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Exhaust Aftertreatment Using Plasma-Assisted Catalysis

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In the field of catalysis, one application that has been classified as a breakthrough technology is the catalytic reduction of NO_x in oxygen-rich environments using hydrocarbons [1]. This breakthrough will require dramatic improvements in both catalyst and engine technology, but the benefits will be substantial for energy efficiency and a cleaner environment. Engine and automobile companies are placing greater emphasis on the diesel engine because of its potential for saving fuel resources and reducing CO_2 emissions. The modern direct-injection diesel engine offers demonstrated fuel economy advantages unmatched by any other commercially-viable engine. The main drawback of diesel engines is exhaust emissions. A modification of existing oxidation catalyst/engine technology is being used to address the CO, hydrocarbon and particulates. However, no satisfactory solution currently exists for NO_x. Diesel engines operate under net oxidizing conditions, thus rendering conventional three-way catalytic converters ineffective for the controlling the NO_x emission. NO_x reduction catalysts, using ammonia as a reductant, do exist for oxygen-rich exhausts; however, for transportation applications, the use of on-board hydrocarbon fuels is a more feasible, cost-effective, and environmentally-sound approach.

Selective catalytic reduction (SCR) by hydrocarbons [2] is one of the leading catalytic aftertreatment technologies for the reduction of NO_x in lean-burn engine exhaust (often referred to as "lean-NO_x"). The objective is to chemically reduce the pollutant molecules of NO_x to benign molecules such as N_2. Aftertreament schemes have focused a great deal on the reduction of NO because the NO_x in engine exhaust is composed primarily of NO. Recent studies, however, have shown that the oxidation of NO to NO_2 serves an important role in enhancing the efficiency for reduction of NO_x to N_2. It has become apparent that preconverting NO to NO_2 could improve both the efficiency and durability of lean-NO_x catalysts. A non-thermal plasma is an efficient means for selective partial oxidation of NO to NO_2. The use of a non-thermal plasma in combination with a lean-NO_x catalyst opens the opportunity for catalysts that are more efficient and more durable compared to conventional catalysts [3].

The plasma inside a fluorescent lamp is perhaps the most common example of a non-thermal plasma. A non-thermal plasma is an electrically energized gas in which the average kinetic energy of the electrons is much higher than that of the gas molecules. The kinetic energy of the electrons is deposited primarily into the major gas components N_2, O_2, H_2O and CO_2. The most useful deposition of energy is associated with the production of N, O and OH radicals through electron-impact dissociation. Oxidation is the dominant process for gas mixtures containing dilute concentrations of NO in mixtures of N_2, O_2 and H_2O, particularly when the O_2 concentration is 5% or higher. In the absence of hydrocarbons, the O radicals will oxidize NO to NO_2, and the OH radicals will further oxidize NO_2 to nitric acid. In plasma-assisted catalysis it is important that the plasma oxidize NO to NO_2 without further producing acids.

Hydrocarbons play an important role in the selective reduction of NO_x to N_2 over the catalyst. The hydrocarbons also play an important role in the selective partial oxidation of NO to NO_2 in the plasma. In the presence of hydrocarbons, the NO is mainly oxidized to NO_2 by

$$NO + HO_2 \rightarrow NO_2 + OH$$
$$NO + ROO \rightarrow NO_2 + RO$$

where R is a hydrocarbon radical. The O and OH radicals produced by electron-impact dissociation are consumed mainly by reactions with the hydrocarbons rather than with NO. Nitric acid formation is minimized because the OH radical reacts preferentially with the hydrocarbon rather than with NO_2. The hydrocarbons lower the energy cost for the oxidation of NO by converting O and OH to HO_2; the OH radical is then reproduced when NO is oxidized by HO_2. This cyclic process leads to a very efficient utilization of the plasma-produced radicals and minimizes the electrical energy required by the plasma.

Figure 1 shows one of the possible embodiments of a plasma-assisted catalyst processor. There are many ways of producing a non-thermal plasma. The schematic shown in Figure 1 shows a plasma produced by short pulses of high voltage on a metal wire inside a metallic cylinder. The plasma serves to oxidize the NO and hydrocarbons to NO_2 and partially-oxidized hydrocarbon products, respectively. The plasma-conversion products are then reduced over the catalyst to N_2, CO_2 and H_2O.

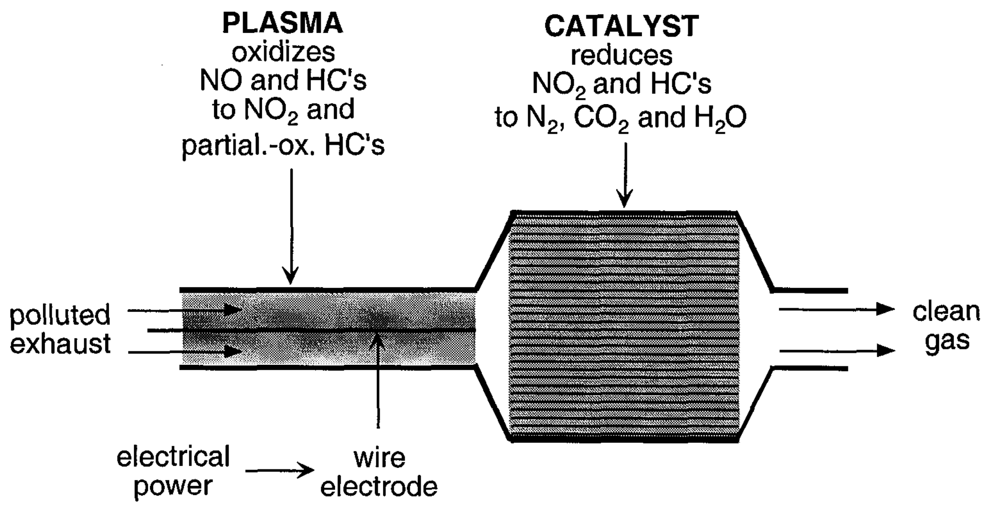

Figure 1. The plasma-assisted catalytic reduction process. Plasma-assisted catalysis has the potential to efficiently reduce NO_x and/or particulates without requiring precious metals or low-sulfur fuel. US Patents: No. 5,711,147, No. 5,891,409, No. 5,893,267.

Figure 2 shows Fourier Transform Infrared (FTIR) spectra illustrating the effect of catalyst, plasma and plasma-plus-catalyst combination on the NO_x and hydrocarbons. In this example, propene is used as the hydrocarbon reductant. When the electrical power to the plasma reactor is turned off and the 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"). When the electrical power to the plasma reactor is turned on, the NO is oxidized to NO_2 and the propene is partially oxidized to formaldehyde, as shown in the third box ("plasma only"). When the NO_2-containing gas stream from the plasma is then passed through the same catalyst, both the NO_x and the hydrocarbons are eliminated, as shown in the bottom box ("plasma + catalyst"). The plasma-plus-catalyst combination efficiently removes NO_x and hydrocarbons under conditions in which the plasma or the catalyst alone is ineffective.

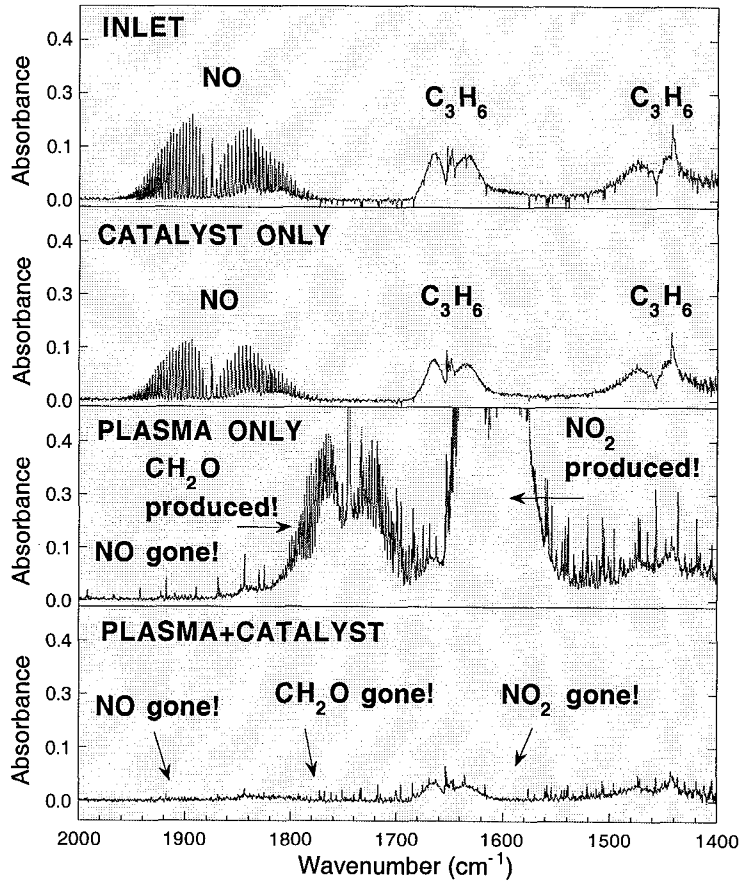

Figure 2. Fourier Transform Infrared (FTIR) spectroscopy data showing the effect of catalyst, plasma and plasma-plus-catalyst combination on the NO_x and hydrocarbons. The plasma-plus-catalyst combination efficiently removes NO_x and hydrocarbons under conditions where the plasma or the catalyst alone is ineffective.

There is a heated debate between engine and oil companies over the need to reduce sulfur in the fuel so that catalyst technologies can efficiently reduce tailpipe emissions of NO_x. State-of-the-art lean-NO_x catalysts require precious metals (e.g., platinum) to convert NO_x to N_2 with high efficiency, particularly at the relatively low temperatures (300 C and below) of diesel engine exhaust. In addition to oxidizing NO to NO_2, the precious metal is very effective in oxidizing SO_2 to SO_3. The SO_3 forms sulfate on the catalyst sites, leading to degradation of the NO_x reduction. The SO_3 also leads to the production of sulfuric acid, which adds to particulate emission. Furthermore, the precious metal is also very active in the oxidation of the hydrocarbons; this results in a decrease in the availability of the hydrocarbon as a reductant for NO_x.

Plasma-assisted catalysis can efficiently reduce NO_x without requiring precious metals or low-sulfur fuel. The plasma oxidizes NO to NO_2, but does not oxidize SO_2 to SO_3. This makes the plasma-assisted process more tolerant to the sulfur content of fuel compared to conventional lean-NO_x technologies. Furthermore, in a plasma, the hydrocarbons are converted to partially oxygenated hydrocarbons, but not completely oxidized to CO_x and H_2O. For some catalysts, the partially oxygenated hydrocarbons could be more effective compared to the original hydrocarbons in reducing NO_x to N_2. The plasma can efficiently oxidize NO to NO_2 over a wide range of temperature without depleting the amount of hydrocarbon available for reduction of NO_x to N_2.

In addition to lean-NO_x catalysis, NO_2 also plays an important role in other exhaust aftertreatment technologies. In lean-NO_x traps, the catalytic oxidation of NO to NO_2 on precious metals is followed by the formation of a nitrate on alkali or alkaline earth metal oxides [4]. In continuously regenerated particulate traps (CRT), a precious metal catalyst is used to oxidize NO to NO_2 upstream of a particulate filter; the NO_2 is then utilized to oxidize the carbon fraction of the trapped particulates [5]. The lean-NO_x trap and CRT technologies require low sulfur fuel because the catalyst component that is active in converting NO to NO_2 is also active in converting SO_2 to SO_3. The sulfur tolerance of these aftertreatment technologies can be substantially improved by using a non-thermal plasma for the selective partial oxidation of NO to NO_2.

References:

[1] "Breakthrough Catalytic Technologies: The Future," Chapter 12 in R.M. Heck and R.J. Farrauto, **Catalytic Air Pollution Control: Commercial Technology** (Van Nostrand Reinhold, New York, 1995) ISBN 0-442-01782-0.

[2] "Selective Catalytic Reduction of NO_x with N-Free Reductants", M. Shelef, Chem. Rev. **95**, 209 (1995).

[3] "Plasma-Assisted Catalytic Reduction of NO_x," B.M. Penetrante, R.M. Brusasco, B.T. Merritt, W.J. Pitz, G.E. Vogtlin, M.C. Kung, H.H. Kung, C.Z. Wan and K.E. Voss, SAE Paper Number 982508 (1998).

[4] "The New Concept 3-Way Catalyst for Automotive Lean-Burn Engine - NO_x Storage and Reduction Catalyst", N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, et al., *Catalysis Today* **27**, 63 (1996).

[5] Cooper, B.J., Jung, H.J. and Thoss, J.E., "Treatment of Diesel Exhaust Gases", US Patent 4,902,487 (February 20, 1990).

Acknowledgments

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Exhaust Aftertreatment Using Plasma-Assisted Catalysis

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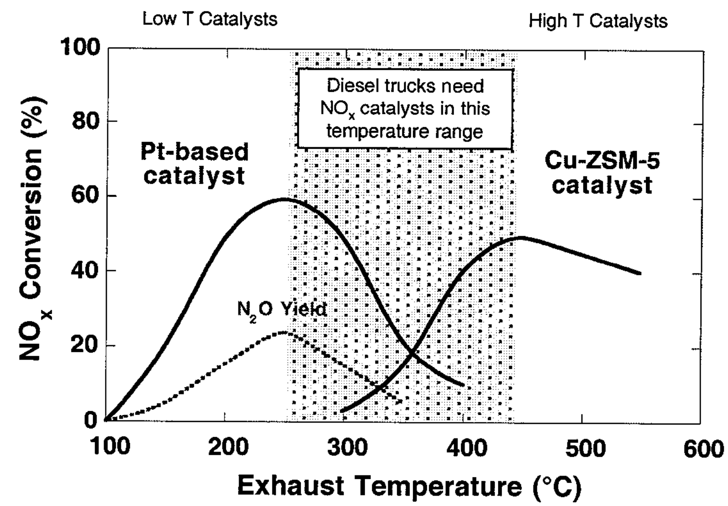
Lean-NO_x Catalysts

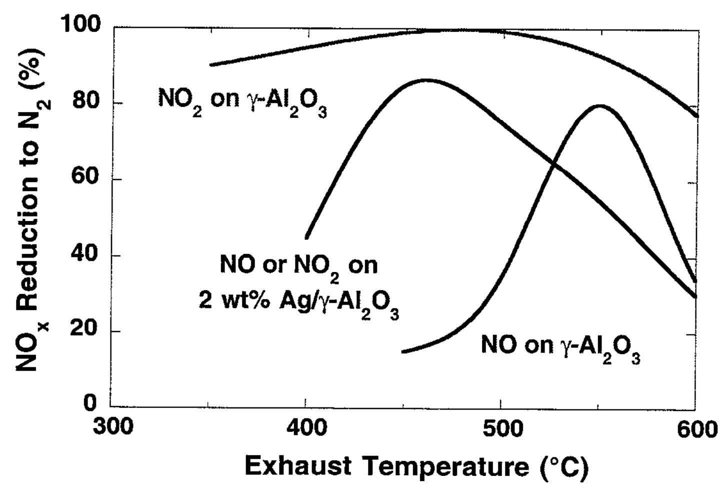


[R.M. Heck and R.J. Farrauto, *Catalytic Air Pollution Control: Commercial Technology* (1995)]

Lean-NO_x Catalysts

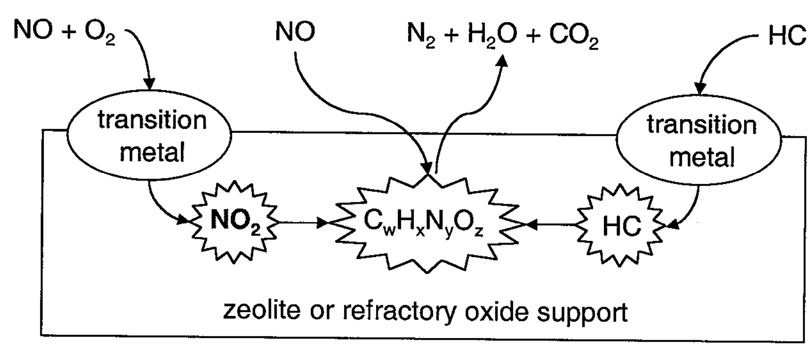
Advantages	Disadvantages
• Can use on-board HC • Good resistance to sulfur • Good durability of low T cat.	• Narrow temperature range • Void of NO_x conversion between low and high T cats. • N_2O formation with low T cat. • Low durability of high T cat.

NO_2 plays an important role in increasing the temperature range for lean-NO_x catalysis



[K.A. Bethe and H.H. Kung, "Supported Ag Catalyst for the Lean Reduction of NO with C_3H_6", *J. Catal.* 172, 93 (1997)]

Lean-NO_x Catalyst



The oxidation of NO to NO_2 also plays an important role in other aftertreatment technologies

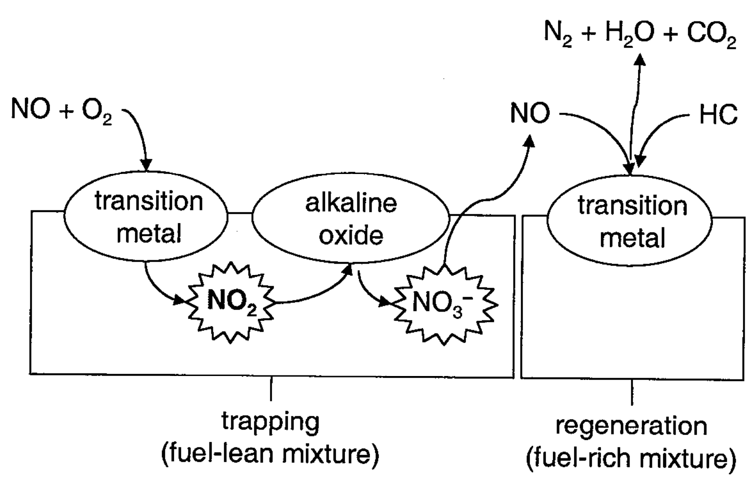
Lean-NO_x Trap

- The conversion to NO_2 is an essential step in the operation of lean-NO_x traps.

CRT

- NO_2 is responsible for the regeneration of continuously regenerated particulate traps.

Lean-NO_x Trap



Lean-NO_x Traps

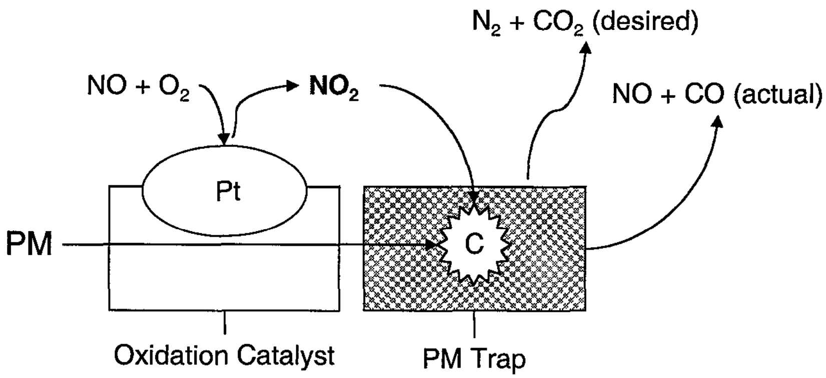
Advantages

- Active in 250 - 450°C range
- High NO_x conversion demonstrated

Disadvantages

- Easily deactivated by sulfur in the fuel
- HC slip during regeneration
- Possible high fuel penalty

Continuously Regenerated Particulate Trap (CRT)



CRTs

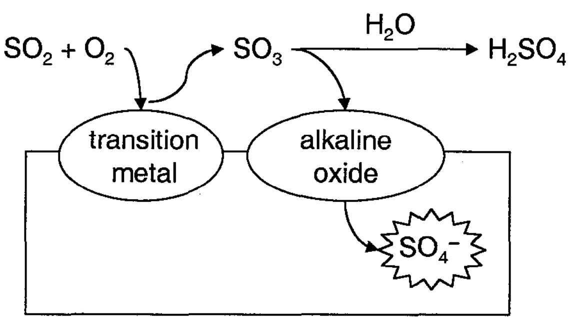
Advantages

- Trap regeneration scheme is passive
- Good performance demonstrated on low sulfur exhaust

Disadvantages

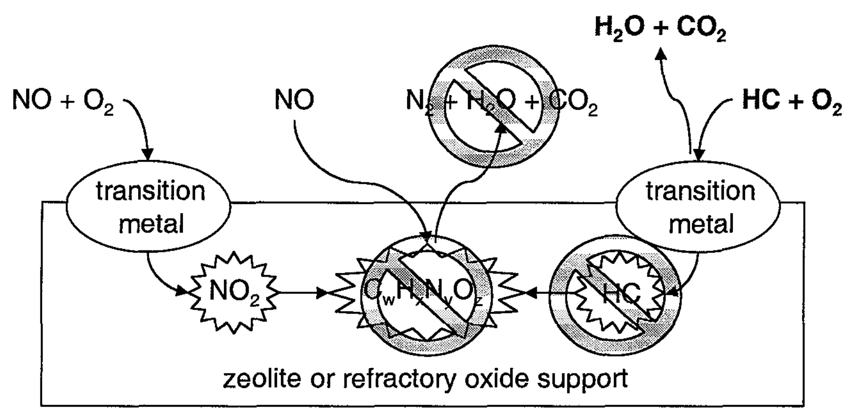
- Requires low sulfur fuel
- Requires Pt-loaded catalyst for oxidation of NO to NO_2

Catalysts that are effective in oxidizing NO to NO_2 are also good at oxidizing SO_2 to SO_3



SO_3 leads to degradation of NO_x trap efficiency and production of particulates in CRTs.

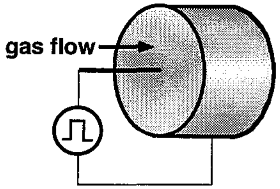
Catalysts that are effective in oxidizing NO to NO_2 are also good at oxidizing HCs to CO_2 and H_2O



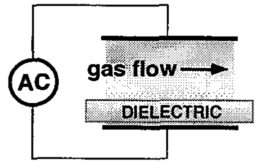
Oxidation of HCs leads to depletion of the reductant available for NO_x reduction in lean-NO_x catalysts.

Non-thermal plasmas can be used for the selective partial oxidation of NO to NO_2

Pulsed Corona



Dielectric Barrier



- Electrodes in atmospheric-pressure gas stream.
- High voltage is applied to accelerate the electrons.
- Hot electrons dissociate the background gas molecules to produce oxidizing radicals.
  - For example: $e + O_2 \rightarrow e + O + O$
    $O + NO \rightarrow NO_2$

[B.M. Penetrante *et al.*, "Plasma-Assisted Catalytic Reduction of NO_x", *SAE Paper 982508* (1998)]

How to produce a non-thermal plasma

- Apply high voltage (DC, AC or pulsed) to exhaust gas.
- Make sure electrical energy is consumed in accelerating electrons only. Avoid heating the gas above ambient to minimize electrical energy penalty.
- Electrons transfer energy to gas molecules by collisions, resulting in:
  - dissociation of N_2: $e + N_2 \rightarrow e + N + N$
  - dissociation of O_2: $e + O_2 \rightarrow e + O + O$
  - dissociation of H_2O: $e + H_2O \rightarrow e + OH + H$
- Only electrons do the useful work.
  - "HOT" electrons -- "COLD" gas

[B.M. Penetrante and S. E. Schultheis, *Non-Thermal Plasma Techniques for Pollution Control* (Springer-Verlag, New York, 1993)]

The hot electrons do not react directly with the NO_x molecules

- With 100's to 1000's of ppm of NO_x in the gas, the probability for direct dissociation of NO_x by the hot electrons is less than 1%!
- The hot electrons will collide mostly with the background N_2 and O_2 molecules.

The plasma can lead to chemical reduction and/or chemical oxidation

- Chemical Reduction

$$e + N_2 \rightarrow e + N + N$$
$$N + NO \rightarrow N_2 + O$$

- Chemical Oxidation

$$e + O_2 \rightarrow e + O + O$$
$$O + NO \rightarrow NO_2$$

Oxidation is the dominant process in the plasma whenever the exhaust gas contains O_2

[B.M. Penetrante *et al.*, "Fundamental Limits on NO_x Reduction by Plasma, *SAE Paper 971715* (1997)]

Hydrocarbons promote the selective oxidation of NO to NO_2 in a plasma

- Hydrocarbons react with O and OH to produce HO_2 and RO_2 (R = HCO, CH_3O, etc)
- NO converted to NO_2 by reaction with HO_2 and RO_2
  - $NO + HO_2 \rightarrow NO_2 + OH$
  - $NO + RO_2 \rightarrow NO_2 + RO$

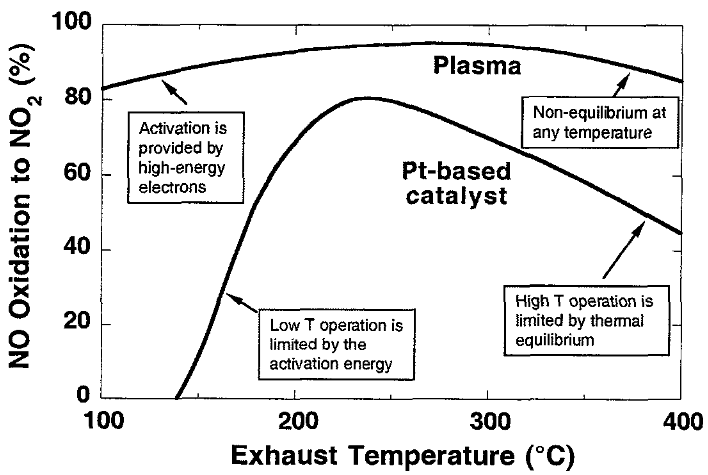
[B.M. Penetrante *et al.*, "Effect of Hydrocarbons on Plasma Treatment of NO_x", in *Proceedings of 1997 Diesel Engine Emissions Reduction Workshop*]

Hydrocarbons play three important roles in the plasma oxidation of NO to NO_2

- The plasma decomposition of one hydrocarbon molecule leads to the oxidation of many NO molecules.
  - Electrical power requirement for conversion of NO to NO_2 is reduced significantly.
- The hydrocarbons scavenge the OH radicals to prevent the conversion of NO_2 to nitric acid.
- The hydrocarbons scavenge the O and OH radicals to prevent the oxidation of SO_2 to SO_3.

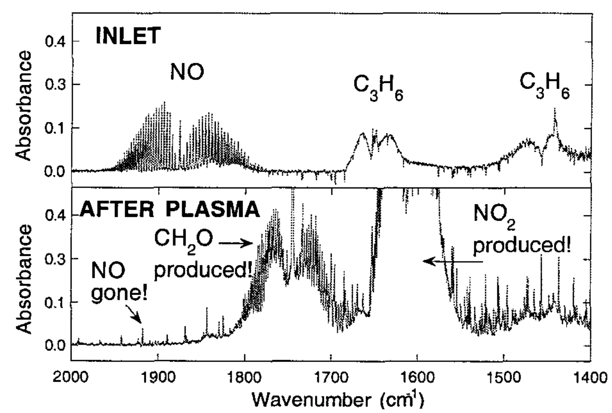
[B.M. Penetrante *et al.*, "Effect of Hydrocarbons on Plasma Treatment of NO_x", in *Proceedings of 1997 Diesel Engine Emissions Reduction Workshop*]

A non-thermal plasma can selectively oxidize NO to NO_2 over a wide temperature range



[based on Figs. 3-4 of B.M. Penetrante *et al.*, "Multi-Stage Selective Catalytic Reduction of NO_x in Lean-Burn Exhaust", in *Proceedings of 1997 Diesel Engine Emissions Reduction Workshop*]

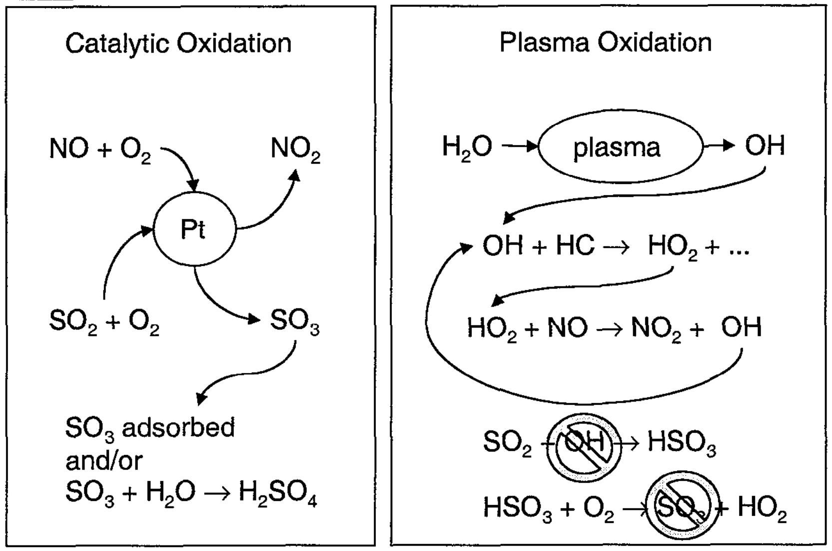
A non-thermal plasma can oxidize NO to NO_2 without depleting the HCs required for lean-NO_x catalysis



The partially-oxidized HCs are still effective for NO_x reduction in lean-NO_x catalysts.

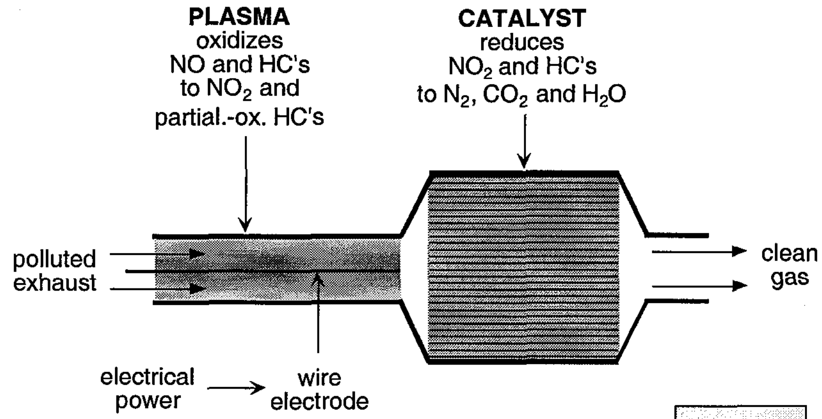
[B.M. Penetrante *et al.*, "Plasma-Assisted Catalytic Reduction of NO_x", *SAE Paper 982508* (1998)]

A non-thermal plasma can oxidize NO to NO_2 without oxidizing SO_2 to SO_3



[B.M. Penetrante *et al.*, "Sulfur Tolerance of Selective Partial Oxidation of NO to NO_2 in a Plasma", *SAE Paper 1999-01-3687* (1999)]

A non-thermal plasma can be used to enhance lean-NO_x catalysis



U.S. Patents
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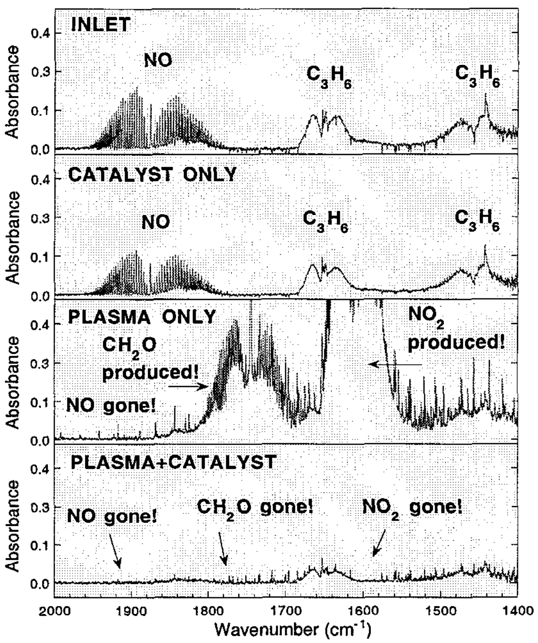
[B.M. Penetrante *et al.*, "Plasma-Assisted Catalytic Reduction of NO_x", *SAE Paper 982508* (1998)]



[B.M. Penetrante *et al.*, "Plasma-Assisted Heterogeneous Catalysis for NO_x Reduction in Lean-Burn Engine Exhaust", in *Proceedings of 1997 Diesel Engine Emissions Reduction Workshop*]

Conclusions

- The oxidation of NO to NO_2 plays an important role in several aftertreatment technologies.
  - Lean-NO_x catalysts
  - Lean-NO_x traps
  - Continuously regenerated particulate traps
- Plasma oxidation overcomes some of the problems encountered in conventional catalysis.
  - Wide temperature window
  - Does not deplete the hydrocarbons necessary for lean-NO_x catalysis
  - Tolerant of the sulfur content of the fuel