

Modeling Species Inhibition and Competitive Adsorption in Urea-SCR Catalysts

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ABSTRACT

Although the urea-SCR technology exhibits high NO_x reduction efficiency over a wide range of temperatures among the lean NO_x reduction technologies, further improvement in low-temperature performance is required to meet the future emission standards and to lower the system cost. In order to improve the catalyst technologies and optimize the system performance, it is critical to understand the reaction mechanisms and catalyst behaviors with respect to operating conditions. Urea-SCR catalysts exhibit poor NO_x reduction performance at low temperature operating conditions ($T < 150^{\circ}\text{C}$). We postulate that the poor performance is either due to NH₃ storage inhibition by species like hydrocarbons or due to competitive adsorption between NH₃ and other adsorbates such as H₂O and hydrocarbons in the exhaust stream. In this paper we attempt to develop one-dimensional models to characterize inhibition and competitive adsorption in Fe-zeolite based urea-SCR catalysts based on bench reactor experiments. We further use the competitive adsorption (CA) model to develop a standard SCR model based on previously identified kinetics. Simulation results indicate that the CA model predicts catalyst outlet NO and NH₃ concentrations with minimal root mean square error.

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INTRODUCTION

Exhaust aftertreatment is essential, in conjunction with engine technologies such as exhaust gas recirculation, in order to meet the stringent emission standards proposed by United States Environmental Protection Agency (EPA) for 2010 [1]. For vehicles powered by heavy duty diesel engines, the limits are 0.2 gm/bhp-hr of nitrogen oxides (NO_x) and 0.01 gm/bhp-hr of particulate matter (PM). Selective catalytic reduction (SCR) using ammonia as a reductant is a proven NO_x reduction technology in stationary sources such as power-plants and boilers [2,3,4,5,6], and SCR using urea in meeting the Euro IV NO_x regulations for heavy duty diesel engines [7,8,9] in Europe. The reductant which selectively reduces NO_x in the exhaust is NH₃, which is produced on-board through the injection of urea solution into the exhaust pipe upstream of the SCR catalyst. Under ideal circumstances, the urea droplets evaporate and decompose into NH₃ and HNCO. The HNCO in turn hydrolyzes to form CO₂ and another molecule of NH₃. A small fraction of the hydrolysis happens in the exhaust pipe, but HNCO hydrolyzes completely on the active sites of the catalyst [10].

Engine exhaust temperature has become much cooler due to advanced combustion technologies. Therefore, it is critical

to improve the low temperature performance of NO_x reduction catalysts. Factors that affect NO_x conversion in SCR catalysts at low temperatures include (a) Hydrocarbon slip from DOC-DPF during engine cold start inhibiting SCR reaction pathways [11] and (b) Competitive adsorption between NH₃ and various adsorbates such as H₂O, NO₂ and hydrocarbons as suggested in the literature [14,15,16].

The presence of H₂O slows the standard SCR reaction but has little effect on the fast SCR rate. It has been reported that water inhibits NO oxidation on zeolites at temperatures where SCR reactions take place [12,13]. This in turn inhibits the formation of NO₂, which is reported as a key player in enhancing the NO_x conversion on Fe-zeolites [13,14,15,16]. The difference in efficiency between the fast and standard SCR reactions is greatest at low temperature, so it is reasonable to consider whether poor NO oxidation at low temperature is responsible. Some authors have suggested that the NO oxidation reaction is far too slow to be significant in the standard SCR reaction mechanism [17]. Under more realistic diesel exhaust conditions, our results indicate that while the steady state NO oxidation in the absence of ammonia is in fact slower than the overall standard SCR reaction, it is certainly fast enough to contribute to the

observed loss in efficiency at low temperature if, for example, more than one reaction pathway exists. Alternatively the presence of ammonia under SCR conditions results in a complete loss of NO_2 via the fast SCR reaction which may increase the net NO_2 formation by reducing or eliminating the reverse reaction. It therefore seems at least plausible that the inhibition of NO oxidation contributes to the loss in standard SCR efficiency of NO_x reduction that we observe with added water. Similarly, hydrocarbon adsorption on base-metal zeolites is a potential problem, as it can reduce durability and lower NO_x conversion efficiency [18,19]. In the case of toluene, as we discuss below, adsorption of relatively small amounts at low temperatures produces a severe inhibition of both the NO oxidation and the standard SCR reactions. The presence of NO with excess oxygen in lean exhaust requires consideration of the NO oxidation reaction for any practical kinetic modeling effort. In any event, in lean exhaust gases containing high NO and oxygen content the NO oxidation reaction is inevitable and must be accounted for. Motivated by these findings we have investigated in detail the inhibition of NO oxidation by hydrocarbons on Fe-zeolites. Also, this paper presents a test plan to probe the effect of adsorbates that compete with NH_3 for active sites and develop a competitive adsorption model based on the test data. The paper also introduces the development of a standard SCR model based on competitive adsorption kinetics involving NH_3 and H_2O .

EXPERIMENTAL SET-UP

The reactor consisted of a straight 25 mm outer diameter quartz tube long enough to stick out of both ends of our temperature programmable furnace (Lindbergh Blue). The catalyst itself was a core (2.5cm by 2.2cm dia.-9.3cm³ volume) drilled out of a commercially available SCR catalyst from Umicore with a cell density of 400 cells per square inch and a wall thickness of 6.5 milli-inches. A few strands of fiber glass thread were wrapped around the monolith to ensure a tight fit and prevent gas from bypassing the catalyst. The catalyst was placed close to the downstream end of the reactor, and a few glass beads were added upstream to help equalize the gas temperature. A type K thermocouple was placed approximately 1-2 mm downstream of the output face of the monolith to monitor the catalyst out gas temperature. Analysis was done using an FTIR spectrometer (Nicolet, Magna 750) equipped with a heated White cell (2 meter path length, 200 cm³ volume, 150°C) as shown in Figure 1.

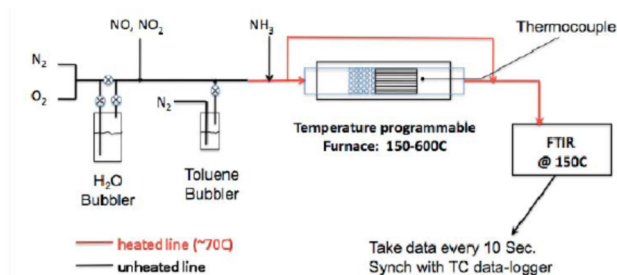


Figure 1. A schematic of the reactor set-up for steady state tests on the Fe-zeolite monolith core.

Data was recorded every few seconds using OMNIC series software from Nicolet. The spectra were analyzed with OMNIC quant pad software using a method developed in-house. The internal gas temperature was recorded every 15 seconds, and this data was synchronized up with the concentration vs. time plots generated by the series software. For all experiments the overall flow was held at 4.5 standard liters per minute, for a gas-hourly space velocity of approximately 30,000/hr. Our standard simulated exhaust for SCR experiments calls for 14% O_2 , 5% CO_2 , 5% H_2O , 350 ppm NH_3 and 350 ppm NO_x as mix of NO_2 and NO. This is the standard steady state CLEERS protocol. CLEERS (Cross-cut Lean Exhaust Emissions Reduction Simulation, www.cleers.org) is a project team comprising of the industry, academia and national laboratories sponsored by the US Department of Energy. Other details of the test set-up can be found in [20].

HYDROCARBON INHIBITION OF SCR REACTIONS

From our recent inhibition tests using H_2O , we observed that H_2O inhibits standard SCR reaction at low temperatures [21]. In that work, we concluded that the inhibition effect on standard SCR occurs through the NO oxidation route, as we observed considerable effect of H_2O at low temperatures and at various H_2O percents. Models to predict H_2O effect on NO oxidation were developed and validated. To probe the effect of hydrocarbons on NO_x reduction performance in a Fe-ZSM5 urea-SCR catalyst, toluene (an aromatic hydrocarbon) and n-dodecane (a long chain hydrocarbon) were considered. We did not observe any effect of propene on NO_x conversion during both steady state and transient tests. Figure 2 shows the effect of n-dodecane and toluene on NO_x conversion. The feed stream included 175 ppm NO, 175 ppm NO_2 , 350 ppm NH_3 , 50 ppm toluene (350C1), 29 ppm n-dodecane (~350C1), 14% O_2 , 2% H_2O at a space velocity of 29000/hr, simulating a fast-SCR reaction.

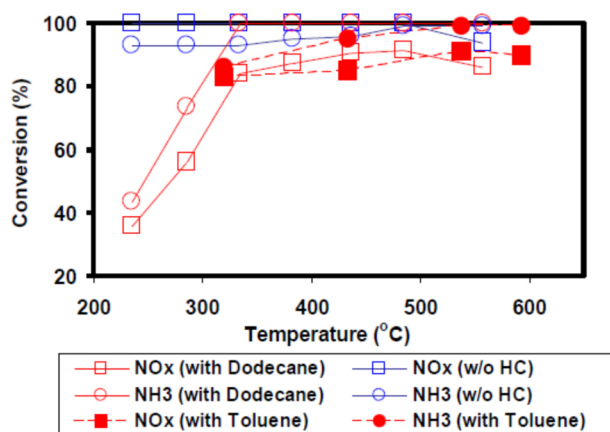


Figure 2. Effect of n-dodecane and toluene on NO_x conversion

It can be seen that n-dodecane has a considerable effect on the NO_x conversion, inhibiting SCR reactions at temperatures ranging from 200°C-300°C. Higher CO and CO₂ concentrations were measured downstream of the reactor when the reactor was heated up to 500°C after each data point. This was due to the oxidation of stored n-dodecane, further validating the assumption that stored hydrocarbons inhibit SCR performance between 200°C-300°C (and hence the drop in performance as shown in Figure 2) and oxidize at higher temperatures. Heating up the sample before moving to a different data point also helped us to approximate zero initial conditions for the storage states in the model. To investigate the effect of hydrocarbons under near-vehicle conditions, several temperature ramp experiments with 29 ppm n-dodecane (350C1) in the feed, were also conducted. The initial furnace temperature was set to 550° C, and the temperature was steadily ramped down to 150° C over a 75 minute period. The temperature was held at 150° C for 30 minutes before ramping back up to 550° C over 75 minutes. The 30-minute hold time was necessary to allow the actual catalyst temperature to stabilize, as the measured temperature lagged significantly behind the furnace set-point during the latter stages of the downward ramp. After the first cycle we held the temperature at 550° C while the experimental conditions were modified and then repeated the cycle. Comparing the two downward ramps is largely indicative of the effect of gas phase n-dodecane, as none is initially stored on the catalyst. The results show that n-dodecane has a considerable effect on NO_x conversion, even during the downward temperature ramps, thus indicating that hydrocarbons inhibit NH₃ storage or competitively adsorb with NH₃ for active sites and affect various NO_x reaction pathways on the SCR catalyst. A sample time history of a temperature ramp experiment is shown in Figure 3.

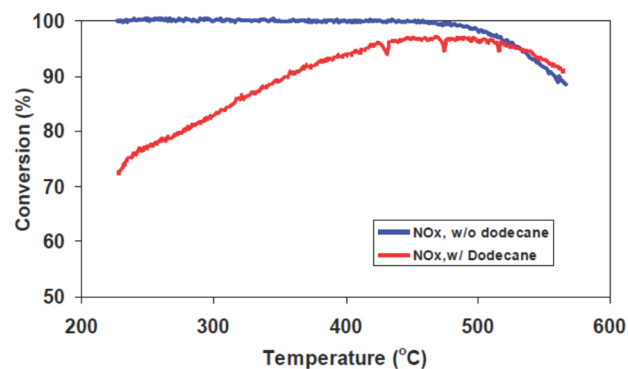


Figure 3. Effect of n-dodecane on NO_x conversion during temperature ramp tests

Toluene inhibition of SCR reaction pathways was discussed in detail in our previous reports [20]. The presence of toluene slows the standard SCR reaction much more effectively than the fast SCR, which suggests that different mechanisms may be in effect, one of them might be the suppression of NO oxidation reaction by toluene which contributes to the loss in NO_x conversion efficiency of the standard SCR reaction (similar to H₂O inhibition). Motivated by these findings, we developed a model to predict toluene's inhibition of NO oxidation to NO₂. A detailed discussion on toluene storage model is reported elsewhere [20, 21]. Here NO₂ adsorption is not included in the model. A single site toluene storage model was developed using the rate parameters obtained from Langmuir isotherms, in the reactor model shown in E1. To predict toluene inhibition of NO oxidation, a kinetic model similar in form to H₂O inhibition model [21] was developed as shown in E1. The model contains a term in the denominator, which represents the inhibition effect of hydrocarbon adsorption (storage) on NO oxidation.

$$r_{inh,tol} = \frac{k_{f,oxi}(c_{NO}c_{O_2}^{0.5} - \frac{c_{NO_2}}{K_{eq}})}{1 + K_{tol} \frac{\theta_{tol}}{1 - \theta_{tol}}} \quad E1$$

The rate parameters for the toluene inhibition model are given in Table 1. Data from a dry temperature ramp test with 350 ppm NO, 14% O₂ and 25 ppm of toluene (350 C1) was used to validate the inhibition model.

The downward temperature ramp data was used to validate the inhibition model as shown in Figure 4. A comparison between H₂O inhibition and toluene inhibition of NO oxidation (not shown here) indicates that a very small amount of toluene (25 ppm) has nearly as much effect as 1.6% water. More severe impacts on NO oxidation efficiency