

Title: Design and Evaluation of Metal Supported Zeolite Catalysts for Methane Dehydroaromatization and Partial Methane Oxidation

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Date: Tuesday November 11th, 2025 (12 PM)

Abstract

Zeolites in their aluminosilicate forms are often used as microporous supports to host metal centers that mediate catalytic reactions such as methane dehydroaromatization (DHA) and partial methane oxidation (PMO). The atomic and bulk properties of zeolite materials, including the bulk density and local arrangements of both Al centers and silanol defects in the lattice, determine metal speciation and dispersion and, consequently, influence measured catalytic rates, selectivity, and stability. Molybdenum domains supported on medium-pore MFI zeolites (i.e., Mo-MFI) have been shown to catalyze methane DHA to equilibrium conversion (~10% at 973 K) with high selectivity to aromatics and dihydrogen (~60–80%), but exposure to high-temperature oxidative regeneration conditions leads to irreversible catalyst deactivation. Assessment of the relevant metal-zeolite structural transformations that occur during catalyst deactivation and regeneration is therefore essential to provide guidance for the purposeful design of stable and regenerable materials. Moreover, support properties (e.g., lattice Al arrangement) and pretreatment conditions have been shown to influence the formation of various Cu structures supported on small-pore chabazite (CHA) zeolites (i.e., Cu-CHA), relevant materials for stoichiometric and continuous PMO reactions. The dearth of methods to simultaneously identify and quantify such sites poses difficulties in relating distinct Cu site types to measured PMO yields and selectivities. Herein, we develop structure-function relations for Mo- and Cu-zeolites that provide new understanding regarding their structural evolution and reactivity for methane DHA and PMO, respectively. Quantitative characterization methods, such as H₂ temperature programmed reduction (TPR), are combined with kinetic measurements to identify metal-zeolite properties that influence the deactivation of Mo-MFI during methane DHA reaction-regeneration cycles, leading to the synthesis of Mo-zeolites with improved long-term stability. These characterization methods were

then adapted and extended to study Cu-CHA materials to interpret how methanol synthesis yields and selectivity depend on various Cu structures formed in Cu-CHA.

The deactivation mechanism of Mo-MFI catalysts during methane DHA reaction-regeneration cycles was first investigated by combining characterization methods and kinetic measurements on materials exposed to successive DHA reaction-regeneration cycles. H₂ TPR methods were developed to quantify and monitor changes to ion-exchanged Mo species, which are precursors to active sites for methane DHA. The titration of H⁺ sites using NH₃, on a suite of Mo-MFI materials with increasing Mo content (0.5–7 wt.%), evinces that proximal Al site arrangements, which can be quantified by Co²⁺ titration, preferentially exchange Mo as [MoO₂]²⁺ sites over binuclear [Mo₂O₅]²⁺ and over Mo species exchanged at isolated Al sites (i.e., [MoO₂OH]⁺), providing guidance on atomic-scale zeolite support properties that govern Mo dispersion. Initial benzene forward formation rates (per Mo; 950 K) measured on Mo-MFI catalysts systematically decrease with increasing numbers of reaction-regeneration cycles. Furthermore, H₂ TPR, H⁺ site titration, and ²⁷Al NMR characterization data show that exposure of Mo-MFI to hydrothermal aging conditions (>823 K, >2 kPa H₂O) during regeneration leads to irreversible removal of framework Al, and their associated H⁺ sites, consequently decreasing the fraction of ion-exchanged Mo and the formation of DHA-inactive aluminum molybdate domains. These findings demonstrate that preserving framework Al sites for Mo redispersion is required to improve catalyst stability through successive DHA reaction-regeneration cycles, which can be achieved by synthesizing zeolite supports with improved hydrothermal stability.

Mo supported on small-pore zeolites (e.g., CHA) were synthesized and evaluated for methane DHA cyclic operation. H₂ and ethene yields are similar in Mo-CHA compared to Mo-MFI, while aromatic formation rates (per Mo; 950 K) are lower due to diffusional barriers imposed by small CHA pore windows (~0.38 nm diam.) on the transport of larger aromatic molecules (~0.59 nm diam.). These intrazeolite diffusion restrictions are alleviated by synthesizing nanosheet (~20–100 nm) and mesoporous CHA materials that allow aromatic products to egress CHA crystallites at faster rates relative to their sequential reactions to form polyaromatic deposits that become entrapped within CHA micropores, resulting in higher benzene formation rates and selectivities. Importantly, aromatics formation rates measured on Mo-CHA materials remain invariant across successive DHA reaction-regeneration cycles. H₂ TPR and high-resolution transmission electron microscopy (HRTEM) demonstrate that, in contrast to Mo-MFI, fractions of

ion-exchanged Mo sites do not decrease and crystalline structures do not noticeably degrade in Mo-CHA catalysts exposed to several DHA reaction-regeneration cycles, demonstrating the potential of these catalysts to endure industrial operation in envisioned commercial methane DHA applications. Moreover, Mo supported on various zeolite topologies (e.g., TON, BEA, KFI) were synthesized and interrogated to evaluate the role of the zeolite framework topology on measured rates and selectivity, revealing that the zeolite spatial constraints that govern the stability of reactive intermediates and transition states (i.e., largest cavity diameter) and the ability of bulky product molecules to egress from crystallites (i.e., pore limiting diameter) together influence the extent to which aromatic products continue to react to form carbonaceous deposits (i.e., coke). Taken together, the characterization and kinetic evaluation of Mo-zeolites demonstrates that the stability of anchoring sites in zeolite lattices that disperse Mo species strongly influences the long-term stability of the catalyst, while zeolite framework topology and crystallite-scale properties influence aromatics and coke selectivity.

We then discuss H₂ TPR methods to characterize the variety of Cu sites formed on Cu-CHA materials and their consequences for stoichiometric PMO cycles. Cu-CHA samples containing only mononuclear Cu^{II} species (i.e., Z₂Cu^{II}) at varying densities were synthesized to study the reduction mechanism of Cu^{II} to Cu^I during H₂ TPR (203–823 K). TPR profiles show multiple features with increasing Z₂Cu^{II} density, concurrent with a shift in the reduction peak maximum temperature to lower temperatures. Isothermal reduction experiments (2.5 kPa H₂, 423–648 K) revealed that the Z₂Cu^{II} reduction process has a second-order dependence in Cu with kinetics described by non-mean field kinetic behavior, evidenced by rate constants that increase with Cu density and a fraction of recalcitrant Cu^{II} sites that do not reduce under isothermal reduction treatment temperatures below 723 K. These kinetic analyses, combined with H₂ reaction order measurements, are used to propose plausible mechanisms that describe the one-electron reduction of Z₂Cu^{II} sites to ZCu^I/ZH⁺ with a two-electron reductant (i.e., H₂) and allow identifying the influence of Cu density and temperature on this H₂-assisted reduction process. Taken together, we conclude that, although H₂ TPR can be used to quantify the fraction of Cu^{II} species, the peak maximum temperature reflects the kinetics of a non-mean field reduction process and thus cannot be assigned unambiguously to a specific Cu site type. H₂ TPR methods were then combined with pre-reduction treatments (i.e., CO, CH₄) designed to selectively reduce different subsets of Cu^{II} site types present initially, in order to quantify the amount of mononuclear and binuclear Cu

species formed in CHA zeolites with predominantly isolated H^+ sites (as quantified by Co^{2+} titration). Our results show that the formation of binuclear Cu sites is kinetically limited by the migration of mononuclear Cu precursors (i.e., $ZCuOH$) that prevent the formation of thermodynamically favored species predicted by DFT-calculated phase diagrams. Consequently, the fraction of binuclear Cu sites increases with increasing Cu content and O_2 activation time and result in higher methanol yields and selectivities, due to lower barriers of CH_4 activation on binuclear than mononuclear Cu sites and lower numbers of $ZCuOH$ sites that facilitate overoxidation reactions.

This work describes a conceptual framework to develop structure-function relations for metal-zeolite catalysts by combining the synthesis of zeolites with tailored bulk and atomic-scale properties and the development of quantitative methods to characterize distinct active site structures and their precursor states. The evolution of metal site speciation and its zeolite host were correlated with (un)desired methane conversion reaction pathways by monitoring the structural changes of both exchanged or supported metal domains and binding sites in the zeolite support during post-synthetic treatments and after exposure to industrially relevant conditions. This approach also led to the synthesis of non-conventional catalysts with improved long-term stability offering orthogonal catalyst design routes necessary for the commercialization of methane conversion technologies. Ultimately, this thesis demonstrates how examination of the physicochemical material properties governing the interaction between metal species and their zeolitic anchoring sites, as well as their response to environment conditions, provide guidance on the design and treatment strategies for tuning catalytic rates, selectivity, and stability for methane conversion applications.