ABSTRACT

Parekh, Atish A. PhD., Purdue University, August 2016. Exploring the Mechanistic Landscape of Nitric Oxide Oxidation and Ammonia Selective Catalytic Reduction of Nitric Oxide on Cu-Zeolites via Kinetic and Spectroscopic Characterization. Major Professors: Fabio H. Ribeiro and W. Nicholas Delgass

Increasingly stringent regulations to reduce emissions of nitrogen oxides (NO_x) from exhausts of heavy-duty diesel engines has set the stage to delve into a detailed investigation of engine after-treatment catalysts in order to understand the chemistry during their operation and design the next generation of catalytic formulations to meet future requirements. Small-pore Cu- and Fe-exchanged SSZ-13 catalysts with chabazite (CHA) topology are able to sustain high catalytic rates for selective catalytic reduction (SCR) even after exposure to harsh hydrothermal conditions present in diesel exhaust. Probing the redox behavior and the active site requirements for standard SCR on Cu-SSZ-13 catalysts using a combination of infrared (FTIR) and *operando* x-ray absorption (XAS) spectroscopies, kinetic measurements and density functional theory (DFT) calculations forms the basis for this dissertation.

The effect of each standard SCR reactant (NO, NH_3 and O_2) on the Cu(I) – Cu(II) redox chemistry and the reaction rates was studied via steady state *operando* XAS experiments. Changing the feed concentration of one of the NO, NH_3 and O_2 reactants at a time showed that while NH_3 and O_2 participated in the reduction of Cu(II) to Cu(I) and re-oxidation of Cu(I) to Cu(II), respectively, NO was involved in both parts of the redox cycle. Together, NO and NH_3 acted as the co-reductants for Cu(II) via the NO assisted dissociation of a N-H bond in a Cu-bound NH_3 molecule, while the combination of NO and O_2 completed the catalytic cycle by re-oxidation of Cu(I).

We studied the re-oxidation of Cu(I) to Cu(II) in the standard SCR mechanism by O_2 and NO_2 titration experiments. Two Cu-SSZ-13 catalysts with the same Cu:Al ratio (0.08-0.09) and type of exchanged Cu^{2+} ions charge-compensated by a pair of framework Al atoms but different Si:Al ratio (4.5, 15) were reduced with NO and NH_3 to Cu(I). Following this reduction, both catalysts were oxidized either in 10% O_2 or 90 ppm NO_2 under isothermal conditions. Oxidation with O_2 followed second order kinetics in the instantaneous Cu(I) fraction for both catalysts, suggesting the involvement of two Cu(I) moieties for O_2 oxidation. Further, a smaller second order rate constant (1.79 min^{-1}) and a greater final Cu(I) fraction (0.26) for the low Al (Si:Al = 15) catalyst compared to the corresponding values (8.16 min^{-1} and 0.15) for the high Al (Si:Al = 4.5) catalyst indicated an underlying dependence of the Cu(I) oxidation with O_2 on the Al distribution and hence, the proximity of Cu ions. In contrast, oxidation with NO_2 was a first order process with identical rate constants of 0.8 min^{-1} for both samples, showing that NO_2 oxidation was independent of the Al distribution or Cu proximity and occurred on isolated Cu(I) ions. Thus, standard SCR, which involves oxidation with O_2, is limited by the pairing ability of Cu ions at dilute Cu or Al contents and hence, controlled by the oxidation half-cycle. Fast SCR, on the other hand, proceeds via oxidation with NO_2, engaging all the Cu ions in the catalyst independent of its Cu or Al contents.

Additionally, a second type of isolated Cu species, $[CuOH]^+$ ions charge-compensated at isolated Al sites, are exchanged in catalysts with dilute Al contents (i.e. high Si:Al) following the saturation of paired Al sites with Cu^{2+} ions, which are thermodynamically preferred over isolated Al sites during ion exchange. NH_3 titration differentiated between the two sites and showed that two protons were replaced per exchanged Cu^{2+}, whereas one proton was replaced per exchanged $[CuOH]^+$ ion. Further, reduction of each Cu^{2+} generated an additional proton, whereas $[CuOH]^+$

ions did not generate extra protons. FTIR spectra on a series of samples with Si:Al = 15 detected the O-H vibration associated with $[CuOH]^+$ ions at 3651 cm^{-1}, and showed a quantitative increase in its peak area with Cu loading beyond the saturation limit of Cu^{2+} (Cu:Al = 0.1, Si:Al = 15). *In situ* oxidizing (20% O_2, 673 K) or reducing (He, 673 K or 3.5% H_2, 523 K) treatments for two representative samples consisting of exclusively Cu^{2+} or predominantly $[CuOH]^+$ (i.e. 80% of the total exchanged Cu) ions exposed differences in their chemical behavior and showed that $[CuOH]^+$ ions are more reducible compared to Cu^{2+}. The two Cu species, however, are indistinguishable during standard SCR catalysis based on the measured apparent kinetics (E_{app}, apparent orders for NO, NH_3, O_2 and turnover rates), steady state Cu(I)-Cu(II) fractions from *operando* XAS spectra and DFT energetics for the standard SCR pathway on both sites. These observations were rationalized by DFT calculations, which showed that solvation by NH_3 under reaction conditions nullified the differences between the two types of Cu species.

The importance of nitrates for the oxidation of NO by O_2 on Cu-ZSM-5 under dry conditions was determined in a separate study using steady state isotope transient kinetic analysis in a custom-designed *operando* FTIR reactor. Three different nitrate peaks at 1626 cm^{-1}, 1601 cm^{-1} and 1567 cm^{-1} were observed under steady state dry NO oxidation conditions. Simultaneous monitoring of the surface nitrates using FTIR and the reactor effluent using mass spectrometer (MS) showed that NO_2 was produced from the decomposition of surface nitrates by NO. ^{15}NO labeling experiments confirmed that NO and NO_2 were in quasi-equilibrium through nitrates on the catalyst surface, and suggested that the bridged/bidentate nitrate at 1626 cm^{-1} is a likely intermediate for dry NO oxidation on Cu-ZSM-5.