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Low-Temperature Standard-SCR over Cu-SSZ-13: Selective Inhibition of the Oxidation Half-Cycle by Mild Hydrothermal Aging

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Abstract

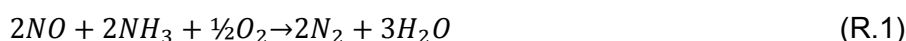
The impact of mild hydrothermal aging (HTA) on low-temperature (150–200 °C) Standard-SCR is investigated using transient response methods and transient kinetic analysis. We decouple the Reduction and the Oxidation Half-Cycles (RHC and OHC) of the Standard-SCR redox mechanism to study them independently. While the RHC rates are essentially unaffected, OHC is inhibited by mild HTA. By equating the estimated rate expressions (both 2nd order in Cu sites, OHC with O₂ as the sole oxidant), we predict exactly the steady-state low-temperature Standard-SCR performance in terms of both NO conversion and bed-average Cu redox state, as well as the detrimental effect of mild HTA on the DeNO_x efficiency. We also demonstrate that the DeNO_x activity of the aged catalyst can be precisely restored by incrementing the oxygen partial pressure in proportion to the drop of the OHC rate constant, as predicted by our simple two-reaction model. These findings offer valuable insights into the design of next-generation urea-SCR exhaust gas aftertreatment (EGA) systems featuring enhanced cold-start performance and durability under aging conditions.



Keywords: NH₃-SCR, Hydrothermal Aging, Cu-SSZ-13, Transient Response Methods, Recovery of Activity

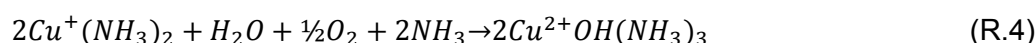
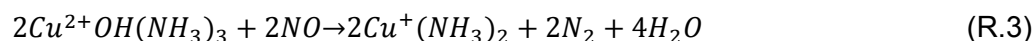
1. Introduction

Nitrogen oxides (NO_x) in Diesel engine vehicles' exhausts – both light- and heavy-duty – remain a critical challenge for human health and the environment^{1,2}. In this context, maintaining high deNO_x performance at low temperatures is particularly important, since the SCR catalyst is often required to operate during cold-start and other low-load driving conditions, where hydrothermal aging can further deteriorate activity^{3,4}. This leads to a continuous interest in Ammonia-Selective Catalytic Reduction (NH₃-SCR), a well-established technology, which reduces NO_x to harmless N₂ through the use of aqueous urea^{5,6}. The main reactions are the Standard-SCR, where NO, NH₃, and O₂ are combined (R.1), and Fast-SCR (R.2), involving NO₂.



The state-of-the-art SCR catalysts for mobile applications are metals-exchanged zeolites, in particular copper-chabazite, a small-pore type zeolite such as Cu-SSZ-13⁷. They are characterized by high selectivity to nitrogen, a wide operating temperature range, and hydrothermal stability⁷⁻⁹. Copper-exchanged zeolites are usually preferred to iron-zeolites due to their higher low-temperature activity ($T \leq 250^\circ\text{C}$)¹⁰ even in the absence of NO₂ (produced by the upstream Diesel Oxidation Catalyst, DOC), which is necessary for Fast-SCR to occur (R.2).

It is well-established that Standard-SCR works with a Cu/redox mechanism at low temperatures¹¹⁻¹⁵, composed of Reduction and Oxidation Half-Cycles (RHC and OHC, respectively), where isolated copper ions cycle between Cu²⁺ and Cu⁺. Recent works¹⁴⁻¹⁸ demonstrated the low-T reaction stoichiometries for RHC and OHC (reported as R.3 and R.4); summed, they lead to the Standard-SCR reaction (R.1).



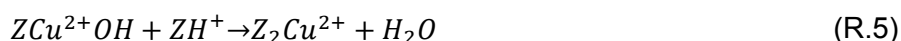
The RHC is characterized by an equimolar consumption of NO and NH₃, production of nitrogen, and Cu²⁺ reduction to Cu¹⁺ (NO:NH₃:Cu²⁺=1:1:1), involving two-proximate ammonia-solvated Cu ions^{14,19-22}. The OHC (R.4) works in the presence of sole oxygen and is promoted by water that acts as a proton transfer molecule, as recently confirmed through DFT calculations by Contaldo et al.²³: O₂ is activated by two diamino Cu⁺ complexes $Cu^+(NH_3)_2$ to form a μ -oxo Cu²⁺-dimer $Cu_2^{2+}(NH_3)_4O_2$,



while H₂O is oxidized to H₂O₂, which acts as an oxygen shuttle to oxidize an additional pair of Cu²⁺ (NH₃)₂.

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Notice that reactions (R.3) and (R.4) rely on NH₃-solvated mobile Cu²⁺OH moieties, originating from ZCu²⁺OH framework-bound species, but the SCR-active sites precursors also include the bidentate Z₂Cu²⁺ species (Z is the AlO₄⁻ of the zeolite framework), which are also thermodynamically favored. The Cu speciation, in fact, depends on the catalyst formulation²⁴ (i.e., on the Si/Al and the Cu/Al ratios) and/or on the extent of aging^{25–27}. Indeed, because the upstream DOC and Diesel Particulate Filter (DPF) generate exothermic reactions during hydrocarbon and soot oxidation, the downstream NH₃-SCR catalyst is exposed to higher temperatures in the presence of water and oxygen^{28,29}. If the temperature is limited to 600–700 °C, it results in mild Hydrothermal Aging (HTA) of the catalyst: the dealumination of the zeolite is minimal in these conditions^{30,31}. Instead, during mild HTA, the Cu speciation is shifted, with a combination of the single-bonded copper atoms with a Brønsted Acid Site (BAS) to form the double-bonded copper atom:



Different methods have been used to quantify this phenomenon (e.g., NH₃ titration³², NO₂ desorption³³, H₂-TPR³⁴, EPR²⁵), but a correlation with the loss of performance of the SCR catalyst is still difficult to identify. Indeed, it is known that over Cu-SSZ-13 NO conversion slightly decreases under mild HTA^{8,9,25}, but a correlation with the shift in copper speciation remains to be established, to our knowledge. Wenig et al.³⁵ have combined steady-state Standard-SCR data and *Operando* XAS over Cu-CHA and Cu-AEI: at low T, they report a drop of the oxidized copper fraction during Standard-SCR with HTA, e.g., at 150 °C over Cu-CHA from ~30 to 0 %. Zhang et al.³⁶ have prepared samples with different Cu speciation (ZCu²⁺OH fraction from 73 to 86 %), and have seen that, with HTA, the catalyst with the lowest ZCu²⁺OH had the lowest loss of performance. Deka et al.³⁷ have shown how classical mild HTA slightly worsens the DeNO_x performances at low T, and mild HTA in H₂-ICE conditions (high water content and/or H₂ slip presence) further decreases the performances. Experimental and modeling work from Zheleznyak et al.³⁸ has indicated that Z₂Cu²⁺ sites are inactive in NO oxidation.

Additionally, the effect of mild HTA on the two half-cycles of the redox mechanism (RHC and OHC) has been studied under different conditions. Gramigni et al.²⁰, Daya et al.¹⁷, and Nasello et al.³⁹ have all demonstrated that the RHC over different-aged Cu-CHA catalysts with diverse Cu loadings and SAR is hardly affected by mild HTA up to 350 °C, both in dry and wet conditions. This is possibly due to the hydrolysis reaction – i.e., (R.5) reverse –, which is not kinetically limited when the RHC is taking place, as shown by DFT calculations by Hu et al.⁴⁰. Deka et al.⁴¹ have investigated a field-aged catalyst at high temperatures: while confirming that aging does not have an impact on RHC, they show instead that the OHC is greatly affected. The activation energy of the Standard-SCR of the Degreened sample is shown to be between the RHC and the OHC activation energies, while for



the field-aged, the Standard-SCR E_A was almost equal to the E_A of the OHC only, suggesting its role as the Rate Determining Step (RDS).

In this work, we focus on how mild HTA affects both the RHC and the OHC, coupling transient tests in laboratory-controlled conditions with kinetic analysis. This will allow us, using Transient Response Methods and a simple two-reaction model, to predict the behavior of the catalyst and its performance during mild HTA. Also, we propose a methodology to recover the activity over the aged catalyst based on the findings reported here and in previous works.

2. Materials and Methods

2.1. Experimental set-up

The experiments are conducted over two Cu-SSZ-13 samples with the same copper loading (2.6 % w/w) and Silica-to-Alumina Ratio (SAR, equal to 30), both quantified by ICP-MS. The two samples were provided by Cummins Inc. in the form of washcoated honeycomb monoliths; catalytic powders were scratched from the monolith, characterized by ICP analysis and loaded in the test reactor.

The first sample was conditioned at 550 °C for four hours at 10 % v/v of both H₂O and O₂ in N₂. Conversely, the second sample went through a mild hydrothermal aging protocol: 650 °C for 50 h under the same inlet gas conditions. In the following, the two samples will be called Degreened and Aged (shortened to deg and aged in the figures).

In the kinetic experiments, two quartz tubular reactors (ID = 6 mm) are loaded with 32 mg of catalyst powders diluted with 98 mg of cordierite powders. Both the samples and the cordierite are sieved to 140-200 mesh to avoid internal mass transfer limitations. The overall load of Cu in the reactor is 13.0 μmol in all the experiments. A thermocouple (K-type) is placed on top of the catalyst bed, assuring correct contact between the two, and is used to control the electric furnace to set the reactor temperature. The reactor has three feed lines: a main one with He and two lines connected to six-way valves. These valves are used to step feed and remove the main gas species. Indeed, by a simple switch, we are able to feed NO, NO₂, NH₃, and/or O₂; when not needed, we feed helium at the same flow rate. The main line of helium can be switched to a saturator in order to have water vapor in the line. The reactor outlet line is split into two online gas analyzers: a UV analyzer (ABB Limas 11HW) and a mass spectrometer (Hiden QGA). The first is used to measure the NO, NO₂, and NH₃, while the second measures N₂, Ar (used as pulse-valve tracer), O₂, and H₂O concentrations. All the lines are heated at 180 °C to prevent water condensation and/or ammonium nitrate formation.



2.2. Experimental procedures

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The Transient Response Methods (TRMs) used in this work resemble those of our recent works^{16,39}. A quick recap of the procedures is reported here with details on the specific experimental conditions:

- **NO₂ adsorption + TPD:** after a pre-oxidation of the catalyst at 550 °C with 8.0 % v/v of O₂ in He, the temperature is set to 150 °C and 500 ppm of NO₂ in He are fed to the reactor. The GHSV is set to 266,250 cm³ h⁻¹ g_{cat}⁻¹ (STP). Nitrates are formed and stored on the catalyst via disproportionation of NO₂ with the formation of NO^{42,43}. After a purge in He, the catalyst undergoes a Temperature-Programmed Desorption (TPD) up to 550 °C with a heating rate of 15 °C min⁻¹. This protocol is used to evaluate the copper speciation (ZCu²⁺OH and Z₂Cu²⁺) by assuming that the ZCu²⁺OH fraction is equal to the ratio of the NO₂ released upon nitrates decomposition during the TPD to the total reducible Cu present in the sample⁴⁴.
- **Reduction Half-Cycle:** the catalyst is pre-oxidized at 550 °C with 8.0 % v/v of O₂ in He for 1 h, followed by cooling to the desired temperature (150, 175, or 200 °C). The GHSV is set to 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP). Once the test temperature is reached, we inject 2.0 % v/v of H₂O via the saturator if the experiment is in wet feed conditions. Then we also feed 500 ppm of NH₃ in He until reaching full saturation of the catalyst, to decouple the RHC from the NH₃ adsorption on the catalyst^{14,20,21}. As soon as the catalyst is fully saturated, NO (500 ppm) is added to monitor the transient consumption (and the associated nitrogen production) and, thus, the RHC dynamics under isothermal conditions. We also calculate the amounts of NO consumed and N₂ produced by integrating the outlet concentration traces over time.
- **Oxidation Half-Cycle:** the catalyst is fully reduced with 500 ppm of NO, 500 ppm of NH₃, and 2 % of H₂O in He and then oxidized with 1.0 % v/v of O₂ and 2.0 % of H₂O in He. Like for the RHC tests, the GHSV is equal to 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP). The process is continuously repeated by changing the duration of the oxidation step (e.g., 1 min, 7 min, 1 h, etc.), to assess the temporal evolution of the oxidized copper fraction¹⁶. By integrating the amount of NO consumed and N₂ produced during the reduction step, which follows each oxidation at different times, and exploiting the Cu²⁺:NO:N₂ = 1:1:1 molar ratios, the Cu²⁺ fraction is computed as in Equation (1):

$$\sigma = \frac{Cu^{2+}}{Cu_{tot}} = \frac{mean(n_{NO}^{cons}, n_{N_2}^{prod})}{n_{Cu_{tot}}} \quad (1)$$

- **Standard-SCR:** after pre-reduction with 500 ppm of NO, 500 ppm of NH₃, and 0.0-2.0 % v/v of H₂O in He, 8.0 % v/v of O₂ is added to the NO+NH₃ feed stream to start the Standard-SCR activity; conditions are kept stable to ensure steady-state NO conversion. After two hours, we shut off oxygen to induce a final NO+NH₃ reduction step and, thus, quantify the bed-average Cu oxidized fraction reached under steady-state Standard-SCR conditions. The



procedure is described in detail by Nasello et al.¹⁶. Additional tests were performed feeding 4.0 and 5.8 % of O₂ during Standard-SCR.

2.3. Transient Kinetic Analysis

The Transient Kinetic Analysis (TKA) of the RHC, OHC, and Standard-SCR data is the same as that applied in recent publications^{16,39}. The plug flow test reactor is modelled as a series of 20 isobaric and isothermal CSTRs, each of them associated with a transient mass balance equation in Cu²⁺, NO, and N₂, as previously reported¹⁶. The RHC rate equation, as in Equation (2), is written assuming first order kinetics in NO, zeroth order in NH₃ (due to catalyst saturation), and second order in the oxidized copper fraction (σ)^{17,20,21}. Instead, for the OHC rate, Equation (3), we assume first order in O₂, zeroth order in NO, and second order in the reduced copper fraction ($1 - \sigma$)^{16,17}. A first order in ($1 - \sigma$) is also used to further prove that is not consistent in low T OHC. In Equations (2) and (3), y_{NO}^{ref} and $y_{O_2}^{ref}$ are the reference concentration for NO and O₂, set to 500 ppm and 8.0 % v/v, respectively.

$$r_{RHC} = k_{RHC} \frac{y_{NO}}{y_{NO}^{ref}} \sigma^2 \quad (2)$$

$$r_{OHC} = k_{OHC} \frac{y_{O_2}}{y_{O_2}^{ref}} (1 - \sigma)^2 \quad (3)$$

Normalization of the rate constants by the reference NO and O₂ mole fractions makes the rate constants equal to TORs at reference conditions, thus facilitating the comparison of the RHC and OHC rates.

It is worth mentioning that the effects of H₂O concentration and NH₃ solvation of Cu^{II} sites are herein lumped in the two rate constants k_{RHC} and k_{OHC} . While the effect of H₂O feed contents will be assessed directly by carrying out tests under both wet (H₂O = 2% v/v) and dry (H₂O = 0% v/v) feed-gas conditions, the effects of ammonia concentration and Cu solvation are not investigated in this work. Nevertheless, Usberti et al.⁴⁵ demonstrated in a recent publication that, if the catalyst is fully saturated with NH₃, Cu²⁺ reduction transients (RHC) are essentially unaffected by changing the gas-phase ammonia concentration. On the contrary, inhibition of the low-temperature Standard-SCR activity was observed when increasing the NH₃/NO feed ratio from 1 to 1.5 and 2; accordingly, this effect was ascribed to ammonia inhibition of the sole OHC. In this paper, in order to assess the effect of the catalyst aging, the OHC will be investigated independently by dedicated transient tests.



3. Results and Discussion

3.1. Effect of mild HTA on Cu speciation and NO conversion

The NO₂ adsorption + TPD experimental protocol is applied to the degreened and aged samples to assess their Cu²⁺ speciation. Results are reported in the supplementary material as Figure SI.1.

During the TPD, the Degreened and the Aged samples released 10.4 and 4.9 μmol of NO₂, which correspond to a ZCu²⁺OH fraction of 80.0 and 37.7 %, respectively. As previously stated, mild HTA reduces the amount of ZCu²⁺OH, converting them into double-bonded Z₂Cu²⁺ sites³³. These values are in line with experimental and modeling work from Daya et al.²⁷, where they used NH₃ adsorption + TPD for the characterization, and from Iacobone et al.³³.

The NO conversion during steady-state Standard-SCR at 150, 175, and 200 °C over the Degreened and Aged samples is plotted in Fig. 1. As anticipated in the Introduction, mild HTA results in a measurable loss of DeNO_x activity across the entire temperature range studied. Specifically, the NO conversion drops from 33.7 to 24.9 % at 150 °C, and from 75.9 to 68.8 % at 200 °C. This motivates the subsequent investigation of the two half-cycles of the redox mechanism (RHC and OHC) with the goal of identifying which is responsible for the observed activity loss.

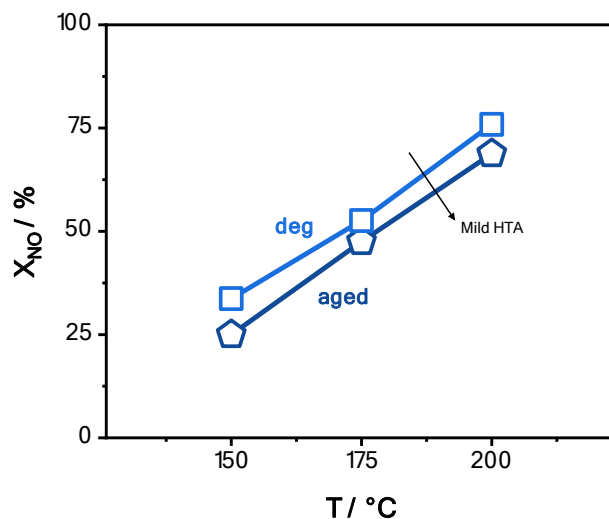


Figure 1 – NO conversion during the Standard-SCR protocol on Degreened and Aged catalysts at 150, 175, and 200 °C. Symbols: squares for degreened, pentagons for aged sample. Feed: GHSV = 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP); NO = 500 ppm, NH₃ = 500 ppm, O₂ = 8.0 % v/v and H₂O = 2.0 % v/v in He.



3.2. Effect of mild HTA on low-T RHC

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In a recent work³⁹, we explored the effect of Mild HTA on the Reduction-Half Cycle in a wider temperature range (135–350 °C), both in dry and wet feed conditions. We have confirmed the marginal effect of hydrothermal aging on the Cu reduction rate, the inhibition due to the presence of water, and that a rate expression second order in the oxidized copper fraction, as seen in Equation (2), accurately predicts the transient dynamics.

In this work, we run the same experiments on this new set of catalysts, focusing on the 150–200 °C range in wet conditions (H₂O = 2.0 % v/v). The empty symbols in Fig. 2 show the experimental data collected during the Reduction Half-Cycle protocol applied to the Degreened (panels A, B, C) and to the Aged samples (panels D, E, F), at three temperatures.

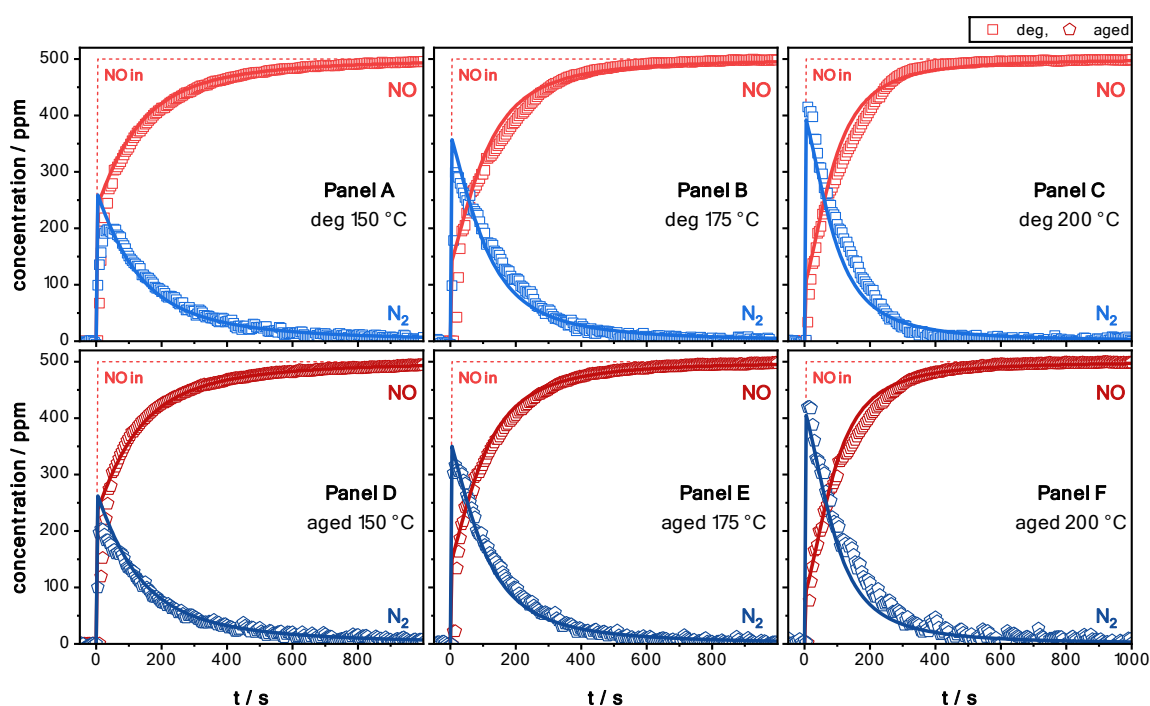


Figure 2 – NO and N₂ dynamics during the RHC protocol on Degreened and Aged samples. Panels: A) deg 150 °C, B) deg 175 °C, C) deg 200 °C, D) aged 150 °C, E) aged 175 °C, F) aged 200 °C. Symbols: experimental data (red for NO, blue for N₂, squares for deg, pentagons for aged). Solid lines: model fit. Feed: GHSV = 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP); NO = 500 ppm, NH₃ = 500 ppm and H₂O = 2.0 % v/v in He.

When a step feed of 500 ppm of NO and 500 ppm of NH₃ is fed to a pre-oxidized NH₃-saturated sample, a N₂ peak is produced while NO is consumed. As the catalyst approaches full reduction, NO approaches the feed concentration value, while N₂ is no longer produced. These dynamics become faster by progressively increasing temperature: a positive effect of temperature on the reduction process is apparent, as NO and N₂ concentrations approach their asymptotic levels faster (approximately 800, 600, and 400 s, respectively, for 150, 175, and 200 °C).



Comparing data obtained over the two samples (for clarity, Fig. SI.2 of the SI shows the superimpositions of the experimental data), the negligible effect of mild HTA on the RHC transients is clearly apparent across the 150-200 °C range. Table SI.1 reports the integral values of NO converted and N₂ released in the different experiments, which are slightly lower than the total amount of copper present in the reactor. This could be associated with two different aspects: i) the catalyst not being fully oxidized at t = 0 s of the transients due to ammonia oxidation during the pre-treatment (when NH₃+O₂ are fed to pre-oxidize and saturate the catalyst); ii) part of the Cu in the catalysts can be present as Cu oxides (namely, CuOx) and not involved in the redox cycle. This last explanation is in line with Yao and coworkers⁴⁶, who reported a significant CuOx content for samples with high Cu loading (≥ 2.0 % w/w).

In agreement with recent publications³⁹, transient kinetic analysis of the data in Fig. 2 provides a quantitative evaluation of the RHC rate. In Fig. 2, the solid lines for NO and N₂ illustrate the model fit obtained with these rate constants. Table 1 shows the respective rate constants estimated by the experimental data fit over the two samples at different temperatures.

k_{RHC} / s^{-1}	Degreened	Aged
150 °C	4.6 E-03	4.3 E-03
175 °C	6.7 E-03	6.9 E-03
200 °C	10.6 E-03	10.3 E-03

Table 1 – RHC rate constants over the Degreened and the Aged samples at the three studied temperatures.

In line with the previous discussion, the rate constants increase with increasing temperature and are almost identical between the two samples. Figure SI.3 shows the corresponding Arrhenius plots: the estimated activation energy of the Degreened is 27.7 kJ mol⁻¹, while for the Aged catalyst it is 29.1 kJ mol⁻¹. As expected, the two E_A are similar since no promotion or inhibition by mild HTA is observed on RHC. This can be explained by the occurrence of the hydrolysis reaction⁴⁰: Z₂Cu²⁺ sites are converted back to ZCu²⁺OH at a rate faster than the RHC and, thus, not kinetically relevant. These findings clearly indicate that RHC cannot be considered responsible for the low-temperature activity loss associated with the aging process.

3.3. Effect of mild HTA on low-T OHC

A novelty of this work lies in addressing the effect of mild HTA on the low-temperature Oxidation Half-Cycle. Fig. 3 shows the experimental data (empty symbols) collected with the OHC protocol over the Degreened (panels A, B, C) and over the Aged (panels D, E, F) samples at 150, 175, and 200 °C.



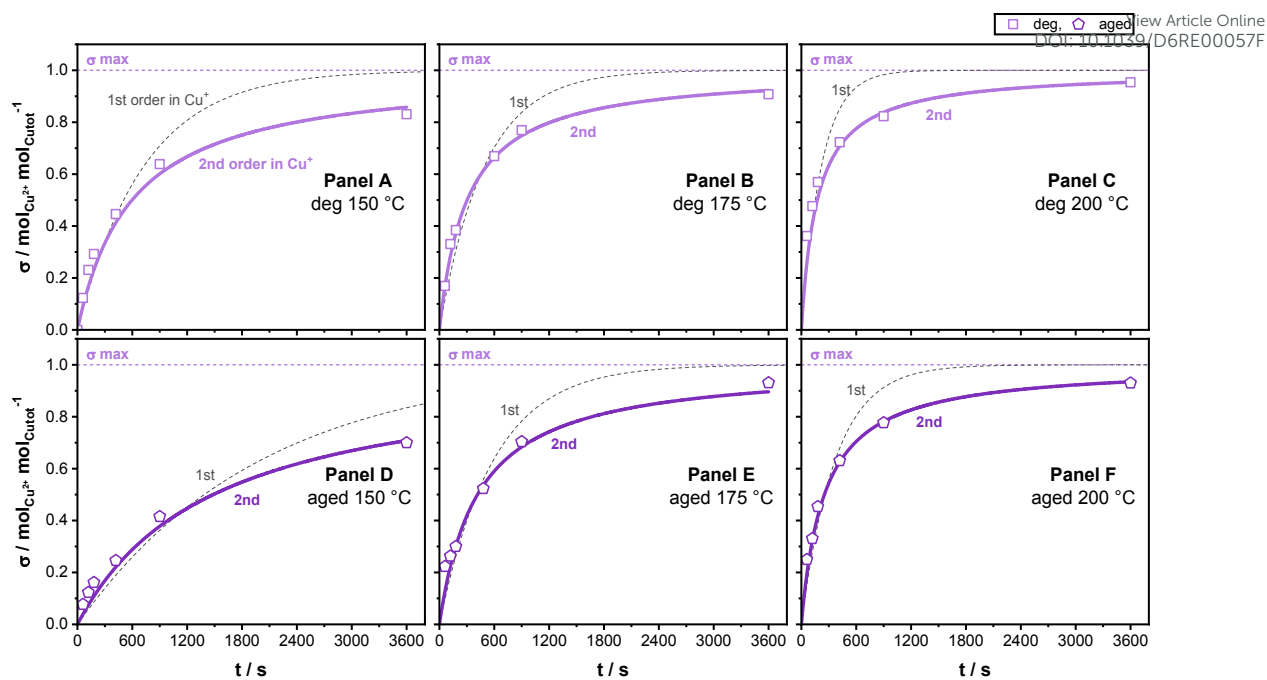


Figure 3 – Transient profiles of σ (Cu^{2+} fraction) vs. oxidation time during the OHC protocol on Degreened and Aged catalysts. Panels: A) deg 150 °C, B) deg 175 °C, C) deg 200 °C, D) aged 150 °C, E) aged 175 °C, F) aged 200 °C. Symbols: experimental data (squares for deg, pentagons for aged). Solid lines: 2nd order in Cu^+ model fit (used in this work). Gray dashed lines: 1st order in Cu^+ model fit. Feed: $\text{GHSV} = 450,000 \text{ cm}^3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ (STP); $\text{O}_2 = 1.0 \text{ \% v/v}$ and $\text{H}_2\text{O} = 2.0 \text{ \% v/v}$ in He.

As shown in Fig. 3, the longer the oxygen exposure time, the higher the catalyst oxidation extent. Full oxidation is approached only over the Degreened sample at 200 °C, after 1 h, due to the low O_2 partial pressure employed in these tests. The 1.0 % v/v concentration of oxygen is chosen specifically for the purpose of slowing down the OHC to improve the evaluation of the respective rate constant. Indeed, we have previously assessed¹⁶ the linear dependence of the OHC rate on the oxygen concentration. Increasing the temperature, we observe a faster oxidation of the Cu sites, in line with previous findings on different catalysts¹⁶.

Comparing the data for the two samples (the experimental dataset at 150 °C is available in Table SI.2), we can see that the oxidation of the Aged sample is always slower than the Degreened across the whole set of investigated temperatures. When coupled with the almost negligible HTA effect detected for the RHC, this result ascribes the typical deNO_x performance loss following mild HTA to the inhibition of the OHC only. This will be further discussed and supported in Section 3.4, where we combine RHC and OHC into the overall Standard-SCR reaction.

Eventually, TKA is applied to the OHC experiments in Fig. 3, fitting the second order OHC rate model (Eq. 3) to the data and estimating the rate constants. Table 2 lists the k_{OHC} estimates, and the solid lines in Fig. 3 show the respective transient fit. Just as a comparison, the gray dashed lines show



instead the fit assuming a 1st order in reduced Cu in the r_{OHC} . As previously assessed¹⁶ the quality of the fit is much worse, confirming the validity of the second order OHC kinetics.

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k_{OHC} / s^{-1}	Degreened	Aged
150 °C	6.7 E-03	2.8 E-03
175 °C	13.2 E-03	8.4 E-03
200 °C	23.0 E-03	15.9 E-03

Table 2 – OHC rate constants over the Degreened and the Aged samples at the three studied temperatures.

In agreement with the previous discussion, the k_{OHC} estimates are consistently smaller over the Aged sample, while a positive temperature effect is observed over both samples. Indeed, the Arrhenius plot in Fig. SI.4 yields an activation energy of 41.1 kJ mol⁻¹ for the Degreened sample, in agreement with the value reported by Paolucci et al.¹⁵ (~35 kJ mol⁻¹) from AIMD simulations of $\text{Cu}^+(\text{NH}_3)_2$ diffusion. In contrast, the Aged sample exhibits a greater activation energy of 58.0 kJ mol⁻¹, comparable to that reported by Deka et al.⁴¹ using similar transient response experiments. These activation energies show that the OHC over the Degreened catalyst is kinetically more favorable, whereas mild HTA makes the reaction less facile, requiring about 40 % more energy to proceed. Overall, these results identify the OHC as the sole aging-sensitive component of the low-temperature redox cycle.

3.4. Combination of RHC and OHC in the Standard-SCR

To close the redox cycle, we herein proceed to combine RHC and OHC kinetics studied independently to analyze the Standard-SCR and the related mild HTA effect. Fig. 4 shows the experimental data of the Standard-SCR protocol over the Degreened (panels A) and over the Aged (panels B) samples at 200 °C. In addition, Fig. SI.5 and SI.6 show the corresponding results at 150 and 175 °C, respectively.



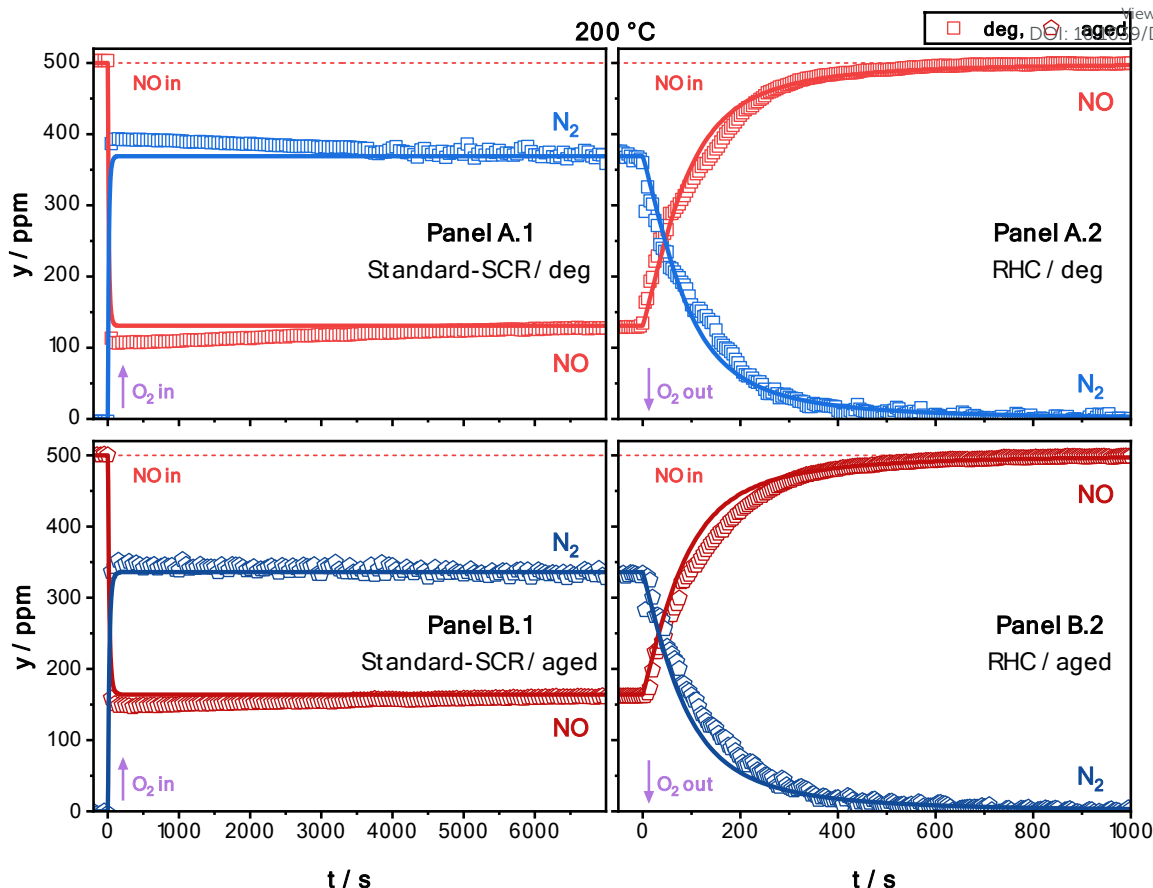
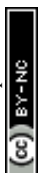


Figure 4 – NO and N₂ transient outlet concentration profiles during the Standard-SCR protocol on Degreened and Aged samples at 200 °C. Panels: A) Degreened, B) Aged, 1) Standard-SCR, 2) RHC following Standard-SCR. Symbols: experimental data (red for NO, blue for N₂, squares for deg, pentagons for aged). Solid lines: model fit. Feed: GHSV = 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP); NO = 500 ppm, NH₃ = 500 ppm, O₂ = 8.0-0.0 % v/v and H₂O = 2.0 % v/v in He.

After the pre-reduction of the catalyst with NO+NH₃, we cofeed 8.0 % v/v of O₂ to activate the Standard-SCR activity, reaching steady-state conditions after a short transient, as shown in the first column of Fig. 4. At 200 °C, the NO conversions (X_{NO}) are equal to 75.9 and 68.8 % for the Degreened and the Aged catalyst, respectively. As expected, and discussed in the Introduction, mild HTA reduced the X_{NO} . After two hours, the oxygen is once again removed to fully reduce the oxidized copper sites present during the steady-state Standard-SCR reaction. This is depicted in the second column of Fig. 4 by the transient NO and N₂ profiles for the two samples. At 200 °C, we assess bed-average fractions of Cu²⁺ sites (σ_{ss}) at steady-state Standard-SCR of 66.9 and 61.5 %. As expected, mild HTA also decreased the Cu²⁺ fraction, and this is confirmed at all the temperatures investigated, as shown in Table 3, consistent with the slower OHC.



Steady-state Standard-SCR	$X_{NO} / \%$				$\sigma_{SS} / \%$			
	Degreened		Aged		Degreened		Aged	
	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model
150 °C	33.7	33.2	24.9	25.0	55.4	55.9	47.7	47.8
175 °C	52.6	51.8	47.5	46.8	61.5	61.5	56.1	56.3
200 °C	75.9	73.8	68.8	67.2	66.9	66.9	61.5	61.6

Table 3 – Experimental and simulated NO conversion (X_{NO}) and bed-average oxidized Cu fraction (σ_{SS}) during steady-state Standard-SCR over the Degreened and the Aged samples at the three studied temperatures: 150, 175, and 200 °C. Feed: GHSV = 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP); NO = 500 ppm, NH₃ = 500 ppm, O₂ = 8.0 % v/v and H₂O = 2.0 % v/v in He. The experimental X_{NO} for Degreened and Aged samples are the same as shown in Fig. 1.

Based on the rate expressions (2) and (3), and using the independently estimated rate constants, we proceed to simulate the Standard-SCR activity. The model relies on equating the r_{RHC} and the r_{OHC} in order to compute X_{NO} and σ_{SS} . For the two catalyst samples, the solid lines in Fig. 4 show the model predictive simulations at 200 °C using the rate constants of Tables 1 and 2. A match of similar quality is illustrated in Figures SI.5 and SI.6 for the data at 150 and 175 °C. Table 3 reports the model predictions of X_{NO} and σ_{SS} , compared to the experimental data. The mean absolute error for X_{NO} is 1.0 %, while it is 0.2 % for σ_{SS} . Clearly, our approach enables an accurate prediction of both the NO conversion and the oxidized copper fraction at steady-state Standard-SCR conditions. It is important to note that such an accurate match is achieved even though the OHC transient experiments were conducted at 1.0 % v/v O₂, whereas the Standard-SCR tests were carried out at 8.0 %, which validates the linear dependence of r_{OHC} on oxygen concentration. Additionally, this confirms the reliability of the redox kinetic model in accurately describing the Standard-SCR conditions over both the Degreened and the Aged samples. In particular, the model correctly predicts both the loss of low-T NO conversion and the decreased oxidized copper fraction under mild HTA solely via the inhibition of low-T OHC.

Recently, Gao and coworkers⁴⁷ have proposed a complementary NO-active OHC route wherein NO and O₂ would re-oxidize the diamine Cu⁺ species to form Cu²⁺ nitrates, subsequently decomposed by NO according to a Fast-SCR pathway: this is essentially identical to the mechanism originally published by Janssens et al.¹¹. Using transient response methods like those herein applied, Gao and coworkers studied the Cu oxidation kinetics at very low temperatures (75-120 °C) over a single catalyst formulation, finding that the NO+O₂ OHC is faster than the O₂-only OHC under wet feed conditions (but not under dry feed conditions). By a complex extrapolation of these data to the temperatures of interest for SCR (185-230 °C), they concluded that account of such a parallel NO-active OHC pathway, although not the dominant oxidation mechanism, is necessary to improve the



kinetic description of the Standard-SCR reaction with respect to our model based on RHC + O₂-only OHC (NO silent). In our view, the results of the transient kinetic analysis herein reported (see Fig. 4 and Table 3) prove that, over the present industrial catalysts, a NO-silent OHC mechanism fully and predictively explains the steady-state Standard-SCR activity both in terms of NO conversion and of bed-average Cu redox state, without the need for invoking additional Cu⁺ oxidation routes. The contribution of a NO-to-nitrate OHC pathway, if any, is negligible in our experimental conditions: its addition to the redox model would only overparameterize it. This conclusion is also in line with results previously published for other Cu-CHA catalysts with different Cu loadings and SAR^{16,45}.

3.5. Oxygen-based recovery of activity

Since mild HTA affects only the OHC, we attempted to engineer a recovery of activity. Given the first order dependence on oxygen in Equation (3), a linear increment of the OHC rate is expected upon increasing the O₂ concentration. Considering that the rate constant decreases under mild HTA, to preserve the same OHC rate, the oxygen concentration must therefore be increased as follows:

$$y_{O_2} = \frac{k_{OHC}^{deg}}{k_{OHC}^{aged}} y_{O_2}^{deg} \quad (4)$$

To challenge this assumption, we first replicated the Standard-SCR protocol at 4.0 % v/v of O₂ over the Degreened and Aged samples at 200 °C. Fig. SI.7 shows the experimental results: for the Degreened catalyst, we record a 62.0 % NO conversion and 56.5 % bed-average Cu²⁺ fraction, while for the Aged catalyst, they are lowered to 53.7 and 52.0 %, respectively. The redox model is once again able to predict the Standard-SCR conditions also at this lower O₂ concentration, as visible from the solid lines in Fig. SI.7, which are superimposed on experimental data. These experiments can be used as a further validation of our model under conditions different from those of Fig. 4.

Then, we run an additional Standard-SCR experiment over the Aged sample, feeding a higher oxygen concentration. By using Equation (4) and the OHC rate constants at 200 °C in Table 2, the activity recovery should be achieved with $y_{O_2} = 5.8$ % in the feed. Fig. SI.8 shows the results of this test, while the bar plot in Fig. 5 compares the results of the different experiments. With $y_{O_2} = 5.8$ %, we achieve a full recovery of the activity: X_{NO} is 61.8 % and σ_{SS} is 57.0 %, i.e., essentially identical to the Degreened catalyst performances at 4.0 % v/v of O₂.



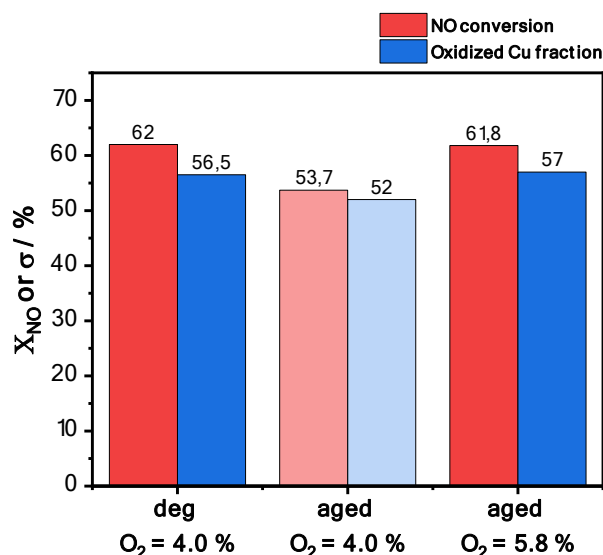


Figure 5 – NO conversion (X_{NO} , in red) and oxidized copper fraction (σ_{ss} , in blue) at steady-state Standard-SCR over the Degreened and Aged samples at 200 °C and different O₂ concentrations (4.0 and 5.8 % v/v). The highlighted columns represent the recovery of activity on the Aged sample (with respect to the Degreened) by increasing the O₂ partial pressure. Feed: GHSV = 450,000 cm³ h⁻¹ g_{cat}⁻¹ (STP); NO = 500 ppm, NH₃ = 500 ppm, O₂ = 4.0/5.8 % v/v and H₂O = 2.0 % v/v in He.

Thus, by a simple increment of the O₂ concentration, we can fully restore the performance of the catalyst; also, we are able to predict this behavior by a simple two-reaction model. In production aftertreatment systems that use SCR catalysts, the upstream O₂ concentration can in principle be tuned by modifying the engine combustion strategy, allowing some adjustments in the oxygen level delivered to the SCR catalyst under low-temperature operating conditions. The model presented in this work can therefore be practically used as part of an onboard model-based control strategy to estimate the O₂ level that best compensates for hydrothermal aging and helps minimize system-level NO_x emissions.

As a final note, we estimate the apparent kinetic orders of NO and oxygen in Standard-SCR. Using the RHC and OHC rate equations with the fitted parameters, for both our investigated catalysts, we have computed the steady-state Standard-SCR rate at different NO (100-2000 ppm) concentrations with fixed O₂ (8 %), and then at different O₂ (1-20 % v/v) concentrations with fixed NO (500 ppm). The results are plotted in Fig. SI.9A and B, respectively. Indeed, by differentiating the $\log_{10} r_{SCR}$, as in Fig. SI.10, we find fractional orders between 0 and 1 for both NO and O₂, confirming that the Standard-SCR mechanism does not exhibit a clear RDS under the investigated conditions, with both RHC and OHC being kinetically relevant. We also show that the kinetic orders with respect to NO and O₂ vary significantly with operating conditions. As expected, at low NO and high O₂ concentrations, where the RDS is the RHC, the rate orders get close to those of the RHC rate (i.e., 1st order in NO and 0th order in O₂), as in Eq. (2). Instead, at high NO and low O₂, where the OHC



becomes rate determining, we see a decrease in the NO order towards zero and an increase in the O₂ order, thus approaching Eq. (3).

3.6. Combined effect of H₂O and HTA on RHC, OHC, and Standard-SCR

The H₂O effect on the RHC and OHC kinetics was independently studied in previous works by some of us^{16,22}, testing Cu-CHA samples varying in SAR. In this work, to check the combined effects of water and catalyst aging, we have run tests in dry-gas conditions for both RHC, OHC, and Standard-SCR over the Degreened and the Aged samples. The data collected were compared with those obtained under wet feed conditions.

For the RHC, Fig. SI.11 shows the data at 150, 175, and 200 °C for both samples, while Table SI.3 reports the rate constants obtained from the model fit of these data. The RHC rate constants of both Degreened and Aged samples obtained under dry conditions are greater than the ones obtained in wet conditions under all the investigated conditions, in line with previous findings on different catalyst samples^{16,39}: the presence of water inhibits the RHC in high SAR samples due to entropy losses in presence of water being far greater than the enthalpic stabilization, as DFT calculations demonstrated⁴⁸. Additionally, in dry-gas conditions, the mild HTA of the Aged sample does not have a significant impact on the RHC rate constants, as shown by the Arrhenius plot in Fig. SI.12A.

For the Standard-SCR, Table SI.4 reports steady-state NO conversions and oxidized copper fractions at three temperatures over the two catalysts. Small differences in NO conversion between the dry-gas and the wet conditions are observed, while the presence of H₂O clearly promotes the oxidation state of the catalyst. This is once again in line with the high SAR sample in Nasello et al.¹⁶.

In this dry-gas case, following the procedure of our recent papers^{45,49}, we have estimated the k_{OHC} based on the equivalence between RHC and OHC reaction rates ($r_{RHC} = r_{OHC} = r_{SCR}$) at steady-state Standard-SCR. The estimates are reported in Table SI.5. Comparing them with the estimates obtained in wet conditions, we can clearly conclude that H₂O promotes the OHC both over the Degreened and the Aged sample. Furthermore, also in dry-gas conditions, the mild HTA inhibits only the OHC, as visible in the Arrhenius plot of Fig. SI.12B.

The H₂O inhibition of the RHC and the H₂O promotion of the OHC explain the apparently paradoxical observation of a marginal H₂O effect on the NO conversion at steady-state Standard-SCR conditions, accompanied, however, by a promotion of the Cu oxidation state. As further validation of this concept, we have simulated the steady-state Standard-SCR conversion at different feed NO feed concentrations (100-2000 ppm), both in dry and wet feed conditions, as shown in Fig. SI.13. These simulations are fully in line with the low-temperature data by Ottinger et al.⁵⁰, who studied experimentally the H₂O effect on Standard SCR at different NO feed concentrations. At low NO concentrations, the presence of water inhibits the NO conversion, while at high feed NO



concentrations, a promotion is apparent. This complex behavior is nicely captured by our simple two reaction model: at low y_{NO}^{in} , in fact, the RHC, which is indeed inhibited by H_2O , is slow and kinetically controls the Standard-SCR activity; instead, at high y_{NO}^{in} , the OHC, which is promoted by H_2O , becomes rate controlling. Notably, this dual role of H_2O (RHC-inhibiting, OHC-promoting) remains valid also after mild HTA, and, most importantly, HTA consistently inhibits only the OHC, regardless of the presence or absence of H_2O .

4. Conclusions

Herein, we have investigated the effect of mild HTA on the low-temperature Standard-SCR (150-200 °C) by applying transient response methods and kinetic modeling to study the RHC and the OHC independently, eventually combining them into the full redox cycle of the Standard-SCR reaction.

- We have confirmed on a different set of catalysts that the low temperature **Reduction Half-Cycle** is essentially unaffected by mild HTA, due to the hydrolysis reaction shifting Z_2Cu^{2+} to $ZCu^{2+}OH$. The second order kinetics in oxidized copper sites are confirmed. The activation energies of the Degreened and Aged samples are comparable.
- The novelty of this work lies in assessing the effect of mild HTA on the low temperature **Oxidation Half-Cycle**. By Transient Kinetic Analysis, we show that the OHC is slower over the Aged sample in comparison to the Degreened sample. In fact, both the oxidized copper fraction at SCR steady state and the OHC rate constant k_{OHC} are consistently smaller over the Aged catalyst. The second order in the reduced copper sites is confirmed for the OHC rate, also in the case of the present industrial catalysts with high Cu loading. The activation energy of the Aged sample is 40 % higher than that of the Degreened catalyst, indicating that the reaction is kinetically hindered by mild HTA.
- As in previous work, the combination of RHC and OHC kinetics to close the redox cycle of the low-temperature **Standard-SCR** is again successful. Using the independent estimates of k_{RHC} and k_{OHC} , we predict the steady-state low-T NO conversion and bed-average oxidized Cu fraction over both the Degreened and the Aged industrial catalysts at all temperatures with a mean absolute error of only 0.6 %. This rules out the need for complementary “NO-active” OHC pathways to describe the Standard SCR activity, as proposed in recent literature. Notably, this also implies that the inhibitory effect of mild HTA on the OHC is responsible for (and fully explains) the observed adverse HTA effect on the overall Standard-SCR activity.
- Based on this evidence of a direct correlation between mild HTA and OHC and recalling that the OHC rate is first order in oxygen, we have engineered an **Oxygen-based Recovery of Activity**. By increasing the oxygen partial pressure over the Aged sample proportionally to the ratio of the k_{OHC} of the Degreened and Aged samples, we were able not only to restore



the steady-state NO conversion but also the bed-average Cu²⁺ fraction to the same values of the Degreened catalyst operated at the lower oxygen concentration.

- We have repeated the RHC and Standard-SCR experiments in the **absence of H₂O in the feed**. In line with our previous work, we have confirmed that water has an inhibiting effect on the RHC (due to the high SAR) but a promoting effect on the OHC. This results in unchanged NO conversion but enhanced Cu oxidation state during steady-state Standard-SCR over both the Degreened and the Aged samples when H₂O is included in the feed stream.

Overall, this study identifies OHC as the sole aging-sensitive step of the SCR redox mechanism. It also provides a simple but mechanistically grounded and, most of all, predictive kinetic framework linking HTA-induced Cu speciation changes to catalyst performance. The ability to fully restore the NH₃-SCR activity of an aged catalyst through oxygen management highlights the practical relevance of this understanding for designing more durable NH₃-SCR systems and improved control strategies of real exhaust aftertreatment systems.

Notably, the present work is focused on a specific Cu-SSZ-13 formulation, although representative of industrial NH₃-SCR catalysts. In principle, the observed selective inhibition of the OHC by mild HTA may depend on zeolite framework, Cu loading, and Silica-to-Alumina ratio, suggesting that further investigation of different Cu-zeolite systems is warranted to generalize the present conclusions.

Conflicts of interest

There are no conflicts of interest to declare.

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Data availability statements

The data supporting this article are included in the main text and the Supplementary Information. Additional data are not available. The SI contains catalyst characterization, Arrhenius plots, Standard-SCR activity, conversion rates, and dry-gas data.

With kind regards,

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