

Topic number: 4.

A SIMPLE MODEL OF THE SURFACE OXIDATION OF *NO* IN *NO*₂

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Herein we investigate the surface kinetics responsible for the conversion of *NO* into *NO*₂ on a Pyrex surface. To this purpose, a capacitively coupled RF oxygen plasma is first created in a cylindrical tube of inner radius $R_t = 0.8$ cm for about 1h. During this period adsorption of *O* atoms on the surface takes place. In the end of the treatment the chemisorption sites are assumed to be fully occupied by chemisorbed *O* atoms, in agreement with the calculations from [1]. The discharge is then turned off and the tube is filled with a mixture of *NO* and *Ar* or *N*₂. *NO* can then react with the adsorbed *O* atoms, thus forming *NO*₂. During this process, the time evolution of the concentrations of *NO* and *NO*₂ is measured simultaneously by quantum cascade laser absorption spectroscopy (QCLAS) in the sealed tube after the plasma treatment. The experimental results and details of the measurements are reported in [2].

A simple surface model was developed in order to interpret the experimental results. The basis of the model is the same as described in [1]. In particular, the surface is considered to be fully covered with adsorption sites, which can hold atoms or molecules either due to physisorption or to chemisorption. Recombination essentially takes place at the ‘active’ chemisorption sites. The most simple surface kinetic scheme describing the conversion of *NO* in *NO*₂ takes into account only two surface reactions,



Here, O_S denotes a chemisorbed oxygen atom, $(NO)_S$ a chemisorbed *NO* molecule, S_V a vacant chemisorption site, and *NO* and *NO*₂ the corresponding gas phase molecules.

The time evolution of the concentration of the gas phase molecules can be calculated from the solution to the following coupled system of equations:

$$\frac{d[NO]}{dt} = \frac{2}{R_t} \{ -r_1 \theta_S^O - r_2 (1 - \theta_S^O - \theta_S^{NO}) \} [S],$$

$$\frac{d[NO_2]}{dt} = \frac{2}{R_t} \theta_S^O r_1 [S],$$

$$\frac{d\theta_S^O}{dt} = -\theta_S^O r_1,$$

$$\frac{d\theta_S^{NO}}{dt} = r_2 (1 - \theta_S^O - \theta_S^{NO}),$$

where $[S]$ is the surface density of chemisorptions sites and $\theta_S^M = [M_S]/[S]$ is the fractional coverage of chemisorption sites by species *M*. In turn, the (time-dependent) reaction rates r_1 and r_2 are given by [1]

$$r_1 = \frac{\phi_{NO}}{[S]} \varphi k_1^0 \exp\left(-\frac{E_1}{RT_W}\right),$$

$$r_2 = \frac{\phi_{NO}}{[S]} \varphi k_2^0 \exp\left(-\frac{E_2}{RT_W}\right),$$

ϕ_{NO} is the flow of gas phase molecules of NO to the wall, T_W is the wall temperature, R is the gas constant, E_1 is the activation energy for recombination, E_2 is the activation energy for chemisorption, and the pre-exponential factors k_i^0 ($i = 1, 2$) are related to an elementary sticking coefficient on the adsorption sites (occupied or vacant) and correct the formulas for directional effects and other unknown phenomena.

Figure 1 shows the comparison between the experimental data and the calculations performed using a density of physisorption sites $[F] = 1.5 \times 10^{15} \text{ cm}^{-2}$, $\varphi = 1.5 \times 10^{-1}$, $E_1 = 24 \text{ kJ/mol}$, $E_2 = 0 \text{ kJ/mol}$, $k_1^0 = 10^{-3}$, $k_2^0 = 2 \times 10^{-8}$, $T_g = T_W = 298 \text{ K}$, and for an initial concentration of NO corresponding to a partial pressure of $0.01 \times 530 \text{ Pa}$. Notice that the values for $[F]$, E_1 and E_2 are typical values in recombination studies [1], whereas the value of φ is larger than used in [1] but very close to the one proposed in [3]. The pre-exponential factor k_1^0 is significantly lower than proposed for recombination in pure gases [1]. Nevertheless, a value of 1.5×10^{-2} was suggested in [4] for the similar reaction with CO, *i.e.*, $\text{CO} + \text{O}_S \rightarrow \text{CO}_2 + \text{S}_V$.

As shown in figure 1, process (1) describes well the behavior of the measured species up to times of the order of 2000 s. However, it does not suffice to explain the results for longer times. As a matter of fact, there is a slow loss of N-containing species, as previously noted in [2]. In the present model this is described by the slow reaction (2), which has a very low pre-exponential factor (k_2^0), indicating that chemisorption of NO is not very efficient. This conclusion is in qualitative agreement with the data from [2] and other preliminary experiments made at the LPP. However, reaction (2) is likely to be only an effective way of describing these losses, which can take place as well due to adsorption of NO_2 or by a more complex sequence of reactions.

The figure on the right illustrates the fractional coverage of chemisorption sites, indicating that O_S is progressively replaced by chemisorbed NO molecules. Work is in progress to gather more experimental data, as well as to refine the model with the inclusion of additional reactions, such as NO_2 adsorption, physisorption, diffusion and Langmuir-Hinshelwood recombination.

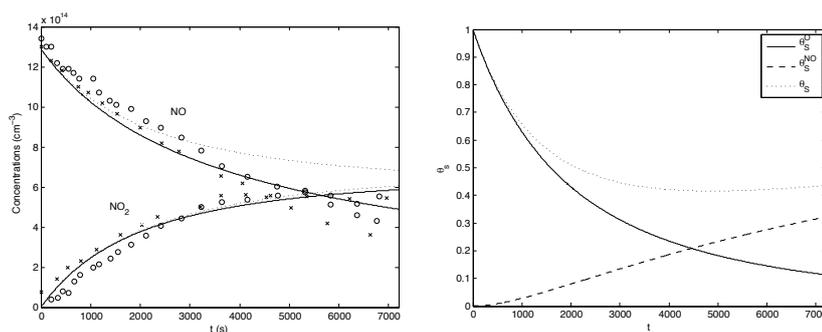


Fig. 1: Left figure: experimental (points) and calculated (curves) concentrations of NO and NO_2 as a function of time, using reaction (1) only (\cdots) or reactions (1) and (2) simultaneously ($—$). Right figure: fractional coverage of adsorption sites with O atoms (θ_S^O), NO molecules (θ_S^{NO}) and total ($\theta_S = \theta_S^O + \theta_S^{NO}$)

References

- [1] V. Guerra, 2007 IEEE Trans. Plasma Sci. **35** 1397.
- [2] O. Guaitella, M. Hübner, S. Welzel, D. Marinov, J. Röpcke and A. Rousseau, 2010 submitted for publication.
- [3] G. Cartry, L. Magne and G. Cernogora, 2000 J. Phys. D: Appl. Phys. **33** 1303.
- [4] V. Kovalev, N. Afonina and V. Gromov, 2002 “Rarefied Gas Dynamics”, AIP Conference proceedings **663**, A. D. Ketsdever and E. P. Muntz (Editors) 1001.