O₂</th>
<th>60 kPa O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO order</td>
<td>NH₃ order</td>
<td>NO order</td>
</tr>
<tr>
<td>Cu-CHA-0.078</td>
<td></td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Cu-CHA-0.17</td>
<td>0.3</td>
<td>-0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Cu-CHA-0.29</td>
<td>0.2</td>
<td>-0.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

a Other reaction conditions: 0.030 kPa NH₃, 7 kPa CO₂, 1 kPa H₂O and balance N₂ at 473 K
b Other reaction conditions: 0.030 kPa NO, 7 kPa CO₂, 1 kPa H₂O and balance N₂ at 473 K
Uncertainties are ± 0.1.
**Figure S9.** Steady-state SCR rate (per Cu) versus O$_2$ pressure on Cu-CHA-X samples (light-to-dark shading as X increases), along with best fit lines representing O$_2$ reaction orders, in the pressure ranges of (a) 1–4 kPa O$_2$, (b) 5–15 kPa O$_2$, and (c) 40–60 kPa O$_2$. For Cu-CHA-0.78, Cu-CHA-0.084, and Cu-CHA-0.10, the O$_2$ reaction order in the low O$_2$ pressure range was instead reported from 2-5 kPa O$_2$ improve experimental accuracy, due to the low (~1%) NO conversion at 1 kPa O$_2$ for these samples.
Figure S10. Steady-state SCR rate (per Cu) versus NH$_3$ pressure on Cu-CHA-0.078, Cu-CHA-0.17, and Cu-CHA-0.29 (light-to-dark shading as X increases), along with best fit lines representing NH$_3$ reaction orders, at various O$_2$ pressures: (a) 1 kPa O$_2$ (Cu-CHA-0.078 was omitted due to noisier measurements in this case), (b) 10 kPa O$_2$, (c) 60 kPa O$_2$. 
Figure S11. Steady-state SCR rate (per Cu) versus NO pressure on Cu-CHA-0.078, Cu-CHA-0.17, and Cu-CHA-0.29 (light-to-dark shading as X increases), along with best fit lines representing NO reaction orders, at various O₂ pressures: a) 1 kPa O₂ (Cu-CHA-0.078 was omitted due to noisier measurements in this case), b) 10 kPa O₂, c) 60 kPa O₂.
Section S.6. *In operando* XANES spectra of Cu-CHA-0.23 with varying O₂ pressure

**Figure S12.** *In-operando* XANES spectra measured at 1 kPa O₂, 5 kPa O₂, 10 kPa O₂, 30 kPa O₂, and 60 kPa O₂ (light to dark with increasing O₂ pressure). The balance gas compositions were 0.030 kPa NH₃, 0.030 kPa NO, 2 kPa H₂O, 7 kPa CO₂, and balance N₂. Linear combination fitting to Cu(I) and Cu(II) standards was performed as previously reported [1].
Section S.7. Transient O₂-assisted oxidation of pre-reduced Cu-CHA-X samples: Models to fit rate data and corresponding XANES spectra

As described in our previous study [2], the transient decrease of Cu¹ with time (Fig. 4, main text) is best described by the following rate law, assuming an integral power on [Cu¹]:

$$\frac{d[\text{Cu}^1(t)]}{dt} = -2k_{\text{ox}}[\text{Cu}^1(t)]^2$$

(S7)

In order to account for the unoxidizable Cu¹ fraction (denoted as [Cu¹(∞)]) observed in XANES spectra at the end of the transient O₂-assisted oxidation experiments (Figs. S13-S19), we define the concentration of Cu¹ that can participate in the oxidation reaction as:

$$[\text{Cu}^1(t)]_{\text{corr}} = [\text{Cu}^1(t)] - [\text{Cu}^1(\infty)]$$

(S8)

$$\frac{d[\text{Cu}^1(t)]_{\text{corr}}}{dt} = -2k_{\text{ox}}[\text{Cu}^1(t)]_{\text{corr}}^2$$

(S9)

Since [Cu¹(t)]corr is the concentration of Cu¹ that is oxidizable by O₂ as a function of time, Eq. (S9) can be integrated from 0 to t, and subsequently rearranged to yield:

$$\text{Cu}^1 \text{ Fraction} = \frac{[\text{Cu}^1(t)]}{[\text{Cu}_{\text{total}}]} = \frac{1 - [\text{Cu}^1(\infty)]/[\text{Cu}^1(0)]}{1 + 2k_{\text{ox}}([\text{Cu}^1(0)] - [\text{Cu}^1(\infty)])t} + \frac{[\text{Cu}^1(\infty)]}{[\text{Cu}^1(0)]}$$

(S10)

where $k_{\text{ox}}$ and [Cu¹(∞)] are the fitted parameters. For each data series, [Cu¹(∞)] is set equal to the Cu¹ fraction of the final time point, and non-linear least-squares regression was used to obtain the best-fit parameter of $k_{\text{ox}}$ (listed in Table 3, main text).
Figure S13. Time-resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.078 (473 K, 10 kPa O\textsubscript{2}) after treatment in 0.030 kPa NO and 0.030 kPa NH\textsubscript{3} at 473 K. A total of 40 spectra were collected in 20 second intervals. The first 10 spectra are plotted for clarity.

Figure S14. Time-resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.10 (473 K, 10 kPa O\textsubscript{2}) after treatment in 0.030 kPa NO and 0.030 kPa NH\textsubscript{3} at 473 K. A total of 40 spectra were collected in 20 second intervals. The first 10 spectra are plotted for clarity.
Figure S15. Time-resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.17 (473 K, 10 kPa O₂) after treatment in 0.030 kPa NO and 0.030 kPa NH₃ at 473 K. A total of 40 spectra were collected in 14.5 second intervals. The first 10 spectra are plotted for clarity.

Figure S16. Time-resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.23 (473 K, 10 kPa O₂) after treatment in 0.030 kPa NO and 0.030 kPa NH₃ at 473 K. A total of 30 spectra were collected in 21.5 second intervals. The first 10 spectra are plotted for clarity.
Figure S17. Time-resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.29 (473 K, 10 kPa O₂) after treatment in 0.030 kPa NO and 0.030 kPa NH₃ at 473 K. A total of 39 spectra were collected in 14.5 second intervals. The first 10 spectra are plotted for clarity.

Figure S18. Time resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.31 (473 K, 10 kPa O₂) after treatment in 0.030 kPa NO and 0.030 kPa NH₃ at 473 K. A total of 32 spectra were collected in 21.5 second intervals. The first 10 spectra are plotted for clarity.
Figure S19. Time-resolved XANES spectra measured during the transient oxidation of Cu-CHA-0.35 (473 K, 10 kPa O₂) after treatment in 0.030 kPa NO and 0.030 kPa NH₃ at 473 K. A total of 30 spectra were collected in 21.5 second intervals. The first 10 spectra are plotted for clarity.
Section S.8. Transient NO+NH$_3$-assisted reduction of oxidized Cu-CHA-X samples: Models to fit rate data and corresponding XANES spectra

The transient decrease in Cu$^{II}$ during reduction in NO and NH$_3$ can be described by a rate law that is first-order in Cu:

$$\frac{d[Cu^{II}(t)]}{dt} = -k_{\text{red}}[Cu^{II}(t)]$$ \hspace{1cm} (S11)

In some samples studied, XANES spectra at the end of the transient NO+NH$_3$-assisted reduction experiments (Figs. S20-S24) showed small percentages ($\leq 10\%$) of Cu$^{II}$ that were not reduced, although we note that these values are within the uncertainty of the linear combination XANES fitting procedure. For the purposes of modeling the data in Figure 6 (main text), we define the fraction of Cu that are able to reduce as:

$$[Cu^{II}(t)]_{\text{corr}} = [Cu^{II}(t)] - [Cu^{II}(\infty)]$$ \hspace{1cm} (S12)

$$\frac{d[Cu^{II}(t)]_{\text{corr}}}{dt} = -k_{\text{red}}[Cu^{II}(t)]_{\text{corr}}$$ \hspace{1cm} (S13)

Integration of Eq. (S13) yields the following expression:

$$Cu^{II} \text{ Fraction} = \frac{[Cu^{II}(t)]}{[Cu_{\text{total}}]} = \frac{[Cu^{II}]-[Cu^{II}(\infty)]}{[Cu_{\text{total}}]} e^{-k_{\text{red}}t} + \frac{[Cu^{II}(\infty)]}{[Cu_{\text{total}}]}$$ \hspace{1cm} (S14)

Where $k_{\text{red}}$ and $[Cu^{II}(\infty)]$ are fitted parameters. For each data series, $[Cu^{II}(\infty)]$ was set equal to the Cu$^{II}$ fraction of the final time point, and non-linear least-squares regression was used to obtain the best-fit parameter of $k_{\text{red}}$ (listed in Table 3, main text).

The transient reduction rate constants measured here were compared to a similar experiment reported in the literature by Liu et al. [8] using the following approximations. First, their reported initial rate of NO and NH$_3$ reduction (1.7 mmol NO g$^{-1}$ h$^{-1}$ at 0.05 kPa NO and 423 K) was converted to the units of our reduction rate constant:

$$1.7 \frac{\text{mmol NO}}{\text{g h}} \times \frac{1 \text{ g cat}}{0.02 \text{ g Cu}} \times \frac{63.546 \text{ g Cu}}{\text{mol}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1 \text{ mol}}{1000 \text{ mmol}} = 0.0015 \frac{\text{mol NO}}{\text{mol Cu s}}$$ \hspace{1cm} (S15)
Next, the Arrhenius equation was applied to estimate this rate at 473 K, assuming an activation energy of 70 kJ/mol, which is consistent with reported apparent activation energies for low-temperature SCR in the reduction-limited regime [2,9]:

\[
\frac{r_{NO,473K}}{r_{NO,423K}} = e^{\frac{E_a}{R} \left( \frac{1}{423} - \frac{1}{473} \right)} = 0.012 \ \frac{\text{mol NO}}{\text{mol Cu} \ \text{s}}
\] (S16)

Finally, it was assumed that transient NO and NH\(_3\) reduction is first-order in NO, and this rate was scaled by the ratio of NO pressures in the two experiments (3/5) to achieve the final estimate for the rate constant of 0.007 s\(^{-1}\), which is quantitatively consistent with our measurement.

**Figure S20.** Time-resolved XANES spectra measured during the transient reduction of Cu-CHA-0.078 (473 K, 0.030 kPa NH\(_3\), 0.030 kPa NO) after treatment in 20 kPa O\(_2\) at 673 K. A total of 30 spectra were collected in 16.5 second intervals. The first 10 spectra are plotted for clarity.
Figure S21. Time-resolved XANES spectra measured during the transient reduction of Cu-CHA-0.084 (473 K, 0.030 kPa NH₃, 0.030 kPa NO) after treatment in 20 kPa O₂ at 673 K. A total of 37 spectra were collected in 22.5 second intervals. The first 10 spectra are plotted for clarity.

Figure S22. Time-resolved XANES spectra measured during the transient reduction of Cu-CHA-0.17 (473 K, 0.030 kPa NH₃, 0.030 kPa NO) after treatment in 20 kPa O₂ at 673 K. A total of 40 spectra were collected in 14.5 second intervals. The first 10 spectra are plotted for clarity.
Figure S23. Time-resolved XANES spectra measured during the transient reduction of Cu-CHA-0.23 (473 K, 0.030 kPa NH₃, 0.030 kPa NO) after treatment in 20 kPa O₂ at 673 K. A total of 54 spectra were collected in 22.5 second intervals. The first 10 spectra are plotted for clarity.

Figure S24. Time-resolved XANES spectra measured during the transient reduction of Cu-CHA-0.35 (473 K, 0.030 kPa NH₃, 0.030 kPa NO) after treatment in 20 kPa O₂ at 673 K. A total of 21 spectra were collected in 22.5 second intervals. The first 10 spectra are plotted for clarity.
Section S.9. References


