

# PLASMA-ASSISTED HETEROGENEOUS CATALYSIS FOR NO<sub>x</sub> REDUCTION IN LEAN-BURN ENGINE EXHAUST

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## INTRODUCTION

The NO<sub>x</sub> in engine exhausts is composed primarily of NO. Consequently, aftertreatment schemes have focused a great deal on the reduction of NO. Recent developments in catalytic control of NO<sub>x</sub> are revealing the significance of NO<sub>2</sub> as an intermediary for achieving higher NO<sub>x</sub> removal efficiencies.

The leading catalytic technologies for removal of NO<sub>x</sub> from lean-burn engine exhausts are the lean-NO<sub>x</sub> SCR catalyst [1-2] and the lean-NO<sub>x</sub> trap [3-5].

Selective catalytic reduction (SCR) is based on the reaction of NO with hydrocarbon species activated on the catalyst surface. Many studies now suggest that the conversion of NO to NO<sub>2</sub> is an important intermediate step in the reduction of NO<sub>x</sub> to N<sub>2</sub> [6-10]. The formation of NO<sub>2</sub> has been found to be a necessary but not a sufficient condition for the SCR of NO.

The lean-NO<sub>x</sub> trap involves the catalytic oxidation of NO to NO<sub>2</sub>, followed by the formation of a nitrate on the surface. The nitrate stored on the surface is decomposed by periodically operating under rich-burn condition and so the released NO<sub>x</sub> is reduced.

Both lean-NO<sub>x</sub> SCR and lean-NO<sub>x</sub> trap technologies require low sulfur fuel because catalysts that are active in converting NO to NO<sub>2</sub> are also active in converting SO<sub>2</sub> to SO<sub>3</sub>. SO<sub>3</sub> leads to the formation of sulfuric acid and sulfates that increase the particulates in the exhaust and poison the active sites on the catalyst.

This paper discusses the combination of a plasma with a catalyst to improve the reduction of NO<sub>x</sub> under lean-burn conditions. We have been investigating the effects of a plasma on the NO<sub>x</sub> reduction activity and temperature operating

window of various catalytic materials. One of our goals is to develop a fundamental understanding of the interaction between the gas-phase plasma chemistry and the heterogeneous chemistry on the catalyst surface. We have observed that plasma assisted heterogeneous catalysis can facilitate NO<sub>x</sub> reduction under conditions that normally make it difficult for either the plasma or the catalyst to function by itself. By systematically varying the plasma electrode and catalyst configuration, we have been able to elucidate the process by which the plasma chemistry affects the chemical reduction of NO<sub>x</sub> on the catalyst surface.

We have discovered that the main effect of the plasma is to induce the gas-phase oxidation of NO to NO<sub>2</sub>. The reduction of NO<sub>x</sub> to N<sub>2</sub> is then accomplished by heterogeneous reaction of O with activated hydrocarbons on the catalyst surface. The use of a plasma opens the opportunity for a new class of catalysts that are potentially more durable, more active, more selective and more sulfur-tolerant compared to conventional lean-NO<sub>x</sub> catalysts.

## TEST SETUP

Figure 1 shows one of the possible embodiments of the plasma-assisted catalyst processor. In this setup the plasma reactor is located upstream of the catalyst reactor. The same result is achieved if the catalyst is placed inside the plasma reactor.

The plasma reactor used in our study is a pulsed corona discharge reactor consisting of a metal wire inside a metal cylinder. The power supply is a magnetic pulse compression system that delivers up to 30 kV output into 100 ns pulses at repetition rates up to the kilohertz range. The catalyst structures we have investigated consisted of either a pellet bed or a monolith.

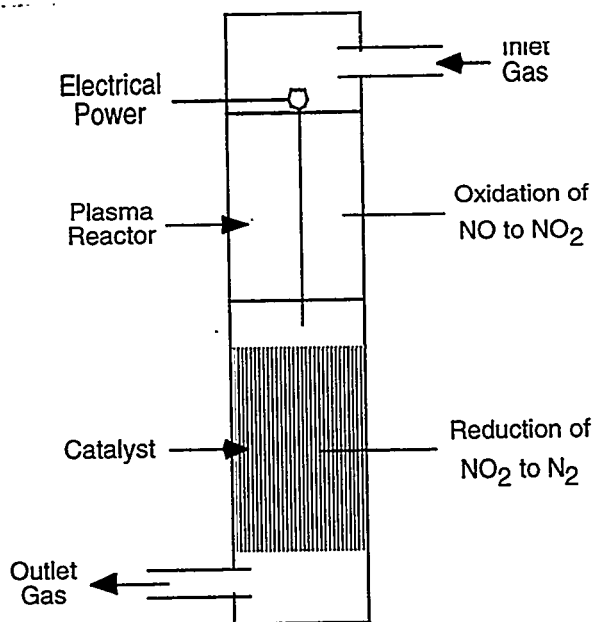


Figure 1. An embodiment of the plasma-assisted SCR process. The same result is achieved if the catalyst is placed inside the plasma reactor.

Heater bands and thermocouples are used to provide active control of the plasma/catalyst processor temperature. The processor temperature can be adjusted from room temperature up to 5000C. This has been used to investigate the operating temperature window of the process.

The separate plasma/catalyst configuration in Figure 1 is very flexible. Although we have used a pulsed corona reactor, this type of reactor is not necessarily the only type that produces the same effect. It can be used with any type of plasma reactor and does not require a specific type of high-voltage power supply. All electrical discharge plasma reactors accomplish essentially the same gas-phase plasma chemistry for the same gas mixture [11-12].

The separate plasma/catalyst configuration is also very flexible with respect to the catalyst support structure. It can be used with a bed of catalyst pellets or a monolith. For monolith structures, any L/D (length/diameter) ratio can be accommodated.

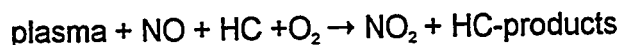
Tests of the plasma/catalyst processor have been done using both a simulated exhaust gas mixture and a real diesel engine exhaust. A gas

blending manifold is used to custom make gas streams consisting of  $N_2$ ,  $O_2$ ,  $H_2O$ ,  $CO_2$ , hydrocarbons, and  $NO_x$ . These gases are metered through mass flow controllers which permit exact control of the flow rate. After mixing in the manifold, the gas then passes through a temperature controlled heater which preheats the gas to the processor temperature. The use of custom-made gas mixtures is necessary for studying the effect of the gas composition on the gas-phase plasma chemistry and the activity of the catalyst. The effect of various gas components on the process products and process efficiency can thus be studied.

The plasma/catalyst processor is also connected to a generator set consisting of a Cummins B5.9 diesel engine. This enables us to test the process on a real diesel exhaust.

## HOW THE PROCESS WORKS

The plasma-assisted catalytic reduction of  $NO_x$  is accomplished in essentially two steps. First, the plasma oxidizes  $NO$  to  $NO_2$  in the presence of a hydrocarbon:



where HC refers to a hydrocarbon and HC-products refers to partially oxidized hydrocarbons. Second, the catalyst reduces  $NO_2$  to  $N_2$  by selective reduction using the hydrocarbons:

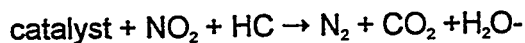


Figure 2 shows the FTIR spectra of the process for a model exhaust gas consisting of 500 ppm  $NO$ , 1000 PPM ( $C_3$ ) propene, 10%  $O_2$  and balance  $N_2$ . The plasma/catalyst processor temperature is 3000C.

The spectrum of the inlet gas is shown in the top box of Figure 2. When the electrical power to the plasma reactor is turned off and this gas mixture is passed through the catalyst, the efficiencies for both the  $NO_x$  reduction and the hydrocarbon oxidation are very low, as shown in the second box ("catalyst only"). The  $NO_x$  reduction at this temperature is very low in spite of the relatively large amount of hydrocarbons available for the catalyst to do SCR.

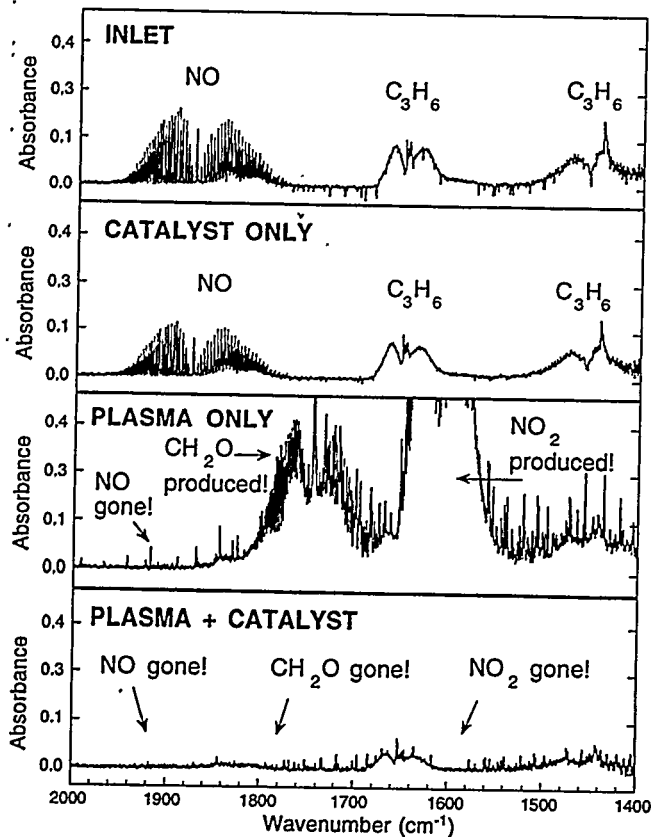


Figure 2. FTIR spectra showing the plasma-assisted catalytic reduction of  $\text{NO}_x$ .

When the electrical power to the plasma reactor is turned on, the  $\text{NO}$  is oxidized to  $\text{NO}_2$  and the propene is partially oxidized to formaldehyde, as shown in the third box ("plasma only"). The  $\text{NO}_x$  reduction is still very low. The same amount of total  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) is left in the gas stream.

When the  $\text{NO}_2$ -containing gas stream from the plasma is then passed through the same catalyst, both the  $\text{NO}_x$  and the hydrocarbons are eliminated, as shown in the bottom box ("plasma + catalyst"). This is true chemical reduction of  $\text{NO}_2$  to  $\text{N}_2$ , and not just absorption of  $\text{NO}_2$  on the catalyst surface. Both the original hydrocarbon and the partially oxidized hydrocarbons are eliminated in the process of reducing  $\text{NO}_2$  to  $\text{N}_2$ .

## KEY FEATURES

There are three key features in the plasma-assisted catalytic reduction of  $\text{NO}_x$ .

First, the plasma oxidation process is partial.

This means the plasma oxidizes  $\text{NO}$  to  $\text{NO}_2$  but does not further oxidize  $\text{NO}_2$  to nitric acid. The plasma also produces some partially oxygenated hydrocarbons, but does not completely oxidize the hydrocarbons to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Second, the plasma oxidation process is selective. This means the plasma oxidizes  $\text{NO}$  to  $\text{NO}_2$ , but does not oxidize  $\text{SO}_2$  to  $\text{SO}_3$ . This makes the plasma-assisted process more tolerant to the sulfur content of fuel compared to conventional lean- $\text{NO}_x$  technologies.

Third, by using a plasma to change the composition of  $\text{NO}_x$  from  $\text{NO}$  to  $\text{NO}_2$ , one can take advantage of a new class of catalysts that are potentially more durable and more active than conventional lean- $\text{NO}_x$  catalysts.

## ROLE OF HYDROCARBONS IN THE PLASMA

The use of a plasma does not automatically guarantee the efficient oxidation of  $\text{NO}$  to  $\text{NO}_2$ .

In exhausts containing both  $\text{O}_2$  and  $\text{H}_2\text{O}$ , the plasma produces not only  $\text{O}$  radicals but also  $\text{OH}$  radicals. The  $\text{O}$  radical can be effective in oxidizing  $\text{NO}$  to  $\text{NO}_2$ . However, the  $\text{OH}$  radical can further oxidize  $\text{NO}_2$  to nitric acid. This acid formation is not a desired part of the plasma process and has to be prevented.

The production of  $\text{O}$  radicals from electron-impact dissociation of  $\text{O}_2$  has an associated cost in electrical energy. The oxidation of one  $\text{NO}$  molecule will require at least one  $\text{O}$  radical:



For temperatures typical of engine exhausts, the oxidation of  $\text{NO}$  to  $\text{NO}_2$  by the  $\text{O}$  radical becomes very inefficient. At high temperatures (for example,  $3000^\circ\text{C}$ ), the  $\text{NO}$  to  $\text{NO}_2$  reaction is counteracted by the reduction reaction

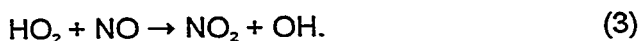


The  $\text{OH}$  radical can prevent the back conversion reaction (2), but does this at the expense of converting  $\text{NO}_2$  to nitric acid.

The hydrocarbon plays several important roles in

the plasma. The presence of the hydrocarbon prevents the formation of acid products and increases the efficiency for NO to NO<sub>2</sub> oxidation.

The hydrocarbon promotes the selective partial oxidation of NO to NO<sub>2</sub>. Instead of reacting with NO and NO<sub>2</sub>, the O and OH radicals preferentially react with the hydrocarbons. The hydrocarbons react with O and OH to produce HO<sub>2</sub> and RO<sub>2</sub>, where R is a hydrocarbon radical such as HCO and CH<sub>3</sub>O-. It is then the HO<sub>2</sub> and RO<sub>2</sub> radicals that oxidize NO to NO<sub>2</sub>. For instance,



The OH radical is reproduced when NO is oxidized by HO<sub>2</sub>. This OH radical will in turn decompose another hydrocarbon molecule and lead to the production of more HO<sub>2</sub> and RO<sub>2</sub> radicals. The decomposition of one hydrocarbon molecule leads to the oxidation of several NO molecules. The electrical energy requirement for conversion of NO to NO<sub>2</sub> is therefore decreased significantly.

Because the OH radical reacts preferentially with the hydrocarbon, the oxidation of NO<sub>2</sub> to nitric acid is prevented. If SO<sub>2</sub> is present in the exhaust, scav-enging of the O and OH radicals by the hydrocarbons will also prevent the oxidation of SO<sub>2</sub> to SO<sub>3</sub>.

The hydrocarbon serves important roles not only on the catalyst, but also in the plasma. For lean burn gasoline engine exhausts, the hydrocarbons are already present - mostly in the form of propene - typically at C<sub>3</sub> concentrations about twice that of NO. For diesel exhausts, the emitted gaseous hydrocarbon levels are much lower. However, the volatile organic fraction of the particulates could be a useful source of additional hydrocarbons.

## PROCESS PRODUCTS

Conventional low-temperature lean-NO<sub>x</sub> catalysts, such as those based on Pt, can achieve NO<sub>x</sub> reduction at the expense of producing N<sub>2</sub>O.

Figure 3 shows the concentrations of the N<sub>x</sub>O<sub>y</sub> species after the plasma/catalyst processor as a function of the input electrical energy density in

the plasma. Without the plasma (energy density = 0), only 20%NO<sub>x</sub> reduction is achieved by the catalyst. This is shown by the decrease in NO concentration, from 500 down to 400 ppm. This NO removal is true chemical reduction of NO to N<sub>2</sub>. Both the NO<sub>2</sub> and N<sub>2</sub>O concentrations are negligible.

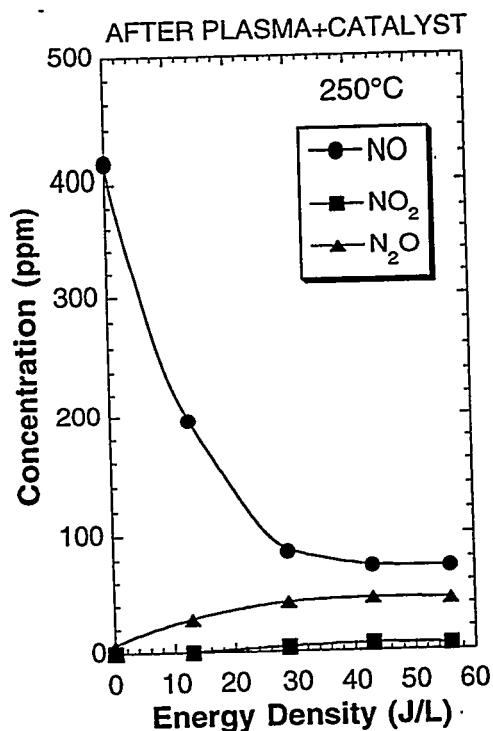


Figure 3. Plasma-assisted catalytic reduction of NO<sub>x</sub> in a model exhaust gas at 2500C.

As the electrical energy density input to the plasma is increased, more NO is removed by conversion to NO<sub>2</sub>. As the NO<sub>2</sub>-containing stream goes through the catalyst, the NO<sub>2</sub> is reduced, mostly to N<sub>2</sub>. As shown in Figure 3, the NO<sub>2</sub> concentration is very low after the plasma + catalyst. Also, only a relatively small amount of N<sub>2</sub>O is produced at 250°C and below, even when the overall NO<sub>x</sub> removal efficiency is high. At temperatures of 3000C and above, the formation of N<sub>2</sub>O is negligible.

As mentioned previously, the presence of hydrocarbons prevents the formation of nitric acid and SO<sub>3</sub> in the plasma.

## TREATMENT OF REAL DIESEL EXHAUST

Figure 4(a) shows the efficiency for plasma oxidation of NO to NO<sub>2</sub>, presented as a function of the electrical energy density in the plasma. Figure 4(b) shows the efficiency for reduction of NO<sub>x</sub> to N<sub>2</sub>, after the plasma and catalyst.

The results using the exhaust from a Cummins diesel engine are compared to those taken using the model exhaust gas. The processing of the real diesel exhaust and the simulated exhaust show very similar results in both the plasma and the catalyst.

## CONCLUSIONS

Plasma-assisted heterogeneous catalysis can enhance the NO<sub>x</sub> reduction under conditions that normally make it difficult for either the plasma or the catalyst to function by itself. By systematically varying the plasma electrode and catalyst configuration, we have been able to elucidate the process by which the gas-phase plasma chemistry affects the chemical reduction of NO<sub>x</sub> on the catalyst surface. Our results are consistent with recent studies that reveal the significance of NO<sub>2</sub> as an intermediary for achieving higher NO<sub>x</sub> removal efficiencies. We have shown that the main effect of the plasma is to enhance the gas-phase oxidation of NO to NO<sub>2</sub>. The reduction of NO<sub>x</sub> to N<sub>2</sub> is then accomplished by the heterogeneous reaction of NO<sub>2</sub> with activated hydrocarbons on the catalyst surface. The use of a plasma opens the opportunity for a new class of catalysts that are potentially more durable, more active, more selective, and more sulfur-tolerant compared to conventional lean-NO<sub>x</sub> catalysts.

Lean-NO<sub>x</sub> catalysts are inherently multi-functional when targeted towards NO. Recent studies have been devoted to separating the oxidative and reductive functions of the catalyst in a multi-stage system [13]. This method works fine for systems that require hydrocarbon addition; the hydrocarbon can be injected between the oxidation catalyst and the reduction catalyst. For a lean-burn exhaust that already has a significant amount of hydrocarbons, the oxidation catalyst for NO is also active for the oxidation of the hydrocarbon; this results in a decrease in the

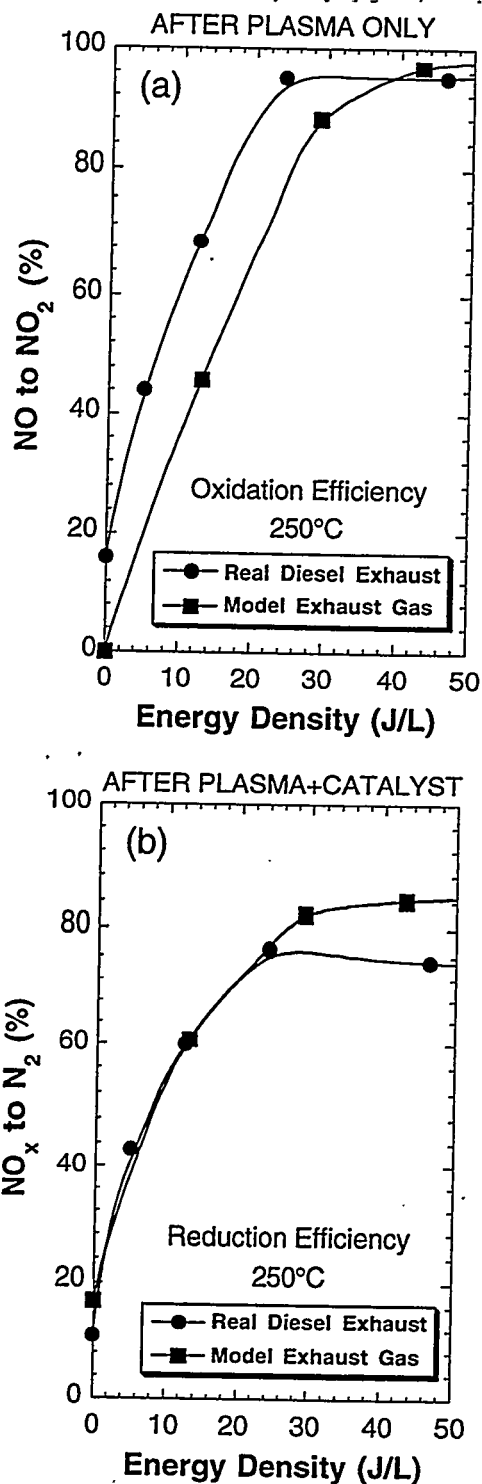


Figure 4. (a) Plasma oxidation efficiency and (b) NO<sub>x</sub> reduction efficiency, in a real diesel exhaust compared to those in the model exhaust gas.

efficiency of the hydrocarbon reductant. With plasma-assisted catalysis there is no longer a need to develop catalysts that can oxidize NO to NO<sub>2</sub> but not oxidize the hydrocarbon reductant. This method is also more tolerant to the sulfur content of the fuel because it will not oxidize SO<sub>2</sub>. The function of the catalyst can be greatly simplified by focusing on the reduction of NO<sub>2</sub>. Plasma-assisted NO<sub>x</sub> reduction can also work with both lean-NO<sub>x</sub> SCR and lean-NO<sub>x</sub> trap technologies:

The plasma-assisted catalytic reduction process is very flexible. It can be implemented with any type of plasma reactor and does not require a specific type of electrical power supply. This flexibility gives us the freedom to choose the least expensive and most durable plasma reactor power supply combination. The process can also accommodate any catalyst support structure. We can choose to put a bed of catalyst pellets inside the plasma reactor, or put a catalyst monolith downstream of the plasma reactor. In the latter case, the volumes of the plasma and the catalyst can be optimized separately.

## ACKNOWLEDGMENTS

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