Assessment of passive NOx adsorbers for diesel applications

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Introduction

Selective catalytic reduction (SCR) with urea injection is highly effective for NO_x reduction on diesel engines after the system is warmed up. However, the NO_x emissions can be high following a cold start, requiring heat-up strategies on the vehicle that consume extra fuel. Low temperature NO_x adsorbers (LTNA) have been explored that store NO_x during a cold start and release it at higher temperatures when the SCR system is operational.

Materials and Methods

The first-generation LTNA samples contained high loadings of Pt (3 to 6 g/L) and oxidized NO to NO_2 to form nitrates. A relatively recent technology (dCSC^{TM} from Johnson Matthey Inc.) contained 3.3 g/L Pd and 0.9 g/L Pt and stored NO as nitrites [1, 2]. The catalysts were prepared on cordierite substrates (62 cells per sq cm). For each technology, a 2.54 cm x 2.54 cm sample was installed in a flow reactor and evaluated at 27K hr^{-1} with 100 ppm NO, 10% O_2, and 5% CO_2 and H_2O. To simulate the Ford Super Duty diesel truck during the first 2 phases of the FTP-75, the catalyst bed temperature was ramped from ca. 90°C to 240°C before stabilizing at 200°C. The temperature was then ramped to 350°C to simulate a US06 test. HC trapping capability was also evaluated by adding 250 ppm C_2H_4 to the feedgas. The samples were evaluated fresh and after thermal aging in the flow reactor. The Pd-rich LTNA was also assessed for sulfur tolerance and desulfation performance. Analysis was performed with a 1 Hz MKS FTIR analyzer equipped with a sample line heated to 191°C.

Results and Discussion

After aging at 700°C under lean conditions, the Pt-rich technologies stored NO_x effectively at 120-150°C, released most of the stored NO_x as NO_2 between 250 and 350°C, and required final temperatures of 400 to 450°C to purge completely and maximize performance on the next test. In contrast, the aged Pd-rich LTNA stored NO effectively starting at 90°C, released much of the stored NO_x as NO between 150 and 200°C, and required a final temperature near 350°C to purge completely. The Pd-rich LTNA also stored and converted C_2H_4 effectively. The storage of NO_2 as nitrates on the Pd-rich LTNA at 150°C was degraded by SO_2, but the storage of NO as nitrites between 90 and 120°C was fairly robust to the SO_2. After aging 24 hrs at 600°C followed by 15 hrs at 700°C and 17 hrs at 740°C lean, the Pd-rich LTNA was evaluated on 5 consecutive temperature ramps. After 1 hour at 750°C lean, the sample was tested again. Since the urea/SCR system on the vehicle is functional after 200 seconds on the FTP-75, the average NO_x storage efficiency during the initial 200 seconds of a temperature ramp was determined. Table 1 shows the average NO_x storage efficiency for the first 200 seconds, the C_2H_4 adsorbed after a test was initiated, and the average C_2H_4 efficiency over the 2-phase simulation for the six tests. The 200 s NO_x storage efficiency on the first test was an impressive 89%. However, the NO_x storage efficiency, HC adsorbed, and overall HC efficiency dropped over the next 3 tests before stabilizing. After the hour at 750°C lean, the NO_x efficiency increased back to 86%, and the amount of C_2H_4 adsorbed also increased.

Table 1. 200 s NO_x efficiency, HC adsorbed, and 2-Phase HC efficiency for Pd-rich LTNA

	Ave NO_x eff Initial 200 s	**C_2H_4 stored (g/L)**	**Ave C_2H_4 eff Phase 1+2**
Test 1 (@17 hr 740°C lean)	89	0.42	87.4
Test 2	84	0.39	85.8
Test 3	82	0.37	85.1
Test 4	74	0.34	84.4
Test 5	77	0.35	83.4
Test 6 (@ 1h 750°C lean)	86	0.39	82.6

These results indicate that the Pd-rich LTNA needs to be highly oxidized for maximum NO_x and HC storage performance. The performance loss from run-to-run was attributed to the reduction of the oxidized Pd from reacting with the NO and C_2H_4 at low temperatures to produce NO_2 and CO, as shown in Figure 1. CH_4 oxidation was used to probe the oxidation state of the Pd and confirmed that the Pd had been partially reduced by the lean ramp tests.

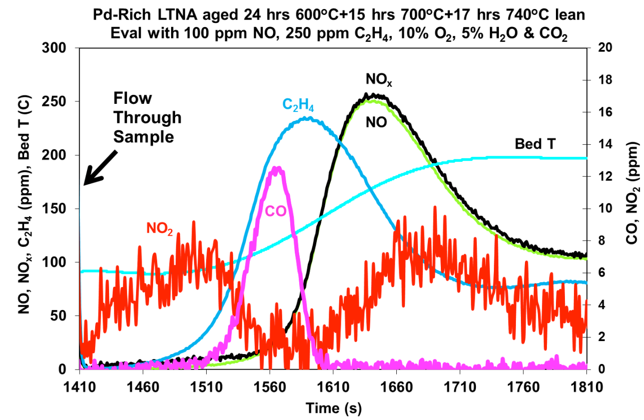

Figure 1. NO, NO_2, NO_x, C_2H_4, CO, and bed temperature during a transient temperature test

Significance

The Pd-rich LTNA catalyst was effective for storing NO and C_2H_4 after sulfur poisoning and after thermal aging at temperatures as high as 740°C. Periodic hot lean exposures (e.g., DPF regenerations) are needed for maximum storage performance.

References

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2. Chen., H.-Y.,Mulla, S., E. Weigert, K. Camm, T. Ballinger, J. Cox, and P. Blakeman, "Cold Start Concept (CSC^{TM}): A Novel Catalyst for Cold Start Emission Control",SAE2013-01-0535.