Structure-activity relationships in NH₃-SCR over Cu/SSZ-13 as probed by reaction kinetics and EPR studies

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Introduction
Selective catalytic reduction (SCR) of NOx with ammonia using metal-exchanged molecular sieves with a Chabazite (CHA) structure has recently been commercialized on diesel vehicles [1-3]. Catalysts with outstanding SCR performance (activity, hydrothermal stability, etc.) include the aluminosilicate zeolite, SSZ-13, with ion-exchanged Cu. Apart from the commercial success, detailed catalyst structures, reaction mechanisms, and structure-activity relationships are still lacking. In the current study, we use Electron Paramagnetic Resonance (EPR), a technique ideally suited for studying Cu²⁺ exchanged zeolites, to study hydrated Cu-SSZ-13 catalysts at various Cu loadings in order to gain further insights into their locations. Also, NH₃-SCR and NH₃ oxidation kinetics are investigated over these catalysts at high space velocity conditions for the development of structure-activity relationships.

Materials and Methods
Na/SSZ-13 was synthesized using a procedure detailed in reference [2]. After exchange of Na⁺ for NH₄⁺, aqueous CuSO₄ solutions with varying concentrations were used to prepare Cu/SSZ-13 catalysts with Cu loadings of 1.31, 2.59, 3.43, 4.67 and 5.15 wt.% (ion exchange (IE) levels were determined as 23%, 45%, 60%, 80% and 90%, respectively). Reaction tests were performed using a plug-flow reactor and products were measured using an online FTIR detector. Catalysts were characterized with surface area/pore volume measurements, temperature programmed reduction (TPR), electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and chemisorption monitored with FTIR.

Results and Discussion
Fig. 1(a) presents EPR results of the Cu-SSZ-13 samples at 155K. Low temperatures were used for the measurements in order to decrease Cu²⁺ ion mobility and allow only dipole-dipole interactions to be monitored. These results are consistent with an octahedral coordination of Cu²⁺ ions and, as shown in the insert, the integrated signal areas are linearly dependent on IE levels further confirming that Cu in all samples are predominately EPR active Cu²⁺ monomers. The observed dipolar broadening in the spectra, can be used to estimate the fraction of the copper population that has a nearest neighbor within some distance range. This analysis gives three Cu-Cu distance groups, i.e. >20, 5-10 and 4-5 Å (none fell in the 10-20 Å range) as a function of Cu loading as shown graphically in Fig. 1(b). Along with TPR results, the EPR studies demonstrate the presence of Cu²⁺ ions in at least two locations within the SSZ-13 zeolite cages. At low ion-exchange levels (e.g. IE 23%), Cu²⁺ ions are far apart suggesting one Cu⁺ ion within one hexagonal unit cell, and coordinated with lattice oxygen atoms of the CHA zeolite 6-membered rings. As the Cu loading increases, it is possible for two Cu²⁺ ions to reside in one unit cell. The estimated Cu-Cu distances from EPR, as well as TPR results suggest some Cu²⁺ ions are located in the large CHA cages and close to 8-membered rings.

Standard NH₃-SCR reaction kinetics were measured at high space velocities. Within the differential kinetic regime and in the absence of inter-particles diffusion limitations, NOx TOF decreases with increasing Cu loading, indicating that the reaction kinetics are controlled by intra-particle diffusion limitations. Catalyst effectiveness factors are estimated using the Thiele relationship, yielding reasonable estimated effective diffusivities of the reactants by comparing to CH₄ diffusivities within 4Å molecular sieves. These results suggest that for the CHA SCR system, both washcoat and pore diffusion limitations should be considered during practical applications.

For the much slower, non-selective NH₃ oxidation, reaction rates increase with increasing Cu loading. This behavior is attributed to: (1) weaker interaction between Cu ions and the zeolite framework at higher Cu loadings that allows more facile Cu²⁺ ↔ Cu⁺ redox cycling thus facilitating NH₃ oxidation; and (2) at higher Cu loadings, the catalytic centers are located closer to pore openings and, thus, more accessible to reactants. Even under differential reaction conditions free from inter-particle limitation, two kinetic regimes are found with dramatically different apparent activation energies below and above 523 K. This is due either to a change in the rate limiting mechanism or, alternatively, a change in the nature of the active site (e.g., coordination of the Cu ion catalytic centers).

References