ABSTRACT

Jones, Casey B. Ph.D., Purdue University, July 2021. Active Site and Zeolite Topological Requirements for the Low-Temperature Selective Catalytic Reduction of NO_X on Cu-Zeolites. Major Professors: Rajamani Gounder and Fabio H. Ribeiro.

The selective catalytic reduction (SCR) of NO_X (x = 1,2) using Cu-exchanged zeolites is used commercially for the abatement of NO_X from on-road lean-burn diesel engines. At the low exhaust temperatures during cold-start and idle operation (<523 K), the SCR reaction proceeds via a Cu^{2+}/Cu^{+} redox cycle of NH_3-solvated and mobilized Cu ions. Reduction of Cu^{2+} species proceeds via NO-assisted reduction of isolated NH_3-solvated Cu^{2+} ions. To complete Cu^{+} to Cu^{2+} oxidation, two $[Cu(NH_3)_2]^{+}$ species react together with O_2 to form a dimeric O_2-bridged Cu^{2+} species that is subsequently reduced by NO and NH_3 to complete the SCR catalytic turnover. NH_3-solvated Cu ion species are nominally isolated under *ex-situ* conditions, however, motivating the critical research question studied in this work regarding how Cu ion mobility and dynamic interconversion of mononuclear and binuclear active sites facilitate SCR chemistry. In particular, this work focuses on understanding how active site proximity, zeolite pore connectivity and dimensionality, and catalyst poisons impact the number and reactivity of active Cu sites.

Steady-state SCR kinetics (473 K) measured at fixed gas conditions (10 kPa O_2) on a series of Cu-chabazite (CHA) zeolites with varied density of isolated Cu ions (0.078-0.35 Cu per 10^3 Å^3) exhibit non-single site behavior because of changes in the kinetic relevance of Cu^{+} oxidation and Cu^{2+} reduction half-cycles, and the non-mean field nature of the Cu^{+} oxidation process. Measurement of SCR rates at dioxygen pressures (1-60 kPa O_2) far removed from typical operating conditions (3-17 kPa O_2) allows isolating the kinetic behavior under primarily Cu^{+} oxidation-limited and Cu^{2+} reduction-limited conditions, and estimating rate parameters for these two regimes by regressing SCR rates as a function of O_2 pressure to an empirical Langmuirian rate expression. Apparent rate constants that are first-order in O_2 (k_{first}) increase systematically with Cu density, consistent with the dual-site Cu^{+} oxidation mechanism. Apparent rate constants that are zero-order in O_2 (k_{zero}) show a weak dependence on Cu density, similar to the fraction of Cu that can be oxidized by O_2 at 473 K in transient experiments, suggesting that changes in k_{zero} reflect changes in the fraction of active Cu given the single-site nature of Cu^{2+}

reduction mechanisms. The measured apparent activation energy in the Cu^+ oxidation limit ($E_{app,first}$) increases systematically with Cu density, highlighting the non-mean field nature of Cu^+ oxidation over the range of Cu densities studied. The measured apparent activation energies in the Cu^{2+} reduction limit are constant above a threshold Cu density (0.17 Cu per 10^3 $Å^3$), consistent with mean-field behavior, but begin to deviate at lower densities (0.084-0.10 Cu per 10^3 $Å^3$).

A series of Cu-zeolites with 2D (LEV, FER) and 1D (MOR) pore connectivity were synthesized to quantify how the framework topology and pore structure influences the mobility and reactivity of Cu ions during SCR. When compared to Cu-CHA, a 3D pore structure, values of k_{first} and k_{zero} (per total Cu) were several factors lower on the 2D and 1D zeolites, indicating that decreasing the effective volumetric footprint of Cu ions during SCR decreases both the rate of dual-site Cu^+ oxidation and the fraction of Cu^+ that oxidizes. When compared to other 3D double-six membered ring (d6r) zeolites with different pore shape (AEI) and size (AFX), rates (per total Cu) were generally a factor of 1.5 to 2 times higher on Cu-CHA, indicating that the open pore structure of cylindrical cages in CHA are favorable for low-temperature SCR reactivity.

The arrangement and density of framework Al atoms in CHA influences low-temperature SCR, as the framework Al atoms mediate Cu ion mobility and the arrangement of Al in the framework determines the chemical identity of the Cu active site precursors as either $[CuOH]^+$ exchanged at an isolated framework Al center or Cu^{2+} exchanged at paired framework Al in a six-membered ring (6-MR). Synthesis of CHA zeolites with mixtures of Na^+ and $TMAda^+$ provides a strategy to alter the amount of Al centers in 6-MR paired configurations, because Na^+ co-occludes in 6-MR voids adjacent to $TMAda^+$ occluded within the *cha* cage. In contrast, synthesis of CHA zeolites with mixtures of K^+ and $TMAda^+$ results in primarily 6-MR isolated Al configurations because K^+ cations displace $TMAda^+$ from residing in *cha* cages. Thus, the use of different mixtures of organic and inorganic structure directing agents (SDAs) provide routes to synthesize CHA zeolites that favor the formation of either $[CuOH]^+$ or Cu^{2+} species. The Cu speciation influences both hydrothermal stability and resistance to sulfur poisoning. SO_2 is a catalyst poison ubiquitous in automotive exhaust and is found to bind to $[CuOH]^+$ sites more strongly than Cu^{2+} sites, both before and after high-temperature de-sulfation treatments.

Together, these findings reveal several of the important structural and active site requirements for low-temperature NO_X SCR with NH_3 on Cu-zeolites. The non-mean field nature of the SCR redox cycle on Cu^{2+}/Cu^{+} ion sites, and the requirement for Cu ions to be located in proximal and accessible locations of zeolite void spaces becomes more favorable in 3D highly connected pore structures, highlighting a primary reason why low-temperature SCR rates (per Cu) are higher on Cu-CHA than on other Cu-zeolites. The synthetic procedures presented here to influence the Al arrangement in CHA zeolites provide new strategies to alter the speciation and density of isolated Cu ion sites, even among Cu-CHA zeolites of nominally identical elemental composition, which have implications for the stability and resistance to poisons of the catalyst under realistic operating conditions. Together, synthetic strategies to manipulate the proximity of active sites, methods to quantify transient and steady-state kinetics, and *in situ* and *operando* characterization are invaluable tools to study and understand the non-mean field dynamic interconversion of isolated and multinuclear sites during low-temperature SCR catalysis.