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Mechanisms of Sulfur Poisoning of NOx Adsorber Materials: Final Report of a CRADA Between PNNL and Cummins Incorporated

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Mechanisms of Sulfur Poisoning of NO_x Adsorber Materials

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Abstract

The control of NOx (NO and NO_2) emissions from so-called 'lean-burn' vehicle engines remains a challenge. The now commercial NO_x adsorber (also known as lean-NO_x trap (LNT) and NOx storage reduction (NSR) catalyst) technology is based upon the concept of storing NOx as nitrates over storage components, typically alkali or alkaline-earth species such as barium, during a lean-burn operation cycle and then reducing the stored nitrates to N_2 during fuel-rich conditions over a precious metal catalyst. In part via this successful five-year CRADA project between PNNL and Cummins Inc. (CRADA PNNL/213), Cummins and the Johnson/Matthey Company commercialized this technology on the 2007 Dodge Ram pickup truck. In particular, this CRADA has focused on problems arising from either or both thermal and SO_2 deactivation which were impeding the ability of the technology to meet durability standards. The results obtained in this CRADA have provided an essential understanding of these deactivation processes thereby leading to materials and process improvements that enabled the commercialization effort.

The objective of this project has been to identify a clear pathway to robust NO_x after-treatment solutions for light-duty diesel engines. The project focussed on understanding and characterizing the NOx storage, release and conversion of existing NO_x adsorber materials. The impact of sulfur on these processes was studied, with special attention given to methods of regenerating the catalyst in the presence of sulfur and the effects of these regeneration treatments on long-term catalyst durability. Model catalysts and more fully formulated catalysts were both studied. The goal of this project has been to identify and understand the deactivation mechanisms of LNT materials in order to provide more robust systems for diesel after-treatment systems that will meet the key emission standards for NO_x. Furthermore, the project aimed to

provide information critical to evaluating used systems to quantify and diagnose the extent of their degradation.

This final report briefly highlights many of the technical accomplishments and documents the productivity of the program in terms of external recognition, peer-reviewed scientific publications (10 total), reports (7 total), and presentations (19 total).

Objectives

- Develop and apply characterization tools to probe the chemical and physical properties of NO_x adsorber catalyst materials for studies of deactivation due to sulfur poisoning and/or thermal aging. Utilize this information to develop mechanistic models that account for NOx adsorber performance degradation.
- Develop protocols and tools for failure analysis of field-aged materials.
- Provide input on new catalyst formulations; verify improved performance through materials characterizations, and laboratory and engine testing.

Introduction

The NO_x adsorber (also known as lean-NO_x trap – LNT) technology is based upon the concept of storing NOx as nitrates over storage components, typically barium species, during a lean-burn operation cycle and then reducing the stored nitrates to N_2 during fuel-rich conditions over a precious metal catalyst [1]. This technology has been recognized as one of the most promising approaches for meeting stringent NOx emission standards for diesel vehicles within the Environmental Protection Agency's (EPA's) 2007/2010 mandated limits. However, problems arising from either or both thermal and SO_2 deactivation must be addressed to meet durability standards. Therefore, an understanding of these processes will be crucial for the development of the LNT technology.

This project has been focused on the identification and the understanding of the important degradation mechanism(s) of the catalyst materials used in LNTs. 'Simple' and 'Enhanced Model' $Pt/BaO/Al_2O_3$ samples were investigated. In particular, the changes in physicochemical properties related to the reaction performances of these LNT materials, due to the effects of high temperature operation and sulfur poisoning, has been researched. By comparing results obtained on 'Simple Model' $Pt/BaO/Al_2O_3$ with 'Enhanced Model' materials, we have developed an understanding of the role of various additives on the deactivation processes. Studies have also been performed on the real commercial samples being used in a Dodge Ram truck with a Cummins diesel emission control system. However, the results about these 'commercial samples' will not be covered in this report. Following a brief description of our experimental approach, we will present a few highlights from some of the work performed in this CRADA with more details about these results provided in publications/reports/presentations lists presented at the end of the report.

Approach

In a microcatalytic reactor system designed and constructed during the first year of this project (Figure 1a), LNT performance was evaluated in a fixed bed reactor operated under continuous lean-rich cycling. Rapid lean-rich switching was enabled just prior to the elevated temperature zone (furnace) where the LNT materials are contained in quartz tubing. After removing water, the effluent of the reactor can be analyzed by mass spectrometry and by a chemiluminescent NOx analyzer. A typical baseline performance testing protocol is illustrated in Figure 1b. In this case, the sample is heated to a reaction temperature in flowing He, the feed switched to a 'lean-NOx' mixture containing oxygen and NO, as well as CO_2 and/or H_2O. After an extended period (15 minutes or more), multiple rich/lean cycles of 1 and 4 minute duration, respectively, are run and NOx removal performance is assessed after at least 3 of these are completed. In the LNT technology, the state of the system is constantly changing so that performance depends on when it is measured. As such, we measure NOx removal efficiencies in at least three different ways as illustrated in Figure 1b. "Lean conversion (4 minutes)" and "lean conversion (30 minutes)" measures NOx removal efficiencies for the first 4 minutes and first 30 minutes of the lean-period, respectively.

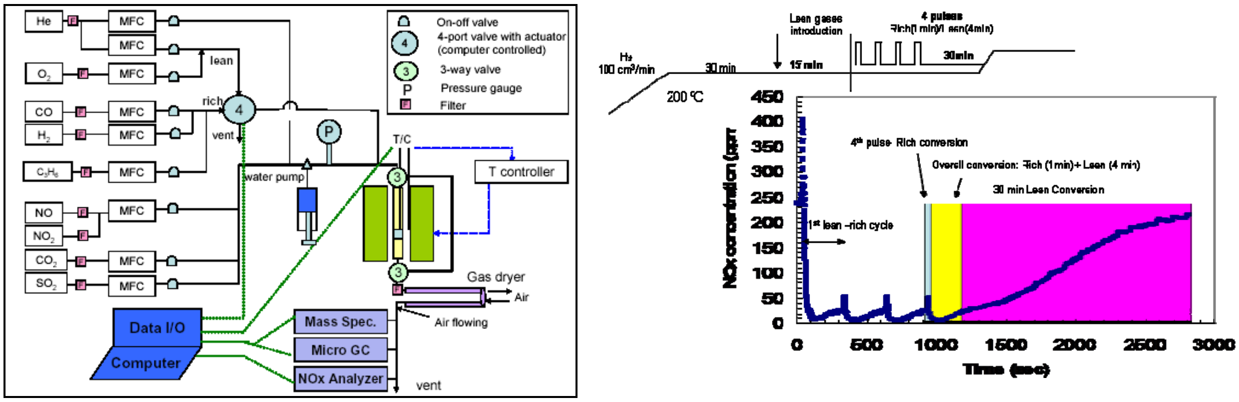

Figure 1. (a) A schematic of the microreactor constructed for this project's studies, and (b) a common reaction protocol used here along with example data where the performance assessments are defined.

In addition, material treatments such as SO_2 aging, and post mortem catalyst characterizations were conducted in the same test stand without exposing the catalyst sample to air. We have established a reaction protocol, which evaluates the performance of samples after various thermal aging and sulfation condition. In this way, we are able to identify optimum de-sulfation treatments to rejuvenate catalyst activities.

State-of-the-art catalyst characterization techniques such as XRD, XPS, TEM/EDS, BET/pore size distribution, and temperature programmed desorption/reaction (TPD/TPRX) were utilized to probe the changes in physicochemical properties of the catalyst samples under deactivating conditions; *e.g.*, thermal aging and SO_2 treatment. Specifically, H_2 TPRX (temperature programmed reaction), in situ Sulfur K-edge XANES (X-ray absorption near edge spectroscopy) and TR-XRD (time-resolved x-ray diffraction) methods were used extensively to quantify the levels, speciation and phase of sulfur on the model adsorber material ($Pt\text{-}BaO/Al_2O_3$ and $Pt\text{-}BaO/CeO_2$) as a function of desulfation process.

Results

Correlation of Pt particle size with the NOx storage performance during thermal aging

We established a direct relationship between Pt particle size and NOx storage performance by correlating the results of *in-situ* time resolved XRD, TEM, FTIR measurements after CO adsorption, with NOx storage performance measurements for samples treated under oxidizing condition at elevated temperature (700, 800 and 900 °C). *In-situ* XRD results provided direct evidence and established the temperature range at which growth of Pt particles occurs. As demonstrated in Figure 2, we obtained the change of Pt crystallite size and the total peak area for the major Pt XRD peak of the 'Simple Model' LNT sample by analyzing the Pt(111) peak using the Scherrer equation. For all calcination temperatures studied, Pt crystallite size increased abruptly within 1 hr, followed by the steady growth with time. As the temperature increased further, the rate of Pt phase growth increased. Both CO adsorption and TEM results were entirely consistent with the *in-situ* XRD data. These results are also in good agreement with previous studies [2] that concluded that Pt sintering rates are exponentially dependent on temperature and linearly on time.

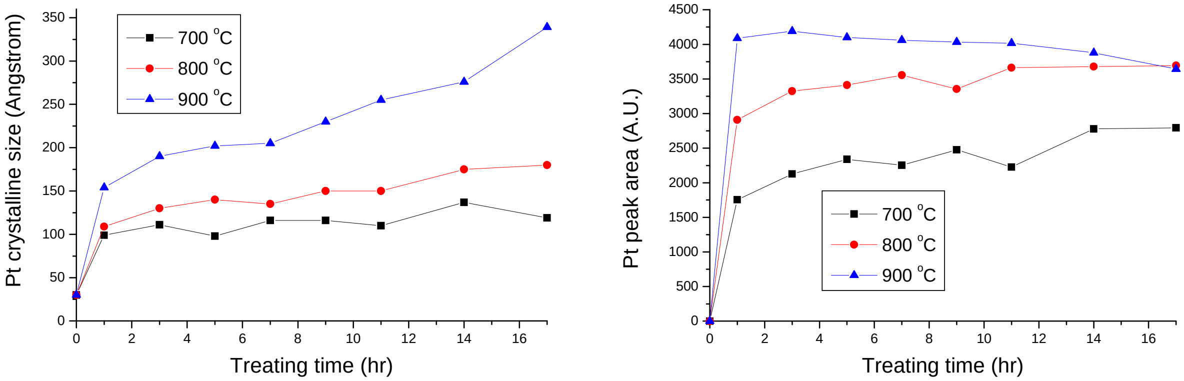

Figure 2. (a) Change of the Pt particle crystallite size, obtained using the Scherrer equation on the *in-situ* XRD data for the 'Simple Model' catalyst, as a function of calcination temperature and treatment time. (b) A plot of the total area of a principle XRD Pt peak as a function of calcination temperature and time.

Figure 3 shows the activity results of the same sample obtained following similar thermal treatments for various times at 700, 800 and 900 °C. With increasing calcination temperatures, the NOx conversion decreases significantly. Note especially that NOx conversion drops significantly within 1 hour, followed by a slower decrease with oxygen treatment time. Recalling the just-described results from the *in-situ* XRD experiments, we find that the NOx storage performance can be directly correlated with the changing Pt particle size; more specifically, greater NOx storage performance is observed for samples with small sized Pt particles, and deteriorates rapidly as the Pt particles sinter during the thermal treatment. For the case of the 'Enhanced Model' sample in which Pt sintering is inhibited to a large extent, the NOx storage performance is maintained to higher temperatures relative to the 'Simple Model', providing further support for the conclusion that the inhibition of Pt sintering at elevated temperature is a key factor to designing more durable NOx adsorber catalysts.

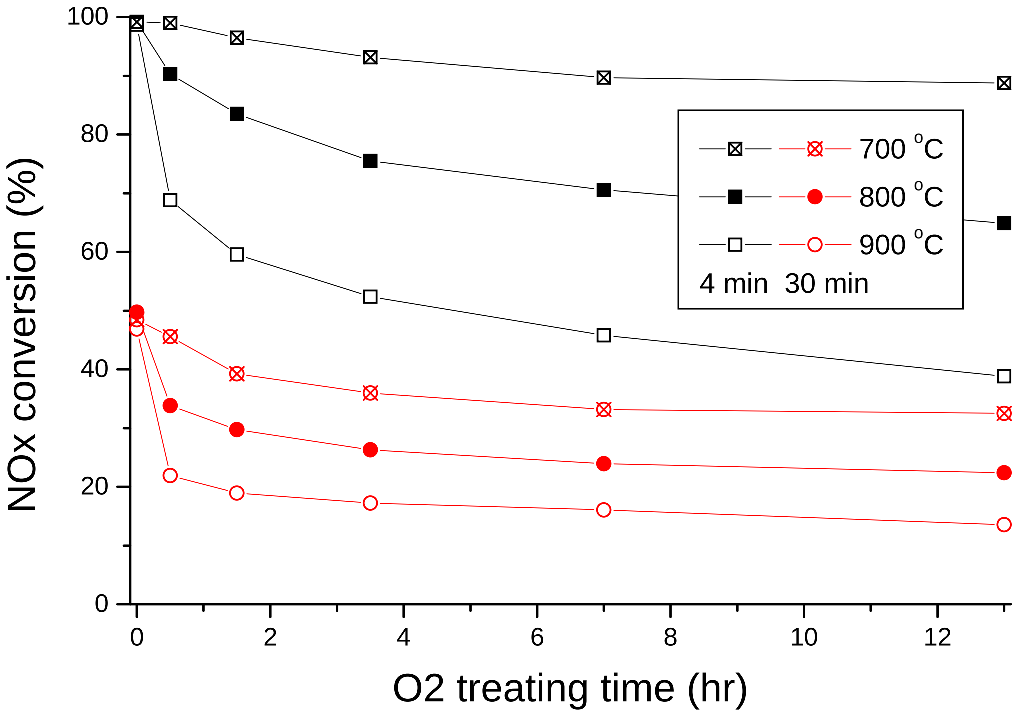

Figure 3. Change of NOx storage performance (4 min and 30 min conversion) as a function of calcination temperature and time.

Reaction Protocol to de-couple effects of thermal aging and de-sulfation

In order to regenerate the LNT catalysts to remove sulfate species that poison the material, a high temperature de-sulfation process is required. Physical and chemical property changes in the material due to removal of sulfates and/or due to the required high temperatures of de-sulfation are unavoidable. Thus, there is a trade-off in regenerating activity by removing the sulfur species while, on the other hand, potentially decreasing it due to thermal deactivation. Furthermore, it becomes difficult to distinguish what is responsible for deactivation in this case. Therefore, a reaction protocol was established to de-couple these two effects. After running the reaction in the presence or absence of SO_2, the catalyst was treated at higher temperature, followed by a 2nd evaluation of the activity without SO_2. Comparison of the activities with/without SO_2 and before/after the higher temperature 'desulfation' treatment allowed us to estimate the contribution to the activity changes from the two potential sources of deactivation. The NOx conversions of both the 'Simple' and 'Enhanced Model LNTs started to decline above 700 °C in the absence of SO_2 in the reactant gas mixture due to thermal deactivation (Pt sintering as shown above). When SO_2 is added to the reactant, it appears that the conversion after de-sulfation follows those of thermally aged samples above 700 °C, indicating that the de-sulfation is essentially complete above this temperature, and that deactivation is due to thermal aging. On the other hand, the 'Enhanced Model' LNT showed more complete recovery of performance at lower temperatures than the 'Simple Model' material, where the thermal aging did not occur to a significant extent. In addition, XPS analysis of post-reaction samples showed that the 'Enhanced Model' sample showed a more rapid decrease of sulfur species as sulfate on the surface than the 'Simple' one, which can explain their differing performance observed after the desulfation process. Thus, we showed that our new reaction procotol allows for the decoupling of thermal aging and sulfur effects, allowing for the identification of optimum condition where the thermal aging is minimized, while the de-sulfation is correspondingly maximized.

Segregation of BaO/Al_2O_3 upon H_2O contact

Recent work from a group at Ford research labs [3] reported that Ba^{2+} ions in a $BaAl_2O_4$ phase, formed by high temperature calcination, leached out from the alumina support material to form a crystalline $BaCO_3$ phase upon contact with H_2O, probably due to an interaction of carbonic ions dissolved in liquid H_2O. However, as shown in the XRD patterns of Figure 4, we determined that, irrespective of the initial barium phase (highly dispersed BaO and/or $BaCO_3$, or $BaAl_2O_4$), a liquid H_2O treatment at room temperature facilitates segregation of Ba from the Al_2O_3 support to produce large crystallites of $BaCO_3$. The segregation process at the microstructural level was clearly evident in the TEM micrographs (not shown), where two distinctly different and distinguishable phases exist. EDX analysis indicated that two phases were aluminum oxide and barium-containing. This finding may have considerable relevance to the practical NOx-trap system, since H_2O condensation is known to regularly occur in exhaust systems during start-up and shut-down of the engine [3].

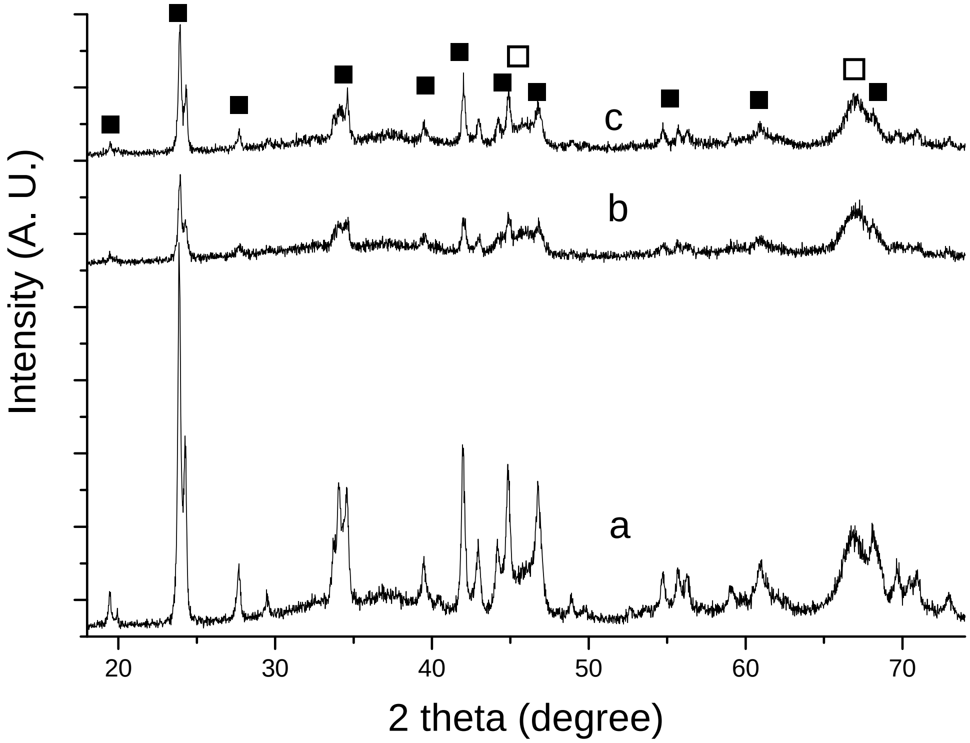

Figure 4. XRD patterns of H_2O-treated 20 wt% BaO/Al_2O_3 samples pre-calcined at 500 °C (a), 900 °C (b) and 1000 °C (c). (■: $BaCO_3$, □: γ-Al_2O_3)

Another important implication of our findings is relevant to the synthesis of NOx trap catalysts. Commonly, the conventional incipient wetness impregnation method is used to sequentially add Pt to alumina-supported baria [4]. During the Pt deposition step from an aqueous solution, the BaO-Al_2O_3 material is unavoidably in contact with liquid water, leading to formation of Ba species that are different from Pt-free Ba samples.

Effect of barium loading on the de-sulfation of Pt-BaO/Al_2O_3

We have previously shown that NOx adsorption/desorption chemistry is strongly dependent on the loading of barium on the basis of Fourier Transform Infrared Spectroscopy (FTIR) and NO_2 temperature programmed desorption (TPD) experiments [5]. With reference to these results, we addressed an important question about how the sulfation and desulfation chemistry varies as a function of barium content in the LNT formulation. For this, we performed a multi-technique study, using H_2 temperature programmed reaction, synchrotron time resolved x-ray diffraction (TR-XRD), sulfur K-edge x-ray absorption near-edge spectroscopy (XANES), and transmission electron microscopy (TEM).

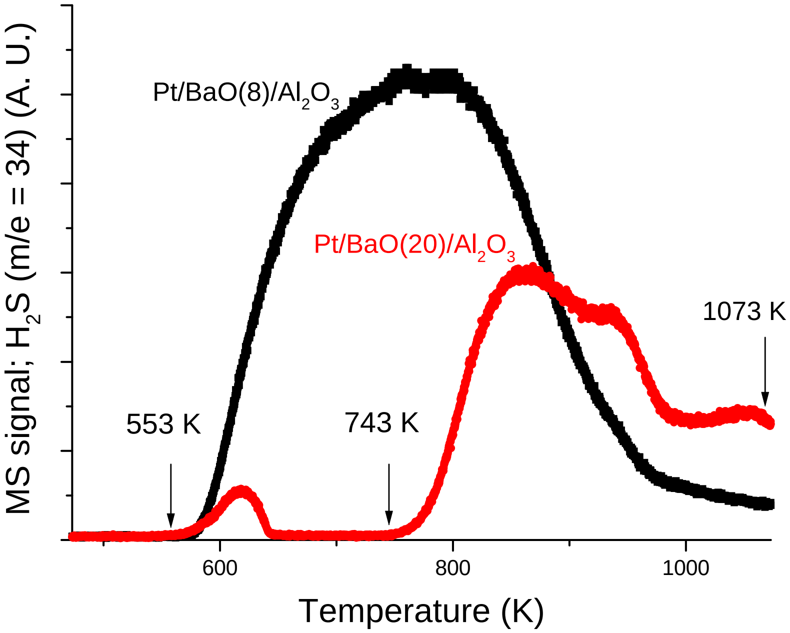

Figure 5. H_2 TPRX spectra for 5g/L Pt-BaO(8)/Al_2O_3 and 5g/L Pt-BaO(20)/Al_2O_3 samples.

Our previous work [5] has clearly shown that two kinds of barium nitrate species (surface and bulk barium nitrates) are formed upon NOx uptake, and the relative distribution of these nitrate species depends on the barium loading. In particular, an 8 wt% BaO/Al_2O_3 sample will contain primarily surface nitrates, while a significant quantity of both surface and bulk nitrates were present for a 20wt% BaO/Al_2O_3 sample following NOx adsorption. As H_2 TPRX results demonstrate in Figure 5, sulfated Pt-BaO(8)/Al_2O_3, consisting of predominantly of surface BaO/$BaCO_3$ species, displays more facile desulfation by H_2 at lower temperature than sulfated

Pt-BaO(20)/Al_2O_3, a material containing primarily bulk BaO/$BaCO_3$ species. Furthermore, after desulfation the amount of residual sulfur species on the former material is much less than on the latter as evidenced by S K-edge XANES and TEM/EDX results. After high temperature desulfation for both samples, residual sulfur exists in a reduced form, primarily as fairly large BaS particles. This suggests that the initial morphology differences between these two samples plays a critical role in determining the extent of desulfation and the temperature at which it occurs, potentially providing important information for the development of more sulfur resistant LNT catalyst systems.

Sequential high temperature reduction, low temperature hydrolysis for the regeneration of sulfated NO_x trap catalysts

Water is known to promote desulfation of LNT catalysts; however, it has also been shown to have a negative effect on catalytic performance via the promotion of Pt sintering. In addition as discussed above, our group [6] has demonstrated that the NOx uptake efficiency is adversely affected by the growth of platinum particles arising from thermal aging. Hence, Pt sintering is detrimental to the performance of these LNT catalysts. Even more important is the irreversible nature of this deactivation process since the sintered Pt particles cannot be re-dispersed. To explore ways to prevent such sintering, we designed a desulfation process in which H_2 and H_2O are separately introduced in two sequential steps: desulfation with H_2 only at high temperatures (up to 800 °C), followed by H_2O treatment at lower temperatures (maximum of 300 °C). The first step transforms the sulfate species into sulfides and even desorbs some of the sulfur as H_2S, while minimizing the Pt sintering. In the 2nd step, the thus formed BaS reacts with H_2O in a hydrolysis reaction to form BaO and additional H_2S. The second process is regarded as a key factor for promoting irreversible Pt sintering behavior.

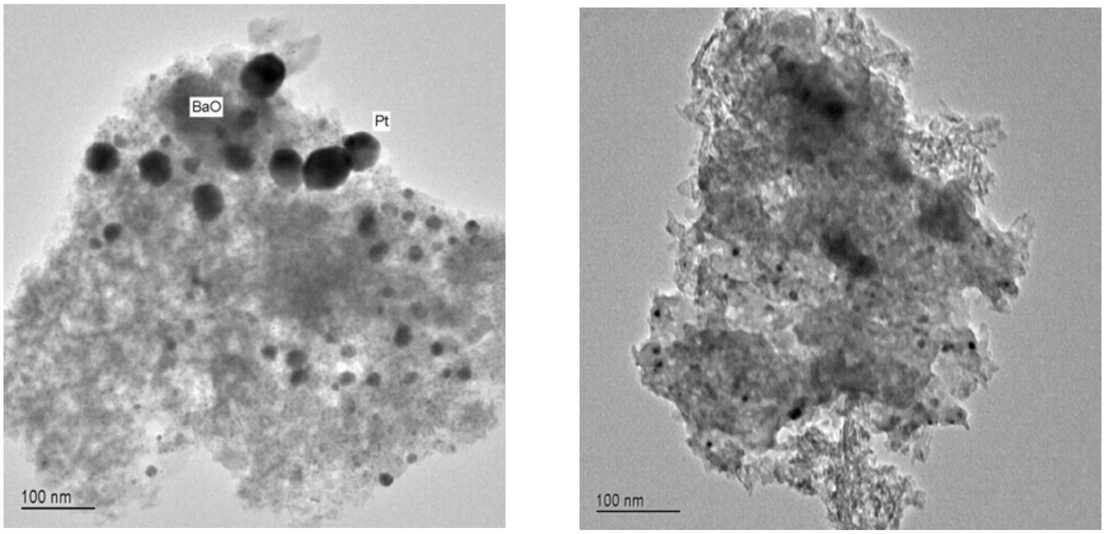

Figure 6. TEM images of PtBaAl_$H_2 \rightarrow H_2O$ (a) and PtBaAl_H_2/H_2O (b) samples.

By using this sequential desulfation process, we can significantly decrease the levels of Pt sintering as shown in TEM pictures of Figure 6, while the amount of sulfur removed from the sample is less than cooperative desulfation with H_2 and H_2O. The NO_x uptake results showed similar NO_x uptake performance for catalysts desulfated cooperatively with H_2 and H_2O or sequentially. Although the amount of H_2S desorbed during the cooperative desulfation process is larger than that of sequential one under the experimental conditions presented here, a modification of the two-step desulfation protocol may offer a means to improve the desulfation efficiency while maintaining the lack of Pt particle size growth. This can be achieved by optimizing the experimental conditions, in particular H_2O concentration and hydrolysis temperature.

Promotional effects of H_2O treatment on fresh and thermally aged Pt-BaO/Al_2O_3 lean NOx trap catalysts

As noted above, simple liquid water treatment applied to fresh and thermally aged Pt(2wt%)-BaO(20wt%)/Al_2O_3 lean NO_x trap catalysts at room temperature induces morphological and structural changes in the barium species as followed by XRD and TEM analysis. During the water treatment, liquid water sufficient to fill the catalyst pore volume is brought into contact with the samples. It was found that irrespective of the original barium chemical state (highly dispersed BaO or crystalline $BaAl_2O_4$), exposing the sample to this liquid water treatment promotes the formation of $BaCO_3$ crystallites (about 15 – 25 nm of its size) without changing the Pt particle size as demonstrated in XRD and TEM. Such transformations of the barium species are found to significantly promote NO_x uptake from 250 °C to 450 °C as shown in Figure 7. All three H_2O-treated samples (7b) show higher NO_x uptake for short-term and long-term performance compared with their non-treated counterparts (7a). The increase in the NO_x uptake for the water-treated samples can be attributed to an enhanced Pt-Ba interaction through the redistribution of barium species.

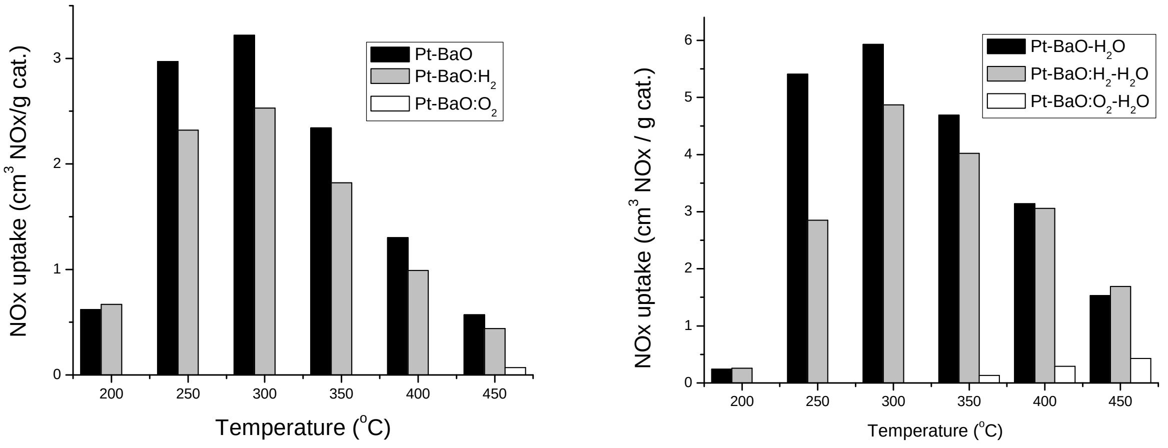

Figure 7. Comparison of NOx uptake as a function of temperature up to 20% breakthrough of the inlet NO concentration for Pt-BaO/Al_2O_3, Pt-BaO/Al_2O_3–H_2 (thermally aged with H_2) and Pt-BaO/Al_2O_3-O_2 (thermally aged with O_2) samples (a) and their water treated samples (b).

The roles of Pt and BaO in the sulfation of Pt/BaO/Al_2O_3 lean NO_x trap materials

The roles of barium oxide and platinum during the sulfation of Pt-BaO/Al_2O_3 lean NOx trap catalysts were investigated by S K edge XANES (X-ray absorption near-edge spectroscopy) and Pt L_{III} XAFS (X-ray absorption fine structure). All of the samples studied (Al_2O_3, BaO/Al_2O_3, Pt/Al_2O_3 and $Pt\text{-}BaO/Al_2O_3$) were pre-sulfated prior to the X-ray absorption measurements.

Figure 8 compares the S XANES spectra obtained for Al_2O_3, BaO(8 or 20)/Al_2O_3 samples, in the presence and absence of Pt, after the same SO_2/O_2 sulfation processes. For the case of the Al_2O_3 support itself, two peaks are observed near 2478 eV and 2482 eV, which can be assigned to aluminum sulfites (SO_3^{2-}) and aluminum sulfates (SO_4^{2-}), respectively. The intensity of the white line at 2482 eV for sulfated Al_2O_3 is much smaller than in samples containing Pt or BaO, implyng that all SO_2 dosed was not fully adsorbed on Al_2O_3. The greater intensity for the Pt- and Ba-containing samples is consistent with the results of SO_2 breakthrough measurements indicating that all dosed SO_2 was adsorbed by Pt/Al_2O_3 and Pt-BaO(8 or 20)/Al_2O_3 up to sulfation levels of 2.5 g/L. Thus, both Pt and barium oxide play a critical role in promoting sulfation for the catalysts supported on alumina.

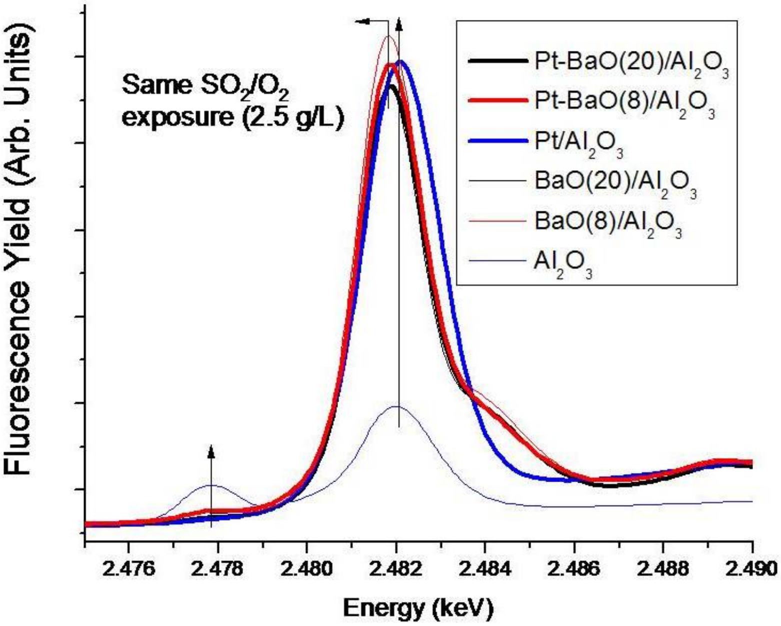

Figure 8. Sulfur K-edge XANES spectra of Al_2O_3, Pt/Al_2O_3, BaO(8 or 20)/ Al_2O_3 and Pt-BaO(8 or 20)/Al_2O_3, each sample having been given an equivalent sulfation exposure of 2.5 g/L.

The 8 wt% and 20 wt% BaO on Al_2O_3 materials are estimated to correspond to 0.26 and 0.75 ML coverages of BaO on the alumina surface [7]. Therefore, significant areas of the alumina surface would still be available for SO_2 to adsorb to form aluminum sulfates. Despite this, the essentially identical peak shapes of the primary S XANES feature for the barium loaded samples, clearly showing that SO_2 preferentially favors the formation of barium sulfates as long as barium remains available for this reaction. It can be summarized that barium oxide itself has the ability to directly form barium sulfate even in the absence of Pt and gas phase oxygen. In the platinum-containing samples, the presence of Pt-O species plays an important role in the formation of sulfate species. However, when oxygen is absent from the gas phase, the sulfation route that involves Pt-O is eliminated after the initially present Pt-O species are completely consumed.

Effect of sulfation levels on the desulfation behavior of pre-sulfated Pt-BaO/Al_2O_3 lean NOx trap catalyst

As described above, our group [8] has reported that desulfation processes for sulfated Pt-BaO/Al_2O_3 LNT materials show a strong dependence on barium loading and, moreover, occur more facilely over at lower loadings. We recently performed experiments aimed at investigating the desulfation with H_2 as a function of sulfur loading. Thus, pre-sulfated Pt(2wt%)-BaO(20wt%)/ Al_2O_3 with various sulfur loading (S/Ba = 0.12, 0.31 and 0.62) were prepared and investigated by using combined H_2 TPRX, XPS, *in-situ* sulfur K-edge XANES and synchrotron TR-XRD techniques. It was found that the amount of H_2S desorbed resulting from the desulfation is not proportional to the amount of initial sulfur loading based on H_2 TPRX results as shown in Figure 9.

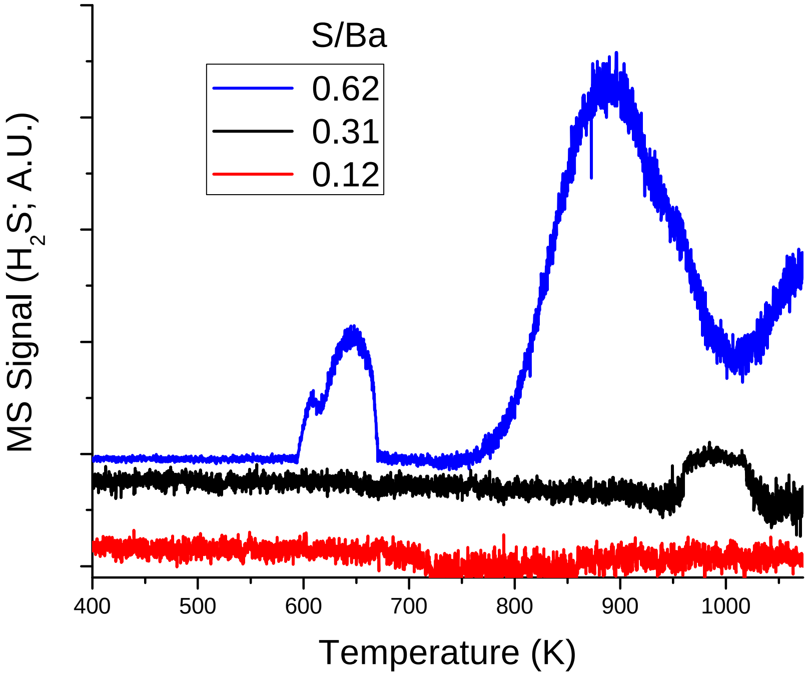

Figure 9. H_2 TRPX spectra for Pt-BaO/Al_2O_3 with different sulfation levels, with S/Ba of 0.12, 0.31 and 0.62.

Especially, *in-situ* sulfur K-edge XANES and TR-XRD results showed that the sulfur species loaded initially, i.e. at lower sulfur loading, have a tendency to be transformed to BaS phase and remain in the catalyst, rather than being removed as H_2S from the catalyst. On the other hand, the sulfur species deposited exceeding some level (at least S/Ba = 0.31) was desorbed as the form of H_2S, thus the relative portion of the residual sulfide species is much less than that of the sample with low sulfur loading. Unlike the sample with high sulfur loading (S/Ba = 0.62), H_2O did not promote the desulfation over the sample with S/Ba of 0.12, implying that the formed BaS species originating from the low sulfur loading are more stable against H_2O. It can be concluded that the sulfur species at low sulfur loading are less likely to be removed as H_2S and have more tendency to be transformed to sulfide species (as BaS) on the material, based on the various characterization results.

Excellent sulfur resistance of Pt/BaO/CeO$_2$ lean NO$_x$ trap materials

We investigated the NO$_x$ storage behavior of Pt-BaO/CeO$_2$ catalysts, especially in the presence of SO$_2$. High surface area CeO$_2$ (~ 110 m^2/g) with a rod like morphology was synthesized and used as a support. The Pt-BaO/CeO$_2$ sample demonstrated slightly higher NO$_x$ uptake in the entire temperature range studied compared with Pt-BaO/γ-Al$_2$O$_3$. More importantly, this ceria-based catalyst showed higher sulfur tolerance than the alumina-based one as shown in Figure 10. The time of complete NO$_x$ uptake was maintained even after exposing the sample to ~3 g/L of SO$_2$. The same sulfur exposure, on the other hand, eliminated the complete NO$_x$ uptake time on the alumina-based NO$_x$ storage catalysts. TEM images (not shown) provided no evidence of either Pt sintering or BaS phase formation during reductive de-sulfation up to 600°C on the ceria based catalyst, while the same process over the alumina-based catalyst resulted in both a significant increase in the average Pt cluster size and the agglomeration of a newly-formed BaS phase into large crystallites. XPS results revealed the presence of about 5 times more residual sulfur after reductive de-sulfation at 600°C on the alumina based catalysts in comparison with the ceria-based ones. All of these results strongly support that, besides their superior intrinsic NO$_x$ uptake properties, ceria based catalysts have a) much higher sulfur tolerance and b) excellent resistance against Pt sintering when they are compared to the widely used alumina based catalysts.

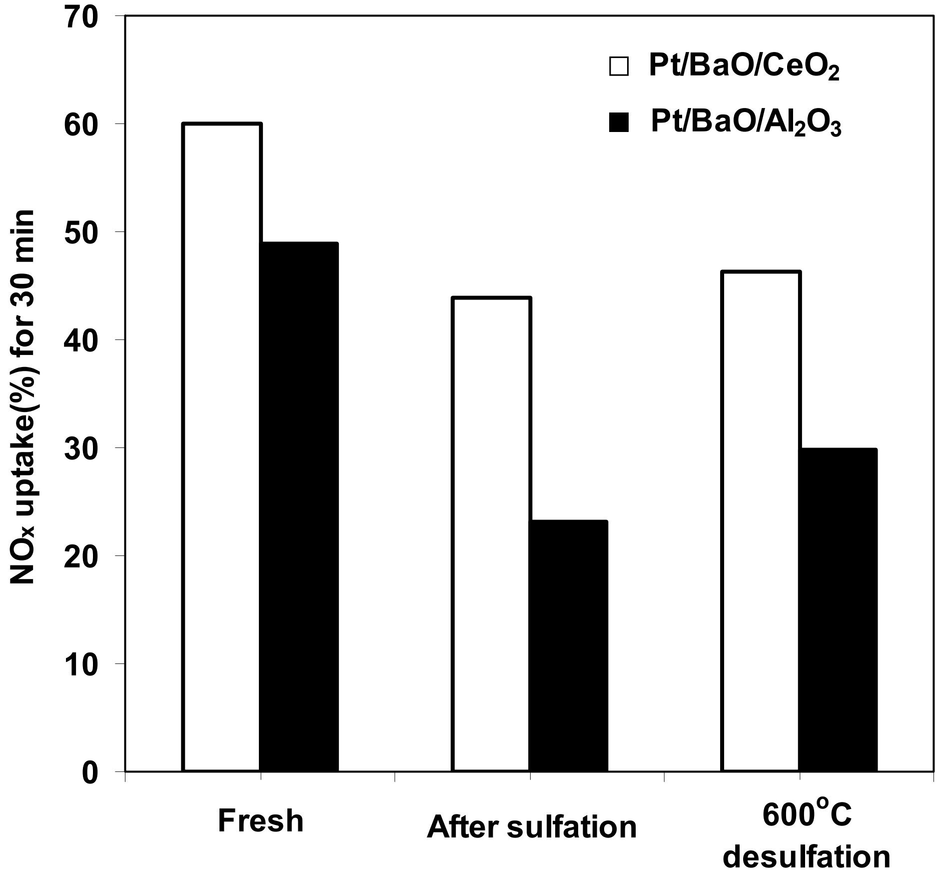

Figure 10. NOx uptake (%) for 30 min over Pt-BaO/CeO$_2$ and Pt-BaO/Al$_2$O$_3$.

Conclusions

PNNL and its CRADA partners from Cummins Inc. and Johnson Matthey have carried out a program to study the mechanisms of deactivation of the materials proposed for use in lean NO_x traps (LNT) arising from thermal aging and SO_2 poisoning. Results demonstrate a strong correlation between Pt particle size growth, induced by thermal treatments, and activity strongly suggesting that this is a predominant mechanism for permanent deactivation. Sulfur was also shown to have strongly negative albeit reversible effects on catalyst performance. Thus, effective catalyst regeneration was shown to be a balance between the need for high temperatures to promote sulfur removal and the need to prevent extended time at high temperatures where irreversible Pt sintering takes place. We found that SO_2 affected NOx adsorption/desorption chemistry differently depending on catalyst composition. For example, our results demonstrated that complete desulfation of the barium species in Pt-BaO(20)/Al_2O_3 is difficult due to the relative inaccessibility of sulfate species in the interior region of the particulate Ba phase. Therefore, it was found that the lower barium loadings provide for more optimum conditions for the removal of sulfur and, correspondingly, reduced deactivating effects. By using a novel reaction protocol to decouple thermal deactivation and de-sulfation, it was found that an 'Enhanced Model' LNT material possesses the ability to de-sulfate at lower temperature where Pt sintering is minimized, thus recovering NOx storage performance more readily and completely after deactivation due to sulfur poisoning. To understand these processes mechanistically, a combination of S XANES and Pt XAFS experiments allowed us to elucidate the roles in the sulfation processes of each component in the LNT catalyst. In other work, it was shown that water treatment promoted the NO_x uptake significantly for the fresh and thermally aged LNT materials. By using a sequential desulfation process, *i.e.*, high temperature desulfation and low temperature hydrolysis, we obtained significantly decreased levels of Pt sintering . By using *in-situ* characterization techniques, we determined that the sulfur species at low sulfur loading is less likely to be removed and has a greater tendency to be transformed to a refractory BaS phase that was very difficult to de-sulfate. Very recently, we have found that CeO_2-supported LNT catalysts have better intrinsic NOx uptake, in addition to a much higher sulfur tolerance and resistance to Pt sintering than alumina-supported counterparts. Overall, these results have provided invaluable information to mitigate critical stability issues in LNT catalysts.

Literature Cited

1. Epling, W. S.; Campbell, L. E.; Yezerets, A.; Currier, N. W.; Parks, J. E. *Catal. Rev.–Sci. Eng.* 2004, **46**, 163.
2. Bartholomew, C. H. *Appl. Catal. A* 2001, **212**, 17.
3. Graham, G.W.; Jen, H.-W.; Theis, J.R.; McCabe, R.W. *Catal. Lett.* 2004, **93**, 3.
4. (a) Olsson, L.; Fridell, E. *J. Catal.* 2002, **210**, 340; (b) Arena, G.E.; Bianchini, A.; Centi, G.; Vazzana, F. *Topics in Catal.* 2001, **16/17**, 157.
5. Szanyi, J.; Kwak, J.H.; Kim, D.H.; Burton, S.D.; Peden, C.H.F., *J. Phys. Chem. B* 2005, **107**, 27.
6. Kim, D.H.; Chin, Y.-H.; Muntean, G.; Yezeretz, A.; Currier, N.; Epling, W.; Chen, H.-Y.; Hess H.; Peden, C.H.F. *Ind. Eng. Chem. Res.* 2006, **45**, 4415.
7. Yi, C.-W.; Kwak, J. H.; Peden, C.H.F.; Wang, C.M.; Szanyi, J. *J. Phys. Chem. C*, 2007, **111**, 14942.

8. Kim, D.H.; Szanyi, J.; Kwak, J.H.; Szailer, T.; Hanson, J.C.; Wang, C.M.; Peden, C.H.F. *J. Phys. Chem. B*, 2006, **110**, 10441.

Special Recognition & Awards

1. 2009 American Chemical Society Team Innovation Award to CRADA team members Hai-Ying Chen (JM), Neal W. Currier (Cummins), Howard S. Hess (JM), Bradlee J. Stroia (Cummins), and Aleksey Yezerets (Cummins).
2. 2007 – Letter from John Wall, Cummins Vice President and Chief Technical Officer, thanking PNNL for their research contributions to Cummins' and Johnson/Matthey's successful commercialization of the lean NOx trap technology on the 2007 Dodge Ram pickup truck.
3. 2004 Advanced Combustion Engine R&D Special Recognition Award "For technical excellence and admirable collegiality in inter-laboratory collaborative research".

Journal Publications

1. J.H. Kwak, D.H. Kim, J. Szanyi and C.H.F. Peden, "Excellent sulfur resistance of Pt/BaO/CeO_2 lean NOx trap catalysts", Appl. Catal. B. **84** (2008) 545.
2. D.H. Kim, J.H. Kwak, J. Szanyi, S.J. Cho and C.H.F. Peden, "Roles of Pt and BaO in the sulfation of Pt/BaO/Al_2O_3 lean NOx trap materials: sulfur K-edge XANES and Pt L_{III} XAFS studies", J. Phys. Chem. C **112** (2008) 2981.
3. D.H. Kim, J.H. Kwak, X. Wang, J. Szanyi and C.H.F. Peden," Sequential high temperature reduction, low temperature hydrolysis for the regeneration of sulfated lean NOx trap catalysts", Catal. Today **136** (2008) 183.
4. D.H. Kim, Y.-H. Chin, J.H. Kwak and C.H.F. Peden, "Promotional effects of H_2O treatment on NO_x storage over fresh and thermally aged Pt-BaO/Al_2O_3 lean NO_x trap catalysts", Catal. Letters **124** (2008) 39.
5. D.H. Kim, Y.-H. Chin, G.G. Muntean, A. Yezeretz, N.W. Currier, W.S. Epling, H.-Y. Chen, H. Hess, and C.H.F. Peden, "Relationship of Pt particle size with the NO_x storage performance over thermally aged Pt/BaO/Al_2O_3 lean NO_x trap catalysts", Ind. Eng. Chem. Res. **45** (2006) 4415.
6. D.H. Kim, Y.-H. Chin, G.G. Muntean, A. Yezeretz, N.W. Currier, W.S. Epling, H.-Y. Chen, H. Hess, and C.H.F. Peden, "Design of reaction protocol for de-coupling the desulfation and thermal aging effects during regeneration of Pt-BaO/Al_2O_3 lean NO_x trap catalysts", Ind. Eng. Chem. Res. **46** (2007) 2735.
7. R.L. Vander Wal, A. Yezerets, N.W. Currier, D.H. Kim, and C.M. Wang, "HR-TEM Study of Diesel Soot Collected from Diesel Particulate Filters", Carbon **45** (2007) 70.
8. D.H. Kim, J. Szanyi, J.H. Kwak, T. Szailer, J.C. Hanson, C.M. Wang, C.H.F. Peden, "Effect of Barium Loading on the De-sulfation of Pt-BaO/Al_2O_3 Studied by H_2 TPRX, TEM, Sulfur K-edge XANES and *In-situ* TR-XRD." J. Phys. Chem. B **110** (2006) 10441.
9. D. H. Kim, Y.-H. Chin, J.-H. Kwak, J. Szanyi, and C.H.F. Peden, "Changes in Ba phases in BaO/Al_2O_3 upon thermal aging and H_2O treatment", Catal. Letters **105** (2005) 259.
10. A. Yezerets, N.W. Currier, D.H. Kim, H. Eadler, W.S. Epling, and C.H.F. Peden, "Differential kinetic analysis of diesel particulate matter (soot) oxidation by oxygen using a step–response technique", Appl. Catal. B **61** (2005) 120.

Reports

1. D.H. Kim, G.G. Muntean, C.H.F. Peden, K. Howden, R.J. Stafford, J.H. Stang, A. Yezerets, N. Currier, H.Y. Chen and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials" in *Combustion and Emission Control for Advanced CIDI Engines: 2008 Annual Progress Report*, (2009) in press.
2. D.H. Kim, X.Q. Wang, G.G. Muntean, C.H.F. Peden, K. Howden, R.J. Stafford, J.H. Stang, A. Yezerets, W.S. Epling, N. Currier, H.Y. Chen and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials" in *Combustion and Emission Control for Advanced CIDI Engines: 2007 Annual Progress Report*, (2008) 154.
3. Do Heui Kim, Xianqin Wang, George Muntean, Charles Peden, Ken Howden, Randy Stafford, John Stang, Aleksey Yezerets, Neil Currier, Haiying Chen, Howard Hess, and Andrew Walker, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", in *Combustion and Emission Control for Advanced CIDI Engines: FY2006 Annual Progress Report* (2007) 142.
4. Do Heui Kim, Janos Szanyi, Ja Hun Kwak, Tamas Szailer, Jon C. Hanson, Chongmin Wang, and Charles H.F. Peden, "Sulfur K-edge XANES and TR-XRD studies of Pt-BaO/Al_2O_3 lean NOx trap catalysts: Effects of barium loading on desulfation", National Synchrotron Light Source Activity Report 2006, 2-36.
5. D.H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, K. Howden, R.J. Stafford, J.H. Stang, A. Yezerets, W.S. Epling, N. Currier, H.Y. Chen, H. Hess, and D. Lafyatis, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials" in *Combustion and Emission Control for Advanced CIDI Engines: 2005 Annual Progress Report* (2006) 151.
6. D.H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, K. Howden, R.J. Stafford, J.H. Stang, A. Yezerets, W.S. Epling, N. Currier, H.Y. Chen, H. Hess, and D. Lafyatis, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials" in *Combustion and Emission Control for Advanced CIDI Engines: 2004 Annual Progress Report* (2005) 184.
7. Y.-H. Chin, D.H. Kim, G.G. Muntean, C.H.F. Peden, L.C. Broering, R.J. Stafford, J.H. Stang, H. Chen, B. Cooper, H. Hess, and D. Lafyatis, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials". in *Combustion and Emission Control for Advanced CIDI Engines: 2003 Annual Progress Report* (2004) 141.

Presentations

1. D. H. Kim, G.G. Muntean, C.H.F. Peden, N. Currier, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Deactivation mechanism of NOx storage materials arising from thermal aging and sulfur poisoning and a reaction protocol to de-couple these effects", presentation at the DEER conference, Dearborn, MI, August 2008.
2. D.H. Kim, J.H. Kwak, J. Szanyi, Xianqin Wang, J. Hanson, C.H.F. Peden, "Understanding the desulfation behavior of Pt-BaO/Al_2O_3 lean NOx trap catalysts studied by H_2 TPRX, in situ S XANES and TR-XRD", 14th ICC (International Congress on Catalysis), Seoul, S. Korea, July 2008.
3. D. H. Kim, X. Wang, G.G. Muntean, C.H.F. Peden, N. Currier, B. Epling, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Washinton DC, June 2008.

4. D. H. Kim, "Fundamental Understanding of sulfation/desulfation mechanisms over Pt-BaO/Al_2O_3 lean NOx trap catalysts" CLEERS (Cross-cut lean exhaust emission reduction simulation) conference, December 2007 (**invited talk**).
5. D.H. Kim, J.H. Kwak, J. Szanyi, Xianqin Wang, J. Hanson, William Epling, C.H.F. Peden, "The use of in situ synchrotron techniques to study desulfation processes of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts", 2007 AIChE annual meeting, Salt Lake City, UT, November 2007.
6. D.H. Kim, J.H. Kwak, J. Szanyi, X. Wang, J.C. Hanson, and C.H.F. Peden, "Barium loading effects on the Desulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts: an *in situ* Sulfur XANES and TR-XRD Study", presentation at the 20th Meeting of the North American Catalysis Society, Houston, TX, June 2007.
7. D.H. Kim, X. Wang, G.G. Muntean, C.H.F. Peden, N. Currier, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", presentation at the DOE Advanced Combustion Engine and Emission Control Review, Washington DC, June 2007.
8. X. Wang, D.H. Kim, J.H. Kwak, C.M. Wang, J. Szanyi, and C.H.F. Peden, "Peculiar Changes in Pt Accessibility and Morphology for Pt/BaO-Al_2O_3 Lean NOx Trap Catalysts with Different Sulfation Levels", presentation at the AIChE Annual Meeting, San Francisco, CA, November 2006.
9. D.H. Kim, J.H. Kwak, J. Szanyi, T. Szailer, J.C. Hanson, C.H.F. Peden, "Effect of Barium loading on the NOx storage and Desulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts", presentation at the 2006 Pacific Coast Catalysis Society Meeting, Seattle, WA, September 2006.
10. D.H. Kim, J.H. Kwak, J. Szanyi, T. Szailer, J.C. Hanson, C.H.F. Peden, "Effect of Barium loading on the NOx storage and Desulfation of Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts", presentation at the 2006 Diesel Engine Emissions Reduction Conference, Detroit, MI, August 2006.
11. D. H. Kim, X. Wang, G.G. Muntean, C.H.F. Peden, N. Currier, B. Epling, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Argonne, IL, May 2006.
12. A. Yezerets, N. Currier, W.S. Epling, D.H. Kim, C.H.F. Peden, G.G. Muntean, C.M. Wang, S.D. Burton, and R.L. Vander Wal, "Toward Fuel Efficient DPF systems-Understanding the soot oxidation process", presentation at the 2005 Diesel Engine Emissions Reduction Conference, Chicago, IL, August 2005.
13. D.H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, R.J. Stafford, J. Stang, A. Yezerets, W.S. Epling, N. Currier, H. Chen, H. Hess, O. Kresnawahjuesa, and D. Lafyatis, "Investigations of SO_2 Poisoning and Thermal Aging Mechanisms for Pt/BaO/Al_2O_3 Lean NOx Trap Catalysts", presentation at the 19th North America Meeting on Catalysis, Philadelphia, PA, May 2005.
14. D. H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, N. Currier, B. Epling, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, and H. Hess, "Mechanisms of Sulfur Poisoning of NOx Adsorber Materials", presentation at the DOE Combustion and Emission Control Review, Argonne, IL, April 2005.

15. D.H. Kim, Y.-H. Chin, J.H. Kwak, J. Szanyi, and C.H.F. Peden, “Segregation of Ba Phase in BaO/Al_2O_3 upon H_2O Treatment”, presentation at the American Institute of Chemical Engineers (AIChE) Annual Meeting, Austin, TX, November 2004.
16. D. H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, N. Currier, B. Epling, R. Stafford, J. Stang, A. Yezerets, H.-Y. Chen, H. Hess, and D. Lafyatis, “Mechanisms of Sulfur Poisoning of NOx Adsorber Materials”, presentation at the DOE Combustion and Emission Control Review, Argonne, IL, May 2004.
17. D. H. Kim, Y.-H. Chin, G.G. Muntean, and C.H.F. Peden, “Effect of Thermal Aging and SO_2 Treatment on the Physicochemical Properties of NO_x Adsorber Materials”, presentation at 2003 National Laboratory Catalysis Conference (NLCAT), Oak Ridge, TN, October 2003.
18. G.G. Muntean and C.H.F. Peden, “Diesel Engine Emission Control Science at Pacific Northwest National Laboratory”, presentation at Ford Scientific Research Laboratories, Dearborn, MI, June 2003 (**invited talk**).
19. D. H. Kim, Y.-H. Chin, G.G. Muntean, C.H.F. Peden, L. Broering, R. Stafford, J. Stang, H.-Y. Chen, B. Cooper, H. Hess and D. Lafyatis, “Mechanisms of Sulfur Poisoning of NOx Adsorber Materials”, presentation at the DOE Combustion and Emission Control Review, Argonne, IL, May 2003.

Acronyms

BET: Branauer-Emmet-Teller particle surface area and pore-size measurement method.
CRADA: cooperative research and development agreement
EDS: energy dispersive [x-ray] spectroscopy
EPA: Environmental Protection Agency
LNT: lean-NOx trap
NOx: nitrogen oxides (NO and NO_2)
PNNL: Pacific Northwest National Laboratory
SMSI: strong metal support interaction
TEM: transmission electron microscopy
TGA: thermal gravimetric analysis
TPD/TPRX: temperature programmed desorption/temperature programmed reaction
XAFS: x-ray absorption fine structure
XANES: x-ray absorption near edge spectroscopy
XPS: x-ray photoelectron spectroscopy
XRD: x-ray diffraction