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EFFECT OF HYDROCARBONS ON PLASMA TREATMENT OF NO_x

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Abstract: This paper examines how hydrocarbons affect the non-thermal plasma treatment of NO_x in lean-burn engine exhausts. We have found that the NO is mainly oxidized to NO_2 by

$$NO + HO_2 \rightarrow NO_2 + OH$$
$$NO + RO_2 \rightarrow NO_2 + RO$$

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. 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 for the selective partial oxidation of NO to NO_2. This result suggests that gas-phase reactions in the plasma alone cannot lead to the chemical reduction of NO_x. Any reduction of NO_x to N_2 can only be accomplished through heterogeneous reactions of NO_2 with surfaces or particulates.

I. Introduction

Lean-burn gasoline engine exhausts contain a significant amount of hydrocarbons in the form of propene. Diesel engine exhausts contain little gaseous hydrocarbon; however, they contain a significant amount of liquid-phase hydrocarbons (known as the volatile organic fraction) in the particulates.

The objective of this paper is to examine the fate of NO_x when an exhaust gas mixture that contains hydrocarbons is subjected to a plasma. We will show that the hydrocarbons promote the oxidation of NO to NO_2, but not the reduction of NO to N_2. The oxidation of NO to NO_2 is strongly coupled with the hydrocarbon oxidation chemistry. This result suggests that gas-phase reactions in the plasma alone cannot lead to the chemical reduction of NO_x. Any reduction of NO_x to N_2 can only be accomplished through heterogeneous reactions of NO_2 with surfaces or particulates.

II. Test Setup

Previous studies [1-3] 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.

The plasma reactor used this study is a pulsed corona consisting of a 1.5 mm diameter wire in a 60 mm diameter metal tube 300 mm long. Heater bands and thermocouples provide active control of the processor temperature. The power supply is a magnetic pulse compression system capable of delivering up to 30 kV output into 100 ns pulses at variable repetition rates to the kilohertz range. The electrical energy deposition into the gas was determined by monitoring the electrical parameters associated with the discharge.

The experiments were performed in a flow-through configuration. We prepared a mixture containing trace amounts of NO and hydrocarbons and recorded the composition of the effluent gas as a function of input electrical energy density. The input energy density, Joules per standard liter (J/L), is the ratio of discharge power to gas flow rate at standard conditions (25°C and 1 atm). The gas blending manifold allowed us to custom make gas streams consisting of N_2, O_2, propene and

NO_x. We metered these gases through mass flow controllers which permited exact control of flow rate. We used calibrated gas mixtures of either hydrocarbons or NO in N_2. This arrangement allowed us to blend in small concentrations of the trace components using mass flow controllers. After mixing in the manifold, the gas then passed through a temperature controlled heater which preheated the gas to the processor temperature. We monitored the outlet gas composition with a Fourier Transform Infrared (FTIR) spectrometer. We heated the absorption cell to 120°C to avoid condensation of any water byproduct.

III. Plasma Process Without Hydrocarbons

Lean-burn engine exhausts contain high concentrations of oxygen, rendering conventional catalytic converters ineffective for the treatment of NO_x. A critical issue in the application of plasma-based methods to cars and trucks is whether the NO is removed by reduction to benign gases such as N_2, or by oxidation to NO_2 and nitric acid. To avoid the need for scrubbing of process products, the desired method of NO removal is by chemical reduction to N_2.

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:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S,^2D) \quad (1)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^3P,^1D) \quad (2)$$

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 lead to the chemical reduction of NO:

$$N(^4S) + NO \rightarrow N_2 + O \quad (3)$$

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.[1-3] Under this condition the rate for dissociation of O_2 is much higher compared to the dissociation of N_2.[4] The dissociation of O_2 will produce only oxidative radicals. The ground-state oxygen atom, $O(^3P)$, will convert NO to NO_2 via

$$O(^3P) + NO + M \rightarrow NO_2 + M \quad (4)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (5a)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (5b)$$

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

$$O(^1D) + H_2O \rightarrow 2\ OH \quad (6)$$

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

(b) Under conditions optimum for the dissociation of N_2, the production of the reducing species, $N(^4S)$, also leads to the production of the metastable atomic nitrogen, $N(^2D)$.[5] The $N(^2D)$ species can lead to undesired reactions in the presence of O_2. Rather than reducing NO, the $N(^2D)$ species would react with O_2 to produce NO:

$$N(^2D) + O_2 \rightarrow NO + O \quad (7)$$

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.

We examined the plasma processing of 100 ppm NO in 10% O_2 and balance N_2, without hydrocarbons. 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). For the 100°C case, about 60% of the NO is 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.

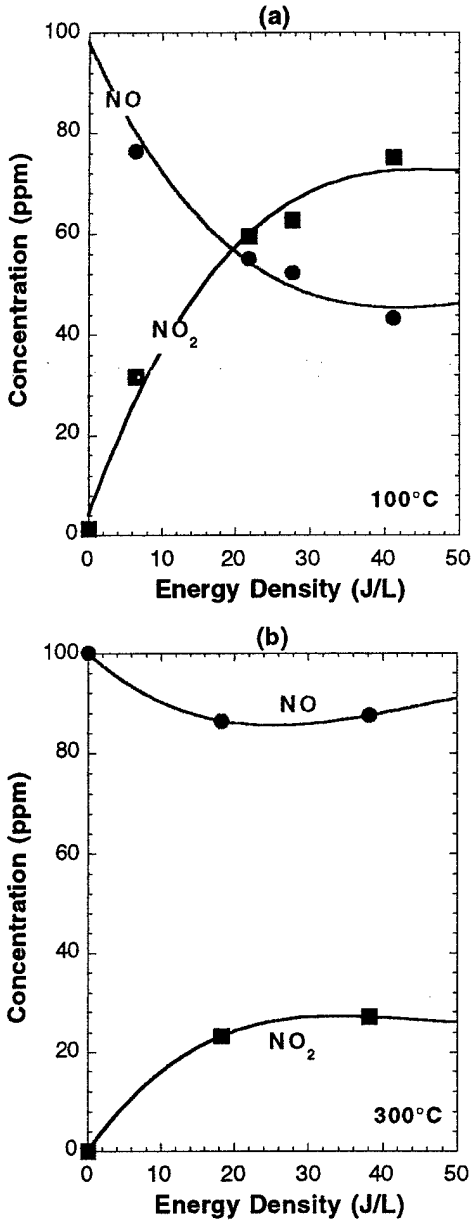

Figure 1. Effect of temperature on the plasma oxidation of NO in the absence of hydrocarbons. Plasma processing of 100 ppm NO in 10% O_2, balance N_2, at (a) 100°C and (b) 300°C.

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

$$O + NO_2 \rightarrow NO + O_2 \qquad (8)$$

Without hydrocarbons the oxidation of NO by the O radical is not efficient at high temperatures.

IV. Plasma Process With Hydrocarbons

We next examined the effect of hydrocarbons on the plasma processing of NO. Propene was used as a representative hydrocarbon. The gas mixture contained 500 ppm NO in 10% O_2 and balance N_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). 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.

The oxidation of NO to NO_2 is coupled with the hydrocarbon oxidation chemistry and will be discussed in the following section.

V. Oxidation Chemistry

This section will discuss the hydrocarbon oxidation chemistry, using propene as the representative hydrocarbon.

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

$$C_3H_6 + O \rightarrow C_2H_5 + HCO \qquad (9)$$

$$C_3H_6 + O \rightarrow CH_2CO + CH_3 + H \qquad (10)$$

$$C_3H_6 + O \rightarrow CH_3CHCO + H + H \qquad (11)$$

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): $O + NO \rightarrow NO_2$.

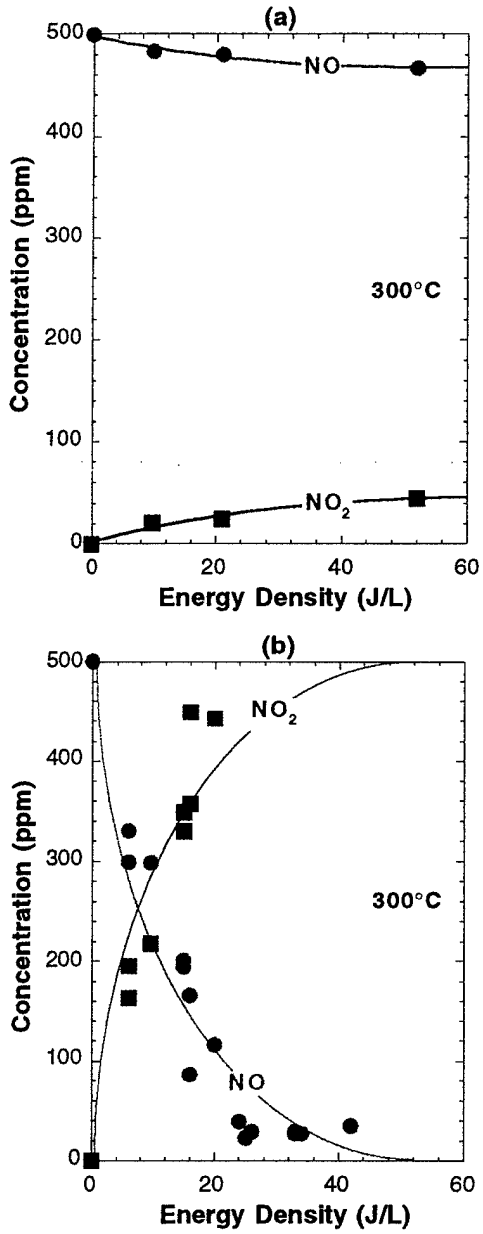

Figure 2. Effect of propene on the plasma oxidation of NO at 300°C. Plasma processing of 500 ppm NO in 10% O_2, balance N_2, (a) without propene, and (b) with 1000 ppm propene.

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 of 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:

$$C_3H_6 + OH \rightarrow C_3H_6OH \quad (12)$$

$$C_3H_6 + OH \rightarrow C_3H_5 + H_2O \quad (13)$$

where C_3H_5 radical symbolized 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

$$NO + HO_2 \rightarrow NO_2 + OH \quad (14)$$

This is also the main reaction that converts NO to NO_2. The HO_2 radicals are also produced from reactions involving hydrocarbon intermediates of propene oxidation:

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2 \quad (15)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (16)$$

$$HCO + O_2 \rightarrow CO + HO_2 \quad (17)$$

$$H + O_2 \rightarrow HO_2 \quad (18)$$

Therefore, the propene supplies HO_2 radicals which convert NO to NO_2. Without the propene, the main reaction to convert NO to NO_2 are reactions (4) and (5): $O + NO \rightarrow NO_2$.

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 which 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:

$$NO + OH \rightarrow HONO \quad (19)$$

$$NO_2 + OH \rightarrow HONO_2 \quad (20)$$

At 300°C, during the time when the propene is being consumed most rapidly, only about 6% of the OH is reacting with NO and NO_2 while the remainder is reacting mostly with propene and its aldehydic intermediate products. At 100°C, 15% of the OH is reacting with NO and NO_2, while the remainder reacting mostly with propene and

aldehydic intermediates. The rate constants for these reactions are much slower than for propene + OH reactions, so that OH reacts mainly with propene rather than NO and NO_2.

VI. Conclusions

The objective of this paper was to examine the fate of NO when a lean-burn exhaust gas that contains hydrocarbons is subjected to a non-thermal plasma. We have found that the NO is mainly oxidized to NO_2 by

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

$$NO + RO_2 \rightarrow NO_2 + RO$$

where R is a hydrocarbon radical. The oxidation of NO to NO_2 is coupled with the hydrocarbon oxidation chemistry. The O and OH radicals are consumed mainly by reactions with the hydrocarbons rather than with NO. Only oxidizing radicals in the form of HO_2 and RO_2 are produced during the breakup of the hydrocarbons. 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 for the selective partial oxidation of NO to NO_2. This result suggests that gas-phase reactions in the plasma alone cannot lead to the chemical reduction of NO_x. Any reduction of NO_x to N_2 can only be accomplished through heterogeneous reactions of NO_2 with surfaces or particulates.

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