

Deconvolving the Standard-SCR Redox Mechanism on Copper-Zeolites for Catalyst Insight and Development

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Significance and Relevance

We investigates NH_3 -SCR over Cu-CHA zeolite catalysts, the state-of-the-art technology for NO_x abatement in Diesel vehicles. By independently studying the two redox half-cycles of Standard-SCR using transient kinetic analysis, we assess the role of copper redox state (Cu^{II}/Cu^{I}) and clarify so far controversial effects of water feed content, hydrothermal aging, and catalyst formulation on the Standard-SCR activity, enabling improved predictions of the steady-state NO_x conversion. These findings help to optimize the SCR catalysts, contributing to enhanced DeNOx performance of emissions control technologies for cleaner Diesel vehicles.

Preferred and 2nd choice for the topic: <u>Fundamental advances in understanding catalysis</u> (or Automotive and stationary emission control) Preferred presentation: Oral only

Introduction and Motivations

Ammonia-Selective Catalytic Reduction (NH₃-SCR) is the state-of-the-art aftertreatment technology for Diesel-fuelled vehicles complying with Euro 6/7 standards. These systems nowadays implement copper-exchanged zeolite catalysts, which exhibit high DeNOx activity in a wide temperature range, high selectivity to N₂ and good hydrothermal stability. The Standard-SCR ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$) reaction mechanism, however, is still debated and not fully understood, even though a general consensus on a Cu redox mechanism has been reached. To convert NO to N₂, copper is reduced from Cu^{II} to Cu^I in the Reduction Half-Cycle (RHC)¹. Then, to restore the activity of the catalyst, the Cu^I sites are oxidized back to Cu^{II} by oxygen only in the Oxidation Half-Cycle (OHC)².

The transient response approach proposed by our group enables to study independently the kinetics of the two half-cycles, which are then combined to predict the Standard-SCR steady-state performances³. Herein we show that by separately assessing the impact of operating conditions and catalyst parameters, such as H_2O presence, catalyst hydrothermal aging, zeolite SAR and Cu loading, on the rates of the two half-cycles, we can clarify so far confusing and controversial effects on the overall Standard-SCR activity at steady state.

Materials and Methods

We have tested Cu-Chabazite (Cu-CHA) catalysts characterized by different exchanged-copper contents (between 0.8 and 2.3 wt%), silica-to-alumina ratios (SAR, between 10 and 25), and Hydrothermal Aging extents (HTA, conditioned or aged). In addition, different reaction conditions have been explored: H_2O presence (0-2 v%), NO feed concentration (300-500 ppm), O_2 concentration (1-8 v%) and temperature (135-500 °C). The reference catalyst was Cu = 1.8 wt% and SAR = 25 (called 1.8Cu-CHA25).

Transient kinetic tests have been run to study independently the RHC (feeding equimolar concentrations of NO and NH₃), the OHC (by oxidizing the sample with O₂ across different time intervals), and the Standard-SCR reaction (NO+NH₃+O₂ feed, followed by oxygen removal to titrate the bed-average steady-state oxidized copper fraction)³. More experimental details are provided in ³.

A UV gas analyser and a mass spectrometer are used to monitor the temporal evolution of the gas species concentrations. These data undergo Transient Kinetic Analysis (TKA) based on a plug flow reactor model, implemented as a cascade of 20 CSTRs. This model includes the following rate equations for the RHC and OHC³:

(1)
$$r_{RHC} = k_{RHC} \left(\frac{y_{NO}}{y_{NO}^{ref}} \right) \sigma^2$$
 (2) $r_{OHC} = k_{OHC} \left(\frac{y_{O_2}}{y_{O_2}^{ref}} \right) (1 - \sigma)^2$

where k are the respective rate constants, y are the molar fractions, $y_{NO}^{ref} = 500 \, ppm$, $y_{O_2}^{ref} = 8 \, \%$, and σ is the fraction of oxidized copper sites.



Results and Discussion

For each catalyst sample, TKA of the transient data collected in both reduction and oxidation conditions is performed to estimate the rate constants for RHC and OHC, respectively. k_{RHC} is estimated by fitting the NO and N₂ dynamics during the RHC transients. Instead, k_{OHC} is obtained from the evolution in time of the oxidized copper fraction during the OHC runs. Figure 1a) and 1b) show the RHC and OHC rate constants for the 1.8Cu-CHA25 catalyst in wet and dry feed conditions (2 and 0 v% H₂O, respectively). Over this sample, H₂O has a modest inhibiting effect on RHC, but a stronger promoting effect on OHC.

Fig. 1c and 1d show that, by combining these two independently estimated rate constants, it is possible to predict with good accuracy both the NO conversion and the bed-average oxidized Cu fraction at Standard-SCR steady state in both dry and wet conditions. Furthermore, the estimated rate constants correctly predict the slightly improved NO conversion and the incremented oxidized copper fraction in wet conditions. Studying just the steady-state activity would lead instead to the erroneous conclusion that H₂O has no significant impact on Standard SCR.



Figure 1 a) RHC rate constants, b) OHC rate constants, c) NO conversion and d) bed-average steady-state oxidized copper fraction. 2Cu-CHA25 sample. Dry and wet conditions: $H_2O=0-2 v\%$, grey squares and blue triangles, respectively. Dotted lines for kinetic fits and transparent solid line for simulations. Feed: NO = NH₃ = 500 ppm and O₂ = 8% in He. T-range = 150-200 °C. W_{cat} = 32 mg, Q = 240 cm³/min (STP)

A similar methodology has been applied to elucidate the effects of hydrothermal aging, zeolite SAR, and Cu loading in Cu-CHA. HTA does not affect RHC, while it inhibits the OHC, thus determining a loss in both NO conversion and Cu^{II} fraction at Standard SCR steady state. Decreasing SAR (higher aluminium content) promotes RHC but leaves OHC unchanged, thus leading to higher NO conversions but to decreased oxidized Cu fractions at steady state. On incrementing the Cu loading, a strong OHC promotion is apparent, while the effect on the RHC is more complex.

Finally, on extending the experimental and modelling analysis to temperatures above 220°C we have found that the well-known "seagull" shape of the NO light-off curves typical of Cu-CHA catalysts is associated with a drop of the OHC rates between 250 and 350 °C. On the contrary, the RHC rates increased monotonically with increasing temperature, following a regular Arrhenius trend.

In conclusion, our original methodology based on decoupling the RHC and the OHC of the Standard-SCR redox mechanism by transient methods can provide valuable phenomenological insight into the effects of reaction variables and catalyst formulation parameters. Such effects, which are clearly distinct (and often opposite) for the two half cycles of the SCR redox mechanism, would remain inaccessible if focusing only on steady-state activity data.

References

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Acknowledgements

This work was financially supported by Johnson Matthey.