INFLUENCE OF CHABAZITE ZEOLITE MATERIAL PROPERTIES ON METAL-OXO ACTIVE SITE DISTRIBUTIONS FOR PARTIAL METHANE OXIDATION

by

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Partial methane oxidation (PMO) to methanol is a desirable route for upgrading natural and shale gas resources to liquid chemical intermediates and has been extensively studied on Cu-zeolites. Prior work has studied the stoichiometric PMO reaction on O_2-activated Cu-zeolites, leading to several proposals for candidate O_x-bridged Cu active site structures. More recent studies have investigated the catalytic PMO reaction and have reported that Cu-chabazite (CHA) zeolites tend to exhibit the highest methane oxidation rate (per Cu) among other Cu-zeolite topologies. Multiple studies have reported that decreasing the Cu site density and increasing the framework Al density increase the selectivity towards methanol, but have proposed different mechanistic explanations. Here, we study the influence of Cu active site distribution, which was altered by varying the extraframework Cu site density and the arrangement of framework Al atoms, on the kinetic parameters governing continuous PMO. The number of redox active Cu species was quantified through linear combination fitting of XANES spectra collected under *in situ* and transient conditions after reactant (O_2) cut-off, and the Cu speciation was investigated with XAS. Total methane oxidation rates and individual product formation rates (CH_3OH, CO, CO_2), normalized per total Cu, increased with Cu density because this influenced the speciation of Cu formed during the reaction. All Cu-CHA samples showed PMO rates that were nearly first-order in CH_4 pressure, consistent with prior reports that C-H activation in CH_4 is the rate limiting step. Samples with differing framework Al arrangement, but fixed extraframework Cu density, showed formation rates of over-oxidation products (e.g., CO_2) that had different apparent reaction orders in O_2, implying differences in the Cu active sites formed during reaction. Changes to Cu oxidation states were monitored with *in situ* XAS. Samples were first subjected to an oxidative pretreatment (723 K, 5 kPa O_2) and then to catalytic PMO conditions to reach steady-state. Steady-state XANES spectra collected after O_2 was removed from the reactant stream showed the expected reduction from Cu(II) to Cu(I), and the fraction of CH_4-reducible Cu(II) sites decreased with increasing Cu content; increasing the CH_4 pressure ten-fold increased the number of CH_4-reducible sites by a factor of ~1.5. These spectroscopic and kinetic observations suggest there are a mixture of Cu site

types that are present during catalysis, each with different intrinsic reactivity toward CH_4 and selectivity to CH_3OH. To rationalize these observations, a reaction mechanism is proposed for a two-site model and used to derive rate expressions that describe apparent reaction orders for the total CH_4 oxidation rate and product formation rates on Cu-CHA zeolites of varying Cu content.

Additional routes for CH_4 activation include partial CH_4 oxidation over Fe zeolites that convert CH_4 at ambient temperature following an activation in nitrous oxide (N_2O), or through CH_4 dehydroaromatization (DHA) to benzene over Mo zeolites under non-oxidative conditions. Prior work on PMO over Fe-zeolites has identified candidate active site structures, but the influence of zeolite structural properties on ion-exchanged Fe speciation remains unclear. This work sought to understand the interaction of Fe with the zeolite framework during solvent-assisted deposition procedures and subsequent thermal treatments. In pursuit of this objective, Fe uptake isotherms were measured, and Fe speciation was characterized with UV-Vis spectroscopy and H_2 temperature programmed reduction (H_2 TPR). Increased framework Al site pairing increased the uptake of Fe in CHA zeolites, and high temperature treatments (723 K) resulted in the formation of oligomeric Fe structures as indicated by UV-vis. In CH_4 DHA over Mo-MFI, a principal challenge is the irreversible loss of catalytic reactivity with repeated reaction-regeneration cycles, attributed to dealumination of the zeolite structure during high-temperature oxidative regeneration treatments that produce steam. CHA zeolites are known to be more resistant to dealumination than MFI, but its smaller pore structure prevents diffusion of benzene and other aromatic products leading to rapid coking. This work attempted to address the diffusion limitations for benzene in Mo-CHA by synthesizing crystals with nanoscale dimensions by incorporating a surfactant into the crystallization procedure, generating solids with a flake-like morphology.

The overarching strategy in this work was to influence the speciation of metal sites and complexes in zeolites by controlling the density and arrangement of anionic Al anchoring sites within the framework and the density of extraframework metal species. In the case of Cu-zeolites, the amount of Cu present on the material influences the structures that form during catalysis that influences both the rate and selectivity of catalytic PMO.