

3. MATERIALS FOR EXHAUST AFTERTREATMENT

A. Materials for Exhaust Aftertreatment

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Objectives

- Develop advanced materials applied for diesel engine aftertreatment systems that will comply with future emission regulations.
- Assess impact of phosphorus on oxidation, lean-NO_x, NO_x adsorber (LNT) and urea-SCR (selective catalytic reduction) catalysts.
- Identify diesel particulate filter (DPF) substrate materials that have high durability and filtration efficiency with minimum impact on engine efficiency.

Approach

- Assess impact of phosphorous on aftertreatment systems by comparing fresh and aged catalyst performance using a fuel burner and a bench test system.
- LNT: Evaluate phosphorus impact on NO oxidation, NO_x storage and reduction functions.
- Urea-SCR: Evaluate phosphorus impact on zeolite and vanadia based catalysts using temperature and NH₃/NO_x ratio sweeps.
- Oxidation catalyst: Develop a correlation between bench and field in terms of deactivation mechanisms.
- Use previously developed test protocol to evaluate filtration efficiency and pressure drop of catalyzed and uncatalyzed DPF samples from various suppliers.

Accomplishments

- Completed lean-NO_x project (unfinished tasks carried over from last year).
 - Sulfur impacts on catalytic performance more severely than phosphorus.
 - Paraffins contributed lean-NO_x catalysis; however, benzene and mono-cyclo-paraffin were not active reductants, whereas aromatics and dicyclo-paraffin inhibited the catalytic reaction.

- Identified the cause of LNT deactivation due to phosphorus exposure.
 - NO_x storage capacity function was affected first and more severely than NO oxidation and NO_x reduction.
 - Phosphorus impacted the NO_x storage function more at low NO_x slip than at high NO_x slip conditions.
 - A model was used to estimate the impact of phosphorus deactivation on fuel penalty for the LNT.
- Identified the cause of vanadia- and zeolite-based SCR catalysts deactivation due to phosphorus exposure.
 - Phosphorus similarly impacted both NH₃ and NO conversions.
 - Zeolite catalyst showed higher phosphorus tolerance initially, but both catalysts had similar deactivation after extended exposure.
 - Speculate that phosphorus blocked NH₃ adsorption sites, which prevented NO reduction.
- Found that phosphorus impacted LNTs more than SCR, but presented a challenge for both catalyst technologies.
- Identified a promising DPF substrate material with filtration efficiency larger than 95% and pressure drop significantly lower than conventional cordierite material.

Future Direction

- Capture intellectual property and identify a partner for commercialization (lean-NO_x project).
- Assess impact of combination of phosphorus, sulfur, and thermal deactivation on oxicat, LNT, and SCR catalysts.
- Explore mitigation strategies for phosphorus, sulfur, and thermal deactivation phenomena.
- Evaluate the effect of thermal deactivation on filtration efficiency of new DPF substrate materials.

Introduction

The objective of this project is to develop and evaluate materials that will be utilized in aftertreatment systems for diesel engine applications to comply with future government emission regulations. The materials include catalysts for NO_x abatement and filtration media for particulate matter control. This year's focus is on the determination of the effect of phosphorus deactivation on the performance of LNTs, SCR catalysts and oxidation catalysts, and on identifying diesel particulate filter (DPF) substrate materials that have high durability and filtration efficiency with minimum impact on engine efficiency.

Approach

Catalyst Deactivation

The study was focused on identifying the impact of phosphorus exposure on catalyst formulations by testing the performance of fresh and aged catalysts. The aged catalysts were prepared by exposing to phosphorus in a diesel fuel burner using a diesel fuel doped with tricresyl phosphate that mimicked the effect of phosphorus from combusted lube oil. Using

x-ray fluorescence (XRF), we analyzed the amount of phosphorus adsorbed as a result of this exposure.

PM Trap

A developed test protocol was used to evaluate filtration efficiency and pressure drop of catalyzed and uncatalyzed DPF samples from various suppliers. In order to test DPF core samples that are supplied in sizes larger than 1 in. × 3 in., we designed and built a new chemical reactor with the capability to hold samples up to 2 in. × 6 in.

Results

Catalyst Deactivation

Lean-NO_x Catalyst Durability: Durability studies using sulfur and phosphorus aging have been performed on the Lean-NO_x catalyst developed from the previous study. Phosphorus was introduced to the sample using a diesel fuel burner burning phosphorus-blended zero-sulfur fuel, and the NO_x reduction performance was tested after each exposure increment. NO_x reduction of the catalyst maintained more than 40% NO_x conversion after reaching 30,000 h engine-equivalent (C15 engine)

phosphorus exposure (Figure 1). Phosphorus content of the aged samples was quantified using XRF.

Sulfur was introduced by SO₂ exposure directly using a bench test system, monitoring the NO_x reduction performance as a function of time-on-stream with SO₂. Sulfur content of the exposed samples has been quantified using a LECO CS-200 Carbon/Sulfur Determinator. NO_x reduction performance of the catalyst was reduced to ~30% NO_x reduction after 100-h engine-equivalent (C15 engine) sulfur exposure.

The negative impact of sulfur exposure was more pronounced than that of phosphorus exposure, both in magnitude and rate of degradation. Understanding the effects of sulfur and phosphorus provided insight into the development of catalyst materials and led to mitigation options best suited for the intended environment.

Lean-NO_x Catalyst Sensitivity to Diesel Fuel Components: A reductant study over the selected combination catalyst has demonstrated much lower activity when diesel fuel was used as a reductant compared to the desired reductant (example: dodecane). The influence of diesel fuel components on NO_x reduction performance has been investigated using a bench test system to determine the source of the activity loss (test condition: 500 ppm NO_x, 3000 ppm liquid hydrocarbons as C₁, 7% H₂O, 9% O₂, 50 ppm propene, 500 ppm CO, and 8% CO₂ with 35,000 h⁻¹ space velocity). Mixtures were prepared such as 80% of dodecane and 20% of various organic hydrocarbons, including paraffin, isoparaffin, aromatic, diaromatic, and combinations thereof. Isoparaffins (max. 74% NO_x reduction) showed NO_x reduction performance at a similar level to dodecane (77%) (Figure 2). Monoaromatics and variations on

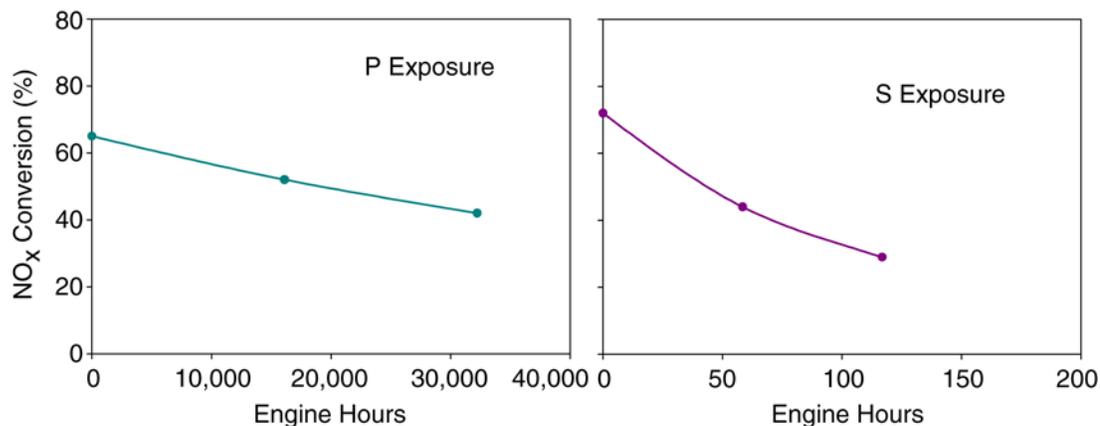


Figure 1. The effect of phosphorus and sulfur on the developed lean-NO_x catalyst performance based on C15 Caterpillar engine equivalent hours exposure.

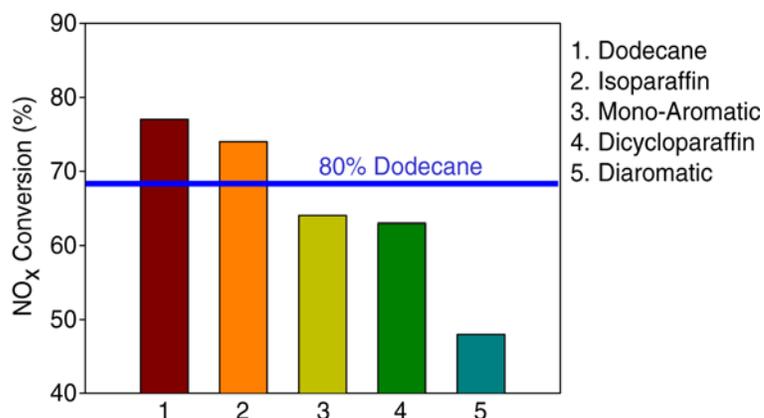


Figure 2. The effect of diesel component on lean-NO_x catalyst performance (20% of diesel components mixed with dodecane).

paraffins had a neutral effect on the NO_x reduction performance. Among the types of reductants tested, diaromatics strongly hindered the performance of the combination catalyst (48%), also shifting the operation temperature to a higher temperature range. Understanding the effects of fuel components provided insight into the development of catalyst materials as well as a fuel processor to obtain the proper reductant from diesel fuel to supply to the catalyst for maximum performance.

NO_x Adsorber Catalyst Durability: A series of model LNTs were prepared by coating 400-cpsi cordierite monolith cores with γ -Al₂O₃ washcoat. The cores were then dipped in cerium acetate solution, dried, then calcined at 550°C for 5 h to give a loading of 20 wt % CeO₂. The process was repeated with a barium acetate solution to give a loading of 11 wt % BaO, and then with platinum/rhenium nitrate solution, resulting in a loading of 5 wt % platinum and 0.6 wt % rhenium. The finished catalysts were reduced in 5% H₂ at 350°C for 2 h. The finished catalysts were tested for NO_x conversion using a laboratory reactor with 1-in. diameter by 3-in.-long catalyst cores at a space velocity of 55,000 h⁻¹. Each sample was degreased at 275°C for 20 min in a reducing gas (2.5% H₂, 2.5% CO, 5% CO₂, 5% H₂O, balanced with N₂), then switched to an oxidizing mix (12% O₂, 5% CO₂, 5% H₂O, balanced with N₂). The 200-ppm NO_x (10% NO₂) was added to load the samples with NO_x. After saturating the samples with NO_x at 275°C, the LNTs were ramped to 425°C in the oxidizing mix without the NO_x, regenerated in the reducing gas, and reloaded with NO_x. After determining the initial performance of the model LNT, the sample was exposed to 3.6 g/L of phosphorus using a diesel fuel burner with phosphorus-doped fuel at 250°C. The aged sample was then reanalyzed for NO_x conversion in the lab reactor. The aging process was repeated to increase phosphorus exposure to 10 g/L.

The NO oxidation to NO₂, NO_x storage, and NO_x reduction function of the NO_x adsorbers was tested after loading with 3.6 and 10 g/L phosphorus, with and without a blank monolith in front as a phosphorus getter. Results indicate that phosphorus degrades LNTs. The NO oxidation function was not affected by the exposure of 3.6 g/L phosphorus; however, the NO to NO₂ conversion dropped from 45% to about 35% after exposure to 10 g/L phosphorus.

In contrast to the relatively stable NO oxidation to NO₂ function, a significant impact was observed on the catalyst NO_x storage capacity even on exposure to 3.6 g/L of phosphorus. Figure 3 shows that at 20% NO slip, the moles of NO_x stored per mole of available barium in the LNT dropped by 65%. Furthermore at a constant storage capacity of 0.05 moles NO_x/mole barium, the NO_x slip increased from 6% on a fresh LNT to 30% after 3.6 g/L phosphorous, and to 90% after exposure to 10 g/L phosphorous.

The reduction of NO to N₂ under the rich condition was negatively affected by the loss of NO_x storage capacity. Figure 4 shows the NO_x storage capacity at 80% slip of a series of fresh LNTs

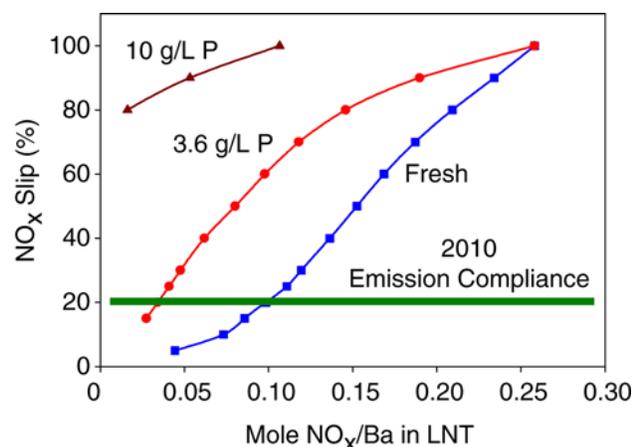


Figure 3. The effect of phosphorus exposure on LNT NO_x storage for three different phosphorus exposures.

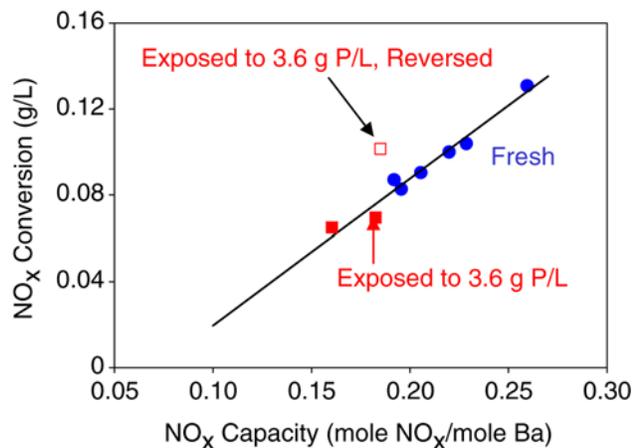


Figure 4. The effect of phosphorus exposure on LNT reduction of NO_x in a rich gas stream.

plotted against the amount of NO_x conversion. A straight line was fit to the data with a correlation coefficient of 0.968. Exposing the catalysts to 3.6 g/L phosphorus reduced the storage capacity and thus decreased the NO_x reduction. However, testing the LNTs in the opposite direction from which they were exposed to phosphorus revealed a significant boost in NO_x conversion from 0.0695 to 0.1014 g/L. When the LNT cores are exposed to phosphorus, the phosphorus tends to deposit in a nonuniform profile with the greatest amount of phosphorus in the front of the core and less phosphorus in the rear. Any NO_x introduced to the front of this aged sample cannot be adsorbed until it gets far enough into the core where phosphorus is not blocking the adsorption sites. Upon switching to rich gas, the front section of the aged LNT has no NO_x to release, and thus no reduction occurs. If NO_x containing gas is introduced at the rear of the core, NO_x begins storing immediately inside the new entrance of the sample because of the low phosphorus part of the sample. In this case, when the system is swept by rich gas, the upstream section of the LNT has stored NO_x to release, and the rhenium in the downstream (high phosphorus part of the sample) can reduce the NO_x to N_2 . Thus the rhenium in the LNT appears to remain active for NO reduction even if no NO_x is stored due to the phosphorus-blocking adsorption sites.

Results from this first phase of study show that phosphorus deactivation may become a significant source of deactivation as durability requirements become increasingly stringent. For LNTs, the NO_x storage capacity function is affected first and most strongly.

SCR Catalyst durability: Zeolite- and vanadia-based SCR catalysts were provided by a catalyst supplier. The samples were degreened according to the company's recommended procedure prior to testing. Both sets of samples were evaluated using a temperature ramp from 100 to 550°C in lean conditions at an NH_3/NO_x ratio of 1.11. After determining the initial activity of the SCR catalysts, samples were exposed to 3.6 g/L of phosphorus using the previously described diesel fuel burner with phosphorus-doped fuel at 250°C. The aged sample was then re-analyzed for NO_x conversion in the lab reactor. The aging process was repeated to increase phosphorus exposure to 10 g/L. Figure 5 shows the results over the fresh and 3.6-g/L phosphorus-exposed vanadia-based samples.

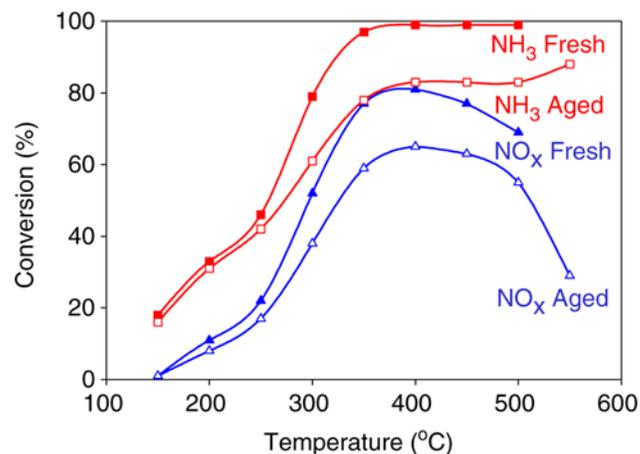


Figure 5. The effect of 3.6-g/L phosphorus exposure on NH_3 and NO_x conversion over vanadia SCR.

The results shown in Figure 5 indicate the vanadia-based SCR catalyst is strongly impacted by 3.6-g/L phosphorus exposure, especially at temperatures above 300°C. Both NO_x and NH_3 conversions are impacted, and to the same degree. As the temperature is increased above 450°C, the NH_3 oxidation reaction becomes significant over this catalyst, and thus the NO_x conversion decreases due to ammonia reacting to become NO. In other results (not shown), the rate of ammonia oxidation appears to increase relative to the rate of the SCR reaction with phosphorus exposure. As the phosphorus begins to block active sites, the first sites lost will be those involving adjacent pairs of vanadia for NO_x reduction, and the other vanadia sites will be available for a longer period of phosphorus exposure. Since the SCR reaction requires two adjacent vanadia sites and ammonia oxidation only requires one site, this could explain the observed effect on relative rates (NH_3 oxidation vs NO_x reduction).

The same tests were run with the zeolite-based SCR. Figure 6 shows the results over the fresh and 3.6-g/L phosphorus exposed zeolite-based catalysts. Compared to Figure 5, the zeolite appears to be less affected by this level of phosphorus than the vanadia catalyst. The effect of phosphorus seems to be relatively constant across a range of temperatures in this case. Both the NO_x and NH_3 conversions are affected to a similar degree. Unlike the vanadia sample, the zeolite catalyst does not show a significant drop in NO_x conversion at temperatures above 450°C due to ammonia oxidation.

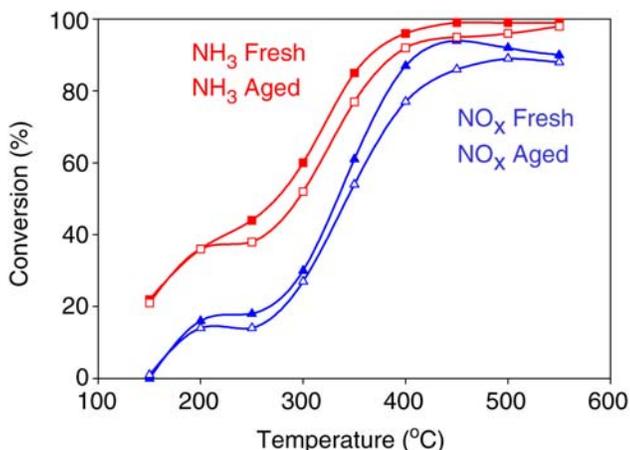


Figure 6. The effect of 3.6-g/L phosphorus exposure on NH₃ and NO_x conversion over zeolite SCR.

The results from tests of fresh and aged samples of both types were then compared using an Arrhenius type plot assuming pseudo first-order kinetics. The results in Figure 7 show that similar kinetics for the SCR reaction occur on both catalyst types.

Below 400°C, the impact of phosphorus on the reaction rate is lower because a significant portion of the SCR reaction takes place in the bulk, where the phosphorus does not penetrate. At temperatures above 400°C more and more of the reaction relatively occurs on the top surface of the catalyst, which is also where most of the phosphorus is deposited.

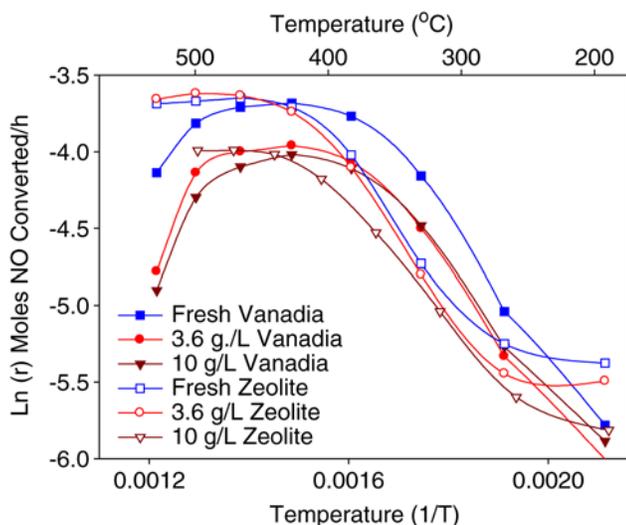


Figure 7. Kinetics of the SCR reaction over fresh and aged catalysts.

The differences between fresh and aged curves of the same type formulation are typical of what is observed when a physical blockage of active sites leads to activity loss. Results over the vanadia sample show that it loses significant activity on exposure to 3.6 g/L phosphorus, but it shows a smaller decline as the exposure is increased to 10 g/L. In contrast, the zeolite is not affected significantly by exposure to 3.6 g/L phosphorus, but the activity significantly decreases as the exposure increases to 10 g/L. Interestingly, increasing the temperature after phosphorus exposure seems to help the zeolite sample regain some of its activity but hurts the vanadia sample, possibly due to increased ammonia oxidation over the latter.

Phosphorus Adsorption

The amount of phosphorus that each type of formulation adsorbed after being exposed to 10 g/L phosphorus was determined by XRF. Results are shown in Figure 8.

The total amount of phosphorus adsorbed did not differ significantly from one catalyst type to the other, and the total amount adsorbed was about 15% of the phosphorus to which the sample was exposed. Similar deposition profiles were also determined for all the types of NO_x reduction catalysts tested. Out of the total amount of phosphorus that was adsorbed by a sample, most of it (65%) adsorbed on the front third of the core, 25% was adsorbed by the middle third, and 10% or less was adsorbed by the bottom third of the sample.

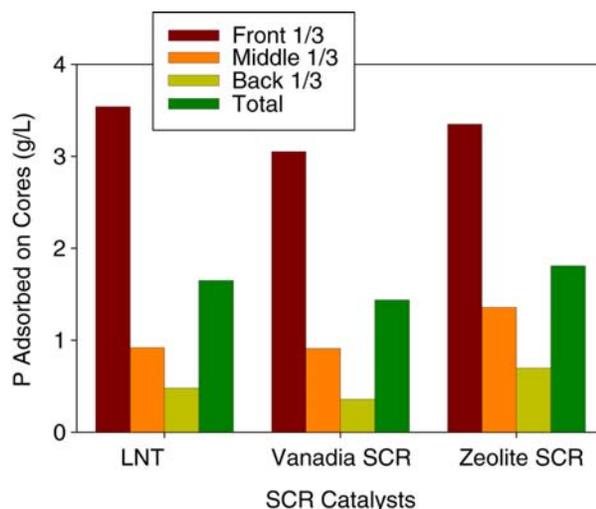


Figure 8. XRF analysis of phosphorus adsorption on NO_x reduction technologies.

PM Trap

Various catalyzed and uncatalyzed DPF materials were obtained from suppliers to screen filtration efficiency and backpressure. Filtration efficiency was determined using a Scanning Mobility Particle Sizer (SMPS), and backpressure was measured using a pressure transducer.

Figure 9 shows the filtration efficiencies of both the new DPF substrate and cordierite. Both graphs are averages of several fresh uncatalyzed DPF samples. The data shows that the filtration efficiencies of both materials are greater than 95%.

Figure 10 shows the results of pressure drop as a function of particulate loading time. The arrows notes backpressure measurements bypassing the DPF samples. The measurements were taken before and after loading the sample with particulate matter to account for variations as a function of particulates produced by the fuel burner. The data show that the new DPF substrate yields substantially lower pressure drop during particulate-loading than Cordierite and for the new material substrate.

Figure 11 shows filtration efficiency of the new DPF substrate material. The filtration efficiency of the catalyzed samples maintain above 98% throughout the particulate-loading process.

To examine the effect of catalyst coating on the pressure drop of the new substrate material, the pressure drop was measured over both catalyzed and uncatalyzed samples (Figure 12). Uncatalyzed sample shows lower pressure drop within 20 min of the test; however, the pressure drop significantly increases as a function of particulate loading time. The catalyzed sample shows opposite pressure drop

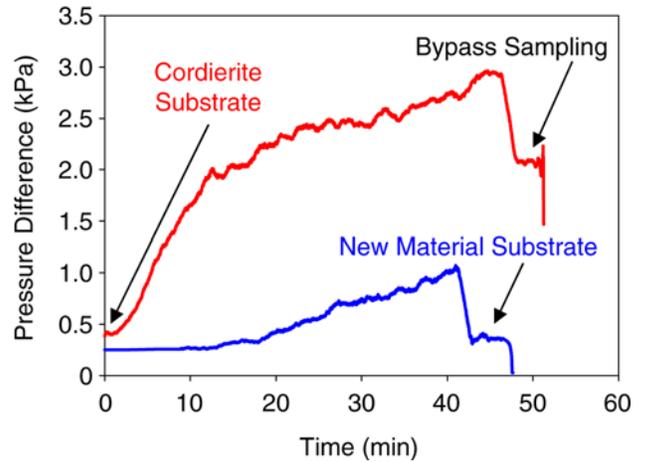


Figure 10. Pressure drop as a function of particulate-loading time for both Cordierite and for the new material substrate.

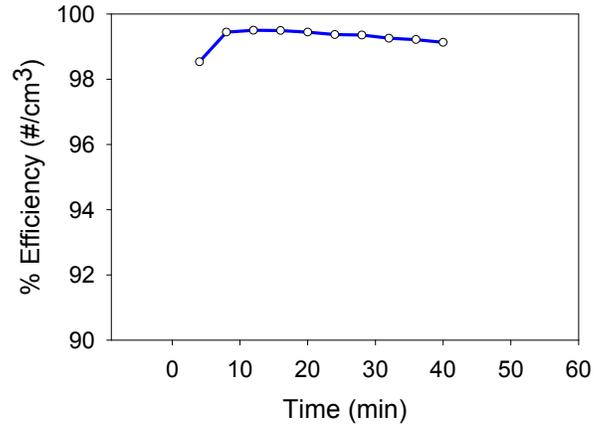


Figure 11. Filtration efficiency of the new catalyzed DPF substrate material.

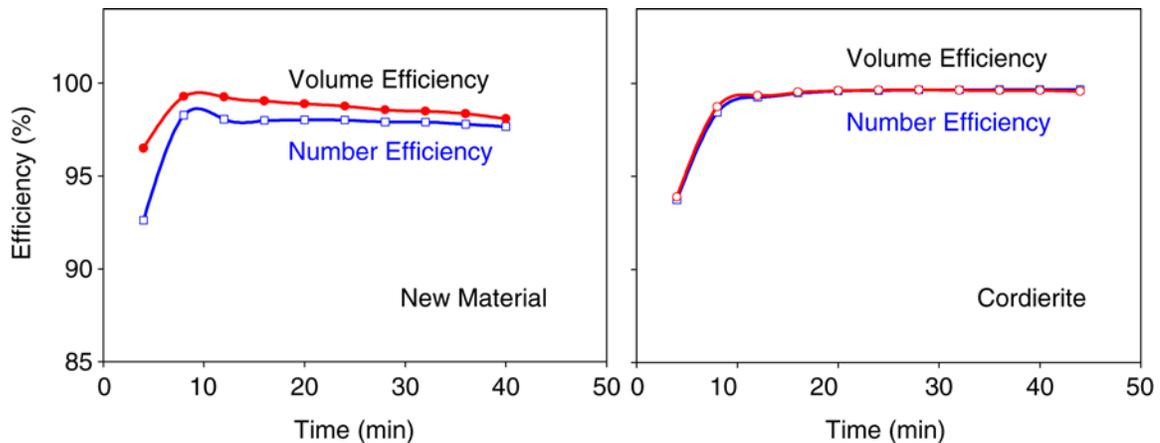


Figure 9. Filtration efficiency of fresh uncatalyzed samples of the new material and of cordierite (average of several samples).

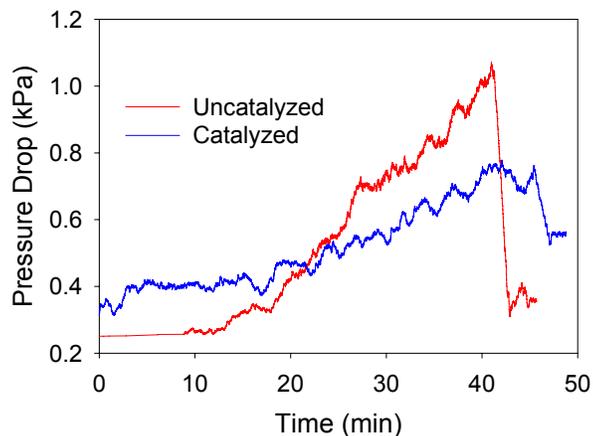


Figure 12. Pressure drop for catalyzed and uncatalyzed fresh samples of the new material substrate.

profile. The sample yields higher backpressure in the early stages of particulate loading, but the pressure drop rate decreases in the late stages of particulate loading possibly because the coated catalyst enhances regenerating soot collected in the sample.

Conclusions

Lean-NO_x Catalyst

The project was completed with the assessments of catalyst durability and diesel fuel component effect on the developed catalyst formulation. The catalyst is relatively durable to phosphorus deactivation but vulnerable to sulfur deactivation. The mitigation plan was developed to minimize the sulfur deactivation. The technology is ready to transfer to an organization specialized in retrofit applications.

Catalyst Durability

Results from the catalyst deactivation study showed that phosphorus exposure by itself can lead to loss of catalyst activity. The loss of activity

appears to be tied to a physical blockage of surface active sites by the phosphorus compound. Most of the phosphorus adsorbs on the inlet side of the catalyst, whereas the adsorbed phosphorus concentration is lower at the outlet. For LNTs, the phosphorus blocks the adsorption of NO₂ on storage sites. For SCR, the phosphorus prevents NH₃ from adsorbing. The impact of phosphorus is greater on LNT activity than it is for SCR, but the resulting loss of activity can lead to a loss of fuel economy in both cases.

PM Trap

A promising material was identified that provides filtration efficiency larger than 95% with low pressure drop. In addition, catalyst coating did not present adverse effect on pressure drop.

Publications and Presentations

R. G. Silver, M. Stefanick, and A. Alletag, "Impact of Phosphorus on NO_x Aftertreatment Catalysts," poster presentation at 2005 DEER meeting, Chicago, Illinois (2005).

R. G. Silver, M. Stefanick, J. M. Faas, and S. Zenskova, "Impact of Phosphorus Exposure on Lean NO_x Trap Performance," presented at the 19th Annual Meeting of the North American Catalysis Society, Philadelphia (2005).

P. Park and C. Boyer, "Effect of SO₂ on the Activity over Ag/γ-Al₂O₃ Catalysts for NO_x Reduction in Lean Conditions," presented at the 19th Annual Meeting of the North American Catalysis Society, Philadelphia (2005).

P. Park and C. Boyer, "Effect of SO₂ on the Activity over Ag/γ-Al₂O₃ Catalysts for NO_x Reduction in Lean Conditions," *Appl. Catal. B.*, **59**, 27–34, 2005.