The Impact of Urea on Hydrothermally Aged Cu/Zeolite SCR Catalysts

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Introduction

Selective Catalytic Reduction (SCR) of NOx with aqueous urea and a Catalyzed Diesel Particulate Filter (CDPF) has been considered as one of the emission control systems for diesel vehicles required to meet Federal Tier 2 and California LEVII emission standards [1]. Zeolite SCR catalysts that are used for stationary sources have been studied widely for use on vehicles. However, conditions such as temperature and flow rate are very different between the stationary and vehicle sources. One of the major differences is that the SCR catalysts may have to sustain high temperatures associated with CDPF regeneration on vehicles. It has been found that base metal/zeolite SCR catalysts, that are engine-aged with urea injection deactivate in a more complicated manner than hydrothermal aging alone [2]. In this paper, the impact of urea along with high temperature on Cu/zeolite SCR catalysts are investigated in a lab flow reactor. The results of this study provide valuable information on the durability of SCR catalysts for vehicle applications and suggest that future investigations of SCR catalysts should consider more realistic conditions for the vehicle application.

Materials and Methods

The SCR catalysts, CatA and CatB, in this study were fully formulated monolith Cu/zeolites. The catalysts were aged at the selected temperature for 30 to 60 minutes in three different ways in a laboratory-scale flow reactor: hydrothermal aging only, hydrothermal aging following wetting of the catalyst core with urea ("wet urea" + hydrothermal), and hydrothermal aging following urea wetting and drying at room temperature overnight ("dry urea" + hydrothermal). The steady state NOx performance was measured from 170°C to 550°C in the flow reactor connected to an FTIR instrument from MIDAC Corporation with a heated sample cell system for gas analysis. Simulated diesel exhaust gas was flowed through the sample core at space velocities of 30K h^{-1}, with a composition as shown in Table 1. The selected aged catalysts were also characterized using solid state ^{27}Al-NMR.

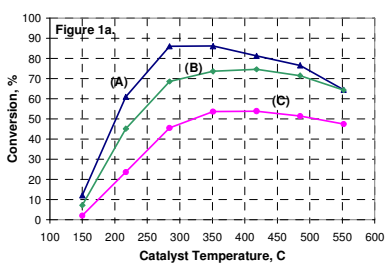
Results and Discussion

The steady state NOx conversion of CatA aged at 860°C for 30 minutes for the three conditions described above are shown in Figure 1a. The sample aged with "wet urea" was deactivated the most. Comparing to the NOx activity of sample aged hydrothermal only, there was up to 18% and 41% decrease in activity for samples aged with "dry urea" and "wet urea" respectively. CatA was also aged at 670°C for 60 minutes hydrothermally without urea, and with "wet urea" + hydrothermal aging. Unlike the samples aged at 860°C, the activity of CatA samples aged at 670°C were very similar regardless of the aging. This indicated that the urea did not deactivate the catalyst beyond the thermal deterioration at 670°C for CatA. The three different aging conditions were also conducted on CatB samples at 770°C for 30 min and the NOx activity after the aging is shown in Figure 1b. Similar to CatA, the CatB sample aged with "wet urea" was deactivated the most. However, the decrease of NOx activity for CatB aged with "wet urea" was at most 17% compared to the sample hydrothermally aged without urea, and there was no significant difference in NOx activity between the samples aged hydrothermally without urea and with "dry urea" except at 150°C. The smaller decrease in activity for CatB could have been due to the lower aging temperature. This suggested that the impact of urea on SCR catalyst durability increased with the aging temperature.

Selected CatB samples, fresh, hydrothermally aged without urea and with "wet urea" were analyzed by solid state ^{27}Al-NMR. The results showed no significant structure change of tetrahedral aluminum from fresh sample for CatB aged at 770 °C for 30 min. However, the "wet urea" sample aged at 770 °C for 30 min had reduced tetrahedral aluminum, indicating dealumination of the zeolite. The NMR analysis suggested that dealumination was the deactivation mechanism for the sample aged with urea.

Table 1. Composition of simulated diesel exhaust gas for SCR activity measurement.

Component	O_2	H_2O	CO_2	NO	NH_3	N_2
Concentration	14%	4.5%	5%	350 ppm	350 ppm	Balance



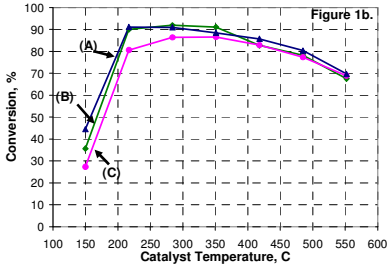


Figure 1a. Steady state NOx conversion of CatA after aging at 860°C for 30 min.
Figure 1b. Steady state NOx conversion of CatB after aging at 770°C for 30 min.
(A) hydrothermal aging only, (B) "dry urea" + hydrothermal aging, (C) "wet urea" + hydrothermal aging.

Conclusions

The combination of urea and high temperature exposure increased the deactiviation of Cu/zeolite SCR catalysts beyond hydrothermal aging alone. Immediate high temperature exposure following wetting of the catalyst core with urea caused more deterioration than if the core was allowed dry at room temperature overnight. The impact of urea on SCR catalyst durability increased with the aging temperature. NMR analysis suggested that aging with urea will cause more dealumination of zeolite for Cu/zeolite SCR catalysts.

References

1. C. Lambert, R. Hammerle, R, McGill, M. Khair and C. Sharp, SAE 2004-01-1292 (2004).
2. Yisun Cheng, Lifeng Xu, Jon Hangas, Mark Jagner, and Christine Lambert, SAE 07PFL-397, in press, (2007)