

# **IN SITU DRIFT ANALYSIS COUPLED TO NON THERMAL PLASMA AT ATMOSPHERIC PRESSURE ON THE DECOMPOSITION OF VOLATILE ORGANIC COMPOUNDS**

ANTHONY RODRIGUES, ELODIE FOURRÉ, JEAN-MICHEL TATIBOUËT

*Institut de chimie des Milieux et Matériaux de Poitiers, UMR CNRS 7285  
Université de Poitiers, Ecole Nationale Supérieure d'Ingénieurs de Poitiers  
1 rue Marcel Doré, 86073 Poitiers Cedex 9*

Corresponding author's e-mail: [elodie.fourre@univ-poitiers.fr](mailto:elodie.fourre@univ-poitiers.fr)

## **ABSTRACT**

An innovative in situ infrared cell (DRIFT) able to study the surface of a material exposed to a non-thermal plasma at atmospheric pressure has been developed and implemented in the laboratory following a collaborative work [1]. The first successful results were obtained from the real time observation of 4 volatile organic compounds (VOCs) decomposition (isopropanol, acetone, ethanol and toluene) on 3 metal oxide surfaces ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>). Here, we present the results of the plasma treatment of isopropanol (IPA) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which led to its oxidation in acetone. Upon prolonged plasma treatment time, acetone decomposed into carboxylic acids. On TiO<sub>2</sub> and CeO<sub>2</sub> surface, it led to the formation of acetic and/or formic acids. Ozone and CO<sub>2</sub> were also observed on the ceria surface.

These preliminary studies highlight the originality of this new system regarding in-situ surface characterization during non thermal plasma treatment at atmospheric pressure.

## **1. INTRODUCTION**

For the last two decades, non thermal atmospheric plasma (NTAP) has been the subject of many investigations for a wide range of applications, going from surface modification (etching, deposition of thin film, oxidation, functionalization...) to life science related to environmental issues and biomedical applications [2], [3]. The main reason for this eagerness comes from the great potential of a NTAP in terms of energy efficiency, flexibility, low pollution and capability to create new products with ecological advantages. More recently, due to a greater concern on environmental issues, research on waste gas treatment, volatile organic compounds (VOCs)

removal has been largely studied. In particular, the presence of a catalyst in the plasma discharge resulted in a synergistic effect and improved VOCs conversion [4], [5].

However, if research has shown tremendous results on VOCs conversion, a few points remain unclear. It concerns essentially the interactions between the chemical species created in the plasma discharge and a material. The willingness to identify active species in the plasma discharge is very challenging. It is a complex field of research, as the species concentration, nature and power input are dependent of the plasma reactor configuration, chemical and electrical parameters. Already, research has been dedicated to identify species in the gaseous phase of plasma by spectroscopic methods but the identification of the interactions between active species and a catalyst surface has been scarcely investigated [5]. The test reactions studied in this work concerned the removal of isopropanol (IPA) and acetone from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and CeO<sub>2</sub> surfaces by non thermal plasma. These two VOCs have been already studied and published in the literature but the results were essentially based on the analysis of the outlet gas composition. IPA conversion by non thermal plasma leads to the formation of acetone, formaldehyde (when the reaction is incomplete), CO<sub>2</sub> and H<sub>2</sub>O [7], [8]. In the case of acetone decomposition, CO<sub>2</sub>, CO, traces of formic acid and formaldehyde were detected in water plasma at atmospheric pressure [9] and via photocatalytic treatment [10]. Acetone is also an intermediate product of IPA oxidation by non thermal plasma.

In the present study, a new designed in situ DRIFT cell allowing recording IR spectra of material surfaces in presence of a non-thermal plasma (DBD type) under controlled atmosphere flow was used to follow the transformation of

volatile organic compounds on different metal oxide surfaces. Acetone and isopropanol were adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and CeO<sub>2</sub> surfaces and the impact of the plasma discharge on the conversion of those two pollutants was studied under real time conditions via infrared analysis.

## 2. EXPERIMENTAL

An home-made IR cell equipped with ZnSe windows was designed to contain a dielectric barrier discharge (DBD) reactor (Fig.1). The volumic DBD plasma was generated between a tip electrode (diameter 0.5mm) and a plate electrode (10mm × 10mm) which were connected to a high voltage power amplifier (Trek, 20/20A) coupled to a function generator (TTi TG1010A). The electrodes were separated from each other by a dielectric material (PEEK) of 0.8mm thickness. Experiments were carried out in an airtight cell with the possibility to vary the chemical and electrical parameters. FTIR Spectrometer Frontier (PerkinElmer), equipped with a MCT detector, was used to record spectra in the range of 4000–900 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The cell was purged with the desired gas for 10 min before the initiation of the plasma discharge. IR spectra of the sample wafer were then recorded in reflection mode as a function of the DBD plasma treatment time. IR spectra were recorded when the plasma was ignited and over a period of time going from 20 min to 8 hours. The experiments were carried out under "dynamic" conditions at a flow rate of 30mL/min which was constantly running in the cell chamber. The power injected in the reactor was determined by the analysis of the Lissajous graph that reports the charge  $Q_m$  transferred to the plasma as a function of the applied voltage ( $U_a$ ).

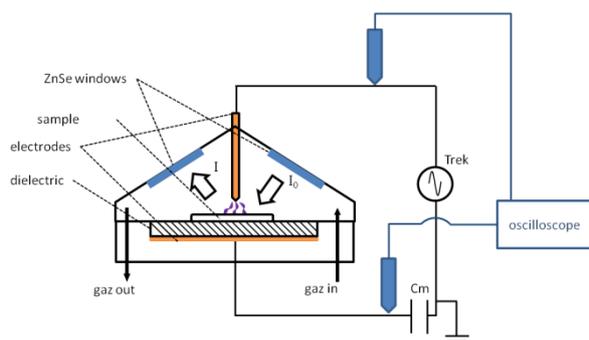


Figure 1 : Schematic of the IR/plasma cell

The energy injected,  $E$  (per impulsion) was calculated from the integration of the area

formed by the Lissajous graph (Manley method) [11]. The energy allowed the calculation of the power (in W) as well as the specific energy  $E_{spe}$  (in J.L<sup>-1</sup>) following equation (1) and (2), where  $f$  is the frequency (Hz) and  $D$  the gas flow rate (L/s):

$$P = E \times f \quad (1)$$

$$E_{spe} = \frac{P}{D} \quad (2)$$

The power was set at 24mW (12kV, 500Hz).

## 3. RESULTS AND DISCUSSION

Independently of the catalyst chemical nature, the predominant bands of isopropanol adsorption, corresponding to the C-H asymmetric and symmetric stretch ( $\nu$ -as and  $\nu$ -s) are detected in the 3000-2970cm<sup>-1</sup> region and the methyl C-H asymmetric and symmetric bends ( $\delta$ -as and  $\delta$ -s) in the 1470-1380cm<sup>-1</sup> region (figures 2, 3 and 4). Between 1245 and 1255cm<sup>-1</sup>,  $\delta$ -O-H from undissociated IPA is identified. Other components around 1145 and 1075cm<sup>-1</sup> are related to the C-O stretch and C-C skeletal of isopropoxide species. Finally,  $\rho$ -CH<sub>3</sub> at ~950cm<sup>-1</sup> is observed on the three surfaces [12], [13], [14]. As soon as the discharge is initiated, the bands corresponding to the methyl group stretch (2975-2885 cm<sup>-1</sup> region) decrease with the treatment time for the three surfaces. A small and broad band at 3240-3245cm<sup>-1</sup> is emerging after 5 minutes treatment (20mins for Al<sub>2</sub>O<sub>3</sub>) corresponding to the O-H stretch of acids.

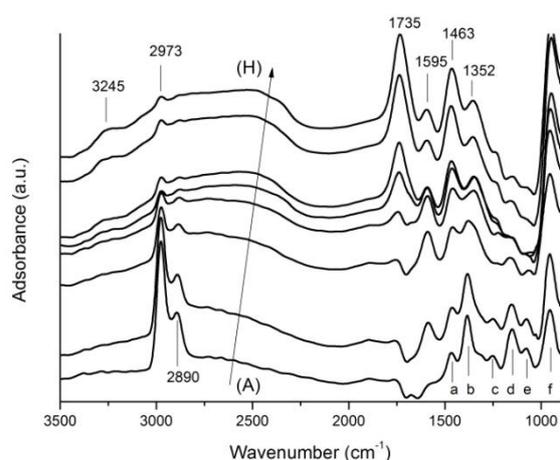


Figure 2: In situ IR spectra of the evolution of isopropanol on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a function of plasma treatment time. (A) 10 minutes of IPA adsorption; (B) to (H) 1, 5, 10, 20, 30, 45 and 60mins of plasma treatment. a: 1462 cm<sup>-1</sup>, b: 1382 cm<sup>-1</sup>, c: 1247 cm<sup>-1</sup>, d: 1149 cm<sup>-1</sup>, e: 1075 cm<sup>-1</sup>, f: 953 cm<sup>-1</sup>.

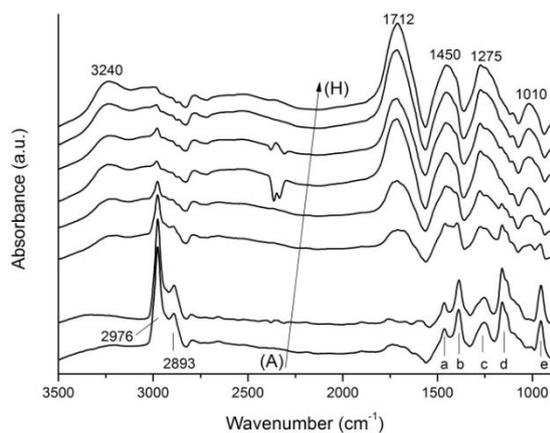


Figure 3: In situ IR spectra of the evolution of isopropanol on  $\text{CeO}_2$  as a function of plasma treatment time. (A) 10mins of IPA adsorption; (B) to (H) 1, 5, 10, 20, 30, 45 and 60mins of plasma treatment. : a:  $1468\text{cm}^{-1}$ , b:  $1387\text{cm}^{-1}$ , c:  $1251\text{cm}^{-1}$ , d:  $1153\text{cm}^{-1}$ , e:  $950\text{cm}^{-1}$ .

This band is even more prominent on  $\text{Al}_2\text{O}_3$  where it produces a very broad band in the  $3300\text{-}2200\text{cm}^{-1}$  region and similarly, but less evident, on  $\text{TiO}_2$  and  $\text{CeO}_2$ .

In the lower region, the analysis is more difficult due to the overlapping of the bands. However, it is possible to identify the progressive formation of C=O group (ketone and/or carboxylic acid) centred at  $1712$ ,  $1735$  and  $1764\text{cm}^{-1}$  for  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  respectively, from 1 to 60mins treatment. In the case of  $\text{TiO}_2$ , the band position is a little high for a ketone and corresponds to the adsorption of a carbonate [15].

Bands of methyl bending vibrations evolve differently. On  $\text{Al}_2\text{O}_3$  surface, figure 2, an increase and a broadening of the  $\delta$ -as C-H band ( $1463\text{cm}^{-1}$ ), a decrease/shift of  $\delta$ -s C-H band ( $1382\text{cm}^{-1}$ ) to  $1350\text{cm}^{-1}$  is observed as a function of the treatment time. The band at  $1350\text{cm}^{-1}$  emerging after 5 mins is related to the methyl bending vibrations of acetone. The absorptions at  $1595$  and  $1463\text{cm}^{-1}$  [16] are assigned to anti-symmetric and symmetric  $\text{COO}^-$  bending vibrations, respectively. A small shoulder at  $1235\text{cm}^{-1}$  also appeared after 20mins treatment and is assigned to acetone formation [1]. A small residual contribution remained at  $1149$  and  $1075\text{cm}^{-1}$  corresponding to C-O and C-C skeletal bonds stretch. These observations show that isopropoxide species formed by the dissociative adsorption of isopropanol give rise to acetone and acetic acid on  $\text{Al}_2\text{O}_3$  when treated by non thermal plasma.

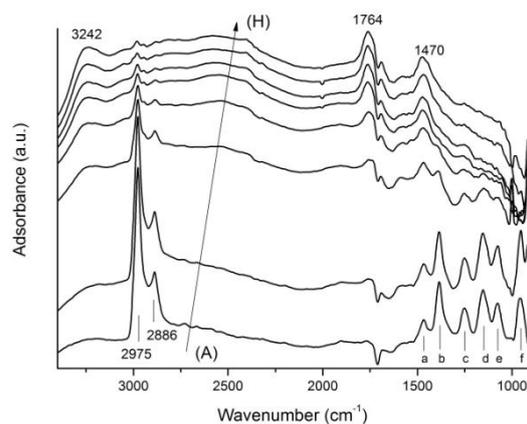


Figure 4: In situ IR spectra of the evolution of isopropanol on  $\text{TiO}_2$  as a function of plasma treatment time. (A) 10mins of IPA adsorption; (B) to (H) 1, 5, 10, 20, 30, 45 and 60mins of plasma treatment; a:  $1466\text{cm}^{-1}$ , b:  $1385\text{cm}^{-1}$ , c:  $1253\text{cm}^{-1}$ , d:  $1153\text{cm}^{-1}$ , e:  $1075\text{cm}^{-1}$ , f:  $956\text{cm}^{-1}$ .

On  $\text{TiO}_2$ , figure 4, an increase and a broadening of the  $\delta$ -as C-H band ( $1470\text{cm}^{-1}$ ) and the total disappearance of  $\delta$ -s C-H band ( $1385\text{cm}^{-1}$ ) are observed as a function of the plasma treatment time. The IPA bands at lower wavenumbers ( $1385\text{-}956\text{cm}^{-1}$ ) progressively weaken till complete disappearance as the plasma treatment time increased. From these observations, plasma treatment of IPA on  $\text{TiO}_2$  leads to the formation of formic acid. From 5 to 20mins treatment, a band at  $1001\text{cm}^{-1}$  emerged and was attributed to ozone adsorption on the surface [17].

On  $\text{CeO}_2$ , figure 3, the band corresponding to the  $\delta$ -as bending mode of methyl is evolving and broadening as a function of the plasma treatment time, while the  $\delta$ -s of methyl is progressively decreasing and merging with the  $\delta$ -as of  $\text{CH}_3$ . In the same time, a band is growing at  $1275\text{cm}^{-1}$ , which overlaps the band at  $1251\text{cm}^{-1}$  ( $\delta$ -OH of IPA) and is attributed to the OH bending vibration mode of acids. The C-O stretch of IPA decreases with the plasma treatment time and after 5mins, a new band is emerging at  $1010\text{cm}^{-1}$  which is attributed to ozonide from ozone adsorption [17]. Additionally, it was possible to identify  $\text{CO}_2$  adsorption/desorption bands ( $2350\text{cm}^{-1}$ ). However, it is difficult to assess if acetone is formed on  $\text{CeO}_2$  surface due to the overlapping of the peaks. As for  $\text{Al}_2\text{O}_3$ , it is difficult to differentiate acetic acid from formic acid.

The adsorption spectra of acetone on the three surfaces resulted in similar profiles and only one adsorption spectrum is displayed on figure 5. It allows us to confirm the decomposition of IPA into acetone on  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$ . When

comparing the adsorption and the 60mins plasma treatment ( $\text{TiO}_2$ ) spectra, figure 5, it clearly shows that only formic acid is adsorbed at the surface since no bending modes of methyl are observed.

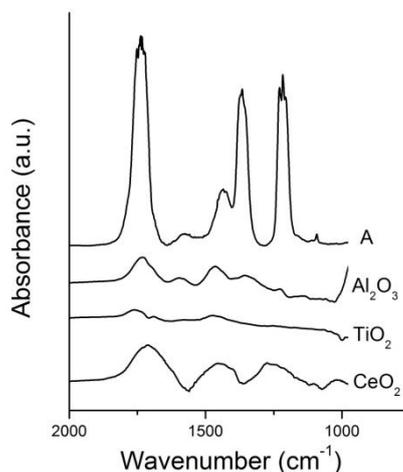


Figure 5: (A) IR spectra of acetone adsorption (10mins) on  $\text{CeO}_2$ . The 3 other spectra are of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{CeO}_2$  after 10mins adsorption IPA followed by 60mins of plasma treatment.

#### 4. CONCLUSION

This new promising system of catalysts surface characterisation, combining non thermal plasma and infrared spectroscopy, has been successfully applied to the in situ characterisation of surface species during plasma treatment and has proven to be efficient. The plasma treatment of IPA molecules adsorbed on  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{CeO}_2$  surfaces led to the formation of acetone, acetic acid and formic acid. On  $\text{CeO}_2$  and  $\text{TiO}_2$  surface, only acids were detected while  $\text{Al}_2\text{O}_3$  showed a small presence of acetone at its surface. On  $\text{CeO}_2$  and  $\text{TiO}_2$ , ozone was detected and a small contribution of  $\text{CO}_2$  on  $\text{CeO}_2$  was observed.

#### REFERENCES

- [1] M. Rivallan, E. Fourré, S. Aiello, J.-M. Tatibouët, F. Thibault-Starzyk, " Insights into the Mechanisms of Isopropanol Conversion on  $\gamma\text{-Al}_2\text{O}_3$  by Dielectric Barrier Discharge", *Plasma Process Polym.*, **9**, 850-854, 2012
- [2] A.Bogaerts, E.Neyts, R. Gijbels, J. Van der Mullen, "Gas discharge plasmas and their applications", *Spectro. Acta Part B*, **57**, 609–658, 2002
- [3] C. Tendero, C. Tixier, P. Tristant, J. Desmaison, P. Leprince, "Atmospheric pressure plasmas: A review", *Spectro. Acta Part B*, **61**, 2-30, 2002
- [4] J. Van Durme, J. Dewulf, C. Leys, H. Van Langenhove, "" *Appl. Cat. B: Env.* **78** (2008) 324–333; (b) Hyun- Ha K., *Plasma Process. Polym.*, **1**, 91-110, 2004
- [5] A. M. Vandenbroucke, R. Morent, N. De Geyter, C. Leys, "Non-thermal plasmas for non-catalytic and catalytic VOC abatement", *J. Hazard. Mater.* **195**, 30-54, 2011
- [6] C. Miron, M. A. Bratescu, N. Saito, O. Takai, "Time-resolved Optical Emission Spectroscopy in Water Electrical Discharges", *Plasma Chem Plasma Process*, **30**, 619–631, 2010
- [7] J. Jarrige and P. Vervisch, "Decomposition of three volatile organic compounds by nanosecond pulsed corona discharge study of by product formation and influence of high voltage pulse parameters", *J. appl. Phys.*, **99**, 113303, 2006
- [8] J. Karuppiah, L. Sivachandiran, R.Karvembu, Ch.Subrahmanyam, "Catalytic non-thermal plasma reactor for the abatement of low concentrations of isopropanol", *Chem. Eng. J.*, **165**, 194–199, 2012
- [9] Narengerile, T.Watanabe, "Acetone decomposition by water plasmas at atmospheric pressure", *Chem. Eng. Sci.*, **69**, 296–303, 2012
- [10] Ș. Neațu, E. Sacaliuc-Pârvolescu, F. Lévy, V.I. Pârvolescu, "Photocatalytic decomposition of acetone over dc-magnetron sputtering supported vanadia/ $\text{TiO}_2$  catalysts", *Catal. Today* **142**, 165-169, 2009
- [11] Manley T C, "The electric characteristics of the ozonator discharge", *Trans. Electrochem. Soc.* **84** 83–96, 1943
- [12] M. del Arco, S. Gutiérrez, C. Martin and V. Rives, "FTIR study of isopropanol reactivity on calcined layered double hydroxides", *Phys. Chem. Chem. Phys.*, **3**, 119-126, 2001
- [13] V. Ermini, E. Finocchio, S. Sechi, G. Busca, S. Rossini, "An FT-IR and flow reactor study of the conversion of propane on  $\gamma\text{-Al}_2\text{O}_3$  in oxygen-containing atmosphere", *Appl. Cat. A: General*, **190**, 157-167, 2000
- [14] M.I. Zaki, G.A.M. Hussein, H.A. El-ammawy, S.A.A. Mansour, "Effect of foreign ion additives on ceria surface reactivity towards isopropanol adsorption and decomposition: an infrared investigation", *J. Mol. Cat.*, **57**, 367-378, 1990
- [15] J. Coates, " Interpretation of IR spectra", *Encyclopedia of Analytical Chemistry*, R.A. Meyers, 10815-10837, 2000
- [16] M.A. Hasan, M.I. Zaki, L.Pasupulety, "Oxide-catalyzed conversion of acetic acid into acetone: an FTIR spectroscopic investigation", *Appl. Cat. A*, **243**, 81-92, 2003
- [17] K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko, "IR spectra of adsorbed ozone", *Colloid Surface A* **101**, 153-158, 1995