

NON-THERMAL PLASMA TREATMENT OF AUTOMOTIVE EXHAUST GASES

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Abstract:

Treatment of NO_x in diesel engine exhaust represents a big opportunity for the environmental application of low-temperature plasmas. In this paper NO_x conversion to N₂ was investigated by Plasma/Catalyst System. Catalytic activity was enhanced by the assistance of plasma, and the plasma/Catalyst system showed higher NO_x conversion. It is shown that the plasma by itself cannot chemically reduce NO_x to N₂ in the highly oxidizing environment of a diesel engine exhaust. To implement the reduction of NO_x to N₂, it is necessary to combine the plasma with a heterogeneous process that can chemically reduce NO₂ to N₂.

Keywords: Plasmacatalytic process; Volatile organic compounds; Non-thermal electrical discharge, NO_x Removal.

Introduction:

Nitrogen oxides (NO_x) {the sum of nitric oxide (NO) and nitrogen dioxide (NO₂)} are mixtures of compounds of nitrogen and oxygen generally found in effluents from combustion sources. NO_x is a precursor to ozone or smog in atmosphere, greenhouse effect gas, and is believed to be a major contributor to acidic deposition of acid rain.[1-2]

Increasingly stringent air quality standards will require future car engines to be equipped with exhaust after treatment systems capable of decreasing the emission of nitrogen oxides (NO_x). The conventional three way catalyst (TWC) was ineffective for the NO_x treatment because of the significant oxygen and water

vapor levels in lean exhaust. A tremendous amount of investigation has been carried out for a couple of decades in developing catalysts for deNO_x reactions in lean conditions. However, until now no durable catalyst for the reduction of nitric oxides in these exhaust gases could be found. NO_x-traps as well as some other catalyst materials suffer from sulphur poisoning causing e.g. a continuous reduction of the NO_x storage capacity. Ultra-low sulphur fuel would be necessary to utilize these catalysts. [1]

Selective catalytic reduction (SCR) using an ammonia based additive as the reducing agent is able to reduce NO_x-emissions by more than 50 %. Using optimized catalyst materials this process works excellent for temperatures above 200 °C. In on-road testing with Diesel trucks more than 70 % NO_x-reduction were demonstrated with urea-SCR-systems. [4] For cars, however, future regulations may require NO_x-reduction at exhaust gas temperatures well below 170 °C. In addition the necessity of an additional reducing agent might not be accepted for personnel cars. Therefore the application of non-thermal plasmas (NTP) for automotive exhaust gas cleaning has widely been investigated. [2]

NTP induced selective catalytic reduction of nitric oxides (NO_x), oxidation of hydrocarbons (HC) and continuous regeneration of soot traps were demonstrated. These applications are based on non-thermal plasma processes generating O and OH-radicals, which react with HC and NO. [2]

Non-Thermal Plasma

Plasma is a partially or fully ionized gas containing electrons, ions, and neutral atoms or molecules, also called the fourth state of matter [4]. Non-thermal plasma (NTP) is a new concept of application of gas-phase oxidation processes that can destroy air pollutants. It is an extensively studied advanced oxidation technology (AOT) that envisions production of highly reactive gas-phase free radicals, such as ·O(³P) and ·OH that can initiate and sustain a

complex chemistry of pollutant destruction reactions. It is often produced by creating electrical discharges in a dielectric barrier electrode arrangement (commonly known as DBD or SDP reactor) and is referred to as a discharge occurring in an open space between two insulated electrodes connected to a source of high voltage alternating current. The geometry of such reactors is either planar or cylindrical with a configuration similar to that of a parallel-plate or a cylindrical capacitor, respectively. Usually, one or both metal electrodes are covered with a dielectric material (Pyrex, quartz, ceramics etc.) that separates them from a thin gas layer. The presence of a dielectric splits the electrical discharges into numerous micro discharges of high instantaneous current and spatially distributes them over the discharge area and, hence, increases the homogeneity of NTP. [4]

Plasma Reactors:

The three different kinds of electrical discharge reactors are used in generation of non-thermal plasma and are shown in fig (1).

In the pulsed corona reactor shown schematically in fig 1(a), the reactor is driven by very short pulses of high voltage, thus creating short-lived discharge plasmas that consist of energetic electrons, which in turn produce the radicals responsible for the decomposition of the undesirable molecules. In a dielectric discharge reactor. One or both of the electrodes are covered with a thin dielectric layer, such as glass or alumina. Dielectric barrier discharge reactors. are now routinely used to produce commercial quantities of ozone. [7]

Whereas in the pulsed corona method the transient behavior of the plasma is controlled by the applied voltage pulse, The plasma that takes place in a dielectric barrier discharge self-extinguishes when charge build up on the dielectric layer reduces the local electric field. The reactor shown in fig1 (b) combines the fast-rising voltage pulse of a pulsed corona reactor and the self-extinguishing characteristic

of a dielectric barrier discharge reactor. The dielectric-pellet bed reactor, shown schematically in fig1(c), employs a reactor packed with dielectric pellet. When external high voltage is applied, the pellets are polarized, and an intense electric field is formed around each pellet contact point. Many pulsed discharge take place around each contact point of the dielectric pellets. Because the pellets are packed close together, there is possibility that the electric field in the micro discharges are significantly enhanced, thus potentially increasing the radical production efficiency. [7]

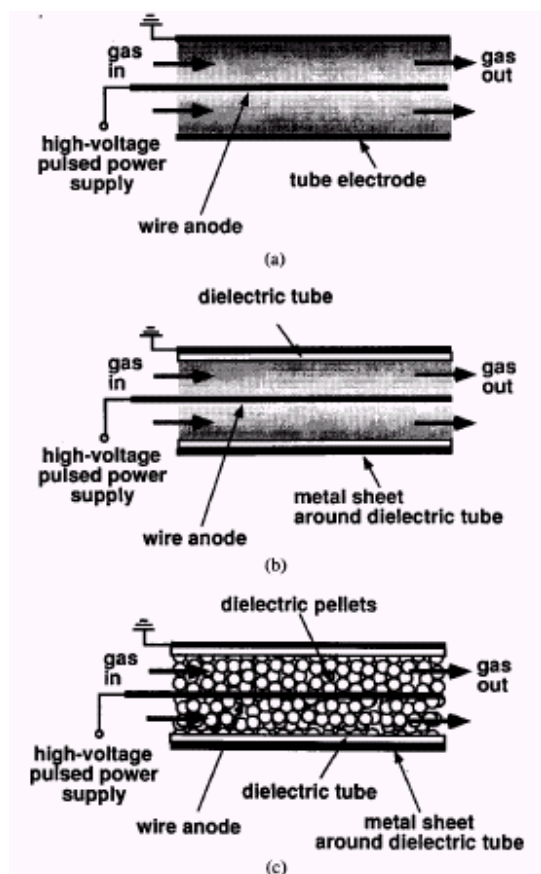
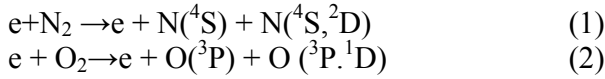


Fig.1. Electrical discharge reactors (a) pulsed corona, (b) dielectric barrier discharge, and (c) dielectric-pellet bed. [7]

NO_x Conversion Chemistry in the Plasma

Oxidation is the dominant process in the plasma for exhausts containing dilute concentrations of NO in mixtures of N₂, O₂ and

H₂O, particularly when the O₂ concentration is 5% or higher. [3] 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:

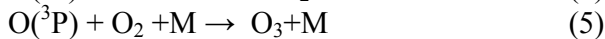
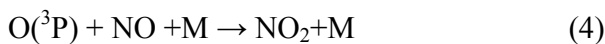


Where N(⁴S) and N(²D) are ground-state and metastable excited-state nitrogen atoms, respectively, and O(³P) (simply referred to as O) and O(¹D) are ground-state and metastable excited-state oxygen atoms, respectively. The N(⁴S) is the only plasma-produced species that could effectively lead to the chemical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



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 [6±8]. Under this condition the rate for electron-impact dissociation of O₂ is much higher compared to that of N₂. The dissociation of O₂ will produce only oxidative radicals. The ground-state oxygen atom, O(³P), will convert NO to NO₂ via



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



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. 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:



Because of the large rate constant for reaction (8) and the large concentration of O₂ relative to NO, the N(²D) species preferentially reacts with O₂ to produce NO. In an oxygen-rich 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. [2-3]

The number of NO molecules converted to NO₂ 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. 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:



Because of reaction (9), the oxidation of NO by the O radical is not efficient at high temperatures. At typical engine exhaust temperatures, the efficiency for conversion of NO to NO₂ is very poor in the absence of hydrocarbons in the gas stream. Figure 1a shows a comparison of our experiment to our chemical kinetics model for the case of plasma processing of 500 p.p.m. NO in 10% O₂, balance N₂ at 300 °C, without any hydrocarbon. Even with high electrical energy input, the maximum oxidation of NO to NO₂ in the plasma at 300 °C is only 10%. Back-conversion

of NO₂ to NO by the O radical is responsible for the low oxidation efficiency. [2-3]

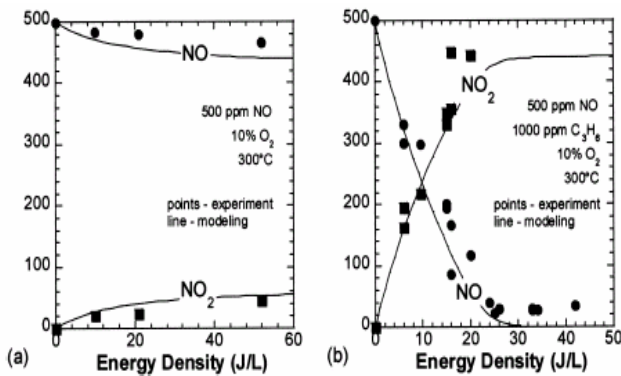
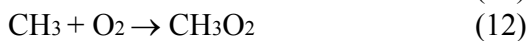
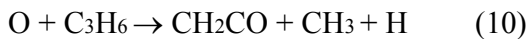
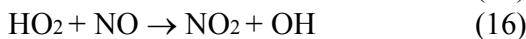
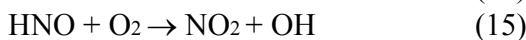
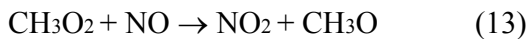


Fig.2. Plasma processing of :(a) 500 p.p.m. NO in 10% O₂, balance N₂ at 300°C, and (b) 500 p.p.m. NO, 1000 p.p.m. C₃H₆ in 10% O₂ balance N₂ at 300°C. [2]

The efficiency of NO-oxidation decreases with increasing temperature. When hydrocarbons other than methane are present in the gas mixture, O-radicals preferably react with hydrocarbon molecules thereby initiating a reaction chain forming several oxidizing radicals. One such reaction chain proposed for propylene e.g. is



Oxidation of NO can proceed according to



Similar reaction chains were proposed for ethylene. It is common to all these reaction chains, that one O-radical induces the oxidation of several NO-molecules and that reactions of NO₂ are suppressed as long as the hydrocarbon concentrations are high enough scavenge the O-radicals generated by electron collisions. Therefore the energy requirements for the oxidation of NO to NO₂ are reduced, and much

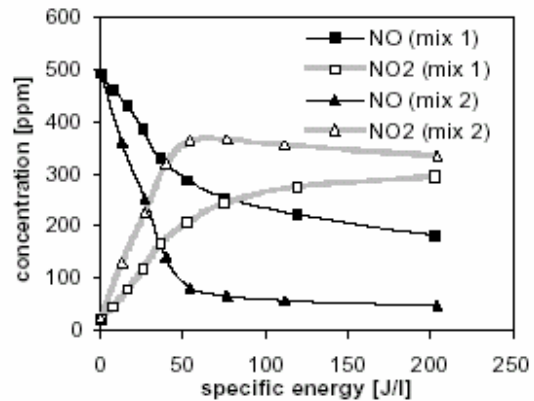


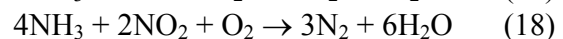
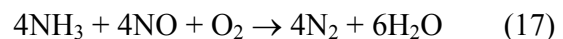
Figure 3: DBD-induced conversion of NO to NO₂. Gas mixture (mole fractions), [N₂]/[O₂]/[H₂O] = 0.72/0.18/0.10, volume flow 10 slm, gas temperature 100 °C. mix 1 – without C₂H₄, mix 2 – [C₂H₄]₀ = 500 ppm. [3]

higher NO₂-concentrations can be obtained (Figure 3). These effects were not only observed in synthetic gas mixtures where hydrocarbons with double bonds are present, but were observed in real Diesel exhaust, too. While NO-oxidation to NO₂ is improved by hydrocarbons, SO₂-oxidation to SO₃ is suppressed. [2-3]

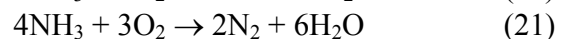
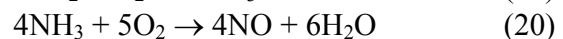
Plasma-Assisted Catalytic Reduction of NO_x

Selective catalytic reduction (SCR) by hydrocarbons is one of the leading catalytic after-treatment technologies for the reduction of NO_x in lean-burn engine exhaust (often referred to as 'lean-NO_x'). [6]

Many challenges exist when applying catalysis/Catalysts to fuel combustion processes (stationary applications) for NO_x emission control. The basic chemistry involves the following reactions: [6]



Selective or desired reactions

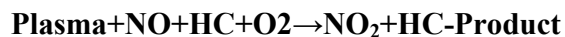


Ammonia or in some cases urea reacts selectively to reduce the NO_x. The non-selective reaction consumes the reagent and reduces the NO_x conversion.

In situations where sulfur compounds are present, the conversion to SO₃ must be minimized to prevent salt formation and deposits on heat transfer surfaces, which reduce the heat transfer efficiency. In mobile applications, the SO₃ must also be minimized since this leads to increased particulates. [6]

After-treatment schemes have focused a great deal on the reduction of NO because the NO_x in engine exhaust is composed primarily of NO. However, catalyst studies have shown that the oxidation of NO to NO₂ serves an important role in enhancing the efficiency for reduction of NO_x to N₂. It has become apparent that preconverting NO to NO₂ could improve both the efficiency and durability of lean-NO_x catalysts. A low-temperature plasma can be an efficient means for selective partial oxidation of NO to NO₂. The use of a low-temperature plasma in combination with a lean-NO_x catalyst opens the opportunity for catalysts that are more efficient and more durable compared to conventional catalysts. [2-8]

The plasma-assisted catalytic reduction of NO_x is accomplished in essentially two steps. First, the plasma oxidizes NO to NO₂ in the presence of a hydrocarbon: [2]



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: [2]



Figure (4) is a schematic of a plasma-assisted catalyst processor. There are many ways of producing a low-temperature plasma. In Fig.4 the plasma reactor is located upstream

of the catalyst reactor. The same result is achieved if the catalyst is placed inside the plasma reactor. [2]

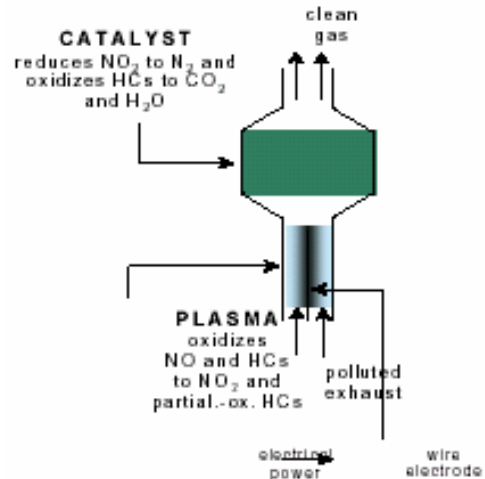


Fig. 4 The plasma-assisted catalytic reduction process. [2]

Figure (5) shows Fourier transform infrared (FTIR) spectra illustrating the effect of catalyst, plasma and plasma-plus-catalyst combination on the NO_x and hydrocarbons. In this example, propene is used as the hydrocarbon reductant. When the electrical power to the plasma reactor is turned off and the gas mixture is passed through the catalyst, the efficiencies for both the NO_x reduction and the hydrocarbon oxidation are very low, as shown in the second box ('catalyst only'). When the electrical power to the plasma reactor is turned on, the NO is oxidized to NO₂ and the propene is partially oxidized to formaldehyde, as shown in the third box ('plasma only'). When the NO₂-containing gas stream from the plasma is then passed through the same catalyst, both the NO_x and the hydrocarbons are eliminated, as shown in the bottom box ('plasma-catalyst'). The plasma-plus-catalyst combination efficiently removes NO_x and hydrocarbons under conditions in which the plasma or the catalyst alone is ineffective. [2]

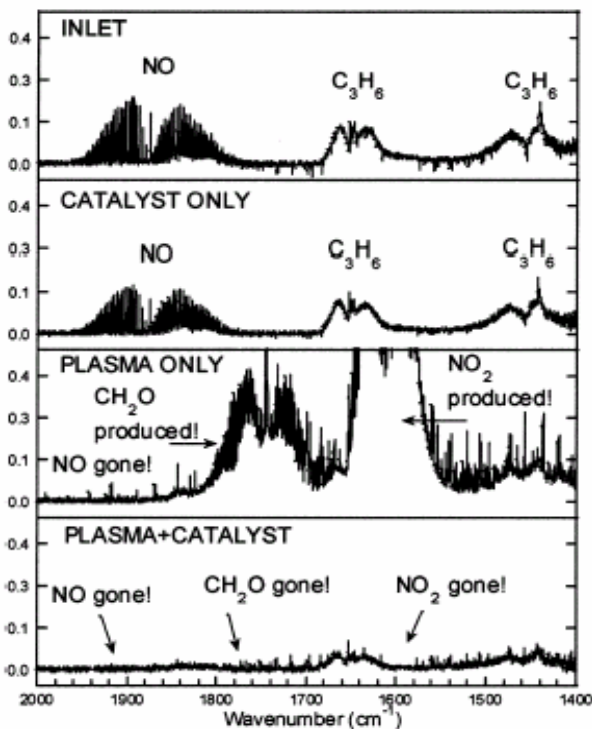


Fig. 5 Fourier Transform Infrared (FTIR) spectroscopy data showing the effect of catalyst, plasma and plasma+catalyst combination on the NOx and hydrocarbons. [2]

Summary and conclusions

NTP-methods have the potential for improved exhaust gas cleaning for cars, because they enable oxidation of noxious compounds at low exhaust gas temperatures. In the case of hydrocarbons and soot these oxidation processes directly reduce emissions. The catalytic reduction of nitrogen oxides at low exhaust gas temperatures is enabled by oxidation of NO to NO₂ or by partial oxidation of hydrocarbons working as a reducing agent.

A low-temperature plasma by itself can not chemically reduce NO_x to N₂ in the highly oxidizing environment of a diesel engine exhaust. To implement the reduction of NO_x to N₂, it is necessary to combine the plasma with a heterogeneous process that can chemically reduce NO₂ to N₂. The selective partial oxidation of NO to NO₂ in a plasma can be utilized to enhance the reduction of NO_x to N₂

by a catalyst. One of the approaches currently offering the greatest hope of reducing NO_x in diesel exhaust is a catalyst working in conjunction with a low temperature plasma.

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