SAE TECHNICAL PAPER SERIES

982508

Plasma-Assisted Catalytic Reduction of NO_x

B. M. Penetrante, R. M. Brusasco, B. T. Merritt, W. J. Pitz and G. E. Vogtlin
Lawrence Livermore National Laboratory

M. C. Kung and H. H. Kung
Center for Catalysis and Surface Science, Northwestern University

C. Z. Wan and K. E. Voss
Engelhard Corporation

**Reprinted From: Plasma Exhaust Aftertreatment
(SP-1395)**

*The Engineering Society
For Advancing Mobility
Land Sea Air and Space®
INTERNATIONAL®*

**International Fall Fuels and Lubricants
Meeting and Exposition
San Francisco, California
October 19-22, 1998**

400 Commonwealth Drive, Warrendale, PA 15096-0001 U.S.A. Tel: (724) 776-4841 Fax: (724) 776-5760

The appearance of this ISSN code at the bottom of this page indicates SAE's consent that copies of the paper may be made for personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay a $7.00 per article copy fee through the Copyright Clearance Center, Inc. Operations Center, 222 Rosewood Drive, Danvers, MA 01923 for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale.

SAE routinely stocks printed papers for a period of three years following date of publication. Direct your orders to SAE Customer Sales and Satisfaction Department.

Quantity reprint rates can be obtained from the Customer Sales and Satisfaction Department.

To request permission to reprint a technical paper or permission to use copyrighted SAE publications in other works, contact the SAE Publications Group.

GLOBAL MOBILITY DATABASE

All SAE papers, standards, and selected books are abstracted and indexed in the Global Mobility Database

No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

ISSN 0148-7191
Copyright 1998 Society of Automotive Engineers, Inc.

Positions and opinions advanced in this paper are those of the author(s) and not necessarily those of SAE. The author is solely responsible for the content of the paper. A process is available by which discussions will be printed with the paper if it is published in SAE Transactions. For permission to publish this paper in full or in part, contact the SAE Publications Group.

Persons wishing to submit papers to be considered for presentation or publication through SAE should send the manuscript or a 300 word abstract of a proposed manuscript to: Secretary, Engineering Meetings Board, SAE.

Printed in USA

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 074-0188*

1. AGENCY USE ONLY (Leave blank)	**2. REPORT DATE** October 1998	**3. REPORT TYPE AND DATES COVERED** Technical report

4. TITLE AND SUBTITLE Plasma-Assisted Catalytic Reduction of NOx	**5. FUNDING NUMBERS** N/A
6. AUTHOR(S) 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	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) SAE International 400 Commonwealth Drive, Warrendale, PA 15096 Lawrence Livermore National Laboratory Center for Catalysis and Surface Science, Northwestern University Engelhard Corporation	**8. PERFORMING ORGANIZATION REPORT NUMBER** N/A
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203	**10. SPONSORING / MONITORING AGENCY REPORT NUMBER** N/A

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited.	**12b. DISTRIBUTION CODE** A

13. ABSTRACT ***(Maximum 200 Words)***

Many studies suggest that lean-NO_x SCR proceeds via oxidation of NO to NO_2 by oxygen, followed by the reaction of the NO_2 with hydrocarbons. On catalysts that are not very effective in catalyzing the equilibration of NO+O2 and NO2, the rate of N2 formation is substantially higher when the input NO_x is NO_2 instead of NO. The apparent bifunctional mechanism in the SCR of NO_x has prompted the use of mechanically mixed catalyst components, in which one component is used to accelerate the oxidation of NO to NO_2, and another component catalyzes the reaction between NO_2 and the hydrocarbon. Catalysts that previously were regarded as inactive for NO_x reduction could therefore become efficient when mixed with an oxidation catalyst. Preconverting NO to NO_2 opens the opportunity for a wider range of SCR catalysts and perhaps improves the durability of these catalysts. This paper describes the use of a non-thermal plasma as an efficient means for selective partial oxidation of NO to NO_2. When combined with some types of SCR catalyst, the plasma can greatly enhance the NO_x reduction and eliminate some of the deficiencies encountered in an entirely catalyst-based approach.

14. SUBJECT TERMS SERDP, SERDP Collection, NOx, SCR, plasma-assisted catalysis	**15. NUMBER OF PAGES** 10
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT unclass	**18. SECURITY CLASSIFICATION OF THIS PAGE** unclass	**19. SECURITY CLASSIFICATION OF ABSTRACT** unclass	**20. LIMITATION OF ABSTRACT** UL

982508

Plasma-Assisted Catalytic Reduction of NO_x

B. M. Penetrante, R. M. Brusasco, B. T. Merritt, W. J. Pitz and G. E. Vogtlin
Lawrence Livermore National Laboratory

M. C. Kung and H. H. Kung
Center for Catalysis and Surface Science, Northwestern University

C. Z. Wan and K. E. Voss
Engelhard Corporation

ABSTRACT

Many studies suggest that lean-NO_x SCR proceeds via oxidation of NO to NO_2 by oxygen, followed by the reaction of the NO_2 with hydrocarbons. On catalysts that are not very effective in catalyzing the equilibration of $NO+O_2$ and NO_2, the rate of N_2 formation is substantially higher when the input NO_x is NO_2 instead of NO. The apparent bifunctional mechanism in the SCR of NO_x has prompted the use of mechanically mixed catalyst components, in which one component is used to accelerate the oxidation of NO to NO_2, and another component catalyzes the reaction between NO_2 and the hydrocarbon. Catalysts that previously were regarded as inactive for NO_x reduction could therefore become efficient when mixed with an oxidation catalyst. Preconverting NO to NO_2 opens the opportunity for a wider range of SCR catalysts and perhaps improves the durability of these catalysts. This paper describes the use of a non-thermal plasma as an efficient means for selective partial oxidation of NO to NO_2. When combined with some types of SCR catalyst, the plasma can greatly enhance the NO_x reduction and eliminate some of the deficiencies encountered in an entirely catalyst-based approach.

I. INTRODUCTION

Lean-burn engines have attracted considerable attention because of their high fuel efficiency and lower emission of carbon dioxide. These engines operate under net oxidizing conditions, thus rendering conventional three-way catalysts ineffective for controlling the NO_x emission. The NO_x in engine exhaust is composed primarily of NO; consequently, aftertreament schemes have focused a great deal on the reduction of NO. Selective catalytic reduction (SCR) by hydrocarbons [1-2] is one of the leading catalytic aftertreatment technologies for the reduction of NO_x in lean-burn engine exhaust. In lean-NO_x SCR, the oxidation of NO to NO_2 serves an important role in enhancing the efficiency for reduction of NO_x to N_2.

This paper describes the use of a non-thermal plasma as an efficient means for selective partial oxidation of NO to NO_2. A short background on the significance of NO_2 in lean-NO_x SCR is given in Section II. The mechanism of plasma oxidation of NO to NO_2 is described in Section III. It is discussed why the plasma, by itself, cannot lead to the chemical reduction of NO_x to N_2 in lean-burn gas mixtures. The role of hydrocarbons in the plasma oxidation process is explained. In combination with some types of SCR catalyst, the plasma can greatly enhance the NO_x reduction. The plasma-assisted catalytic reduction process is described in Section IV. An example is then presented to demonstrate the improvement in NO_x reduction efficiency that can be accomplished by combining a representative SCR catalyst with a plasma.

II. SIGNIFICANCE OF NO_2 IN LEAN-NO_x SCR

Many studies suggest that lean-NO_x SCR proceeds via oxidation of NO to NO_2 by oxygen, followed by the reaction of the NO_2 with hydrocarbons [3-13]. On catalysts that are not very effective in catalyzing the equilibration of $NO+O_2$ and NO_2, the rate of N_2 formation is substantially higher when the input NO_x is NO_2 instead of NO. This has been observed on Na-ZSM-5 [9], Ce-ZSM-5 [9], γ-Al_2O_3 [3], H-ZSM-5 [3], ZrO_2 [14], and Ga_2O_3 [14]. It has also been observed that Group II metal oxides in general are much more effective in the SCR of NO_2 compared to NO [15].

The apparent bifunctional mechanism in the SCR of NO_x has prompted the use of mechanically mixed catalyst components, in which one component (for example, Mn_2O_3 or Mn_3O_4) is used to accelerate the oxidation of NO to NO_2 and another component (for example, Sn-ZSM-5 or In/Al_2O_3) catalyzes the reaction between NO_2 and the hydrocarbon [16-18]. Catalysts that previously were regarded as inactive for NO_x reduction could therefore become efficient when mixed with an oxidation catalyst.

The apparent role of NO_2 in the SCR of NO_x has also prompted the use of a multi-stage system in which an oxidation catalyst (for example, Pt-MFI zeolite) is used upstream of a reduction catalyst (for example, In-MFI or Zn-MFI zeolite) [19-20]. This latter method works fine particularly 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 efficiency of the hydrocarbon reductant.

It has been pointed out by Bethke et al. [21] and Chajar et al. [22] that the formation of gas phase NO_2 does not necessarily precede the formation of N_2. On catalysts such as Al_2O_3 that are less active in the oxidation of NO to NO_2, Bethke et al. [21] suggests that the N_2 production is higher using NO_2 than NO because of the higher surface coverage of adsorbed NO_2. The adsorbed NO_2 forms an adsorbed oxidized N-containing hydrocarbon intermediate. The reaction of this intermediate with NO is then the principal route to the production of N_2. For catalysts that deactivate due to coking, NO_2 helps maintain the activity by removing the surface carbonaceous species, resulting in an impression that NO_2 is a reagent for N_2 production. In any case, it is apparent that preconverting NO to NO_2 opens the opportunity for a wider range of SCR catalysts and perhaps improves the durability of these catalysts.

III. PLASMA PROCESS

A non-thermal plasma [23-25] is a very effective means for oxidizing NO to NO_2 in the gas-phase under lean-burn engine exhaust conditions. The use of a plasma can improve the NO_x reduction efficiency and eliminate some of the deficiencies encountered in an entirely catalyst-based approach. The plasma can oxidize NO to NO without depleting the amount of hydrocarbons available for SCR of NO_2 to N_2. The function of the SCR catalyst can thus be greatly simplified by focusing on the reduction of NO_2 by the hydrocarbon. Furthermore, the plasma can oxidize NO without oxidizing SO_2, thus making the process tolerant to the sulfur content of the fuel.

Previous studies [26-28] have shown that all electrical discharge plasma reactors produce a plasma with an average electron kinetic energy of around 3-6 eV. The plasma chemistry in discharge plasma reactors is therefore very similar regardless of electrode structure or the way the voltage is delivered to the reactor.

TEST SETUP – 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 electrical energy deposition into the gas is determined by monitoring the electrical parameters associated with the discharge. To obtain pulse energies a digital oscilloscope records both the voltage and current profiles. We measure the total current which contains both the discharge current and the current associated with charging the capacitance of the reactor. A computer data acquisition system reads the voltage and current profiles and integrates the product of the voltage and discharge current over the pulse duration to yield the pulse energy. The determination of the power input to the gas takes into account the capacitor charging current correction. The power input to the plasma processor was varied by changing either the pulse energy or pulse repetition frequency.

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 500°C. This has been used to investigate the operating temperature window of the process. The catalyst structures we have investigated in combination with the plasma consisted of either a pellet bed or a monolith.

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 permitted exact control of the flow rate. After mixing in the manifold, the gas then passes through a temperature controlled heater which preheated 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 gas composition is monitored with a chemiluminescent NO_x analyzer and a Fourier Transform Infrared (FTIR) spectrometer. Because our gas samples contain water in some experiments, we heat the FTIR cell (6-m path White cell) to 120°C to avoid condensation. In addition, we use a heated sample gas dilution and conditioning unit before the NO_x analyzer.

The plasma 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.

PLASMA WITHOUT HYDROCARBONS – In the plasma, oxidation is the dominant process for exhausts 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. The kinetic energy of the electrons is deposited primarily into the major gas components, N_2 and O_2. The most useful deposition of energy is associated with the production of N and O radicals through electron-impact dissociation:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S, ^2D) \qquad \text{(Eq. 1)}$$

$$e + O_2 \rightarrow e + O(^3P) + O(^3P, ^1D) \qquad \text{(Eq. 2)}$$

where $N(^4S)$ and $N(^2D)$ are ground-state and metastable excited-state nitrogen atoms, respectively, and $O(^3P)$ (simply referred to as O) and $O(^1D)$ are ground-state and metastable excited-state oxygen atoms, respectively. The $N(^4S)$ is the only plasma-produced species that could effectively lead to the chemical reduction of NO [24,29]:

$$N(^4S) + NO \rightarrow N_2 + O \qquad \text{(Eq. 3)}$$

In the presence of O_2, the oxidation pathway becomes dominant for two reasons:

a. The dissociation energy of O_2 is smaller than that of N_2. For electrical discharge plasma reactors, the average electron kinetic energy is low, around 3-6 eV.[26-28] Under this condition the rate for dissociation of O_2 is much higher compared to the dissociation of N_2.[23-24] The dissociation of O_2 will produce only oxidative radicals. The ground-state oxygen atom, $O(^3P)$, will convert NO to NO_2 via

$$O(^3P) + NO + M \rightarrow NO_2 + M \qquad \text{(Eq. 4)}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad \text{(Eq. 5a)}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad \text{(Eq. 5b)}$$

The metastable oxygen atom, $O(^1D)$, will react with H_2O to produce OH radicals:

$$O(^1D) + H_2O \rightarrow 2\,OH \qquad \text{(Eq. 6)}$$

The OH radicals will convert NO and NO_2 to nitrous and nitric acid, respectively.

b. High electron energies are required to optimize the production of $N(^4S)$ by electron-impact dissociation of N_2. Under conditions optimum for the dissociation of N_2, a large number of excited nitrogen atoms, $N(^2D)$, is produced [30-31]. The $N(^2D)$ species can lead to undesired reactions in the presence of O_2. Rather than reduce NO, the $N(^2D)$ species would react with O_2 to produce NO:

$$N(^2D) + O_2 \rightarrow NO + O \qquad \text{(Eq. 7)}$$

Because of the large rate constant [32] for reaction (7) and the large concentration of O_2 relative to NO, the $N(^2D)$ species preferentially reacts with O_2 to produce NO. In a lean-burn exhaust, the production of NO by $N(^2D)$ will counterbalance the reduction of NO by $N(^4S)$, thus effectively leaving oxidation as the only pathway for NO conversion. The effect of $N(^2D)$ on the NO_x conversion chemistry has been validated in comparison with experiments [24].

We examined the plasma processing of 100 ppm NO in a dry mixture of 10% O_2 and balance N_2, without hydrocarbons. The purpose of this experiment was to determine the efficiency for plasma oxidation of NO to NO_2 by the O radical. The NO_x concentrations for the cases at 100°C and 300°C are shown in Figures 1(a) and 1(b), respectively. They are plotted as a function of electrical energy density (J/L), which is the electrical power delivered to the plasma divided by the gas flow rate. The lines shown in the figures are fits to the experimental data points. For the 100°C case, about 60% of the NO are converted to NO_2 at energy densities of 40 J/L and above. For the 300°C case, the conversion of NO to NO_2 is only around 20% even at the high energy densities.

For a given energy density input, the NO_x conversion chemistry in the plasma is accomplished in tens of milliseconds. The plasma reactions can therefore accommodate very high space velocities. The factors that determine the products of the plasma chemistry are the energy density input, gas composition and gas temperature. Under some conditions, if the radical production rate in the plasma is too high and the initial NO_x concentration is low, some of the radicals could end up forming NO_x.

The efficiency for oxidation of NO to NO_2 drops as the temperature is increased. At high temperatures, the NO to NO_2 oxidation reaction is counteracted by the reduction reaction:

$$O + NO_2 \rightarrow NO + O_2 \qquad \text{(Eq. 8)}$$

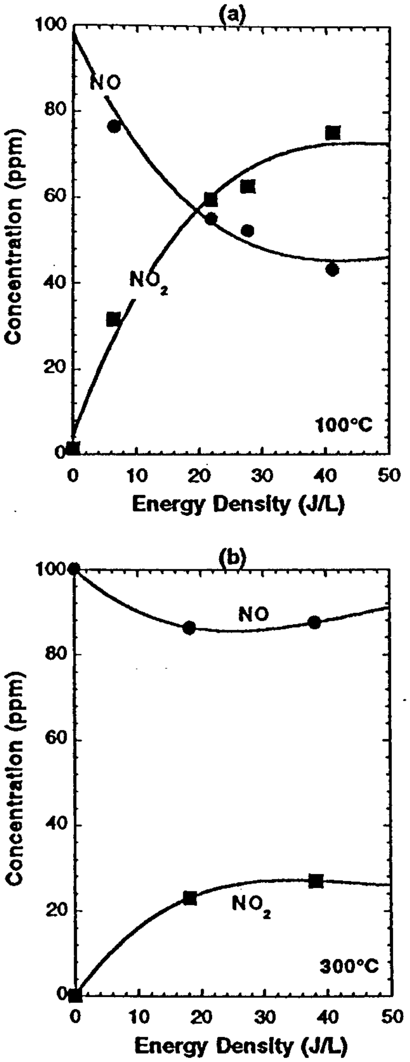

Figure 1. Effect of temperature on the plasma oxidation of NO in the absence of hydrocarbons. Plasma processing of 100 ppm NO in 10% O_2, balance N_2, at (a) 100°C and (b) 300°C.

Because of reaction (8), the oxidation of NO by the O radical is not efficient at high temperatures. We will show in the next section that the NO oxidation efficiency in the plasma can improve dramatically in the presence of hydrocarbons.

PLASMA WITH HYDROCARBONS – We next examined the effect of hydrocarbons on the plasma processing of NO. Propene was used as a representative hydrocarbon. The dry gas mixture contained 500 ppm NO in 10% O_2 and balance N_2. The purpose of this experiment was to determine how the hydrocarbon affects the plasma oxidation of NO to NO_2.

The NO_x concentrations for the cases without propene and with 1000 ppm propene are shown in Figures 2(a) and 2(b), respectively, for processing at 300°C.

For the case without propene (Figure 2(a)), less than 20% of the NO is converted to NO_2 even at the high energy densities. This is consistent with the previous observation shown in Figure 1(b).

The number of NO molecules converted to NO_2 is determined by the number of O radicals produced by the plasma, not by the initial NO concentration. The number of O radicals is determined only by the energy density input to the plasma.

At high temperatures, the efficiency for conversion of NO to NO_2 is poor in the absence of hydrocarbons in the gas stream. Figure 2(b) shows the NO_x concentrations when 1000 ppm of propene is added to this gas stream. The main fate of NO in the plasma in the presence of hydrocarbons is the oxidation of NO to NO_2.

In the absence of hydrocarbons, the number of NO molecules oxidized to NO_2 is determined by the number of O radicals, which is proportional to the energy density input to the plasma. Backconversion of NO_2 to NO by the O radical via reaction (8) decreases the oxidation efficiency. In the presence of hydrocarbons, the radical responsible for the oxidation of NO to NO_2 is no longer the O radical. It will be shown in the following chemical kinetics analysis that the HO_2 is the radical that oxidizes NO to NO_2 when the plasma processing is done in the presence of hydrocarbons. The number of HO_2 radicals produced in the plasma is a function of both the energy density input to the plasma and the hydrocarbon concentration in the gas stream.

The experiments were interpreted with a detailed chemical kinetics model for propene oxidation [33-35] which included reactions to treat the plasma [23] and NO_x kinetics. Thermodynamic properties for the relevant radicals and stable parents were obtained by group additivity using THERM [36] with updated H/C/O groups and bond dissociation groups [37]. The thermochemical data allow accurate calculation of reverse reaction rate constants by microscopic reversibility. The C_3 mechanism was updated in a number of ways. The reactions involving propane were updated from Ref. [38]. The NO_x submechanism from GRI Mech™ [39] has been added to the C_3 mechanism. Most of the reaction rate constants were taken from Refs. [40] and [41].

In the very early stages of reaction the propene is mainly consumed by the O atom:

$$C_3H_6 + O \rightarrow C_2H_5 + HCO \qquad \text{(Eq. 9)}$$

$$C_3H_6 + O \rightarrow CH_2CO + CH_3 + H \qquad \text{(Eq. 10)}$$

$$C_3H_6 + O \rightarrow CH_3CHCO + H + H \qquad \text{(Eq. 11)}$$

Abstraction reactions by O atoms do not contribute significantly to propene consumption at the low temperatures encountered in this study because of the higher activation energy of abstraction reactions compared to addition reactions.

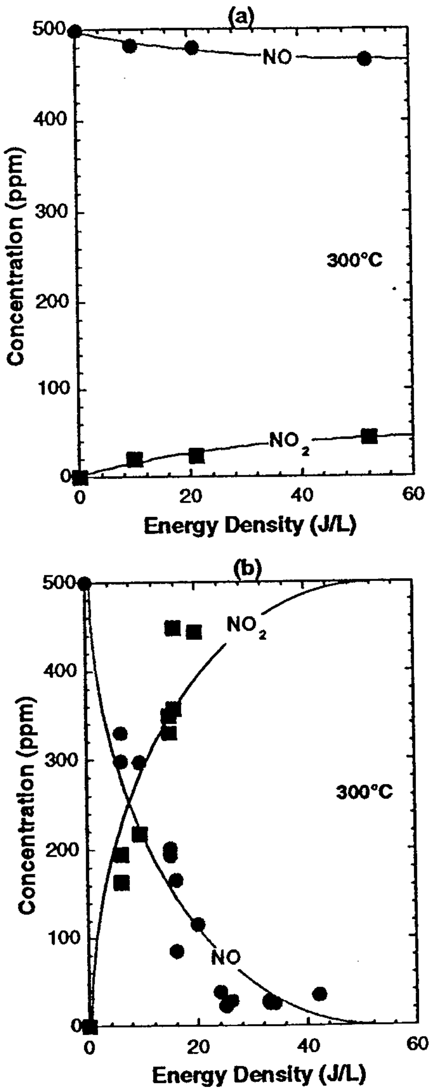

Figure 2. Effect of propene on the plasma oxidation of NO at 300°C. Plasma processing of 500 ppm NO in 10% O_2, balance N_2, (a) without propene, and (b) with 1000 ppm propene.

Of the total reaction with O atom, reaction (9) contributes 50%, and reactions (10) and (11) contribute 25% each. The O atoms are consumed more effectively by reactions (9)-(11) than reactions (4) and (5): $O + NO \rightarrow NO_2$.

At 300°C and early in the reaction, about 98% of the O atoms react with propene compared to 2% with NO. The rate constants for propene + O are much faster than that for NO + O. This result means that the propene consumes most of the O atoms that might otherwise react with NO to form NO_2.

After the initial stages of reaction, the OH radical rather than O atom becomes the main radical consuming propene:

$$C_3H_6 + OH \rightarrow C_3H_6OH \qquad \text{(Eq. 12)}$$

$$C_3H_6 + OH \rightarrow C_3H_5 + H_2O \qquad \text{(Eq. 13)}$$

where the C_3H_5 radical symbolizes all three isomers, which were distinguished individually in the reaction mechanism. The switch from O atom reactions to OH reactions is mainly due to OH being produced by the reaction

$$NO + HO_2 \rightarrow NO_2 + OH \qquad \text{(Eq. 14)}$$

Reaction (14) is also the main reaction that converts NO to NO_2.

In the presence of H_2O, electron-impact dissociation of H_2O would produce additional OH radicals. The metastable oxygen atom, $O(^1D)$, will react with H_2O to also produce OH radicals via reaction (6). These OH radicals will decompose the hydrocarbons, for example via reactions (12) and (13), and produce hydrocarbon radicals that convert NO to NO_2 in the presence of O_2.

The HO_2 radicals are also produced from reactions involving hydrocarbon intermediates of propene oxidation:

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \qquad \text{(Eq. 15)}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad \text{(Eq. 16)}$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad \text{(Eq. 17)}$$

$$H + O_2 \rightarrow HO_2 \qquad \text{(Eq. 18)}$$

Therefore, the propene supplies HO_2 radicals that convert NO to NO_2. Without the propene, the main reaction to convert NO to NO_2 are reactions (4) and (5): $O + NO \rightarrow NO_2$. Radical-radical reactions involving O and OH (such as $OH + O \rightarrow HO_2$) are not important because of the low concentrations of these radicals.

Nearly all the O atoms for conversion are supplied by electron impact, which has an associated cost in electrical energy. The propene lowers the energy requirement by production of HO_2 radicals that then become the main radical for conversion of NO to NO_2.

The OH produced from reaction (6) can also react with NO and NO_2 to form their related acids:

$$NO + OH \rightarrow HONO \qquad \text{(Eq. 19)}$$

$$NO_2 + OH \rightarrow HONO_2 \qquad \text{(Eq. 20)}$$

At 300°C, during the time when the propene is being consumed most rapidly, only about 6% of the OH react with NO and NO_2 while the remainder react mostly with propene and its aldehydic intermediate products. At 100°C, 15% of the OH react with NO and NO_2, while the remainder react mostly with propene and aldehydic intermediates. The rate constants for the NO_x + OH reactions are much slower than for propene + OH reactions, so that OH reacts mainly with propene rather than NO and NO_2 [42].

Because the OH radical reacts preferentially with the hydrocarbon, the oxidation of NO_2 to nitric acid is minimized. If SO_2 is present in the exhaust, scavenging of the O and OH radicals by the hydrocarbons will also minimize the oxidation of SO_2 to SO_3. Experimental data demonstrating how hydrocarbons prevent the oxidation of SO_2 to SO_3 will be shown in another paper.

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_1 concentrations about six times 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.

The hydrocarbons play three important functions in the plasma: (1) the hydrocarbons lower the energy cost for oxidation of NO to NO_2, (2) the hydrocarbons minimize the formation of acid products, and (3) the hydrocarbons prevent the oxidation of SO_2 to SO_3.

Figure 3 shows the efficiency for plasma oxidation of NO to NO_2 in a model exhaust gas consisting of 500 ppm NO, 1000 ppm C_3H_6, 10% O_2 and balance N_2. The plasma oxidation of NO in the presence of hydrocarbons can have high efficiency over a wide range of temperatures. In comparison, catalytic oxidation of NO to NO_2, e.g. using a Pt-based catalyst, can be accomplished only over a much narrower range of temperature.

IV. PLASMA-ASSISTED CATALYSIS

PROCESS – 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:

$$\text{plasma} + NO + HC + O_2 \rightarrow NO_2 + \text{HC-products}$$

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:

$$\text{catalyst} + NO_2 + HC \rightarrow N_2 + CO_2 + H_2O.$$

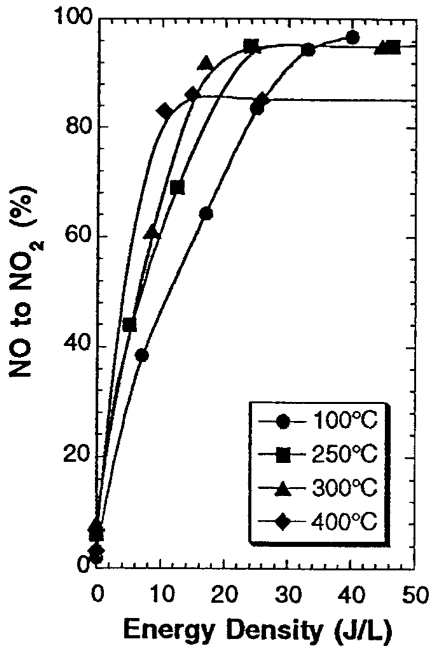

Figure 3. Oxidation of NO to NO_2 in a plasma. Gas mixture: 500 ppm NO, 1000 ppm C_3H6, 10% O_2, balance N_2.

There are three key features in the plasma-assisted catalytic reduction of NO_x.

- First, the plasma oxidation process is partial. This means the plasma oxidizes NO to NO_2 but does not further oxidize NO_2 to nitric acid. The plasma also produces some partially oxygenated hydrocarbons, but does not completely oxidize the hydrocarbons to CO_2 and H_2O. For some catalysts, the partially oxygenated hydrocarbons are much more effective compared to the original hydrocarbons in reducing NO_x to N_2.
- Second, the plasma oxidation process is selective. This means 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.
- Third, by using a plasma to change the composition of NO_x from NO to NO_2, one can take advantage of a new class of catalysts that are potentially more durable and more active than conventional lean-NO_x catalysts.

TEST SETUP – Figure 4 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.

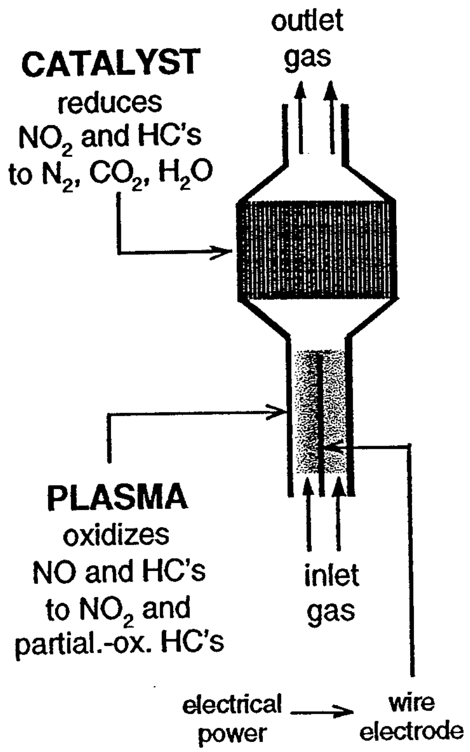

Figure 4. An embodiment of the plasma-assisted catalytic reduction process. The same result is achieved if the catalyst is placed inside the plasma reactor.

The separate plasma/catalyst configuration shown in Figure 4 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 [26-28].

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 exhaust from a Cummins B5.9 diesel engine.

CATALYST – The aim of this paper is to demonstrate the improvement in NO_x reduction efficiency that can be accomplished by combining an SCR catalyst with a plasma. For this purpose we have chosen γ-Al_2O_3 as a representative SCR catalyst for three reasons. First, many groups have shown that γ-Al_2O_3 is much more active as an SCR catalyst for the reduction of NO_2 compared to NO [3,43-47]. γ-Al_2O_3 is one of the best non-proprietary materials for taking advantage of the presence of

NO_2. Second, several studies [48-49] comparing a wide variety of SCR catalysts, including zeolites and metal oxides, have found γ-Al_2O_3 to be one of the most active for NO_x reduction by hydrocarbons. Third, γ-Al_2O_3 can be prepared in a hydrothermally stable form, thus making it a suitable catalyst or catalyst support for a practical device. Studies using a real diesel engine exhaust have shown that γ-Al_2O_3 retains its NO_x reduction activity over a long period of time [50].

In plasma-assisted catalysis, the NO_x to N_2 conversion is determined by the catalyst. Catalyst characterization has been done using a He background gas to establish real conversion of NO_x to N_2.

Combining a plasma with γ-Al_2O_3 can provide NO_x reduction efficiencies much higher than those achieved by the conventional approach of loading a metal on γ-Al_2O_3. Figure 5(a) shows the NO reduction to N_2 for γ-Al_2O_3. The temperature operating window occurs at a high temperature and is narrow. The addition of 2 wt% Ag to γ-Al_2O_3 increases the NO reduction in the lower temperature region, as shown in Figure 5(b). When the input gas feed contains NO_2 instead of NO, the NO_x reduction activity over γ-Al_2O_3 increases dramatically over a wide range of temperature, as shown in Figure 5(c).

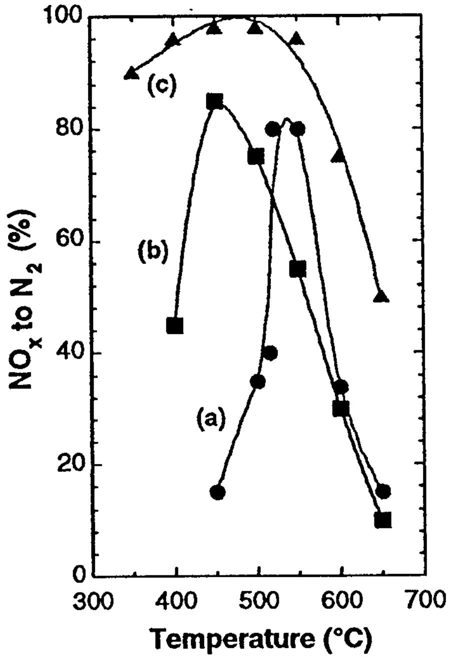

Figure 5. NO_x reduction to N_2 as a function of temperature. (a) NO over γ-Al_2O_3, (b) NO or NO_2 over 2 wt% Ag/Al_2O_3, (c) NO_2 over γ-Al_2O_3. Catalyst weight, 0.25 g. Dry gas feed, 1000 ppm NO or NO_2, 1000 ppm C_3H6, 6% O_2, balance He at 100 mL/min. Space velocity = 12,000 /hr. Data taken from Ref. [46].

Figure 6(a) shows the NO reduction to N_2 for 2 wt% Co/Al_2O_3. With the same catalyst, the reduction activity in the lower temperature region is increased when the input gas feed contains NO_2 instead of NO, as shown in Figure 6(b). However, when NO_2 is used with pure γ-Al_2O_3, the NO_x reduction activity is higher over a much wider range of temperature, as shown in Figure 6(c).

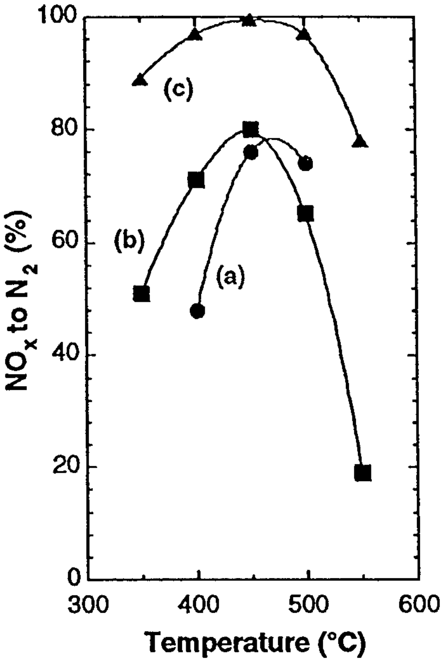

Figure 6. NO_x reduction to N_2 as a function of temperature. (a) NO over 2 wt% Co/Al_2O_3, (b) NO_2 over 2 wt% Co/Al_2O_3, (c) NO_2 over γ-Al_2O_3. Catalyst weight, 0.25 g. Dry gas feed, 1000 ppm NO or NO_2, 1000 ppm C_3H6, 5% O_2, balance He at 100 mL/min. Space velocity = 12,000 /hr. Data taken from Ref. [47].

Figure 7 shows the NO_x reduction to N_2 over a monolith washcoated with γ-Al_2O_3. The NO_x reduction is much higher when the input NO_x is NO_2 instead of NO.

Figures 5-7 illustrate how the conversion of NO to NO_2 can significantly increase the SCR activity. The gas feeds used were dry. It is known that H_2O degrades the SCR activity of γ-Al_2O_3. The negative effect of H_2O on the SCR activity of various catalysts, and how the effect can be overcome, is an important topic that is outside the scope of this paper. In the next section we will show the SCR activity of γ-Al_2O_3 for a real diesel engine exhaust, which contains about 5% H_2O.

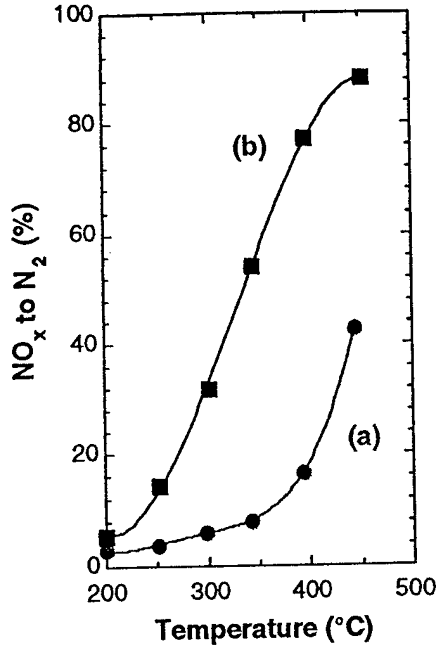

Figure 7. Selective catalytic reduction of NO_x over a monolith washcoated with γ-Al_2O_3. Space velocity = 18,000 /hr. L/D = 3. Dry gas feed. Gas mixture: 1000 ppm C_3H_6, 10% O_2, balance N_2. (a) Input NO_x consisting of 500 ppm NO, (b) Input NO_x consisting of 500 ppm NO_2.

DIESEL ENGINE EXHAUST DATA – Figure 8 shows data on plasma-assisted catalytic reduction of NO_x using a slipstream of the exhaust from a Cummins B5.9 diesel engine. The reactor used in this run consisted of a pulsed corona plasma reactor packed with γ-Al_2O_3 pellets. The total plasma + catalyst reactor volume was 0.5 L. A Cummins B5.9 diesel engine running with a 95 kW load was used as the source of NO_x. The engine-out NO_x was 600 ppm. The exhaust temperature was typically between 350 - 400°C when the engine load is 95 kW. The temperature of the plasma/catalyst reactor was set at 370°C. Propene was used as the hydrocarbon reductant, with a C1/NO_x ratio of 5. Figure 8 shows the amount of NO_x reduction at space velocities of 12,000 and 18,000 /hr. The NO_x reduction increases dramatically as the energy density delivered to the plasma is increased.

We have chosen γ-Al_2O_3 as a representative SCR catalyst that works very well in combination with a plasma. However, it is not necessarily the best catalyst for this purpose.

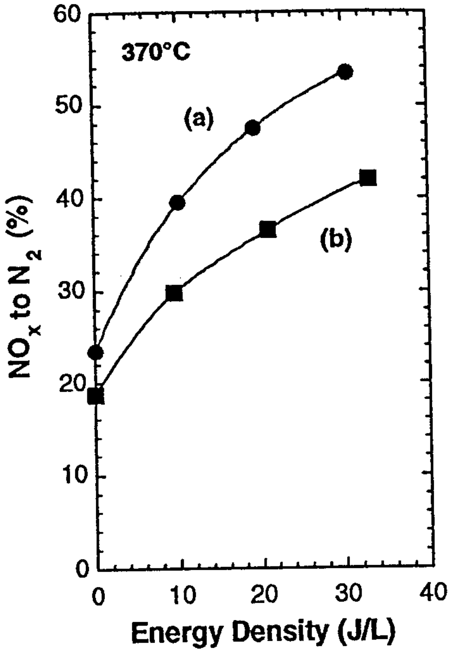

Figure 8. Plasma-assisted catalytic reduction of NO_x at 370°C in a pulsed corona plasma reactor packed with γ-Al_2O_3 pellets. Total plasma+catalyst reactor volume = 0.5 L. The NO_x reduction is shown as a function of the energy density input to the plasma. A Cummins B5.9 diesel engine running with a 95 kW load was used as the source of NO_x. Propene reductant C1/NO_x = 5. Space velocity: (a) 12,000 /hr, and (b) 18,000 /hr.

Actual exhaust from a diesel engine contains around 10% CO_2 and 5% or more H_2O, in addition to the 10% O_2. The H_2O component is known to decrease the SCR efficiency of γ-Al_2O_3. Some studies suggest that it is possible to overcome the detrimental effect of H_2O on SCR activity. For example, Maunala et al. [18] have observed that the activity of In/ Al_2O_3 remains high even in the presence of H_2O when the input NO_x is NO_2.

V. CONCLUSIONS

The oxidation of NO to NO_2 serves an important role in enhancing the efficiency for SCR of NO_x to N_2. A non-thermal plasma is a very effective means for oxidizing NO to NO_2 in the gas-phase under lean-burn engine exhaust conditions. When combined with some types of SCR catalyst, the plasma can greatly enhance the NO_x reduction and eliminate some of the deficiencies encountered in an entirely catalyst-based approach. The plasma can efficiently oxidize NO to NO_2 over a wide range of temperature without depleting the amount of hydrocarbons available for SCR of NO_2 to N_2. Furthermore, in the presence of hydrocarbons the plasma can oxidize NO without oxidizing SO_2, thus making the process tolerant to the sulfur content of the fuel. Experimental data demonstrating the sulfur tolerance of the hydrocarbon-enhanced plasma oxidation process will be shown in another paper.

ACKNOWLEDGMENTS

The work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the DOE Office of Basic Energy Sciences, the DOE Office of Fossil Energy, the Strategic Environmental Research and Development Program, and a Cooperative Research and Development Agreement with Cummins Engine Company. The work at Northwestern University was supported by the Chemical Sciences Division of the DOE Office of Basic Energy Sciences.

REFERENCES

1. Shelef, M., "Selective Catalytic Reduction of NO$_x$ With N-Free Reductants", *Chem. Rev.* 95, 209 (1995).
2. Tabata, T., Kokitsu, M., and Okada, O., "Study on Patent Literature of Catalysts for a New NO$_x$ Removal Process", *Catal. Today* 22, 147 (1994).
3. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M., "Selective Reduction of Nitrogen Monoxide with Propane over Alumina and HZSM-5 Zeolite - Effect of Oxygen and Nitrogen Dioxide Intermediate", *Appl. Catal.* 70, L15 (1991).
4. Petunchi, J.O. and Hall, W.K., "On the Role of Nitrogen Dioxide in the Mechanism of the Selective Reduction of NO$_x$ over Cu-ZSM-5 Zeolite", *Appl. Catal. B: Environmental* 2, L17 (1993).
5. Petunchi, J.O., Sill, G., and Hall, W.K., "Studies of the Selective Reduction of Nitric Oxide by Hydrocarbons", *Appl. Catal. B: Environmental* 2, 303 (1993).
6. Valyon, J. and Hall, W.K., "Studies of the Surface Species Formed from NO on Copper Zeolites" *J. Phys. Chem.* 97, 1204 (1993).
7. Sasaki, M., Hamada, H., Kintaichi, Y., and Ito, T., "Role of Oxygen in Selective Reduction of Nitrogen Monoxide by Propane over Zeolite and Alumina-Based Catalysts" *Catal. Lett.* 15, 297 (1992).
8. Shelef, M., Montreuil, C.N., and Jen, H.W., "NO$_2$ Formation Over Cu-ZSM-5 and the Selective Catalytic Reduction of NO", *Catal. Lett.* 26, 277 (1994).
9. Yokoyama, C. and Misono, M., "Catalytic Reduction of Nitrogen Oxides by Propene in the Presence of Oxygen over Cerium Ion-Exchanged Zeolites: 2. Mechanistic Study of Roles of Oxygen and Doped Metals", *J.Catal.* 150, 9 (1994).
10. Bamwenda, G.R., Ogata, A., Obuchi, A., Takahashi, H., and Mizuno, K., "Selective Reduction of NO$_2$ by Propylene in Excess Oxygen Over Rh/Al$_2$O$_3$. Drift Spectroscopy and Activity Studies", *React. Kinet. Catal. Lett.* 56, 311 (1995).
11. Lukyanov, D.B., Sill, G., Ditri, J.L., and Hall, W.K., "Comparison of Catalyzed and Homogeneous Reactions of Hydrocarbons for Selective Catalytic Reduction (SCR) of NOx", *J.Catal.* 153, 265 (1995).
12. Beutel, T., Adelman, B.J., Lei, G.D., and Sachtler, W.M.H., "Potential Reaction Intermediates of NO$_x$ Reduction with Propane over Cu/ZSM-5", *Catal. Lett.* 32, 83 (1995).
13. Ansell, G.P., Diwell, A.F., Golunski, S.E., Hayes, J.W., Rajaram, R.R., Truex, T.J., and Walker, A.P., "Mechanism of the Lean NO$_x$ Reaction over Cu/ZSM-5" *Appl. Catal. B* 2, 81 (1993).
14. Kung, M., Bethke, K., Alt, D., Yang, B. and Kung, H., in *NO$_x$ Reduction*, ACS Symposium Series (1995).
15. Shimokawabe, M., Ohi, A., and Takezawa, N., "Catalytic Reduction of Nitrogen Dioxide with Propene in the Presence and Absence of Oxygen Over Various Metal Oxides", *React. Kinet. Catal. Lett.* 52, 393 (1994).
16. Hirao, Y., Yokoyama, C., and Misono, M., "Enhancement by Water Vapour of Catalytic Reduction of NO by Propene Over Mechanically Mixed Mn$_2$O$_3$ and Sn-ZSM-5", *Chem. Comm.* March 7, 597 (1996).
17. Misono, M., Hirao, Y., and Yokoyama, C., "Reduction of Nitrogen Oxides with Hydrocarbons Catalyzed by Bifunctional Catalysts", *Catal. Today* 38, 157 (1997).
18. Maunala, T., Kintaichi, Y., Inaba, M., Haneda, M., Sato, K, and Hamada, H., "Enhanced Activity of In and Ga-Supported Sol-Gel Alumina Catalysts for NO Reduction by Hydrocarbons in Lean Conditions", *Appl. Catal. B: Environmental* 15, 291 (1998).
19. Iwamoto, M., Hernandez, A.M., and Zengyo, T., "Oxidation of NO to NO$_2$ on a Pt-MFI Zeolite and Subsequent Reduction of NO$_x$ by C$_2$H$_4$ on an In-MFI Zeolite: a Novel De-NO$_x$ Strategy in Excess Oxygen", *Chem. Comm.* Jan 7, 37 (1997).
20. Iwamoto, M. and Zengyo, T., "Highly Selective Reduction of NO in Excess Oxygen through the Intermediate Addition of Reductant (IAR) Between Pt- and Zn-MFI Zeolites", *Chem. Lett.* 1283 (1997).
21. Bethke, K.A., Li, C., Kung, M.C., Yang, B., et al., "The Role of NO$_2$ in the Reduction of NO by Hydrocarbon over Cu-ZrO$_2$ and Cu-ZSM-5 Catalysts", *Catal. Lett.* 31, 287 (1995).
22. Chajar, Z., Primet, M., Praliaud, H., Chevrier, M., Gauthier, C., and Mathis, F., "Nitrogen Dioxide Effect in the Reduction of Nitric Oxide by Propane in Oxidizing Atmosphere", *Catal. Lett.* 28, 33 (1994).
23. Penetrante, B.M., in "Non-Thermal Plasma Techniques for Pollution Control - Part A: Overview, Fundamentals and Supporting Technologies" (B.M. Penetrante and S.E. Schultheis, Eds.), p. 65. Springer-Verlag, Berlin Heidelberg New York, 1993.
24. Penetrante, B.M., Bardsley, J.N., and Hsiao, M.C., "Kinetic Analysis of Non-Thermal Plasmas Used for Pollution Control", *Jap. J. Appl. Phys.* 36, 5007 (1997).
25. Penetrante, B.M., Hsiao, M.C., Bardsley, J.N., Merritt, B.T., Vogtlin, G.E., Kuthi, A., Burkhart, C.P., and Bayless, J.R., "Identification of Mechanisms for Decomposition of Air Pollutants by Non-Thermal Plasma Processing", *Plasma Sources Sci. Tech.* 6, 251 (1997).
26. Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Vogtlin, G.E., Wallman, P.H., Neiger, M., Wolf, O., Hammer, T. and Broer, S., "Pulsed Corona and Dielectric-Barrier Discharge Processing of NO in N$_2$", *Appl. Phys. Lett.* 68, 3719 (1996).
27. Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Vogtlin, G.E., Wallman, P.H., Kuthi A., Burkhart, C.P., and Bayless, J.R., "Electron-Impact Dissociation of Molecular Nitrogen in Atmospheric-Pressure Non-Thermal Plasma Reactors", *Appl. Phys. Lett.* 67, 3096 (1995).
28. Penetrante, B.M., Hsiao, M.C., Merritt, B.T., Vogtlin, G.E. and Wallman, P.H., "Comparison of Electrical Discharge Techniques for Non-Thermal Plasma Processing of NO in N$_2$.", *IEEE Trans. Plasma Sci.* 23, 679 (1995).
29. Penetrante, B.M., Hsiao, M.C., Merritt, B.T., and Vogtlin, G.E., "Fundamental Limits on NO$_x$ Reduction by Plasma", *SAE Paper* 971715 (1997).
30. Zipf, E.C., Espy, P.J. and Boyle, C.F., "The Excitation and Collisional Deactivation of Metastable N(2P) Atoms in Auroras", *J. Geophys. Res.* 85, 687 (1980).
31. Cosby, P.C., "Electron-impact Dissociation of Nitrogen", *J. Chem. Phys.* 98, 9544 (1993).
32. Schofield, K., "Critically Evaluated Rate Constants for Gaseous Reactions of Several Electronically Excited Species", *J. Phys. Chem. Ref. Data* 8, 723 (1979).
33. Wilk, R.D., Cernansky, N.P., Pitz, W.J. and Westbrook,

C.K., "Propene Oxidation at Low and Intermediate Temperatures - A Detailed Chemical Kinetic Study", *Combust. Flame* 77, 145 (1989).

34. Koert, D.N., Pitz, W.J. and Bozzelli, J.W., "Chemical Kinetic Modeling of High Pressure Propane Oxidation and Comparison to Experimental Results", Twenty-Sixth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1996, p. 633-640.
35. Pitz, W.J., Westbrook, C.K. and Leppard, W.R., "Autoignition Chemistry of C4 Olefins Under Motored Engine Conditions: A Comparison of Experimental and Modeling Results", *SAE Paper 912315* (1991).
36. Ritter, E.R. and Bozzelli, J.W.," THERM - Thermodynamic Property Estimation for Gas Phase Radicals and Molecules", *Int. J. Chem. Kinet.* 23, 767 (1991).
37. Lay, T.H., Bozzelli, J.W., Dean, A.M. and Ritter, E.R., "Hydrogen Atom Bond Increments for Calculation of Thermodynamic Properties of Hydrocarbon Radical Species", *J. Phys. Chem.* 99, 14514 (1995).
38. Marinov, N.M., Castaldi, M.J., Melius, C.F. and Tsang, W., "Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Premixed Propane Flame", *Comb. Sci. Tech.* 28, 295 (1997).
39. Bowman, C.T., Hanson, R.K., Davidson, D.F., Gardiner, Jr., W.C., Lissianski, V., Smith, G.P., Golden, D.M., Frenklach, M. and M. Goldenberg, http://www.me.berkeley.edu/gri_mech, 1997.
40. Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, Jr., R.F., Kerr, J.A. and Troe, J., "Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry", *J. Phys. Chem. Ref. Data* 26, 521 (1997).
41. Dean, A.M. and Bozzelli, J.W., "Combustion Chemistry of Nitrogen", in *Combustion Chemistry II*, ed. W. Gardiner, Jr. (Springer-Verlag, New York, 1997).
42. Pitz, W.J., Penetrante, B.M., Hsiao, M.C. and Vogtlin, G.E., "Simultaneous Oxidation of NO and Hydrocarbons in a Non-Thermal Plasma", *1997 Fall Meeting of the Western States Section of the Combustion Institute.*
43. Radtke, F., Koeppel, R.A., and Baiker, A., "Harmful By-Products in Selective Catalytic Reduction of Nitrogen Oxides by Olefins over Alumina", *Catal. Lett.* 28, 131 (1994).
44. Kung, M., Lee, J.-H., Chu-Kung, A., and Kung, H.H., in "Proceedings, 11th International Congress on Catalysis-40th Anniversary" (J.W. Hightower, W.N. Delgass, E. Iglesia, and A.T. Bell, Eds), Vol. 101, p. 701. Elsevier, Amsterdam, 1996.
45. Radtke, F., Koeppel, R.A., Minardi, E.G., and Baiker, A., "Catalytic Reduction of Nitrogen Oxides by Olefins in the Presence of Oxygen over Copper/Alumina: Influence of Copper Loading and Formation of Byproducts", *J. Catal.* 167, 127 (1997).
46. Bethe, K.A and Kung, H.H., "Supported Ag Catalyst for the Lean Reduction of NO with C_3H_6", *J. Catal.* 172, 93 (1997).
47. Yan, J.-Y., Kung, M.C., Sachtler, W.M.H., and Kung, H.H., "Co/Al_2O_3 Lean NO_x Reduction Catalyst", *J. Catal.* 172, 178 (1997).
48. Misono, M. and Kondo, K., "Catalytic Removal of Nitrogen Monoxide over Rare-Earth Ion-Exchanged Zeolites in the Presence of Propene and Oxygen", *Chem. Lett.* June, 1001 (1991).
49. Hamada, H., "Selective Reduction of NO by Hydrocarbons and Oxygenated Hydrocarbons over Metal Oxide Catalysts", *Catal. Today* 22, 21 (1994).
50. Tabata, M., Tsuchida, H., Miyamoto, K., Yoshinari, T., et al., "Reduction of NO_x in Diesel Exhaust with Methanol over Alumina Catalyst", *Appl. Catal. B: Environmental* 6, 169 (1995).