A Study of Chemical Aging Effects on HDD SCR Catalyst Performance

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Introduction

Increasingly stringent PM and NOx emissions regulations for Heavy Duty Diesel engines presents a challenge to the emission control community. To meet the durability requirement of these regulations, an improved understanding of the impact of chemical deactivation on catalyst activity in this application is necessary. A study by Johnson Matthey, Scania and Lubrizol showed little effect of oil derived contaminants on V based SCR after simulated aging equivalent to 100,000 km [1]. On the other hand, a 30% decline in NOx conversion after simulating 420,000 km has also been reported on similar catalyst [2]. Work by Bunting et al on DOCs have shown the impact of phosphorus (P) on catalyst activity varies with introduction method, and intake manifold injection of P results in deactivation similar to a field aged catalyst [3]. Promising SCR activity, including tolerance to thermal deactivation, has been shown with a delaminated Fe_2O_3-pillared clay in the absence of SO_2 [4]. In this work, a set of iron-zeolite based SCR catalysts was exposed to P and S at 210 and 450°C in the laboratory, and the impact on NOx reduction was evaluated. Comparisons were made to SCR samples exposed only to P [5], to see the extent of interactions between P and S.

Materials and Methods

One inch diameter monolith cores were chemically aged using a diesel fuel burner running on doped fuel, which exposed samples to 5 and 10g / L of substrate for both P and S. Depending on engine oil consumption and catalyst size, this amount can correspond to 800,000 and 1,600,000 km, respectively. This procedure simulates the intake manifold injection of P mentioned earlier and results in the introduction of combusted P and S over the sample. Catalyst performance was evaluated at a GHSV of 60,000/h using temperature and NO_2/NOx ratio sweep tests with simulated diesel exhaust, including 8.0% CO_2, 9.5% O_2, 240 ppm NO, 60 ppm NO_2, 333 ppm NH_3, 5% H_2O, and balance N_2. Gases were analyzed with an FTIR.

Results and Discussion

The amount of P adsorbed on the catalysts after aging and testing were determined by XRF analysis and reported in Table 1. The majority of the P is adsorbed on the front of the SCR. Increasing the exposure temperature increases the amount of P adsorbed and the depth of penetration into the core. A similar analysis for S showed no adsorption at 210°C exposure.

Table 1. Results from XRF analysis of adsorbed P (g/L) as a function of exposure temperature and location after exposure to 10 g/L P and S.

Exposure Temperature (°C)	Front (g/L P)	Middle (g/L P)	Rear (g/L P)
210	6.2	1.9	1.3
450	6.9	5.8	3.0

Figure 1 shows the effect of P and S on relative NOx activity during a temperature ramp as a function of exposure level. In all cases, as exposure levels increase activity loss accelerates. Compared to deactivation due to P alone, the initial activity loss increased more than 10% with the addition of S at an exposure level of 10 g/L (A vs. B curve). After the initial test ramp to 550°C, a repeat test showed significant activity recovery (B vs C curve). Increasing the exposure temperature increased the deactivation due to S effects, so that the activity loss appears more linear with increasing exposure level (C vs. D curve). Higher exposure temperature also made it more difficult to recover lost activity after aging. Analysis of the data suggests deactivation is mainly due to fouling of NH_3 adsorption sites by P while S affects NOx interaction with NH_3.

Significance

Details of the deactivation of iron- zeolite based SCR catalyst were obtained from the lab bench by studying the effect of P and S exposure. SCR catalyst deactivation accelerated as exposure levels increased; at the lower exposure temperature some of the activity lost due to S could be recovered by increasing catalyst bed temperature. Deactivation due to P was more significant and permanent than the loss due to S.

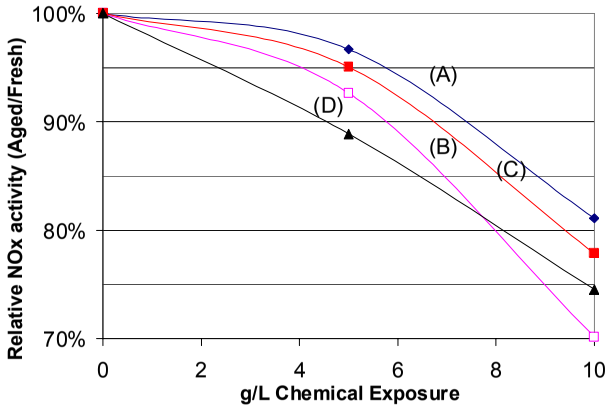

Figure 1. Relative NOx conversion (Aged/Fresh activity) at 440°C as a function of P and S exposure level and exhaust temperature: (A) exposed to P alone at 210°C, initial activity test; (B) exposed to both at 210°C, initial activity test; (C) Exposed to both at 210°C, repeated activity test; (D) Exposed to both at 450°C, repeated activity test.

References

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