



Oxidation of propene from air by atmospheric plasma-catalytic hybrid system

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Abstract: The pulsed dielectric barrier discharge (DBD) combined with the palladium supported on alumina beads, was investigated for propene (C₃H₆) removal from air. The effects of thermal-catalysis, plasma-catalysis (in-plasma catalysis and post-plasma catalysis), and plasma-alone on the propene removal were compared. Results are presented in the terms of C₃H₆ removal efficiency, energy consumption, and by-products production. Temperature dependence studies (20–250 °C) show that in all conditions of input plasma energy density explored (23–148 J L⁻¹), the plasma-catalysis systems exhibit better propene conversion efficiencies than the thermal catalysis at low temperature (60% at 20 °C). Plasma-alone treatment has a similar effectiveness compared to plasma-catalysis at room temperature, but it leads to the formation of high by-products concentrations. It appears that in the plasma-catalyst system, C₃H₆ removal was the most efficient, whatever was the configuration used, and it was helpful to minimize by-products formation.

Keywords: non-thermal plasma; C₃H₆ oxidation; palladium catalyst.

INTRODUCTION

Volatile organic compounds (VOCs) are an important category of air pollutants and therefore, they have become a serious problem, damaging the human health and the environment in general. The well-established technologies for the removal of VOCs, namely thermal and catalytic oxidation, require a substantial supply of thermal energy (200–800 °C) and are not well adapted and also are energetically expensive in the case of the moderate gas flow rates containing low VOCs concentrations.^{1–3}

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As an alternative to the conventional VOCs removal techniques, the atmospheric non-thermal plasma (NTP) technology received the increasing interest during the last decades for the removal of dilute VOCs from many sources. The main advantage of these non-equilibrium plasmas consists of 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 the gas heating, as in thermal processes. However, NTP technology for indoor air treatment has the disadvantage, because it produces the undesirable by-products such as ozone, aldehyde, and NO_x .⁴⁻⁶ To overcome the by-products formation and to increase the energy efficiency, NTP could take the advantage of its synergetic effect through the combination with heterogeneous catalysts. This combination can be either single-stage (in-plasma catalysis) or two stages (post-plasma catalysis). Such a combination helps to bring down the disadvantages of both catalytic and plasma treatments.^{7,8}

In this study, the dielectric-barrier discharge (DBD) reactor, combined to 1 wt.% of $\text{Pd}/\text{Al}_2\text{O}_3$ beads catalyst, were investigated for the removal of propene from air at the atmospheric pressure. Reported results, as a function of the gas temperature and the input plasma energy density, consider the catalyst effect, the plasma effect and the plasma-catalyst effect on the efficiency of propene conversion. Systematic investigations were carried out in order to select the optimal positioning of the catalyst regarding the plasma discharge.

EXPERIMENTAL

Catalyst preparation

The catalysts based on palladium supported on alumina beads (1 wt.% of $\text{Pd}/\text{Al}_2\text{O}_3$) were prepared by the impregnation method as described in details elsewhere.⁸ The aqueous solution of tetraaminepalladium(II) nitrate (5 wt.% of Pd, Strem Chemicals) and alumina beads (1 mm diameter, SASOL) were stirred in the rotary evaporator for 3 h at 50 °C, under atmospheric pressure. Then, the sample catalyst was dried for 12 h at 120 °C and calcined for 4 h at 500 °C at a heating rate of about 3°C per min under air flow.

Catalysts characterization

Surface area/porosity measurements were conducted using a Micromeritics ASAP 2010 apparatus with N_2 as the sorbate at -196 °C. All the samples were outgassed prior to analysis at 300 °C under vacuum (5×10^{-3} Torr) for 3 h. The total specific surface areas were determined by the multipoint BET (Brunauer–Emmett–Teller) method. Mesoporosity was evaluated by the Barret–Joyner–Halenda (BJH) method.

X-Ray powder diffraction (XRD) analyses were conducted by a Bruker D5005 powder diffractometer scanning, using $\text{CuK}\alpha$ radiation. The samples were scanned at a rate of 0.02° per step in the 2θ range of 4–80° (scan time = 2s per step). The applied voltage and current were 50 kV and 35 mA, respectively. Diffraction patterns were assigned using Joint Committee on Powder Diffraction Standards (JCPDS) cards supplied by the International Centre for Diffraction Database (ICDD). The average crystallite sizes of Al_2O_3 support and Pd-supported catalysts were estimated using the Scherrer equation:

$$d_i = \frac{k \lambda}{\beta \cos \theta}$$

where d_i is the mean size of the ordered (crystalline) domains of (i) Al_2O_3 or/and PdO and Pd , which may be smaller or equal to the grain size, k (0.9) is the shape factor, λ (0.154 nm) is the X-ray wavelength, β is the line broadening at half maximum intensity (FWHM) in rad and θ is the Bragg angle.

Chemical states of the atoms in the catalyst surface were investigated by the X-ray photoelectron spectroscopy (XPS) on an AXIS Ultra DLD spectrometer produced by Kratos Analytical, operating with Al ($\text{K}\alpha$) radiation. XPS data were calibrated using the binding energy of C 1s (284.6 eV) as the standard. The XPS core level spectra were analyzed with a fitting routine, which decomposes each spectrum into individual, mixed Gaussian–Lorentzian peaks using a Shirley background subtraction over the energy range of the fit. The surface composition was calculated from the integrated peaks, using empirical cross-section factors for XPS (C 1s = 1, O 1s = 2.93, Al 2p = 0.54, Pd 3d ($3d_{5/2} + 3d_{3/2}$) = 16.04).

Plasma-catalysis system

The plasma reactor we used is a cylindrical DBD shown in Fig. 1. That configuration gives the possibility to combine the catalyst with the plasma reactor in two different ways: by introducing the catalyst in the discharge zone (in-plasma catalysis, IPC) or by placing the catalyst downstream the discharge zone (post-plasma catalysis, PPC). The plasma reactor was powered by a pulsed sub-microsecond high voltage generator delivering HV amplitude (up to 20 kV) at frequency up to 200 Hz. The electrical characterization of plasma (energy deposition) was performed by the current and voltage measurements. The discharge pulse energy was measured with a capacitive circuit. The energy deposition in the plasma reactor (J L^{-1}) is given by $E_d = E_p Q^{-1} f$, in which, E_p is the discharge pulse energy, f the pulse repetition rate, and Q is the gas flow rate at standard conditions (25 °C and 1 atm). The experiments were conducted maintaining the constant discharge pulse energy E_p at about 80 mJ and in varying the

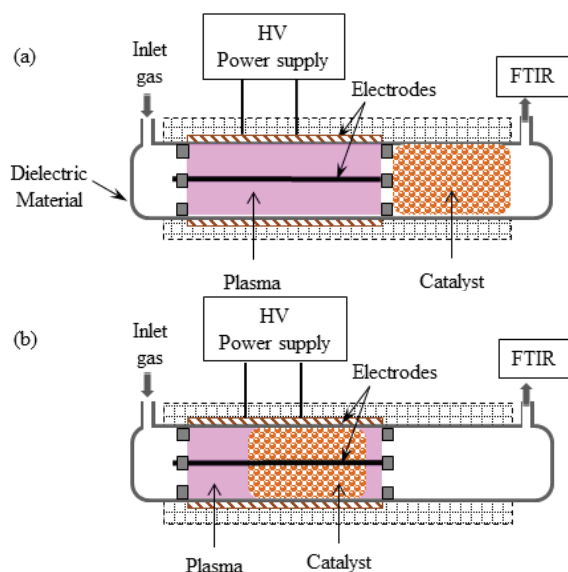


Fig. 1. Schematic view of the plasma-catalyst reactor: a) post-plasma catalysis; b) in-plasma catalysis.

pulse repetition frequency in the range 30–190 Hz, and as a consequence the desired energy deposition ranged from 23 to 148 J L⁻¹.

Experimental conditions

The propene oxidation was performed in a continuous flow fixed-bed reactor in the temperature range 20–250 °C. The total flow through the catalyst bed was kept at 1 L min⁻¹, leading a weight hourly space velocity of about 15000 h⁻¹. The initial propene concentration was fixed at about 1000 ppm.

The reactant and reaction products were analyzed *in-situ* using the FTIR spectrometer (Nicolet 6700, Thermo-Scientific).

RESULTS AND DISCUSSION

The N₂ adsorption/desorption analysis show that both the BET surface area and the total pore volume increases with the alumina sphere diameter, corresponding to the mesoporous materials. The XRD patterns suggest the formation of the alumina phase with the presence of the characteristic peaks for γ -Al₂O₃ phase. The XRD analysis also confirms a small Pd metal peak to be present along with the major PdO peaks. However, the XPS analyzes shows only the Pd²⁺ peak, corresponding to the PdO phase, probably because the amount of the exposed Pd metal is too small to be picked up by XPS. Thus, it can be expected that the exchange or equilibration should occur on the surface of PdO at lower temperatures, as PdO is quite stable and does not easily change the oxidation state of a metal.⁹ XPS results also showed the formation of palladium species in a higher oxidation state, probably PdO₂ (338 eV), inducing the formation of new interfacial sites for the oxidation reaction.¹⁰

Fig. 2 shows the typical FTIR spectra illustrating the plasma and plasma-catalysis processing of air-C₃H₆ mixture at 150 °C an energy deposition of 55

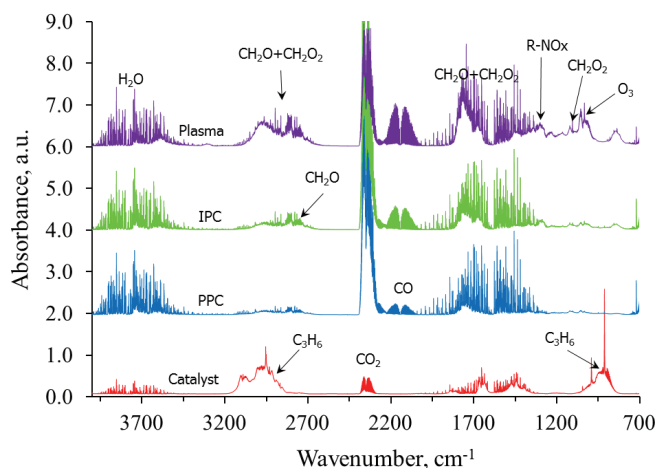


Fig. 2. Typical FTIR spectra for plasma and plasma-catalytic processing of air-C₃H₆ mixture (150 °C, 55 J L⁻¹).

J L^{-1} . In addition to CO and CO_2 , the other detected gaseous carbon-containing compounds are formaldehyde (HCHO), formic acid (HCOOH), and nitric acid (HNO_3). At higher temperature, the nitric acid decomposition leads to the formation of NO and NO_2 .

Before comparing the effect of the thermal catalysis, plasma-catalysis (IPC and PPC), and plasma alone on the propene removal, the preliminary studies with alumina beads were performed. In the absence of plasma, the alumina beads show a high activity at $450\text{ }^\circ\text{C}$ and above. The propene conversion over alumina alone was about 60 % with CO_2 , H_2O and CO which are the reaction products. For 1 wt.% of $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, the temperature of total propene oxidation was drastically reduced to $250\text{ }^\circ\text{C}$ leading to CO_2 and H_2O .

The effect of the energy deposition on propene conversion was studied as function of temperature in the range $23\text{--}148\text{ J L}^{-1}$. The results indicated that propene could be converted by plasma at low temperature. However, the reaction by-products were HCHO , HCOOH , CO and O_3 . In the plasma-catalyst system, the interaction of the catalyst active phase, with the reactive species produced by the plasma, changed the catalyst activity by the increasing of the conversion efficiency and the decrease of the concentration of by-products. In some cases, the plasma-catalyst system in IPC configuration is better than the plasma-catalyst system in PPC configuration. This could be explained by the interaction of the catalyst active phase with the reactive species produced by plasma ($\cdot\text{O}$, $\cdot\text{OH}$, $\cdot\text{O}_2$, etc.) in IPC configuration. In this study, only the data obtained at 148 J L^{-1} will be presented.

Fig. 3 shows the comparisons between the thermal and the plasma-catalysis for the removal of propene from air using both configurations: in-plasma cat-

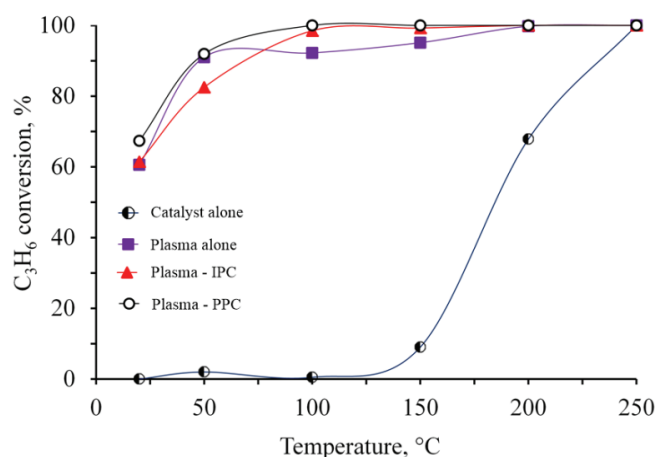


Fig. 3. Thermal, plasma, and plasma-catalytic conversion efficiency of C_3H_6 in air as a function of temperature ($E_d = 148\text{ J L}^{-1}$).

alysis and post-plasma catalysis. We can note that the removal of propene by the thermal catalysis has a threshold temperature of 150 °C and increases steadily with the temperature reaching 100 % removal at 250 °C. The processing of propene using plasma discharge (with and without catalyst) exhibits a lower threshold temperature and the reactions take place at room temperature. Larger conversion efficiencies were observed with the plasma-catalysis systems at any temperature, over the range 20–150 °C as illustrated in Fig. 3. At room temperature, the plasma-alone and the plasma-catalysis (IPC and PPC) exhibit 60 % of propene conversion, compared to 0 % for thermal-catalysis. While the conversion efficiencies are quite similar, the nature and the amounts of the end-products observed are different.

The total propene conversion was achieved at 100°C (IPC and PPC) and 200 °C (plasma alone) leading to the production of the by-products such as CO, HCHO, HCOOH, O₃ and NO_x.

Fig. 4–7 show the amounts of CO, CO₂, HCHO and HCOOH respectively, produced in the case of the plasma alone and the plasma-catalysis (IPC and PPC) processing of the air-propene mixture as a function of temperature.

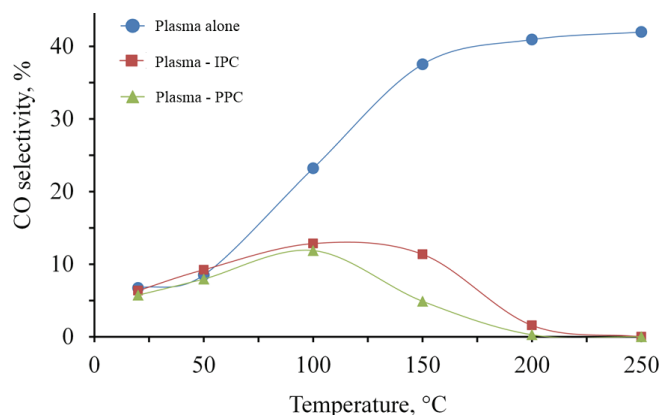


Fig. 4. CO selectivity according to temperature at input density energy 148 J L⁻¹.

At low temperature (<100 °C), CO selectivity is quite similar for IPC and PPC configurations. At higher temperature, CO concentration drastically increased in the case of plasma-alone and slightly decreased when plasma was combined to catalyst over two configurations. We observe that the addition of the catalyst to the plasma in both IPC and PPC configurations increased the CO₂ selectivity to about 60 %, when comparing to the thermal-catalysis at 150 °C.

At a given temperature in the range of 20–250 °C, the concentrations of formaldehyde (HCHO) and formic acid (HCOOH), derived from the partial oxidation of propene, decrease when the catalyst is combined with plasma. We obs-

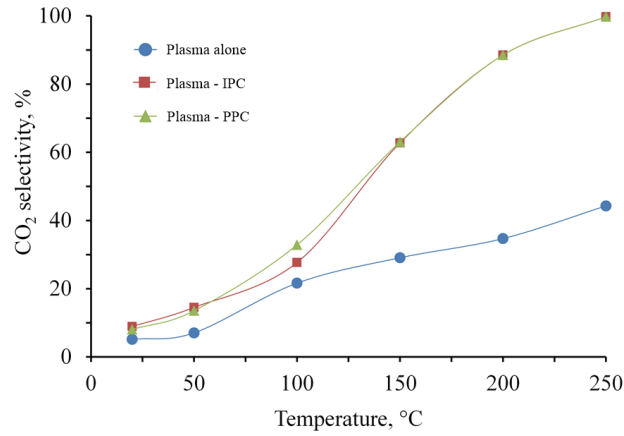


Fig. 5. CO₂ selectivity according to temperature at input density energy 148 J L⁻¹.

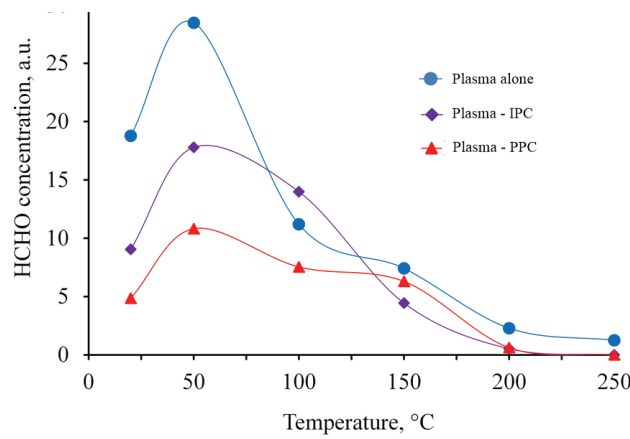


Fig. 6. HCHO concentration according to temperature at input density energy 148 J L⁻¹.

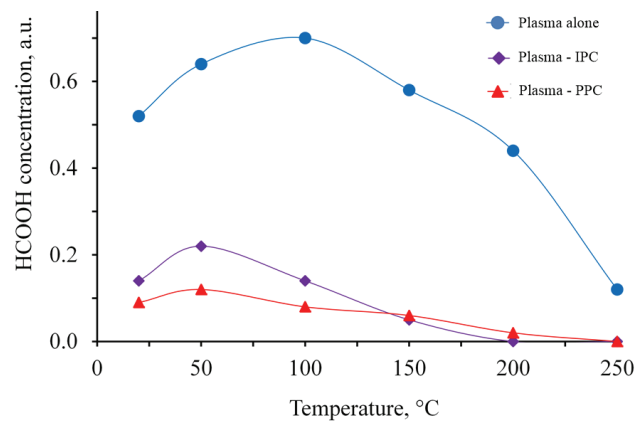


Fig. 7. HCOOH concentration according to temperature at input density energy 148 J L⁻¹.

erve that the concentrations of these by-products could be drastically reduced by increasing the plasma energy density.

CONCLUSIONS

In this research, the thermal catalysis, the plasma-catalysis (IPC and PPC), and the plasma-alone processing of the air-propene mixture were investigated as the function of temperature and of plasma energy deposition. Alumina and palladium supported on alumina beads (1 wt.% of Pd/Al₂O₃) catalysts were used in combination with the sub-microsecond pulsed dielectric barrier discharge. The plasma-catalysis systems exhibit better propene conversion efficiencies than the thermal catalysis at low temperature. The plasma-alone treatment has a similar effectiveness to the plasma-catalysis at room temperature (up to 60 % propene conversion) but leads to the formation of the high concentration of by-products such as carbon monoxide, formaldehyde and formic acid. The total conversion of propene was achieved at 100 °C in plasma-catalysis case and 250 °C in catalysis alone case. It has been shown that at a given energy density, the plasma-catalyst was helpful in minimizing the by-products formation. The plasma-catalytic conversion processes could be explained by the specific plasma-induced interactions between plasma reactive species (O₃, O, OH,...) and the catalyst active phase at low temperature, whereas at higher temperature the thermal activation of the catalyst becomes important, overtaking the contribution of the plasma-activated processes.

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ИЗВОД

ОКСИДАЦИЈА ПРОПАНА У ВАЗДУХУ АТМОСФЕРСКИМ ПЛАЗМА-КАТАЛИТИЧКИМ СИСТЕМОМ

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Метода пулсне диелектричне баријере (DBD), у комбинацији са паладијумом на носачу од алуминијумских перли, испитана је у циљу уклањања пропена из ваздуха. Поређени су ефекти термалне катализе, катализе плазмом и саме плазме на уклањање пропена. Резултати су поређени у односу на ефикасност уклањања пропена, потрошњу енергије и стварање споредних производа. Проучавање зависности од температуре (20–250 °C) показало је да је у било којим испитиваним условима уклањање пропена помоћу катализе плазмом ефикасније од термалне катализе. Третман самом плазмом је на собној температури ефикасан слично као и катализа плазмом, али има превише споредних производа. Катализа плазмом се показала као најнефективнија.

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