Mechanism of the Poisoning Action Of Sulfur on Catalytically Active Pd(100)

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(Received 6 June 2001; published 19 November 2001)

The influence of sulfur adsorbates on the stereodynamics of surface reactions is evaluated for the associative desorption of D_2 from Pd(100). The experimental results show that translational and rotational steering is more effective than at the clean surface, which implies that the potential energy surface (PES) for the reaction shows a larger spatial extension into the vacuum than for the clean surface. A significant polar corrugation of the PES becomes evident at high J'' states. At $J'' = 8$ a very strong coverage dependence of the alignment with $A_0^{(2)} = 0.07 \pm 0.06$ at the clean surface and $A_0^{(2)} = 0.60 \pm 0.11$ at $\Theta_S = 0.5$ monolayer is observed. This coverage dependence indicates a shift of the reaction site from the bridge to the c-type hollow position at a sulfur coverage of more than $\Theta_S = 0.25$ monolayer.

The poisoning of catalytically active surfaces by adsorbate atoms is a fundamental, but often unwanted, phenomenon. Despite many observations of this effect on surface reactions the mechanism of this poisoning action is still largely unknown. Recently, a theoretical study of the dissociation reaction of hydrogen on sulfur-covered Pd(100) was performed [1,2]. A six-dimensional potential energy surface (PES) is obtained from density functional theory with generalized gradient corrections for the exchange-correlation energy. The investigation shows that the presence of sulfur introduces reaction barriers in the entrance channel and thereby changes the dissociation probability of approaching hydrogen molecules. Different barriers evolve at various locations within the surface unit cell with heights between 100 meV at a hollow site and more than 2.5 eV atop S atoms, while at the clean Pd(100) surface the reaction paths above the bridge and hollow sites are not activated [3]. The heights decrease with lateral distance from the S atoms. Thus an increase of the sulfur coverage leads to a decrease of the number of reaction paths without and with low barrier.

Molecular dynamics calculations of the reaction have been performed on this highly corrugated PES [4,5]. It is found that, due to the high corrugation, translational steering [6] is effective up to kinetic energies of about 0.5 eV. When detailed balance arguments are invoked, the mean kinetic energies obtained from this calculation agree well with experimental observations of desorbing molecules [7]. Discrepancies arise, however, when the sticking probability is considered. The molecular dynamics calculation predicts, in good agreement with the experimental results of Burke and Madix [8], that for $\Theta_S > 0.25$ ML (monolayer) dissociative sticking essentially does not occur at thermal energies, because at higher sulfur coverage the minimum barrier in the entrance channel rises to above 2 eV. In an earlier molecular beam experiment Rendulic *et al.* [9], on the other hand, reported the observation of finite dissociative sticking at a nominal sulfur coverage of $\Theta_S = 0.5$ ML. Further, in associative desorption, molecules with kinetic energies corresponding to the calculated high barriers are not found [7]. A very sensitive test of the topology of the PES regarding its azimuthal and polar corrugation can be performed by evaluating the spatial alignment of associatively formed molecules. In this paper we present results of the first measurement of a preferred angular momentum alignment of associatively desorbing molecules from a catalytically poisoned metal surface.

The experimental setup has been described in detail previously [10]. Briefly, the experiments are performed in an ultrahigh vacuum chamber at a base pressure of less than 2×10^{-10} mbar. Order and cleanliness of the surface are determined by low-energy electron diffraction (LEED) and Auger spectroscopy. Adsorbates are removed when necessary by soft Ar^+ ion sputtering at low energy and low current density. After sputtering, the surface is allowed to anneal. For the preparation of a well-defined sulfur adlayer the palladium surface is exposed to hydrogen sulfide at $T_S = 690$ K. After dosing, the order and amount of sulfur on the surface is controlled again with LEED and Auger spectroscopy. The amount of sulfur is determined from the Auger peak ratio of sulfur (152 eV) and palladium (330 eV). For a $c(2 \times 2)$ S/Pd(100) LEED pattern Auger peak ratios of I_{152}/I_{330} between 0.65 and 0.75 are observed. We thus correlate a ratio of 0.7 to a sulfur coverage of $\Theta_S = 0.5$ ML. Deuterium atoms are supplied to the surface by atomic permeation through the bulk of the 1-mm-thick sample. The crystal can radiatively be heated between 300 and 950 K, and is kept at $T_S = 690$ K for the experiments in this paper.

Rovibrational state selective detection of desorbing molecules is performed by vacuum ultraviolet (VUV) laser induced fluorescence. D_2 is electronically excited in the $B^1\Sigma_u^+(v', J') \leftarrow X^1\Sigma_g^+(v'', J'')$ Lyman system with radiation tunable in the $\lambda = 106-110$ nm spectral range. The fluorescence is detected perpendicular to both the surface normal and the direction of the VUV laser beam. Information about the rotational alignment is obtained by measuring the fluorescence intensity with the VUV probe laser beam being polarized parallel ($I_\parallel$) and perpendicular

($I_\perp$) to the surface normal. From this measurement an anisotropy P can be derived by $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$. Following Greene and Zare [11], the intensities $I_\parallel$ and $I_\perp$ are related to alignment factors for cylindrical symmetry, $A_0^{(k)}$, via

$$I = SC \sum_{k_a, k_d, k} A_0^{(k)} \epsilon(k_a, k_d, k, 0, \Omega) \omega(k_a, k_d, k; J_i, J_e, J_f),$$

(1)

where S denotes the product of the Hönl-London factors of the participating transitions from the initial state J_i to the electronically excited state J_e by laser excitation, and, further, from this state to the final rotational state J_f by the fluorescence from the excited to the ground state. C is proportional to the population in the initial state, and ω denotes the angular momentum coupling factor, which can be obtained from Eqs. (8)–(12) in Ref. [11]. The geometrical factors $\epsilon(\Omega)$ are tabulated for the present setup in Ref. [12]. The summation runs over all possible combinations of the multipole moments k_a and k_d of the absorbed and detected photons, respectively. k is the multipole moment of the combined transition. When the emitted fluorescence is not analyzed with respect to its polarization, as in this case, one has to sum $\epsilon(\Omega)$ over the two possible polarization directions of the fluorescence. Equation (1) has to be evaluated for $I_\parallel$ and $I_\perp$. The quadrupole alignment factor $A_0^{(2)}$ is then connected to the experimentally observed fluorescence anisotropy P by [13,14]

$$A_0^{(2)} = \frac{-a + bP}{c - dP},$$

(2)

where a, b, c, and d are easily computable linear combinations of the products of $\epsilon(\Omega)$ and $\omega(k, J)$. A positive rotational alignment describes an ensemble of molecules in a helicoptering motion with their rotational axis preferentially parallel to the surface normal. Negative $A_0^{(2)}$ characterizes molecules in a cartwheeling motion having the rotational axis preferentially perpendicular to the surface normal.

The fluorescence anisotropy is determined via R and P branch lines of appropriate Lyman bands. The experimentally observed alignment of D_2 molecules desorbing in the vibrational ground state from the sulfur-covered surface ($\Theta_S \approx 0.5$ ML) is shown in Fig. 1. $A_0^{(2)}$ is found to be positive, and its value increases with the increasing rotational quantum state J''. The molecules thus desorb preferentially with their J'' vectors parallel to the surface normal, in a helicopter-type motion. For $J'' = 8$ the observed rotational alignment of $A_0^{(2)} = 0.60$ indicates that upon leaving the surface 89% of the molecules are in magnetic substates with $m_J \geq J/2$, thus being in a helicopter-type motion, while 11% are in states with $m_J < J/2$ being in a cartwheeling motion. Results of a quantum dynamical calculation [5] of hydrogen dissociation on S/Pd(100) on the six-dimensional PES
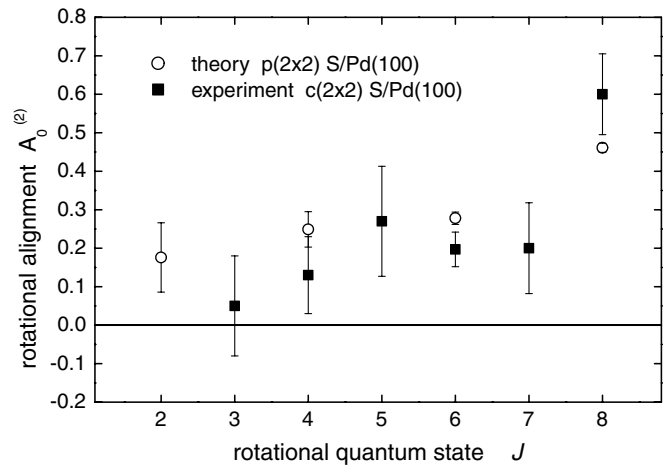

FIG. 1. Rotational alignment of D_2 desorbing from S/Pd(100). Experimental data (solid squares) are taken at a $c(2 \times 2)$ adlayer while theoretical results are calculated for hydrogen desorption from a $p(2 \times 2)$ S coverage (open circles).

are also shown in Fig. 1. These results also show a positive alignment and are generally in good agreement with the experimentally observed alignment. The low quadrupole alignment observed for the low-J'' states can be explained by an efficient rotational steering [15,16] into a favorable geometry, which is most effective at low rotational states. The PES calculated for this reaction extends above the S atoms up to 3.9 Å into the vacuum, measured from the fourfold hollow position, significantly more than a top Pd atoms at the clean surface (≈ 2 Å) [6]. The experimentally observed change of $A_0^{(2)}$ with J'' is larger than theoretically predicted. The rotational steering is thus more effective than expected from the quantum dynamical calculation on the *ab initio* PES [5], which may be caused by an even larger corrugation of the PES. The calculations are, however, performed for a $p(2 \times 2)$ reconstruction of S on Pd(100) and thus for a coverage of a quarter monolayer, while the experiments are carried out for a nominal coverage of $\Theta_S = 0.5$ ML. For rotational states up to $J'' = 6$ the alignment of D_2 molecules desorbing from the S-poisoned surface is generally lower than that for desorption from the clean surface [13,14]. This is again in accordance with the topology of the PES for the S-covered surface which generally shows a larger extension along the direction of the surface normal than that for the clean Pd(100) surface [2,3,17]. While for the clean palladium surface the rotational alignment significantly decreases from $J'' = 5$ to $J'' = 8$, such behavior is not observed for the sulfur-poisoned surface. This may be caused by the height and position of the barriers on the S-covered surface, which prevent the efficient rotational-translational energy transfer from taking place [14].

Measurements for the clean and the $c(2 \times 2)$ sulfur-covered surfaces show very different results of the quadrupole alignment for higher rotational states. In this

study a rotational alignment of $A_0^{(2)} = (0.07 \pm 0.06)$ is derived for D_2 ($J'' = 8$) desorbing from the clean surface, supporting the result of an earlier study where $A_0^{(2)} = (-0.03 \pm 0.14)$ was reported [14]. On clean Pd(100), D_2 ($J'' = 8$) thus desorbs with nearly isotropic distribution of the J'' vectors. At the sulfur-covered surface, on the other hand, a value of $A_0^{(2)} = (0.60 \pm 0.11)$ is observed, describing a strongly helicoptering motion of the molecules. Results of $A_0^{(2)}$, with dependence on the sulfur coverage, are shown in Fig. 2. The rotational alignment increases at first nearly linearly with increasing sulfur coverage up to a value of $A_0^{(2)} = 0.47 \pm 0.07$ at $\Theta_S = 0.25$ to 0.3 ML and then saturates at $A_0^{(2)} = 0.6$ at $\Theta_S = 0.5$ ML. The alignment of $A_0^{(2)} = 0.47$ at $\Theta_S = 0.25$ ML is in excellent agreement with that calculated quantum dynamically for the $p(2 \times 2)$ sulfur-covered Pd(100) surface [5]. The larger alignment observed at $\Theta_S = 0.5$ ML implies that the polar corrugation is higher than at $\Theta_S = 0.25$ ML, as theoretically expected.

A theoretical analysis of the poisoning mechanism of sulfur has been performed only for certain highly symmetric atomic S adlayers [2]. Also the quantum dynamic calculation of the association reaction has been carried out [2] only on the symmetric $p(2 \times 2)$ S/Pd(100) surface. When the sulfur coverage is increased from zero up to $\Theta_S = 0.5$ ML, not only highly symmetric adsorption sites and overlayer structures are occupied by the S atoms, but initially a random distribution of atoms is formed. This situation has, however, not yet been treated by a rigorous theoretical analysis. In order to assess the poisoning action of S atoms we performed a Monte Carlo simulation of the available reaction sites for the deuterium association reaction as a function of sulfur coverage [18]. This may be considered a crude simplification of the problem; however, the *ab initio* PES shows very different activation barriers for typical sites within the surface unit cell [2]. The lowest barriers of $E_b = 100$ and 150 meV are reported for p-type hollow and bridge sites, with next-nearest neighbor S atoms, respectively, while for c-type hollow sites a barrier of $E_b = 2.5$ eV is calculated. In the simulation a reaction at each site is assumed to be associated with a specific population distribution $\sigma_\alpha(m_J)$ of the m_J states. The total m_J population distribution in the desorption flux averaged over all reaction sites is then given by

$$\sigma_{\text{tot}}(m_J) = \sum_\alpha \nu_\alpha n_\alpha \sigma_\alpha(m_J), \qquad (3)$$

where $\nu_\alpha \sim \exp(-E_{b\alpha}/k_B T)$ takes the barrier height $E_{b\alpha}$ at each site into account and n_α describes the relative abundancy of the reaction channel α. The rotational alignment is then obtained from

$$A_0^{(2)} = \sum_{m_J} \left(\frac{3m_J^2}{J(J+1)} - 1 \right) \sigma_{\text{tot}}(m_J). \qquad (4)$$

In all cases considered, reaction on patches of sulfur-free palladium and at sites in the vicinity of S atoms is taken into account. For the clean areas a parabolic m_J population distribution σ_{clean} derived from the observed alignment of $A_0^{(2)} = 0.07$ is used. For the fully developed S adlayers, σ_{poisoned} is taken either from theoretical calculations [5] or from the experimental data observed in this study, depending on the coverage and the specific model. Again, only $A_0^{(2)}$ is used to characterize the m_J population distribution. An extensive discussion of the procedure and results for a variety of different models is given elsewhere [18].

In Fig. 2 the results of three different but typical models for the active reaction site are shown. If the reactions occur only at clean areas and at hollow sites separated from an S atom only by a Pd-Pd bridge (c-type hollow sites), model 1, a rapid rise of the alignment with increasing S coverage is obtained (dashed line in Fig. 2). Already at $\Theta_S = 0.2$ ML the final value of $A_0^{(2)} = 0.6$ is reached. This model obviously does not match the experimental results, which is also not expected due to the high barrier at this site. In a second model, the reaction at bridge sites which are twice as abundant as hollow sites is considered. Again, reactions at noninfluenced sites and sites influenced by S atoms are taken into account. Bridge sites directly adjacent to an S atom show extremely high barriers for reaction [2] and thus do not contribute. For bridge sites influenced by two next-nearest neighbor S atoms an alignment of $A_0^{(2)} = 0.5$ is taken. Both the present experimental observation at $\Theta_S = 0.25$ ML and the theoretical calculation for the $p(2 \times 2)$ S-covered surface yield this value. For bridge sites influenced by just one S atom a value of $A_0^{(2)} = 0.35$ is calculated; see Ref. [18]. The alignment obtained for this model 2 as a function of S coverage is shown as a dotted line in Fig. 2. Up to $\Theta_S = 0.4$ ML the experimental results are very well described
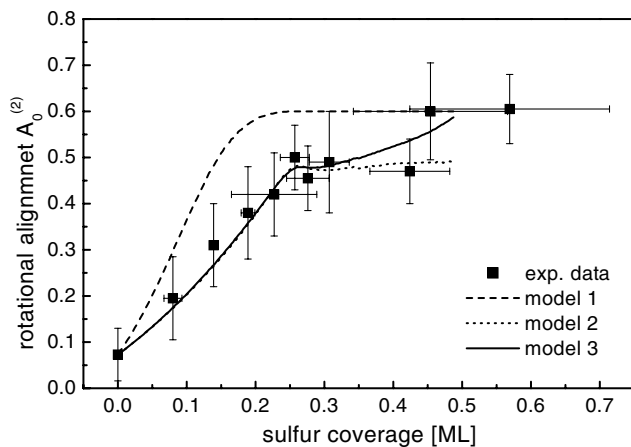

FIG. 2. The rotational alignment of D_2 ($v'' = 0, J'' = 8$) as a function of sulfur coverage. The experimental results are represented by solid squares. The model calculations describe reactions at different sites: c-type hollow sites (model 1), bridge sites (model 2), and a combination of both (model 3).

by this model. Only the highest value of $A_0^{(2)} = 0.6$ at $\Theta_S = 0.5$ ML cannot be reproduced. However, at this coverage, reactive bridge sites are no longer available. Therefore only a model which considers both reactions at bridge and at c-type hollow sites may describe completely the experimentally observed alignment. The solid line in Fig. 2 shows the result of such a simulation. Up to $\Theta_S = 0.25$ ML the reaction occurs at the bridge sites as before, and the solid line coincides with that of model 2. Different from model 2, the simulated alignment now continues to increase slowly up to $A_0^{(2)} = 0.6$ at $\Theta_S = 0.5$ ML. Above $\Theta_S = 0.25$ ML the reactive bridge sites cease to exist and the reaction has to occur at c-type hollow sites. This is also reflected in the coverage dependence of the rotational alignment. The c-type hollow sites contribute to the reaction only at sulfur coverages higher than $\Theta_S = 0.25$ ML. This behavior is not surprising, because at the c-type hollow sites a barrier height of $E_b \sim 2.5$ eV has to be surmounted, compared to a height of only 150 meV at the reactive bridge sites [2]. Thus, only at high-S coverages, when bridge sites are no longer available, do reactions at c-type hollow sites contribute to the associative desorption of D_2. It may be noted that reactions at p-type hollow sites, despite showing the lowest barrier, are not significant at any coverage. They represent a discernible fraction of reaction sites influenced by S atoms only at low coverages up to 0.2 ML; however, their fraction never exceeds 9% of the available reaction sites [18].

The coverage dependence of the rotational alignment yields insight into the microscopic mechanism of the poisoning action of sulfur adlayers on catalytically active metals, in this case Pd(100): energetic barriers against the reaction evolve, the polar corrugation significantly increases, while the azimuth remains small. That is different from another system with high barriers, clean Cu(111), where the azimuthal corrugation was found to be large [19,20]. Sulfur acts locally, thus at low coverages the catalytic reaction on clean patches may still prevail. With increasing sulfur coverage the reaction site changes within the surface unit cell from the bridge to the c-type hollow site, but only when reactive bridge sites cease to exist. Quantum dynamical calculations [5] of the reaction dynamics on a six-dimensional *ab initio* potential energy surface [2] agree well with the present experimental observations, although it seems that the corrugation of the potential is even larger than that of the *ab initio* PES.

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