

## Adsorbed and Gas Phase Study of the Oxidation of Isopropanol on TiO<sub>2</sub> Using Non Thermal Plasma for Surface Regeneration

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Plasma driven catalysis is a promising technology for the abatement of volatile organic compounds in air, however, little is known about the mechanisms and phenomena taking place upon the plasma-pollutant interactions. A post plasma configuration is used to study the regeneration of the TiO<sub>2</sub> surface -ozone being the main oxidative species- hence limiting the ozonation effect from the real synergic effect between non thermal plasma (NTP) and catalysis in a packed bed reactor model. More importantly, the contributions of the gas phase and of the adsorbed phase are independently monitored using two parallel systems. The complementary analysis of the gas phase composition by FT-IR and the in situ surface analysis of the adsorbent/catalyst by DRIFTS are used to propose an oxidation mechanism for a model COV, isopropanol.

The peculiarity of the system in place lies in the fact that the plasma is not continuously generated. The pollutant is initially concentrated on the surface of the catalyst and a temporary discharge is then generated to regenerate the surface by mineralization of the adsorbed organic species.

The adsorption and oxidation properties of isopropanol (IPA) are monitored using two parallel experimental setups, crucial to understanding the performance and mechanism of surface regeneration by NTP. In the gas phase apparatus, the system consists of a dielectric barrier discharge (DBD) reactor, a catalytic reactor and the FT-IR cell in series (figure 1), enabling the analysis of the gas phase composition at the output of the catalytic reactor.

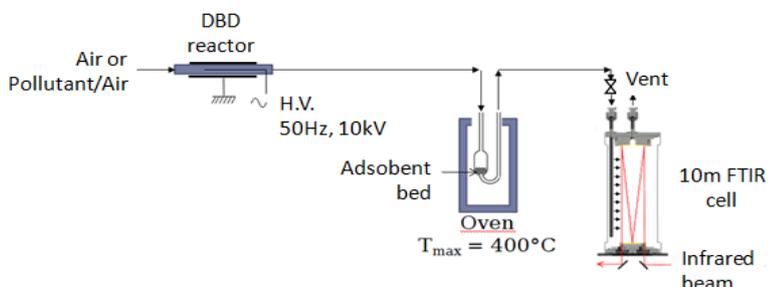


Figure 1 Schematic representation of the gas phase experimental setup

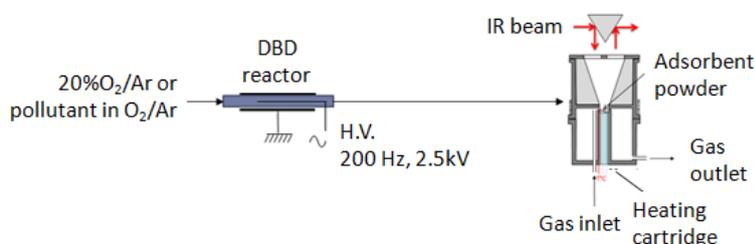


Figure 2. Schematic representation of the adsorbed phase experimental setup

In the solid phase apparatus, the adsorbent bed is located inside the DRIFTS cell (figure 2), also placed downstream from the plasma reactor, and the contact between the gas and the solid is monitored in situ, allowing a real time analysis of the phenomenon taking place on the surface.

IPA, commonly found in confined air is tested on TiO<sub>2</sub>, also known for its photocatalysis potential [1,2]. The gas phase study shows an adsorption capacity of 240 μmol per gram of TiO<sub>2</sub> and a mineralization efficiency of 2%, a transient production of acetone is also observed in the gas phase when the plasma is switched on. The DRIFTS experiments are performed in similar conditions and using the

same experimental steps, these have shown that IPA adsorbs on the surface via two different mechanisms, a dissociative process and a non dissociative process. The dissociative adsorption results in the formation of monodentate isopropoxy groups and surface hydroxyl species and the non dissociative adsorption giving rise to strongly bonded isopropanol and weakly hydrogen bonded isopropanol (figure 3) [3,4,5].

The adsorbed phase study of the ozonation step shows that acetone is the main intermediate in the oxidation route of isopropanol into CO<sub>2</sub> and CO. Surface kinetics are studied and show that the rate constant for IPA consumption on TiO<sub>2</sub> via plasma enhanced catalysis is  $1.34 \times 10^{-3} \text{ s}^{-1}$ , twice more efficient than photocatalysis alone [5].

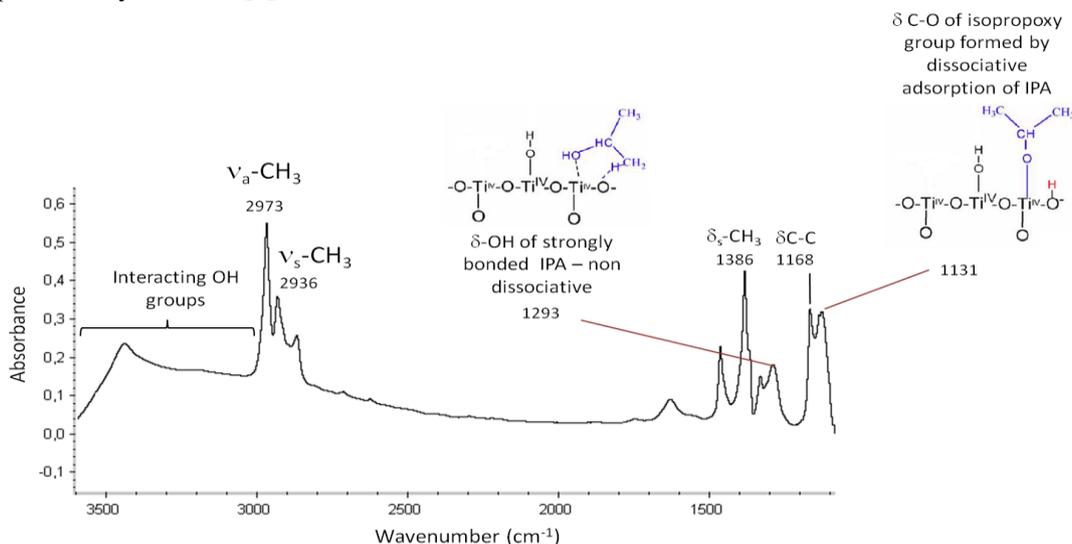


Fig. 3 Absorbance spectrum of IPA adsorbed on TiO<sub>2</sub>

It is concluded from the study of IPA adsorption and plasma on TiO<sub>2</sub> that acetone is the main intermediate and single route of IPA oxidation on TiO<sub>2</sub>. Acetone and formate species accumulate on the TiO<sub>2</sub> surface during the ozonation step and the mineralization of IPA is not complete. When the surface is saturated with IPA beforehand, the plasma will not lead to a complete mineralization. Two hypotheses are put forward:

- 1) IPA is in competition with acetone, it has a higher heat of adsorption on TiO<sub>2</sub> than acetone. The acetone formed during the ozonation cannot be readsorbed on TiO<sub>2</sub> due to a residual IPA content in the gas phase which will maintain the coverage of IPA close to one. This explains the initial desorption of acetone observed in the gas phase study during plasma. When the IPA coverage decreases sufficiently, acetone can readsorb on the surface and lead to further oxidation, and/or
- 2) acetone is less reactive than IPA towards ozone.

For further elucidation, a study of the adsorption and reactivity of acetone during plasma is performed and analysed by the complementary analytical methods, FT-IR and DRIFTS. A mechanism is then proposed for the oxidation of IPA on TiO<sub>2</sub> whereby two types of sites, denoted s<sub>1</sub> and s<sub>2</sub>, are distinguished and only one leads to the complete oxidation of IPA.

This double analytical approach is unique in providing information on the one hand (FT-IR), about the performance of the process in terms of adsorption capacity of materials, oxidation efficiency and surface regeneration and on the other hand (DRIFTS), reaction kinetics in terms of reaction constants, mechanisms of adsorption and oxidation, surface coverage, intermediates formed and species that remain adsorbed on the surface. A quantitative analysis of the gas phase composition and the real time analysis of the phenomena taking place on the surface are necessary to propose a complete oxidation mechanism for a model COV, here IPA.

## References

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