Isothermal desorption of O$_2$ from Ag(001)

F. Buatier de Mongeot *, M. Rocca, U. Valbusa

CFSBT-CNR and INFN, Dipartimento di Fisica dell’Università di Genova. Via Dodecaneso 33. 16146 Genova. Italy

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Abstract

The relevant parameters which characterise molecular desorption of O$_2$-Ag(001) have been determined under isothermal conditions in the low coverage limit, using the beam-flag method. We find a desorption order $n=1.07 \pm 0.10$, a desorption energy $E_{\text{des}} = 0.50 \pm 0.12$ eV and a pre-exponential factor $v_{\text{des}} = 10^{13.3\pm5.5} \text{s}^{-1}$. Such values compare well with the thermal desorption parameters present in literature for molecular oxygen adsorbed on Ag(110). The much lower dissociative adsorption probability of O$_2$ on Ag(001) is therefore due to the existence of a different dissociation mechanism and not to a difference in the desorption probability compared with Ag(110).

Keywords: Low index single crystal surfaces; Molecule–solid reactions; Oxygen; Silver; Sticking; Thermal desorption spectroscopy

1. Introduction

The O$_2$–Ag system has been intensely studied in the past due to the importance of silver as a catalyst for the epoxidation reaction of ethylene. Mostly, the reactive Ag(110) surface was studied [1,2], or the close-packed Ag(111) face, which turns out to be extremely inert towards oxygen [1,3]. The Ag(001) face was little studied and it was believed to have a very low reactivity, comparable to the (111) surface [4]. A recent molecular beam study showed that, contrary to expectation, the activation barrier for molecular chemisorption on Ag(001) is comparable to the one of Ag(110) [5]. At $T=100$ K oxygen adsorption occurs non-dissociatively, overcoming an activation barrier placed between the physisorption and the chemisorption molecular well. The initial sticking coefficient $S_0$ is therefore strongly dependent on the impact energy of the molecules, rising from $3 \times 10^{-4}$ to 0.61 when $E_i$ increases from 0.025 to 0.8 eV. The molecules, once chemisorbed, are thermally stable on the surface up to $T_\text{z} \approx 165$ K in the low coverage regime. Dissociation is mediated by the molecularly chemisorbed precursor. The much smaller dissociative sticking coefficient on Ag(001) is then explained with a very high desorption probability compared with dissociation ($P_{\text{diss}}(001) = 4.4 \times 10^{-3}$ at $T=300$ K) [5].

It is of interest to measure the parameters which characterise molecular oxygen desorption from Ag(001) so that a direct comparison with the well-studied O$_2$–Ag(110) system can be made, in order to understand why a strongly different dissociation probability is found on the two Ag faces ($P_{\text{diss}}(110) = 0.63$ at $T=300$ K) [5]. Performing an isothermal desorption experiment would be...
extremely instructive as the extraction of the desorption parameters is straightforward and needs no complicated analysis. Only a few isothermal desorption experiments have been reported so far. In most of them the adsorbate coverage was monitored as a function of time through its Auger signal [6–8]. Unfortunately, this method cannot be applied to systems where the electron beam induces dissociation and desorption of the adsorbate, as is the case of O₂–Ag [4]. Other groups [9–11] attached the sample to a specially designed holder and, using a fast control electronics, could raise the crystal temperature in a step-wise manner, monitoring the desorption flux with a mass spectrometer. Recently, isothermal desorption of NH₃ from Cu(001) was studied by recording the surface NH₃ coverage as a function of time with time-resolved electron energy loss spectroscopy while dosing the surface with a modulated supersonic molecular beam [12]. Unfortunately, all these techniques have constraints which limit their applicability to the study of special cases.

In this paper we will show that isothermal desorption data can be obtained in a simple way by dosing the sample with a supersonic molecular beam at a temperature where desorption is significant, and recording with a mass spectrometer the partial pressure rise when the beam is flagged off. A straightforward analysis of the desorption data is developed which gives the desorption parameters (pre-exponential factor, desorption energy and desorption order) of O₂–Ag(001). Isothermal desorption spectra similar to the ones shown in this paper were observed also for C₄H₆–Pt(111) in the multilayer regime, but no quantitative analysis of the data was attempted in that case [13].

2. Experimental

The present experiments were performed with the same apparatus used for the previous investigations of O₂–Ag(001) [5], O₂–Ag(110) [2] and O₂–Ag(111) [3]; the details of this set-up are described in Ref. [14]. The apparatus is equipped with a supersonic molecular beam, and allows one to perform King Wells (KW) measurements of the sticking coefficient [15], high-resolution electron energy loss spectroscopy (EELS) and thermal desorption spectroscopy (TDS). The oxygen was dosed with the supersonic molecular beam; by varying the nozzle temperature and by seeding in He the impact energies $E_i$ of the O₂ molecules could be increased up to 0.8 eV. The beam is collimated so that only the central portion of the crystal surface is exposed. The beam can be intercepted with the flags F₁ and F₂ (see inset of Fig. 1). The flags are made of ceramics and are therefore inert towards oxygen. The O₂ coverage, θ, which in the following will be expressed in monolayers (1 ML = 1.2 x 10¹⁵ cm⁻²), was determined by the KW uptake, whereby the molecular beam flux is measured with a spinning rotor gauge. The O₂ partial pressure in the experimental chamber was monitored with a quadrupole mass spectrometer (QMS) mounted in a non-line-of-sight configuration with respect to the sample surface.

3. Results and discussion

In Fig. 1 a typical isothermal desorption measurement is reported. The surface temperature is
kept constant at $T=190$ K, where desorption is already significant. At time $t_0$, the flag F1 (see inset in Fig. 1) is opened, the beam enters the main chamber and the oxygen pressure rises to $P_1$. At time $t_1$ also the F2 flag is opened and the clean surface is exposed to the beam. A drop in the oxygen pressure is observed because a considerable fraction of the impinging molecules is adsorbed, and therefore does not contribute to the measured background. At this temperature desorption is significant, so that the uptake rate can be expressed as:

$$\frac{d\Theta}{dt} = S(\Theta,T,E_i)\Phi - R_{\text{des}}(\Theta,T) = S(\Theta,T,E_i)\Phi - \Theta K_{\text{des}}(\Theta,T),$$

where $\Phi$ is the oxygen beam flux, $\Theta$ the surface coverage, $R_{\text{des}}$ and $K_{\text{des}}$ are, respectively, the desorption rate (expressed in ML s$^{-1}$) and desorption frequency (expressed in s$^{-1}$). After about 10 s of exposure the oxygen pressure returns to $P_1$ because equilibrium between adsorption and desorption is achieved and the surface coverage reaches a steady state value $\Theta_{ss}$:

$$\Theta_{ss}(T) = \frac{S(\Theta_{ss},T,E_i)\Phi}{K_{\text{des}}(\Theta_{ss},T)}.$$  

As soon as the flag F2 is closed (at time $t_2$), an increase in the oxygen partial pressure is observed, owing to the desorption of the adsorbed oxygen molecules. Due to the very low $O_2$ dissociation probability on Ag(001), adsorption and desorption occur essentially reversibly, and adsorption–desorption cycles can thus be repeated several times. The desorption rate $R_{\text{des}}$ can be obtained from the measured pressure rise after the flag F2 is closed at time $t_2$, and is calibrated against the known molecular beam flux $\Phi$:

$$R_{\text{des}}(t) = \frac{P(t)}{P_1 - P_0} \Phi t > t_2.$$  

The equilibrium coverage $\Theta_{eq}$ can be derived by time integration of $R_{\text{des}}$ (for the present measurement it is 0.02 ML), while the surface coverage at time $t > t_2$ is:

$$\Theta(t) = \Theta_{eq}(T) - \int_{t_2}^{t} R_{\text{des}}(\tau) \, d\tau.$$  

It is now possible to obtain the $\Theta$ dependence of $R_{\text{des}}$ so that, in the framework of the Polanyi–Wigner model [16], the desorption rate can be expressed as:

$$R_{\text{des}} = v_{\text{des}} \Theta^n \exp \left(-\frac{E_{\text{des}}}{KT}\right),$$

where the desorption parameters are, in general, coverage dependent; in the low coverage limit, as in the present experiment, such an effect is, however, usually weak or negligible [17]. In Fig. 2 the dependence of $\log(R_{\text{des}})$ from $\log(\Theta)$ is reported for the data of Fig. 1. The apparent drop in $R_{\text{des}}$ at high coverages, immediately after closing the F2 flag, is an artifact which arises from the finite response time of the pumping system ($\tau_p=0.2$ s); those data points will therefore be excluded in the following analysis. According to Eq. (5) the intercept of the fit gives the quantity $\log(v_{\text{des}}) - E_{\text{des}}/KT$, while from the slope of the data points we derive in a direct way the desorption order $n$ which is $0.94 \pm 0.15$. A unity desorption

![Fig. 2. Plot of the isothermal desorption rate $R_{\text{des}}$ versus $O_2$ coverage. From the slope of the data points the desorption order $n$ is obtained. From the intercept, the quantity $\log(v_{\text{des}}) - E_{\text{des}}/KT$ is derived. The drop of $R_{\text{des}}$ at high coverages is due to the finite response time of the pumping system and is not included in the fit.](image-url)
order is indeed what we would expect for a non-recombinative desorption process in the low coverage limit, where lateral interactions are negligible [16]. In order to obtain the desorption parameters $E_{\text{des}}$ and $v_{\text{des}}$ from the intercept $(\log(v_{\text{des}})-E_{\text{des}}/KT)$, the isothermal desorption experiment has to be repeated at different surface temperatures. In Fig. 3 the intercepts obtained for $T$ in a range 169 to 200 K are reported in an Arrhenius plot. The points are the average value of several measurements. The uncertainty on the measurements performed at higher temperatures is larger because the equilibrium coverage (and thus the desorption signal) is lower.

The desorption energy can be derived from the slope of the points in Fig. 3. It is $E_{\text{des}} = 0.50 \pm 0.12$ eV, while $v_{\text{des}} = 10^{13.3 \pm 3.5}$ s$^{-1}$ is obtained from the intercept. The desorption order, averaged over the measurements at different $T$, comes out as $n = 1.07 \pm 0.10$. Within the error limits we found no temperature dependence of the desorption parameters. Measurements over a wider temperature range would be needed in order to evidence the existence of such a shift. Broadening the temperature range would, moreover, help in reducing the error on the determination of the desorption parameters. It was, unfortunately, not possible to further extend the measurements at higher temperatures because the desorption time constant becomes comparable to the response time $\tau_p$ of the pumping system and, moreover, the desorption signal is degraded due to the lower $\Theta_{eq}$. On the other hand, performing measurements at temperatures lower than 169 K is difficult because the desorption rate becomes too low.

It is interesting to compare the result of the present isothermal desorption experiment with those of a conventional TDS measurement of $O_2$ desorption from Ag(001) [18]. In this case we find $E_{\text{des}} = 0.44$ eV, while $v_{\text{des}} = 10^{10}$ s$^{-1}$ in the low coverage limit. For increasing coverages, $v_{\text{des}}$ decreases by orders of magnitude. As a consequence of the detailed balance principle, the strong decrease of $v_{\text{des}}$ with $\Theta$ also affects the coverage dependence of the sticking coefficient, which drops by several decades. Within error limits therefore, the present isothermal determination of the desorption parameters, which is valid in the very low coverage limit, is compatible with the results of a conventional TDS experiment, with the advantage that complicated modeling of the desorption spectra can be avoided.

We can now compare this result with the value obtained in a TPD experiment for $O_2$–Ag(110) where $E_{\text{des}} = 469$ meV was found [1]. In the analysis of the TPD data, the desorption order was assumed to be unity and a desorption pre-exponential factor of $10^{13}$ s$^{-1}$ was imposed (a typical value for first order desorption processes). We can thus conclude that the desorption parameters we find for $O_2$–Ag(001) are comparable with the ones of $O_2$–Ag(110). This indicates that, on Ag(001), oxygen follows a different dissociation route, otherwise the observed great dissimilarity of the dissociation probability on the two Ag faces could not be reconciled. Indeed recent data suggest that on Ag(001) the dissociation of oxygen should only occur at special defect sites which are identified with kinks, while molecules adsorbed on terrace sites desorb intact [19].

4. Conclusion

In conclusion, we determined under isothermal conditions the relevant parameters which affect
O₂ desorption from Ag(001). The measurement was done following the King–Wells scheme, but at a temperature where the desorption rate is significant. A simple analysis of the desorption spectra has been developed, which yields in a straightforward way the desorption order \( n = 1.07 \pm 0.10 \), the desorption energy \( E_{\text{des}} = 0.50 \pm 0.12 \) eV and the pre-exponential factor \( \nu_{\text{des}} = 10^{13.3 \pm 3.5} \) s⁻¹. The desorption parameters we find for O₂–Ag(001) are comparable with the ones of O₂–Ag(110). We can therefore conclude that the much lower value of the dissociation probability on Ag(001) \( (P_{\text{diss}} = 4.4 \times 10^{-3}) \) compared with Ag(110) \( (P_{\text{diss}} = 0.63) \) is due to a different dissociation mechanism and not to a difference in the desorption parameters.

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