Performance Characterization of Cu/Zeolite and Fe/Zeolite Catalysts for the Selective Catalytic Reduction of NOx

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Introduction

Reduction of nitrogen oxides (NOx) in the lean exhaust gas of diesel engines is not trivial. The well-known reaction chemistry of a typical precious metal three-way catalyst (TWC) is not effective for NOx conversion in lean exhaust. Urea-based Selective Catalytic Reduction (SCR) has the potential to meet U.S. Diesel Tier 2 Bin 5 emission standards for NOx in 2010 [1]. The reduction of NOx with either ammonia (NH_3) or urea has been used extensively for stationary source emission control. NOx reduction is possible due to the high selectivity of the NH_3 and NOx reaction to form elemental N_2. Urea decomposes to NH_3 following a well-known two-step decomposition process involving thermolysis and hydrolysis. The U.S. Tier 2 Bin 5 NOx standard represents a challenging 90+% reduction from previous standards. The varying operating and driving conditions of light-duty and heavy-duty vehicles make it necessary to customize catalyst features to the application. Generally, light-duty applications require SCR catalysts to function well at low temperatures (<350°C) whereas heavy-duty applications require functionality at higher temperature (>350°C) and high space velocity. One major thermal durability requirement of SCR formulations involves withstanding the high temperature process of regenerating particulate filters from accumulated soot. On the basis of performance, three important parameters for the selecting the proper SCR formulation involves the exhaust temperature profile, the NO_2/NOx ratio, and the amount of NH_3 stored on the catalyst surface. In addition to thermal durability, this paper reviews a detailed comparison between the basic catalytic activity of Cu/Zeolite and Fe/Zeolite formulations, and their resistance to poisons such as sulfur and hydrocarbons.

Materials and Methods

Fundamental catalyst activity data were obtained using a laboratory-scale flow reactor system. A round sample core of 1" diameter by 1" long was taken from a washcoated Cu/Zeolite and Fe/Zeolite monolith obtained from a supplier. The catalyst temperature was maintained with a tube furnace. Simulated diesel exhaust gas was flowed through the sample core consisting of 350ppm NOx, 350ppm NH_3, 14% O_2, 5% H_2O, 5% CO_2, and balance N_2. The total gas flow rate was 6.44 liters per minutes resulting in a gas hourly space velocity (GHSV) equal to 30,000/hr. A Nicolet FTIR instrument with a heat sample cell was used at the outlet of the reactor to measure NO, NO_2, N_2O, NH_3, H_2O, and CO_2 concentrations. Before evaluation, all catalysts were hydrothermally aged at 670°C for 64 hours in the presence of 5% H_2O, 14% O_2, 5% CO_2, and balance N_2.

Results and Discussion

Performance plots in Figure 1 show the active temperature range for Cu, Fe, and vanadium based SCR catalysts, the impact from high temperature 1 hour aging, the influence of stored NH_3 on low temperature activity, and the NOx conversion sensitivity to exhaust NO_2 fraction. The following main conclusions emerge from this study: **a)** Base metal/zeolite SCR formulations were found to be more thermally stable than vanadium based catalysts, **b)** The never-to-exceed temperature for Cu/Zeolite was established to be 775°C, while for Fe/Zeolite it was higher (925°C), **c)** NOx conversion for both Cu and Fe/Zeolite SCR catalysts are a strong functions of NH_3 storage capacity, **d)** low temperature NOx performance of both Cu/Zeolite and Fe/Zeolite was improved with the increase in NO_2 fraction. However, the Fe formulation was more sensitive to the NO_2/NOx ratio.

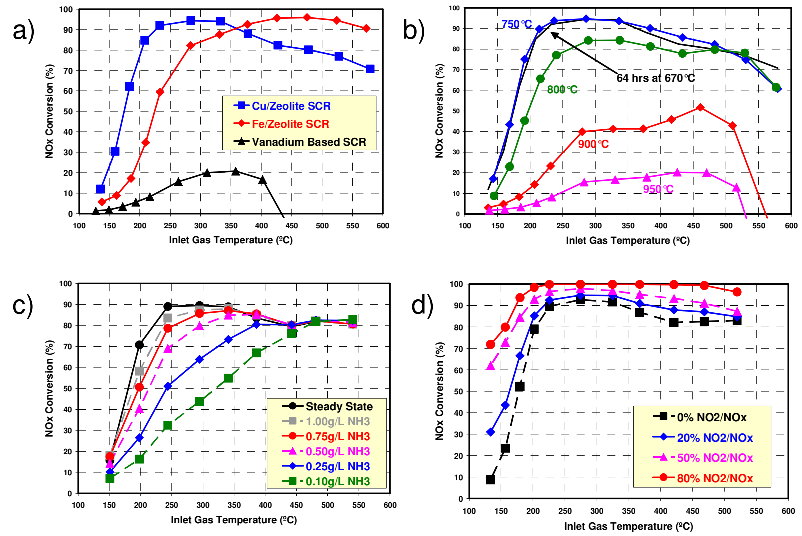

Figure 1. **a)** NOx conversion over Cu, Fe, and Vanadium based SCR formulations, **b)** Cu/Zeolite NOx conversion after 1 hour aging from 750°C – 950°C, **c)** Cu/Zeolite NOx conversion as function of exposed NH_3, **d)** Cu/Zeolite NOx conversion versus NO_2/NOx ratio. Note: SCR catalysts aged at 670°C for 64 hours in a) – d).

Significance

The transient driving nature of light-duty and heavy-duty vehicles makes it necessary to understand the key SCR functions and durability limitations under various operating conditions. Results in this study highlight main differences between Cu/Zeolite and Fe/Zeolite SCR formulations and provides insight into key parameters impacting NOx conversion.

References

1. Christine K. Lambert, Paul M. Liang, and Robert H. Hammerle, *Using Diesel Aftertreatment Models to Guide System Design for Tier II Emission Standards,* SAE 2002-01-1868.