

Redox kinetics for the low-temperature NH₃-SCR and N₂O formation over Cu-CHA catalysts

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Highlights

- Independent analysis of RHC and OHC transients predicts Cu-CHA STD-SCR activity.
- Low-T N₂O production over Cu-CHA catalysts is related to a side Cu reduction step.
- NO, O₂, and GHSV effects are predicted by dual-site RHC-OHC redox mechanisms.

1. Introduction

NH₃-SCR over copper-exchanged zeolite is the state-of-the-art process for NO_x abatement from mobile sources. Recently, significant effort in the scientific literature has been focused on elucidating the low-temperature ($\leq 220^\circ\text{C}$) Standard SCR (STD-SCR) mechanism. It is well established that Cu sites are involved in a redox process, cycling between Cu^{II} to Cu^I in the reduction half cycle (RHC) and from Cu^I to Cu^{II} in the oxidation half cycle (OHC); nevertheless, the mechanism remains unclear in terms of intermediates and whether single Cu ions or Cu dimers are involved. Based on transient response methods (TRM) and kinetic modelling, Tronconi and co-workers [1,2] and Daya et al. [3] proposed dual-site mechanisms for both half-cycles over Cu-CHA catalysts, demonstrating that independent kinetic analysis of the RHC and the OHC transients results in accurately simulating the NO conversion and the average oxidized Cu fraction at steady-state of STD-SCR. This work explores the effects of temperature, feed composition and Gas Hourly Space Velocity (GHSV) on both RHC and OHC to generalize the proposed redox model. Undesired N₂O formation is also included in the kinetic analysis.

2. Methods

Experimental runs have been carried out over monolith samples coated with a model Cu-CHA catalyst (Cu loading 1.67% w/w ICP, SAR=25), placed in a stainless-steel tubular reactor and tested between 150-200°C and GHSV \approx 40000-120000 h⁻¹. The TRM protocol was composed by: I) pre-oxidation with O₂ (8%) and NH₃ (500 ppm) in 2.3% H₂O+N₂; II) reduction of the fully oxidized catalyst with NO (300-600 ppm) and NH₃ (500 ppm) in 2.3% H₂O+N₂ to titrate all the reducible Cu sites; III) STD-SCR, adding O₂ (1-12%) to NO and NH₃ in 2.3% H₂O+N₂, IV) a second reduction step, shutting-off O₂, to evaluate the bed-average Cu^{II} fraction at STD-SCR steady-state (σ). Data are fitted by the PFR transient integral model (cascade of 20 CSTRs) proposed by Tronconi and co-workers [1,2] assuming: a) the RHC rate to be 1st and 2nd order in the NO concentration and the Cu^{II} fraction ($r_{RHC} = k_{RHC}(y_{NO})\sigma^2$); b) the OHC rate to be 1st and 2nd order in O₂ concentration and in reduced Cu fraction ($r_{OHC} = k_{OHC}(y_{O_2})(1-\sigma)^2$). As a novelty, the present model incorporates the kinetics of N₂O production, assumed as an unselective Cu reduction step with rate 1st order in NO and with an undefined nth order in the oxidized Cu fraction ($r_{RHC_N_2O} = k_{RHC_N_2O}(y_{NO})\sigma^n$). Finally, NO conversions, bed-average oxidized Cu fractions, and N₂O productions at STD-SCR steady-state are used as experimental responses of a non-linear multi-response least-squares regression to estimate the rate parameters ($k_{i, T_{ref}}$ and $E_{i, ACT}$ of a modified Arrhenius form, where i=RHC, OHC and RHC_N₂O and T_{ref}=200°C) that best fit the collected data.

3. Results and discussion

TRM tests, addressing the effects of temperature (150-175-200°C), NO (300-500-600 ppm), O₂ (1-2-4-8-12%) feed concentrations, and space velocity (40000-60000-80000-120000 h⁻¹), were found to be in line with the kinetic analysis performed by Tronconi and co-workers over powdered Cu-CHA catalysts [1,2]. This confirms the kinetic dependences assumed by the proposed mechanism: the NO

concentration affects only the RHC rate with a 1st order dependence, while OHC proceeds via a “NO silent” mechanism, involving oxygen only. Furthermore, both half-cycles occur according to a dual-site mechanism, with dynamics compatible with 2nd order dependences on Cu^{II} (RHC) and Cu^I (OHC) fractions. N₂O is confirmed to be the product of a side RHC reaction, following an apparent 3rd order dependence on the oxidized Cu fraction and a 1st order dependence in NO. This assumption allows both to nicely match the N₂O formation dynamics during the reduction step and to predict the steady-state N₂O make during the STD-SCR phase. Based on the successful analysis of the redox transients, we derive a novel steady-state STD-SCR rate expression, Eq.1, by equating the RHC and OHC rates (neglecting the small contribution of the N₂O production); the N₂O rate expression is shown by Eq.2.

Steady-state data covering the effects of space velocity, temperature, pressure, NO and O₂ feed concentrations are used as experimental responses of a global regression, for a total of 30 kinetic runs. By minimizing the sum of the squared errors between experimental and simulated data, we obtain a single set of kinetic parameter estimates for the RHC, RHC_N₂O and OHC rate expressions (6 adaptive parameters, $k_{i,Tref}$ and $E_{i,ACT}$). Fit results are shown as parity plots in Figure 1, comparing experimental data and model simulations with the fitted kinetics for NO conversion (panel A, covering a wide range between 20% and 90%), average oxidized Cu fraction σ (panel B), and N₂O make (panel C) at STD-SCR steady-state. These results highlight the adequacy of the proposed low-temperature redox model in accurately predicting the Standard SCR over a wide range of conditions, with minimal and randomly distributed errors (average of ~3-4% on the NO conversion and average Cu fraction and of 0.25 ppm on the N₂O production). Notably, the kinetics from the global regression allow not only to effectively simulate the STD-SCR steady-state, but also the dynamics observed during the transients redox tests over the whole range of investigated operating conditions.

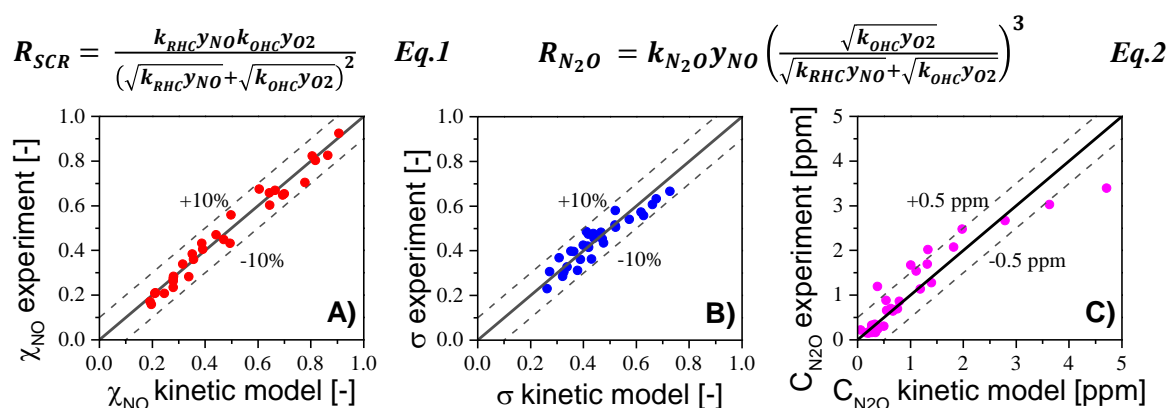


Figure 1. Experimental and simulated STD-SCR NO conversions (A), average oxidized Cu fractions (B) and N₂O make (C) varying T (150→200°C), GHSV (40000→120000 h⁻¹) and NO (300→600 ppm) and O₂ (1→12%) feed concentrations.

4. Conclusions

Results from this work highlight the significance of independently studying the two half-cycles of the low-T redox mechanism of NH₃-SCR over Cu-zeolite catalysts. This approach has enabled us to identify the kinetics of Cu reduction, Cu oxidation, and side N₂O production, resulting in the accurate prediction of the low-T activity of a model Cu-CHA catalyst under a wide range of representative conditions.

References

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Keywords

“NH₃-SCR”; “Cu zeolite”; “redox mechanism”; “kinetics”.