



HAL
open science

Plasma Assisted Catalyst for NO_x Remediation from Lean Gas Exhaust

Ahmed Khacef, Patrick da Costa, Gérald Djéga-Mariadassou

► **To cite this version:**

Ahmed Khacef, Patrick da Costa, Gérald Djéga-Mariadassou. Plasma Assisted Catalyst for NO_x Remediation from Lean Gas Exhaust. *Journal of Engineering and Technology Research*, 2013, 1 (1), pp.112-122. hal-00918937

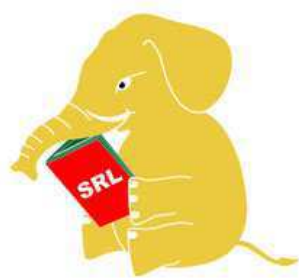
HAL Id: hal-00918937

<https://hal.science/hal-00918937v1>

Submitted on 16 Dec 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Scientia Research Library

Journal of Engineering And Technology Research
, 2013, 1 (1):112-122

<http://www.scientiaresearchlibrary.com/archive.php>

Plasma assisted catalyst for NO_x remediation from lean gas exhaust

Ahmed Khacef^{1*}, Patrick Da Costa², Gérald Djéga-Mariadassou³

¹GREMI - Groupe de Recherche sur l'Energétique des Milieux Ionisés UMR 7344, CNRS - Université d'Orléans, 14 rue d'Issoudun, BP 6744, 45067, Orléans Cedex 02, France

²IJLRA, Université Pierre et Marie Curie, UPMC Sorbonne Université, UMR 7190, 2 place de la gare de ceinture, 78210 Saint Cyr l'école, France

³On leave from UPMC Paris 6, Université Pierre et Marie Curie, Laboratoire Réactivité de Surface, UMR CNRS 7609, 4 place Jussieu, Case 178 Tour 54-55, 75252 Paris Cedex 05, France.

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/O₂/hydrocarbons in N₂ 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 deNO_x: NO oxidation to NO₂ and hydrocarbon activation through the partial oxidation to aldehyde and/or alcohol were observed. The NO_x 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 deNO_x reaction which is in full accordance with the proposed model. It can be seen that the NTP is activating the low temperature deNO_x function of alumina while providing a wide operating temperature window for deNO_x reaction.

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

INTRODUCTION

The air pollutants such as nitrogen oxides NO_x (NO and NO₂) 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 NO_x, unburned hydrocarbons (UHC) and fine particle matter (PM). The selective reduction of NO_x to N₂ and the total oxidation of VOCs to CO₂ and H₂O are still a matter of intensive research and no stable and sufficiently active catalyst has yet been designed to reduce the NO_x (NO+NO₂) 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, NO_x and SO₂ [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-catalysis which 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 NO₂ 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 deNO_x process for multiple reasons [1-2, 5, 14-17]. First, UHCs enhance the gas phase oxidation of NO to NO₂ 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 NO_x. Thirdly, UHCs prevent the oxidation of SO₂ 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 NO_x to N₂.

In this present paper, we report experimental studies on the NO_x conversion chemistry in lean automotive exhaust gases by a sub- μ s 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.

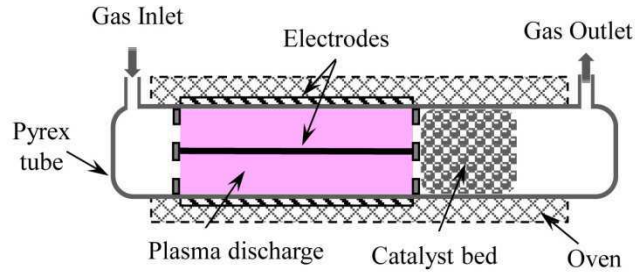


Fig. 1: Schematic overview of the plasma-catalyst configurations: PPC (a) and IPC (b).

The DBD reactor was driven by a high-voltage pulse generator delivering output voltage up to 30 kV into 0.1 to 0.5 μ s 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 NO_x 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 $E_d = (E_p/Q) \cdot f$, 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 the instantaneous discharge power and discharge pulse energy is given in the figure 2 for input voltage of 14 kV.

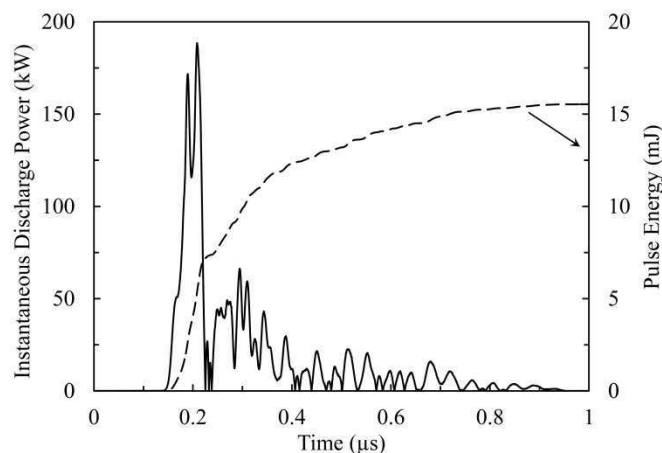


Fig. 2: Time behavior of the instantaneous discharge power and discharge pulse energy (input voltage = 14 kV).

NO_x 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 engine exhausts. Typically, the N₂-based mixture consists of O₂, H₂O, NO, hydrocarbons (C₃H₆, C₃H₈, n-C₁₀, 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: O₂ (10%), H₂O (10%), NO (500 ppm), NO₂ (500 ppm), C₃H₆ (2000 ppm), C₃H₈ (150 ppm), n-C₁₀ (1100 ppm), toluene (450 ppm), and N₂ as balance.

The reactor outflow was analyzed using a set of specific detectors. A NO_x analyzer (Eco Physics CLD 700 AL) allowed the simultaneous detection of NO, NO₂ and NO_x. The hydrocarbon concentration was followed by gas micro-chromatography (Agilent G2890A). This apparatus allowed also the analysis of various gases such as H₂, O₂, N₂, CO, and CO₂, 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 mm multiple pass absorption cell.

RESULT AND DISCUSSION

During plasma discharge in typical exhausts contain N₂, O₂, and H₂O with NO (the major form of NO_x), primary radicals (N, OH, and O) are created by electron-impact reactions and rapidly consumed by reactions in the remediation pathway. Secondary radicals (HO₂, NO₃, and O₃) 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 NO_x. Attention has now turned to studying the chemistry occurring when a hydrocarbon is added to the mixture, promoting the conversion of NO to NO₂. Detailed kinetic schemes and discussions of the mechanisms involved in gas phase chemistry in the plasma processing O₂, NO, N₂, and HC mixtures were studied extensively [19-22].

Figure 3 show the concentrations of NO and NO₂ at 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 NO₂. Less than 50% of the initial NO is converted to NO₂ 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 NO₂ concentration resulting in an almost constant NO_x level.

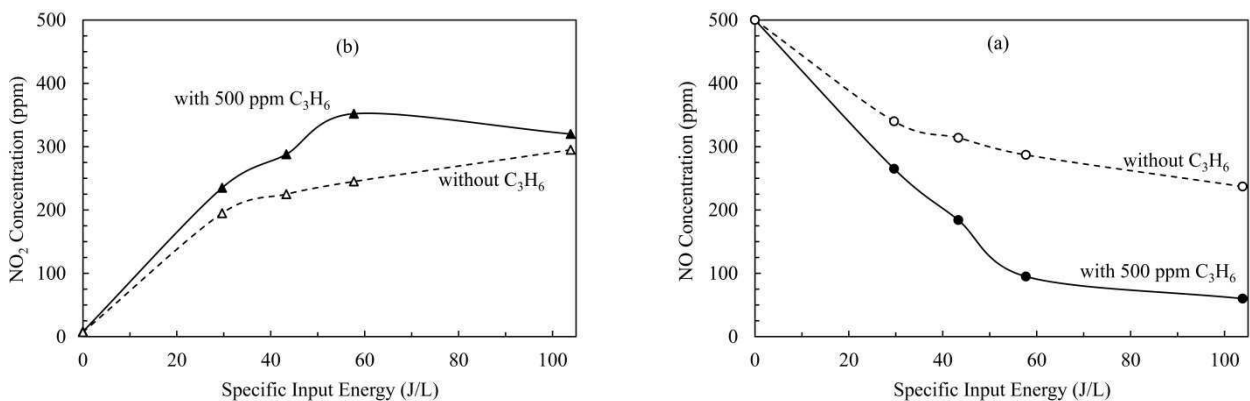


Fig. 3: Effect of input energy density on the plasma oxidation of NO to NO₂ at room temperature (500 ppm NO in 19.6% O₂, balance N₂, without and with 500 ppm propene).

UHCs, currently present in diesel exhausts, significantly influence NO_x 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 $\text{SIE} = 90 \text{ J/L}$, 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. The HO_2 radical 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-NO_x type (CH_3ONO , CH_3ONO_2), nitromethane (CH_3NO_2), formic acid (CH_2O_2), propylene oxide ($\text{C}_3\text{H}_6\text{O}$), 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 results obtained at the exit of pulsed-DBD in dry gas mixture are shown in figures 4 and 5.

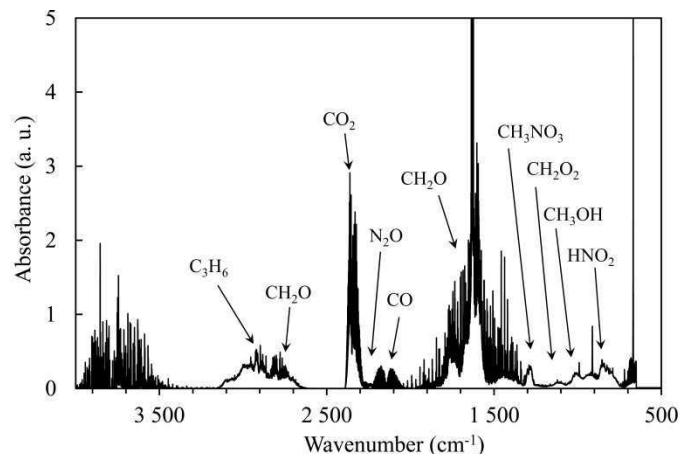


Fig. 4: Typical FTIR spectrum of the products from pulsed DBD processing (27 J/L input energy density, room temperature) of O_2 (10%)- NO (500 ppm)- C_3H_6 (1500ppm)- N_2 .

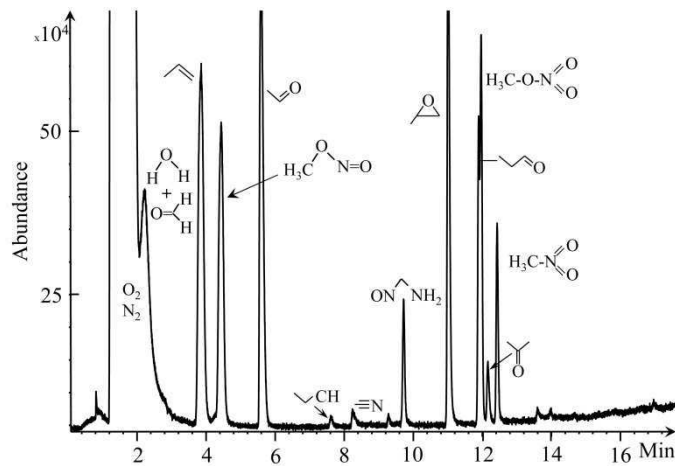


Fig. 5: Typical chromatogram plot of a gas phase from pulsed DBD processing (36 J/L, 150°C) of O₂ (8 %)-NO (300 ppm)-C₃H₆ (450 ppm)-N₂.

When the gas mixture was heated, the NO to NO₂ oxidation reaction is counteracted at high temperature by the reduction reaction as shown in figure 6. In these C₃H₆-O₂-NO-N₂ mixtures, the maximum efficiency for oxidation of NO to NO₂ increases as the C₁/NO_x ratio is increased. A C₁/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 in the gas phase even at temperature as high as 400°C.

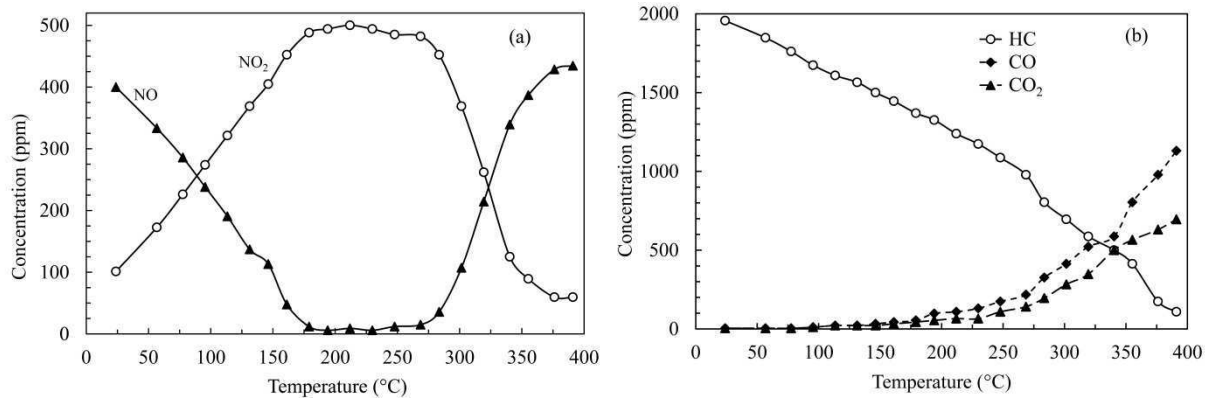


Fig. 6: Species concentrations as a function of the gas temperature at the exit of HV-pulsed DBD at 36 J/L. Gas mixture: C₃H₆ (2000 ppm)-NO (500 ppm)-O₂ (8 % vol.)-N₂.

The need for an effective after-treatment process capable to reduce NO_x under lean conditions has produced a large interest in plasma assisted catalytic reduction. From the literature, it was found that catalyst such as γ -Al₂O₃ 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 deNO_x catalysis, a deNO_x reaction model is required. A three function catalyst model for hydrocarbon (HC) SCR of NO_x 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 temperature programmed 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 NO₂. The second

function F2 is the mild oxidation of HC through organic nitrogen-containing intermediates (R-NO_x) 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 N₂ assisted by the oxidation of reductants to CO₂/H₂O 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.

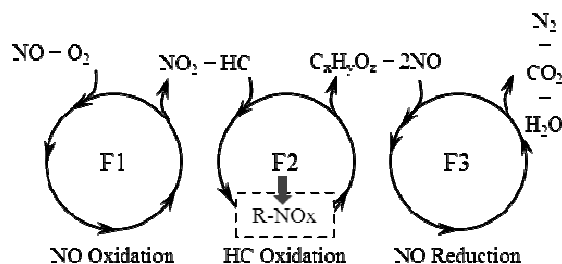


Fig. 7: General scheme of the three-function model designing deNO_x catalysis in presence of non-reactive HC as reductant [19].

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 NO₂ as well as the partial oxidation of hydrocarbons. The presence of the UHCs in the exhaust is very important for the plasma-catalytic deNO_x process for multiple reasons. First, UHCs enhance the gas phase oxidation of NO to NO₂ (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-NO_x (figures 4 and 5) useful for the catalytic reduction of NO_x. For some catalysts, the partially oxygenated hydrocarbons are much more effective compared to original hydrocarbons in reducing NO_x to N₂. Thirdly, UHCs prevent the oxidation of SO₂ 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+}/CeO₂-ZrO₂ 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 deNO_x process by providing oxygenates and nitro-compounds to catalyst from low temperature, the conversion of NO_x 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 deNO_x 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-NO_x 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 NO_x remediation. Furthermore, plasma is able to provide both NO₂ and C_xH_yO_z intermediate species at low temperature. However, the behavior of the R-NO_x species formed in the plasma still remains to be studied. The NO_x removal leads mainly to dinitrogen as reported previously [25].

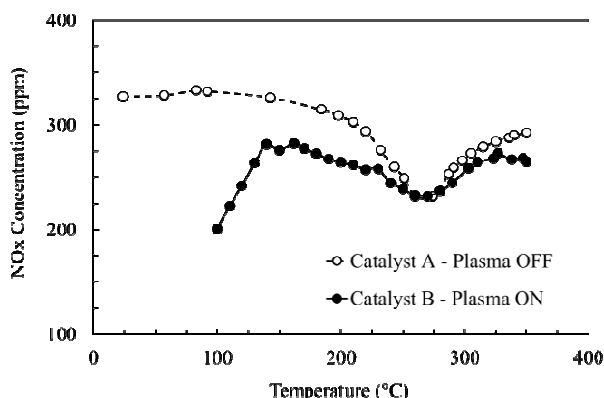


Fig. 8: NO_x concentration versus reaction temperature in the presence of plasma (36 J.L⁻¹ (Catalyst B) and in the absence of plasma (Catalyst A) during a TPSR (1°C.min⁻¹ of NO (340 ppm) - O₂ (8%) - C₃H₆ (1900 ppm) - GHSV=45000 h⁻¹

The experiments of coupling a NTP reactor with a catalyst (Alumina) for catalytic-assisted deNO_x has been carried out by flowing a C₃H₆- NO-O₂-N₂ 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 NO_x versus temperature is also reported.

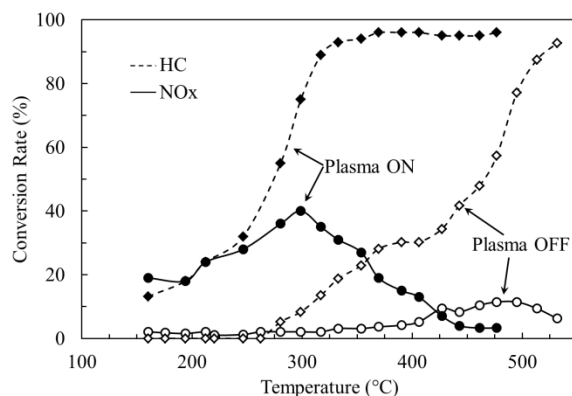


Fig. 9: NO_x and global HC conversions as a function of temperature: NO (500 ppm), C₃H₆ (2000 ppm), O₂ (8 vol%), N₂. Catalyst: Al₂O₃, GHSV:54 000 h⁻¹.

In the absence of plasma, Al₂O₃ only begins to be active in deNO_x, at high temperatures, starting at 350°C, with a NO_x conversion of about 10% above 425°C (Figure xx). Furthermore, HCs are oxidized to CO₂/H₂O from 270°C, that is, before NO activation on alumina. In accordance with the model, the deNO_x process is poor (low turnover of the function F3 catalytic cycle) because of the lack of reducer at high temperature.

In the presence of plasma, NO_x conversion starts at a low temperature, simultaneously with the total oxidation of HC to CO₂/H₂O. The NO_x 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 NO_x reduction reaction. It can be seen that the NTP is activating the low-temperature deNO_x function of alumina while providing a wide operating temperature window for deNO_x reaction.

CONCLUSION

The NTP-catalytic reactor for deNO_x 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 deNO_x device (as far the catalyst has been designed in order to possess three catalytic functions):

- (i) the conversion of NO to NO₂
- (ii) the production of oxygenated compounds C_xH_yO_z and organic intermediates R-NO_x that are able to decompose to oxygenates.

It has been shown that in addition to NO₂, plasma processing of a mixture containing O₂-NO-H₂O-HC-N₂ leads to the production of aldehydes (CH₃CHO, CH₂O), alcohols (CH₃OH), nitrate and intermediate organic nitroso compounds of R-NO_x type (CH₃ONO, CH₃ONO₂), nitromethane (CH₃NO₂), formic acid (CH₂O₂), propylene oxide (C₃H₆O), and to some extent of acids (HNO₂, HNO₃). Formations of such molecules are predicted by kinetic models of NTP.

NO_x 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 N₂-based mixture consists of O₂, H₂O, NO, and HCs (C₃H₆, C₃H₈, C₇H₈, and n-C₁₀). In all cases, the plasma reactor has been shown to deliver to the catalyst reactor a rich mixture of NO₂, oxygenates, and intermediate organic nitroso compounds, completely consumed during the deNO_x catalytic process and leading to efficient NO_x abatements and allowing the extension of the temperature windows of deNO_x reaction from room temperature.

ACKNOWLEDGMENTS

The authors greatly acknowledge all engineers from PSA Peugeot-Citroën and Renault who worked on the subject with the LRS and GREMI laboratories.

REFERENCES

- [1] BM Penetrante; RM Brusasco; BTMerrit; WJPitz; GEVogtlin; MCKung; HHKung; CZ Wan; KEVoss, SAE Technical Paper 982508, **1998**. 57-66.
- [2] ML Balmer;R Tonkin; S Yoon; A Kolwaite; S Barlow; GMaupin; J Hoard,SAE Technical Paper 1999-01-3640, **1999**, 67-73.
- [3] M Higashi; S Uchida; NSuzuki; KFujii,IEEE Trans. Plasma Sci., **1992**,20,1-1

- [4] BM Penetrante; RM Brusasco; BT Merrit; WJ Pitz; GE Vogtlin; SAETechnical Paper 1999-01-3637, **1999**, 45-50.
- [5] A Khacef; JM Cormier; JM Pouvesle, *J. Phys. D: Appl. Phys.***2002**, 35, 1491-1498.
- [6] A.Khacef;JM Cormier *J. Phys. D: Appl. Phys.*,**2006**, 39, 1078-1083.
- [7] HH Kim, *Plasma Process. Polym.* **2004**, 1, 91-110.
- [8] JY Park; JG Jung; JS Kim; GH Rim; KS Kim, *IEEE Trans. Plasma Science*, **2003**, 31, 1349–1354 U Roland; F Holzer; FD Kopinke, *Appl. Catal. B: Environm.*, **2005**, 58, 217-226
- [9] V Demidiouk; SI Moon; JO Chae,*Catal. Commun.*, **2003**, 4, 51-56
- [10] A Baylet; P Marécot; DDuprez; XJeandel; K Lombaert; JM Tatibouët, *Appl. Catal. B: Environ.*, **2012**, 113-114, 31-36
- [11] EM Van Veldhuizen, *Electrical discharge for environment purpose. Fundamentals and applications*, Nova Science Publishers Inc, **2000**, New York.
- [12] JS Chang; PL Lawless; T Yamamoto, *IEEE Trans. Plasma Sci.*, **1991**, 19, 1152-1166.
- [13] BM Penetrante; MC Hsiao; JNBardsley; BT Merrit; GE Vogtlin; PH Wallman; A Kuthi; CP Burkhardt; JR Bayless, *Pure & Appl. Chem.*,**1996**, 68, 1083-1087
- [14] HH Shin; WS Yoon, *SAE Technical Paper* **2000-01-2969**, 2000, 103-110.
- [15] R Dorai; MJ Kushner, *SAE Technical Paper* **1999-01-3683**, 1999, 81-87.
- [16] EA Filimonova; YH Kim; SH Hong;YH Song, *J. Phys. D: Appl. Phys.*, **2002**, 35, 2795-2807.
- [17] A Khacef; JM Cormier; JM Pouvesle, *Eur. Phys. J. Appl. Phys.*,**2006**, 33, 195-198.
- [18] G Djéga-Mariadassou; F Baudin; A Khacef; P Da Costa, *Plasma Chemistry and Catalysis in Gases and Liquids*, Eds VI Parvulescu; M Magureanu; P Lukes, Wiley VCH, **2012**, 89-129
- [19] G Lombardi; NBlin-Simiand; FJorand; L Magne; S Pasquiers; C Postel; JR Vacher, *Plasma Chem. Plasma Process.*, 27, **2007**, 414-445.
- [20] R Dorai; MJ Kushner, *J. Phys. D: Appl. Phys.*, **2003**, 36, 1075-1083.
- [21] AR Martin; JT Shawcross; JC Whitehead, *J. Phys. D: Appl. Phys.*, **2004**, 37, 42-49.
- [22] R Dorai; MJ Kushner, *J. Appl. Phys.*, **2000**, 88, 3739-3747.
- [23] O Gorce; HJurado; C Thomas; G Djéga-Mariadassou; AKhacef; JM Cormier; JM Pouvesle; G Blanchard; S Calvo; Y Lendresse, *SAE TechnicalPaper* **2001-01-3508**, 2001, 47-51.
- [24] F Baudin, *PhD Thesis, Université Pierre et Marie Curie paris, France*), **2005**.
- [25] G Djéga-Mariadassou; F Fajardie; JF Tempère; JM Manoli; O Touret; GBlanchard; J. Mol. Catal. A, **2000**, 161, 179-189

[27] G. Djéga-Mariadassou; M Berger; O Gorce; JW Park; H Pernot; C Potvin; C Thomas; P Da Costa, Past and Present in deNO_x Catalysis, Studies in surface Science and Catalysis, **2007**, 171, Eds P Granger and VI Parvulescu, Elsevier, the Netherlands, 145-173

[28] O Gorce; C Thomas; G. Djéga-Mariadassou; G Blanchard, French Patent Registered #0009678, (**2000**).