

Low-Temperature redox kinetics for NH₃-SCR and N₂O formation over Cu-CHA catalysts

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Significance and Relevance

Results from this work highlight the significance of independently studying the two half-cycles of the low-T redox mechanism of NH_3 -SCR over Cu-zeolite catalysts. This approach enables to identify the kinetics of Cu reduction, Cu oxidation, and side N_2O production, resulting in the accurate prediction of the low-T SCR activity of a model Cu-CHA catalyst across a wide range of representative conditions.

Preferred and 2nd choice for the topic:

<u>Automotive and stationary emission control</u> (or Fundamental advances in understanding catalysis) Preferred presentation: <u>Oral preferred or Short Oral</u>

Introduction and Motivations

NH₃-SCR over copper-exchanged zeolite is the state-of-the-art process for NOx abatement from the exhaust gases of mobile sources. Recent literature works have been focused on the low-temperature (\leq 220 °C) Standard-SCR (STD-SCR) mechanism. It has been established that Cu active sites cycle 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). Using Transient Response Methods (TRM), operando spectroscopy, Density functional Theory (DFT) and kinetic modelling, Tronconi and co-workers^{1,2} and Daya et al.³ proposed a dual-site mechanisms for both half-cycles, demonstrating that independent kinetic analysis of the RHC and of the OHC transients results in accurately simulating the NO conversion and the average oxidized Cu fraction at steady-state of STD-SCR. This work generalizes the proposed redox model, exploring the effects of temperature, Gas Hourly Space Velocity (GHSV), feed composition, pressure and washcoat loading on the Standard-SCR activity and on the undesired N₂O formation of a model honeycomb monolith Cu-CHA catalyst.

Materials and Methods

Experimental runs have been performed over monolith samples coated with a model Cu-CHA catalyst (1.67 % w/w Cu, SAR=25), placed in a stainless-steel tubular reactor, and tested at 150→200°C and GHSV≈40-120 kh⁻¹. The TRM protocol included: I) pre-oxidation with O₂ (8%) and NH₃ (500 ppm); II) reduction of the fully oxidized catalyst with NO (300-600 ppm) and NH₃ (500 ppm); III) STD-SCR, adding O₂ (1-12%) to NO and NH₃, IV) a second reduction step, shutting-off O₂ after STD-SCR steady-state, allowing the evaluation of the bed-average Cu^{II} fraction at STD-SCR steady-state ($\sigma = Cu^{II} / Cu_{TOT}$). All tests were carried out in 2.3% H₂O using N₂ as diluent. Data were fitted by the PFR transient integral reactor model proposed by Nasello et al.¹ assuming: a) the RHC rate to be 1st and 2nd order in the NO concentration and the Cu^{III} fraction ($r_{RHC} = k_{RHC}(y_{NO})\sigma^2$); b) the OHC rate to be 1st order in O₂ and 2nd order in reduced Cu fraction ($r_{OHC} = k_{OHC}(y_{O_2})(1-\sigma)^2$). N₂O production kinetics at low temperature was added as an unselective Cu reduction step with rate 1st order in NO and with undefined nth order in the oxidized Cu fraction ($r_{N_2O} = k_{N_2O}(y_{NO})\sigma^n$). Finally, NO conversions, bed-average oxidized Cu fractions, and N₂O productions at STD-SCR steady-state were used as experimental responses in a multi-response non-linear least-squares regression to estimate the rate parameters that best fit the collected data.



Results and Discussion

TRM tests performed between 150 and 200°C allowed to collect NO conversions, oxidized Cu fractions and N₂O outlet concentrations at STD-SCR steady-state under different operating conditions. The activity shown by the catalyst is the result of the kinetic equilibrium reached between reduction and oxidation reaction rates ($r_{RHC} = r_{OHC}$). Combining the two rate expressions while neglecting the influence of the N₂O production on the overall NO conversion (only few ppm of N₂O produced), we derived the rate expression of the low-T Standard SCR shown in Eq.1. N₂O was 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 (steady-state rate expression shown by Eq.2). These assumptions allow 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.

Collected steady-state data are used as experimental responses of a global regression, for a total of 48 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 $E_{act,i}$). 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 production (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 ~3-5% on the NO conversion and average Cu fraction and of 0.25 ppm on the N₂O production). The model accurately describes the effects of temperature (150 \rightarrow 200°C), NO (300 \rightarrow 600 ppm) and O₂ (1 \rightarrow 12%) concentrations, space velocity (40 \rightarrow 120 kh⁻¹), and pressure (1 \rightarrow 3 bara). Furthermore, the model was able to predict the results obtained over a monolith with increased washcoat loading. 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 transient 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 (C) varying T (150→200 °C), GHSV (40→120 kh⁻¹), NO (300→600 ppm), O₂ (1→12 %) concentrations, and pressure (1→3 bara).

References

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