

PULSED DBD-CATALYST HYBRID REACTOR FOR ENVIRONMENTAL CLEAN-UP: VOCS OXIDATION IN AIR AT LOW TEMPERATURE

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ABSTRACT

The combination of pulsed dielectric barrier discharge with palladium supported on alumina catalysts (0.5 and 1 wt%Pd) was investigated for the oxidation of volatile organic compounds (CH₄, C₃H₆, and C₇H₈) in air at atmospheric pressure, temperature up to 500°C, and input plasma energy up to 145 J/L. The plasma-catalysis interaction revealed the benefit effect of the plasma on the CH₄, C₃H₆, and C₇H₈ oxidation even at low temperature leading to high selectivity in CO₂ than only-plasma reaction. At room temperature, the plasma could activate both alumina and Pd/Al₂O₃ catalysts. For such systems, the light-off curves were shifted toward lower temperatures as the plasma input energy increased. At a given energy, the plasma-catalyst was helpful in minimizing the by-products formation. At low temperature, these mechanisms could be explained by the plasma-induced interactions between reactive species and catalyst active sites whereas at higher temperature the thermal processes become predominant overtaking the contribution of the plasma-activated processes.

1. INTRODUCTION

Volatile organic compounds (VOCs) are an important category of air pollutants and therefore, become a serious problem for damaging the human health and the environment. The well-established technologies for VOCs abatement, thermal and catalytic oxidation [1], require a substantial supply of thermal energy (200-800°C) which makes them unsuitable and energetically expensive for the treatment of low pollutant concentrations at moderate gas flow rates.

As an alternative to catalytic oxidation, atmospheric non-thermal plasma (NTP) such dielectric barrier and corona discharges have been extensively investigated in the field of pollution control and reviewed [2-4]. The main advantage of these non-equilibrium plasmas consists in the ability to generate high energy electrons, while keeping the background gas close to room temperature. Thus, a highly reactive environment is created without spending energy on gas heating as in thermal processes. However, NTP technology for indoor air treatment has the disadvantage to produce undesirable by-products such as ozone, aldehyde, and NO_x [5-6]. To overcome the by-products formation and increasing energy efficiency, NTP could take advantage of its synergetic effect through combination with heterogeneous catalysts. This combination can be either single-stage (in-plasma catalysis, IPC) or two stages (post-plasma catalysis, PPC). Such a combination helps to bring down the disadvantages of both catalytic and plasma treatments [7-9].

In this paper, cylindrical DBD reactor combined with Pd/Al₂O₃ catalyst were investigated for the removal of CH₄, C₃H₆, and C₇H₈ from air at atmospheric pressure. Reported results, as a function of gas temperature and specific input plasma energy, concern the catalyst effect, the plasma effect and the combined plasma-catalyst effect on the conversion efficiency of these molecules. Systematic investigations were carried out in order to select the optimal positioning of the catalyst regarding the plasma discharges.

2. EXPERIMENTAL

The plasma reactor is a cylindrical DBD that can give the possibility to combine catalyst with plasma reactor in IPC or PPC as shown in Fig. 1.

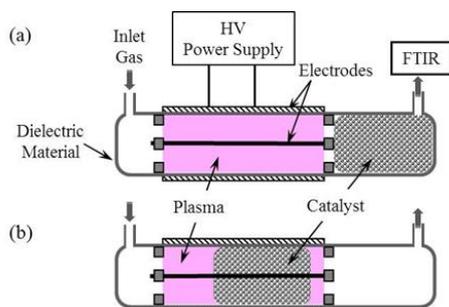


Fig. 1. Schematic view of the plasma-catalyst reactor: (a) Post-Plasma Catalysis (PPC), (b) In-Plasma Catalysis (IPC).

The plasma reactor was driven by a pulsed sub-microsecond high voltage generator delivering output HV up to 20 kV into 0.5 μ s pulses (FWHM) at a maximum frequency of about 200 Hz. Electrical characterization of plasma was performed by current-voltage measurements using a HV probe having an attenuation ratio of 1000:1 (Tektronix P6015A) and current probe having 10 ns rise time (Pearson 4001), respectively. The energy consumption of the plasma reactor was evaluated through the specific input energy (J/L) which is the energy deposited per unit volume of gas in the reactor and is given by $SIE = (E_p \cdot f) / Q$ (E_p is the discharge pulse energy, f the pulse frequency, and Q the total gas flow rate). Experiments were conducted by maintaining E_p constant at about 13 mJ then; the maximum desired specific input energy reach the value of 145 J/L.

Palladium supported catalysts (0.5 and 1 wt% Pd) were prepared by impregnation of Al_2O_3 beads (diam. 1.0 and 1.8 mm; Sasol Germany GmbH) by an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ (STREM Chemicals Inc.).

The catalysts structure was scanned by XRD (Bruker D5005 powder diffractometer using $Cu K\alpha$ radiation). Fig. 2 shows an example of these characterizations. The atoms chemical states in the catalyst surface were investigated by XPS (AXIS Ultra DLD spectrometer marketed by Kratos Analytical, operating with $Al K\alpha$ radiation). The surface area/porosity measurements were evaluated by the multipoint BET and BJH methods. Finally, Pd metal loading was determined by ICP-OES using an ACTIVA spectrometer (Horiba Jobin Yvon).

CH_4 , C_3H_6 , and C_7H_8 oxidation was performed in a continuous flow fixed-bed reactor for

temperature up to 500°C at a total flow through the catalyst bed kept to 1 L/min (weight hourly space velocity of about 15 000 h^{-1}). Initial VOCs concentrations have been fixed at 1000 ppm.

The reactant and reaction products were analysed in-situ using an Ft-IR spectrometer (Nicolet 6700, Thermo-Scientific).

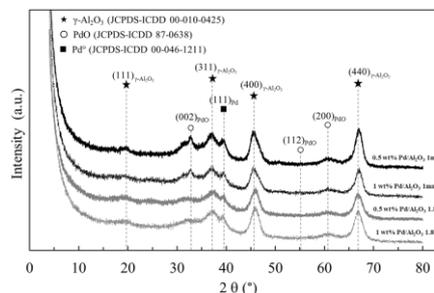


Fig.2. XRD patterns of the Pd/Al_2O_3 (0.5 and 1wt%, diameter 1 and 1.8 mm), and the corresponding patterns of Al_2O_3 , PdO and Pd .

3. RESULTS

Preliminary study of the CH_4 catalytic oxidation shows that Al_2O_3 , by itself, does not exhibit any catalytic activity for CH_4 conversion at temperature lower than 500°C. Moreover, the catalytic activity (Pd/Al_2O_3) increases by decreasing the particle size and increasing the Pd load, according to the following sentences: 1wt% Pd/Al_2O_3 (1.0 mm) > 1wt% Pd/Al_2O_3 (1.8 mm) ~ 0.5wt% Pd/Al_2O_3 (1.0 mm) > 0.5wt% Pd/Al_2O_3 (1.8 mm).

For plasma-alone experiments, CH_4 conversion reached a maximum of 67% with CO , CO_2 , O_3 , and HNO_3 as main products. When combined to catalyst, results revealed the benefit effect of plasma on the oxidation of CH_4 even at low temperature. It is clearly shown that, at room temperature, the plasma could activate both alumina and Pd/Al_2O_3 catalysts leading the enhancement of the catalytic performances: CH_4 conversion up to 5% was measured (non-activity without plasma even at 500°C). As shown in Fig. 3, catalytic performances were significantly enhanced when plasma is used. Compared with plasma-off case, improvements of about 200% and 40% were measured at 300 and 350°C, respectively. As the specific input energy increased, the CH_4 conversion curves have been shifted toward lower temperature. Although the difference is weak, the IPC configuration seems to be more efficient compared with PPC. In all cases, the reaction using Pd/Al_2O_3 catalyst becomes more selective in CO_2 formation than the reaction in plasma alone and, at high temperature O_3 and HNO_3 disappears in favour of NO_x .

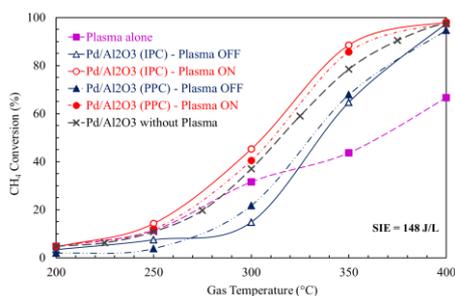


Fig. 3. CH_4 conversion vs gas temperature at $\text{SIE}=148 \text{ J/L}$ for plasma and plasma-catalysis (IPC vs. PPC): $[\text{CH}_4]_0=1000 \text{ ppm}$.

Fig. 4 shows typical Ft-IR spectra illustrating the catalyst, plasma and plasma-catalysis processing of air- C_3H_6 mixture. Similar spectra were observed for C_7H_8 . In addition to CO and CO_2 , the detected other gaseous carbon-containing compounds are formaldehyde (CH_2O), formic acid (CH_2O_2), methyl nitrate (CH_3NO_3), and nitric acid (HNO_3). At higher temperature, nitric acid decomposition leads to the formation of NO and NO_2 .

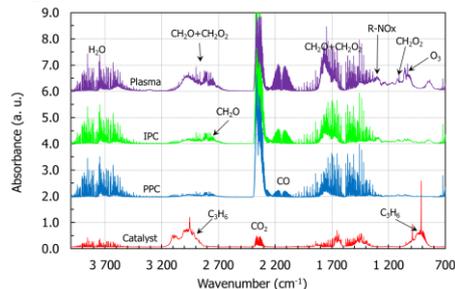


Fig. 4. Typical Ft-IR spectra for catalytic, plasma and plasma-catalyst processing of air- C_3H_6 mixture (150°C , 54 J/L)

Contrary to methane, alumina alone shows a high activity for C_3H_6 and C_7H_8 oxidation at temperature higher than 400°C : conversion of about 50% for both molecules at 400°C with CO_2 , H_2O , and CO as reaction products. By addition of 1 wt%Pd on the support a huge increase in the performance was observed and the temperature of the total oxidation was drastically reduced to 250°C .

Figs. 5 and 6 show comparison between thermal, plasma, and plasma-catalysis (IPC and PPC) conversion of propene and toluene, respectively. We can note that the thermal catalysis has a threshold temperature (130 and 150°C for C_3H_6 and C_7H_8 , respectively) and increases steadily with increasing temperature reaching 100% removal at 250°C . Processing both C_3H_6 and C_7H_8 using plasma discharges (with and without catalyst) exhibit a lower threshold temperature and the reactions take place from room temperature. Higher conversion efficiencies were observed with plasma-catalysis systems whatever the temperature together with high temperature

dependence over the range $20\text{-}150^\circ\text{C}$ as illustrated in the figures.

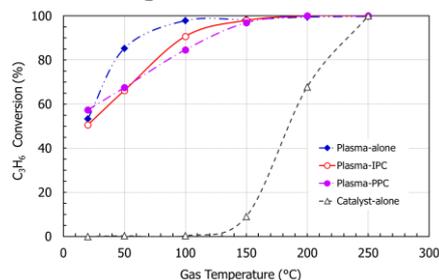


Fig. 5. Thermal, plasma, and plasma-catalytic conversion of C_3H_6 in air as a function of gas temperature ($\text{Ed}=54 \text{ J/L}$).

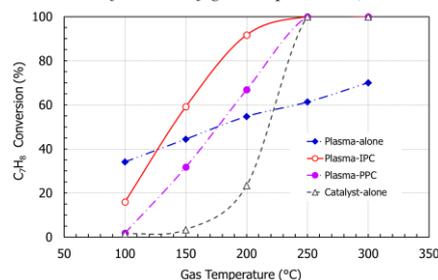


Fig. 6. Thermal, plasma, and plasma-catalytic conversion of C_7H_8 in air as a function of temperature ($\text{Ed}=23 \text{ J/L}$)

At room temperature, plasma-alone and plasma-catalysis (IPC and PPC) exhibit 60% propene conversion compared to 0% for thermal-catalysis. While the conversion efficiencies are quiet similar, the nature and the amounts of end-products observed are different. Total C_3H_6 conversion was achieved at 100°C leading to the production of CO , CH_2O , CH_2O_2 , CH_3NO_3 , O_3 , and NO_x . Propene and toluene conversion efficiency increased with increasing the plasma energy density. As example, at a given temperature (100°C as example), the toluene conversion reached 34, 69, and 82% at input energy density of 23, 84 and 145 J/L , respectively. Placing the catalyst in the discharge zone (IPC) resulted in higher C_7H_8 conversion compared to PPC (10-30% improvement depending of the energy density). It was found that in IPC configuration; the catalyst could be activated by high energy species produced by the plasma and convert toluene by using intermediate species such as O_3 .

Fig. 7 shows the amounts of CO , CH_2O , and CH_2O_2 respectively, produced in the case of plasma-alone and plasma-catalysis processing of air- C_3H_6 mixture as the gas temperature increase. At low temperature ($<100^\circ\text{C}$), CO concentrations are quiet similar for IPC and PPC configurations. At higher temperature, CO concentration drastically increased in case of plasma-alone and slightly decreased when plasma was combined to catalyst. We observe that the addition of the

catalyst to the plasma increased the CO₂ selectivity to about 85-90% when comparing to thermal-catalysis at 150°C.

At a given temperature in the range 20-250°C, the concentrations of formaldehyde and formic acid derived from the partial oxidation of propene decrease when the catalyst is combined to plasma. We observe that increasing the plasma energy density could drastically reduce the concentrations of by-products.

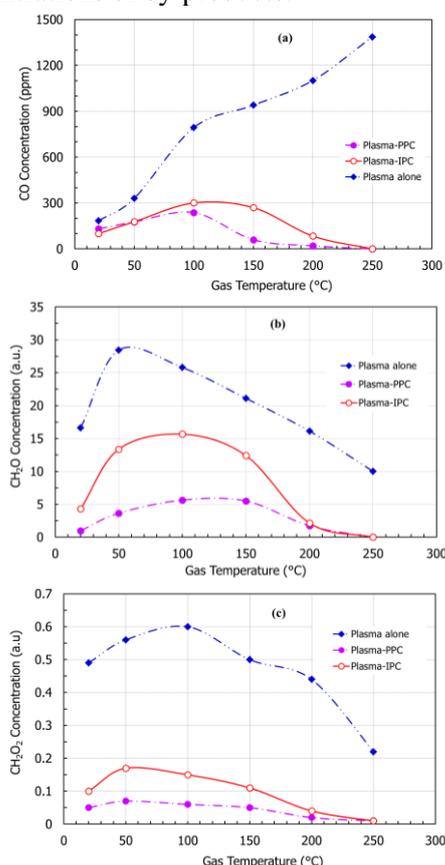


Fig 7: (a) Carbone monoxide, (b) formaldehyde, and (c) formic acid concentrations vs temperature (SIE= 54J/L)

4. SUMMARY

CH₄, C₃H₆, and C₇H₈ oxidation in air by catalysis (Pd/Al₂O₃), plasma, and plasma-catalysis systems have been investigated in wide range of temperature and plasma input energy. Whatever the molecule studied, the plasma significantly enhanced the catalytic activity even at low temperature leading to high CO₂/CO selectivity. Performance of the system was slightly better when the catalyst was located in the discharge area. As example, total C₃H₆ conversion was measured at 100°C when it occurs at 250°C for thermal catalysis. At room temperature and for given input energy, the catalyst was helpful in minimizing the by-products issued from plasma (CO, CH₂O, CH₂O₂, HNO₂).

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