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Impact of redox conditions on thermal deactivation of NO_x traps for diesel

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Abstract

Performance of NO_x traps after high-temperature treatments in different redox environments was studied. Two types of treatments were considered: aging and pretreatment. Lean and rich agings were examined for a model NO_x trap, Pt–Ba/Al_2O_3. These were done at 950 °C for 3 h, in air and in 1% H_2/N_2, respectively. Lean aging had a severe impact on NO_x trap performance, including HC and CO oxidation, and NH_3 and N_2O formation. Rich aging had minimal impact on performance, compared to fresh/degreened performance. Deactivation from lean aging was essentially irreversible due to Pt sintering, but Pt remained dispersed with the rich aging. Pretreatments were examined for a commercially feasible fully formulated NO_x trap and two model NO_x traps, Pt–Ba/Al_2O_3 and Pt–Ba–Ce/Al_2O_3. Pretreatments were done at 600 °C for 10 min, and used feed gas that simulated diesel exhaust under several conditions. Lean pretreatment severely suppressed NO_x, HC, CO, NH_3 and N_2O activities for the ceria-containing NO_x traps, but had no impact on Pt–Ba/Al_2O_3. Subsequently, a relatively mild rich pretreatment reversed this deactivation, which appears to be due to a form of Pt–ceria interaction, an effect that is well known from early work on three-way catalysts. Practical applications of results of this work are discussed with respect to NO_x traps for light-duty diesel vehicles.
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Keywords: NO_x storage; NO_x reduction; Pt–Ba/Al_2O_3; Pt–Ba–Ce/Al_2O_3; Ceria; Thermal deactivation

1. Introduction

Diesel and lean-burn gasoline engines are considered attractive alternatives to conventional gasoline to improve fuel economy and reduce CO_2 emissions for light duty vehicles. A major challenge is abatement of NO_x ($NO + NO_2$) emissions. This is difficult in the O_2-rich exhaust of lean-burn engines. Lean NO_x traps have been an important aftertreatment technology under development to address this [1–3]. Recently, NO_x traps have been produced for lean burn gasoline passenger cars, but this application is limited. A key obstacle in the way of more widespread implementation of NO_x traps is durability. This is particularly the case for diesel vehicles. They require high NO_x conversion at lower temperature than that needed for lean-burn gasoline, for example, ~150–300 °C for diesel compared to ~300–600 °C for gasoline. NO_x trap activity at the lower temperatures is particularly sensitive to catalyst deactivation.

One source of deactivation is sulfur [4,5]. Vehicle exhaust contains low levels (ppm) of SO_2. This is derived primarily from combustion of organic sulfur contaminants in fuel. Sulfates accumulate on NO_x storage sites, and degrade performance. Periodically, sulfate is purged from the trap to restore NO_x performance. Sulfate purging (deSO_x) as well as the more frequent NO_x purging (deNO_x) is accomplished by running the engine rich, however, much higher temperatures are needed for deSO_x. For example, ~600–750 °C is typical for deSO_x, where normal operating temperatures are sufficient for deNO_x. In addition, a deSO_x event requires longer time, 5–10 min, compared to a few seconds for a deNO_x event.

Another source of deactivation is thermal, which is the subject of this work. In particular, we examined effects of feed gas redox character during high temperature on NO_x trap

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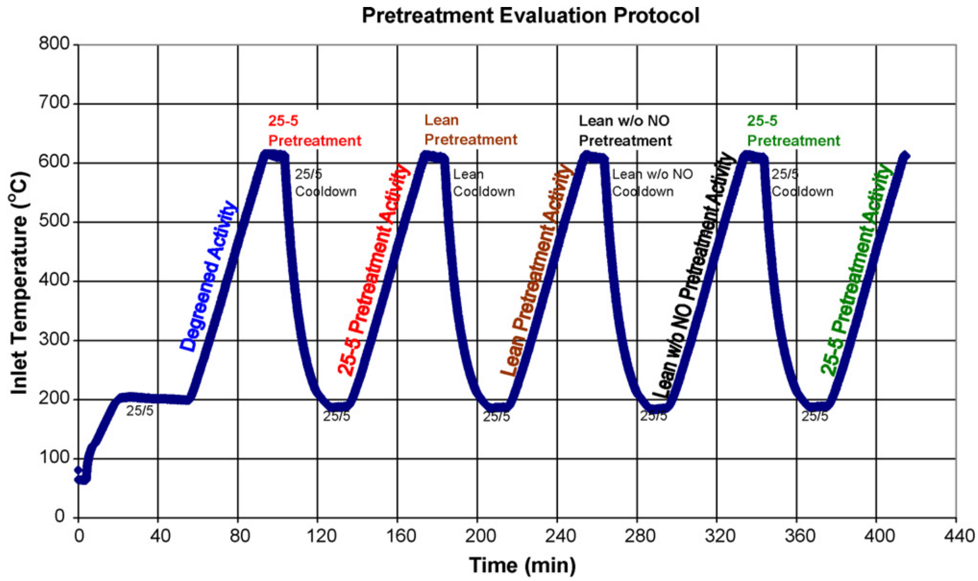

Fig. 1. Pretreatment evaluation procedure.

performance. We evaluated effects of aging, as well as shorter-term high-temperature exposure. In diesel applications, NO_x traps require high temperature for sulfate purging, as described above, and for regeneration of a downstream soot filter. The former requires a reducing (rich) environment, and the latter an oxidizing (lean) environment. Practical implications of this work are discussed.

2. Experimental

2.1. NO_x trap samples

Two model NO_x traps and one fully formulated NO_x trap, all prepared by a commercial catalyst supplier, were examined. Both model traps contained Pt and $BaCO_3$ supported on γ-Al_2O_3. One also contained ceria (CeO_2). These two model traps will be referred to as Pt–Ba/Al_2O_3 and Pt–Ba–Ce/Al_2O_3. The fully formulated trap contained Pt, $BaCO_3$ and ceria on γ-Al_2O_3, however, its entire composition is proprietary. This trap will be referred to as supplier formulated, or simply supplier. All NO_x traps were provided as washcoated cordierite monoliths with 400 cells/in.^{2}. Their Pt loadings were ~100 g/ft^3.

Table 1
Simulated diesel exhaust gas composition used for NO_x trap activity evaluations

Feed gas components	Lean concentrations	Rich concentrations
NO_x	500 ppm	500 ppm
C_3H_6	100 ppm	1650 ppm
CO	500 ppm	4.0%
H_2	167 ppm	1.3%
O_2	10%	1%
CO_2	5%	5%
H_2O	5%	5%
N_2	Balance	Balance

2.2. Activity testing

An integral flow reactor was used to measure NO_x trap activity. NO_x trap test samples were (3/4) in. diameter × 3 in. long monolith cores cut from larger sample bricks. The reactor had a quartz flow tube in which a test sample was placed. Thermocouples were located in the feed gas ((3/4) in. before the sample inlet) and in the sample (1 in. behind the inlet face). Temperature was controlled primarily with a large tube furnace (29 in. long) that surrounded the flow tube. The sample zone was isothermal with $\Delta T < 10$ °C at 600 °C. The flow tube had a bypass line to allow measurement of inlet concentrations for the feed gas components. Feed gas was a simulated diesel exhaust gas mixture. Typical diesel exhaust is lean (O_2-rich), however, NO_x traps periodically require rich exhaust to release and reduce stored NO_x. Compositions for the lean and rich feed gas mixtures are described in Table 1.

Activity data were collected over a temperature range of 150–600 °C, measured at the sample inlet. Temperature was ramped at 10 °C/min. Space velocity was 30,000/h. Feed gas composition was cycled between lean and rich, 25 and 5 s, respectively, which is called 25–5. FTIR was used to measure NO, NO_2, NH_3, N_2O, C_3H_6, and CO concentrations. Its pathlength was 3.25 m. Resolution was 0.5 cm^{-1}. The FTIR gas cell was ~150 cm^3 in volume, and gas flow was ~3 l/min. Measurement frequency was ~1 Hz. Conversions for NO_x, HC and CO were calculated as $[(C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}}] \times 100\%$, where C is concentration averaged over one 25–5 cycle. Formation for NH_3 and N_2O were calculated as $[C_{\text{outlet}}^{NH_3}/C_{\text{inlet}}^{NO_x}] \times 100\%$ and $[2C_{\text{outlet}}^{N_2O}/C_{\text{inlet}}^{NO_x}] \times 100\%$, respectively.

Degreening was performed on all samples, fresh and aged, prior to activity testing. Samples were degreened in the flow reactor by holding inlet temperature at 600 °C for 0.5–1 h. Feed gas was cycled at 25–5, which was also performed during heating and cooling.

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