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

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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 (γ-Al₂O₃, TiO₂, CeO₂). Here, we present the results of the plasma treatment of isopropanol (IPA) on γ-Al₂O₃, which led to its oxidation in acetone. Upon prolonged plasma treatment time, acetone decomposed into carboxylic acids. On TiO₂ and CeO₂ surface, it led to the formation of acetic and/or formic acids. Ozone and CO₂ 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 γ-Al₂O₃, TiO₂ and CeO₂ 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), CO₂ and H₂O [7], [8]. In the case of acetone decomposition, CO₂, 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 γ-Al₂O₃, TiO₂, and CeO₂ 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⁻¹ with a resolution of 4 cm⁻¹. 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, transferred to the plasma as a function of the applied voltage (U).

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 Eₚₑₛₑ (in J.L⁻¹) 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 (ν-as and ν-s) are detected in the 3000-2970 cm⁻¹ region and the methyl C-H asymmetric and symmetric bends (δ-as and δ-s) in the 1470-1380 cm⁻¹ region (figures 2, 3 and 4). Between 1245 and 1255 cm⁻¹, δ-O-H from undissociated IPA is identified. Other components around 1145 and 1075 cm⁻¹ are related to the C-O stretch and C-C skeletal of isopropoxide species. Finally, ρ-CH₃ at ~950 cm⁻¹ 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⁻¹ region) decrease with the treatment time for the three surfaces. A small and broad band at 3240-3245 cm⁻¹ is emerging after 5 minutes treatment (20mins for Al₂O₃) corresponding to the O-H stretch of acids.

![Figure 1: Schematic of the IR/plasma cell](image)

**Figure 2:** In situ IR spectra of the evolution of isopropanol on γ-Al₂O₃ as a function of plasma treatment time. (A) 10 minutes of IPA adsorption; (B) to (H) 1, 5, 10, 20, 30, 45 and 60 mins of plasma treatment. a: 1462 cm⁻¹, b: 1382 cm⁻¹, c: 1247 cm⁻¹, d: 1149 cm⁻¹, e: 1075 cm⁻¹, f: 953 cm⁻¹.
This band is even more prominent on Al₂O₃ where it produces a very broad band in the 3300-
2200cm⁻¹ region and similarly, but less evident, on TiO₂ and CeO₂.

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 cm⁻¹ for CeO₂, Al₂O₃ and TiO₂ respectively, from 1 to 60 mins treatment. In the case of TiO₂, 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 Al₂O₃ surface, figure 2, an increase and a broadening of the δ-as C-H band (1463 cm⁻¹), a decrease/shift of δ-s C-H band (1382 cm⁻¹) to 1350 cm⁻¹ is observed as a function of the treatment time. The band at 1350 cm⁻¹ emerging after 5 mins is related to the methyl bending vibrations of acetone. The absorptions at 1595 and 1463 cm⁻¹ [16] are assigned to antisymmetric and symmetric COO⁻ bending vibrations, respectively. A small shoulder at 1235 cm⁻¹ also appeared after 20 mins treatment and is assigned to acetone formation [1]. A small residual contribution remained at 1149 and 1075 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 Al₂O₃ when treated by non thermal plasma.

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 Al₂O₃ and CeO₂. When

On TiO₂, figure 4, an increase and a broadening of the δ-as C-H band (1470 cm⁻¹) and the total disappearance of δ-s C-H band (1385 cm⁻¹) are observed as a function of the plasma treatment time. The IPA bands at lower wavenumbers (1385-956 cm⁻¹) progressively weaken till complete disappearance as the plasma treatment time increased. From these observations, plasma treatment of IPA on TiO₂ leads to the formation of formic acid. From 5 to 20 mins treatment, a band at 1001 cm⁻¹ emerged and was attributed to ozone adsorption on the surface [17].

On CeO₂, figure 3, the band corresponding to the δ-as bending mode of methyl is evolving and broadening as a function of the plasma treatment time, while the δ-s of methyl is progressively decreasing and merging with the δ-as of CH₃. In the same time, a band is growing at 1275 cm⁻¹, which overlaps the band at 1251 cm⁻¹ (δ-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 cm⁻¹ which is attributed to ozone from ozone adsorption [17]. Additionally, it was possible to identify CO₂ adsorption/desorption bands (2350 cm⁻¹). However, it is difficult to assess if acetone is formed on CeO₂ surface due to the overlapping of the peaks. As for Al₂O₃, it is difficult to differentiate acetic acid from formic acid.
comparing the adsorption and the 60mins plasma treatment (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 CeO$_2$. The 3 other spectra are of Al$_2$O$_3$, TiO$_2$ and 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 Al$_2$O$_3$, TiO$_2$ and CeO$_2$ surfaces led to the formation of acetone, acetic acid and formic acid. On CeO$_2$ and TiO$_2$ surface, only acids were detected while Al$_2$O$_3$ showed a small presence of acetone at its surface. On CeO$_2$ and TiO$_2$, ozone was detected and a small contribution of CO$_2$ on CeO$_2$ was observed.

REFERENCES