Mobility of ammonia in zeolites relevant to NOx emission control catalysts

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Introduction
Ammonia selective catalytic reduction (SCR) is an important emission control technology for removing NOx from lean-burn engines. Zeolites are an important class of material used in many SCR catalyst technologies.[1] Two key reactions occurring on zeolite based SCR catalysts are shown below.

\[ 4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \]  \hspace{1cm} \text{Eq 1}

\[ \text{NH}_3 + \text{H}^+(\text{ion}) \rightarrow \text{NH}_4^+(\text{ion}) \]  \hspace{1cm} \text{Eq 2}

Equation 1 shows the standard comproportionation reaction between NH3 and NO leading to formation of N2, which is catalyzed by transition metal ions residing at ion-exchange sites in the zeolite pores. These microporous materials also contain residual protons in ion-exchange sites, which have a high propensity to retain ammonia as shown in Eq 2.[2] Together, Eqs 1 and 2 constitute two competing pathways for consumption of ammonia in the pre-steady state operational regime. The degree to which Eq 2 competes with Eq 1 depends on the relative rates of Eq 1 (occurring at the SCR active site) and Eq 2 (occurring at the Bronsted acid sites).

Ammonia stored as NH4+ can also be used to accomplish NOx conversion under conditions where injection of NH3-equivalents (such as urea) may not be possible or desired. However, this process requires that molecules of ammonia migrate from the ion-exchange sites to the SCR active sites. Thus the efficiency of NOx conversion by stored ammonia may depend on the mobility of ammonia in the zeolite. The rate for temperature-programmed desorption (TPD) of ammonia is also closely connected to the mobility of ammonia in the zeolite, and can be used to extract kinetic information about the migration process. We have collected ammonia-TPD data for a series of commercially common zeolite materials in their H+ form, including those most relevant in ammonia SCR catalysis. Based on a simple kinetic model, the variability in the ammonia migration rate across this series was related to key structural factors in the zeolite framework. Finally, certain performance features in SCR catalysts made from different zeolites may be related in part to differences in ammonia mobility in the zeolite pores.

Materials and Methods
All of the zeolite materials used in this study were obtained from commercial sources or prepared in-house. The ammonia-TPD measurements were performed using a Micrometrics Instrument Corporation AutoChem II 2920 instrument with a thermal conductivity detector (TCD). The sample was saturated with ammonia at 120°C. Then the temperature was raised to 600°C at a ramp rate of 5°C/min in a flow of 50 mL/min helium.

Results and Discussion
Figure 1(left) shows the ammonia-TPD trace for an H-form zeolite of the CHA framework type. The data is representative in showing two clear regimes for ammonia desorption indicated as peak(a) and peak(b). Figure 1(right) shows the position of peak(a) and peak(b) in temperature vs. the maximum free sphere diameter[3] for six different zeolites. The position of peak(a) is independent of the zeolite framework type. Peak(b) shifts to higher temperature as the size of the pore aperture decreases. This data shows that it is more difficult to desorb NH3 associated with peak(b) as the size of the pore aperture decreases. We consider a simple kinetic model based on the “hopping” of NH3 molecules between ground state binding sites. Fitting this model to the ammonia-TPD data allows us to estimate the kinetic activation parameters. One result is that the estimated entropy of activation for desorption is markedly negative, indicating that the transition state for ammonia migration is more ordered than the ground state. This suggests that a key factor limiting ammonia mobility in zeolites is passage through the pore aperture. This helps to explain why SCR catalysts based on small pore zeolites and large pore zeolites show different behavior with respect to their dependence on stored ammonia.

Figure 1. Left: Ammonia temperature-programmed desorption trace for a representative zeolite (CHA). Right: Temperature at peak NH3 desorption as a function of the maximum free sphere diameter for a series of zeolite frameworks (CHA, MFI, BEA, FAU, MOR, FER). All zeolite samples have SAR = 20–35.

Significance
Temperature-programmed desorption of ammonia yields information about the mobility of ammonia in zeolites. Ammonia storage and mobility are important performance considerations in SCR catalysts based on zeolites.

References