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A COMPARISON OF NO INTERACTION WITH STEPPED Pt AND Ru FIELD EMITTER SURFACES

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Résumé - L'adsorption et la décomposition catalytique de NO à la surface de pointes émettrices de Pt et Ru, ont été étudiées par spectrométrie de masse de désorption de champ pulsée. En l'absence de champ électrique, il y a adsorption moléculaire de NO sur les faces à marches (111) et (001). La dépendance en température des durées de vie avant thermodésorption, a permis d'évaluer l'énergie d'activation ($E_d = 153$ KJ/mol) et le facteur préexponentiel ($\tau_0 = 5 \times 10^{-15}$ sec). Ces valeurs sont représentatives d'une désorption à partir des marches.

La formation d'oxydes de surface à une température de 535 à 602 K, a été observée pour le Pt(001) à marches, mais pas pour la face (111) à marches. La dépendance en temps de l'intensité de PtO$^+$ est due à un mécanisme réactionnel postérieur.

Sur les faces (001) à marches du Ru, il y a adsorption moléculaire et dissociative de NO même à 300 K. À 500 K, le Ru est plus fortement oxydé que le Pt; les ions RuO$^{n+}$ jusqu'à RuO$^{2+}$ sont observés. Cela implique une instabilité du Ru comme catalyseur de la décomposition de NO.

Abstract - The adsorption and the catalytic decomposition of NO on Pt and Ru field emitter surfaces has been studied by pulsed field desorption mass spectrometry (PFDSMS). A molecular adsorption of NO was found on stepped Pt(111) and (001) surfaces in the absence of electrostatic fields. From the temperature dependence of the mean lifetimes before thermal desorption an activation energy $E_d = 153$ KJ/mol and a pre-exponential term $\tau_0 = 5 \times 10^{-15}$ sec have been evaluated. These values are considered as representative for desorption from steps.

The formation of surface oxides at temperatures $T = 535...602$ K was observed for stepped Pt(001), but not for stepped (111) surfaces. The time dependence of the PtO$^+$ intensity is due to a consecutive reaction mechanism.
On stepped Ru(001) surfaces a molecular as well as a dissociative adsorption of NO occurs even at 300 K. At 500 K, Ru is more strongly oxidized than Pt, RuO\textsubscript{x}\textsuperscript{6+} ions up to RuO\textsubscript{3}\textsuperscript{2+} are observed. This implies an instability of Ru as a catalyst for NO decomposition.

I - INTRODUCTION
The platinum metal plays an important role as a component in multifunctional catalysts for nitric oxide removal from automobile exhaust gases. Ruthenium has also gathered interest as a candidate for nitric oxide decomposition. However, it forms volatile oxides, RuO\textsubscript{3} and RuO\textsubscript{4}, under technical conditions thus restricting its practical applicability.

Various surface sensitive techniques have been employed to elucidate the face selectivity of Pt and Ru towards NO decomposition (for a review see /1/).

Recently, a high catalytic activity has been discussed for certain stepped surfaces like Pt (410), as expected from theoretical considerations /2/ and verified in experimental observations /3/.

In this study we compare adsorption and decomposition of NO on the stepped (001) surfaces of Pt and Ru field emitters. We employ pulsed field desorption mass spectrometry (PFDMS) in order to obtain kinetic information about these processes as recently reported for NO desorption from stepped Pt (111) surfaces /4/.

II - EXPERIMENTAL
The PFDMS technique has been described in detail elsewhere /5/. Fast negative pulses of up to 20 kV amplitude are applied to an electrode in front of a Pt or a Ru field emitter tip. Field strengths of the order of some ten V/nm cause the desorption of the adsorbed species. The respective ions are chemically analyzed by time-of-flight mass spectrometry.

Kinetic processes on the field emitter surfaces can be studied by varying the repetition frequency of the pulses, i.e. the time \( t_R \) between the pulses, usually from 100 \( \mu \)sec up to some seconds. Details - including experimental procedures for measurements of the mean lifetime \( \tau \) before thermal desorption - have been published elsewhere /4/.

NO (99.8 % purity) was provided by Messer Griesheim. Both, Pt (Goodfellow Metals, 99.99 % purity) and Ru (spark erosion cut from a boule supplied by Materials Research Corporation) field emitters were (001) oriented. They were cleaned in situ by field evaporation.
III - RESULTS

Fig. 1 shows the results of the reaction time variation measurements. We selected the stepped region in the vicinity of the (001) poles of (001) oriented field emitter tips of Pt and Ru. The measurements have been performed under continuous supply of NO from the gas phase at p = 1.3 x 10^{-5} Pa. The field strength amounts to F = 26 V/nm, sufficient to desorb molecularly adsorbed NO quantitatively with each pulse. Thus, the measured NO^+ ion intensities are proportional to the NO_{ad} surface concentration. Substantial amounts of O_{ad} are removed by the field pulses, so that it cannot accumulate at the surface. O_{ad} appears as PtO^+ or RuO^2+ in the mass spectra. During the field pulses, NO molecules are accelerated by the field, and hit the surface with higher kinetic energy, so that their dissociation rate is enhanced. This part of the ion intensity is calculated and subtracted from the total ion currents of PtO^+ and RuO^2+. We first inspect adsorption of NO on stepped Pt (001), Fig. 1a. Both, molecular and dissociative adsorption take place as shown by the occurrence of NO^+ and PtO^+ ions. At short times, the NO^+ ion intensity increases linearly with t_R. At long times, the NO^+ intensity levels off. This behaviour is characteristic for thermal desorption of NO_{ad} during t_R. If we assume (i) adsorption to be associated with a constant sticking probability and (ii) the thermal desorption to obey first order kinetics, the surface concentration of NO_{ad} develops according to 
\[ c = c_0 (1 - e^{-t/\tau}) \]
Since the measured NO^+ ion intensities display the same time dependence, the mean lifetime \( \tau \) before thermal desorption of NO_{ad} can be determined as that value of \( t_R \) where the NO^+ ion intensity reaches the \( (1 - 1/e) \) level of the constant part at long times. At \( T = 543 \) K we find \( \tau = 0.2 \) sec.

By comparing the intensity increase of NO^+ at short times, i.e. the adsorption rate \( dc/ dt \), with the impingement rate from the gas phase into the monitored area (checked by NO^+ dc field ionization), values of 0.65...0.85 are derived for the sticking probability. These values are in accord with measurements of other authors /6,7/.

We now inspect the property of the stepped (001) surface to partially dissociate the adsorbed NO. We take the PtO^+ ion intensities as a measure for the formation of surface oxide due to dissociation of NO_{ad}. Nitrogen containing ionic metal species are not detected. This is explained by fast recombination and thermal desorption according to 
\[ 2N_{ad} \rightarrow N_2 + g^+ \]
Within the measured time range, the PtO^+ ion intensities are always considerably smaller than the NO^+ intensities. Thus, molecular adsorption prevails over dissociative adsorption. The PtO^+ intensity (from the field free reaction between the pulses) appears with a delay time, which is of about the same value as the time \( \tau = 0.2 \) sec to reach the equilibrium concentration of molecularly adsorbed NO. This is in accord with a consecutive reaction mechanism, where adsorption of NO from the gas phase has to take place before decomposition into O_{ad} can occur. Values for the dissociation probability, w, can be obtained by comparing the measured PtO^+ in-
Fig. 1 - Dependence of ion intensities on reaction time, $t_R$. NO pressure: $1.3 \times 10^{-5}$ Pa, impingement rate: 0.19 molecules/sec into the monitored area.

1a) - $\text{NO}^+$ and $\text{PtO}^+$ ion intensities, Pt tip temperature: 543 K, field strength: 28 V/nm. $\tau$ = mean lifetime of molecularly adsorbed NO.

1b) - Ru$O^2+$ ion intensity, Ru tip temperature: 503 K, field strength: 30 V/nm. For comparison with $\text{PtO}^+$ of fig. 1a, the ion intensity has been related to the same size of the monitored area.

Intensities with the impingement rate. Within the measured time range, $w$ is small. At a time $t_R = 1$ sec, $w$ is of the order of a few percent only.

In fig. 1b we compare the development of the surface oxide on stepped Pt(OCl) with that on stepped Ru(OCl). In contrast to the Pt surface, the oxide build-up on Ru follows normal kinetics as evidenced by a proportional increase of the Ru$O^2+$ intensity with time. Furthermore, the dissociation probability of the NO is considerably higher on the Ru surface. By comparison with the impingement rate from the gas phase we find values of more than 5%. Within the measured time range the surface oxide coverage is far below a monolayer. Further oxidation of Ru is achieved at higher NO gas pressures.

In fig. 2, data of a pulse field strength variation measurement at $p = 5.5 \times 10^{-4}$ Pa and $t_R = 0.25$ sec are shown. At low field strength values, $\text{NO}^+$ ion intensities (ions/sec) dominate. They increase with the rising field strength. This is due to
an increasing field desorption probability of NO$_{ad}$. At high field strengths, however, the NO$^+$ ion intensity decreases drastically. This decrease coincides with high desorption rates of RuO$^{2+}$. We conclude that at high field strengths the surface oxide level is considerably lowered by field desorption. Thus oxygen vacancy sites are created allowing for NO$_{ad}$ dissociation.

At low field strengths, i.e. without destroying the oxide layer by the field pulses, we observe RuO$_{2}^{2+}$ and RuO$_{3}^{2+}$ ions. Their decrease at higher field strengths is more pronounced for RuO$_{3}^{2+}$ than for RuO$_{2}^{2+}$.

![Graph](image.png)

**Fig. 2 - Dependence of ion intensities on desorption field strength. NO pressure: 6.7 x 10$^{-4}$ Pa, Ru tip temperature: 552 K, reaction time: 0.25 sec, i.e. pulse frequency: 4 Hz.**

**IV - DISCUSSION**

Adsorption of NO on stepped (001) field emitter surface of Pt and Ru occurs molecularly as well as dissociatively. On the Pt surface molecular adsorption of NO prevails over dissociative adsorption in the measured time range at $T = 543$ K. The mean lifetime $\tau$ of NO$_{ad}$ before thermal desorption has been measured. We find $\tau = 0.2$ sec at $T = 543$ K. The temperature dependence of $\tau$ has been measured and will be published elsewhere. We found, that the rate parameters of thermal desorption ($E_d = 153$ kJ/mol, $\tau_0 = 5 \times 10^{-15}$ sec) are governed by the presence of steps. This is in accord with observations of other authors /6,7/. Since steps may be active in N-O bond breaking it has to be concluded that molecular adsorption and dissociation are
competitive processes at these sites. Within the measured time range, NO$^+$ and PtO$^+$
intensities are not influenced by each other. Thus, O$_{\text{ad}}$ does not completely block
the step sites for molecular adsorption.

Dissociative adsorption was found at the steps of a (001) Pt surface, but not at the
steps of (111) Pt. There, NO adsorbed only molecularly /4/. Banholzer et al. /2/ de-
veloped a symmetry model for explaining this strong influence of the crystallograph-
ic orientation.

It has been found that the oxide build-up at 543 K essentially begins after the mo-
lecularly adsorbed NO$_{\text{ad}}$ has reached its equilibrium concentration at $\tau = 0.2$ sec.
This behaviour is explained by a consecutive reaction mechanism, involving adsorp-
tion first and decomposition successively. The steep increase of the PtO$^+$ intensity
at long times $t_R$ possibly indicates dissociation kinetics of higher than first order
in NO$_{\text{ad}}$-concentration.

The dissociation probability (compared with the impingement rate from the gas phase)
is considerably higher for clean Ru than for clean Pt. At low pulsed field strengths
the surface layer is not completely removed thus allowing O$_{\text{ad}}$ to accumulate at the
surface and to form an oxide layer where RuO$_2^+$ and RuO$_3^+$ ions can be desorbed from.
It is remarkable that such an oxide layer is built up not only from O$_2$ /8/ but also
from NO. This intense oxidation of the ruthenium restricts its applicability as a
catalyst for NO decomposition, in contrast to platinum which is not so strongly
oxidized.

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