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1 Dynamic probing of plasma-catalytic surface
2 processes: oxidation of toluene on CeO₂

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1 **Abstract**

2 This article reports the use of innovative diagnostics to monitor toluene adsorption and
3 oxidation on CeO₂ surface under Non-Thermal Plasma (NTP) exposure. Two plasma-catalytic
4 configurations are explored, namely: Post-Plasma Catalysis (PPC) and In-Plasma Catalysis
5 (IPC). Since heterogeneous processes are pointed out as key steps of the plasma-catalyst
6 coupling, the catalyst surface has been monitored by two complementary *in-situ* diagnostics: i)
7 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) ii) and Transmission
8 Fourier Transform Infrared Spectroscopy using Sorbent track (ST) device. Dielectric Barrier
9 Discharges (DBD) are used in both PPC and IPC configurations to induce adsorbed toluene
10 oxidation. Toluene in dry air is first adsorbed on the selected catalytic surface: ceria (CeO₂).
11 Subsequently, the plasma is switched on. During the experiment, the ceria surface is
12 monitored by infrared to study toluene adsorption and oxidation mechanisms. The adsorption
13 capacity of toluene on ceria is respectively measured in the configurations of PPC and IPC by
14 DRIFTS and ST. The oxidation of toluene by plasma follows a first-order reaction regardless
15 of plasma configuration and injected power and IPC is more effective for the toluene removal
16 than PPC. Intermediates of toluene (benzyl alcohol, benzaldehyde and benzoic acid) are also
17 identified on the surface and their respective temporal evolutions as a function of the plasma
18 exposure are studied.

19 20 **Keywords**

21 Plasma-catalysis, Adsorption, VOC, Non-Thermal Plasma, Air Treatment, Ceria, Toluene,
22 DRIFTS

1 **1 Introduction**

2 Volatile organic compounds (VOCs) are organic chemical species characterized by high
3 vapor pressures at room temperature, allowing their evaporation in air without decomposition.
4 Atmospheric VOCs result from both biogenic and anthropogenic sources. VOC emissions can
5 affect environment and human health in many ways ^[1], depending on various factors such as
6 the structure of the VOCs, and the exposure parameters. Toluene is one of the most ubiquitous
7 anthropogenic VOCs ^[2]. Due to its neurotoxic effects ^[3] several techniques have been studied
8 in order to remove toluene such as photocatalysis ^[4], adsorption ^[5], bio-filtration ^[6], plasma-
9 catalysis ^[7].

10 Among these methods, non-thermal plasma (NTP) is one of the most attractive due to its
11 energy efficiency ^[8]. Regarding non-thermal plasma, the injected energy is used to generate
12 energetic electrons while the background gas temperature remains close to ambient
13 temperature. The collisions between the high-energy electrons and the background gas
14 generate chemically active species (ions, radicals, excited species, etc) which directly or
15 indirectly react with VOCs and induce oxidation reactions. In order to make reactions more
16 selective and to prevent the formation of undesired by-products, the combination of plasma
17 with heterogeneous catalysis has been addressed ^[9]. The catalysts can be placed downstream
18 the plasma reactor, so-called Post Plasma Catalysis (PPC) ^[10,11], or directly introduced into the
19 active plasma discharge, so-called In-Plasma Catalysis (IPC) ^[12,13]. Irrespectively of the
20 configurations, synergetic effects involving catalytic surface reactions are observed ^[14,15].
21 Former studies pointed out various hypotheses to interpret plasma-catalyst positive interaction,
22 among them ozone formation and decomposition ^[16], adsorption and desorption of organic
23 reactants and plasma generated species ^[17], local heating ^[18], and enhanced interaction of gas-
24 phase radicals with adsorbed pollutants ^[19]. These hypotheses are generally based on the
25 monitoring of reactor outlet gases whereas they all refer to inner reactor processes. This

1 discrepancy motivates the development of *in-situ* diagnostics to deepen our understanding
2 plasma-catalysis.

3 *In-situ* Fourier Transform Infrared (FTIR) spectroscopy allows real time monitoring of
4 processes occurring on the surface of the catalysts. Diffuse Reflectance Infrared Fourier
5 Transform Spectroscopy (DRIFTS) has been used by various authors to investigate adsorbed
6 species and active site evolutions onto catalytic surfaces ^[20-22]. More precisely, in the case of
7 PPC studies ^[23,24], Barakat et al. ^[24] investigated the evolution of adsorbed organics along the
8 plasma-catalytic decomposition of acetone and isopropanol on TiO₂ surface using DRIFTS.
9 Authors evidenced that complete oxidation of isopropanol and acetone is mainly limited by
10 acetone oxidation rate. More recently, Magureanu et al. ^[25] used DRIFTS to address ozone
11 interaction with Ag–Al catalysts supported on quartz pellets. This approach provided new
12 insights into the determination of active sites for heterogeneous toluene mineralization.
13 Regarding IPC, infrared (IR) absorption spectroscopy in transmission mode can be adapted to
14 directly access the catalysts surface under plasma exposure. Noticeably, Rivallan et al. ^[26]
15 achieved IR *in-situ* measurements combining a Dielectric-barrier discharge (DBD) with Al₂O₃
16 catalyst. Authors performed surface *in-situ* and time resolved monitoring of the oxidation of
17 preliminarily adsorbed IPA. Another effective example can be found in the work of Stere et al.
18 ^[27] who used DRIFTS to study the selective catalytic reduction (SCR) of NO_x on a Ag/Al₂O₃
19 catalyst in the presence of toluene and n-octane where the catalyst was activated by a helium
20 plasma jet at atmospheric pressure. The approaches of *in-situ* IR provide new insights into the
21 catalyst surface during the pollutant adsorption and plasma induced oxidation process.
22 Coupling this technique with *in-situ* plasma allowed real-time monitoring of (i) primary
23 pollutants adsorption on the surface of the catalyst and (ii) the production of intermediates.

24 Our group recently reported a new approach to monitor adsorption and surface oxidation
25 of pollutants under direct plasma exposure ^[28]. To that end, a new experimental device was

1 constructed and named Sorbent Track (ST). More precisely, the DBD is generated in contact
2 with a catalytic pellet and transmission-FTIR measurements are performed throughout the
3 plasma exposed pellet. Coupling this technique with *in-situ* plasma allowed real-time
4 monitoring of species adsorbed, produced and removed from the catalyst surface. The
5 sorbent-TRACK system made in our laboratory provides a quantitative insight to the
6 heterogeneous processes of plasma catalysis [28].

7 In the present paper, adsorption and oxidation of toluene on ceria is reported under plasma
8 exposure in two different configurations using surface monitoring diagnostics: In-Plasma
9 Configuration (IPC) is studied using Sorbent TRACK; Post-Plasma Configuration (PPC) is
10 studied using DRIFTS. With these two configurations, toluene was adsorbed up to its
11 breakthrough onto CeO₂. Reversibly and irreversibly adsorbed toluene fractions are quantified
12 and compared for IPC and PPC. The influence of plasma position and injected power are also
13 investigated during the plasma oxidation process to know which configuration is more
14 effective for toluene removal. Real time evolution of adsorbed intermediates of toluene is also
15 reported.

16 **2 Experimental set up**

17 **2.1 Gas flow preparation and materials**

18 Toluene used in this study is provided by sigma Aldrich (34866, CHROMASOLV®, for
19 HPLC, 99.9%). A 5.7 ml/min air flow were sent through the way (1) connected with the
20 toluene bubbler of 273.15 K and the obtained toluene concentration at the bubbler outlet is
21 8964 ppm. A 494.3 ml/min air flow was sent through the way (2). Once the two ways were
22 mixed together the concentration of toluene is 100 ppm with a flow rate of 500 mL min⁻¹. The
23 material used as catalyst consists in CeO₂ powder (99.95% trace rare earth metals basis, sigma

1 Aldrich) with a specific surface area of $84 \pm 5 \text{ m}^2/\text{g}$ measured by Brunauer-Emmett-Teller
2 (BET) method (Coulter SA3100). In the DRIFTS experiments, 25.0 mg of CeO_2 powder are
3 introduced into the sample holder. In the case of Sorbent Track experiments, CeO_2 powder
4 has been compacted to a wafer (25.0 mg of CeO_2 , $\text{Ø} = 7 \text{ mm}$, thickness of 0.3 mm).

5 The experimental procedure is composed of four steps: i) thermal treatment of the catalyst
6 at 400°C to remove water and other adsorbed hydrocarbon species; ii) adsorption of 100 ppm
7 toluene onto the catalyst until saturation of the sorption sites; iii) flushing with dry air flow to
8 remove reversibly adsorbed toluene; iv) surface exposition to *in-situ* plasma or *post-situ*
9 plasma for two hours.

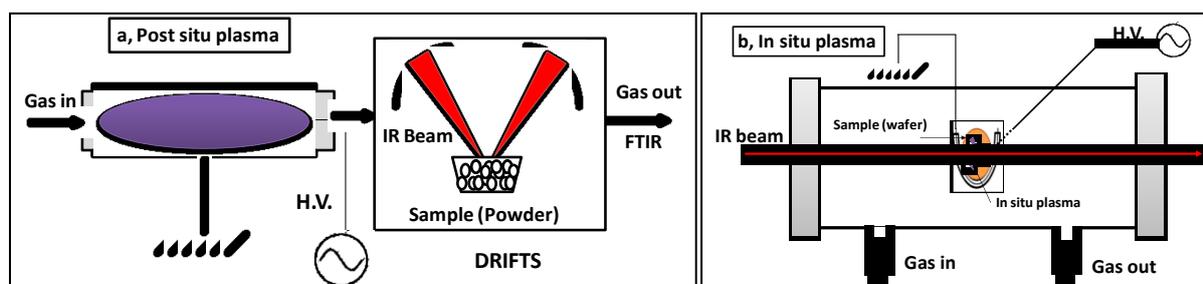
10 **2.2 Post-Plasma (PPC) and In-Plasma (IPC) set-up**

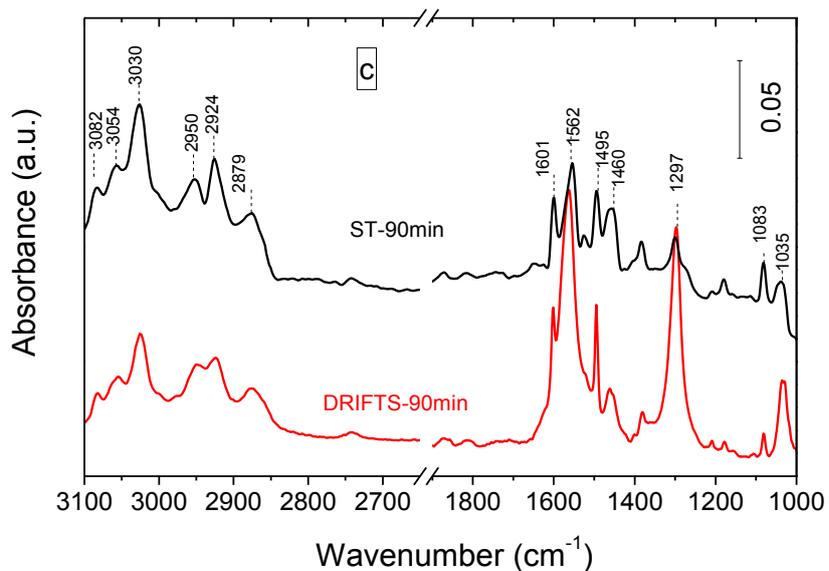
11 The post situ plasma set-up is described in Figure 1a. For the *post-situ* plasma experiment,
12 the DBD is placed upstream the catalyst bed. It consists of Pyrex glass tube of 23.5 cm length,
13 3.3 mm external diameter and 1.7 mm inner diameter. The high voltage electrode is a tungsten
14 wire of 0.2 mm thickness placed in the middle of the tube. The ground electrode consists in a
15 copper sheet wrapped around the dielectric Pyrex tube. The sample holder of DRIFTS
16 consists in a ceramic crucible in which a few milligrams (ca. 25.0 mg) of the solid to be
17 studied are placed. The cell contains a thermocouple and a heating resistor, a gas inlet and
18 outlet, and ZnSe windows to allow the IR beam to enter and exit the cell. The infrared beam is
19 focused by series of mirrors and the radiation diffused by the powder is collected by
20 ellipsoidal mirrors and sent to the detector. The distance between the tail of plasma and the
21 sample is 180 cm and the flow time of the active species before anchoring the catalyst is about
22 6 s. The detection and quantification of the gas phase species is performed using high
23 resolution Nicolet 6700 Fourier Transform Infrared spectrometer (FTIR) equipped with a 10
24 m optical-path White cell and a cooled MCT (mercury cadmium telluride) detector.

1 The *in-situ* plasma set-up is described in Figure 1a. Sorbent Track cell is composed of a
2 glass cylinder carrying a toroidal sample holder in its center where the ceria pellet is placed in
3 the form of a self-supported wafer. The heating system gives a maximum temperature of 573
4 K on the sample. The plasma reactor consists of a Pyrex glass tube of 5.8 mm inner diameter,
5 8 mm outside diameter. The inner electrode (H.V.) consists of a copper wire of 30 μm and the
6 outer electrode is a copper wire of 30 μm placed in the center of sample holder. More details
7 of ST cell can be found in our previous study [28].

8 100 ppm of toluene diluted in air are sent into the DRIFTS or ST cell to saturated ceria
9 surface. For PPC, the ceria surface is monitored by Diffuse Reflectance Infrared Fourier
10 Transform Spectroscopy (DRIFTS) and the gas phase is measured using Fourier Transform
11 Infrared Spectroscopy (FTIR). For IPC, the ceria surface is monitored by transmission FTIR.
12 Figure 1c represents the absorbance spectra obtained by DRIFTS and ST when the ceria
13 surface is saturated by toluene. The bands at 3030, 3054 and 3082 cm^{-1} are assigned to
14 toluene C–H aromatic and the C–H stretching from the toluene methyl group are detected at
15 2950, 2924 and 2879 cm^{-1} . The bands at 1495, 1460, 1562 and 1601 cm^{-1} are attributed to the
16 C=C stretching in the toluene aromatic ring. A small contribution at 1081 and 1032 cm^{-1}
17 could be attributed to in-plane toluene C–H bending. The intense band at 1297 cm^{-1} might be
18 assigned to toluene Ar-C stretching or to the twisting mode of methylene as proposed by
19 Busca et al. [29]. Finally, a weak overtone in the 2000–1800 cm^{-1} region is detected.

20

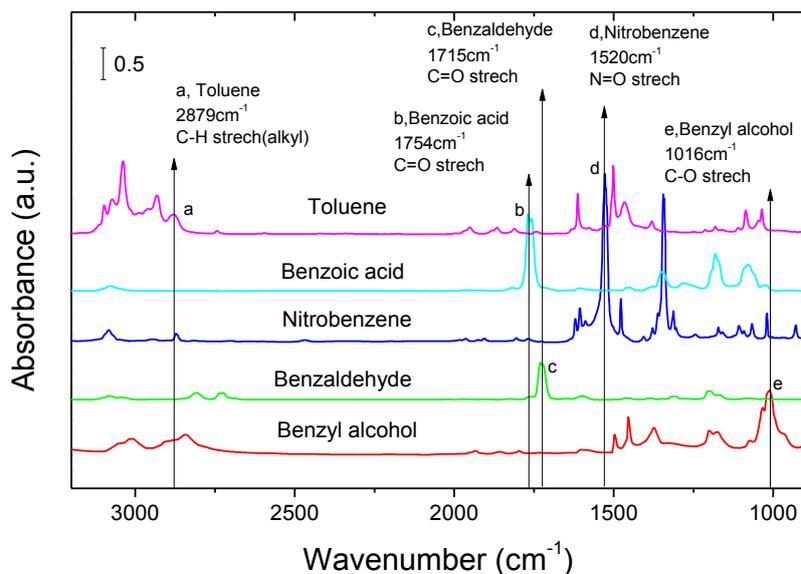




1
 2 **Figure 1 - Schematic representation of experimental setups of PPC (a) and of IPC (b) and infrared absorbance**
 3 **spectra (c) of toluene adsorbed on ceria surface obtained by DRIFTS (red line) and ST (black line).**

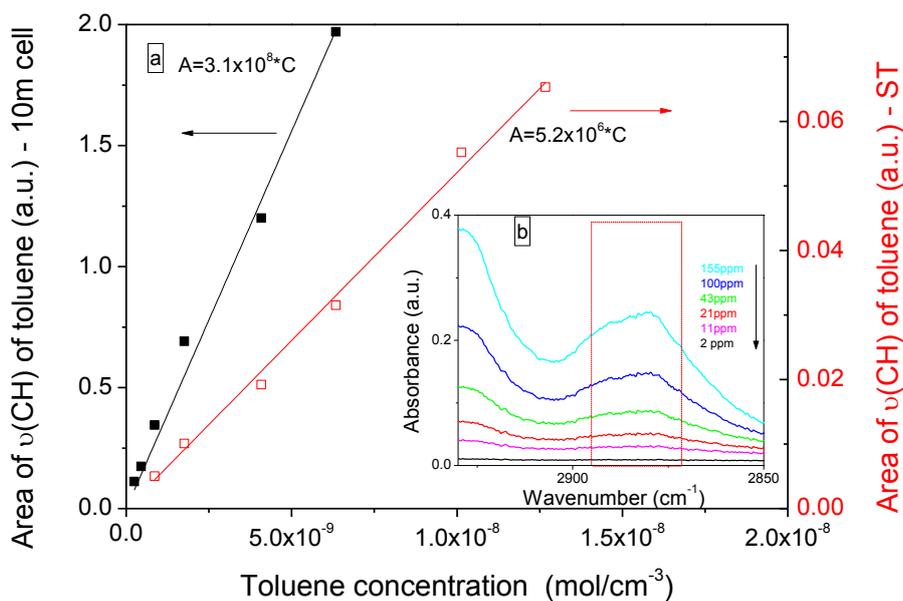
4 ***2.3 Toluene quantification and intermediates identification***

5 Figure 2 represents the FTIR spectra of toluene and potential intermediates of toluene
 6 oxidation: benzoic acid, nitrobenzene, benzaldehyde and benzyl alcohol. In order to avoid
 7 overlapping, the bands of 2879 cm^{-1} ($\nu(\text{C-H})$ of toluene), 1754 cm^{-1} ($\nu(\text{C=O})$ of benzoic acid),
 8 1715 cm^{-1} ($\nu(\text{C=O})$ of benzaldehyde), 1520 cm^{-1} ($\nu(\text{N=O})$ of nitrobenzene) and 1016 cm^{-1}
 9 ($\nu(\text{C-O})$ of benzyl alcohol) are respectively chosen to monitor the respective evolution of
 10 these adsorbed intermediates on ceria surface.



1
 2 **Figure 2 - FTIR spectra of toluene (a), benzoic acid (b), nitrobenzene (c), benzaldehyde (d) and benzyl alcohol (e).**
 3 **Bands of 2879 cm⁻¹ (ν(C-H) of toluene), 1754 cm⁻¹ (ν(C=O) of benzoic acid), 1715 cm⁻¹ (ν(C=O) of benzaldehyde), 1520**
 4 **cm⁻¹ (ν(N=O) of nitrobenzene) and 1016 cm⁻¹ (ν(C-O) of benzyl alcohol) are respectively chosen.**

5 For toluene, calibration curves (Figure 3) were obtained by passing the standard gases in
 6 air at different known concentrations (155, 100, 43, 21, 11 and 2ppm), through the 10 m white
 7 gas cell (black line in Figure 3a) or ST system (red line in Figure 3a). The fitting function is
 8 shown in Figure 3a, where the unit ppm was converted to mol/cm³. The spectral region
 9 selected for toluene (ν(C-H)) calibration is 2895.3-2871.1 cm⁻¹.



1 Figure 3 - a) Corresponding toluene calibration curve (the spectral region of $\nu(\text{C-H})$ selected for toluene
2 calibration is $2895.3\text{-}2871.1\text{ cm}^{-1}$); b) Toluene FTIR spectra in the gas phase obtained in a 10 m White cell or ST with
3 inlet toluene at a concentration of 155, 100, 43, 21, 11 and 2ppm in dry air (the unit ppm was converted to mol/cm^3).

4 According to Lambert- Beer Law,

$$A_{\text{toluene}} = \epsilon_{\text{toluene}} \cdot L \cdot C_{\text{toluene}} \quad \text{Equation 1}$$

5 For 10 m white gas cell, according to the slope of 3.1×10^8 obtained in Figure 3b,

$$A_{\text{toluene}} = 3.1 \times 10^5 \sigma_{\text{toluene}} \quad \text{Equation 2}$$

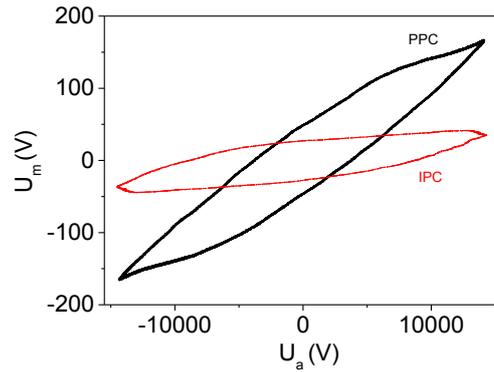
6 Where σ_{toluene} are the $L \times C$ product expressed in $\text{mol} \cdot \text{cm}^{-2}$

7 For Sorbent-TRACK system, L is 16 cm and with the slope of 5.2×10^6 obtained in Figure
8 3b,

$$A_{\text{toluene}} = 3.2 \times 10^5 \sigma_{\text{toluene}} \quad \text{Equation 3}$$

9 **2.4 Electrical parameters measurement**

10 For both configurations, the electrical parameters were measured via two high voltage
11 probes (LeCroy, PPE20KV-CC) connected to a digital oscilloscope (LeCroy WaveSurfer
12 64Xs-A, 600 MHz). A measurement capacitance (C_m) of 680 pF is placed in serie with the
13 DBD reactors. The injected power is obtained from the Lissajous figures, corresponding to the
14 plotting of the transported electric charges through the discharge as a function of the
15 periodical applied voltage. Experimentally, charges are delivered from the voltage drop across
16 the reactor and the average electric energy dissipated in a discharge cycle is proportional to
17 the area of the characteristic Lissajous figure (Figure 4). In order to tune the specific input
18 energy (SIE), the voltage applied is varied, but the frequency is kept constant at 50 Hz.



1

2 **Figure 4 - Example of Lissajous figure obtained from IPC (red) and PPC (black) to calculate injected powers. It**
 3 **is obtained by applying a voltage of 15 kV and a frequency of 50 Hz in a typical DBD reactor under air flow**
 4 **(500ml/min) by means of a sinusoidal power supply. Injected powers are respectively 130 and 145 mW for IPC and**
 5 **PPC.**

6 **3 Results and discussions**

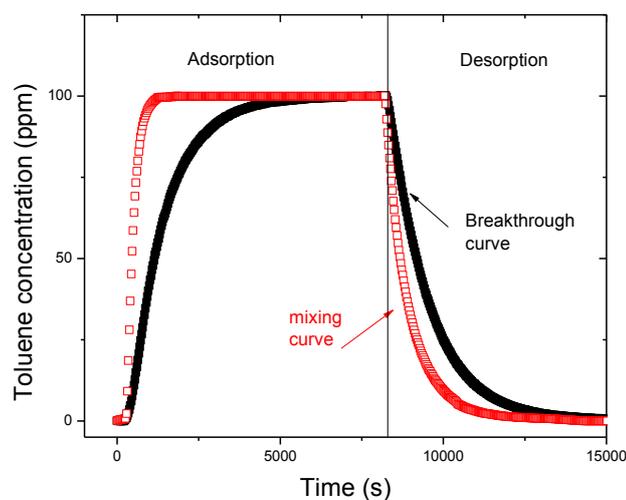
7 **3.1 Toluene adsorption and desorption**

8 The toluene adsorption on ceria has been studied using two experimental set-ups: PPC
 9 and IPC. The purpose is to follow the evolution of toluene adsorption onto ceria, to determine
 10 the toluene adsorption capacity and to compare PPC and IPC approaches.

11 **Post-Plasma (PPC) set-up**

12 In order to saturate CeO₂ surface with the selected model VOC, 100 ppm of toluene
 13 diluted in air are sent into the cell (DRIFTS), with a total flow rate of 500 mL/min : gas phase
 14 measurements using FTIR and adsorbed phase measurements using DRIFTS. In order to
 15 determine ceria surface coverage by toluene, the adsorption capacity is determined from the
 16 FTIR measurements by the previously reported method ^[24]. Quantitative values of irreversibly
 17 and reversibly adsorbed toluene on ceria are determined using breakthrough curves as shown
 18 in Figure 5 in a dedicated experimental set up ^[24]. The mixig curve of the system is
 19 determined by sending the VOC in the empty reactor and is used as a background.

1 Breakthrough curves are established during toluene adsorption and desorption steps. Under
2 dry air and 100 ppm toluene gas phase concentration, $3.4 \pm 0.3 \mu\text{mol}/\text{m}^2$ toluene are initially
3 adsorbed on CeO_2 . The flushing of toluene saturated CeO_2 surface by air leads to the
4 desorption of $2.0 \pm 0.2 \mu\text{mol}/\text{m}^2$ of toluene subsequently considered as reversibly adsorbed.
5 The amount of irreversibly adsorbed toluene on CeO_2 is given by the subtraction of these two
6 values, i.e. $1.4 \pm 0.2 \mu\text{mol}/\text{m}^2$.



7

8 **Figure 5 - Breakthrough curve obtained during adsorption and desorption steps of the experimental procedure**
9 **and used to quantify adsorbed toluene.**

10 Adsorbed phase measurements are monitored by DRIFTS. The Corresponding recorded
11 spectra as a function of time are reported in Figure 6a and the evolution of toluene adsorption
12 capacity is plotted in Figure 6b. The bands assignment was presented in section 2.2. During
13 the toluene adsorption, the intensity of the bands increases as function of adsorption time. No
14 other bands than that attributed to toluene were observed along toluene adsorption using
15 DRIFTS and FTIR. It's shown in this section that since the spectra of adsorbed toluene on
16 ceria could be recorded *in-situ*, the catalyst working can be monitored to investigate the
17 changes of species during the adsorption and plasmas-oxidation. Besides, quantitative
18 analysis of the gases leaving the DRIFTS cell provides additional data: toluene adsorption

1 capacity and by-products formation. A direct quantitative technique to investigate the
2 adsorbed species on catalyst surface by transmission IR using ST is presented in next section.

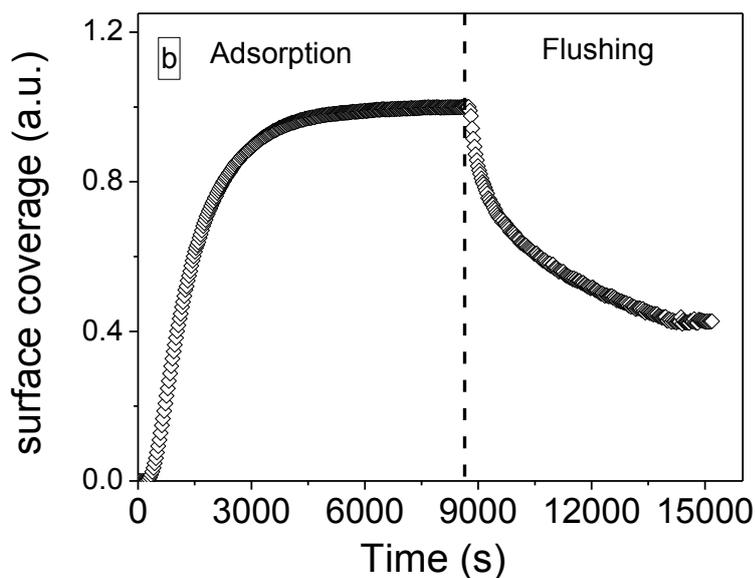
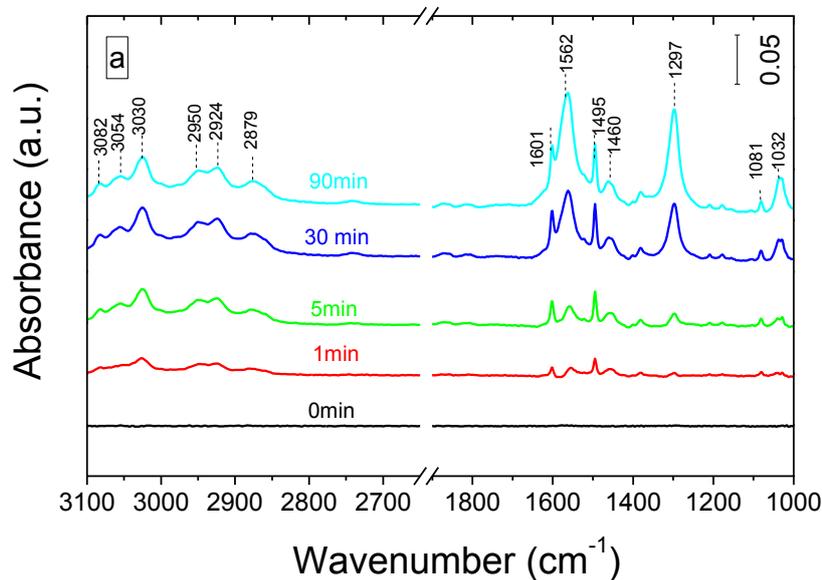


Figure 6 - a) Absorbance spectra recorded by DRIFTS during toluene adsorption on CeO₂. (100 ppm toluene, 500 mL/min air, 25 mg CeO₂); b) the evolution of the adsorption and desorption by air of toluene on CeO₂.

8 *In-Plasma (IPC) set-up*

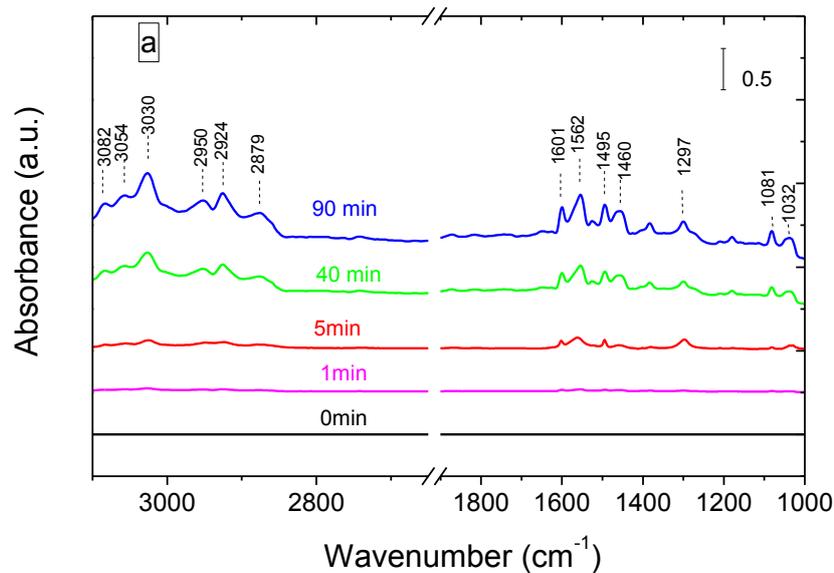
9 For the IPC set-up, the same experiment condition as PPC is used to saturate the ceria
10 surface by toluene. When using Sorbent Track, the quantitative method was presented in

1 section 2.3. In Sorbent-TRACK, toluene molecules may be located on the catalyst and in the
2 gas phase. Hence the absorbance is:

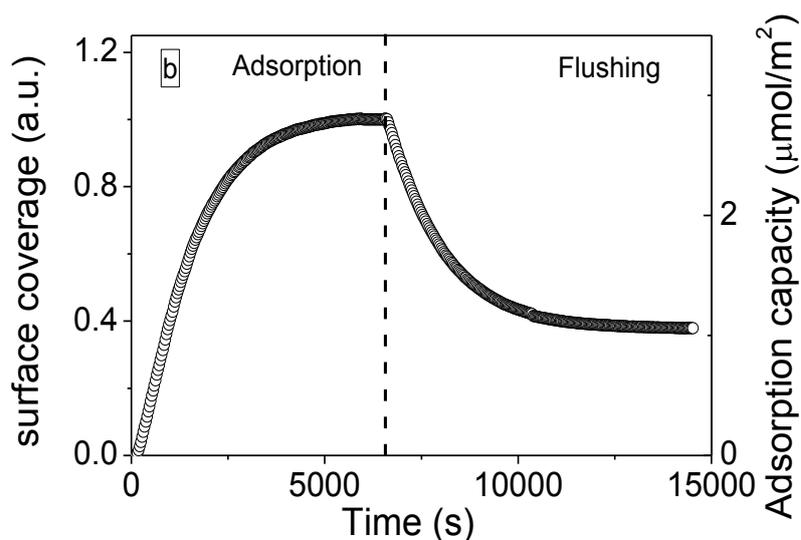
$$A_{\text{toluene}} = 2.7 \times 10^5 (\sigma^{\text{S}_{\text{toluene}}} + \sigma^{\text{G}_{\text{toluene}}}) \quad \text{Equation 4}$$

3 $\sigma^{\text{S}_{\text{toluene}}} + \sigma^{\text{G}_{\text{toluene}}}$ are the optical depth of toluene in the solid and gas phase respectively.

4 In order to evaluate the contribution of the toluene gas phase molecules to the absorbance in
5 ST cell, the infrared spectra of the CeO₂ surface upon toluene adsorption is recorded in Figure
6 7a and the evolution of toluene adsorption capacity is plotted in Figure 7b. With the gas flow
7 of 500ml/min and the volume of ST cell of 460ml, the filling time is about 1 min. So the
8 spectrum recorded at 1 min in Figure 7a by ST is mainly toluene of gas phase. The gas phase
9 contribution of toluene is about 2% of toluene concentration at 90min. In the following
10 (Figure 7b), the concentration of adsorbed toluene has been corrected from the gas phase
11 contribution. Direct FTIR absorption is performed through the ceria sample. The total,
12 reversible and irreversible amount of toluene is respectively determined as 2.9 ± 0.3 , 1.6 ± 0.2 ,
13 and $1.1 \pm 0.2 \mu\text{mol/m}^2$. These values are not significantly different from those obtained in
14 PPC set-up, which confirms the performance of IPC set-up.



15



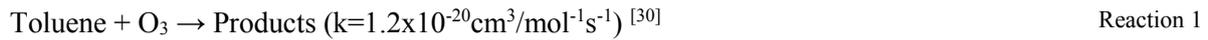
1
2
3 Figure 7 a) Absorbance spectra recorded by Trans-FTIR in Sorbent Track during toluene adsorption on CeO₂.
4 (100 ppm toluene, 500 mL/min air, 25 mg CeO₂); b) the evolution of the adsorption and desorption by air of toluene
5 on CeO₂.

6 **3.2 Comparison of toluene oxidation in IPC and PPC**

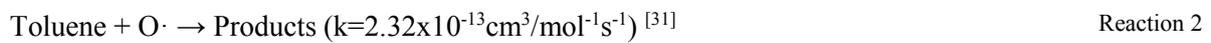
7 Beyond toluene adsorption, which was quantitatively and qualitatively addressed in PPC
8 and IPC configurations of by DRIFTS and ST, toluene oxidation is investigated using these
9 two configurations. Figure 8a shows the temporal evolution of CeO₂ surface coverage by
10 toluene under plasma exposure in IPC and PPC configurations for different plasma input
11 powers. Two main comments can be made: i) an increase of the plasma power leads to an
12 increase of oxidation rate; ii) higher toluene oxidation rate is achieved when there is direct
13 contact between the plasma and cerium oxide surface (IPC). It was checked using a 10 long
14 path cell FTIR absorption spectroscopy that no toluene is detected in the gas phase (sensitivity
15 = 100 ppb), thus toluene desorption in PPC or IPC is excluded here. Meanwhile, the graph of
16 Figure 8a represents concentration of reactants versus time considering a first-order reaction
17 and the reaction rates corresponding input powers have been plotted in Figure 8b. Compared
18 with PPC, the rate constants become higher in IPC. Regardless of the plasma configurations,
19 rate constants are higher with more injected power and linearly increase with power. The

1 slopes η which are respectively $14 \times 10^{-3} \text{ J}^{-1}$ and $7.6 \times 10^{-3} \text{ J}^{-1}$ for IPC and PPC are not much
2 sensitive to the injected power. The η of IPC is almost twice than PPC that higher toluene
3 removal could be achieved with ceria in IPC than PPC under the same injected power.

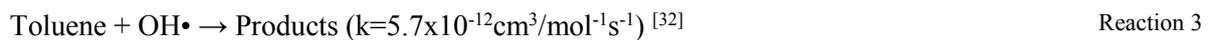
4 Higher toluene removal in IPC can be also confirmed by literature. For PPC, ozone is the
5 most important oxidizing agent from the following reaction:



6 O_3 can be catalytically decomposed into highly active atomic oxygen which is highly active
7 and involved in toluene oxidation:

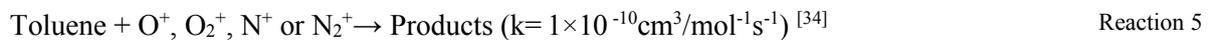
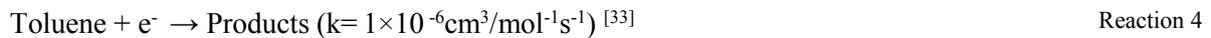


8 Atomic oxygen can also react with water to form hydroxyl radical which is very powerful
9 oxidants that enhance toluene destruction:

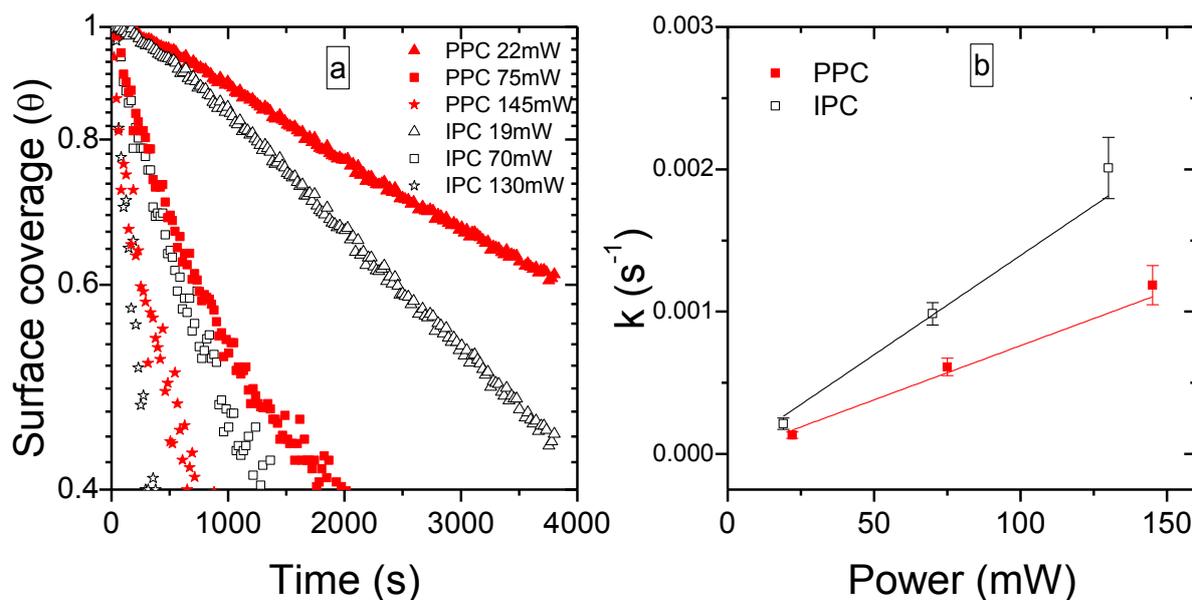


10 As for the IPC, short-life active species should be considered from the following reactions:

11



12 Much more $\text{O} \cdot$ and $\text{OH} \cdot$ radicals can be formed in the IPC, which combines both gas-phase
13 and catalyst surface. Besides of energetic electrons impact, radical attack is another important
14 mechanism with a higher rate constants leading to toluene destruction in the IPC. These could
15 explain that IPC is more effective for toluene removal with ceria than PPC.



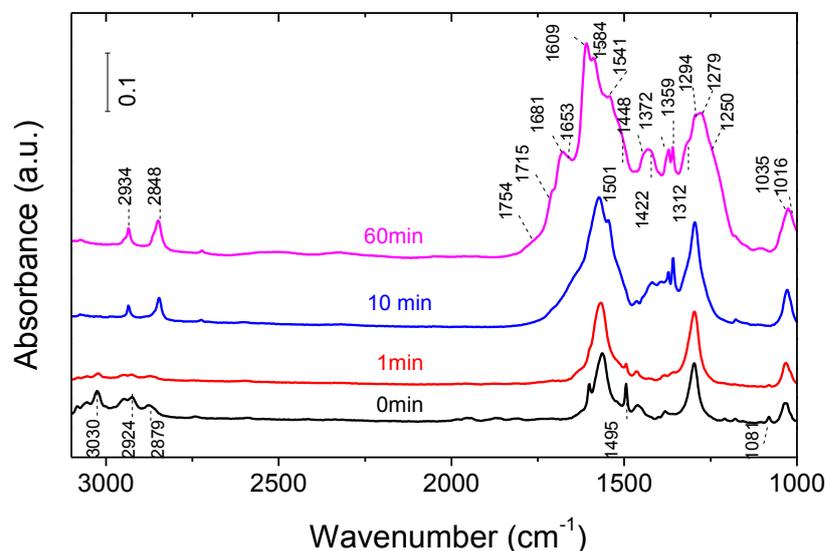
1
 2 Figure 8 - a) Evolution of toluene coverage on CeO₂ during NTP exposure at different injected powers which are
 3 respectively 22, 75 and 145 mW for PPC (red) and 19, 70 and 130 mW for IPC (black) (when ceria surface is
 4 saturated ($\theta=1$), the adsorbed toluene value is 2.95 μmol for 25mg catalysts) and b) the rate constant obtained from
 5 Figure 8a at different injected powers for PPC (red) and IPC (black).

6 **3.3 Adsorbed intermediates study during toluene oxidation**

7 **3.3.1 Adsorbed intermediates formation using PPC**

8 When the plasma is turned on, the catalytic surface is exposed to a flow of long-life
 9 reactive species - mainly ozone; C-H toluene aromatic bands (at around 3100–3000 cm^{-1}
 10 domain) rapidly decrease during the first minute of plasma treatment, as shown in Figure 9.
 11 Some potential by-products were presented in section 2.3 which are used for the following
 12 discussions. The new bands at 2848, 1715, 1653, 1584, 1448, 1312 cm^{-1} increase with time
 13 and can be attributed to adsorbed benzaldehyde [35]. The bands at 2848 and 1715 cm^{-1} could
 14 be attributed to C-H and C=O of benzaldehyde. The bands at 1653, 1584 and 1312 cm^{-1} arise
 15 from the different vibrational modes of aromatic rings. The presence of benzoic acid can be
 16 evidenced by 1754, 1681, 1609, 1584, 1501, 1448, 1422, 1320 cm^{-1} which are respectively
 17 assigned to $\nu(\text{COOH})$, $\nu(\text{CC})+\delta(\text{CH})$ ring (1609, 1584, 1501, 1448 cm^{-1}), $\delta(\text{C-OH})$ and

1 vs(OCO) benzoate [36]. The $\delta(\text{OH})$ at 1372 cm^{-1} [36] and $\nu(\text{CO})$ at 1016 and 1035 cm^{-1} [37]
2 $\nu(\text{CC})+\delta(\text{CH})$ ring at 1609 , 1584 , 1501 [38] can be attributed to benzyl alcohol.

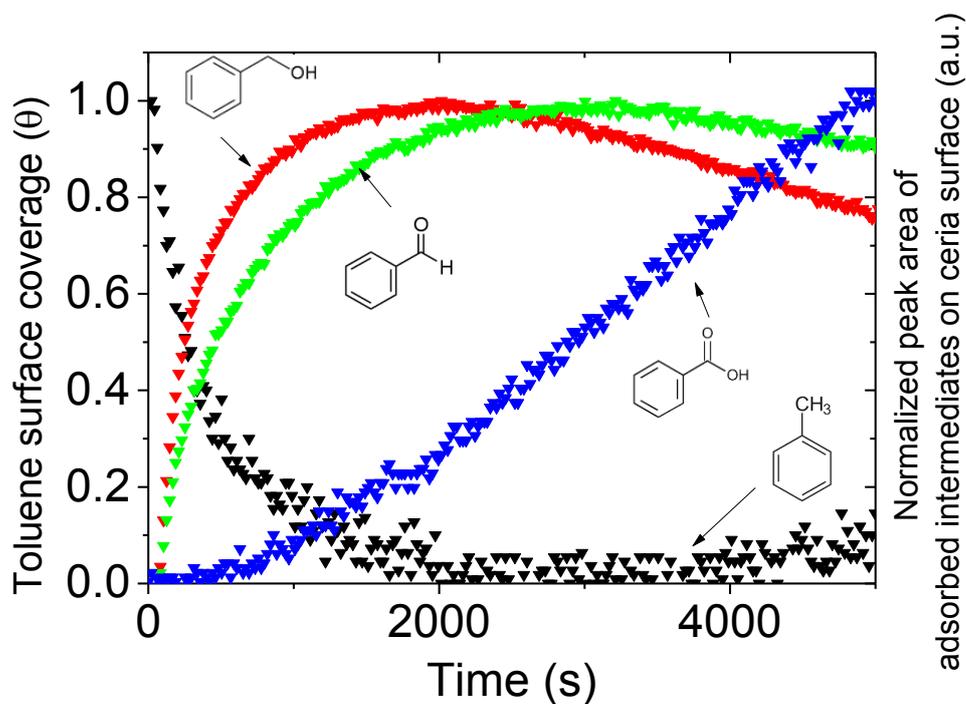


3
4 **Figure 9 - DRIFTS absorbance infrared spectra of surface species adsorbed on CeO₂ during post plasma**
5 **treatment (500 mL/min air, 25 mg CeO₂, 294 K, 50 Hz, 15 kV, 145 mW, 60 min).**

6 Based on the integration of the bands at 2879 cm^{-1} , 1754 cm^{-1} , 1715 cm^{-1} and 1016 cm^{-1}
7 respectively used for toluene, benzoic acid, benzaldehyde and benzyl alcohol surface semi-
8 quantitative investigation, evidences the temporal profiles of toluene and its oxidation
9 products. At $t = 0$ min corresponding to the end of flushing step and the beginning of plasma
10 exposure, CeO₂ surface is saturated with toluene under the corresponding gas phase
11 concentration and θ_{Toluene} is considered as 1, i.e. $1.4\text{ }\mu\text{mol}$ adsorbed per m^2 or $118\text{ }\mu\text{mol}$ of
12 toluene adsorbed per gram of CeO₂. Figure 10 shows a decrease in toluene surface coverage
13 and the formation of adsorbed intermediates such as benzyl alcohol (1016 cm^{-1}),
14 benzaldehyde (1715 cm^{-1}) and benzoic acid (1754 cm^{-1}) as soon as the plasma is turned on.
15 Simultaneously a production of adsorbed benzyl alcohol and benzaldehyde is observed. Their
16 surface concentrations gradually increase until plateau is reached, i.e. ca. 2000s and 3000s
17 respectively after *post-situ* plasma exposure. The evolution of benzoic acid differs from that

1 of benzyl alcohol and benzaldehyde. Indeed, the production of surface benzoic acid starts
2 beyond 500s while no benzoic acid is observed in the gas phase.

3 As mentioned in section 3.2, in PCC ozone is the most important oxidizing agent and it
4 can be catalytically decomposed into highly active atomic oxygen which reacts with water to
5 form hydroxyl radical. The atomic oxygen and hydroxyl radical play an important role during
6 toluene oxidation [33,39–42]. The hydrogen abstraction from the methyl group is the primary
7 pathway in toluene oxidation, leading to a benzyl radical and then forming benzaldehyde and
8 benzyl alcohol, which will be further attacked by an atomic oxygen and hydroxyl radical
9 forming benzoic acid [42]. Toluene and these three initial by-products (benzaldehyde, benzyl
10 alcohol and benzoic acid) were attacked by atomic oxygen and hydroxyl radical addition to
11 the aromatic ring, which resulted in the open of aromatic ring [40]. The compounds generated
12 after ring opening contained several carbonyl bonds (C=O) and alkenyl bonds (C=C), finally
13 leading to the formation of harmless CO₂ and H₂O.



14

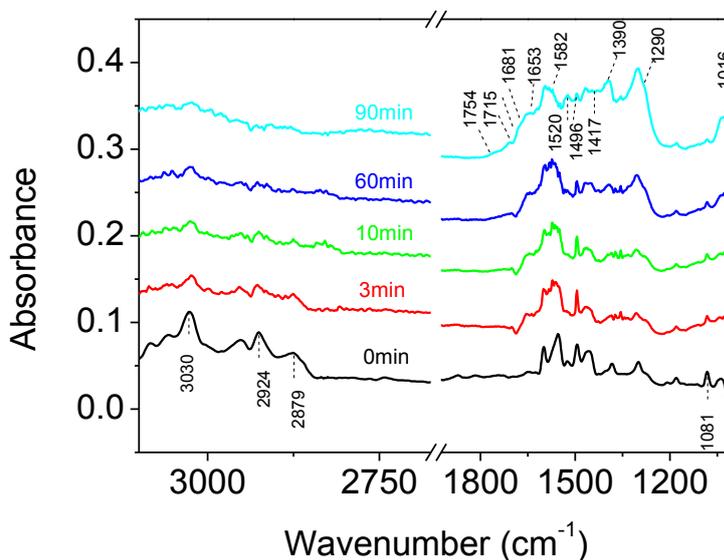
1 **Figure 10 - Evolution of toluene surface coverage on CeO₂ as a function of post-situ NTP exposure time.**
2 **Adsorbed intermediates such as benzyl alcohol (1016 cm⁻¹), benzaldehyde (1715 cm⁻¹) and benzoic acid (1754 cm⁻¹) are**
3 **also plotted.**

4 **3.3.2 Adsorbed intermediates formation using IPC**

5 In the case of the *in-plasma* Configuration, the catalytic surface is simultaneously exposed
6 to short and long life species produced by the plasma. Figure 11, shows the dynamic of
7 spectra recorded by Sorbent-TRACK after the plasma has been turned ON while the evolution
8 of toluene and adsorbed intermediates are plotted in Figure 12. Compared to the PPC
9 configuration, some similar trends have been observed: 1) the C–H aromatic bands (at around
10 3100–3000 cm⁻¹ domain) decreased rapidly at the first minutes of plasma treatment; 2) the
11 presence of benzyl alcohol (1016 cm⁻¹), benzaldehyde (1715 cm⁻¹) and benzoic acid (1754cm⁻¹)
12 have been confirmed by the bands discussed in the previous section. However, the bands in
13 the region of 1600-1700 cm⁻¹, which correspond benzaldehyde are less intense in IPC
14 configuration than in PPC configuration. Moreover, ring opening reactions could be supported
15 by the presence of C=O at a band between 1770-1740 cm⁻¹ which may correspond the
16 carbonyl group [43] and by the increasing and broadening of the 1400-1500 cm⁻¹ band which
17 could be due to various stretching behaviors such as C=C from alkenes [44]. The presence of
18 alkane groups is indicated by the C-H bending vibration between 1380 and 1465 cm⁻¹ and the
19 location of bending vibration of CH₃ groups at 1390 cm⁻¹ could be given as evidence. The
20 bands at 1582, 1520 and 1290 cm⁻¹ could be assigned according to literature [45–47] to surface
21 nitrates species, like nitrobenzene.

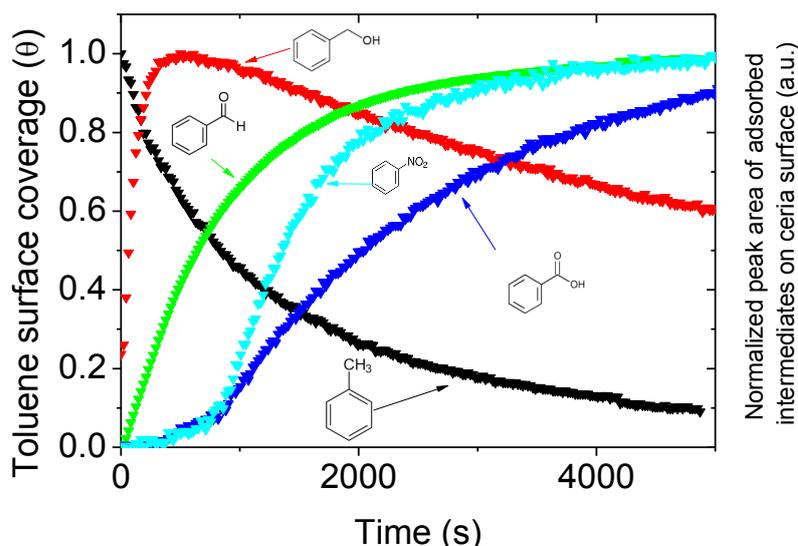
22 The mechanism of toluene oxidation in IPC is more complex than PPC because in IPC
23 toluene could react with short live species, especially electron. The contribution of electron is
24 not negligible as the reaction rate constant (in reaction 4) is important. The authors [33,39,48]
25 propose that the toluene destruction is mainly initiated via the collision between an electron in
26 plasma and toluene molecules with the formation of phenyl radical and methyl. Mean energy

1 of C–C between the methyl group and the aromatic ring is about 4.4 eV [34] while mean
2 energy of the energetic electrons ranges from 1 to 10 eV [49] that C–C can be easily destructed
3 by energetic electrons beyond 4.4 eV. Phenyl radical could react with excited NO_2^\bullet , forming
4 nitrobenzene. The radical attack (atomic oxygen and hydroxyl radical) would occur
5 subsequently and contribute to toluene oxidation and ring opening reactions. Toluene
6 destruction consists of several processes in IPC, and its destruction by energetic electrons and
7 radicals are inseparable and cooperative which make IPC is more effective than PPC for
8 toluene removal.



9

10 **Figure 11 - Transmission infrared absorbance spectra of surface species adsorbed on CeO₂ during post plasma**
11 **treatment using Sorbent Track (500 mL/min air, 15 mg CeO₂, 294 K, 50 Hz, 10 kV, 70mW, 90 min).**



1
 2 **Figure 12 - Evolution of toluene surface coverage on CeO₂ as a function of *in-situ* NTP exposure time. Adsorbed**
 3 **intermediates such as benzyl alcohol (1016 cm⁻¹), benzaldehyde (1715 cm⁻¹), benzoic acid (1754 cm⁻¹) and nitrobenzene**
 4 **(1520 cm⁻¹) are also plotted.**

5 **4 Conclusion**

6 In this study, we present the dynamic *in-situ* monitoring of the adsorption followed by the
 7 oxidation of toluene adsorbed on Ceria under plasma exposure in two different plasma
 8 configurations: In-Plasma and Post-Plasma Configurations where the catalyst is located in
 9 contact with the plasma or downstream the plasma.

10 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Trans-FTIR
 11 have been respectively used to monitor the ceria surface in the post-situ plasma (PPC) and *in-*
 12 *situ* plasma (IPC) configuration. A new dedicated device, Sorbent-TRACK has been set-up to
 13 perform Trans-FTIR experiments in IPC configuration. The adsorption of toluene on ceria
 14 was quantitatively and qualitatively analyzed in the configuration of PPC and IPC by DRIFTS
 15 and ST respectively and the adsorption capacity is respectively 1.4 ± 0.2 and 1.1 ± 0.2
 16 $\mu\text{mol}/\text{m}^2$. It was found that the toluene oxidation by plasma is a first-order reaction and IPC is
 17 more effective for the toluene removal than PPC. Regardless of the plasma configurations,

1 rate constants increase linearly with injected power. The adsorbed intermediates were also
2 monitored by DRIFTS and transmission IR. The long live species and short live species lead
3 to different intermediates formation and evolution which could explain the higher efficiency
4 of toluene removal in IPC.

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8 reference ANR-11-IDEX-0004-02.

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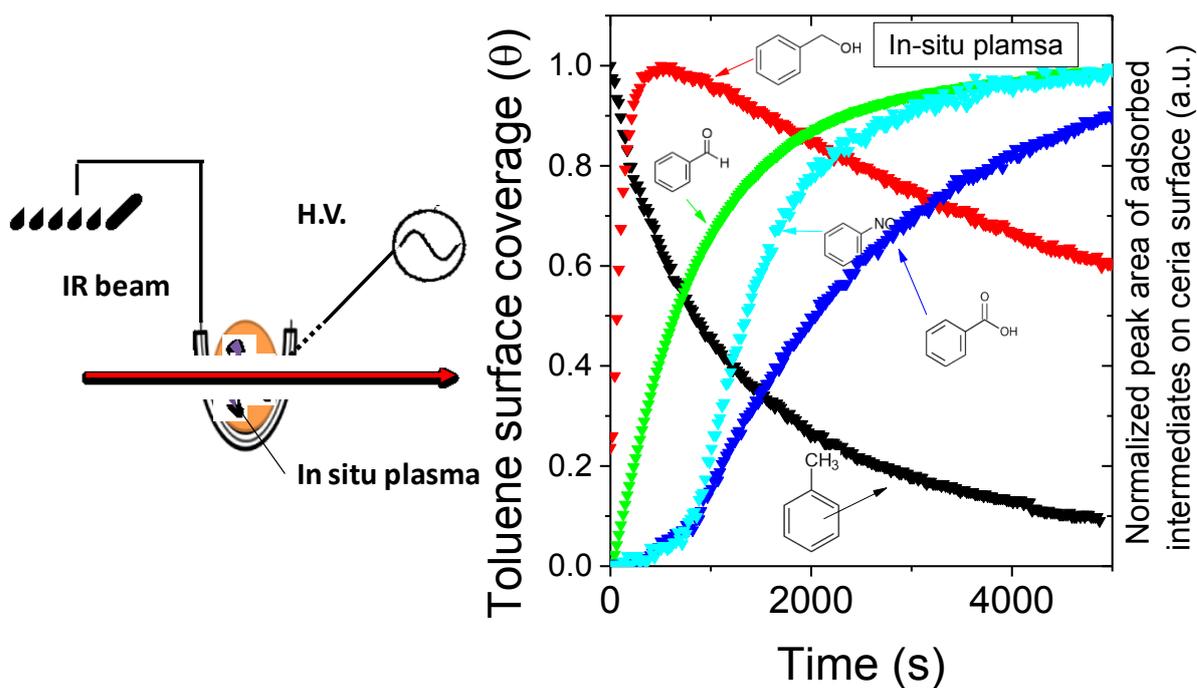
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1

2 Table of Contents

3 Toluene adsorption and oxidation on CeO₂ surface by Non-thermal plasma (NTP) is *in-*
4 *situ* monitored using infrared (IR) diagnostics (Diffuse Reflectance Infrared Fourier
5 Transform Spectroscopy (DRIFTS) and transmission mode). The oxidation of toluene by
6 plasma follows a first-order reaction regardless of plasma configuration and injected power. It
7 was found that IPC was more effective for the toluene removal than PPC. Interestingly,
8 toluene abatement and reaction intermediate formations are characterized *in-situ* throughout
9 the heterogeneous oxidation reaction advancement.



10

11

12