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W. Addy Majewski
Diesel Controls Ltd.

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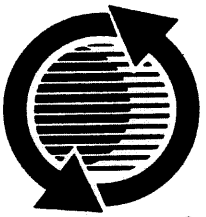

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ABSTRACT

Two catalyst formulations were tested on a diesel engine. A Fourier Transform Infrared (FTIR) analyzer was used to measure concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2). Other exhaust gas components were measured by conventional analyzers.

The results indicate that nitrogen oxides (NO_x) undergo complex chemical reactions in the diesel oxidation catalyst (DOC). The increase of NO_2 occurring at a certain temperature range is accompanied by a decrease of the total NO_x emission. NO_2 is probably an important itermediate product in the lean NO_x catalyst reaction chain.

INTRODUCTION

Catalytic reduction of NO_x under lean conditions became the research focus for both diesel and automotive applications. Surprisingly, very little data is published on the role of NO_2 in the nitrogen oxides catalysis. Majority of experimental work is limited to the total NO_x measurements only and attempts are made to interpret the results in terms of NO reactions. On the other hand, it is a known fact that precious metal catalysts can oxidize NO to NO_2 in diesel exhaust *[9,10]*. As a result a significant fraction of NO_x may be present as NO_2. Because NO_2 exhibits high chemical activity, it may deserve more attention in the NO_x catalysis models.

From the underground mining perspective the oxidation of nitric oxide to nitrogen dioxide may be a counterproductive process. Occupational Health and Safety standards legislating the ambient air quality regulate each nitrogen oxide separately. Exposure limits of NO_2 are about ten times lower than those for NO. The Mine Safety and Health Administration has proposed permissible exposure limits of 3 ppm for NO_2 and 25 ppm for NO for mines in the U.S.*[8]*.

The purpose of this paper was to study the influence of different catalyst formulations and engine conditions on the transformations of NO_x and generation of NO_2 in diesel exhaust gas. To interpret the experimental data a discussion of several possible nitrogen oxides reactions was necessary. Some of the reactions are those occurring in the "lean NO_x catalyst".

Investigation of nitrogen oxides reactions has been made possible with the introduction of high accuracy exhaust gas analyzers. Effects of DOCs upon nitrogen oxides emission were researched by means of a Fourier Transform Infrared instrument. The experimental part has been performed at the USBM's Diesel Emissions Research Laboratory. Catalyst samples were tested on a diesel engine over a slow engine load ramp with temperatures increasing from 150 to 550 °C. Nitrogen oxides, sulfur dioxide, carbon monoxide and hydrocarbons were measured at the inlet and outlet of each catalyst.

Two catalyst samples were investigated: a platinum and a palladium based formulation. The samples were prepared for this study by Diesel Controls Limited.

EXPERIMENTAL METHODS

APPARATUS - All testing was conducted in the USBM's Diesel Emissions Research Laboratory (DERL). A schematic of its sampling system is shown in Fig.1. A brief description of the apparatus used during this testing is given below and described in more detail elsewhere *[1-4]*.

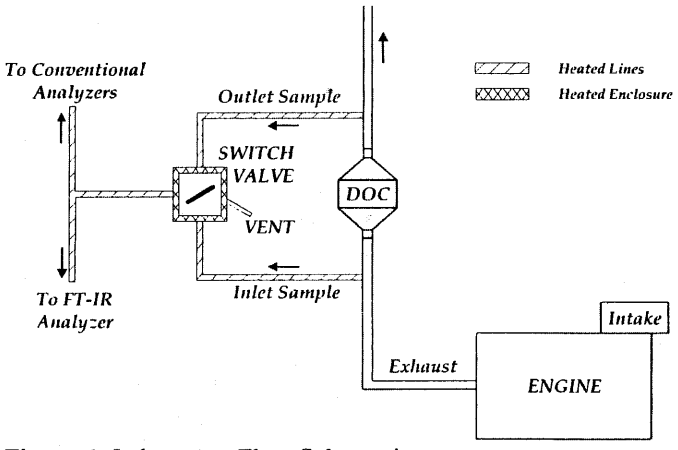

Figure 1. Laboratory Flow Schematic

TEST ENGINE - The evaluations reported here were made by installing DOCs in the exhaust stream of a 7-liter, pre-chamber, naturally aspirated, Caterpillar 3304 mining diesel engine. For standard U.S. Mine Safety and Health Administration (MSHA) test conditions, the maximum power rating of this engine is 75 kW (100 hp) at 37 Hz (2200 rpm).

During the evaluations, the engine's intake air was controlled to SAE standard conditions of 100 kPa (402 "H_2O) and 25°C (77°F).

The fuel used throughout all of the testing was commercially available, low-sulfur (<0.05%) fuel, and conforms to the 1993 U.S. Environmental Protection Agency (EPA) regulation for diesel fuels *[5]*.

GASEOUS EMISSIONS SAMPLING SYSTEM - Emissions of carbon monoxide and carbon dioxide were measured using a Pierburg BINOS-2000 non dispersive infrared analyzer, while gaseous hydrocarbons were measured using a Pierburg FID PM-2000 flame ionization analyzer. A Rosemount 880 nondispersive infra-red analyzer was used to measure SO_2 emissions, and an Oxymat PM-2000 paramagnetic analyzer was used to measure O_2.

A Nicolet Rega 7000 FTIR Spectrometer exhaust gas analyzer *[6,7]* was used to measure the NO and NO_2 emissions during these tests. Unlike the conventional analyzers, the FTIR analyzer is able to measure the exhaust concentrations of both NO and NO_2 directly, concurrently, and in the same sample. Since there is no full scale or "ranges" on the FTIR, the accuracy is based on the calibration gas used. In this case, the accuracy of the NO measurement was ±15 ppm, and NO_2 was ±2 ppm.

Continuous samples of gas-phase emissions were taken via an exhaust flow-switching configuration consisting of a heated enclosure (containing flow-switching valves) and three heated sample lines as illustrated in Fig.1. Using this sampling system, it was possible to sample the gaseous emissions alternately from the engine exhaust upstream of the DOC, and from the exhaust downstream of the DOC, without stopping the engine to insert or remove the DOC. This is accomplished by a set of valves which divert the sample to heated lines which convey the samples to the traditional and FTIR exhaust gas analyzers. A vent line is used to maintain constant flow conditions in the upstream and downstream sample lines regardless of which sample arm is being used.

Several other species can be included in the FTIR measuring program. Other nitrogen compounds measured in this study by FTIR and mentioned in the further discussion were ammonia and nitrous oxide.

ENGINE OPERATING CONDITIONS

Chemical reactions, such as oxidation, tend to occur more rapidly at higher temperatures. The temperature of diesel exhaust depends upon engine load, so that the performance of a DOC depends critically upon the engine used and its duty cycle as well as the location of the DOC with respect to the exhaust manifold. For this reason, it is important to evaluate aftertreatment devices over a range of exhaust temperatures. "Ramp" tests are conducted to screen aftertreatment devices. The test is performed at a constant engine speed of 1500 rpm. Emissions are measured while increasing the engine load from 27 N·m (20 lb-ft) to 325 N·m (240 lb-ft) at a very slow rate: 0.019 N·m/s (5/6 lb-ft/min). The corresponding rate of change of temperature of the DOC is about 0.025°C/s (2.7°F/min). Fig.2 shows the actual progress of torque and exhaust temperature during a typical ramp. One ramp test was conducted on each DOC. The results from these tests were similar to the results from ramp tests previously conducted on other DOCs *[9]*.

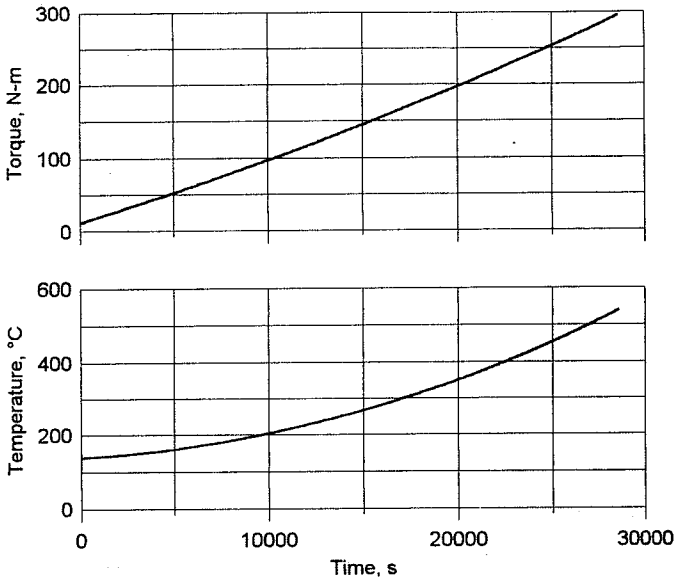

Figure 2. Temperature and Engine Load During a Ramp Evaluation

Fig.3 illustrates the concentration of CO measured as a function of exhaust temperature. Gas concentration measurements are taken every 20 seconds yielding the total of about 1400 measuring points during one ramp test. The sampling location is alternated every 10 minutes.

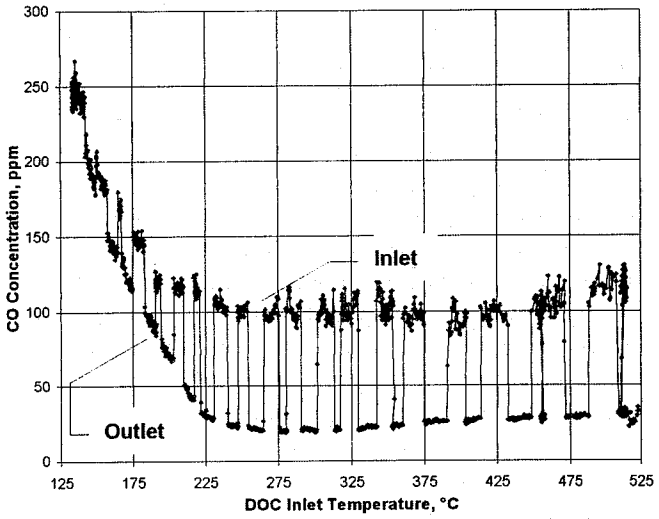

Figure 3. Carbon Monoxide Sampling During a Ramp Test Illustrating Inlet/Outlet Switching

Interpolation gives an excellent indication of what the measured concentrations are throughout the entire sampling period. Note that beyond 140°C (284° F) the concentration of CO is less downstream (Outlet) than upstream (Inlet), reflecting the oxidation of CO by the DOC. At higher temperatures more than 75% of the CO is removed. The purpose of this illustration is to convey the general idea of determining the influence of the DOC upon emissions through the use of the switching method described. The situations to be discussed further involve NO_2 and NO and are somewhat more complex so that it is helpful to keep the overall technique in mind.

Graphs used in the further discussion are curve fitted representations of experimental data.

CATALYTIC CONVERTERS

Two catalytic converters were tested. Both of them had the same γ-alumina washcoat but different precious metals formulation. Some data on both units are listed in Table 1.

Table 1
Technical Data on the Catalytic Converters

	Pt Catalyst	Pd Catalyst
Substrate type	Metallic	
Diameter, mm	149.2	
Length, mm	90	
Volume, dm^3	1.578	
Cell density, cm^{-2}	30	
Washcoat	γ-Al_2O_3	
W/c loading, g/dm^3	100	
Precious metal	Platinum	Palladium
Metal loading, g/dm^3	1.4	2.1

Both catalysts were tested at the constant engine speed of 1500 rpm. The resulting exhaust gas space velocity in each catalyst was approximately constant and amounted to 165000 Sm^3/m^3h.

Both units underwent the following, 2-step, preconditioning cycle prior to tests:

(1) 240 minutes long diesel engine preaging at 200°C with 5-minute long, 400°C temperature peaks every 30 min. High sulfur fuel (approx. 0.3% S) was used for the engine preaging.

(2) 60 minute oven heat treatment at 500°C in air atmosphere.

CATALYST PERFORMANCE: CO, HC AND SO_2

The two catalyst formulations differed significantly in their oxidation activity. Results pertaining to the oxidation of carbon monoxide, gas phase hydrocarbons and sulfur dioxide are plotted as concentrations in Fig.4. The top left plot - carbon monoxide on the platinum catalyst - represents exactly the same set of data which was already shown in Fig.3. The same data is plotted in terms of conversions in Fig.5.

High conversions of hydrocarbons and CO are very desirable performance characteristics of the diesel catalyst. High conversion of sulfur dioxide leads to the generation of sulfuric acid and an increase in particulate emission what is commonly perceived as a negative effect. Because of the Environmental Protection Agency's diesel particulate regulations, low sulfate formation became a target for the design of diesel catalyst formulation.

The platinum formulation (Fig.4 and 5 left) exhibited both good conversions and low light-off temperatures in respect to carbon monoxide and hydrocarbons. Unfortunately, the SO_2 conversion was also high, especially at higher temperatures. The palladium catalyst (Fig.4 and 5 right) features virtually no activity for the SO_2 oxidation. The penalty is a significantly higher light-off temperature for both carbon monoxide and hydrocarbons.

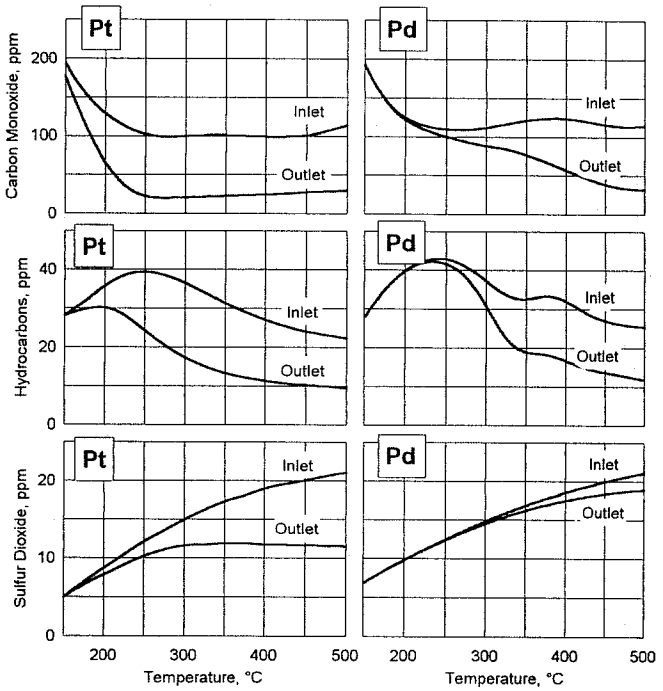

Figure 4. Concentrations of Carbon Monoxide, Hydrocarbons and Sulfur Dioxide on Pt and Pd Catalyst

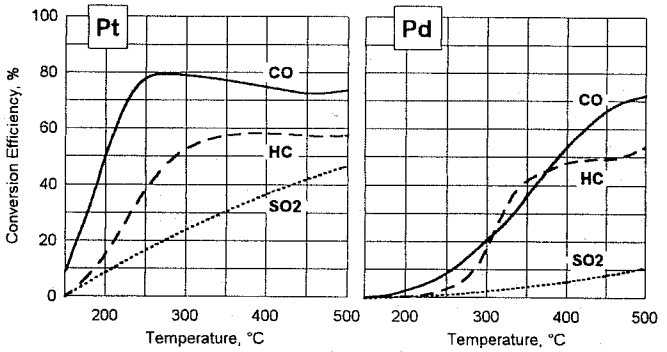

Figure 5. Conversions of Carbon Monoxide, Hydrocarbons and Sulfur Dioxide on Pt and Pd Catalyst

An interesting feature visible in the conversion graph (Fig.5) is the maximum conversion of carbon monoxide on the Pt catalyst, taking place at 275°C. Also the hydrocarbons conversion shows a maximum, although less pronounced, at about 375°C. Conversions of all species on the palladium catalyst continuously increase with temperature and do not exhibit a maximum.

CATALYST PERFORMANCE: NITROGEN OXIDES

Inlet and outlet concentrations of nitric oxide and nitrogen dioxide as a function of the DOC inlet temperature during the ramp test are shown in Fig.6. Plots on the left and right side represent results on the platinum and palladium catalysts, respectively. The top graphs display NO concentrations. The bottom graphs depict NO_2 data.

The platinum catalyst promotes the oxidation of nitric oxide to nitrogen dioxide accordingly to reaction Eq.(1):

$$NO + \tfrac{1}{2} O_2 \leftrightarrow NO_2 \qquad (1)$$

The equilibrium concentration of NO based on this reaction under the conditions present in the exhaust is also plotted in Fig.6. The process described by Eq.1 has already been the subject of previous studies *[9,10]*. The NO oxidation was confirmed in this work and is visible in the Pt plots (Fig.6) at temperatures of 250°C and higher. NO concentration decreases at the outlet from the DOC and the NO_2 concentration increases at corresponding temperatures. Conversion of NO reaches a maximum at 360°C. A peak NO_2 concentration at this temperature occurs (lower graph). Concentrations of NO (upper graph) at the DOC outlet are significantly lower than those at the DOC inlet with the maximum difference occurring at about 380°C.

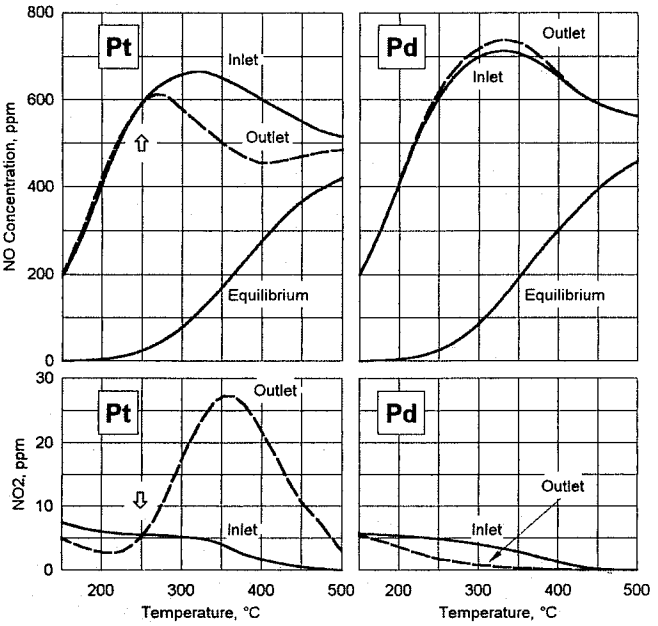

Figure 6. Nitrogen Oxides Concentration

At temperatures higher than 360-380°C the NO oxidation rate slows down. Less difference between the inlet and outlet NO concentrations is observed and the NO_2 concentration at the DOC outlet decreases. It is believed that this behavior is the result of thermodynamic limitations. Reaction Eq.(1) is an equilibrium reaction. A double-head arrow has been used in Eq.(1) to indicate that NO will not react completely with oxygen to form NO_2. Rather, an equilibrium composition can be reached where the system becomes thermodynamically stable. In such an equilibrium product mixture the reaction will not proceed any further. Concentrations of reactants in the equilibrium state are correlated by the reaction equilibrium constant K_p. The equilibrium constant can be calculated from thermochemical properties of reactants. It depends on temperature and therefore the calculations must be done for several temperatures within a given range. The exact thermodynamic formulas are given in the section Theoretical Considerations, Eq.(14)-(16).

Such thermodynamic calculations have been performed for reaction Eq.(1). The equilibrium constant was calculated for temperatures from 150 to 500°C. Then, the NO equilibrium concentration was calculated and plotted in Fig.6 (upper graph). The inlet concentrations of species were assumed for the calculations. Oxygen concentration in the exhaust gas during tests changed from approximately 17% at 150°C to 7% at 500°C.

The equilibrium line runs below the NO inlet line indicating that the reaction will progress to the right side of Eq.(1). The meaning of the equilibrium curve is that NO will decrease from the *inlet* concentration to the *equilibrium* concentration, in the result of a spontaneous progress of the reaction Eq.(1). At low temperatures, below 200°C, the equilibrium concentration of NO equals practically zero. The reaction can continue until almost the whole amount of nitric oxide present in the system is oxidized to nitrogen dioxide. At higher temperatures the equilibrium concentration of NO increases. When the exhaust temperature approaches 500°C, the inlet and equilibrium curves approach each other and the extent of the reaction progress is seriously limited.

It should be stressed that thermodynamic constraints are in no relation whatsoever to the reaction kinetics. Equilibrium can be perceived as a state that would be reached between reagents in a closed system after an infinitely long time elapsed. Thus, if thermodynamics prevents certain processes from proceeding they cannot occur. However, even if a reaction is feasible from the equilibrium point of view, it may not be fast enough to be completed within a reasonable period of time. It is the function of a catalyst to accelerate slow reactions.

Interesting concentration profiles have been measured on the platinum catalyst at low temperatures. Inlet and outlet curves for both NO and NO_2 cross each other at approximately 250°C. Points of crossing are indicated by vertical arrows in Fig.6. At low temperature the nitric oxide concentration at the outlet from the catalyst is *higher* than that at the inlet. The difference is small and hardly visible in Fig.6. The pertinent section of the curve appears to be just a thicker line. In fact, the outlet curve runs above the inlet one. Altogether, the platinum catalyst generates nitric oxide below 250°C. A similar cross-over of inlet and outlet concentrations happens to nitrogen dioxide. NO_2 outlet concentration at temperatures below 250°C is lower than its inlet concentration indicating an overall reduction occurring in the DOC.

The palladium catalyst results (Fig.6 right) follow the low temperature platinum pattern throughout the tested temperature range. The catalyst generates small amounts of nitric oxide at temperatures between 200 and 425°C. Nitrogen dioxide is reduced in the catalyst within the whole temperature range.

Equilibrium curve for NO oxidation was also calculated and plotted for the Pd catalyst test. The small differences between equilibrium concentrations in both tests are due to slightly different engine baselines (inlet concentrations). Equilibrium curves run *below* the actual concentrations. Consequently, the progress of reaction Eq.(1) must be to the right side of the equation, i.e. NO_2 is generated and NO is consumed in the process. The opposite tendency which was observed on the Pd catalyst as well as on the Pt catalyst at low temperatures indicates that nitrogen oxides chemistry in the diesel catalyst is not limited to the simple oxidation of NO,

Eq.(1). Nitrogen oxides must undergo other than Eq.(1), concurrent reactions.

BALANCE OF NITROGEN OXIDES

The stoichiometry of the oxidation of nitric oxide is given by Eq.(1). One mole of NO reacts with oxygen to produce one mole of NO_2. Under the conditions in diesel exhaust one mole of NO takes the same volume as one mole of NO_2. Consequently, with the reaction progress, an increase of NO_2 concentration by 1 ppm should be accompanied by a decrease of NO concentration of exactly 1 ppm. Total NO_x concentration should not be affected by the transformation of NO into NO_2.

Fig.7 illustrates the nitrogen oxides balance as measured during ramp tests on both catalysts. The same scale is applied for both the Pt and Pd units to emphasize the difference in performance. The top graphs represent changes in NO and NO_2 concentrations as the gas passes through catalysts. The most striking realization is the lack of balance between NO and NO_2 on the Pt catalyst. At temperatures between 350°C and 400°C approximately 20 to 25 ppm of NO_2 is generated. This is accompanied by a disappearance of more than 150 ppm of NO. For each mole of NO_2 generated about seven moles of NO disappear from the system. This ratio between NO_2 generated and NO disappearing from the system was constant at all temperatures where the reduction of NO was taking place. A net reduction of NO_x takes place which is illustrated in the bottom graph in Fig.7. The Pt catalyst is a net NO_x remover at temperatures of 250°C and higher with the maximum conversion efficiency of 22% at about 380°C.

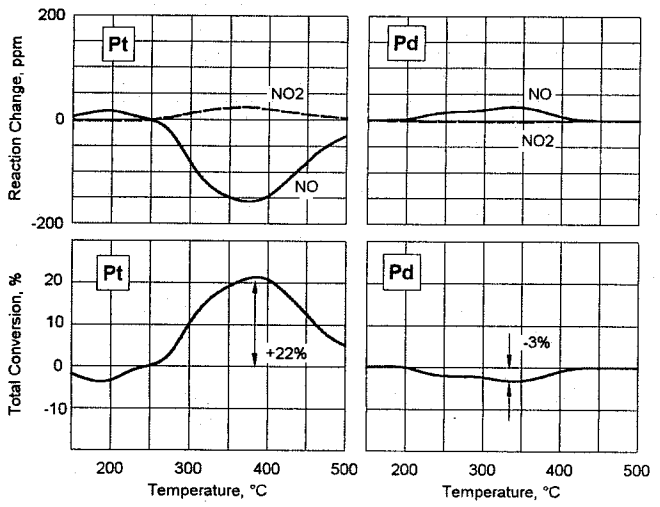

Figure 7. Nitrogen Oxides Balance

The platinum catalyst, as already discussed, shows a reversed performance tendency at low temperatures. NO_2 is removed from the system and NO is generated. The same kind of behaviour is displayed by the Pd catalyst through most of the whole temperature range. The amount of NO generated is bigger than that of NO_2 removed, contributing to a net NO_x generation. The Pd device generates up to 25 ppm of NO (between 200 and 425°C), removing about 3 ppm of NO_2 (all temperatures). There is no constant ratio of NO generated to NO_2 removed. The mechanism of NO generation, although interesting theoretically, is of no practical importance, as the maximum total NO_x generation (negative conversion) on the Pd catalyst amounts to 3% (Fig.7 bottom).

THEORETICAL CONSIDERATIONS

There are many potential reactions of nitrogen oxides in diesel exhaust. Nitrogen compounds present in exhaust gases from internal combustion engines include, beside NO, NO_2 and nitrogen N_2, the nitrous oxide N_2O and ammonia NH_3. Both N_2O and NH_3 were measured by the FTIR instrument. Concentrations of both species were practically equal to zero on both catalysts within the whole temperature range. The insignificant role of N_2O under lean conditions has been reported in literature *[11]*. Performed measurements imply that neither nitrous oxide nor ammonia play an important role in the chemistry of nitrogen oxides in diesel exhaust. Reactions with the formation of any of these species have been excluded from the further discussion. As there is no evidence of hydrogen in exhaust gas under lean conditions, H_2 reactions are not discussed either.

NITROGEN OXIDES REACTIONS - The following are several chemical reactions involving nitrogen oxides which occur or may be occurring in diesel exhaust. Reactions (2) and (3) represent the synthesis of NO_x as happens in the engine cylinder. Reaction (3) is in fact the global reaction standing for processes Eq.(2) + Eq.(1).

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \leftrightarrow NO \qquad (2)$$

$$\tfrac{1}{2}N_2 + O_2 \leftrightarrow NO_2 \qquad (3)$$

An alternative way to generate NO_2 from NO is the disproportionation of nitric oxide, reaction Eq.(4):

$$2NO \leftrightarrow NO_2 + \tfrac{1}{2}N_2 \qquad (4)$$

Nitrogen dioxide may react with exhaust gas components of a reducing character. Equations (5), (6) and (7) are examples of such reactions, where NO_2 reduces to NO. Reactions Eq.(5) and (6) represent oxidation of hydrocarbons and carbon monoxide by NO_2. Eq.(7) depicts the reaction between NO_2 and carbon of diesel particulates.

$$NO_2 + \{HC\} \leftrightarrow NO + CO + H_2O \qquad (5)$$

$$NO_2 + CO \leftrightarrow NO + CO_2 \qquad (6)$$

$$NO_2 + C \leftrightarrow NO + CO \qquad (7)$$

Similar set of reactions may be written for nitric oxide:

$$NO + \{HC\} \leftrightarrow N_2 + CO + H_2O \qquad (8)$$

$$NO + CO \leftrightarrow \tfrac{1}{2}N_2 + CO_2 \qquad (9)$$

$$NO + C \leftrightarrow \tfrac{1}{2}N_2 + CO \qquad (10)$$

Reaction Eq.(8) is considered to be the major mechanism of NO_x reduction on a Pt/Al_2O_3 lean NO_x catalyst *[12]*.

Finally, NO_2 can be reduced directly to N_2, Eq. (11), (12) and (13):

$$NO_2 + \{HC\} \leftrightarrow N_2 + CO + H_2O \qquad (11)$$

$$NO_2 + 2CO \leftrightarrow \tfrac{1}{2}N_2 + 2CO_2 \qquad (12)$$

$$NO_2 + 2C \leftrightarrow \tfrac{1}{2}N_2 + 2CO \qquad (13)$$

The last set of equations is formally a simple sum of previous reactions. For example, reaction Eq.(12) is the sum of reactions Eq.(6) and (9). Despite this formality, the mechanism of reaction Eq.(12) is not necessarily comprised of the processes Eq. (6) and (9). It may not include NO as the intermediate reaction product. Also the reaction kinetics may be different from the kinetics of the formal constituent processes.

REACTIONS THERMODYNAMICS - It is possible to predict the direction of a reaction in a given reacting mixture as well as the equilibrium concentrations of reactants by thermodynamic calculations. From thermochemical properties of pure reactants the *standard Gibbs free energy of reaction* ΔG_r^0 can be calculated. The equilibrium constant of a reaction K_p is related to ΔG_r^0 as follows

$$K_p\langle T\rangle = \exp\left\{\frac{\Delta G_r^0\langle T\rangle}{RT}\right\} \qquad (14)$$

where R is the universal gas constant and T is the absolute temperature in K. Both K_p and ΔG_r^0 are functions of temperature. The equilibrium constant for an equilibrium reaction between ideal-gas species

$$aA + bB + \ldots \leftrightarrow lL + mM + \ldots \qquad (15)$$

can be written as

$$K_p\langle T\rangle = \frac{(P_L)^l (P_M)^m \ldots}{(P_A)^a (P_B)^b \ldots} \qquad (16)$$

where P_i denotes the equilibrium partial pressure of species *i* in atmospheric units. Eq.(16) solved together with the stoichiometric mass balance of the reaction allows for the calculation of equilibrium partial pressures and concentrations in the reacting mixture.

Some of the nitrogen oxides reactions have been collected in Table 2. The standard Gibbs free energy of reaction and logarithms of equilibrium constant are listed for the temperature of 700 K (427°C).

High value of equilibrium constant means that the given reaction may proceed to the right side of its equation. Equilibrium constant close to 1, $\ln(K_p)\approx 0$, indicates that equilibrium concentrations of products and reactants are comparable. The reaction, depending on the actual concentrations, may be in the proximity of its equilibrium point. Eq.(16) must be solved together with the mass balance to find out which direction can the reaction proceed. Very low equilibrium constant (negative $\ln(K_p)$) points that the reaction would proceed to the left side of its equation.

Reaction Eq.(2) - synthesis of NO - is the only reaction with a negative $ln(K_p)$ and the corresponding K_p of $8.2 \cdot 10^{-7}$. The generation of NO from oxygen and nitrogen under conditions in diesel exhaust is not possible. From the thermodynamic reasons the reaction can proceed only to the left side of the equation. NO in diesel exhaust is predisposed to decompose into oxygen and nitrogen. The rate of this reaction, however, is very low. At temperatures below 700°C the speed of spontaneous NO decomposition equals practically zero.

Reaction Eq.(1) - oxidation of NO to NO_2 - is close to its equilibrium point at high temperatures in diesel exhaust. At 427°C the equilibrium constant amounts to $exp(0.9) = 2.4$. The NO equilibrium curve is shown in Fig.6. The speed of NO oxidation on the Pt catalyst was high. Equilibrium constraints limited progress of the reaction at higher temperatures.

The reaction Eq.(4) - disproportionation of NO - shows the logarithm of K_p of 14.87 corresponding to a high value of $K_p = 2.9 \cdot 10^6$. There is no thermodynamic constraint on the progress of this process.

The other reactions in Table 2 present oxidation, by either NO or NO_2, of hydrocarbons, carbon monoxide and carbon of diesel particulates. Dodecane ($n\text{-}C_{12}H_{26}$) served as a representative of hydrocarbons, Eqns.(5a) and (8a). All of the reactions exhibit very high equilibrium constants. Logarithm of K_p varies between 29 and 52.2 yielding equilibrium constants from $3.8 \cdot 10^{12}$ to $4.5 \cdot 10^{22}$. There are no thermodynamic constraints for the oxidation of HC, CO or diesel particulate matter (DPM) by NO_x in diesel exhaust.

Table 2
Nitrogen Oxides Reactions Equilibrium Constant @700K

Reaction		$\Delta G_r^{0,700}$ kcal/gmole	$\ln(K_p^{700})$
$\frac{1}{2}N_2 + \frac{1}{2}O_2 \leftrightarrow NO$	(2)	19.49	-14.0
$NO + \frac{1}{2}O_2 \leftrightarrow NO_2$	(1)	-1.19	0.9
$2NO \leftrightarrow NO_2 + \frac{1}{2}N_2$	(4)	-20.69	14.87
$NO + \frac{1}{25}C_{12}H_{26} \leftrightarrow \leftrightarrow \frac{1}{2}N_2 + \frac{12}{25}CO + \frac{13}{25}H_2O$	(8a)	-70.47	50.7
$NO + CO \leftrightarrow \frac{1}{2}N_2 + CO_2$	(9)	-72.54	52.2
$NO + C \leftrightarrow \frac{1}{2}N_2 + CO$	(10)	-60.96	43.8
$NO_2 + \frac{1}{25}C_{12}H_{26} \leftrightarrow \leftrightarrow NO + \frac{12}{25}CO + \frac{13}{25}H_2O$	(5a)	-49.78	35.8
$NO_2 + CO \leftrightarrow NO + CO_2$	(6)	-51.85	37.3
$NO_2 + C \leftrightarrow NO + CO$	(7)	-40.28	29.0

Nitrogen oxides can undergo several different reactions, as shown in Table 2. Particular reactions compete for NO or NO_2, quantities of which are limited. The consumption of NO_x in different reactions depends on their speed. Equilibrium calculations yield no indication on the reaction speed. The numbers in Table 2 do not indicate which reactions are more likely to occur. It is perfectly possible that a reaction with lower equilibrium constant would proceed faster than a competitive reaction with high equilibrium constant. Speed of reactions can be selectively modified by a catalyst.

DISCUSSION OF NO_X RESULTS

Two patterns in the NO_x performance were occurring. The first one is that of *NO_x reduction* demonstrated by the Pt catalyst at temperatures above 250°C. The other one is the *generation* of small amounts of NO_x occurring on the Pd catalyst as well as on the Pt catalyst at low temperatures.

REDUCTION OF NO_X - The reduction of NO_x was the net effect of a decrease of NO concentration accompanied by an increase of NO_2. The overall performance exhibited by the platinum catalyst and expressed in terms of total NO_x was very similar to a lean NO_x catalyst performance.

One of conceivable mechanisms is that of the selective NO reduction by hydrocarbons in lean NO_x catalysts. It is known that Pt/Al_2O_3 catalysts show the NO_x reduction activity under lean conditions. The conversion curve shows a maximum performance between 300°C and 400°C which is typical for that kind of device. The selective NO reduction mechanism is ussually explained by the reaction with hydrocarbons, Eq.(8), and, possibly, reactions (9) and (10) as well. These processes could have been happening in the Pt catalyst to a certain degree. However, they can not account for the observed NO_2 concentration profiles.

The changes in NO_2 concentration over the temperature range followed in a very systematic manner those of NO. The regularity is well pronounced in the ramp test with platinum catalyst. Changes in concentrations of both NO and NO_2 were plotted in Fig.7 - top left graph. There is a significant coincidence in temperature (250°C) where neither NO_2 nor NO change their concentrations in the catalyst. This is the point, indicated by arrows in Fig.6, where the inlet and outlet concentration profiles of both NO and NO_2 cross. The increase of NO_2 concentration mirrors the decrease of NO with a scaling factor. The scaling factor amounts to 7 and is constant over the whole temperature range where the net reduction of NO_x takes place. Most likely, NO and NO_2 are parts of one reaction chain and their changes are related by some reaction stoichiometry.

The mirroring of NO and NO_2 concentration profiles implies that NO_2 is an important step in the NO_x removal mechanism. The suggested mechanism of NO_x removal begins with the catalytic oxidation of NO to NO_2 by means of oxygen present in the exhaust gas (Eq.(1)). Generated NO_2 reduces thereafter with the formation of nitrogen. Processes yielding the formation of N_2 from NO_2 could be either reactions with other components of diesel exhaust, Eq.(11)-(13), or direct decomposition of NO_2 into nitrogen and oxygen. In reality a combination of all the processes was probably taking place. Reaction with hydrocarbons seems to be confirmed by the maximum of the HC conversion curve in the Pt catalyst, Fig.5. The maximum hydrocarbons conversion correlates with the maximum NO_x conversion from Fig.7. A quantitative analysis, however, shows that the observed NO_x reduction was higher than the corresponding total change of reducing material, including hydrocarbons, CO as well as DPM. The DPM estimate was based on typical particulate emission from the test engine during ramp tests. To explain the NO_x reduction one must assume that some decomposition of NO_2 was happening as well.

The above consecutive $NO \rightarrow NO_2$ model accounts for the correlation in the NO and NO_2 concentration profiles and for the imbalanced but correlated changes of NO and NO_2. It also explains the declining NO_x reduction at higher temperatures by the thermodynamic constraints of the NO oxidation.

A possible parallel process is the disproportionation of NO, Eq.(4). Nitric oxide disappears from the system and nitrogen dioxide is generated. The reaction stoichiometry yields the total NO_x reduction of 50%. It is not possible to conclude if this process was occurring in the Pt catalyst. However, no matter what was its extent, it could account for an NO reduction not exceeding the NO_2 increase multiplied by the stoichiometric factor of 2 (Eq.(4)). As the experimental data show that the NO decrease is 7 times as high as the corresponding NO_2 increase, reaction Eq.(4) can not explain by itself the observed NO_x reduction.

NO_2 may play an important role in the lean NO_x catalyst chemistry. It is commonly known that NO_2 has more oxidizing character than NO. As such, it is more likely to react with exhaust gas hydrocarbons than NO. The quantities of NO_2 are significant, especially in platinum containing catalysts where a large fraction of NO is converted to NO_2. Unfortunately, most of the research done on the lean NO_x catalyst is not concerned with NO_2. Experimental work is usually limited to measurements of the total NO_x and the process mechanisms are explained by reactions of NO.

There are recent literature reports suggesting that NO_2 may be a reaction intermediate in the Cu/ZSM5 lean NO_x catalyst *[12]*. Presence of oxygen was found to be critical for the NO_x reduction. The reaction mechanism was explained by the formation of NO_2 intermediate on the copper sites. So far, there have been no reports on the role of NO_2 in a Pt/Al_2O_3 catalyst. However, the importance of oxygen for the platinum lean NO_x catalyst performance has been reported. Engler et al. *[13]* investigated the influence of the oxygen content on the lean NO_x Pt catalyst performance. They found that in the absence of oxygen no NO_x conversion was taking place. That conclusion could not be explained by the assumed NO reaction model. As the presence of oxygen is a necessary condition in the NO_2 model, Engler's results are in fact another indication that nitrogen dioxide might be a reaction intermediate on the platinum catalyst as well.

GENERATION OF NO - The generation of NO by the palladium catalyst and the platinum catalyst at low temperature is not possible within the discussed set of reactions. Nitrogen dioxide may react with reducing agents to form NO, Eq.(5)-(7). The amount of NO generated, however, cannot be higher than that of NO_2 which disappears from the system. The opposite was recorded in this study. Up to 25 ppm of NO was generated with the accompanying decrease of NO_2 of about 3 ppm.

No constant ratio between the reaction changes of NO and NO_2 was found. Also, the temperature ranges for the two reactions were different, implying that two separate processes were taking place. The decrease of NO_2 was most likely due to its reactions with reducing exhaust gas components, Eq.(5)-(7) and (11)-(13). There was no indication that NO is

oxidized in the Pd catalyst. The engine out NO_2 was significantly reduced in the whole temperature range.

Some NO generation could be attributed to the catalytic oxidation of nitrogenated hydrocarbons. Their sources would be several nitrogen containing lube oil additives *[14]*, products of the nitration of lube oil hydrocarbons by the blowby exhaust gas in the crankcase *[15]* and nitrogen containing compounds of diesel fuel *[16]*. Simple calculations show, however, that this hypothesis would explain NO generation of a few ppm only and cannot account for the NO levels of 25 ppm found in this study. Admittedly, authors do not have a good theory for the mechanism of NO generation in the Pd catalyst.

CONCLUSIONS

(1) The platinum catalyst increased nitrogen dioxide concentration by up to 25 ppm. The increase of NO_2, however, was accompanied by a many times higher decrease of NO. The catalyst exhibited the lean NO_x performance with a maximum nitrogen oxides conversion efficiency of 22%.

(2) The results indicate that NO_2 played an important role in the lean NO_x catalyst reaction mechanism. In the first step NO was catalytically oxidized to NO_2. Generated NO_2 reacted subsequently to N_2 with either hydrocarbons, diesel particulates or CO as well as decomposed. Some disproportionation of NO into N_2 and NO_2 was also possible.

(3) Both NO_2 generation and total NO_x reduction on Pt catalyst show maximum between 350 and 400°C. The declining performance at higher temperatures is attributed to thermodynamic constraints of the oxidation of NO.

(4) Engine out NO_2 was reduced on the palladium catalyst throughout the tested temperature range. This was accompanied by more than equivalent increase of NO. The total NO effect was insignificant from the practical point of view with the maximum NO_x generation of 3%.

(5) Platinum catalyst was very active in respect to CO and hydrocarbons. The activity of the palladium catalyst at high temperatures (400°C) matched that of the Pt DOC, but the light-off temperatures were higher by more than 100°C.

(6) Underground mines experiencing problems with NO_2 levels should use diesel oxidation catalysts tested specifically for the NO/NO_2 shift. Some DOCs might deteriorate the ambient air quality situation while others can effectively reduce the engine out NO_2.

RECOMMENDATION - Most of the experimental work in the lean NO_x catalyst research is limited to total NO_x measurements. It is believed that separate measurements and analysis of NO *and* NO_2 are more appropriate and would cast more light on the catalytic NO_x reduction mechanism in lean exhaust.

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