ABSTRACT

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Title: Synthesis and Characterization of Copper-Exchanged Zeolite Catalysts and Kinetic Studies on NO_x Selective Catalytic Reduction with Ammonia
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Cu-SSZ-13 zeolites are used commercially in diesel engine exhaust after-treatment for abatement of toxic NO_x (x = 1,2) pollutants via selective catalytic reduction (SCR) with NH_3. We aim to piece a detailed understanding of the SCR reaction mechanism and nature of the Cu active site to provide insight into their catalytic performance and guidance on synthesizing materials with improved low temperature (< 473 K) reactivity and stability against deactivation (e.g. hydrothermal, sulfur oxides). We use computational, titration, spectroscopic, and kinetic techniques to elucidate (1) the presence of two types of Cu^{2+} ions in Cu-SSZ-13 materials, (2) molecular details on how these Cu cations, facilitated by NH_3 solvation, undergo a reduction-oxidation catalytic cycle, and (3) that sulfur oxides poison the two different types of Cu^{2+} ions to different extents at via different mechanisms.

Copper was exchanged onto H-SSZ-13 samples with different Si:Al ratios (4.5, 15, and 25) via liquid-phase ion exchange using $Cu(NO_3)_2$ as the precursor. The speciation of copper started from the most stable Cu^{2+} coordinated to two anionic sites (Z_2Cu) on the zeolite framework to $[CuOH]^+$ coordinated to only one anionic site (ZCuOH) on the zeolite framework with increasing Cu:Al ratios. The number of Z_2Cu and ZCuOH sites was quantified by selective NH_3 titration of the number of residual Brønsted acid sites after Cu exchange, and by quantification of Brønsted acidic Si(OH)Al and CuOH stretching vibrations from IR spectra. Cu-SSZ-13 with similar Cu densities and anionic framework site densities exhibit similar standard SCR rates, apparent activation energies, and orders regardless of the fraction of Z_2Cu and ZCuOH sites, indicating that both sites are equally active within measurable error for SCR.

The standard SCR reaction uses O_2 as the oxidant ($4NH_3 + 4NO + O_2 \rightarrow 6H_2O + 4N_2$) and involves a Cu(I)/Cu(II) redox cycle, with Cu(II) reduction mediated by NO and NH_3, and Cu(I) oxidation mediated by NO and O_2. In contrast, the fast SCR reaction ($4NH_3 + 2NO + 2NO_2 \rightarrow 6H_2O + 4N_2$) uses NO_2 as the oxidant. Low temperature (437 K) standard SCR reaction kinetics over Cu-SSZ-13 zeolites depend on the spatial density and distribution of Cu ions,

varied by changing the Cu:Al and Si:Al ratio. Facilitated by NH_3 solvation, mobile Cu(I) complexes can dimerize with other Cu(I) complexes within diffusion distances to activate O_2, as demonstrated through X-ray absorption spectroscopy and density functional theory calculations. Monte Carlo simulations are used to define average Cu-Cu distances. In contrast with O_2-assisted oxidation reactions, NO_2 oxidizes single Cu(I) complexes with similar kinetics among samples of varying Cu spatial density. These findings demonstrate that low temperature standard SCR is dependent on Cu spatial density and requires NH_3 solvation to mobilize Cu(I) sites to activate O_2, while in contrast fast SCR uses NO_2 to oxidize single Cu(I) sites.

We also studied the effect of sulfur oxides, a common poison in diesel exhaust, on Cu-SSZ-13 zeolites. Model Cu-SSZ-13 samples were exposed to dry SO_2 and O_2 streams at 473 and 673 K. These Cu-SSZ-13 zeolites were synthesized and characterized to contain distinct Cu active site types, predominantly either divalent Cu^{2+} ions exchanged at proximal anionic framework sites (Z_2Cu), or monovalent $CuOH^+$ complexes exchanged at isolated anionic framework sites (ZCuOH). On the model Z_2Cu sample, SCR turnover rates (473 K, per Cu) catalyst decreased linearly with increasing S content to undetectable values at equimolar S:Cu molar ratios, while apparent activation energies remained constant at ~65 kJ mol^{-1}, consistent with poisoning of each Z_2Cu site with one SO_2-derived intermediate. On the model ZCuOH sample, SCR turnover rates also decreased linearly with increasing S content, yet apparent activation energies decreased monotonically from ~50 to ~10 kJ mol^{-1}, suggesting that multiple phenomena are responsible for the observed poisoning behavior and consistent with findings that SO_2 exposure led to additional storage of SO_2-derived intermediates on non-Cu surface sites. Changes to Cu^{2+} charge transfer features in UV-Visible spectra were more pronounced for SO_2-poisoned ZCuOH than Z_2Cu sites, while X-ray diffraction and micropore volume measurements show evidence of partial occlusion of microporous voids by SO_2-derived deposits, suggesting that deactivation may not only reflect Cu site poisoning. Density functional theory calculations are used to identify the structures and binding energies of different SO_2-derived intermediates at Z_2Cu and ZCuOH sites. It is found that bisulfates are particularly low in energy, and residual Brønsted protons are liberated as these bisulfates are formed. These findings indicate that Z_2Cu sites are more resistant to SO_2 poisoning than ZCuOH sites, and are easier to regenerate once poisoned.