

Production/conversion of molecules on catalytic surfaces under plasma exposure

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Interaction of reactive plasmas with surfaces is an essential issue for a great number of applications [1,2] and especially for plasma/catalyst coupling [3] used for air treatment. However, up to now the basic mechanisms of interaction between plasma species and catalytic surfaces are barely understood. Furthermore, surface properties may be modified by plasma and depend on plasma parameters [4] what means that they can not be studied separately. Surface production and chemical reactions of stable molecules induced by plasma exposure provide important information on the underlying elementary processes such as adsorption, desorption, recombination, surface chemical reactions.

In this work we implement the approach developed in [5] that permits to probe the state of the surface after different plasma exposures. Experimental procedure consists in the pretreatment of the inner surface of the discharge tube using low pressure (~1 mbar) flowing CCP RF discharge in Ar, N₂, O₂ and air. Then the reactor is evacuated and two kinds of experiments are performed: (i) the production of molecules in a pure N₂ or pure O₂ plasma reacting with species adsorbed on the wall during the pre-treatment phase; (ii) the study of molecules losses/conversion on the surfaces by introducing a controlled amount of probe molecules in the reactor. Evolution of the gas phase concentrations of probe molecules and products of heterogeneous reactions is monitored using tunable infrared laser absorption spectroscopy in the closed reactor.

Using this approach it was proven that pure N₂ or air plasma graft stable N atoms to the surface of pyrex discharge tube. These atoms are irreversibly trapped by surface active sites and stay on the surface for a long time after plasma treatment without recombination. Being exposed to pure O₂ plasma, adsorbed atoms react with impinging active oxygen species to produce NO. Fig.1 shows evolution of [NO] in a single O₂ plasma pulse after different pretreatment procedures. Based on the analysis of NO formation kinetics, the lower limit for the density of surface active sites on pyrex was estimated to be $3 \cdot 10^{13} \text{ cm}^{-2}$, i.e. less than 1% of physisorption sites.

Following the (ii) experimental procedure, pyrex surface was probed by introducing the reactor a controlled amount of NO, NO₂ or N₂O molecules after various pretreatment procedures. Concentrations of all the 3 species were simultaneously measured using 3-QCL (Quantum Cascade Lasers diodes) system. It was shown that NO is oxidized into NO₂ on the pyrex surface pretreated by O₂ plasma. From the resulting production of NO₂, the initial

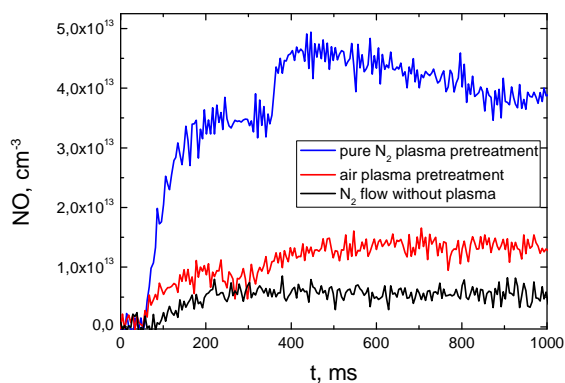


Fig 1. NO production in 300 ms O₂ plasma pulse after pure N₂ plasma (upper curve), air plasma or N₂ neutral flow (lower curve) pretreatment.

coverage of adsorbed O atoms is estimated $[O_{\text{ads}}] \approx 2 \cdot 10^{14} \text{ cm}^{-2}$.

Using the described methodology we study the influence of plasma parameters on the resulting properties of the pretreated surface. The role of discharge power, gas pressure and pretreatment duration is being evaluated. In order to distinguish the influence of long-lived radicals from ion and short-lived species exposure, the surface is pretreated by the flowing discharge afterglow.

The catalytic properties of other materials are also studied with similar experimental procedure. We use quartz discharge tube as well as pyrex tubes with dip-coating of different catalytic materials on its inner surface (TiO_2 , Al_2O_3 , SiO_2).

At the same time the modeling of surface kinetics for our experimental conditions is being performed in order to determine the main elementary processes and their rates (see the abstract of Vasco Guerra *et al.*).

All the data obtained with the RF discharge and the related surface kinetic model give constraints on the surface reaction rates which can be used for a better understanding of the kinetic of a pulsed DC discharge performed with the same surfaces as for the RF discharge.

Using the 3 QCL-system we study the reaction kinetics and mutual conversion of nitrogen oxides in low pressure (1.3 mbar) DC discharge with the aim to find out the main gas phase and (probably) surface processes governing their concentration in plasma. 1% of NO, NO_2 or N_2O is admixed to pure N_2 or air and then a single discharge pulsed ($\tau=1-10 \text{ ms}$, $i=25-150 \text{ mA}$) is applied to the mixture in closed reactor. Concentrations of 3 species are monitored simultaneously with time resolution down to $33 \mu\text{s}$ during plasma ON phase and in the afterglow. Figure 2 shows time evolution of NO, NO_2 and N_2O initially admixed to air.

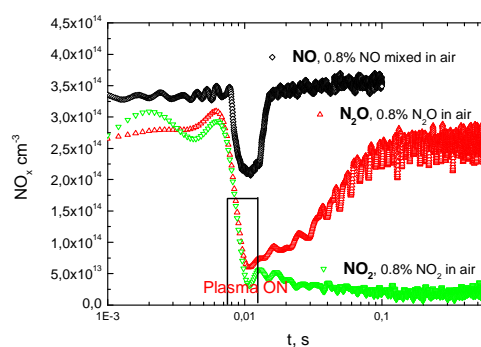


Fig 2. Time evolution of NO, NO_2 and N_2O initially admixed to air. Discharge pulse duration 5 ms, discharge current 150 mA.

Reference

- [1] J van Helden, Zijlmans R, Schram D and Engeln R 2009 *Plasma Sources Sci. Technol.* **18** 02502
- [2] Pejaković D A, Marschall J, Duan L, and Martin M P 2008 *Journal of Thermophysics and Heat Transfer* **22** 178
- [3] F. Thevenet, O. Guaitella, E. Puzenat, J.-M. Herrmann, A. Rousseau, C. Guillard *Catalysis Today* 122 (2007) 186–194
- [4] Carry G, Magne L and Cernogora G 2000 *J. Phys. D: Appl. Phys.* **33** 1303–14
- [5] D Marinov, O Guaitella, A Rousseau and Y Ionikh *J. Phys. D: Appl. Phys.* 43 (2010)