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Catalysis Today 89 (2004) 75–81

CATALYSIS TODAY

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Oxidation of 2-heptanone in air by a DBD-type plasma generated within a honeycomb monolith supported Pt-based catalyst

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Abstract

A plasma-catalyst reactor was used to eliminate a low concentration (180 ppm) of 2-heptanone in air by total oxidation. This VOC is representative of a class of odorous ketones. A DBD-type plasma was generated through a platinum-based catalyst supported on an alumina wash-coated honeycomb monolith by means of a high voltage bi-polar pulsed excitation.

The 2-heptanone elimination efficiency increases with the energy density. More than 97% of 2-heptanone conversion is observed, in dry air condition for an energy density of 200 J/L.

An important synergy effect has been observed between cold plasma and catalyst, the 2-heptanone conversion remaining less than 50% on an uncoated monolith, even at an energy density value higher than 500 J/L.

The presence of water (3 mol%) in the gas phase, slightly decreases the efficiency of the 2-heptanone elimination, but strongly decreases the ozone formation in the 100–300 J/L energy density range.

Keywords: Non-thermal plasma; Catalyst; Volatile organic compound; VOC elimination; Oxidation; Ozone

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1. Introduction

The legislation concerning the gaseous wastes coming from human activity becomes more and more restrictive. In Europe, the protocol of Göteborg (1999) stipulates a strong reduction of hazardous gas emissions such as sulfur and nitric oxides, ammonia and Volatile Organic Compounds (VOC) by 2010. On average, the VOC released in the atmosphere will have to decrease of 35% (see Table 1). The catalytic oxidation is a very efficient technique for the VOC's elimination [1].

Among the different catalysts tested for the VOC elimination those based on noble metals as Pt and Pd present the best performances [2–6]. However, in the case of a high flow of polluted air containing a low concentration of VOC, typically in the range from 1 up to 1000 ppm, an expensive heating of the air flow is needed to reach the catalyst working temperature. Alternatively, a two-stage system can be used to first concentrate the pollutant in the effluent followed by a catalytic reactor, which is then able to work in autothermal conditions, but such a system is very heavy to manage [1].

Our preliminary work have shown that a Pt phase catalyst supported on a alumina wash-coated monolith needs at least 200 °C to eliminate almost completely 1900 ppm of 2-heptanone in air at a GHSV of $2 \times 10^6\ h^{-1}$ [7].

Since the beginning of 1990s, many researches on nitric oxides elimination from diesel and lean burn gasoline engines exhaust gases have shown that the combination of a pulsed electrical discharge with a catalyst is very promising for atmospheric pollutant removal [8]. The use of a non-thermal plasma has been already used in VOC elimination [9,10]. By adding a catalyst to a plasma reactor, it seems possible to avoid some drawbacks of both thermal catalysis (high energy consumption) and plasma alone (ozone formation) and to improve the efficiency of the process.

Only few studies on the plasma and catalyst coupling have been already published on VOC elimination [11–13].

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doi:10.1016/j.cattod.2003.11.042

Table 1
Göteborg protocole

Country	VOC (kT)	Change (%)
Austria	159	−33
Germany	995	−42
Belgium	144	−48
Denmark	85	−36
Spain	669	−73
Croatia	90	+12
France	1100	−41
Ireland	55	−52
Italy	1159	−34
Luxembourg	9	−30
The Netherlands	191	−36
UK	1200	−37
Czech Republic	220	−8
Hungary	137	−3
Poland	800	+8
Slovakia	140	+37
Slovenia	40	0
Switzerland	144	−16

Allowing VOC’s emission in Europe in 2010 in kT and equivalent reduction in comparison with 1998 for each country.

Usually, the catalyst is located either in the plasma zone (packed-bed reactor) or after the plasma zone [13–16]. Whatever the catalyst location, the treatment of high flow of gas as required in industrial processes needs to minimize the pressure drop due to the presence of the pellets. A possible answer is to use a honeycomb monolith to support the catalytically active phase as already successfully used in automotive exhaust gases treatment.

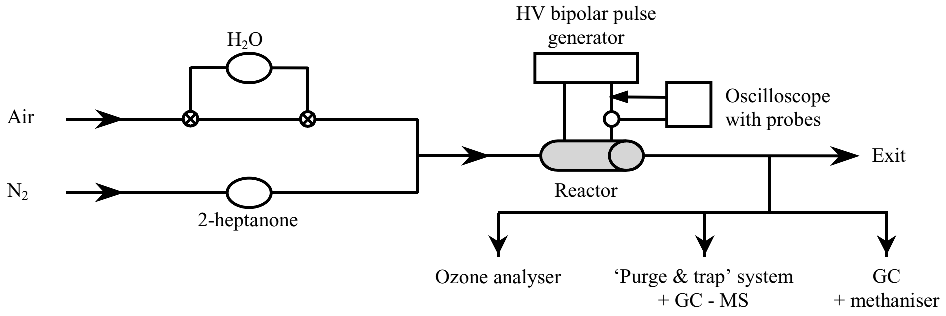
The VOC model molecule we have chosen was the 2-heptanone since it is an odorous molecule contained in various meals such as blue cheese.

2. Experimental

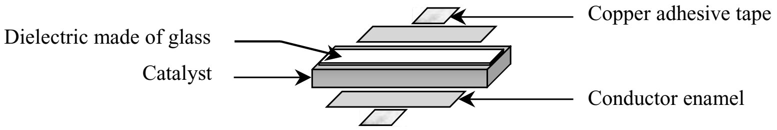
The experimental set-up is made of three parts: the gas mixing part, which allows to make the reactant flow mixture, the hybrid plasma-catalytic reactor, and the analytic system (Scheme 1).

The non-thermal plasma is generated within a honeycomb monolith slice cut parallel to the channels axis, by a dielectric barrier discharge (DBD) in a plane-to-plane geometry, the dielectric barrier being formed by a 2 mm thick glass plate (see Scheme 2). The two planar electrodes (10 cm × 2.5 cm) are made of a conducting enamel painted directly on the monolith for one electrode and on the glass plate face for the other one. The electrodes are connected to a high voltage (HV) bi-polar pulse generator (A2E ENERTRONIC) by using a copper adhesive tape on which the HV wires were soldered. The honeycomb slice has been cut from a 400 cpsi type cordierite monolith (400 channels by square inch) corresponding to about 1 mm^2 for each channel section. This slice is of three channels height with a total thickness of about 4 mm. According to the size of the electrodes and the thickness of the monolith slice, the volume where the plasma is formed is about 10 cm^3. The time evolution of the discharge electrical parameters is measured by using a high-impedance probe (Tektronix P6015A, 75 MHz) for the applied voltage and an inductive probe (Stangenes Industries, 60 MHz) for the current, connected to a fast digital oscilloscope (Lecroy LT374L, 500 MHz, 4 GS/s).

The catalyst, supplied by Infragas S.p.A., is an alumina wash-coated monolith of cordierite ($Mg_2Al_4Si_5O_{18}$) containing 0.3 wt.% of platinum and 7 wt.% of alumina. The catalyst was calcined under air at 650 °C during 8 h and reduced under H_2 (10% H_2 in N_2) at 350 °C during 3 h.



Scheme 1. Experimental set-up.



Scheme 2. Module use for the study.

The 2-heptanone containing air was passing through the monolith with a flow rate of 420 mL/min and can be analyzed on-line.

The CO, CO_2 and CH_4 are analyzed by a gas chromatograph (Varian 3400) equipped with a methanizer and a FID detector.

Ozone formation is continuously monitored by an UV ozone analyzer (O_3 42 M, Environnement SA).

Other products are analyzed by a GC–MS (Perkin–Elmer) apparatus equipped with a "purge and trap" system (ATD 400, Perkin–Elmer). After trapping for various times in the cold trap (−30 °C) filled by Tenax TA^{TM} adsorbent, a thermal rapid desorption under the chromatograph carrier gas flow (He) allows to inject, in the gas chromatograph, the accumulated products in the trap.

According to the trapping duration, our system is able to detect traces amount until the ppb range.

The amount of 2-heptanone and water were controlled by the temperature of the saturators (2-heptanone and water) and by the respective flows (Brooks mass flow controllers) of air and N_2 (see Scheme 1).

The standard conditions are 180 ppm of 2-heptanone in dry or wet air ($H_2O = 3\%$) at ambient temperature (∼24 °C), with a total flow rate of 420 mL/min.

We have check to that the formation of nitric oxides, NO and NO_2 does not exceed 10 ppm at the reactor exit, for the highest energy densities used in our experiments [17].

3. Results and discussion

3.1. Plasma formation within the monolith

A CCD-videocamera equipped with a fast electronic shutter has been used to measure the spatial distribution of the plasma into the inter-electrode volume. It has been found that plasma filaments, following development of streamers across cordierite channel walls, are randomly distributed within the honeycomb structure. These filaments do not appear at the same location from one HV pulse to the other when the discharge is running with a given pulse frequency, so that free radicals ($N^\bullet$, $O^\bullet$, $H^\bullet$, $OH^\bullet$) are created through dissociation of the background gas molecules (N_2, O_2, H_2O) in all the volume between the glass and the lower electrode.

3.2. Electrical parameters

Fig. 1 shows typical waveforms of the current and applied bi-polar voltage pulse to the electrodes, for an absolute voltage peak value, V_P, equal to 17 kV; the current is reversed for a better reading of the figure. The duration of each elementary voltage pulse is about 1 μs. The time evolution of the current corresponds to the following phenomena.

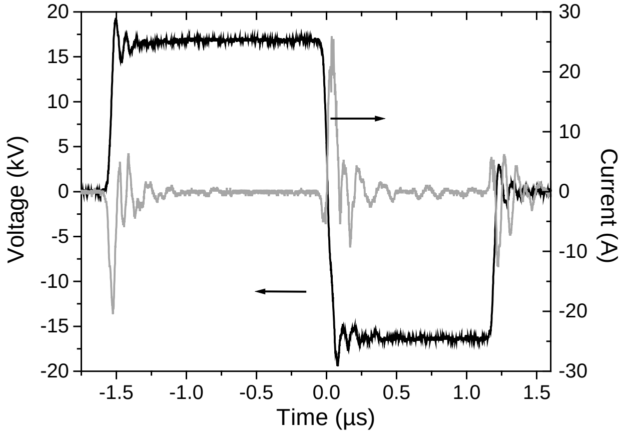


Fig. 1. Time evolution of voltage and current. $V_{PP} = 34$ kV; $f = 132$ Hz; total flow rate = 420 ml/min (GHSV = 1800 h^{-1}); dry air containing 180 ppm of 2-heptanone.

- First, there is a charge of the equivalent capacitance of the discharge structure (4.3 pF) in parallel with the stray capacitance, C_{el}, of the electrical circuit arrangement (first current pulse, negative on the figure). It is believed that no discharge breakdown occurs at this time because the applied voltage is too low. Previous experiments [17] have shown that, for the same discharge structure, no plasma fluorescence was detected by the CCD-camera when V_p is lower than 20 kV. Thus, the value of the peak current measured, 17 A, may result from the charging of the capacitance C_{el} estimated to 20 pF by integrating the current pulse in function of the applied voltage at a low V_p value. It follows that the capacitive current should be only about 10 A, taken into account that the measured voltage growth is 421.5 V/ns. Further works are planned to determine if some microdischarges at the surface of the cordierite monolith could be responsible for the difference between the measured current and the estimated capacitive one.
- Second, the discharge is characterized by a current pulse with a peak value of about 25 A for the conditions of Fig. 1, which develops during the voltage drop from V_P down to $-V_P$ (middle current pulse $V_{PP} = 2V_P$).
- Third, the last pulse corresponds to a displacement current owing to the voltage reset to zero. The minimum voltage drop to apply in order to obtain a well reproducible discharge from pulse to pulse, ${V_{PP}}^{min}$, is a function of the repetition frequency, f, of the bi-polar pulse and also depends on the composition of the gas mixture flowing through the honeycomb structure. For example, ${V_{PP}}^{min} = 26$ kV at $f = 132$ Hz, for dry air.

The results presented in Fig. 2 for $V_{PP} = 34$ kV show that the variation of the repetition frequency of the bi-polar pulse does not significantly modify the discharge peak current, I_C, in the frequency range investigated for a given gas mixture. Moreover, the electrical energy deposited per pulse in the discharge, E_{pulse}, determined from the computation of the electric power and integration over the current pulse duration is approximately constant for a given applied voltage. The

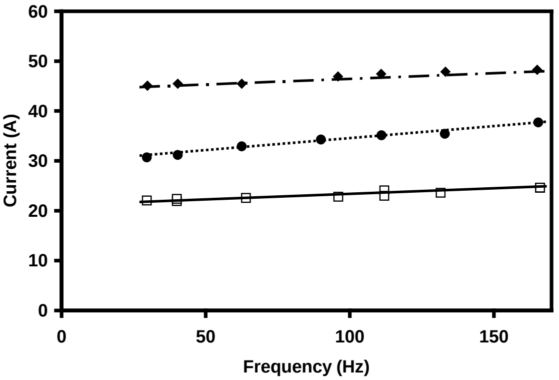


Fig. 2. Maximum of the current in function of the repetition frequency of voltage pulse for various gas phase composition (V_{PP} = 34 kV; GHSV = 1800 h^{-1}). (◆) Nitrogen, (☐) 180 ppm 2-heptanone in dry air and (●) 180 ppm 2-heptanone in wet air (H_2O = 3 mol%).

energy density, E_d (in J/L) deposited in the gas phase in our experimental conditions is plotted in function of V_{PP} in Fig. 3. Whatever the monolith used (uncoated or catalytic), the same results are obtained.

It then appears that the gas phase composition plays an important role in the E_d value, at a given applied voltage and repetition frequency of the bi-polar pulse. However, the presence of the 2-heptanone does not significantly modified the E_d value obtained for dry and wet air.

Typical evolutions of the I_C value in function of the applied voltage V_{PP} are plotted in Fig. 4 for three gas phase composition, i.e. dry nitrogen, dry and wet air (H_2O = 3 mol%) containing 180 ppm of 2-heptanone. When the voltage value increases, the discharge peak current first increases linearly with the same slope for all mixtures, which is a characteristic behavior of a pure capacitance charge. For higher applied voltages, I_C increases with a higher slope, whose value depends on the composition of the gas phase. This behavior was already observed for the same kind of discharge in absence of monolith between the electrodes [18].

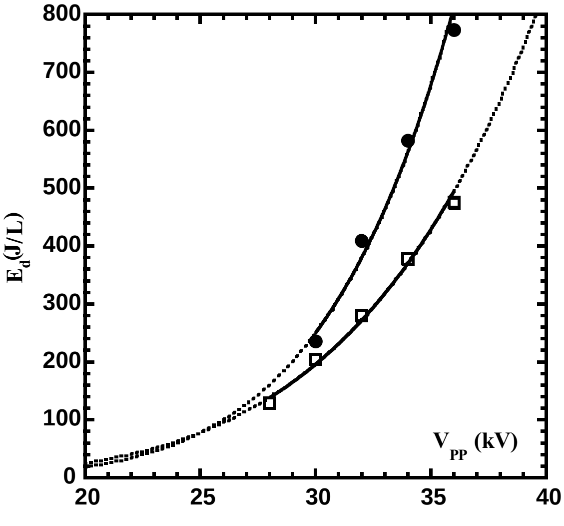


Fig. 3. Energy density E_d in function of the applied voltage (f = 132 Hz; 420 mL/min; 2-heptanone = 180 ppm). (●) Wet air (H_2O = 3 mol%) and (☐) Dry air.

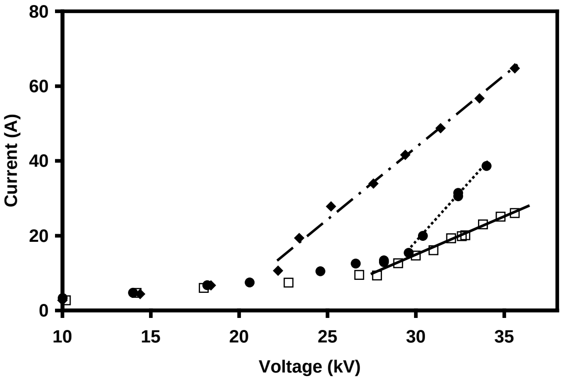


Fig. 4. Maximum of the current in function of the applied voltage (f = 132 Hz; GHSV = 1800 h^{-1}). (◆) Nitrogen, (☐) 180 ppm 2-heptanone in dry air and (●) 180 ppm 2-heptanone in wet air (H_2O = 3 mol%).

3.3. Reactivity

Fig. 5 shows the variation of the 2-heptanone conversion in function of the repetition frequency of the bi-polar voltage pulse in dry air conditions (180 ppm of 2-heptanone in dry air). Whatever the monolith used (uncoated or catalytic), the 2-heptanone conversion increases with the frequency of the repetition of the bi-polar voltage pulse.

According to the low increase of temperature in the reactor (T_{max} = 40 °C, measured on the outer wall of the glass reactor containing the monolith), the improvement in the 2-heptanone conversion can be only assigned to the increase of the energy deposited in the gas phase. At 132 Hz and 34 kV, the 2-heptanone removal reaches 98% with the catalytic monolith whereas the conversion is only 50% with the uncoated monolith, showing the important role of the Pt/Al_2O_3 catalytic phase.

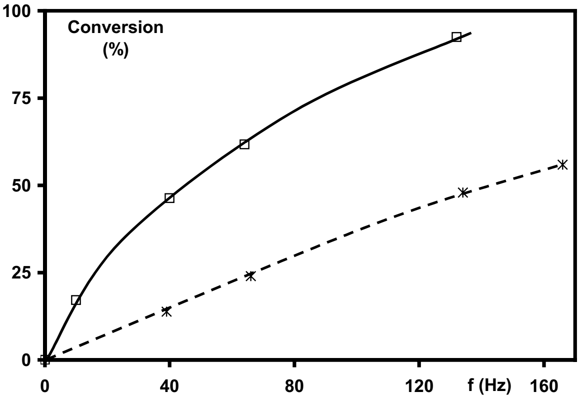


Fig. 5. 2-Heptanone (180 ppm in dry air) conversion on the catalytic monolith (☐) and on uncoated monolith (∗) in function of the repetition frequency of the voltage pulse (V_{PP} = 34 kV, GHSV = 1800 h^{-1}).

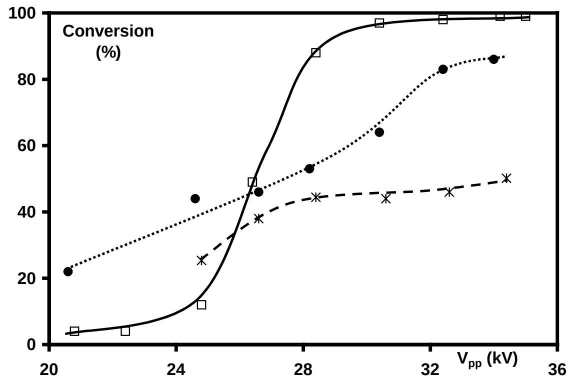


Fig. 6. 2-Heptanone (180 ppm) conversion in function of the applied voltage. (∗) Uncoated monolith (dry air), (☐) catalytic monolith (dry air) and (●) catalytic monolith (wet air) ($f = 132$ Hz; GHSV $= 1800\,h^{-1}$).

A similar result is obtained with variable voltage experiments. The conversion of the 2-heptanone in function of the value of the pulse voltage is shown in Fig. 6. According to Fig. 3, the 2-heptanone conversion starts to increase with the increase of E_d, for dry air conditions. According to the residence time (1.5 s) and to the repetition frequency ($f = 132$ Hz) of the voltage pulse the gas flow is submitted to 198 discharges in the plasma zone, when it is passing through the reactor. This value, which is not enough to remove the 2-heptanone in presence of the uncoated monolith shows the important role played by the catalytic phase for the VOC molecules removal.

The behavior of the 2-heptanone conversion on the catalytic monolith in dry or wet air conditions is different. In wet air conditions, the conversion at low voltages is higher than that in dry air, but the conversion increases with voltages applied more slowly than in dry air, so that at 31 kV the conversion reaches 95% in dry air and only 63% in wet air conditions while the E_d values are 220 and 300 J/L for dry and wet air conditions, respectively. It should be noticed that in wet air conditions, the 2-heptanone conversion is not negligible, even for applied voltages as low as 20–24 kV.

Figs. 7–9 present the carbon balance and the catalytic behavior of 2-heptanone conversion to carbon oxides on the catalytic and uncoated monolith in dry and wet air conditions. The main products observed by gas chromatography are carbon oxides, with small traces of acetic acid, particularly in wet air conditions and for the lowest applied voltages.

After more than 100 h under the plasma, the catalyst presents few traces of carbonaceous deposits on its surface (0.2 wt.%). After solvent extraction and characterization by mass spectrometry these products have been identified to heavy acids and esters containing 10–19 carbon atoms. Those products could be formed by the combination of 2-heptanone fragments due to the partial oxidation at low voltages and can explain the lack of the carbon balance. The formation of such compounds has been already observed, in absence of plasma, at 100 °C on the same kind of catalyst

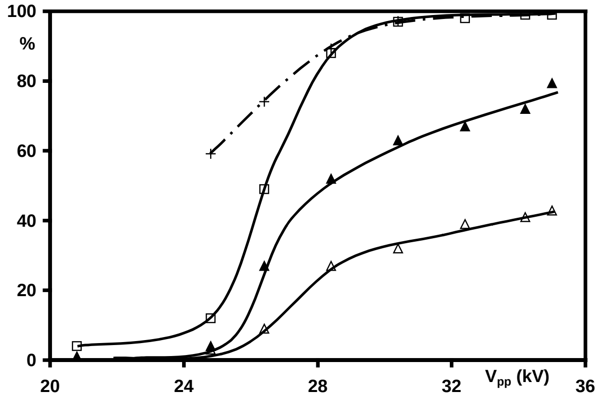


Fig. 7. Catalytic behavior of 2-heptanone (180 ppm in dry air) conversion on the catalytic monolith in function of the applied voltage ($f = 132$ Hz; GHSV $= 1800\,h^{-1}$). (+) Carbon balance, (☐) 2-heptanone conversion, (▲) CO_2 formation (%) and (△) CO formation (%).

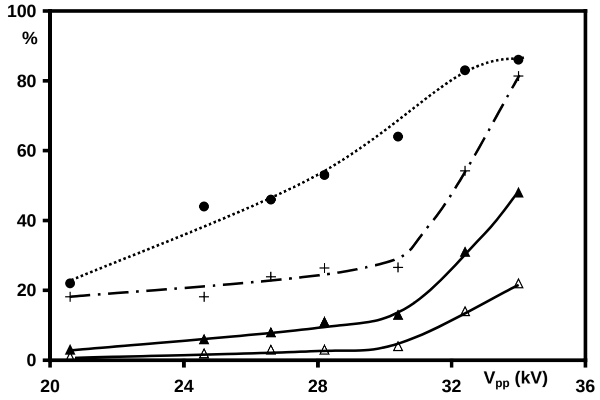


Fig. 8. Catalytic behavior of 2-heptanone (180 ppm in wet air: $H_2O = 3$ mol%) conversion on the catalytic monolith in function of the applied voltage ($f = 132$ Hz; GHSV $= 1800\,h^{-1}$). (+) Carbon balance, (●) 2-heptanone conversion, (▲) CO_2 formation (%) and (△) CO formation (%).

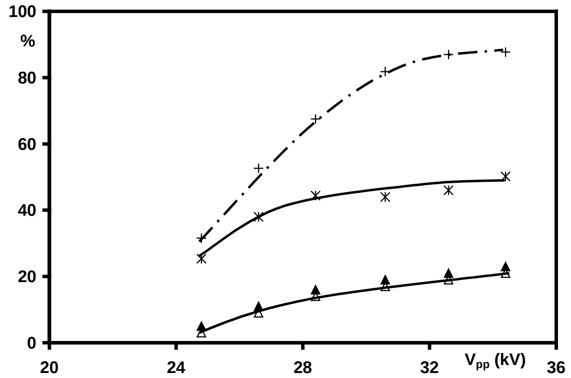


Fig. 9. Catalytic behavior of 2-heptanone (180 ppm in dry air) conversion on the uncoated monolith in function of the applied voltage ($f = 132$ Hz; GHSV $= 1800\,h^{-1}$). (+) Carbon balance, (∗) 2-heptanone conversion, (▲) CO_2 formation (%) and (△) CO formation (%).

Table 2
Conversion of 2-heptanone, CO_2/CO ratio and selectivity (S_x) of carbon oxides formation on the catalyst and uncoated monoliths ($f = 132$ Hz, 2-heptanone = 180 ppm, flow rate = 420 mL/min, wet air = 3 mol% H_2O)[a]

Solid	Gas phase	$V_{pp} = 27$ kV					$V_{pp} = 34$ kV				
		Conversion (%)	CO_2/CO	S_{CO_2} (%)	S_{CO} (%)	CB (%)	Conversion (%)	CO_2/CO	S_{CO_2} (%)	S_{CO} (%)	CB (%)
Monolith	Dry air	38	1.2	29	24	53	50	1.1	46	42	88
Catalyst	Dry air	49	3.0	55	18	73	98	1.8	64	36	100
	Wet air	46	2.8	17	6	23	86	2.2	56	26	82

[a] CB: carbon balance.

[7] and could explain the 2-heptanone conversion observed at low voltages in presence of water (Figs. 6 and 8). In presence of water, this reaction seems to be the main reaction for voltages lower than 30–32 kV, as shown by the poor carbon balance for voltages lower than 32 kV (see Fig. 8).

The CO_2/CO ratio is favored by both the presence of a catalyst and water in the gas phase, and seems to decrease with the conversion (see Table 2). This behavior should result from complex reactions both on the catalyst surface and in the gas phase, but the only small variations in the CO_2/CO ratio when the conversion varies in a large range, strongly suggests that CO_2 and CO are mainly produced by two different ways.

In standard experimental conditions (34 kV; 132 Hz; 420 mL/min; 180 ppm of 2-heptanone), the conversion is maximum in dry air (98%) and is obtained with the catalytic monolith, whereas with the uncoated monolith only 50% of 2-heptanone is transformed. It is then obvious that a high synergy effect exists between the catalyst and the non-thermal plasma.

3.4. Ozone formation

As already observed [18], a non-thermal plasma leads to ozone formation through the production of oxygen atoms by electron collisions on O_2,

$$O_2 + e^- \rightarrow 2O^\bullet + e^-$$

followed by an addition reaction

$$O^\bullet + O_2 + M \rightarrow O_3 + M,\ \text{with}\, M = N_2\ \text{or}\ O_2$$

The influence of the energy density E_d and gas phase composition on the ozone formation is presented in Fig. 10, which shows the comparison between the ozone concentrations obtained with the catalytic monolith in dry and wet air and on the uncoated monolith in dry air. Whatever the system used, the ozone formation follows the same trend, by increasing with the energy density E_d and then passing through a maximum before a rapid decrease until ppb range concentration. The maximum concentration value strongly depends on the conditions used, the lower ozone formation being observed for wet air conditions. The decrease in the ozone formation by increasing the deposited energy in the gas phase could be due to an increase in the temperature but measurements of the gas phase temperature at the exit of the monolith have shown that in our standard conditions at 34 kV, the value is less than 32 °C, whereas the temperature of the outer wall of the reactor, in the plasma zone reaches 40 °C. This difference means that one of the plasma effect is to heat the catalyst rather than the gas phase, and then some hot spots able to decompose ozone can exist on the catalyst surface.

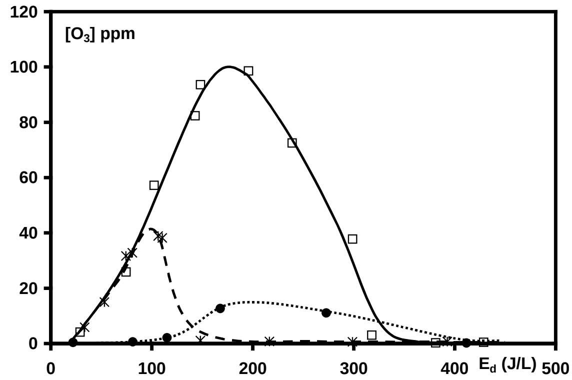


Fig. 10. Variation of the ozone concentration in function of the energy density E_d (2-heptanone = 180 ppm; GHSV = 1800 h^{-1}). (□) Catalytic monolith (dry air), (●) catalytic monolith (wet air) and (∗) uncoated monolith (dry air).

A similar behavior was observed with the uncoated monolith (see Fig. 10) but the maximum of the ozone concentration never exceed 50 ppm (against 100 ppm with the catalytic monolith) suggesting that the ozone formation could occur on the catalyst surface.

The presence of water in the gas phase which induces a drastic decrease in the ozone formation (Fig. 10) could be explained by the following series of radical reactions leading to a fast ozone consumption [18,19]:

(1) $H_2O + e^- \rightarrow H^\bullet + HO^\bullet + e^-$
(2) $H^\bullet + O_3 \rightarrow HO^\bullet + O_2$
(3) $HO^\bullet + O_3 \rightarrow HO_2{}^\bullet + O_2$
(4) $HO_2{}^\bullet + O_3 \rightarrow HO^\bullet + 2O_2$

4. Conclusion

Experiments on 2-heptanone elimination by a plasma-catalytic hybrid reactor have been performed. A non-thermal plasma has been generated within a honeycomb monolith using a high voltage pulse excitation.

A high synergy effect between the catalytic monolith (cordierite honeycomb monolith wash-coated by Pt/Al_2O_3 catalytic phase) and the non-thermal plasma has been evidenced leading to a complete elimination of the 2-heptanone.

The presence of water in the effluent containing the 2-heptanone enhances the CO_2 selectivity and drastically reduces the ozone formation. However a slight decrease in the 2-heptanone elimination has been observed and the formation of a polymeric by-product for the lower applied voltages (lower energy densities).

These results clearly demonstrate that:

- A plasma can be successfully generated within a catalyst.
- A high synergy effect is observed between a cold plasma and an oxidation catalyst.
- The ozone formation is drastically reduced by the presence of water.

These promising results allow to think of the use of this process in industrial or domestic utilization for VOC or odor elimination.

Acknowledgements

The French “Ministère de l’Économie, des Finances et de l’Industrie”, the “Région Poitou−Charentes” and the “Centre de Ressources Technologiques Plasma-Laser” are warmly acknowledged for financial support.

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