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Sequential precursors in dissociative chemisorption: O_2 on Pt(111)

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A physisorbed state for O_2 on Pt(111) has been identified by XPS spectroscopy and demonstrated to be an intrinsic precursor to molecular chemisorption. Combined with the prior demonstration that the molecularly chemisorbed species is a precursor to dissociation, we propose a model of sequential precursors to describe dissociation.

Precursor species have often been invoked to describe the kinetics of adsorption, desorption, and dissociative chemisorption of gases on surfaces. This concept, dating from the seminal papers of Langmuir[1] and Lennard-Jones,[2] is based on the recognition that there may exist a weakly bound molecular state between the gas phase and the strongly chemisorbed or dissociated state. For example, if an incident gas molecule is first trapped in this weakly bound state, fully accommodates with the surface, and then subsequently chemisorbs or dissociates, then this weakly bound and usually mobile species is labeled a precursor. Kinetic models employing such precursor species[3] have been very successful in describing a wide variety of adsorption phenomena, e.g., the independence of the sticking coefficient S with coverage Θ and its decrease with increasing surface temperature T_s and initial gas translational energy E_i.

Two types of intrinsic precursor species (precursors over a bare metal surface) have often been suggested.[3] First, a physisorbed species may be a precursor to molecular chemisorption. Attempts to isolate such species at low T_s have proven both successful[4,5] and unsuccessful,[6] depending upon the exact system. Second, there is accumulating evidence that a molecularly chemisorbed species may act as a precursor to dissociative chemisorption.[7-9] We will show here that both types of precursors exist for O_2-Pt(111). Therefore, the kinetics of dissociation requires a description in terms of two *sequential precursors*.

The adiabatic potential-energy surface (PES) describing the interaction of O_2 with a metal surface can be constructed from three separate diabatic interactions.[9] These three diabatic surfaces extrapolate asymptotically to the $M+O_2$, $M+O_2{}^-$, and $M+2O$ dissociation limits, where M is the metal. This PES can, in principle, have three distinct wells corresponding to physisorption, molecular chemisorption formed by charge transfer from the metal to the O_2, and the atomic well formed by dissociation. Whether barriers actually exist separating these wells depends on the details of the energetics. For some metals, only the dissociated state can be isolated at low T_s.[10] In other cases, a molecularly chemisorbed state is also observed,[7] while in still other cases, all three states have been isolated.[4]

For O_2 interacting with Pt(111), both the atomic state and a molecularly chemisorbed state (resembling a negative ion) have been well characterized by a variety of surface spectroscopies.[9] No physisorbed species has been previously observed. The thermal conversion of the molecularly chemisorbed species into the atomic one, the sensitivity of the initial dissociative chemisorption probability S_0 to step density, and the dependence of S_0 on E_i and T_s all suggest that the molecularly chemisorbed state is a precursor to dissociative chemisorption,[7,8] and this has been studied in detail.[9] While the precursor mechanism dominates the adsorption dynamics at low E_i, an activated quasidirect process for dissociative chemisorption dominates at higher E_i.[11]

In this paper we report x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and thermal-desorption spectroscopy (TDS) measurements for O_2 adsorbed on a Pt(111) crystal at $T_s = 25-100$ K. The Pt(111) surface was cleaned by standard oxidation-anneal cycles and its cleanliness was monitored by the absence of any peaks other than Pt in the XPS and UPS spectra. The sample was cooled by a flowing-liquid-He cryostat and was heated either by radiation or electron bombardment from a filament behind the sample. After initial cooling, the sample could be flashed and then cooled from 900 to $\simeq 25$ K in less than 3 min. This short thermal time constant was essential for cleanliness of the sample at low T_s due to possible background water adsorption. The base pressure of the vacuum system was $\simeq 10^{-10}$ Torr. Relative temperatures were measured by a Chromel-Alumel thermocouple spot welded to the crystal. The absolute scale was calibrated by assigning the TDS peak for multilayer O_2 desorption to 30 K.[5] Dosing of O_2 was accomplished through a multichannel array molecular beam at a gas temperature of 300 K and a 45° incident angle. Relative exposures were determined by the product of the chamber pressure produced by the beam and the exposure time. TDS spectra were obtained with a differentially pumped line-of-sight mass spectrometer which was apertured to observe desorption from the center of the crystal. All XPS binding energies were measured relative to the Pt $4f_{7/2}$ peak at 71.1 eV.[12]

Adsorption of O_2 at $T_s > 150$ K produces a peak at 530.3 eV in the O 1s region of the XPS spectra, while adsorption at $45 < T_s < 130$ K produces a slight shift in the

O 1*s* peak to 530.8 eV. These spectra are in agreement with previous work,[7] and represent the atomic and molecularly chemisorbed species, respectively. However, adsorption at $T_s = 25$ K produces considerably different O 1*s* spectra, with a main peak at 535.8 eV and a weak shake-up satellite at 545.0 eV. The binding energy of the main O 1*s* peak is within 2 eV of that of gas-phase O_2, when corrected by the work function of Pt(111). This implies that the new spectra are those of a weakly interacting or physisorbed O_2 on Pt(111). A similar correlation between the binding energy of gas-phase and weakly interacting condensed (multilayer) species has been noted previously.[13] The large shifts in the XPS spectra between physisorbed and molecularly chemisorbed O_2 allow an easy separation of the two species. In contrast, the variations in the O_2-derived features of the UPS spectra were largely obscured by overlapping of the Pt *d* bands.

Figure 1 shows the integrated intensities of the two main O 1*s* spectral features as functions of O_2 exposure for $T_s = 25$ K. The peak for physisorption (open circles) clearly dominates for all exposures. The initial linear increase in this intensity with exposure indicates that S is independent of coverage Θ. The break in the slope at a relative exposure of 0.22 suggests the onset of multilayer formation. The arrow marks the intensity for saturated adsorption at $T_s = 35$ K. At this T_s desorption of multilayers readily occurs (see below), and independently confirms that a relative exposure of 0.22 corresponds to a saturated monolayer. No change in the O 1*s* binding energy could be observed between the physisorption and multilayer regimes. At $T_s = 25$ K the probability for adsorption into the chemisorbed state is < 0.05 of that into the physisorbed state. This small probability could be due to a parallel direct channel for chemisorption, or it could arise if conversion of the physisorbed species into either the molecularly chemisorbed or dissociated species occurs at steps.

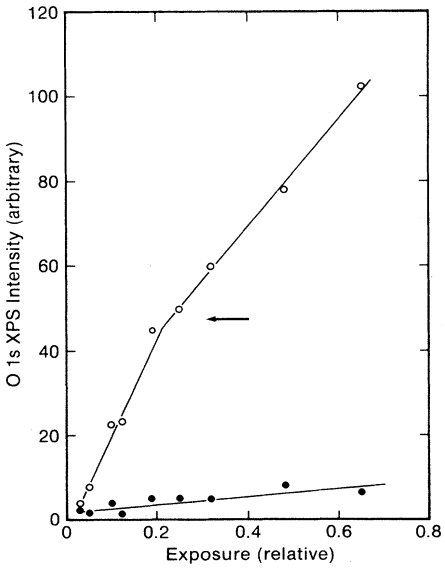

FIG. 1. O 1*s* integrated intensity vs relative exposure for adsorption at $T_s = 25$ K. The open circles are for the feature at 535.8 eV (physisorbed state) and the solid circles are for the feature at 530.8 eV (molecularly chemisorbed state).

TDS spectra as a function of exposure at $T_s = 25$ K are shown in Fig. 2. The peaks at $\simeq 130$ and $\simeq 750$ K are well known and represent desorption from the molecularly chemisorbed state and from associative desorption, respectively. The peak at 45 K is assigned to desorption from the physisorbed state, while the peak at 30 K is assigned to multilayer desorption. The latter assignment is confirmed by the unlimited increase in its intensity with exposure and its onset at a relative exposure of $\simeq 0.25$, in agreement with the XPS determination of monolayer saturation. The physisorption well depth is estimated to be 0.12 eV from the desorption temperatures, assuming a normal preexponential factor of 10^{13} for desorption. For relative exposure < 0.12, no desorption from the physisorbed state is observed. This contradicts the XPS results which indicate that the physisorbed state is the predominant species formed at 25 K, and suggests that thermal conversion to the chemisorbed state during the TDS predominates over desorption at low Θ. In a like manner, thermally induced dissociation of molecularly chemisorbed O_2 during TDS accounts for the associative desorption feature.[7]

Figure 3 shows the O 1*s* integrated intensities for the physisorbed and chemisorbed species as a function of T_s for a relative exposure of 0.1. As noted before, the physisorbed species is principally observed at low T_s. For $T_s > 45$ K only the chemisorbed species is observed and the intensity of this feature decreases approximately exponentially with T_s. In a narrow range of T_s around 38 K both species are observed simultaneously. For relative exposures ≤ 0.1 at $T_s = 25$ K the predominant physisorbed XPS feature is converted quantitatively ($\pm 10\%$) to the chemisorbed XPS feature upon anneal to 80 K. For an exposure of 0.20 only $\simeq 50\%$ of the initial intensity in the physisorbed feature is converted to the chemisorbed feature upon anneal to 80 K. These observations are in full agreement with the TDS spectra, and indicate a coverage-dependent competition between desorption of the physisorbed state and thermal conversion into the

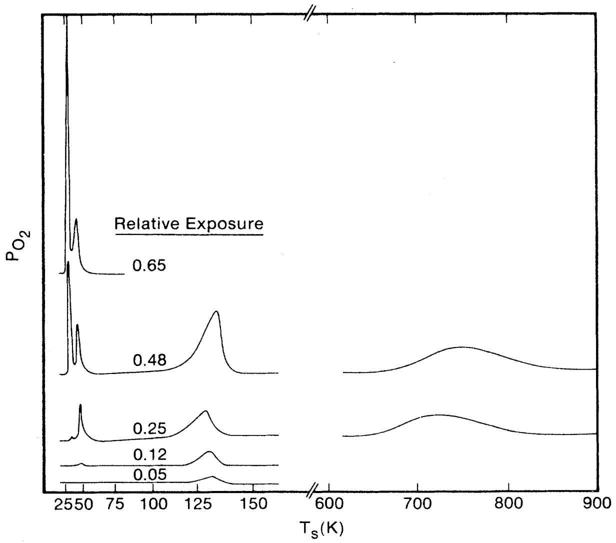

FIG. 2. TDS spectra as a function of relative exposure for adsorption at $T_s = 25$ K.

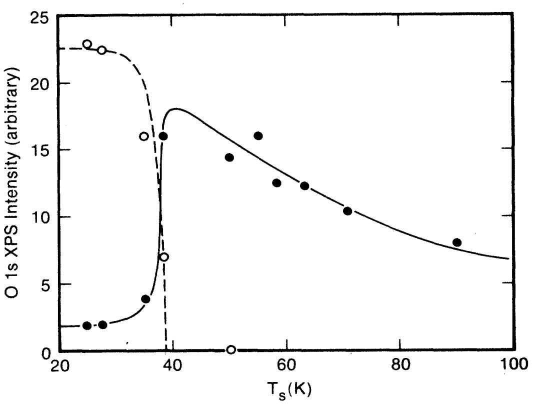

FIG. 3. O 1s integrated intensity as a function of T_s for an exposure of 0.1. The symbols are the same as in Fig. 1. The curves are fits of the precursor model to the data (see text).

molecularly chemisorbed state. Thermal conversion dominates at low Θ. The measured conversion should depend on the heating rate because of the competition between desorption and conversion, presumably decreasing at high heating rates (see kinetic parameters determined later). Only a single heating rate of $\simeq 2$ K/s was used in these studies.

These experimental results all indicate that the physisorbed state is a precursor to molecular chemisorption. This realization, coupled with the prior assignment of the molecularly chemisorbed state as a precursor to dissociation, indicates that the overall path from the gas phase to dissociation must be described in terms of two *sequential precursors*. This is represented schematically by the following kinetic scheme:

$$O_2(g) \underset{k_d}{\overset{P_{\rm trap}}{\rightleftarrows}} P \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} C \xrightarrow{k_a} 2O(a)\ ,$$

where $O_2(g)$ is the gas-phase O_2, P is the physisorbed species, C is the molecularly chemisorbed species, and $O(a)$ is the adsorbed atomic species. $P_{\rm trap}$ is the trapping probability into the physisorbed state and k_i are the various thermal rates.

For the experimental conditions of Fig. 3, $k_{-c} \approx k_a \approx 0$, and the solutions of the kinetic equations are $P(t)=P_0 \exp(-kt)$ and $C(t)=P_0(1+k_d/k_c)^{-1}[1-\exp(-kt)]$, where $k=k_d+k_c$ and P_0 is the product of exposure and $P_{\rm trap}$. A fit of these equations to the data of Fig. 3 (solid and dashed lines) yields the following parameters: $\nu_d/\nu_c=10.6$, $E_d-E_c=11.6$ meV, and $E_c=108$ meV, where ν_i and E_i are the preexponential factors and activation energies in the Arrhenius form of the various rates. These values predict $E_d=119.6$ meV, in agreement with the previous estimate from the TDS spectra. For these fits, it was assumed that $\nu_d=10^{13}$, $t=200$ s (typical time required for the XPS measurements), and $P_0=22.5$. The errors in the fit kinetic parameters are difficult to estimate. Those caused by assuming a fixed t in the analysis, i.e., the neglect in treating the XPS spectrum as a dynamically evolving event are minimal when compared to that due to experimental uncertainties. Note that for this relative exposure of 0.1, the thermal conversion of P to C occurs at $T_s<45$ K, which is where desorption occurs from the physisorbed state in the TDS. Thus, Fig. 3 is in full agreement with the separate conversion experiments. For $T_s>150$ K, where only dissociative chemisorption contributes to sticking, the full kinetic mechanism is readily solved for the sticking coefficient by making the usual steady-state assumptions for P and C, and yields $S=P_{\rm trap}/[1+(k_d/k_c)(1+k_{-c}/k_a)]$. A fit of this equation to the data in Fig. 11 of Ref. 9 yields the following parameters: $\nu_{-c}/\nu_a=20.3$ and $E_{-c}-E_a=56$ meV, where Arrhenius forms are assumed for the rates. This fit uses the kinetic parameters determined in the fit to the data of Fig. 3 and assumes $P_{\rm trap}$ is not a function of T_s. This latter assumption is somewhat suspect, but we have no way to separate this T_s dependence from the kinetic one without performing scattering experiments. The application of the sequential precursor model to fit this data yields slightly different parameters than those in Ref. 9 where a single precursor model was used to analyze the data.

A rapid decrease in S with E_i was observed previously[9,11] and attributed to the energy dependence of $P_{\rm trap}$. One difficulty noted previously in an interpretation based on a single precursor was that this decrease in S with E_i was too rapid when compared to simple models for trapping into the molecularly chemisorbed state. It was suggested[9] that one reasonable explanation for this was that trapping occurred into a more weakly bound state, and this possibility was, in large part, the motivation for the present study. The present observation of initial trapping into the physisorbed state now brings the E_i dependence of $P_{\rm trap}$ into semiquantitative agreement with the trapping models.

We have convincingly demonstrated that the physisorbed state of O_2 on Pt(111) is an intrinsic precursor to molecular chemisorption. This was accomplished by isolating this species at low T_s, observing its thermal conversion to the molecularly chemisorbed species and by observing its effect on the kinetics of adsorption in a T_s regime where the precursor is only a transient, i.e., by observing a decrease in sticking into the molecularly chemisorbed state with increasing T_s and E_i. Coupled with the previous confirmation of the molecularly chemisorbed state as a precursor to dissociative chemisorption, we have proposed a model of *sequential precursors* to describe dissociative chemisorption of O_2 on Pt(111).

The mechanism of sequential precursors is anticipated to be of considerable generality in dissociative chemisorption. Theoretical arguments have been presented previously that the PES topology described for O_2-metal interactions is generally relevant for many molecule-metal interactions,[14,15] and it is just this PES topology which can produce sequential precursors. Previous experiments of O_2 on Ag(110) (Ref. 4) are interpretable in such terms.

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