ADSORPTION OF NO ON Pt STUDIED BY PULSED FIELD DESORPTION MASS SPECTROMETRY

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To cite this version:

HAL Id: jpa-00224418
https://hal.archives-ouvertes.fr/jpa-00224418
Submitted on 1 Jan 1984

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I - INTRODUCTION

The adsorption of nitric oxide on noble metal surfaces has been studied extensively in the past (for a summary see /1/) since it is one of the elemental steps in the catalytic reduction process to molecular nitrogen and oxygen. This reaction is especially important for emissions control in combustion engines. Various surface sensitive techniques including thermal desorption spectroscopy (TPD) /2/ and molecular beam relaxation spectroscopy (MBRS) /3-5/ have been employed to characterize the adsorption states on Pt(111) and to elucidate the kinetics of thermal desorption. The results differ substantially from each other and it is concluded that this is in part due to different densities of step sites in the (111) surfaces. Therefore, it seems worthwhile to extend these investigations and to perform measurements on the stepped surface of a Pt field emitter by means of pulsed field desorption mass spectrometry (PFDMS). This technique has already been successfully employed in similar investigations of CO on Fe /6/.

II - EXPERIMENTAL

The PFDMS apparatus has been described in detail elsewhere /7/. It differs from a normal atom probe in the following manner. Fast negative field pulses (amplitudes up to 20 kV, rise times \( \sim 100 \) ns, repetition rates up to 100 kHz) are applied to a
counter electrode mounted at distances of 0.1mm in front of a field emitter. Adsorbed species are field desorbed, and the chemical nature of the ions is determined by time of flight measurements. Between the pulses, an arbitrary field, usually zero, can be maintained. A channel plate with a probe hole is mounted at the entrance of the flight tube in order to observe the orientation of the tip.

Temperatures are measured by a thermocouple spotwelded to the base of the emitter tip. NO (99.8 % purity) was provided by Messer Griesheim. Pt field emitters were prepared by electrochemical etching of a 0.1 mm wire (99.99 % purity) from Goodfellow Metals and cleaned by field evaporation.

III - EXPERIMENTAL PROCEDURE

The general procedure for providing kinetic data of surface processes in PFDMS is illustrated in Fig. 1. While the field emitter surface is continuously dosed by the gaseous reactant, adsorption takes place only in the field free reaction interval, \( t_R \), between two pulses. At the end of this interval the adsorbed layer is desorbed by a field pulse. If the layer is completely removed by each pulse the measured ion intensity directly represents the surface concentration within the monitored area before the pulse.

By variation of \( t_R \) (usually in the time range 100 \( \mu \)sec... 10 sec) both the kinetic of adsorption and the thermal equilibration of the adlayer are examined. For short times, supply from the gas phase is insufficient to achieve a steady surface concentration. The field pulses interrupt the adsorption process and, thus, the amount of material accumulated on the surface at this instant is measured. For long times (compared with the mean lifetime) a dynamic adsorption thermal desorption equilibrium will be established. Then the surface concentration remains constant with increasing \( t_R \), and consequently, the ion intensity does not increase any further. Assuming the adsorption process to proceed with a constant sticking probability and
thermal desorption to obey first order kinetics the mean lifetime can be measured as the value of $t_R$ at which the $(1-1/e)$ level of the equilibrium coverage is reached.

IV - RESULTS

Using Frenkel's equation,

$$\tau = \tau_0 \times \exp\left(\frac{E_d}{kT}\right),$$

the activation energy, $E_d$, for thermal desorption and the preexponential term, $\tau_0$, can be determined independently by measuring $\tau$ at various temperatures. This has been done for NO, adsorbed on a (100) oriented Pt field emitter surface, containing about 100 atomic sites in the monitored area (Fig. 2). Temperatures were varied in the range between 526 K and 583 K, so that the $\tau$ values occurred in the millisecond time scale. A field strength of 22 V/nm turned out to be sufficient to achieve com-

![Graph](attachment:image.png)

Fig. 2 - Temperature dependence of the mean lifetime of NO adsorbed on a Pt field emitter tip.

plete desorption of the adsorbed NO molecules by each pulse. No other species than NO$^+$ appeared in the mass spectrum, so that the surface concentration of NO$_{ad}$ is directly correlated with the measured ion intensity. The kinetic parameters for the thermal desorption process are found to be $E_d = 139$ kJ/mole and $\tau_0 = 3.8 \times 10^{-15}$ sec.
Recently, three different MBRS studies on the adsorption and thermal desorption of NO from Pt(111) have appeared in the literature /3-5/. There is agreement between the different authors that the measured desorption kinetics refer to the molecular adsorption state of NO. Lin and Somorjai /3/ found a distinct increase in $E_d$ from 120 to 135 kJ/mol and a slight decrease of the preexponential term, $\tau_0$, from $1.6 \times 10^{-14}$ to $7.9 \times 10^{-15}$ sec when replacing a Pt(111) by a stepped Pt(557) surface. This surface consists of six-atom-wide terraces of (111) orientation separated by monoatomic steps of (100) orientation. Campbell et al. /4/ found $E_d = 138$ kJ/mol and $\tau_0 = 3.2 \times 10^{-16}$ sec on a (111) surface and argue that these values are representative of the thermal desorption from defect sites, which are present to about 5% on their surface. Dramatically differing $E_d$ and $\tau_0$ values are found by Serri et al. /5/ ($E_d = 67...138$ kJ/mol and $\tau_0 = 3.2 \times 10^{-10}...3.2 \times 10^{-16}$ sec). Again, step sites seem to play a dominant role in thermal desorption. In addition, these authors also report non-first order desorption rates at surface concentrations below $10^{-2}$ monolayers. This observation was not confirmed in our measurements.

Our field emitter surface contains several % of steps (the actual value depending on the location of the probe hole and on the size of the emitter tip). The kinetic data provided by PFDMS preferentially refer to thermal desorption from these steps, since they exert the strongest bonding to adspecies. Our results are in good agreement with those cited above for the stepped (111) surfaces, and it can be concluded that similar adsorption sites are sampled in both methods, PFDMS and MBRS.

REFERENCES