

Catalytic Consequences of Active Site Speciation, Distribution, Mobility and Stability on Selective Catalytic Reduction of NO_x with Ammonia over Cu-Exchanged Zeolites

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Selective catalytic reduction (SCR) of NO_x using NH₃ as a reductant over Cu-SSZ-13 zeolites is a commercial technology used to meet emissions targets in lean-burn and diesel engine exhaust. Optimization of catalyst design parameters to improve catalyst reactivity and stability against deactivation (hydrothermal and sulfur poisoning) necessitates detailed molecular level understanding of structurally different active Cu sites and the reaction mechanism. With the help of synthetic, titrimetric, spectroscopic, kinetic and computational techniques, we established new molecular level details regarding 1) active Cu site speciation in monomeric and dimeric complexes in Cu-SSZ-13, 2) elementary steps in the catalytic reaction mechanism, 3) and deactivation mechanisms upon hydrothermal treatment and sulfur poisoning.

We have demonstrated that Cu in Cu-SSZ-13 speciates as two distinct isolated sites, nominally divalent Cu^{II} and monovalent [Cu^{II}(OH)]⁺ complexes exchanged at paired Al and isolated Al sites, respectively. This Cu site model accurately described a wide range of zeolite chemical composition, as evidenced by spectroscopic (Infrared and X-ray absorption) and titrimetric characterization of Cu sites under *ex situ* conditions and *in situ* and *operando* SCR reaction conditions. Monovalent [Cu^{II}(OH)]⁺ complexes have been further found to condense to form multinuclear Cu-oxo complexes upon high temperature oxidative treatment, which have been characterized using UV-visible spectroscopy, CO-temperature programmed reduction and dry NO oxidation as a probe reaction. Structurally different isolated Cu sites have different susceptibilities to H₂ and He reductions, but are similarly susceptible to NO + NH₃ reduction and have been found to catalyze NO_x SCR reaction at similar turnover rates (per Cu^{II}; 473 K) via a Cu^{II}/Cu^I redox cycle, as their structurally different identities are masked by NH₃ solvation during reaction.

Molecular level insights on the low temperature Cu^{II}/Cu^I redox mechanism have been obtained using experiments performed *in situ* and *in operando* coupled with theory. Evidence has been provided to show that the Cu^{II} → Cu^I reduction half-cycle involves single-site Cu reduction of isolated Cu^{II} sites with NO+NH₃, which is independent of Cu spatial density. In contrast, the Cu^I → Cu^{II} oxidation half-cycle involves dual-site Cu oxidation with O₂ to form dimeric Cu-oxo complexes, which is dependent on Cu spatial density. Such dual-site oxidation during the SCR Cu^{II}/Cu^I redox cycle requires two Cu^I(NH₃)₂ sites, which is enabled by NH₃ solvation that confers mobility to isolated Cu^I sites and allows reactions between two Cu^I(NH₃)₂ species and O₂. As a result, standard SCR rates depend on Cu

proximity in Cu-SSZ-13 zeolites when Cu^I oxidation steps are kinetically relevant. Additional unresolved pieces of mechanism have been investigated, such as the reactivity of Cu dimers, the types of reaction intermediates involved, and the debated role of Brønsted acid sites in the SCR cycle, to postulate a detailed reaction mechanism. A strategy has been discussed to operate either in oxidation or reduction-limited kinetic regimes, to extract oxidation and reduction rate constants, and better interpret the kinetic differences among Cu-SSZ-13 catalysts.

The stability of active Cu sites upon sulfur oxide poisoning has been assessed by exposing model Cu-zeolite samples to dry SO₂ and O₂ streams at 473 and 673 K, and then analyzing the surface intermediates formed via spectroscopic and kinetic assessments. Model Cu-SSZ-13 zeolites were synthesized to contain distinct Cu active site types, predominantly either divalent Cu^{II} ions exchanged at proximal framework Al (Z₂Cu), or monovalent [Cu^{II}OH]⁺ complexes exchanged at isolated framework Al (ZCuOH). SCR turnover rates (473 K, per Cu) decreased linearly with increasing S content to undetectable values at equimolar S:Cu ratios, consistent with poisoning of each Cu site with one SO₂-derived intermediate. Cu and S K-edge X-ray absorption spectroscopy and density functional theory calculations were used to identify the structures and binding energies of different SO₂-derived intermediates at Z₂Cu and ZCuOH sites, revealing that bisulfates are particularly low in energy, and residual Brønsted protons are liberated at Z₂Cu sites as bisulfates are formed. Molecular dynamics simulations also show that Cu sites bound to one HSO₄⁻ are immobile, but become liberated from the framework and more mobile when bound to two HSO₄⁻. These findings indicate that Z₂Cu sites are more resistant to SO₂ poisoning than ZCuOH sites, and are easier to regenerate once poisoned.

The stability of active Cu sites on various small-pore Cu-zeolites during hydrothermal deactivation (high temperature steaming conditions) has also been assessed by probing the structural and kinetic changes to active Cu sites. Three small-pore, eight-membered ring (8-MR) zeolites of different cage-based topology (CHA, AEI, RTH) have been investigated. With the help of UV-visible spectroscopy to probe the Cu structure, in conjunction with measuring differential reaction kinetics before and after subsequent treatments, it has been suggested that the RTH framework imposes internal transport restrictions, effectively functioning as a 1-D framework during SCR catalysis. Hydrothermal aging of Cu-RTH results in complete deactivation and undetectable SCR rates, despite no changes in long-range structure or micropore volume after hydrothermal aging treatments and subsequent SCR exposure, highlighting beneficial properties conferred by double six-membered ring (D6R) composite building units. Exposure aging conditions and SCR reactants resulted in deleterious structural changes to Cu sites, likely reflecting the formation of inactive copper-aluminate domains. Therefore, the viability of Cu-zeolites for practical low temperature NO_x SCR catalysis cannot be inferred solely from assessments of framework structural integrity after aging treatments, but also require Cu active site and kinetic characterization after aged zeolites are exposed to low temperature SCR conditions.