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Plasma-Assisted Catalytic Reduction of NO$_x$

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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, aftertreatment 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$_2$O$_3$ [3], H-ZSM-5 [3], ZrO$_2$ [14], and Ga$_2$O$_3$ [14]. It has also been observed that Group II metal oxides in general are much more effective in NOx 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.
ZSM-5 or In/Al₂O₃) catalyzes the reaction between NO₂ and the hydrocarbon [16-18]. Catalysts that previously were regarded as inactive for NOₓ reduction could therefore become efficient when mixed with an oxidation catalyst.

The apparent role of NO₂ in the SCR of NOₓ 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 NO₂ does not necessarily precede the formation of N₂. On catalysts such as Al₂O₃ that are less active in the oxidation of NO to NO₂, Bethke et al. [21] suggests that the N₂ production is higher using NO₂ than NO because of the higher surface coverage of adsorbed NO₂. The adsorbed NO₂ forms an adsorbed oxidized N-containing hydrocarbon intermediate. The reaction of this intermediate with NO is then the principal route to the production of N₂. On catalysts that deactivate due to coking, NO₂ helps maintain the activity by removing the surface carbonaceous species, resulting in an impression that NO₂ is a reagent for N₂ production. In any case, it is apparent that preconverting NO to NO₂ 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 NO₂ in the gas-phase under lean-burn engine exhaust conditions. The use of a plasma can improve the NOₓ reduction efficiency and eliminate some of the deficiencies encountered in an entirely catalyst-based approach. The plasma can oxidize NO to NO₂ without depleting the amount of hydrocarbons available for SCR of NO₂ to N₂. The function of the SCR catalyst can thus be greatly simplified by focusing on the reduction of NO₂ by the hydrocarbon. Furthermore, the plasma can oxidize NO without oxidizing SO₂, 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 N₂, O₂, H₂O, CO₂, hydrocarbons and NOₓ. 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 NOₓ 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 NOₓ 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 N2, O2 and H2O, particularly when the O2 concentration is 5% or higher. The kinetic energy of the electrons is deposited primarily into the major gas components, N2 and O2. The most useful deposition of energy is associated with the production of N and O radicals through electron-impact dissociation:

\[ e + N_2 \rightarrow e + N(4S) + N(4S,2D) \]  
\[ e + O_2 \rightarrow e + O(3P) + O(3P,1D) \]

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]:

\[ N(4S) + NO \rightarrow N_2 + O \]  

In the presence of O2, the oxidation pathway becomes dominant for two reasons:

(a) The dissociation energy of O2 is smaller than that of N2. 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 O2 is much higher compared to the dissociation of N2.[23-24] The dissociation of O2 will produce only oxidative radicals. The ground-state oxygen atom, O(3P), will convert NO to NO2 via:

\[ O(3P) + NO + M \rightarrow NO_2 + M \]  
\[ O(3P) + O_2 + M \rightarrow O_3 + M \]  
\[ O_3 + NO \rightarrow NO_2 + O_2 \]

The metastable oxygen atom, O(1D), will react with H2O to produce OH radicals:

\[ O(1D) + H_2O \rightarrow 2 OH \]

The OH radicals will convert NO and NO2 to nitrous and nitric acid, respectively.

(b) High electron energies are required to optimize the production of N(4S) by electron-impact dissociation of N2. Under conditions optimum for the dissociation of N2, 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 O2. Rather than reduce NO, the N(2D) species would react with O2 to produce NO:

\[ N(2D) + O_2 \rightarrow NO + O \]

Because of the large rate constant [32] for reaction (7) and the large concentration of O2 relative to NO, the N(2D) species preferentially reacts with O2 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 NOx 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% O2 and balance N2, without hydrocarbons. The purpose of this experiment was to determine the efficiency for plasma oxidation of NO to NO2 by the O radical. The NOx 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 NO2 at energy densities of 40 J/L and above. For the 300°C case, the conversion of NO to NO2 is only around 20% even at the high energy densities.

For a given energy density input, the NOx 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 NOx concentration is low, some of the radicals could end up forming NOx.

The efficiency for oxidation of NO to NO2 drops as the temperature is increased. At high temperatures, the NO to NO2 oxidation reaction is counteracted by the reduction reaction:

\[ O + NO_2 \rightarrow NO + O_2 \]

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% O2 and balance N2. The purpose of this experiment was to determine how the hydrocarbon affects the plasma oxidation of NO to NO2.
The NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} is poor in the absence of hydrocarbons in the gas stream. Figure 2(b) shows the NO\textsubscript{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\textsubscript{2}.

In the absence of hydrocarbons, the number of NO molecules oxidized to NO\textsubscript{2} is determined by the number
of O radicals, which is proportional to the energy density input to the plasma. Backconversion of NO\textsubscript{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\textsubscript{2} is no longer the O radical. It will be shown in the following chemical kinetics analysis that the HO\textsubscript{2} is the radical that oxidizes NO to NO\textsubscript{2} when the plasma processing is done in the presence of hydrocarbons. The number of HO\textsubscript{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\textsubscript{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\textsubscript{3} mechanism was updated in a number of ways. The reactions involving propane were updated from Ref. [38]. The NO\textsubscript{x} submechanism from GRI Mech\textsuperscript{™} [39] has been added to the C\textsubscript{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:

\[
\text{C}_3\text{H}_6 + O \rightarrow \text{C}_2\text{H}_5 + \text{HCO} \quad (9)
\]
\[
\text{C}_3\text{H}_6 + O \rightarrow \text{CH}_2\text{CO} + \text{CH}_3 + \text{H} \quad (10)
\]
\[
\text{C}_3\text{H}_6 + O \rightarrow \text{CH}_3\text{CHCO} + \text{H} + \text{H} \quad (11)
\]

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.

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\textsubscript{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\textsubscript{2}.

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

\[
\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{C}_3\text{H}_5\text{OH} \quad (12)
\]
\[
\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{C}_3\text{H}_5 + \text{H}_2\text{O} \quad (13)
\]

where the C\textsubscript{3}H\textsubscript{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

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \quad (14)
\]

Reaction (14) is also the main reaction that converts NO to NO\textsubscript{2}.

In the presence of H\textsubscript{2}O, electron-impact dissociation of H\textsubscript{2}O would produce additional OH radicals. The metastable oxygen atom, O(1\textsuperscript{D}), will react with H\textsubscript{2}O 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\textsubscript{2} in the presence of O\textsubscript{2}.

The HO\textsubscript{2} radicals are also produced from reactions involving hydrocarbon intermediates of propene oxidation:

\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \quad (15)
\]
\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \quad (16)
\]
\[
\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \quad (17)
\]
\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad (18)
\]

Therefore, the propene supplies HO\textsubscript{2} radicals that convert NO to NO\textsubscript{2}. Without the propene, the main reaction to convert NO to NO\textsubscript{2} are reactions (4) and (5): O + NO \rightarrow NO\textsubscript{2}. Radical-radical reactions involving O and OH (such as OH + O \rightarrow HO\textsubscript{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\textsubscript{2} radicals that then become the main radical for conversion of NO to NO\textsubscript{2}.

The OH produced from reaction (6) can also react with NO and NO\textsubscript{2} to form their related acids:

\[
\text{NO} + \text{OH} \rightarrow \text{HONO} \quad (19)
\]
\[
\text{NO}_2 + \text{OH} \rightarrow \text{HONO}_2 \quad (20)
\]

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\textsubscript{2} while the remainder react mostly with propene and its aldehydic intermediate products. At
100°C, 15% of the OH react with NO and NO₂, while the remainder react mostly with propene and aldehydic intermediates. The rate constants for the NOₓ + OH reactions are much slower than for propene + OH reactions, so that OH reacts mainly with propene rather than NO and NO₂ [42].

Because the OH radical reacts preferentially with the hydrocarbon, the oxidation of NO₂ to nitric acid is minimized. If SO₂ is present in the exhaust, scavenging of the O and OH radicals by the hydrocarbons will also minimize the oxidation of SO₂ to SO₃. Experimental data demonstrating how hydrocarbons prevent the oxidation of SO₂ to SO₃ 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 C₁ 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 NO₂, (2) the hydrocarbons minimize the formation of acid products, and (3) the hydrocarbons prevent the oxidation of SO₂ to SO₃.

Figure 3 shows the efficiency for plasma oxidation of NO to NO₂ in a model exhaust gas consisting of 500 ppm NO, 1000 ppm C₃H₆, 10% O₂, and balance N₂. 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 NO₂, 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 NOₓ is accomplished in essentially two steps. First, the plasma oxidizes NO to NO₂ in the presence of a hydrocarbon:

\[
\text{plasma} + \text{NO} + \text{HC} + \text{O}_2 \rightarrow \text{NO}_2 + \text{HC-products}
\]

where HC refers to a hydrocarbon and HC-products refers to partially oxidized hydrocarbons. Second, the catalyst reduces NO₂ to N₂ by selective reduction using the hydrocarbons:

\[
\text{catalyst} + \text{NO}_2 + \text{HC} \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

Figure 3. Oxidation of NO to NO₂ in a plasma. Gas mixture: 500 ppm NO, 1000 ppm C₃H₆, 10% O₂, balance N₂.

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

- First, the plasma oxidation process is partial. This means the plasma oxidizes NO to NO₂ but does not further oxidize NO₂ to nitric acid. The plasma also produces some partially oxygenated hydrocarbons, but does not completely oxidize the hydrocarbons to CO₂ and H₂O. For some catalysts, the partially oxygenated hydrocarbons are much more effective compared to the original hydrocarbons in reducing NOₓ to N₂.

- Second, the plasma oxidation process is selective. This means the plasma oxidizes NO to NO₂ but does not oxidize SO₂ to SO₃. This makes the plasma-assisted process more tolerant to the sulfur content of fuel compared to conventional lean-NOₓ technologies.

- Third, by using a plasma to change the composition of NOₓ from NO to NO₂, one can take advantage of a new class of catalysts that are potentially more durable and more active than conventional lean-NOₓ 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\textsubscript{x} reduction efficiency that can be accomplished by combining an SCR catalyst with a plasma. For this purpose we have chosen $\gamma$-Al\textsubscript{2}O\textsubscript{3} as a representative SCR catalyst for three reasons. First, many groups have shown that $\gamma$-Al\textsubscript{2}O\textsubscript{3} is much more active as an SCR catalyst for the reduction of NO\textsubscript{2} compared to NO [3,43-47]. $\gamma$-Al\textsubscript{2}O\textsubscript{3} is one of the best non-proprietary materials for taking advantage of the presence of NO\textsubscript{2}. Second, several studies [48-49] comparing a wide variety of SCR catalysts, including zeolites and metal oxides, have found $\gamma$-Al\textsubscript{2}O\textsubscript{3} to be one of the most active for NO\textsubscript{x} reduction by hydrocarbons. Third, $\gamma$-Al\textsubscript{2}O\textsubscript{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 $\gamma$-Al\textsubscript{2}O\textsubscript{3} retains its NO\textsubscript{x} reduction activity over a long period of time [50].

In plasma-assisted catalysis, the NO\textsubscript{x} to N\textsubscript{2} conversion is determined by the catalyst. Catalyst characterization has been done using a He background gas to establish real conversion of NO\textsubscript{x} to N\textsubscript{2}.

Combining a plasma with $\gamma$-Al\textsubscript{2}O\textsubscript{3} can provide NO\textsubscript{x} reduction efficiencies much higher than those achieved by the conventional approach of loading a metal on $\gamma$-Al\textsubscript{2}O\textsubscript{3}. Figure 5(a) shows the NO reduction to N\textsubscript{2} for $\gamma$-Al\textsubscript{2}O\textsubscript{3}. The temperature operating window occurs at a

Figure 5. NO\textsubscript{x} reduction to N\textsubscript{2} as a function of temperature. (a) NO over $\gamma$-Al\textsubscript{2}O\textsubscript{3}, (b) NO or NO\textsubscript{2} over 2 wt\% Ag/Al\textsubscript{2}O\textsubscript{3}, (c) NO\textsubscript{2} over $\gamma$-Al\textsubscript{2}O\textsubscript{3}. Catalyst weight, 0.25 g. Dry gas feed, 1000 ppm NO or NO\textsubscript{2}, 1000 ppm C\textsubscript{3}H\textsubscript{6}, 6% O\textsubscript{2}, balance He at 100 mL/min. Space velocity = 12,000 hr\textsuperscript{-1}. Data taken from Ref. [46].
The addition of 2 wt% Ag to \( \gamma-Al_2O_3 \) 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 \( \gamma-Al_2O_3 \) increases dramatically over a wide range of temperature, as shown in Figure 5(c).

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 \( \gamma-Al_2O_3\), the NO\(_x\) reduction activity is higher over a much wider range of temperature, as shown in Figure 6(c).

Figure 7 shows the NO\(_x\) reduction to \( N_2 \) over a monolith washcoated with \( \gamma-Al_2O_3\). 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 \( \gamma-Al_2O_3\). 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 \( \gamma-Al_2O_3\) 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 \( \gamma-Al_2O_3\). Space velocity = 18,000 /hr. L/D = 3. Dry gas feed. Gas mixture: 1000 ppm C\(_3\)H\(_6\), 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 \( \gamma-Al_2O_3\) 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\(^\circ\)C when the engine load is 95 kW. The temperature of the plasma/catalyst reactor was set at 370\(^\circ\)C. Propene was used as the hydrocarbon reductant, with a C\(_1\)/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 \( \gamma-Al_2O_3\) 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.

![Plasma-assisted catalytic reduction of NOx at 370°C](image)

**Figure 8.** Plasma-assisted catalytic reduction of NO$_x$ at 370°C in a pulsed corona plasma reactor packed with γ-Al$_2$O$_3$ 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 C$_1$/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$_2$O, in addition to the 10% O$_2$. The H$_2$O component is known to decrease the SCR efficiency of γ-Al$_2$O$_3$. Some studies suggest that it is possible to overcome the detrimental effect of H$_2$O on SCR activity. For example, Maunala et al. [18] have observed that the activity of In/Al$_2$O$_3$ remains high even in the presence of H$_2$O 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.

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