A Fundamental Consideration on NO_x Adsorber Technology for DI Diesel Application

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ABSTRACT

Diesel engines are far more efficient than gasoline engines of comparable size, and emit less greenhouse gases that have been implicated in global warming. In 2000, the US EPA proposed very stringent emissions standards to be introduced in 2007 along with low sulfur (< 15 ppm) diesel fuel. The California Air Resource Board (CARB) has also established the principle that future diesel fueled vehicles should meet the same low emissions standards as gasoline fueled vehicles and the EPA followed suit with its Tier II emissions regulation. Achieving such low emissions cannot be done through engine development and fuel reformulation alone, and requires application of NO_x and particulate matter (PM) aftertreatment control devices. There is a widespread consensus that NO_x adsorbers and particulate filter are required in order for diesel engines to meet the 2007 emissions regulations for NO_x and PM.

In this paper, the key exhaust characteristics from an advanced diesel engine are reviewed. Development of the NO_x adsorber technology is discussed. Spectroscopic techniques are applied to understand the underlying chemical reactions over the catalyst surface during NO_x trapping and regeneration periods. In-situ surface probes are useful in providing not only thermodynamic and kinetics information required for model development but also a fundamental understanding of storage capacity and degradation mechanisms. The distribution of various nitration/sulfation species is related to surface basicity. Surface displacement reactions of carbonates also play roles in affecting the trapping capability of NO_x adsorbers. When ultralow-S fuel is used as a reductant during the regeneration, sulfur induced performance degradation is still observed in

an aged catalyst. Other possible sources related to catalyst deactivation include incomplete reduction of surface nitration, coke formation derived from incomplete hydrocarbon burning, and lubricant formulations. Sulfur management and the direction of future work for the successful implementation of such integrated engine and aftertreatment technology are discussed.

INTRODUCTION

Considerable efforts have been spent through a partnership including resources of government, industry, and institute of higher learning to significantly reduce NO_x and PM emissions while maintaining the superior advantage in fuel economy of diesel engines. Research on plasma-assisted catalytic reduction of NO_x has been reviewed in a number of articles (1-3). The potential of lean NO_x technology for diesel emission control has also been investigated (4-8). PM reduction has been demonstrated with a particulate filter and regeneration of the filter has been a subject of many studies (9-18). NO_x adsorber technology to control NO_x emissions becomes increasingly attractive for many engine manufactures (16-17). Improvements for NO_x adsorber technology have been focused on the development of catalysts with more efficient NO_x conversion and higher capacity for NO_x storage over a wide exhaust gas temperature range and on a fundamental understanding of the deactivation mechanisms of the catalyst. Another important development area has been the hydrocarbon utilization or means to reduce the required fuel penalty. The effectiveness of various reductants (18) and the development of injection systems to provide an optimized reductant (19) were both reported on. There was an effort to develop the optimum time and fuel quantity for the regeneration event (20) when

regeneration was required. Nevertheless, the most critical step though for NO_x adsorber technology is the development of a more sulfur tolerant catalyst, or a sulfur management scheme, even if 15 ppm [S] fuel is available. In addition, selective catalytic reduction (SCR) using urea has grown in economic and technologic importance. Different aspects using SCR for both stationary and mobile applications have also been reviewed in the literature (21-23).

NO_x adsorber technology relies on a storage-reduction approach that involves removal of NO_x from the exhaust under lean conditions by adsorption, followed by periodic regeneration of the adsorbent along with reduction of the released NO_x under rich conditions. This alleviates the need for maintaining a given C₁/NO_x ratio under transient and fluctuating exhaust NO_x levels, as in the case of a transitional lean NO_x catalyst. The key advantages of NO_x adsorber technology include its high efficiency of NO_x conversion (> 85 %) and its wide temperature range of operation. Another benefit is the use of on board diesel fuel as reductant, which exhibits easier enforcement/anti-tampering control and eliminates additional infrastructure such as the case with urea-SCR.

The adsorption of a NO_x adsorber catalyst entails reaction of an acidic gas (NO₂) with a basic adsorbent (oxides or carbonates of alkali and alkaline earth elements, e.g. BaO and BaCO₃) to form nitrate or nitroso-species, both on the catalyst surface. Since NO is known to show slower reactivity with metal oxides than NO₂ and engine-out NO_x primarily consists of NO (90 %), it must first be oxidized to NO₂ over an oxidation catalyst (e.g. Pt based). When the effective storage capacity of the adsorber is below the desirable level, reductant (e.g. diesel fuel) is injected to establish a rich environment. Under this condition, the trapped NO_x is reduced to N₂ following a conventional three-way catalytic conversion principle. The operational temperature range of the NO_x adsorber catalyst is governed by the low and high limits. The low limit is controlled by the light-off temperature required for the catalyst to oxidize NO into NO₂ and the upper limit is determined by the temperature of thermodynamic stability of the trapped nitrogen oxide species (e.g. Ba(NO₃)₂). NO_x adsorbers are generally stable to the hydrothermal conditions encountered in diesel exhaust. However, the adsorbent function (e.g. BaO around Pt sites) is extremely susceptible to deactivation from sulfur oxides in the exhaust by the formation of sulfated species [22] that hinder adsorption sites intended for NO₂ storage [23]. Furthermore, the rich regeneration pulses not sufficient either in reactivity or in temperature to effectively release the SO_x from the adsorber result in a rapid deactivation (from 100 % to 20 % NO_x conversion) as seen when a NO_x adsorber aged with a diesel fuel containing current sulfur levels (0.05 % S).

EMISSION REGULATION/CYCLE DEFINITION

Based on EPA's Tier 2 emission standards that will be phased-in between 2004 and 2009, vehicles are classified based on gross vehicle weight rating (GVWR), and their applications. Passenger cars and light-duty trucks with GVWR less than 8500 lbm are tested on chassis dynamometers using the FTP-75 cycle and Supplemental Federal Test Procedure (SFTP). The engines for heavy-duty vehicles with GVWR above 8500 lbm are tested on engine dynamometers using the US Heavy Duty (US-HD) cycle and Supplemental Emission Test (SET). Medium-duty passenger vehicles (MDPV) and heavy-duty diesel vehicles (HDDV) for GVWR up to 10,000 lbm and 14000 lbm, respectively, can be optionally tested using either light-duty standards or heavy-duty standards.

FTP-75 cycle specifies the vehicle speed over time, and emission standards are in g/mile. Three phases are included in this cycle: 0-505 s cold transient, 506-1372 s cold stabilized, and 0-505 s hot transient. The hot transient phase is a repeat test of the cold transient phase, but with a 10 min soak period following the cold stabilized phase. Emissions from cold and hot start tests are combined using the weighting factors of 0.43 and 0.57, respectively, with an assumption that the stabilized cold phase will have the same emissions as the hot start. Following Tier 2 standards, vehicle manufactures will have a choice to certify a specific vehicle to any of the 8 bins of different stringency. However, the entire vehicle fleet sold by each manufacturer will have to meet the average NO_x standard of 0.07 g/mile.

US-HD cycle specifies the normalized engine speed and torque history with respect to the full-throttle torque curve, and the emission standards are in g/bhp-hr. There is a 20 min cold start transient cycle, followed by a repeat 20 min hot start transient cycle after a 20 min soak period. Unlike the FTP-75 cycle, the cold start emission has a much lower weighting factor, 1/7 vs. 6/7, for the hot start cycle. The NO_x emission standard, 0.2 g/bhp-hr will be phased in between 2007 and 2010. Additionally, SET emission test using Euro III cycle will be required to meet the same FTP standard, and Not-to-Exceed (NTE) to meet 1.5 times the FTP standards.

EXHAUST CHARACTERISTICS

Under FTP-75 and US-HD cycles, engines will undergo very different speed and load history, as well as the exhaust characteristics. The engine calibration, such as the use of EGR, can also influence its exhaust characteristics. An advanced prototype Cummins 5.9L ISB engine equipped with cooled EGR was used to evaluate performance of various NO_x adsorbers.

Figure 1 shows one typical example of the engine-out NO_x contribution vs. engine turbo-out temperature. Based on the thermal management for the aftertreatment system, the catalyst inlet temperature is lower than the turbo-out temperature by 20-50°C. For FTP-75 cycle, about 20 % of NO_x will be emitted below 200°C during the cold-start vs. 7.5 % during the hot-start. Since cold-start represents a significant portion of the overall light-duty emissions, it is essential to improve the low-temperature performance of the NO_x catalyst, particularly for temperatures below 200°C. For US-HD cycle, the majority of NO_x is emitted when the engine turbo-out temperature is above 200°C.

The plot of engine-out NO_x contribution vs. catalyst space velocity is also shown in Figure 1, for catalyst space velocity of two times the engine displacement. For FTP-75 cycle, the majority of NO_x is emitted when the space velocity is below 30 k/hr. For US-HD cycle, a significant portion of NO_x is emitted when the space velocity is 60-70 k/hr. Higher space velocity generally represents higher NO_x loading for the catalyst. All factors including temperature, space velocity and NO_x loading need to be considered for the catalyst sizing in order to minimize the regeneration frequency and the associated fuel penalty.

Concentrations of O₂ and H₂O in engine exhaust are directly related to the engine A/F ratio, which in turn is influenced by EGR configuration. Since NO_x adsorber regeneration requires an O₂-starving environment, the fuel injection penalty can be related to the O₂ flow rate, which is determined by the exhaust flow rate and the O₂ concentration. Figure 2 shows the engine-out O₂ flow rates depicted for FTP-75 and US-HD cycles. It is expected that the H₂O content in exhaust may play a major role on the performance of the NO_x adsorber because most base metal oxides of adsorber materials undergo rapid hydrolysis with H₂O. Dispersion of the precious metal and sorbate ingredients shows strong dependence on the physical state of the supporting material. Figure 2 also shows the engine-out H₂O concentration based on complete combustion and dry ambient air. As indicated by Figure 2, the maximum H₂O concentration is found to be less than 10 %, at low A/F conditions. The average H₂O concentration over the emission cycles is between 4 %-5 %.

ANALYTICAL AND EXPERIMENTAL METHODS

DRIFTS (diffused reflectance FTIR) (24-27) and Raman spectroscopy (27,28) were used to characterize surface adsorbed species. Both are vibrational techniques permitting a sample depth profiling from several to hundred nanometers. A sketch of experimental setups for both techniques is

depicted in Figure 3. During the nitration process, various nitrates and nitrites, including species in different chelation configurations such as uni- or bi-dentate geometry can be identified in the spectra. During the sulfation process, various oxy-sulfur species including sulfites, sulfates, bisulfates and pyrosulfates can be identified and discriminated (29-34). The sensitivity of spectroscopic techniques provides information not only for the vibrational frequencies but also for rotational contours associated with the specific vibrational modes. Surface physisorbed, vapor-like NO₂ (with the P/R branches at 1596/1626 cm⁻¹) and SO₂ (with Q-branch at 1358 cm⁻¹) can be seen in the spectra, particularly for samples operated at relatively low temperatures, < 300°C.

In-situ DRIFTS measurements were conducted by a SpectraTech unit attached to a standard FTIR spectrometer. Within the unit, the incident IR was directed onto the sample through the front portion of a parabolic mirror and the diffused signal was collected through the back portion of the mirror. The powdered sample was sealed under a ZnSe dome and heated by an electric heater mounted underneath the sample cup. The reaction gas flowed through the dome with the desired rates. Surface adsorbed species accumulated on the top two-dimensional overlayer were investigated by exposing catalytic powder to the reaction gas (0.1 % NO₂ or 0.98 % SO₂ in N₂ or air) under the desired conditions of temperatures and flow rates. The spectrum of KBr powder at each specific temperature was used as the background for other spectra collected at the same temperature. All spectra were collected in single-beam mode and ratioed to the single-beam spectrum of KBr background in order to generate the spectra in absorbance unit.

For off-line measurements in DRIFTS, samples were loaded in a packed-bed reactor and exposed to the reaction gas at the desired temperatures. The flow rate in packed-bed reactor was adjusted much larger than the one used for in-situ measurements and all sample particles were exposed to the reaction gas. This was in contrast to in-situ measurements where only the top surface overlayer of a sample was in contact with the reaction gas.

Raman can be a powerful tool to identify surface adsorbed species as long as these surface-mediated species are not significantly fluorescent. Raman data were collected using a Renishaw Ramanscope equipped with two holographic Notch filters, an electrically cooled CCD camera and an Ar⁺ laser. The excitation source was focused onto the sample through a microscope. Laser power was maintained at a low level, <5 mW, in order to avoid any thermal heating.

Both DRIFTS and Raman are generally considered as qualitative techniques. When a well-characterized

internal reference is used, quantitative information may be obtainable. Time sequence of surface buildups of a specific species may also carry some kinetics information. Thus, spectral measurements of a specific absorption band on the catalyst at various times within the stream may reveal a catalyst deactivation mechanism.

Model powder samples for this study, such as BaO, Al₂O₃, CaO were obtained from Alfa without further treatment. Fully formulated NO_x adsorber catalysts, SO_x trap catalyst and catalyzed soot filters for engine tests were obtained from Engelhard.

NO_x ADSORBER FUNDAMENTAL-NO_x STORAGE AND REGENERATION

For BaO-based catalysts, BaO interacts rapidly with moisture and CO₂ in the exhaust to form a mixture of BaCO₃ and Ba(OH)₂. It is found that NO_x conversion increases with increasing O₂ concentration but decreases with increasing CO₂ concentration. It is a general understanding (35,36) that the trapping mechanisms of NO_x adsorbers may involve several routes:

- (1) Oxidation of NO

- (2) Disproportionation of NO₂

- (3) Displacement reactions of carbonates

- (4) Hydrolysis of BaO

- (5) Insertion reactions involving surface hydroxyl groups, such as $\text{>OH} + \text{NO}_2 \rightarrow \text{>ONO}_2\text{H}$.

The burst of NO_x at the beginning of each rich regeneration cycle suggests that the decomposition of metal nitrates may be the first step in the reduction mechanism. Upon reacting with hydrocarbons or other appropriate reductants during the regeneration, Ba(NO₃)₂ appears to first decompose to release NO_x which will then be reduced to N₂. Such NO_x release can be depicted by a desorption process:

It is evident that this desorption process is sensitive to sample temperature. The release NO_x will be reduced to N₂ over precious metal (e.g. Pt) sites with additional available reductants. It was found that base metal oxides (BMOs), physically separated from Pt component, do not exhibit high trapping capacity for NO_x and require more reductants during regeneration. Thus, an intimate contact of Pt and BMOs is apparently essential in determining the overall efficiency in NO_x conversion. Insufficient reductant often leads to high NO release. Trapped NO_x quantity also appears to affect the NO_x reduction. It was determined that loosely trapped nitrated species tend to easily release as NO during regeneration. The reduction reaction also seems to depend on the type of reductants and the reduction temperature, especially for low temperature operations (e.g. <250°C). It appears that it is advantageous to keep the NO_x adsorber near 100 % trapping efficiency during the operation. This tends to minimize the NO release during regeneration. A development of adequate regeneration strategy consisting of optimization of lean NO_x trapping time, regeneration time, lean/rich ratio and space velocity, is critical to a successful application of NO_x adsorber technology.

LOW TEMPERATURE PERFORMANCE IMPROVEMENT

As characterized in Figure 1, the NO_x adsorber catalyst located in the exhaust stream of our test engine spent most of the time during the FTP75 test cycle in the temperature range between 200°C and 250°C. When diesel fuel is used as the reductant to regenerate the adsorber, the light-off temperature may not occur at or below 200°C due to limited oxidation of the fuel at low temperatures. One way to increase the activity is to transform the diesel fuel into light hydrocarbon constituents (C₃-C₈). Table I summarizes the NO_x trapping capacity of a NO_x adsorber regenerated at 250°C using various light hydrocarbons as reductants in a laboratory experiment. As shown in Table I, the light hydrocarbon components (except propylene, more or less equivalent to diesel) are worse reductants than the diesel fuel for low temperature regeneration of a NO_x adsorber.

Another way to improve the low temperature performance of NO_x adsorbers is through a reforming process by converting the diesel fuel into CO and H₂ since CO and H₂ are generally more effective reductants than the hydrocarbons. Cyclic lean-rich experiments were conducted in the laboratory to confirm this hypothesis. A lean gas mixture containing NO, O₂, CO₂ and water was passed through a NO_x adsorber catalyst for two minutes and then the mixture was switched to a rich

exhaust containing CO₂, water and various CO and H₂ mixtures for ten seconds at a constant catalyst inlet temperature. The total quantity of the reductant introduced during the ten seconds regeneration period was equivalent to three times the stoichiometric flux of the NO_x during the lean exposure. The lean-rich switch was repeated more than 15 cycles. The cycle average of the NO_x conversion was calculated based on the total NO_x breakthrough and the total NO_x flux during each measurement. Table II summarizes the experimental results. The syngas was found to be much more active than the diesel. In fact, all syngas samples with various CO and H₂ contents can sufficiently lower the catalyst light off temperatures of the NO_x adsorber below 180°C. It clearly indicates that reforming of diesel fuel to syngas as reductant during the regeneration is an effective way to enhance the low temperature performance of a NO_x adsorber catalyst.

Table I NO_x trapping capacity of NO_x adsorber at 250°C

Reductant	NO _x Capacity at 250°C
ultra-low [S] diesel	0.54 gNO ₂ /l (base case)
propylene	1.04 x base
isobutane	0
o-xylene	0.7 x base
n-octane	0.074 x base
iso-octane	0

Table II Cycle NO_x Conversions of NO_x adsorber with various reductants

Reductant	Cycle NO _x Conversion % (120s Lean / 10s Rich)			
	250°C	225°C	200°C	180°C
ultra-low [S] diesel	92	81	58	5
CO	100	100	93	81
CO/H ₂ = 3	100	100	98	85
CO/H ₂ = 1	100	100	100	95

H ₂ /CO = 3	100	100	100	95
H ₂	100	100	100	95

SPECTROSCOPIC CHARACTERIZATION OF MODEL BULK METAL OXIDES

Surface probe of adsorbing species using spectroscopic techniques is a useful tool to understand the underlying chemistry of the adsorption and the aging mechanism. Temperature and temporal probes of surface species provide not only the kinetics information governing the storage efficiency but also the early indication of catalyst fouling. A database for nitration/sulfation as well as de-nitration/de-sulfation of model metal oxides such as CaO, BaO and Al₂O₃ using DRIFTS and Raman has been established. Such a database can provide knowledge to develop a better and more robust NO_x adsorber catalyst system. The following examples illustrate the capability of surface analyses to elucidate the NO_x and SO_x chemistry of model BMOs.

Figure 4a shows the Raman spectrum of nitrated BaO powder exposed to NO₂ (1000 ppm in air) at 250°C for 1 hour. The spectral patterns of 1060/690 cm⁻¹ features in Figure 4a match well with the bands observed for Ba(NO₃)₂ crystal. The 848 cm⁻¹ band attributed to BaO can be used as an internal reference for quantification. Besides these major bands, three additional weak features, observed at 1765, 1506 and 1423 cm⁻¹ can be assigned as surface nitrated species. As shown in the figure, buildups of the bulk species are significantly larger than the surface species. Raman spectra of nitrated BaO were also studied at various temperatures, ranging from 70°C to 250°C. The buildups of the bulk and surface nitrate species at each temperature were normalized against the integrated strength of the BaO 848 cm⁻¹ band. It is evident that the formation of bulk species is overwhelmingly dominant and more or less insensitive to the temperature of studies as indicated in Figure 4b. It seems that surface nitrate can easily transform into bulk nitrate if sufficient exposure to excess quantity of NO₂ occurs. It is generally understood that bulk nitrates are more difficult to reduce than surface nitrates due to their ionic characteristics. It suggests that avoiding formation of bulk nitrate at low temperatures may be important to improve low temperature performance of NO_x adsorbers. Based on the current data, we can conclude that nitrate formation is by far the most dominant process in the nitration of BMO's and most of the nitrates are bulk-like.

Figure 5 shows the Raman spectra of sulfated BaO powder exposed to SO₂ (998 ppm in air) at 25°C and

320°C under aerobic condition for one hour. Besides the BaO band at 848 cm⁻¹, several sulfated species are observed. At 25°C, the sulfated species are observed at 1685, 1059, 989 and 948 cm⁻¹. The 989 cm⁻¹ band can be assigned as the bulk sulfate while the other bands may be attributed to surface sulfated species. With a ratio to BaO band at 848 cm⁻¹, all buildups of the sulfated species can be normalized. It is interesting to note that the bulk-sulfate formation (the growth of 989 cm⁻¹ band) only occurs at high temperatures. At low temperatures, very little bulk sulfate was formed. At temperatures below 250°C, several surface sulfated species can be seen at 948 (sulfite) and 590 cm⁻¹ (bending modes of sulfated species). The 590 cm⁻¹ band is quite broad indicating the presence of a mixture of bending modes. The 1060 cm⁻¹ band can be attributed to a mixture of bi-sulfate and carbonate. Above 300°C, the strong sulfate band at 989 cm⁻¹ begins to show and the bending band splits into several sharp features located at 648/618 cm⁻¹ and 491/462/454 cm⁻¹. Three additional bands are also present at 967, 918 and 1570 cm⁻¹. The 967/918 cm⁻¹ pair can be attributed to sulfites while the 1570 cm⁻¹ can be attributed to pyro-sulfate formation. Pyro-sulfate bands can be easily observed in Raman. High temperatures seem to favor the formation of sulfates and pyro-sulfates. The temperature dependence of the 989 cm⁻¹ band (bulk sulfates) shows a nonlinear response while the increase of 1060 cm⁻¹ band (bisulfates/carbonates) is almost linear. We conclude that the formation of surface species is dominant in sulfation and the surface accumulation is sensitive to temperature.

NOX ADSORBER CHARACTERIZATION

Catalyst durability is the most critical issue in NOx adsorber development in current aftertreatment technology. Deactivation of NOx adsorbers involves many pathways and S-poisoning is possibly the most recognizable one. Degradation pathways are temperature driven and mostly irreversible in nature, such as the particle size growth of precious metals and the sintering effect of BMOs and/or supporting materials. Some occur at a relatively slow pace, such as the dispersion loss of certain active components. Some may be caused by catalyst fouling due to the incomplete burning of condensed hydrocarbons during the catalyst regeneration. Although catalyst deactivation appears inevitable, it is important to minimize the drastic degradation thus extending catalyst useful life.

Spectroscopic characterization of the inlet portion of catalyst samples following the time sequence of an engine test reveals important information related to catalyst deactivation. Surface changes on catalysts can be characterized using differential DRIFTS, a subtraction of the spectrum of the fresh sample from the spectrum of an aged sample. Both buildups and depletions are observed in differential DRIFTS.

Depletions correspond to spectral changes of certain functionalities displaced by the reaction gas. Our DRIFTS database for model bulk BMOs provides a basis for band assignment. Major DRIFTS bands of various BMOs are listed in Table III. In nitration, the major spectral changes can be seen in the buildups of nitrates and the loss of surface OH. The OH loss must be attributed to surface displacement and insertion reactions with NOx. In sulfation, the major spectral changes occur in the growth of sulfates and surface adsorbed SO₂ and the loss of OH. The loss of OH may also be caused by surface insertion and displacement reactions by SO₂ or SO₃. Typical insertion and displacement reactions of sulfur oxides species are:

Figure 6 shows the spectra of differential DRIFTS before and after the engine aging of a Barium-based NOx adsorber. As shown in the Figure, a series of relatively sharp features, located at 858, 1060, 1750, 2451 and 2822 cm⁻¹, was depleted from the spectrum of the fresh sample. All these bands match well with the spectrum of BaCO₃. It is known that the fresh sample equilibrates with the CO₂ in the air contributing to abundant BaCO₃ absorption bands. Upon exposure to engine exhaust, BaCO₃ can be easily converted into Ba(NO₃)₂. Besides the depletion of BaCO₃, a significant OH loss was also observed. Based on the data in Table III, the relatively sharp depletion at 3746 cm⁻¹ in Figure 6 can be attributed to a loss of type III OH's (following the Knozinger-Ratnasamy classification) associated with Al₂O₃ (30). This type of surface OH's appears to have a high reactivity with SO₂. The reaction most likely undergoes a formation of bi-sulfates, $>\text{—OH} + \text{SO}_3 \rightarrow >\text{—OSO}_2\text{OH}$.

Several buildups related to nitrated and sulfated species are observed in Figure 6. The buildup at 1098 cm⁻¹ can be attributed to sulfate formation. There are two types of nitrate formation. The 1376 cm⁻¹ band corresponds to nitrates located on BaO sites while the 1580 cm⁻¹ band corresponds to nitrates on Al₂O₃ sites. All spectral assignments are based on the database collected for model BMOs. Besides sulfate and nitrate formation, weak features at 2960 and 1470 cm⁻¹ can be assigned to C-H stretchings and bendings. It suggests that condensed hydrocarbon species are accumulated on the surface of the aged sample, particularly in the later time of engine test.

The DRIFTS spectra as a function of time on stream of the inlet portion of the engine aged NOx adsorber catalyst are presented in Figure 6. The configuration of the aftertreatment system used in this engine test is also shown in Figure 7. It contains a SOx trap

followed by a NO_x adsorber and then a catalyzed soot filter to remove PM. Diesel fuel was injected after the SO_x trap but prior to the NO_x adsorber during the regeneration. To minimize the masking effect caused by sulfur poisoning from the fuel, Philips ultra-low S fuel (<3 ppm [S]) was used as both the engine and regeneration hydrocarbons. It was determined that the performance of the NO_x adsorber lost about 10% NO_x conversion efficiency during 350 hours operation in a light-duty cycle. Three major deactivation pathways are speculated. They are: (1) sulfur poisoning from the fuel during regeneration, (2) incomplete reduction of trapped NO_x species, and (3) residuals and coke formation of condensed hydrocarbons from unburned fuel components during regeneration.

Besides the most pronounced 1120 cm⁻¹ band that can be assigned as sulfate formation, the buildup at 1290 cm⁻¹ can be attributed to nitrate formation, particularly on BaO sites. The Cordierite band at 1860 cm⁻¹ can be used as an internal reference for quantification of the change of absorption band. A couple weak features appearing at 2970 and 3020 cm⁻¹ can be related to hydrocarbon bands, possibly resulted from the condensed fuel derived species.

The assignment of the condensed hydrocarbons can also be verified by Raman spectra between the fresh and the aged sample. Figure 8 shows several Raman features at 251, 564/574, 680, 972/1007 and 1193 cm⁻¹ which can be assigned as Cordierite bands. For aged samples, besides a gradual increase of the fluorescence background, two major bands are observed at 1360 and 1588 cm⁻¹ which can be assigned as the typical carbon bands. The fluorescence comes from the aromatic residual of the condensed hydrocarbon species. The intensity ratio between these two carbon bands reflects the aromatic domain size. The Raman nature of these carbon bands has been extensively studied for various carbonaceous materials (37-38). Many excellent reviews have been reported and various phonon models have been developed (39). The Raman ratio between the disordered (the 1350 cm⁻¹ band) and the graphitic band (the 1588 cm⁻¹ band) has been used as a measure for the growth of microcrystallite. It is a good indicator of formation of coke precursor.

Temporal buildups of nitrates, sulfates and hydrocarbons are listed in Figure 9. Nitrate buildup seems to slow down after 200 hrs of operation. Besides a rapid increase at the beginning, the sulfate buildup increases continuously in intensity with time. Further reactions of surface oxy-sulfur species to form pyro- or poly-sulfates following the reactions of $\text{>OH} + \text{SO}_3 \rightarrow \text{>OSO}_2\text{OH}$ and $2\text{>OSO}_2\text{OH} \rightarrow \text{S}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ or $2\text{HSO}_3^- \rightarrow \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O}$ may account for the continuous buildups. The overall buildups of hydrocarbons also grow with time. However, the non-

uniformity of the burning of the injected fuel during operation gives rise to fluctuations in hydrocarbon deposit.

The measured IR buildup (the integrated strength of the specific absorption band) of surface adsorbing species generally relates to the remaining sites available for further adsorption. According to the Elovich adsorption mechanism (40), the surface buildup of a specific species q at a time t may follow an equation of $dq/dt = k \exp(-\beta q)$, where k is the adsorption rate and β is a constant, more or less, independent of pressure and temperature. Since the NO_x conversion efficiency of a NO_x adsorber is proportional to the available adsorption sites on the catalyst surface, the available sites at a time t gradually diminishes if poisons start to occupy the sites. The density of the sites should follow an exponential decay if Elovich adsorption mechanism applies. The NO_x conversion efficiency is proportional to the available active sites on catalyst surface,

$$N(\text{available sites}) \propto N_0 \exp(-[\alpha_S + \alpha_N + \alpha_C]t) \\ \propto N_0 \exp(-\alpha_{\text{all}}t),$$

where N_0 is the total adsorption sites of a fresh catalyst, α_S is the degradation coefficient for S-poisoning, α_N is the degradation coefficient for incomplete regeneration of trapped NO_x sites, and α_C is the degradation coefficient for coke formation and other sintering effects. For simplicity, all thermal instability and sintering effects of Pt and supporting materials can be grouped within the term of α_C .

Assuming all the structural changes caused by α_S , α_N and α_C under the operating conditions are irreversible and independent among one another, the time dependent adsorption kinetics will be

$$kN_0 \exp(-\alpha_i N) = dN/dt \text{ for each adsorbed species.}$$

With an integration of

$$\int \exp(\alpha_i N) dN = N_0 \int k dt,$$

a linear relationship of $\alpha_i \propto \ln(t)$ can be obtained. In IR measurement, α is directly proportional to the absorbance (the integrated signal of a specific functionality). As shown in Figure 8, both nitrate and sulfate buildups exhibit a linear response to $\ln(t)$. The slopes for such linear dependence, $\alpha \propto \ln(t)$, are also found quite similar suggesting a similar mechanism for surface adsorption. We conclude that most IR buildups on NO_x adsorber follow Elovich surface adsorption mechanism.

SO_x TRAP CHARACTERIZATION

SOx TRAP CHARACTERIZATION

Besides the common poisons from fuel, lubricant additives may also contribute to catalyst deactivation. A typical example is the anti-wearing component, ZDDP in oils, can deposit phosphates on the catalyst. Phosphate species have been identified in the front side of the aged SOx trap that is placed upstream of the NOx adsorber. Figure 10 shows DRIFTS spectra of an aged SOx trap as a function of time on stream. The configuration of the aftertreatment system is identical to the one depicted in Figure 6 where the soot filter is located downstream. Two characteristic phosphate bands at 1260 and 1605 cm^{-1} match reasonably well with the spectrum of the aged SOx trap after 260 hr of operation. The phosphorus-contamination is not observed in the backside of SOx trap indicating a strong surface adhesive nature for phosphates. With a comparison to the spectrum of zinc phosphate, the band at 1260 cm^{-1} is slightly shifted to higher energy, indicating a mixture of other phosphate salts including calcium. Whether these phosphate species exhibit detrimental impacts on SOx trap remains to be seen. The phosphorus and ash components from lubricants can be identified in aged catalysts. As shown in Figure 10, the phosphate buildup is not significant at the early time (~50 hr), but grows with a faster rate than sulfates.

SULFUR MANAGEMENT

Sulfur poisoning from the fuel is the most recognizable degradation mechanism in NOx adsorber technology. SOx competes for the active sites available for NOx adsorption to form thermodynamically more stable sulfate species. The sites covered by these sulfated species are difficult to regenerate at normal operation temperatures (e.g. < 500°C). Even with the availability of 15ppm sulfur diesel fuel, NOx adsorber will be totally deactivated without effective sulfur management. In addition to fuel sulfur, sulfur in the lube oil also plays a role in sulfur loading and performance degradation in NOx adsorber.

Two general pathways are currently being explored for sulfur management: (1) the use of a disposable SOx trap that can be replaced or rejuvenated offline periodically, and (2) the use of diesel fuel and high temperature desulfation strategy to desorb the sulfates in order to recover the NOx trapping efficiency. The advantages and disadvantages of both approaches are briefly compared below.

High adsorption capacity and high selectivity for sulfur are the main driving forces for the design of disposable SOx trap. It provides a protection of adsorber catalyst from sulfur poisoning during misfueling which may be an important aspect in the near future. The relatively small size and economic cost are attractive for light-duty applications even with a restriction of limited lifetime. Usable lifetime of SOx trap is dependent on sulfur level in the fuel and the

lube. Designed properly, it would not release any significant secondary emission.

For desulfation approach, the catalytic system requires on-board management to generate a high temperature exhaust (e.g. > 600°C) to release sulfur from the catalyst. It is obvious that secondary emissions, such as hydrogen sulfide and/or sulfur dioxides, will be major concerns. Fuel penalty will be another hurdle that can not be avoided during desulfation. The main advantage is the integration of both trapping functions of NOx and SOx together. Therefore the development requires compromise among NOx storage & conversion, SOx storage & release, and catalyst thermal durability.

In the current development program, one of the efforts was focused on developing a SOx trap with sufficient capacity to protect the NOx adsorber catalyst for at least 20,000 miles operation. The SOx trapping efficiency needs to be maintained near 100% all the time (< 10 ppb break-through), and the stored SOx should not be released during the hottest driving conditions and the rich condition for NOx regeneration. The current development path employs a formulation containing base metals. A SOx trap with a capacity of 20gm SO_2/l and an estimated 15,000 mile lifetime before change-out has been demonstrated in the laboratory. Alternate substrates with high pore volume to improve its capacity are under investigation.

FUTURE WORK AND DIRECTION

Significant progress in NOx adsorber technology has been made in this program, but much work still remains to be accomplished. As mentioned previously, sulfur management is one of the most critical areas where progress still needs to be focused in order to make the NOx adsorber technology plausible. The capacity of a replaceable or off-line regenerable SOx trap needs to be increased to achieve an acceptable service interval. Alternatively, regenerable NOx adsorbers that allow the trapped SOx to be released at high temperatures need to be explored. Durability of a NOx adsorber exposed to periodic high temperature regeneration for SOx removal must be addressed and demonstrated.

Effective use of reductants introduced to the exhaust to optimizing catalyst conversion efficiency and minimizing fuel penalty needs to be emphasized. Reductant dispersion and concentration are important parameters when selecting placement and spray characteristics of an auxiliary injector.

High NOx reduction has been demonstrated through current development efforts. However, a system with acceptable cost has not yet been achieved. Efforts to reduce the size and complexity of the catalyst

system, thereby reducing the overall cost need to continue. Catalyst size reduction and integration should be investigated. Washcoat formulations and substrate geometry and materials are under consideration to further optimize the aftertreatment system.

While NO_x control is one of the main concerns with respect to emissions controls on diesel engines, one does not wish to inadvertently produce any potentially harmful unregulated byproducts as a result of the addition of any new aftertreatment devices. The potential of ammonia (NH₃) generation from adsorbers when HC is injected during regeneration needs to be evaluated.

Component and system reliability and durability have not yet been investigated thoroughly. Both component and system reliability and durability are of great interest to both the manufactures and regulatory agencies. In continuing development efforts, we will keep a close watch on any indicators such as failures or performance deterioration to provide some insight into component and system capability.

CONCLUSIONS

- Spectroscopic techniques, DRIFTS and Raman are valuable tools in catalyst characterization in elucidating the NO_x storage and aging mechanisms of NO_x adsorber catalyst.
- Surface adsorbing species responding to temperature and temporal behaviors provide kinetics information.
- Reforming of on-board diesel fuel to syngas may provide an effective way to enhance low temperature performance of NO_x adsorber.
- The integrated IR buildups of surface nitrate and sulfate species with time on stream suggests an Elovich adsorption mechanism.
- S-contamination, incomplete regeneration and coke formation are responsible for the loss of low temperature performance of NO_x adsorber catalyst even when an ultra low-S fuel (< 3ppm [S]) is used.
- Oil-derived contaminants such as phosphates and metal ash have been observed and their impacts on catalyst performances are under investigation.

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ACRONYMS

P/Q/R: rotational contours of a defined molecular vibration; P, Q and R refer to rotational transitions with change of angular momentum quantum number $\Delta J = -1, 0$ and $+1$, respectively.

ABS: stands for absorbance, which is defined as $\ln(I_0/I)$; I and I_0 are intensities of the transmitted and the incident beams.

OH: hydroxyl group with bending and stretching vibrations around 1630 and 3200–3700 cm⁻¹.

Chemicals: BaO (Barium Oxide), BaCO₃ (Barium Carbonate), Ba(NO₃)₂ (Barium nitrate), CaO (Calcium Oxide), Al₂O₃ (Aluminum Oxide)

Table III Major IR functionalities of model metal oxides

	<u>Al₂O₃</u>	<u>BaO</u>	<u>CaO</u>
<i>Nitration</i>			
Nitrates (cm ⁻¹)	1580	1250/1320/1470	1350/1460
OH change (cm ⁻¹)	sharp loss @3750 broad growth @3600	broad loss @3400 sharp growth @3560/3610	sharp loss @3631 sharp growth @3576
<i>Sulfation</i>			
Sulfates (cm ⁻¹)	1150	1080/1190	
SO ₂ (cm ⁻¹)	1358	1358	
OH loss (cm ⁻¹)	sharp loss @3755/3681	broad loss @3500/3300

Figure 1 Engine-out NOx contribution vs. engine turbo-out temperature and space velocity.

Figure 2 Engine out O_2 flow rate and H_2O concentration history over FTP-75 and US-HD cycles.

Figure 3 Experimental setups for (a) DRIFTS and (b) MicroRaman

Figure 4 Raman response of nitrated species on BaO: (a) spectrum of BaO powder exposed to NO_2 (1000 ppm in air) at 250°C for 1 hr and (b) a plot of nitrate buildups as a function of temperature. All spectra were normalized against BaO band at 848 cm^{-1} .

Figure 5 Raman spectra of BaO powder exposed to SO₂ (998 ppm in air) at 320°C and 25°C for 1 hr.

Differential IR (used@350hr - fresh) of Sample A

Figure 6 Differential DRIFTS spectrum (absorbance of 350 hrs aged – absorbance of fresh) of an engine aged NO_x adsorber.

Figure 7 DRIFTS analysis of engine aged NO_x adsorber as a function of time on stream. The configuration of the aftertreatment system is shown in the top of the figure where the soot filter is located downstream.

Figure 8 Raman analysis of engine aged NO_x adsorber as a function of time on stream.

Figure 9 Buildups of surface nitrated and sulfated species of an engine aged NO_x adsorber as a function of time:

- (a) Buildups of nitrates @1320 cm^{-1} and sulfates @ 1100 cm^{-1}
- (b) Fluctuation of hydrocarbon buildups @2970 cm^{-1}
- (c) Elovich relationship of sulfate buildups @ 1100 cm^{-1} ; (buildups) $\propto \ln(t)$
- (d) Elovich relationship of nitrate buildups @1320 cm^{-1} ; (buildups) $\propto \ln(t)$

Figure 10 DRIFTS spectra of engine aged SOx trap as a function of time on stream