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HAL Id: hal-00918937

https://hal.science/hal-00918937

Submitted on 16 Dec 2013

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ABSTARCT
A non-thermal plasma (NTP) reactor was coupled with a three-function catalyst in order to verify the nature of the effect of the plasma on the catalytic process. A mixture of NO/O_2/hydrocarbons in N_2 was used as a lean model exhaust gas composition. The plasma was found to perform two of the three functions defined in the catalysis model when coupling the plasma reactor to the catalytic deNOx: NO oxidation to NO_2 and hydrocarbon activation through the partial oxidation to aldehyde and/or alcohol were observed. The NOx conversion is higher than 20% between 200 and 360°C, 40% being obtained at 300°C. This behaviour clearly demonstrates the role of the NTP as a promoter of the deNOx reaction which is in full accordance with the proposed model. It can be seen that the NTP is activating the lowtemperature deNOx function of alumina while providing a wide operating temperature window for deNOx reaction.

KeyWords: Non-thermal plasma, Selective catalytic reduction, NOx,

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INTRODUCTION

The air pollutants such as nitrogen oxides NOx (NO and NO_2) and volatile organic compounds (VOC's) are precursor of ozone and remain the most serious hazards to human health among the regulated compounds. Among the existing pollution sources, motor vehicles are seen as the major contributor to air pollution by NOx, unburned hydrocarbons (UHC) and fine particle matter (PM).The selective reduction of NOx to N_2 and the total oxidation of VOCs to CO_2 and H_2O are still a matter of intensive research and no stable and sufficiently active catalyst has yet been designed to reduce the NOx (NO+NO_2) emission from automotive exhaust gases in lean (i.e. oxygen-rich) conditions.

As an alternative to catalytic processes which require high temperatures, non-thermal plasma (NTP) also referred as "non-equilibrium plasma" or "cold plasma", such dielectric barrier discharges (DBD) and corona discharges have been extensively investigated in the field of pollution control and frequently proposed in the literature for the removal of VOCs, NOx and SO_2 [1-8]. In NTP, background gaseous species are chemically excited or dissociated directly by electronic impact, while the temperature of the reactants (i.e. gas temperature) remains relatively low and thus the product distributions far from the chemical equilibrium may be obtained. In that case, the most useful deposition of energy is associated with the production of excited species (atoms, molecules) and activated species (radicals, ions) that eventually lead to the chemical conversion of pollutants.

Although NTPs present attractive properties (low temperature, atmospheric pressure, compactness) and a unique way to induce gas phase reactions by electron collisions, the formation of unwanted by-products and poor energy efficiency are serious obstacle towards their industrial implementation.To overcome these drawbacks, a more effective use of NTP is possible by exploiting its inherent synergetic potential through combination with heterogeneous catalyst as emphasized by different groups [9-11]. This innovative technique called plasma-catalysiswhich combines the advantages of both NTP and catalysis has become a hot topic over the last decade.Catalyst can be combined with plasma in two ways: in-plasma catalysis (IPC), with the catalyst directly into the discharge zone or post-plasma catalysis (PPC), with the catalyst downstream the discharge zone.

The conventional NTP reactors that are widely used for various environmental applications are subdivided according the type of discharge mode (pulse, DC, AC, RF, microwave), presence of a dielectric barrier or catalyst, and geometry (cylinder, plate). It is important to note that the chemical potential of each discharge mode differs enormously from one discharge to another. Roughly speaking, the efficiency of a plasma discharge to remove pollutant from gas stream depends mainly on its ability to produce large amount of active species in the plasma volume. It has been well established that DBD and corona discharge fulfilled that condition [12-13].

For the vehicle exhaust systems, it was established that the observed chemistry in the plasma includes the conversion of NO to NO_2 as well as the partial oxidation of hydrocarbons. The presence of the unburned hydrocarbons (UHCs)in the exhaust is very important for the plasma-catalytic deNOx process for multiple raisons[1-2, 5, 14-17].First, UHCs enhance the gas phase oxidation of NO to $NO_2$and lower the energy cost for this oxidation. Secondly, their partial oxidation leads to produce chemical species such as aldehydes and alcohols useful for the catalytic reduction of NOx. Thirdly, UHCs prevent the oxidation of SO_2 thus making the plasma-catalytic process tolerant to the sulphur content of the fuel.For some catalysts, the partially oxygenated hydrocarbons are much more effective compared to original hydrocarbons in reducing NOx to N_2.

In this present paper, we report experimental studies on the NOx conversion chemistry in lean automotive exhaust gases by a sub-µs pulsed DBDs. Results of plasma and plasma assisted alumina catalyst will be presented to validate a three-function catalyst model.

MATERIAL AND METHODS

DBD reactors in cylindrical configuration combined or not to heterogeneous catalyst have been used. For automotive application, the catalyst materials are usually placed downstream from NTP reactor (PPC: *Post-Plasma Catalysis* or *Plasma-Enhanced Catalysis*) as shown in figure 1. The DBD reactor consisted of a tungsten wire (0.9 mm diameter) centered in a quartz tube (inner and

outer diameters of 11 mm and 13 mm, respectively). A brass mesh covered the dielectric tube and forms the outer electrode. The length of the outer electrode can be adjusted and then determines the active volume of the plasma reactor. The DBD reactor was placed inside a tubular furnace and the gas mixture temperature could be adjusted from room temperature to 500°C.
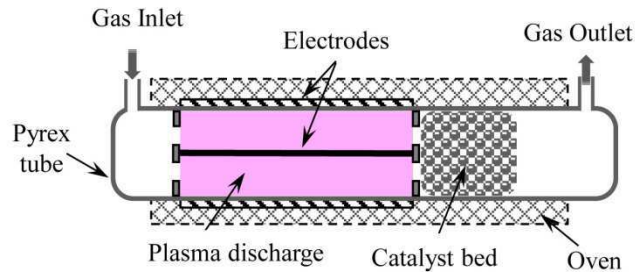

Fig. 1:Schematic overview of the plasma-catalyst configurations: PPC (a) and IPC (b).

The DBD reactor was driven by a high-voltage pulse generatordelivering output voltage up to 30 kV into 0.1 to 0.5 µs pulses (half width at half maximum)at repetition rate up to 200 Hz. Electrical characterization of the plasma was performed by current and voltage measurements using a HV Tektronix P6015A probe and Pearson 4001 current probe having 10 ns rise time, respectively. The electrical energy deposition in the plasma reactor was evaluated through the specific input energy (SIE) which is the parameter commonly used to evaluate the NOx conversion efficiency in the plasma. However, if this parameter is important to characterize the electrical energy consumption of the process we should take into account the way to achieve the chosen energy value [18]. It means that for a specific energy deposited in given plasma reactor, the plasma chemistry strongly depend on the type of the discharge (pulsed or AC voltage for example) and their HV-parameters (amplitude, rise time, duration, and frequency).SIE (J/L) is given by $E_d = (E_p/Q).f$, in which E_p is the discharge pulse energy (J/pulse), f the pulse repetition frequency (Hz), and Q is the gas flow rate (L/s) at standard conditions. The discharge pulse energy could be adjusted by varying the discharge voltage. An example of the time-behavior of theinstantaneous discharge power and discharge pulse energy is given in the figure 2 for input voltage of 14 kV.
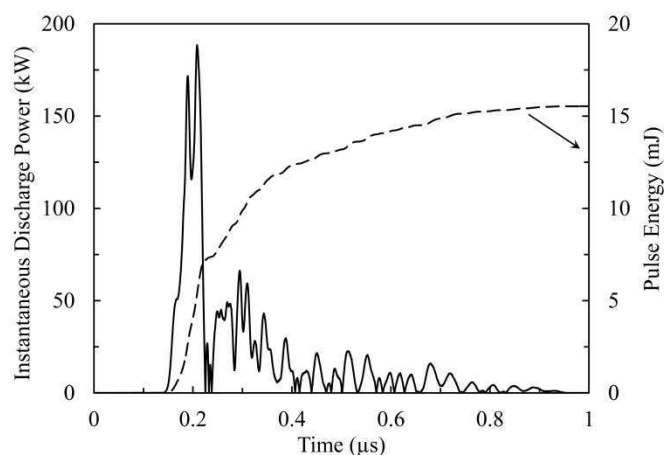

Fig. 2:Time behavior of the instantaneous discharge power and discharge pulse energy (input voltage = 14 kV).

NOx reduction experiments have been conducted to investigate gas mixtures with composition more and more complex. The goal is to reach synthetic gas exhausts simulating diesel and lean-burn gasoline engineexhausts. Typically, the N_2-based mixture consists of O_2, H_2O, NO, hydrocarbons (C_3H_6, C_3H_8, n-C_{10}, and toluene). The gas mixtures were prepared in a gas handling system and their composition was controlled using calibrated high-precision mass flow controllers.Maximum concentration of different gas components is: O_2 (10%), H_2O (10%), NO(500 ppm), NO_2 (500 ppm), C_3H_6 (2000 ppm), C_3H_8 (150ppm), n-C_{10} (1100 ppm), toluene (450ppm), and N_2 as balance.

The reactor outflow was analyzed using a set of specific detectors. A NOx analyzer (Eco Physics CLD 700 AL) allowed the simultaneous detection of NO, NO_2 and NOx. The hydrocarbon concentration was followed by gas micro-chromatography (Agilent G2890A). This apparatus allowed also the analysis of various gases such as H_2, O_2, N_2, CO, and CO_2, in a scale ranging from ppm to %.Additional chemical analysis were performed by using Fourier transform infrared absorption spectrometer (FTIR-Nicolet Magna 550 II) equipped with a heated 10 mmultiple pass absorption cell.

RESULT AND DISCUSSION

During plasma discharge in typical exhausts contain N_2, O_2, and H_2O with NO (the major form of NOx), primary radicals (N, OH, and O) are created by electron-impact reactions and rapidly consumed by reactions in the remediation pathway. Secondary radicals (HO_2, NO_3, and O_3) are not formed by direct electron-impact events but rather by reactions involving the primary radicals. Much effort has already been expended upon the modeling of the removal by plasma of pollutant species from vehicle exhaust streams, particularly the direct removal of NOx. Attention has now turned to studying the chemistry occurring when a hydrocarbon is added to the mixture, promoting the conversion of NO to NO_2. Detailed kinetic schemes and discussions of the mechanisms involved in gas phase chemistry in the plasma processing O_2, NO, N_2, and HC mixtures were studied extensively [19-22].

Figure 3 show the concentrations of NO and NO_2at room temperature as function of the specific input energy for the cases without propene and with 500 ppm propene, respectively. In HC-free mixture, the oxygen radicals are the responsible for the oxidation of NO to NO_2. Less than 50% of the initial NO is converted to NO_2 even for the highest energy densities (up to 103 J/L). The increase of NO conversion obtained with increasing energy deposition is counteracted by the increase in NO_2 concentration resulting in an almost constant NOx level.
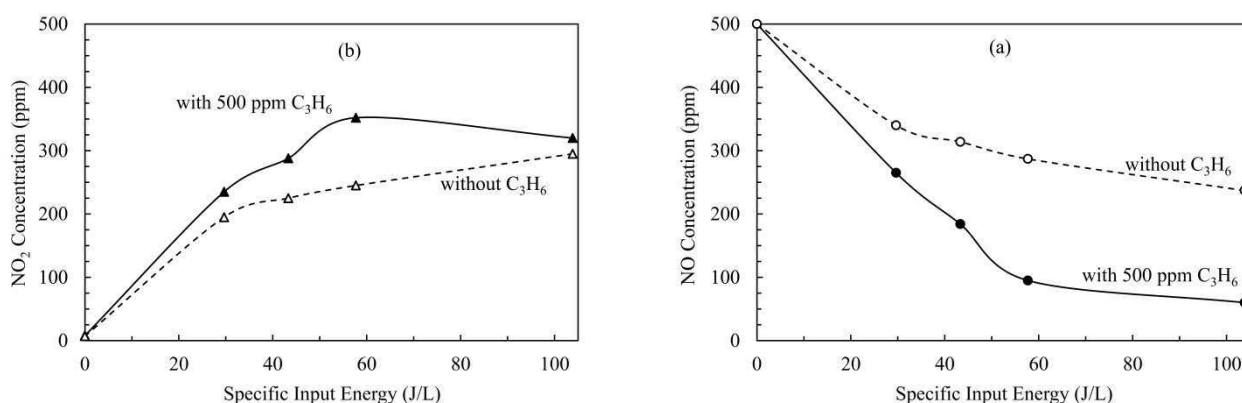

Fig. 3:Effect of input energy density on the plasma oxidation of NO to NO_2at room temperature (500 ppm NO in 19.6% O_2, balance N_2, without and with 500 ppm propene).

UHCs, currently present in diesel exhausts, significantly influenceNOx chemistry during plasma remediation by oxidizing NO into NO_2.This behavior is illustrated in figures 3(a) and 3(b) and shows that at SIE = 90 J/L, the NO removal was improved by nearly a factor 2 when adding 500 ppm of C_3H_6. In that case, the radical responsible for the oxidation of NO to NO_2 is no longer the O radical. From chemical kinetics analysis, Penetrante et al [1] shows that the HO_2 is the radical that oxidizes NO to NO_2 when the plasma processing is done in the presence of hydrocarbons. Globally, the plasma chemistry show that the atomic oxygen produced in the discharge is the initiator of the hydrocarbon chemistry. These reactions produce HC radical intermediates such as RO_2, OH, and HO_2. After the initiation of the kinetic, OH radicals rather than O atoms become the main HC consuming species. Although diesel exhausts are humid with a typical water content of few %, the production of OH radicals by electron impact dissociation of water is slow [23] and the main source of OH comes from the hydrocarbon oxidation chemistry. TheHO_2radical and to a lesser extent peroxy radicals, RO_2, are responsible for the conversion of NO into NO_2 [4]The RO radicals then go on to produce the aldehydes [22].

In addition to NO_2, plasma processing of mixture containing O_2-NO-H_2O-HC-N_2 lead to the production of CO, CO_2, aldehydes (CH_3CHO, CH_2O), alcohols (CH_3OH), nitrate and nitrite compounds of R-NOx type (CH_3ONO, CH_3ONO_2), nitromethane (CH_3NO_2), formic acid (CH_2O_2), propylene oxide (C_3H_6O),and some extent of acids (HNO_2, HNO_3).Formations of such molecules are predicted by kinetic models [17, 20, 22-23] and detected by gas chromatography and FTIR spectroscopy as well [5, 24-25].Examples of FTIR and GC measurement resultsobtained at the exit of pulsed-DBD in dry gas mixture are shown in figures 4 and 5.
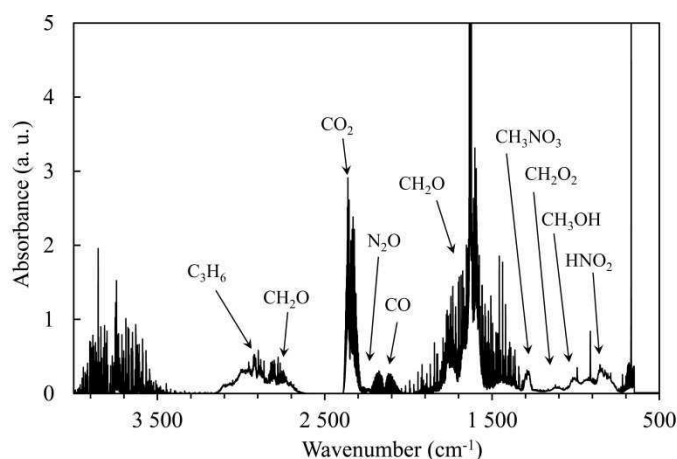

Fig. 4: Typical FTIR spectrum of the products from pulsed DBD processing (27 J/L input energy density, room temperature) of O_2 (10%)-NO (500 ppm)-C_3H_6 (1500ppm)-N_2.
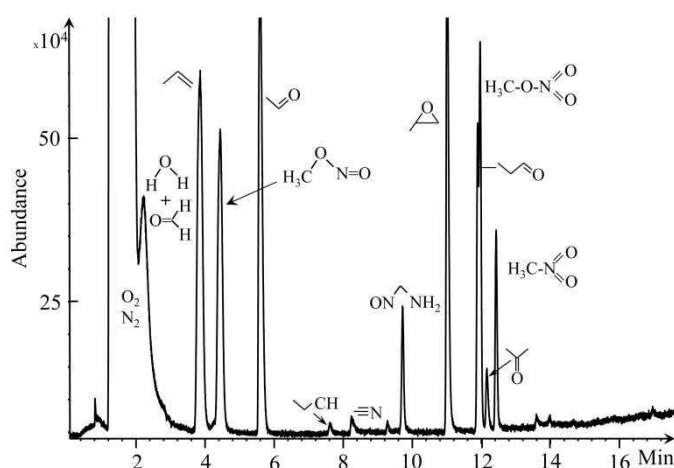
Fig. 5:Typical chromatogram plot of a gas phase from pulsed DBD processing (36 J/L, 150°C) of O_2 (8 %)-NO (300 ppm)-C_3H_6 (450 ppm)-N_2.

When the gas mixture was heated, the NO to NO_2 oxidation reaction is counteracted at high temperature by the reduction reaction as shown in figure 6. In these C_3H_6-O_2-NO-N_2 mixtures, the maximum efficiency for oxidation of NO to NO_2 increases as the C_1/NO_x ratio is increased. A C_1/NO_x ratio of 4 is required to get 80% oxidation efficiency. In the absence of propene, the oxidation efficiency is very low (54%) even at high values of electrical energy density input to the plasma.The evolution of the total HC concentration(FID signal) as a function of the temperature show that some amount of hydrocarbon species remain is the gas phase even at temperature as high as 400°C.
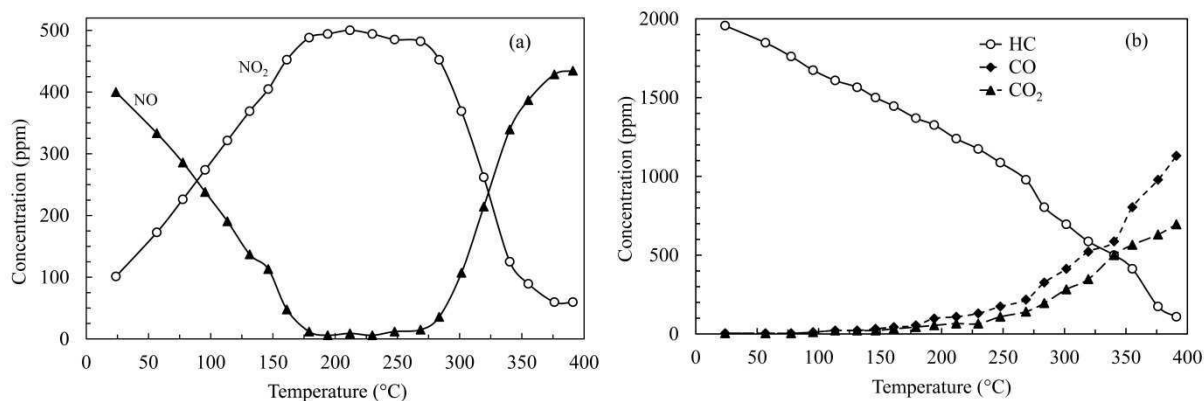

Fig. 6:Species concentrationsas a function of the gas temperature at the exit of HV-pulsed DBD at 36 J/L.Gas mixture: C_3H_6 (2000 ppm)-NO (500 ppm)-O_2 (8 % vol.)-N_2.

The need for an effective after-treatment process capable to reduce NOx under lean conditions has produced a large interest in plasma assisted catalytic reduction. From the literature, it was found that catalyst such as γ-Al_2O_3 and NaY zeolite presented high activity when combined with non-thermal plasma.Authors did not give any interpretation for the observed results, but published the composition of the stabilized gas mixture at the outlet of the plasma reactor, just before the catalytic reactor.In order to understand the role of plasma in deNOx catalysis, a deNOx: reaction model is required. A three function catalyst model for hydrocarbon (HC) SCR of NOx has been previously defined, in the absence of plasma, by Djéga-Mariadassou and coworkers [19, 24, 26, 27]. That model is based on experimental evidence for each function, during temperatureprogrammed surface reactions (TPSR) and has been verified during stationary experiments.A general scheme of the model is shown in figure 7. The first function F1 leads to the oxidation of NO to NO_2. The second

function F2 is the mild oxidation of HC through organic nitrogen-containing intermediates (R-NOx)leading to $C_xH_yO_z$ intermediate species such as aldehydes or alcohols.The 3rd function F3 involves the NO reduction by subsequent formation of N_2 assisted by the oxidation of reductants to CO_2/H_2O over transition metal cations. The previous $C_xH_yO_z$ intermediate species can achieve their own total oxidation by cleaning the adsorbed oxygen species left by NO dissociation. The catalyst has to simultaneously produce, by itself, all these reactions and the three functions have to turn over simultaneously. This reaction corresponds to "a supported homogeneous catalytic process" involving a surface transition metal complex.
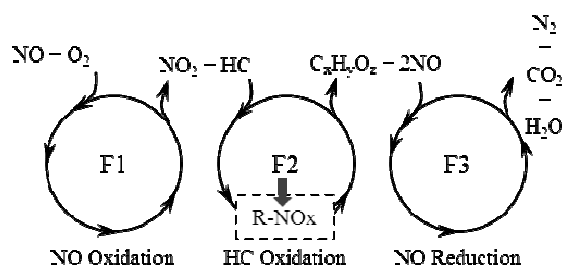

Fig. 7: General scheme of the three-function model designing deNOx catalystin presence of non-reactive HC as reductant [19].

It is very difficult to find the best design of the catalyst to simultaneously initiate the three functions by itself. Thus an external device can be developed to substitute functions F1 and F2, providing the catalyst the good oxygenated species, in the full range of temperature.For the vehicle exhaust systems, it was established that the plasma chemistry includes the conversion of NO to NO_2 as well as the partial oxidation of hydrocarbons. The presence of the UHCs in the exhaust is very important for the plasma-catalytic deNOx process for multiple reasons. First, UHCs enhance the gas phase oxidation of NO to NO_2 (figure 3) and lower the energy cost for this oxidation. Secondly, their partial oxidation leads to produce,in the whole range of reaction temperature, chemical species such as aldehydes, alcohols, and R-NOx(figures 4 and 5) useful for the catalytic reduction of NOx. For some catalysts, the partially oxygenated hydrocarbons are much more effective compared to original hydrocarbons in reducing NOx to N_2. Thirdly, UHCs prevent the oxidation of SO_2 thus making the plasma-catalytic process tolerant to the sulphur content of the fuel. These "intermediate" species are needed for function F1 and F2 and furthermore, for the third function itself.

The three-function model was tested by checking the activity of a complete catalyst (named catalyst A) designed to contain the three functions [26] and a simplified catalyst (named catalyst B) including only the third function F3.The catalyst A is Rh^{x+}/CeO_2-ZrO_2 based material [28], to which a first and a second functions were added. These two kinds of catalysts were found to be stable under the experimental conditions, allowing a reliable evaluation of the effect of the plasma on the catalytic process. In order to check the efficiency and the role of the plasma on the deNOx process by providing oxygenates and nitro-compounds to catalyst from low temperature, the conversion of NOx versus temperature has been conducted with the catalyst "B" in the presence of plasma (plasma ON) and with the catalyst "A" in the absence of plasma (plasma OFF). Results are reported in figure 8. These results show that the deNOx conversion at about 270°C is almost the same for both catalysts. Nevertheless, the behavior between room temperature and 170°C is quite different, due to the probable R-NOx formation in the plasma and their subsequent adsorption on the catalyst support. The NTP could substitute for the first two functions of the complete catalyst "A". As a consequence, catalyst "B" in the presence of plasma was found to be equivalent to catalyst "A" in the absence of plasma. This result demonstrates what can be the role of plasma in non-thermal

plasma assisted catalytic NOx remediation. Furthermore, plasma is able to provide both NO_2 and $C_xH_yO_z$ intermediate species at low temperature. However, the behavior of the R-NOx species formed in the plasma still remains to be studied. The NOx removal leads mainly to dinitrogen as reported previously [25].
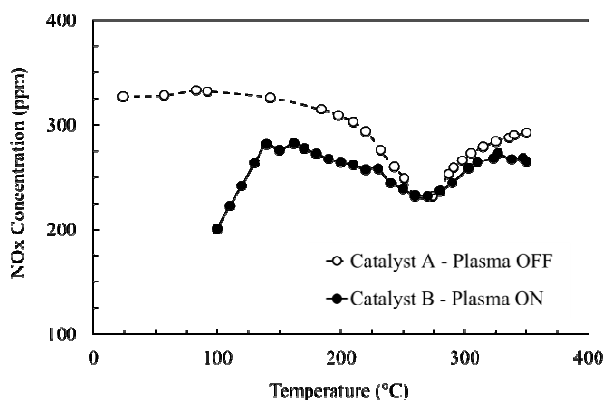

Fig. 8: NOx concentration versus reaction temperature in the presence of plasma (36 J.L^{-1} (Catalyst B) and in the absence of plasma (Catalyst A) during a TPSR (1°C.min^{-1} of NO (340 ppm) - O_2 (8%)- C_3H_6 (1900 ppm) - GHSV=45000 h^{-1}

The experiments of coupling a NTP reactor with a catalyst (Alumina) forcatalytic-assisted deNOxhas been carried out by flowing a C_3H_6- NO-O_2-N_2 mixture in the two successive reactors. Figure 9 shows the conversion of global HC (without discrimination of the nature of compounds), HC being defined as propene, oxygenates $C_xH_yO_z$, and nitrogen-containing species. Conversion of NOx versus temperature is also reported.
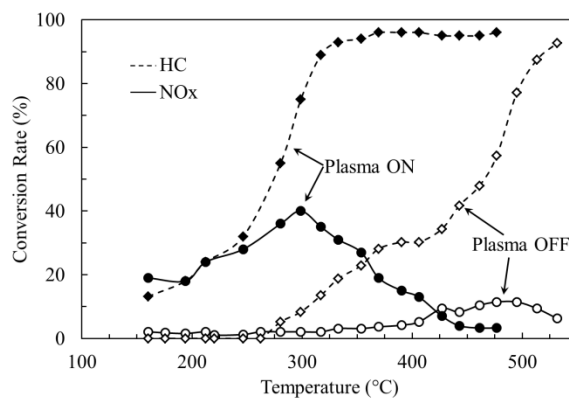

Fig. 9: NOx and global HC conversions as a function of temperature: NO (500 ppm), C_3H_6 (2000 ppm), O_2 (8 vol%), N_2. Catalyst: Al_2O_3, GHSV:54 000 h^{-1}.

In. the absence of plasma, Al_2O_3 only begins to be active in deNOx, at high temperatures, starting at 350°C, with a NOx conversion of about 10% above 425°C (Figure xx). Furthermore, HCs are oxidized to CO_2/H_2O from 270°C, that is, before NO activation on alumina. In accordance with the model, the deNOx process is poor (low turnover of the function F3 catalytic cycle) because of the lack of reducer at high temperature.

ln the presence of plasma, NOx conversion starts at a low temperature, simultaneously with the total oxidation of HC to CO_2/H_2O. The NOx conversion is higher than 20% between 200 and 360°C, 40% being obtained at 300°C. This behaviour clearly demonstrates the role of the NTP as a

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promoter of the NOx reduction reaction. It can be seen that the NTP is activating the low-temperature deNOx function of alumina while providing a wide operating temperature window for deNOx reaction.

CONCLUSION

The NTP-catalytic reactor for deNOx has been illustrated comparing data of the NTP activity on reaction mixtures and the NTP-catalytic reactor coupling.

The NTP plays the role of two of the three functions defined in the catalysis model when coupling the plasma reactor to the catalytic deNOx device (as far the catalyst has been designed in order to possess three catalytic functions):

(i) the conversion of NO to NO_2

(ii) the production of oxygenated compounds $C_xH_yO_z$ and organic intermediates R-NOx that are able to decompose to oxygenates.

It has been shown that in addition to NO_2, plasma processing of a mixture containing O_2-NO-H_2O-HC-N_2 leads to the production of aldehydes (CH_3CHO, CH_2O), alcohols (CH_3OH), nitrate and intermediate organic nitroso compounds of R-NOx type (CH_3ONO, CH_3ONO_2), nitromethane (CH_3NO_2), formic acid (CH_2O_2), propylene oxide (C_3H_6O), and to some extent of acids (HNO_2, HNO_3). Formations of such molecules are predicted by kinetic models of NTP.

NOx reduction experiments have been selected to investigate gas mixtures with increasing the complexity of the compositions mixtures, representative of a real Diesel exhaust mixture. The goal was to produce synthetic gas exhausts simulating diesel and lean-bum gasoline engine exhausts. Typically, the N_2-based mixture consists of O_2, H_2O, NO, and HCs (C_3H_6, C_3H_8, C_7H_8, and n-C_{10}). In all cases, the plasma reactor has been shown to deliver to the catalyst reactor a rich mixture of NO_2, oxygenates, and intermediate organic nitroso compounds, completely consumed during the deNOx catalytic process and leading to efficient NOx abatements and allowing the extension of the temperature windows of deNOx reaction from room temperature.

ACKNOWlLEDGMENTS

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