# Formation of $N_2O$ and $(NO)_2$ during NO adsorption on Au 3D crystals

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The adsorption of NO on Au 3D hemispherical crystals ("field emitter tips") has been studied by means of pulsed field desorption mass spectrometry (PFDMS) under dynamic gas flow conditions and at 300 K. Local chemical probing of ~200 Au sites in the stepped surface region between the central (111) pole and the peripheral (001) plane leads to the detection of $NO^+$, $N_2O^+$ and $(NO)_2^+$ species. Obviously, molecular NO adsorption on stepped Au surfaces can lead to dimerization. Nitrous oxide formation probably occurs via the dimer, $(NO)_2$.

**KEY WORDS:** chemical probing; gold nano-crystals; nitric oxide; nitrous oxide.

## 1. Introduction

Nitric oxide reduction on supported noble metal catalysts frequently leads to unwanted amounts of nitrous oxide ($N_2O$). Various formation mechanisms have been proposed but no general agreement seems to have been reached as yet. The relevant literature published until 1998 has been reviewed by Nieuwenhuys [1] from the viewpoint of a surface science approach to catalysis. More recently, on the basis of Steady state isotopic transient kinetic analysis (SSITKA) of the $NO/O_2/H_2$ reaction over $Pt/SiO_2$ catalysts [2] a mechanistic network of NO conversion into $N_2O$ and $N_2$ has been proposed. The scheme includes dimeric $(NO)_2$ as an intermediate of $N_2O$ formation. Although such dimers have not been explicitly identified by SSITKA, the authors emphasize that the route to $N_2O$ formation, which is fast, must be through a final step involving a coupled intermediate weakly bound to the catalyst surface and in reversible equilibrium with the gas phase. Subsequent calculations using density functional theory (DFT) have indeed shown [3] that the activation barrier for the $NO_{ad} + NO_{ad}$ reaction is considerably lower than the one for the $N_{ad} + NO_{ad}$ reaction.

Studies of the NO reduction over Au based catalysts are scarce. Ueda and Haruta [4] have reported on $N_2O$ formation at 323 K during the NO + CO reaction. Mechanistic aspects in this work have not been addressed. No report on $N_2O$ formation has been made by Deckers *et al.* [5] during a study of the NO + $H_2$ reaction. The authors mention that NO adsorption on $Au/Al_2O_3$ was not detectable by infrared spectroscopy.

We wish here to present first results of an "atom-probe" PFDMS study (Pulsed Field Desorption Mass Spectrometry) on the low-pressure adsorption of NO on pure Au at 300 K. We demonstrate the ultimate sensitivity of the instrument in detecting species like nitrous oxide and dimeric $(NO)_2$ at coverages far below the monolayer limit.

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## 2. Experimental

The experiments were performed in a home-built "atom-probe" device similar to the one described earlier [6]. Standard field ion micrographs were taken by a high resolution CCD-camera (512 × 512 pixels, 18 bit dynamic resolution) using either hydrogen ($H_2$) or neon (Ne) as imaging gas (purity better than 99.999%). NO gas was used in commercially available purity (99.8%). Au tips were electrochemically etched from a Au wire (Ø = 0.13 mm, 99.99%) in an aqueous solution of KCN (20%) at 4.5 V dc. They generally appeared (111) oriented in FIM. Several cycles of annealing, sputtering in Ne at 550 K and low-temperature field evaporation allowed us to obtain clean and defect-free Au tips. An example is given in figure 1.

As described earlier (for a review of high-field methods, see [7]), PFDMS allows for a truly *in-situ* local chemical analysis on selected surfaces of 3D crystals (tips) comprising between some ten and some hundred atomic sites. In the present study, field pulses up to 3V/Å were produced by applying HV pulses (pulse widths 100–200 ns, repetition rates $\leq$ 10 kHz) to a ring-like counter electrode mounted in front of the sample. A channel-plate image intensifier with a central hole is placed in front of the time-of-flight tube to allow for field ion imaging. The sample-hole alignment was such that ~ 200 atomic Au sites (the actual number depending also on the tip radius of curvature) in the area between the (111) pole and the peripheral (001) plane were monitored during the dynamic interaction with NO gas at 300 K.

Figure 2 shows a time scheme of the field pulses. The repetition frequency used in the present study was

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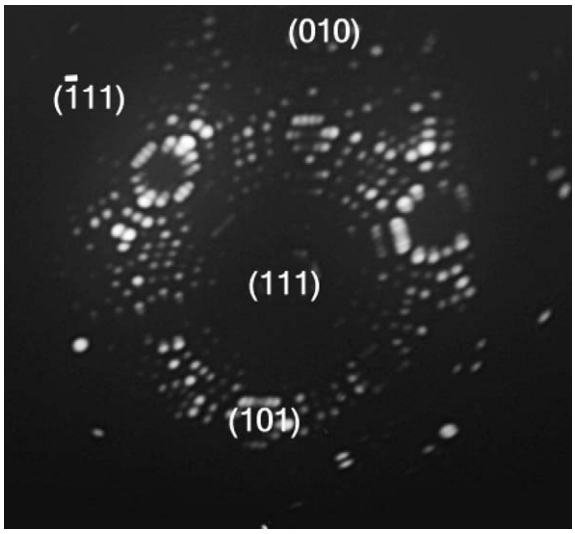


Figure 1. Ne-FIM micrograph at 58 K of a (111) oriented Au tip.

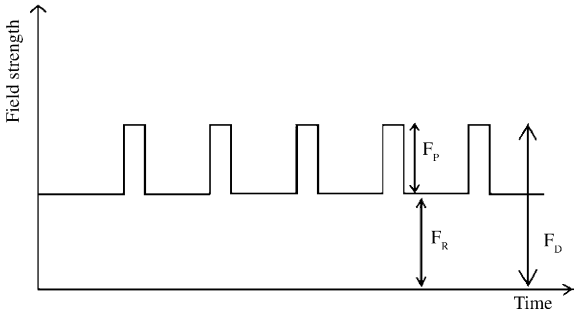


Figure 2. Time scheme of the field pulses. $F_R$: static field, $F_P$: pulsed field and $F_D$: desorption field. $F_R = 0$ for measurements reported here.

$f = 1.66$ kHz corresponding to a reaction time $t_R \sim 600\mu s$. No steady electric field was applied during the experiments. Field pulses lead to desorption of adsorbed species and the respective ions (only those "seen" by the probe hole) are injected into a single-ion detection time-of-flight mass spectrometer.

## 3. Results and discussion

Experiments were performed by exposing a clean (111) oriented Au tip to a dynamic NO gas pressure of $1.3 \times 10^{-7}$ mbar at room temperature. Figure 3 shows the respective time-of-flight mass spectrum obtained while applying field pulses of $\sim 0.7$V/Å. $NO^+$ and $N_2O^+$ dominate the mass spectrum besides smaller amounts of $(NO)_2^+$. No Au field evaporation is seen at these low-field conditions.

Species are field-desorbed from the adsorbed layer built up during the field-free reaction interval, $t_R \sim 600\mu s$. For the chosen gas pressure we expect a maximum ion rate of $\sim 20$ $s^{-1}$ in case of complete field desorption by pulses and for a sticking probability $S = 1$ (we are not aware of literature work in which $S$ was

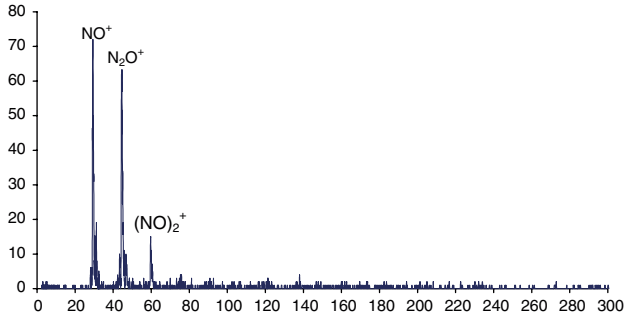


Figure 3. Atom-probe analysis by PFDMS during the interaction of NO with Au. Experimental conditions: $P_{NO} = 1.3 \times 10^{-7}$ mbar, $T = 300$ K, $F_P \sim 0.7$ V/Å, monitored area: ~200 atoms.

explicitly determined). The (total) ion intensity ($NO^+ + N_2O^+ + (NO)_2^+$) amounts to 3 $s^{-1}$. Such a value would be roughly in accordance with (field) desorption from step sites since we can estimate our Au sample to contain between 10 and 15% steps. We point out, however, that such an interpretation completely neglects the influence of surface diffusion into or out of the monitored surface area. It was previously demonstrated see, for example, Ref. [8] that a systematic variation of the pulse field strength can reveal whether or not diffusion is in operation. Usually, high field strengths can suppress the influence of long-range diffusion from the shank of the tip into the crystal apex region. Similar studies at varying pulse height are presently being performed for NO/Au.

The chemical nature of the detected ions suggests NO dimerization to take place:

$$2NO_{ad} \rightleftharpoons (NO)_{2,ad} \quad (1)$$

As discussed above, step sites may be claimed to be involved in this process. In a previous PFDMS study of CO adsorption on Au [9] we have demonstrated the formation of AuCO and $Au(CO)_2$ singly or doubly charged ions suggesting CO twin bound at steps. The intensities of these species was found to depend strongly on the steady field strength applied between pulses and the data could be quantitatively assessed by DFT calculations. In the present study no steady field was applied. With the data at hand, it cannot be excluded that NO is also twin bound to Au (step) atoms and that dimerization to $(NO)_2^+$ occurs during the field pulses.

Nitrous oxide ($N_2O$) formation may be suggested to involve an intermediate $(NO)_{2,ad}$ state.

$$(NO)_{2,ad} \rightleftharpoons N_2O_{ad} + O_{ad} \quad (2)$$

The combination of two $NO_{ad}$ species to form $N_2O_{ad}$ has been recently proposed on the basis of SSITKA results of the $NO/H_2$ reaction on $Pt/SiO_2$ catalysts [2,10]. Subsequent DFT calculations [3] have demonstrated considerably lower activation energies for a (low-temperature) pathway involving intermediate

dimerization than for a direct reaction involving adsorbed nitrogen atoms and NO molecules:

$$N_{ad} + NO_{ad} \rightleftharpoons N_2O_{ad} \quad (3)$$

Thereupon an interesting discussion on the possible influence of surface nitrogen transients has been led by M.W. Roberts [11]. We mention here that $N^+$ was only occasionally detected in the PFDMS experiments suggesting that NO decomposition to $N_{ad}$ + $O_{ad}$ during $t_R = 600\mu s$ at 300 K is a process of low probability on Au. This is also in accordance with results obtained by A. Ueda and M. Haruta [4] according to which $N_2O$ formation during the CO + NO reaction over supported Au catalysts dominates clearly over $N_2$ formation (by recombination of $2N_{ad}$) up to 323 K.

One of the surprising features of our experiments is that no significant amounts of surface oxygen were observed. In fact, according to equation (2) equal amounts of $N_2O^+$ and $O^+$ would have been expected under conditions of high (field) desorption probabilities of the respective neutrals. Since no poisoning effects with time are seen either, we conclude that surface oxygen is absent from the area monitored by the field pulses. The reason might well be associated with rapid surface diffusion. Ample experimental evidence for the formation of highly mobile transient surface oxygen has been obtained by the group of M.W. Roberts [12] and suggested to be important in catalytic oxidation. We hope to find answers to the problem of deficient surface oxygen by future reaction studies in which the pulse repetition frequency will be varied systematically. To this end, we mention that the reaction of NO with oxygen-covered Au surfaces may easily produce $NO_2$ species without concomitant formation of $N_2O$ and $(NO)_2$ [13].

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