**Title:** Synthesis and Characterization of Mononuclear and Binuclear Copper Species in Cu-Exchanged Zeolites for Redox Reactions including Partial Methane Oxidation

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## Abstract

Cu-zeolites have received renewed attention as catalytic materials that facilitate partial methane oxidation (PMO) to methanol, with a variety of mononuclear, binuclear, and multinuclear Cu active site motifs that have been proposed in prior literature. Our approach to more precisely identify and probe the Cu structures that activate $O_2$ and reduce in $CH_4$ relies on the synthesis of model supports with varying composition and well-defined Cu speciation, which also facilitates connections between experimental data and theoretical models. Chabazite (CHA) zeolites are high-symmetry frameworks that contain a single lattice tetrahedral site (T-site), in which $Cu^{2+}$ ions exchange at paired Al sites in a six-membered ring (6-MR) while $CuOH^+$ species exchange at isolated 6-MR Al sites, the latter of which can react to form binuclear $O/O_2$-bridged Cu structures. In this work, Cu-CHA zeolites were synthesized to contain predominantly $Cu^{2+}$ ($Z_2Cu$) or $CuOH^+$ (ZCuOH) species of varying density, or a mixture of $Z_2Cu$ and ZCuOH sites. $Z_2Cu$ and ZCuOH sites were quantified by titration of residual Brønsted acid sites with $NH_3$, which respectively exchange with 2:1 or 1:1 $H^+$:$Cu^{2+}$ stoichiometry. Stoichiometric PMO reaction cycles on Cu-zeolites involved high-temperature (723 K) activation in $O_2$, and then moderate-temperature (473 K) reduction in $CH_4$ and treatment in $H_2O$ (473 K) to extract $CH_3OH$. *In-situ* UV-Visible spectroscopy under oxidizing ($O_2$, 723 K) and reducing (CO, 523 K; $CH_4$, 473 K; He, 723 K) conditions detected the presence of mononuclear and binuclear Cu site types, while *in-situ* Cu K-edge X-ray absorption spectroscopy after such treatments was used to quantify Cu(I) and Cu(II) contents and *in situ* Raman spectroscopy was used to identify the Cu structures formed. ZCuOH, but not $Z_2Cu$ sites, are precursors to binuclear $O/O_2$-bridged Cu sites that form upon $O_2$ activation and subsequently produce methanol after stoichiometric PMO cycles, at yields (per total Cu) that increased systematically with ZCuOH site density. The fraction of Cu(II) sites that undergo auto-reduction in inert at high temperatures (He, 723 K) is identical, within experimental error, to the fraction that reduces in $CH_4$ at temperatures relevant for PMO (473 K), providing a quantitative link between the binuclear Cu site motifs involved in both reaction pathways and motivating

refinement of currently postulated PMO reaction mechanisms. These Cu-CHA zeolites were also studied for other redox chemistries including the selective catalytic reduction (SCR) of $NO_x$ with $NH_3$. *In situ* UV-Visible and X-ray absorption spectroscopies were used to monitor and quantify the transient partial reduction of Cu(II) to Cu(I) during exposure to $NH_3$ (473 K), in concert with titration methods that use NO and $NH_3$ co-reductants to fully reduce all Cu(II) ions that remain after treatment in $NH_3$ alone to the Cu(I) state, providing quantitative evidence that both $Z_2Cu$ and ZCuOH sites are able to reduce in $NH_3$ alone to similar extents as a function of time. These findings provide new insight into the reaction pathways and mechanisms in which $NH_3$ behaves as a reductant of mononuclear Cu(II) sites in zeolites, which are undesired side-reactions that occur during steady-state $NO_x$ SCR and that often unintendedly result in Cu(II) reduction prior to spectroscopic or titrimetric characterization. Overall, the strategy in this dissertation employs synthetic methods to control framework Al density and arrangement in zeolite supports to emphasize extra-framework Cu site motifs of different structure and at different spatial densities, and to interrogate these model materials using a combination of *in situ* spectroscopic techniques together with theory, in order to elucidate active site structure and proximity requirements in redox catalysis. This work demonstrates how quantitative reactivity and site titration data, brought together with an arsenal of tools available in contemporary catalysis research, can provide detailed mechanistic insights into transition metal-catalyzed redox cycles on heterogeneous catalysts.