Oxidation of NO Into NO$_2$ by Surface Adsorbed O Atoms

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Plasma-surface interactions are increasingly recognised as a key factor in explaining molecule production and conversion processes. In order to scrutinise such effects well-defined surface and gas phase conditions are required. Hence, the inner surface of a Pyrex tube was treated by a capacitively coupled RF plasma at low pressure. The post-plasma oxidation of gas mixtures containing 1 % NO into NO$_2$ has been studied by means of quantum cascade laser absorption spectroscopy in the mid-infrared spectral range. The plasma pre-treatment experiments with oxygen containing precursors suggest O atom adsorption on the Pyrex tube with a surface density of $2.7 \times 10^{14}\,\mathrm{cm}^{-2}$. A simple kinetic model was developed and shows good agreement with the measured NO and NO$_2$ gas phase concentrations. In the model a fraction of the surface is considered to be covered with chemisorption sites where atoms and molecules can be adsorbed, whereas they can be removed only by recombination.

1 Introduction

For a wealth of discharge phenomena plasma surface interactions are of considerable importance in addition to kinetic processes in the plasma volume. Focused on environmental applications the use of electric discharges is a promising technique for toxic gas removal, especially when these gases are present at low concentrations [1-6]. Recent concerns about air quality, including NO$_x$ production, have led to a growing number of studies in the field of pollution abatement from gas exhausts. Apart from conventional techniques such as catalysis, scrubbers, and active charcoal, the combination of plasmas with catalysts has been a technical as well as a scientific challenge over the past decade. The plasma-catalyst synergy has been studied in air discharges at low and atmospheric pressure [7-9]. One of the main issues of plasma-catalyst coupling is to understand plasma interaction with the dielectric material, especially the processes involved in the destruction and production of molecules at surfaces, which are mostly unknown.

Using a plasma induced fluorescence technique the loss probability of atomic oxygen has been determined on a silica surface [10]. It was shown that in a pulsed microwave (MW) discharge the loss probability of O atoms at the surface is higher under plasma exposure than just after the discharge extinction. In [11], the loss of O atoms was measured by emission spectroscopy for different dielectric materials. It was found, that on the TiO$_2$ surface O atoms were stored without any recombination and could be desorbed into the gas phase by a strong electric field. At surfaces radicals may recombine but they could also be involved in other chemical reactions such as the production of NO$_x$ species in air plasmas.

Among several studies dealing with the NO$_x$ problem only a few examples are directly focused on the interaction of these species with surfaces. The production of NO in a pulsed DC discharge was shown to be proportional
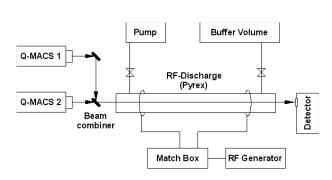
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to the energy density injected into the gas, independently from both pulse duration and plasma current frequency [12]. This NO formation was well fitted by kinetic modelling of the gas phase for high energy densities but small discrepancies were obtained for lower energy values [13]. Provided the injected power values would be sufficiently low enough surface processes could play a more dominant role. The importance of surface reactions for the formation of molecules by recombination has been experimentally demonstrated in a N_2/O_2 plasma [14, 15].

Recently a specially designed capacitive coupled radio-frequency (RF) plasma reactor has been used to investigate the interaction between its inner surface and the gas phase [16]. This experimental setup gives the opportunity to analyse the plasma stimulated deposition of oxygen atoms at a Pyrex surface and its consequences for the NO and NO_2 kinetics by simultaneous time resolved measurements of the concentrations of both molecules. The concentration measurements were performed using mid-infrared quantum cascade laser absorption spectroscopy (QCLAS). The main results are briefly summarised here, whereas the focus of this study is to better understand the destruction and/or production of molecules at the Pyrex surface after the exposure to a RF plasma. In order to interpret the experimental results a simple surface model based on [17] was developed. In the model the surface is considered to be fully covered with adsorption sites, which can be occupied by atoms or molecules either due to both physisorption and chemisorption.

2 Experimental setup

The experiments were carried out in a cylindrical plasma reactor made of Pyrex, length l = 60 cm, inner diameter d = 2 cm (figure 1). The inner surface of the tube is pre-treated by a capacitively coupled RF plasma, f = 13.56 MHz, for 1h at flowing conditions at a pressure of 0.53 mbar. Outside the tube two metallic rings work as electrodes in order to avoid any contact between plasma and metal which could induce additional chemical reactions.
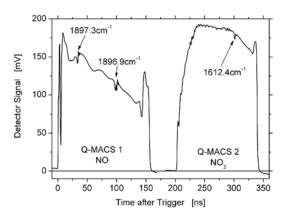

Fig. 1 Experimental set up: RF discharge tube, length l = 60 cm, inner diameter d = 2 cm, combined with a QCLAS system for in-situ concentration measurements of NO and NO_2 [16].

Fig. 2 Two typical QCLAS spectra demonstrating the detection of NO and NO_2.

The pre-treatment plasma was fed with different precursor gases, namely O_2, N_2, Ar, and synthetic air (80 % N_2, 20 % O_2). The injected power was 30 W. After the wall conditioning, the tube was filled with a gas mixture of 1% NO in N_2 or in Ar at a pressure of 5.3 mbar. Next, NO and NO_2 densities are simultaneously measured without plasma during a period of 2 h while the tube was closed.

Using a double quantum cascade laser measurement and control system (QMACS) [18], NO and NO_2 concentrations are monitored by means of absorption lines at 1897 cm^{-1} and 1612 cm^{-1}, respectively (figure 2). To calculate absolute species concentrations, the system was first calibrated using NO and NO_2 at known pressure and concentration [16].

3 Experimental Results

In a first experimental step the Pyrex tube was exposed to Ar and N_2 plasmas. This plasma cleaning without any O atom containing species allows to check, if ion bombardment is able to create free adsorption sites for NO on the Pyrex surface. In both cases no significant decrease of the NO concentration was observed after a gas mixture of 1% NO in N_2 or in Ar was fed into the tube. Thus, it is assumed that under our conditions, NO is not lost on the Pyrex walls even after plasma exposure of the inner surface. In particular, reactions of the type $NO_s + NO \rightarrow$ N + NO_2 do not seem to take place. This behaviour is in good agreement with results reported in the literature [19].

In a different experiment the plasma reactor was pre-treated for 30 min with an Ar plasma followed by a pure O_2 flow without discharge for another 30 min. Similar to the former experiment, the NO concentration remains constant over more than 80 min. This behaviour suggests that O_2 molecules are not adsorbed at the Pyrex surface and/or the possibly adsorbed O_2 could not directly lead to an oxidation of NO at the wall.
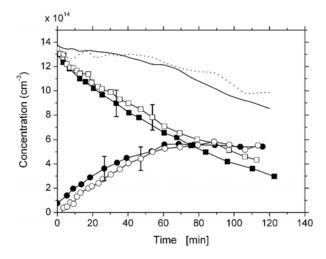

Fig. 3 Time dependence of the NO and NO_2 concentrations after a 1h oxygen plasma pre-treatment of the Pyrex tube. Probe gas: (i) N_2+1% NO (NO, ■, NO_2, ●), (ii) Ar+1%NO (NO, □, NO_2, o), p=5.3 mbar. Upper curves show the sum of the NO and NO_2 concentrations [16].

Complementary to the first experiments a pure O_2 plasma was applied for 60 min in order to scrutinise whether surface oxidation reactions occur after this treatment. Figure 3 shows the results for two types of probing gas (i) 1% of NO in N_2 and (ii) 1% of NO in Ar. In both cases the concentration of NO decreases while NO_2 simultaneously increases. For both experiments a first order exponential fit gives a rate coefficient of 2.3×10^{11} molecules s^{-1} for NO losses. The NO_2 production rate coefficient is nearly the same (2.1×1011 molecules s^{-1} for the experiment in N_2 and 1.9×10^{11} molecules s^{-1} for the experiment in Ar). Therefore it can be concluded, that NO is oxidized into NO_2 by O containing species (O_2, O_2-, or O atoms) adsorbed on the Pyrex surface during the pre-treatment phase.

Notice that during the pre-treatment using an O_2 plasma the temperature of the tube wall rises to about 350 K. Probably, this temperature rise has some influence on the deposition of oxygen containing species and more work is planned in order to verify this dependence. Between the pre-treatment phase and the filling with NO/N_2 the temperature returns to the ambient one and remains constant during the experiment. No considerable heating of the reactor due to the surface reactions has been observed.

As pointed out earlier, O_2 molecules are hardly adsorbed and/or are not involved in the oxidation of NO under our conditions. At the surface O_2- could have been adsorbed under plasma exposure, but the amount of oxygen atoms required to produce the measured NO_2 density of 5.3×10^{14} cm^{-3} would induce a surface charge density as high as 20 $\mu C/cm^2$ leading to a plasma breakdown at the surface during the filling procedure. O atoms involved in the NO oxidation process can thus only originate from atomic oxygen adsorbed during the pre-treatment (designated as O_s further below).

These O_s do not recombine to O_2 and remain at the surface during all pumping and filling procedures. Since the O_s cannot be easily desorbed, NO oxidises at the surface and not in the gas phase. The oxidation to NO_2 with O_s could occur via two different mechanisms:

i) the gas phase NO reacts directly with O_s via a direct pick-up of NO from the gas phase (Eley-Rideal

mechanism)

ii) first NO is adsorbed and then reacts with O_s at the surface (Langmuir-Hinshelwood mechanism)

The experiments with Ar or N_2 plasmas have shown that they are not able to create adsorption sites for NO at the Pyrex surface. The Langmuir-Hinshelwood mechanism could then happen only if the O_2 plasma provides a better cleaning of the surface than a N_2 or Ar plasma.

Whatever the mechanism involved, the rate coefficient is relatively low compared to that one of the NO_2 production at the same pressure in the gas phase. Here according to Atkinson et al. [20] the oxidation of NO into NO_2 is a third order reaction with a rate coefficient $k(298K) = 10^{-31}$ cm^6 molecule^{-2}s^{-1}. Assuming that all adsorbed O atoms would react with the initially available NO molecules in the probing gas (1 % at 5.3 mbar) the production rate would be 8.6×10^{15} molecules s^{-1}. This is 4 orders of magnitude higher than the experimentally observed 2.1×10^{11} molecules s^{-1}.

The limiting factor for the surface oxidation reaction is probably not the surface density of O_s. Assuming that all the O_s stored onto the surface are used to oxidize NO, the oxygen surface density of 2.7×10^{14} cm^{-2} can be estimated by considering a smooth surface at the pretreated tube [16].

The experiments with NO in N_2 or in Ar as feed gas, give the same kinetics for NO and NO_2 (figure 3). The relatively low production rate of NO_2 is thus not limited by a competition between NO and N_2 for adsorption processes and/or direct reactions of N_2 with adsorbed O atoms. The characteristic diffusion time in our conditions is about 1 millisecond. In other words, the transport of NO molecules to the surface cannot be a limiting step.

The NO_2 desorption from the surface is not either the slowest process because the production rate coefficient of NO_2 is about equal to the NO loss rate coefficient (2.1×10^{11} molecules s^{-1} and of 2.3×10^{11} molecules s^{-1}, respectively). However, in the gas phase the sum of the NO and NO_2 concentrations decreases slightly with time. The NO_2 concentration shows saturation at 5.3×10^{14} cm^{-3}. After 120 min about 30% of the N atoms originating from NO was not detected as NO or NO_2 in the gas phase. On a longer time scale NO could be partly adsorbed or both species, NO and NO_2, may be converted into other oxygen containing compounds such as N_2O, NO_3 and N_2O_3. Therefore, for future studies it would be worthwhile monitoring also the concentrations of these compounds, e.g. using a third laser in the experimental set-up.

4 Surface Kinetic Modeling

The simplest surface kinetic scheme describing the conversion of NO in NO_2 takes into account only two surface reactions, $NO + O_S \rightarrow NO_2$ (1) and $NO + S_V \rightarrow (NO)_S$ (2). 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:

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

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

$$\frac{d\,[\Theta_S^O]}{dt} = -\Theta_S^O r_1,$$

$$\frac{d\,[\Theta_S^{NO}]}{dt} = r_2 \left(1 - \Theta_S^O - \Theta_S^{NO} \right),$$

where $[S]$ is the surface density of chemisorptions sites and $\Theta_S^M = [MS]/[S]$ is the fractional coverage of chemisorption sites by species M. The (time-dependent) reaction rates r_1 and r_2 are given by [17]

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

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

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 for the adsorption sites (occupied or vacant) and correct the formulas for directional effects and other unknown phenomena.

Figure 4 shows the comparison between the experimental data and the calculations performed using a density of physisorption sites $[F] = 1.5 \times 10^{15}$ cm^{-2}, the fraction of the surface covered by chemisorption sites $\varphi = 1.7 \times 10^{-1}$, $E_1 = 24$ kJ/mol, $E_2 = 0$ J/mol, $k_1^0 = 1.15 \times 10^{-3}$, $k_2^0 = 3 \times 10^{-8}$, $T_g = T_W = 298$ K, and for an initial concentration of NO corresponding to a partial pressure of 0.01 x 5.3 mbar. Notice that the values for $[F]$, E_1 and E_2 are typical values in recombination studies [17], whereas the value of φ is larger than used in [17] but very close to the one proposed in [21]. The pre-exponential factor k_1^0 is significantly lower than suggested for recombination in pure gases [17]. Nevertheless, a value of 1.5×10^{-2} was suggested in [22] for the similar reaction with CO, i.e., $CO + O_S \rightarrow CO_2 + S_V$.

As shown in figure 4, process (1) describes well the behaviour of the measured species up to times of the order of 2000 s. However, it cannot explain the results for longer times. As a matter of fact, there is a slow loss of N-containing species, as previously noted in [16]. 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. However, reaction (2) may be only one effective way among others of describing these losses, which can take place as well due to adsorption of NO$_2$ or by a more complex sequence of reactions.

Figure 5 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.
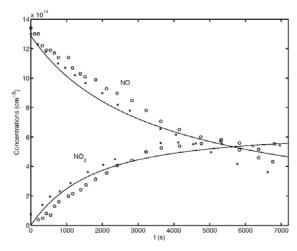

Fig. 4 Experimental (points) and calculated (lines) concentrations of NO and NO$_2$ as a function of time, using reaction (1) only (dotted) or reactions (1) and (2) simultaneously (solid).

Fig. 5 Fractional coverage of adsorption sites with O atoms (Θ_S^O), NO molecules (Θ_S^{NO}) and total ($\Theta_S = \Theta_S^O + \Theta_S^{NO}$).

5   Conclusions

Recently it has been shown that at a Pyrex surface NO is oxidized to NO$_2$ after oxygen containing plasma treatment of the surface. The O atoms produced by a pure O$_2$ or an air plasma are adsorbed at the inner surface and remain available for oxidation reactions at a medium pressure range of a few mbar over several tens of minutes. A pure O$_2$ plasma treatment of the Pyrex material leads to a surface highly saturated with O atoms. Under our conditions NO is probably oxidized to NO$_2$ via an Eley-Rideal mechanism. An effective reaction

rate coefficient of 2.3×10^{11} molecules s^{-1} has been determined. An Ar or N_2 plasma treatment of the Pyrex surface has not led to considerable numbers of adsorption sites for NO [16]. The developed simple surface model accords well with the experimental results. In the model a fraction of the surface is considered to be covered with chemisorption sites where atoms and molecules can be adsorbed, whereas they can be removed only by recombination. In particular, after about 30 min the fractional coverage of adsorption sites with NO molecules is non-negligible and may partially explain the loss of N containing species in the gas phase.

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