Active site requirements in oxidation and reduction halves of the Cu redox cycle during Standard NH₃-Selective Catalytic Reduction of NOx on Cu-SSZ-13

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Effect of Cu density on SCR kinetics: Different kinetic regimes

- Standard SCR rates increases linearly with Cu density at ρCu > 300 mol m⁻³, as would be expected for a reaction catalyzed by single isolated Cu sites
- In contrast, SCR rates vary quadratically with Cu density below ρCu < 300 mol m⁻³ suggesting the dual Cu site behavior in the Cu → Cu²⁺ half-cycle.
- Two kinetic regimes, characterized by distinct kinetic parameters (QO, NO and NH₃ order as well as Eₚ

Mechanistic origin of different kinetic regimes

- Cu²⁺ in the MARI
- Dual site Cu²⁺Cu²⁺ oxidation limiting SCR redox cycle

Cu²⁺ SCR dependence
O₂ order=1
O₂ order=0

Proposed mechanism

- Reduction of single Cu²⁺ site to Cu[NH₂]+, with NO+NH₃
- Oxidation of two mobile Cu[NH₂]+ (within diffusion distance) with O₂ to form NH₃-solvated Cu²⁺ dimer, making O₂-assisted oxidation sensitive to Cu proximity
- Reduction of binuclear Cu²⁺ complex further with NO and NH₃ to form Cu(NH₃)₂ and complete the redox cycle.

Summary

- Solvation with NH₃ confers mobility to Cu(NH₂)+, enabling them to pair and form Cu dimers
- Cu ions supported on zeolite are neither infinitely mobile, as in a homogeneous catalyst, nor segregated into separate ensembles of active and inactive sites, as in a heterogeneous catalyst.

References

- C. Paolucci, I. Khurana, A. A. Parekh, S. Li, A. Shih, H. Li, J. R. Di Iorio, J. D. Albarracin-Caballero, A. Yezerets, J. T. Miller, W. F. Schneider, F. H. Ribeiro, Dynamic Multinuclear Sites Formed by Mobilized Copper Ions in NOx Selective Catalytic Reduction, Science 2017