

# EXPERIMENTAL AND MODELING INVESTIGATION OF AN UNEXPECTED KINETIC REGIME IN COMMERCIAL CU/Z SCR CATALYST

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## *Abstract*

It is well known that a catalytic monolith operates in a kinetic regime at low temperatures and transitions to bulk mass transfer controlled regime at sufficiently high temperatures. The washcoat diffusional regime can also prevail over an intermediate range of temperatures. In this work, we show that the performance of hydrothermally aged commercial Cu-zeolite SCR differs from the conventional sequence of regime transition with temperature. The SCR catalyst operates in a kinetic regime at low temperature. As temperature is increased, the performance transitions to mixed regime and at higher temperature, the performance transitions back to kinetic regime.

## *Keywords*

Diesel emission control, selective catalytic reduction, Ammonia, NO<sub>x</sub> reduction, mass transfer regime.

## **Introduction**

Selective catalytic reduction of NO<sub>x</sub> with ammonia (commonly referred to as NH<sub>3</sub>-SCR or just SCR) has emerged as the technology of choice to meet stringent emissions requirements for a variety of diesel applications world-wide. The most widely used class of NH<sub>3</sub>-SCR catalysts in the US are based on metal exchanged zeolites, especially those exchanged with iron or copper. The commercial NH<sub>3</sub>-SCR catalysts have undergone significant advancements leading to improved stability and performance.

It is a conventional observation that the performance of a catalytic monolith is bounded by two limits: a kinetic regime at low temperature and external mass transfer controlled regime at sufficiently high temperatures. The washcoat diffusional resistance can also be significant over an intermediate range of temperatures. In this study, we demonstrate a phenomenon that differs the conventional observation of regime transition. Specifically, we show that the hydrothermally aged

commercial Cu-zeolite SCR catalyst operates in a kinetic regime at low temperature. The performance operates in a mixed regime at intermediate temperature and transitions to kinetic regime at higher temperatures.

## **Experimental**

Cylindrical samples (approximately 1 inch diameter by 3 inch length and 300 cells/in<sup>2</sup>) were cored from a commercial Cu-zeolite SCR catalyst, belonging to the structural family of Chabazite (CHA). Before each experiment, the samples were hydrothermally aged at 700°C for 60 hours in the feed gas containing 10% O<sub>2</sub>, 8% H<sub>2</sub>O, 7% CO<sub>2</sub> and balance N<sub>2</sub> at 40 k<sup>h-1</sup>. Steady state NH<sub>3</sub>-SCR experiments were carried out to determine the dependence of NO<sub>x</sub> reduction on temperature. During such experiments, the reaction gas feed also included 200 ppm NO<sub>x</sub> and 200 ppm NH<sub>3</sub>. The bench flow reactor experimental set-up used in this work is the same as that described in detail in our earlier work (Henry et al., 2012).

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The catalyst sample was wrapped in Interam® mat which was compressed between the core and the quartz reactor tube. This enabled to prevent any gas bypassing around the catalyst periphery during the experiments. The temperatures of the catalyst and gas were measured by Omega K-type thermocouples. The effluent from the flow reactor was analyzed using an FT-IR spectrometer (MKS 2030 Series)

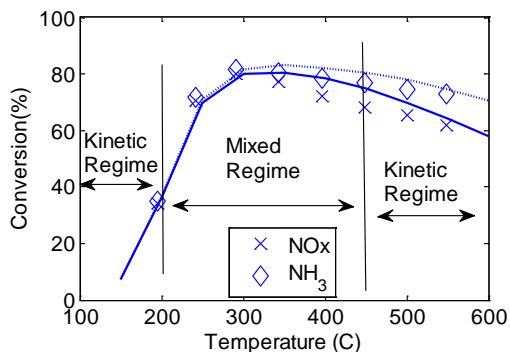


Figure 1. Steady state NO<sub>x</sub> and NH<sub>3</sub> conversions during NH<sub>3</sub>-SCR experiment on commercial Cu-zeolite SCR catalyst with feed: 200 ppm of NO and 200 ppm of NH<sub>3</sub> along with basic components of exhaust gas (10 % O<sub>2</sub>, 8% CO<sub>2</sub>, 7 % H<sub>2</sub>O and balance of N<sub>2</sub>)

### Kinetic Model

In this work, we have followed a global kinetic modeling approach based on the previously published study (Olsson et al., 2008). The rate expression for standard SCR reaction [equation 1] assumes that strongly adsorbed NH<sub>3</sub> reacts with gas-phase or weakly adsorbed NO.

$$\text{Rate} = k\theta C_{\text{NO}} \quad (1)$$

### Result

Figure 1 shows the steady state NO<sub>x</sub> and NH<sub>3</sub> conversions as a function of temperature under the standard SCR conditions (feed NO<sub>2</sub>/NO<sub>x</sub>=0). It is interesting to note that the conversions go through maximum and decrease with temperature above 300 °C. To gain insight into this unexpected behavior, we studied relative contribution of kinetics, bulk diffusion and washcoat diffusion.

Figure 2 shows the quantification of these key processes in terms of resistances. The resistance is defined as an inverse of rate of the process. Thus the process with highest resistance represents overall bottleneck and governs the conversion. The bulk and washcoat diffusional resistances decrease with temperature due to increase in diffusivity. But the reaction resistance increases with temperature showing the importance of kinetics above 400°C. This unusual prevalence of kinetic regime at higher temperature is attributed to the non-

monotonic dependence of reaction rate on temperature. The rate of SCR reaction is a function of rate constant (*k*) and surface coverage of NH<sub>3</sub> (*θ*) [eq. 1]. Though the rate constant (*k*) increases with temperature following Arrhenius dependence; the coverage of NH<sub>3</sub> decreases sharply with temperature. As a result, the reaction rate increases with temperature initially, attains a maximum then decreases.

### Conclusions

In this work, we illustrated an unusual phenomenon where the performance of a commercial Cu-zeolite SCR catalyst does not undergo a classical transition from kinetic to bulk mass transfer controlled regime as temperature increases. Instead, the performance undergoes a transition from kinetic to mixed to kinetic regime, as temperature increases [Figure 1]. This unusual behavior is attributed to the non-monotonic dependence of reaction rate on temperature. The rate of standard SCR increases with temperature initially, attains a maximum and drops sharply above 300 °C due to rapid depopulation of surface NH<sub>3</sub>. The behavior has significant implications for catalyst design and optimization that will be discussed in detail in a forthcoming publication.

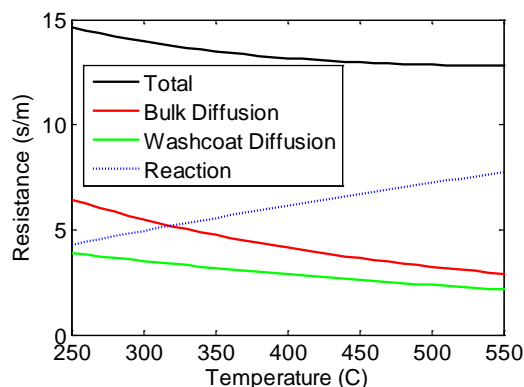


Figure 2. Calculated resistances during NH<sub>3</sub>-SCR on commercial Cu-zeolite SCR catalyst. Feed: 200 ppm of NO and 200 ppm of NH<sub>3</sub> along with basic components of exhaust gas (10 % O<sub>2</sub>, 8% CO<sub>2</sub>, 7 % H<sub>2</sub>O and balance of N<sub>2</sub>)

### References

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