

# **NH<sub>3</sub> storage isotherms: a path toward better models of NH<sub>3</sub> storage on zeolite SCR catalysts**

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## **Introduction**

Copper-exchanged zeolite catalysts active in the selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) by NH<sub>3</sub> have played a key role in making it possible for high efficiency lean-burn engines (such as those running on diesel fuel) to comply with emissions regulations. However, further tightening of emissions standards is requiring still more advances in catalyst performance. Achieving high NO<sub>x</sub> conversion while minimizing NH<sub>3</sub> slip and efficiently utilizing the reductant (such as urea) requires careful management of the NH<sub>3</sub> inventory on the surface of the SCR catalyst. On-board control strategies for NH<sub>3</sub> dosing rely heavily on SCR device models that accurately predict transient NH<sub>3</sub> storage levels. These models must account for a wide range of operating parameters, including temperature, gas composition, and catalyst age, as well as drive-cycle hysteresis. We have found that the widely used laboratory strategies for measuring NH<sub>3</sub> storage characteristics tend to convolute the effects of adsorption energetics, reaction rates, and mass transport, thereby greatly complicating the accurate determination of both the rate controlling steps and their associated kinetic parameters. The resulting models typically do not accurately represent NH<sub>3</sub> storage behavior over a realistic range of operating conditions. To circumvent these challenges, we have measured NH<sub>3</sub> desorption isotherms that isolate just the energetics of the adsorption/desorption process. We have also used a standard thermodynamic relation to estimate adsorption enthalpy as a function of NH<sub>3</sub> coverage from the isotherm data.

## **Materials and Methods**

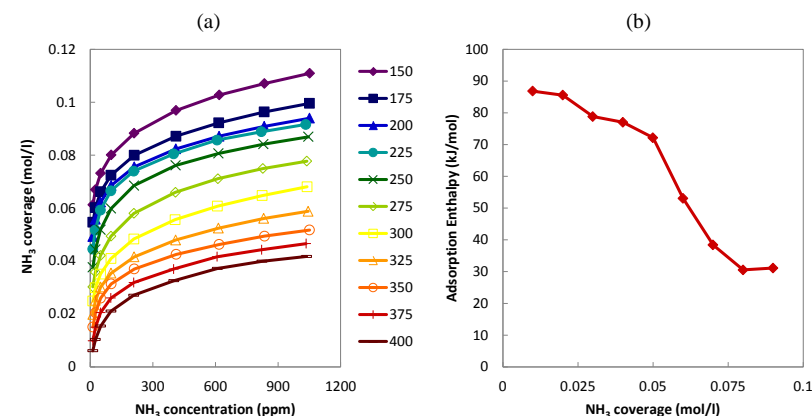
A 2.0 cm diameter by 5.0 cm long core sample was cut from a commercial small pore copper zeolite (intended for use in a General Motors pickup truck). The core sample was degreened for 4 h at 700 °C under a flow of air humidified with 10% H<sub>2</sub>O prior to loading in an automated flow reactor for characterization. Equilibrium NH<sub>3</sub> storage isotherms were measured by integrating the NH<sub>3</sub> released from the catalyst (measured by an FTIR spectrometer) during isothermal step-wise desorption experiments at the following NH<sub>3</sub> concentrations: 1000, 800, 600, 400, 200, 100, 50, 25, and 12.5 ppm. The step-wise desorption experiment was repeated at 11 temperatures spaced in 25 °C increments between 150 and 400 °C. The total gas flow was held fixed to maintain a GHSV of 30,000 h<sup>-1</sup> (based on flows at 0 °C and 1 atm) and included 5% H<sub>2</sub>O and a balance of N<sub>2</sub> in addition to the varying NH<sub>3</sub> concentration. A form of the Clausius-Clapeyron equation

$$\frac{d(\ln P_{\text{NH}_3})}{d(\frac{1}{T})} = \frac{\Delta H_{\text{ads}}}{R}$$

was used to estimate the NH<sub>3</sub> adsorption enthalpy as a function of coverage from the NH<sub>3</sub> isotherms.

## **Results and Discussion**

Figure 1 (a) shows the equilibrium NH<sub>3</sub> storage isotherms measured on the degreened copper zeolite catalyst in the presence of H<sub>2</sub>O. These isotherms were used to calculate adsorption enthalpy as a function of NH<sub>3</sub> stored on the catalyst (Figure 1(b)). The adsorption enthalpy appears to have two plateaus, one at 85 kJ/mol and the other at 30 kJ/mol, consistent with two distinct storage sites. Comparison with model isotherms indicates that the adsorption enthalpy trends are consistent with a two site Langmuir adsorption model. Similar experiments were conducted in the absence of H<sub>2</sub>O and on a catalyst sample that was hydrothermally aged at a higher temperature to capture the effects of H<sub>2</sub>O competition for storage sites and aging on NH<sub>3</sub> adsorption energetics.



**Figure 1.** (a) Equilibrium NH<sub>3</sub> storage isotherms (moles NH<sub>3</sub> stored per liter of catalyst monolith as a function of NH<sub>3</sub> feed concentration) over a range of temperatures in 5% H<sub>2</sub>O, balance N<sub>2</sub>; (b) Estimated adsorption enthalpy as a function of NH<sub>3</sub> coverage as determined from the Clausius-Clapeyron relationship.

## **Significance**

Accurate estimates for NH<sub>3</sub> adsorption-desorption energetics are critical to successful SCR device modeling because their relationship with NH<sub>3</sub> surface storage is exponential. The NH<sub>3</sub> storage isotherm method described here provides direct estimates of these energetics and their functional relationship with NH<sub>3</sub> coverage without any added bias from mass transfer or chemical reaction. This makes it possible to develop more accurate parameter estimates for SCR device models as well as improved physical insight into catalyst surface details that control NO<sub>x</sub> conversion. Combined with independent measurements that include mass transfer and intrinsic kinetics, these energetics estimates can be used to formulate more accurate models of NH<sub>3</sub> SCR catalysts, enabling improved catalyst formulations, emissions control strategies and advanced vehicle architectures.