

Molecules formation with adsorbed O atoms: how to investigate surface reactivity from fundamentals to applications

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The surface reactivity is a key issue for most of the applications of non thermal plasma and especially for air pollution abatement by dielectric barrier discharges. Due to the numerous processes involved in air plasma interacting with surfaces, the understanding of the surface impact requires to gather data collected from many different dedicated experiments. This work shows the interest of measurements performed a lower pressure for a better understanding of atmospheric pressure systems. The O atoms density and life time, its recombination into O₂ or O₃, the exchange of O atoms between gas phase and surface material were all analysed and then used to describe the molecule formation onto the surface such as NO_x, or organic molecule oxidation. The strategy developed through this work for describing the reactivity of one specific radical could be of interest for other reactive radical or molecules produced in plasmas.

Most of the emerging applications of non-thermal plasmas are developed at atmospheric pressure and even some of well established applications running at low pressure tend to move towards higher pressures especially to speed up processes. Surface treatment and functionalization, biomedical applications, gas synthesis as well as air pollution control are among the numerous applications requiring a precise control of the interaction between atmospheric pressure plasma and complex surfaces. However the chemistry involved at atmospheric pressure is far too complex to have a full description of gas phase processes coupled with surface reactions. Moreover data for surface processes are most of the time unknown. The understanding of surface reactivity under atmospheric pressure plasma exposure requires then to separates the mechanisms involved and focus on the most important simple reactions. For this purpose we use a low pressure discharge in mbar range which is more suitable for fundamental studies, and can provide information on specific reactions useful for the later understanding of processes at higher pressure.

The main motivation of our work is the use of plasma coupled with adsorbent material for air pollution control [1]. O atoms are essential for Volatile Organic Compounds (VOC) destruction because they are the main oxidizing species in the gas phase as well as adsorbed phase. O atoms are also the source of ozone which is responsible for additional VOC oxidation. Therefore we are focussing on O atoms and what they become after being produced in the plasma. The recombination into O₂, the ozone formation in gas phase as well as onto the surface, the exchange of O atoms with the surface material, the production of NO, NO₂ as well as the oxidation of VOC and the decomposition of O₃ on porous surfaces are all the processes which were investigated. For this purpose experiments were performed in parallel at atmospheric pressure and medium pressure (mbar range) allowing the use of dedicated procedure for each mechanism separately with the appropriate diagnostic.

The two main discharge setups used consist in a coaxial double Dielectric Barrier Discharge (DBD) at atmospheric pressure and a 60 cm long tube in which a pulsed DC discharge (PDCD) as well as RF-capacitive coupled discharge (RF-CCD) can be ignited at pressures around 1 mbar. The same surfaces are studied in both systems: Pyrex, quartz, TiO₂ and Al₂O₃. Even by focussing only on O atoms reactivity, it was necessary to gather information obtain in simple gas mixture before studying real VOC oxidation. Measurement were then performed in pure oxygen plasma, then with successively pure nitrogen and pure oxygen plasmas, then in pure air and finally in air with VOCs.

Measurements performed in pure oxygen:

Interaction of O_2 plasma with catalytic surfaces was first studied at low pressure. Production and losses of atomic oxygen were investigated by means of actinometry and TALIF in the PDCD. Production of ozone was followed by time resolved broadband UV absorption. Based on these measurements the efficiencies of surface recombination mechanisms (i) $(O+O)_{\text{wall}} \rightarrow O_2$ and (ii) $(O+O_2)_{\text{wall}} \rightarrow O_3$ were determined. The experimental results were interpreted in terms of a self-consistent kinetic model describing the plasma phase and the afterglow. It was found that for high specific surface materials ozone production may account for 25% of the surface losses of atomic oxygen. It should be noted that reaction (ii) was proposed to explain the increased efficiency of O_3 production in DBD interacting with catalytic surfaces [1].

In order to further investigate the mechanisms of surface recombination of oxygen atoms, chemisorption of O on surfaces under O_2 plasma exposure was studied using stable $^{36}O_2$ isotopes as in [2]. It is supposed that chemisorbed O atoms play an important role in surface catalyzed reactions in plasmas, heterogeneous recombination of O is an example of such processes. First the studied surface was exposed to a discharge in $^{36}O_2$ and then adsorbed ^{18}O atoms were titrated by exposing the pretreated surface to $^{32}O_2$ plasma; $^{16}O^{18}O$ produced on the surface were then detected using a mass spectrometer. The described method allowed determination of the $^{18}O_{\text{ads}}$ surface coverage as a function of plasma pretreatment parameters. Adsorption/desorption kinetics of O on different materials was investigated.

All these measurements give the maximum amount of O atoms which could possibly react onto the surface also in air plasmas

Molecules oxidation with adsorbed O atoms:

Reactivity of O_{ads} was investigated in a series of experiments where different surfaces pretreated by O_2 plasma were brought in contact with several probe molecules (NO, C_2H_2 , CO) in the PDCD and the RF-CCD [3]. Destruction of these molecules and formation of oxidation products was followed in-situ using IR laser absorption spectroscopy. It was found that the reactivity of O_{ads} depends on the nature of the surface and the probe molecule, but also on the adsorption sites for one given surface.

All the processes observed at low pressure, NOx formation, C_2H_2 oxidation were also monitored at atmospheric pressure as well as oxidation of other organic molecules such as Isopropanol and Acetone. Three different options of FTIR measurements were used: gas phase analysis, diffusion and transmission analyses directly onto surfaces. These three methods of infrared absorption measurement combined provide information on the oxidation by-product remaining onto the different surfaces under plasma exposure as well as the final species released in the gas phase when oxidation occurs on a surface saturated by adsorbed O atoms, or a surface exposed only to O_3 flow. The different reactivity induced by O atoms directly adsorbed and O atoms obtained from O_3 decomposition can then be distinguished.

All these results together provide a detailed picture of the adsorbed O atoms reactivity which can be expected depending on the surface nature. It is an improvement in the understanding of plasma/catalyst coupling. The strategy used in this work is essential for understanding of basic phenomena that would have been impossible to investigate only with the atmospheric pressure experiment.

References

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