

# Mechanism of Poisoning the Catalytic Activity of Pd(100) by a Sulfur Adlayer

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## Abstract

The modification of the potential-energy surface (PES) of H<sub>2</sub> dissociation over Pd(100) as induced by the presence of a (2×2) S adlayer is investigated by density-functional theory and the linear augmented plane wave method. It is shown that the poisoning effect of S originates from the formation of energy barriers hindering the dissociation of H<sub>2</sub>. The barriers are in the entrance channel of the PES and their magnitude strongly depends on the lateral distance of the H<sub>2</sub> molecule from the S adatoms.

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The modification of the chemical reactivity and selectivity of metal surfaces by adsorbates is a most important ingredient of catalysis. Nevertheless, the understanding of the microscopic mechanism of how adatoms promote or poison certain reactions is grossly incomplete. Hydrogen dissociation has become the benchmark system for theoretical and experimental studies of a simple chemical reaction, and much progress has been made in developing a picture of how H–H bonds are broken on clean metal surfaces, and how new bonds between the hydrogen atoms and the surface are formed [1–8]. However, a quantitative study of the modifications of the potential-energy surface (PES) of hydrogen dissociation on an adlayer-covered surface has not been addressed by theory so far.

The Pd(100) surface is probably the best-suited substrate for an investigation of the mechanism of poisoning a catalytic reaction, because many experimental and theoretical studies exist and form a good body of information to compare to. At the clean Pd(100) surface hydrogen dissociates spontaneously, i.e. dissociation pathways exist which have no hampering energy barrier [8–12]. However, when the surface is covered with sulfur the H<sub>2</sub> sticking probability is reduced by several orders of magnitude [9–11]. The mechanism actualizing this huge poisoning effect is not known. Using density functional theory calculations we show in this Letter that adsorbed sulfur builds up energy barriers which hinder the dissociation, and that, because these energy barriers are located in the entrance channel of the dissociation-reaction pathway, this hinderance is particularly effective.

The influence of adsorbed sulfur on the dissociative adsorption of H<sub>2</sub> has been studied using molecular beam experiments [10], temperature programmed desorption (TPD) of hydrogen molecules adsorbed at  $T = 110$  K [11], and energy resolved studies of molecules desorbing from the surface after penetrating a thin Pd film [9]. The results show that with increasing sulfur coverage  $\Theta_S$  the initial sticking coefficient of H<sub>2</sub> strongly decreases [10,11]. This is true in particular for molecules with low kinetic energy [10] ( $\lesssim 0.1$  eV), as these can adsorb only if non-activated dissociation pathways exist and are accessible. For  $\Theta_S=0.25$  the initial sticking coefficient of molecules with low energies is approximately two orders of magnitude smaller than that for the clean surface [10,11] indicating that for this sulfur cov-

erage non-activated dissociation is nearly completely hindered. When the sulfur coverage is increased the  $H_2$  sticking coefficient reduces even further (at  $\Theta_S = 0.5$  it is about three orders of magnitude smaller than at the clean surface). In addition to this dramatic decrease of the initial sticking coefficient TPD studies [11] observed a decrease of the hydrogen saturation coverage with increasing  $\Theta_S$ . Burke and Madix [11] therefore concluded that sulfur adatoms substantially reduce the hydrogen adsorption energy at sites in their vicinity making these positions unstable against associative desorption. This was also the conclusion of earlier permeation studies of Comsa et al. [9].

Theoretical studies have addressed this problem as well. Feibelman and Hamann [19,20] suggested that the poisoning effect of sulfur is related to the S induced change of the density of states (DOS) at the Fermi level (see also Ref. [21]). A different mechanism which could give rise to a modification of the reactivity by adlayers is the interaction of the  $H_2$  molecule with the adlayer induced electrostatic field [22,23]. In all this work it remained open, how the described effect will modify the hydrogen sticking (by blocking adsorption sites for atomic hydrogen or by building up energy barriers along the dissociation-reaction pathway of  $H_2$ ).

In a previous paper [13] we reported density functional theory calculations of the adsorption energy and geometry of hydrogen at different adsorption sites on clean Pd(100) and on Pd(100) covered with a  $(2 \times 2)$  S adlayer ( $\Theta_S=0.25$ ). The calculations show that the presence of a  $(2 \times 2)$  S adlayer moderately decreases the hydrogen adsorption energy, but the reduction is not sufficient for a strict blocking of hydrogen adsorption sites [13]. The poisoning effect of S is not governed by a decrease of the adsorption energy alone and a complete understanding of poisoning by adsorbed sulfur requires a calculation of the PES for hydrogen dissociation in the presence of a sulfur adlayer. In the present paper we report and discuss such calculations. They were performed using density-functional theory with the generalized gradient approximation (GGA) [14] for the exchange-correlation functional. The full potential linear augmented plane wave (FP-LAPW) method [15,16] is employed for solving the non-relativistic Kohn-Sham equations. In the interstitial region the wave functions are represented by a plane wave expansion up to  $E_{\text{cut}}=11$  Ry, and plane waves up to

$\tilde{E}_{\text{cut}}=169$  Ry are taken into account for the potential representation. For the  $\mathbf{k}$ -integration we used 32 uniformly-spaced points in the two-dimensional Brillouin zone of the  $(2\times 2)$  surface unit cell. We used a supercell geometry and modeled the metal substrate by three-layer slabs which are separated by a 10 Å thick vacuum region. The adsorbates are placed at both sides of the slab. The geometry of the Pd(100)  $(2\times 2)$  S surface is determined by total-energy minimization [13]. This geometry is kept fixed when the H<sub>2</sub> dissociation pathway is studied, which is the appropriate and plausible approach, because the mass mismatch of the different atoms is significant. The most severe approximations in our studies are the thinness of the metal slab. For studies of adsorption energies an accurate treatment of a fcc (100) surface typically requires to take at least five or seven layers into account, when an accuracy of adsorption energies of about 0.1 eV is aimed for. In the present study of hydrogen dissociation we encounter the more fortunate situation, that the PES, which is presented in Fig. 2, and which corresponds to a three-layer Pd slab, is found to be indeed meaningful. This is concluded from calculations at the geometries of the energy barriers and adsorption sites of Fig. 2 using a five- and a seven layer slab (see Table 1). The resulting energies and forces show that the topology of the PES shown in Fig. 2 is correct and that the energy barriers change by less than 0.05 eV when a thicker Pd slab is used. We believe that the high number of valence electrons of Pd and the fact that the Fermi level cuts the *d* band such that the possibility for low energy electron-hole excitations still exists, are responsible for the fortunate situation that the PES of hydrogen dissociation on a Pd crystal is well described by that at thin Pd slabs.

Figure 1 shows the surface unit cell for a sulfur coverage  $\Theta_{\text{S}}=0.25$ . Out of the three hollow sites per unit cell only two are distinct. They are denoted  $\mathbf{h}_1$  and  $\mathbf{h}_2$ . The PES for the H<sub>2</sub> dissociation at a rigid substrate is six dimensional. However, the influence of the  $(2\times 2)$  sulfur adlayer on H<sub>2</sub> dissociation on Pd(100) is well presented by three decisive cuts through the PES (see Fig. 2). These, so-called elbow-plots, are defined as follows. The center-of-mass of the two hydrogen nuclei is fixed over a surface hollow site, and the H–H

axis is kept parallel to surface, which is the energetically most favorable orientation. Then the energy is displayed as a function of the H–H interatomic distance and the height of the H–H center of mass above the surface. Figure 2a shows the results for the dissociation over the hollow site at the clean surface, and Figs. 2b,c are for the  $(2\times 2)\text{S}/\text{Pd}(100)$  substrate at the hollow site  $\mathbf{h}_1$  and the hollow site  $\mathbf{h}_2$ , respectively. The different geometries of these different cuts through the PES are given in the insets. The adsorption height of sulfur adatoms on the  $(2\times 2)$  S covered Pd(100) surface is calculated as  $Z_S=1.24 \text{ \AA}$  above the top Pd layer [13]. The PES of  $\text{H}_2$  dissociation on clean Pd(100) in Fig. 2a gives an example of non-activated dissociation, where the two hydrogen nuclei may follow an always downhill dissociation pathway [8]. The presence of a  $(2\times 2)$  S adlayer on Pd(100) ( $\Theta_S=0.25$ ) changes the dissociation process significantly. The lowest-energy dissociation pathways at the sulfur-covered surface in Fig. 2b,c have energy barriers of 0.1 eV and 0.6 eV. In addition to the dissociation over the hollow sites (Fig. 2b,c), we also considered the dissociation geometry where the center-of-mass of the molecule is situated over the bridge site  $\mathbf{b}$  and the two H atoms point towards the hollow sites  $\mathbf{h}_1$  and  $\mathbf{h}_2$ . At the clean surface this dissociation pathway is also non-activated and the decrease of the potential energy along the dissociation pathway is even steeper than for dissociation over the hollow site [8]. We found that upon sulfur adsorption the dissociation of  $\text{H}_2$  becomes an activated process in this geometry too (the energy barrier is 0.15 eV). In addition to the formation of energy barriers for different adsorption pathways the sulfur adlayer reduces the adsorption energies for atomic hydrogen (see Fig. 2 at larger  $d_{\text{H-H}}$  values). The latter result was discussed in detail in Ref. [13]. The PES shown in Fig. 2 affirms that the poisoning effect of sulfur adatoms for hydrogen dissociation on Pd(100) are determined by the sulfur-induced formation of energy barriers. It is evident and in fact plausible that the height of the barrier strongly depends on the lateral distance of the hydrogen molecule from the sulfur adatoms.

At a first glance it is astonishing that such small energy barriers, which are induced by the sulfur adsorption, can have the pronounced effect on the dissociative adsorption of  $\text{H}_2$  which was alluded to in the introduction. However, the important theoretical result is not

just the heights of the barriers, but also their location. The theory predicts that the energy barriers, which are induced by S adsorption, are in the entrance channel at a height above the top Pd layer of  $Z = 1.8$  and  $1.4 \text{ \AA}$ , and  $d_{\text{H-H}} = 0.78 \text{ \AA}$ . Thus, we encounter a different situation to that found, e.g. for clean Cu and NiAl surfaces [4–6]. The location of the energy barrier in the entrance channel implies (see e.g. Ref. [17]) that for the impinging  $\text{H}_2$  molecule the H–H bond remains practically intact up to the position of the top of the barrier. As a consequence, vibrational and translational degrees of freedom of the  $\text{H}_2$  molecule couple only weakly and the vibrational energy of the impinging  $\text{H}_2$  cannot be utilized to overcome the barrier. For sulfur coverages up to  $\Theta_{\text{S}}=0.25$  we therefore predict that the sticking coefficient shows no strong dependence on the  $\text{H}_2$  vibrational state. We also note that the energy barrier in the entrance channel implies a significant reduction of sticking of low energy (thermal) molecules. The investigations of  $\text{H}_2$  dissociation at clean Pd(100) [8,18] had shown that the large sticking coefficient of  $\text{H}_2$  molecules with energy below about 0.2 eV at Pd(100) results in part from the steering of molecules with initially unfavorable orientations of the molecular axis towards the non-activated dissociation pathways. In the case that energy barriers are induced along those pathways, the phase space of initial conditions that result in a dissociation of low energy hydrogen molecules, and hence the sticking coefficient, shrinks drastically, because in addition to the hindered dissociation along the particular pathway the steering mechanism [18] is also disabled.

In order to identify the microscopic origin of the poisoning effect of sulfur in more detail we analyze the surface electronic structure. At first we recall that the trends of the reactivity of clean metal surfaces for the dissociative adsorption of hydrogen molecules could be explained within a simple chemical bonding model [6]. At noble and transition metal surfaces the presence and magnitude of a dissociation barrier is mainly governed by the direct interaction of the closed-shell orbital structure of the  $\text{H}_2$  molecule with the metal  $d$  states. This interaction is attractive as long as the bonding states of the  $\text{H}_2 \sigma_{\text{g}}$  and the  $\text{H}_2 \sigma_{\text{u}}$  levels with the metal  $d$  band dominate the energetics. The interaction becomes repulsive, i.e. an energy barrier is built up, when the corresponding antibonding states become occupied by

a critical amount. These antibonding states have their main weight just above the  $d$  band edge. Thus, for a true transition metal these antibonding states are practically empty, and a small or vanishing energy barrier results [6,13,8].

In Fig. 3 the densities of states (DOS) at three different lateral positions of the  $\text{H}_2$  molecule are compared; the height above the surface and the H–H distance is taken to be the same ( $Z=1.6 \text{ \AA}$ ,  $d_{\text{H-H}}=0.79 \text{ \AA}$ ). It is evident that the sulfur  $p$  orbitals strongly interact with the Pd  $d$  states, giving rise to a narrow peak just below the Pd  $d$  band edge (at  $\epsilon - \epsilon_{\text{F}} = -4.8 \text{ eV}$ ) and a broad band at higher energies, which has substantial DOS at the Fermi level (see middle panels of Figs. 3b and c). The  $d$  band at the surface Pd atoms is considerably broadened due to the interaction with the S atoms (see lower panels of Figs. 3b and c). The density of  $d$  states close to the Fermi energy is reduced by  $\approx 50 \%$  compared to clean Pd(100) but the value of the DOS at  $\epsilon_{\text{F}}$  remains substantial.

The formation of a small energy barrier for hydrogen dissociation over the  $\mathbf{h}_1$  hollow site due to the presence of the  $(2 \times 2)$  S adlayer can be understood by extending the reactivity model discussed above. A comparison of the DOS at the H atoms in Fig. 3a and b reveals that at the sulfur-covered Pd surface the interaction of the  $\sigma_{\text{g}}$  orbital of the  $\text{H}_2$  molecule with the broadened band of the surface Pd  $d$  states results in a broader distribution of states with an increased weight below the Fermi level. Consequently we encounter a larger occupation of  $\text{H}_2$ –substrate antibonding states. Thus, the repulsive contribution to the  $\text{H}_2$ –surface interaction is increased and thus may give rise to the formation of an energy barrier. A  $\text{H}_2$  molecule hitting the surface over the hollow site  $\mathbf{h}_1$  or  $\mathbf{h}_2$  interacts with the same surface Pd atoms and, hence, the formation of a large barrier over the hollow site  $\mathbf{h}_2$  cannot be explained by sulfur-induced modification of the electronic structure at surface Pd atoms. Intense peaks of the DOS at the H atoms for the configuration where the  $\text{H}_2$  molecule dissociates over the hollow site  $\mathbf{h}_2$  (Fig. 3c) are found at energies of the sulfur related bonding state at  $-4.8 \text{ eV}$  and at the Fermi level. In addition there is a significant contribution of the sulfur adatom to the bonding states of the  $\text{H}_2$   $\sigma_{\text{g}}$ –surface interaction at  $-7 \text{ eV}$  (see arrows in Fig. 3c). These features clearly indicate that the  $\text{H}_2$  molecule interacts

*directly* with states localized at the sulfur adatom. We conclude that the large energy barrier for H<sub>2</sub> dissociation over the hollow site **h<sub>2</sub>** is caused mainly by the repulsion between the occupied H<sub>2</sub>  $\sigma_g$  state and the spatially localized S–Pd bonding band at  $-4.8$  eV. Direct H<sub>2</sub>–S interactions become important because due to the large adsorption height of the S adatoms H–S and H–Pd distances are comparable for larger heights of the H<sub>2</sub> molecule in front of the surface. Indeed, as seen in Fig. 2c the top of the energy barrier is situated at values of  $Z$  close to the sulfur adsorption height.

In conclusion, our DFT calculations of the modification of the PES of H<sub>2</sub> dissociation on Pd(100) due to the presence of a (2×2) sulfur adlayer show that the poisoning effect of sulfur adatoms is governed by the formation of energy barriers which are situated in the entrance channel of the PES. We identified the direct interaction of the H<sub>2</sub> molecule with states at the S adatom as the origin of the large barriers found over hollow sites neighboring the S adatoms; at larger center-of-mass distances to the S adatom the poisoning effect is weaker and results from the modification of the local electronic structure at the surface Pd atoms.



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TABLES

slab	Fig. 2a $E_{\text{ad}}$	Fig.2b $E_{\text{b}}   (F_d, F_Z)$	Fig. 2c $E_{\text{b}}   (F_d, F_Z)$	Fig. 2b,c $E_{\text{ad}}$
3	-0.47	0.09   (-66,-38)	0.56   (-49,-41)	-0.21
5	-0.52	0.10   (-97,-54)	0.59   (-72,-69)	-0.22
7	-0.54	0.09   (-90,-64)	0.59   (-33,-90)	-0.22

TABLE I. Dependence of the barrier heights,  $E_{\text{b}}$ , and adsorption energy at bridge sites,  $E_{\text{ad}}$ , on the thickness of the substrate Pd slab. The positions refer to those of the three-layer calculation as given in Figs. 2a, 2b, and 2c. Units are in eV per  $\text{H}_2$  molecule. Included are the calculated forces between between the hydrogen atoms  $F_d$  and between the  $\text{H}_2$  molecule and the surface  $F_Z$  in units of  $\text{meV}/\text{\AA}$ . Positive values of the force components are directed toward an increase of  $d_{\text{H-H}}$  or  $Z$ .

FIGURES

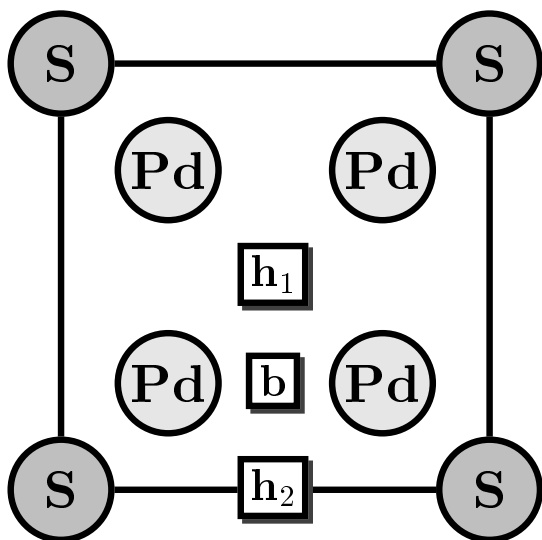


FIG. 1. Surface geometry of  $(2 \times 2)$ S on Pd(100) with the two different hollow sites labeled as  $h_1$  and  $h_2$  and the bridge site  $b$ .

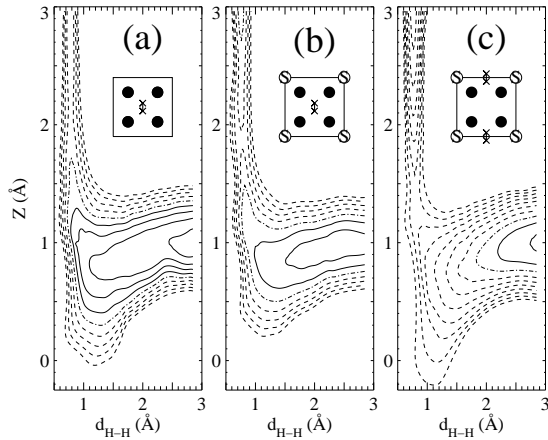


FIG. 2. Cuts through the six-dimensional potential-energy surface (PES) of  $\text{H}_2$  dissociation over the surface hollow site of the clean Pd(100) surface (a) and over the hollow sites  $\mathbf{h}_1$  and  $\mathbf{h}_2$  (c) at  $(2 \times 2)\text{S}/\text{Pd}(100)$ . The energy contours are displayed as a function of the H-H distance,  $d_{\text{H-H}}$ , and the height of the H-H center of mass above the center of the top Pd layer,  $Z$ . The geometry of each dissociation pathway is indicated in the inset. Positive values of the potential energy are given by dashed, negative ones by solid lines. The zero of energy is given as a dot-dashed line. The interval between adjacent contours is 0.1 eV.

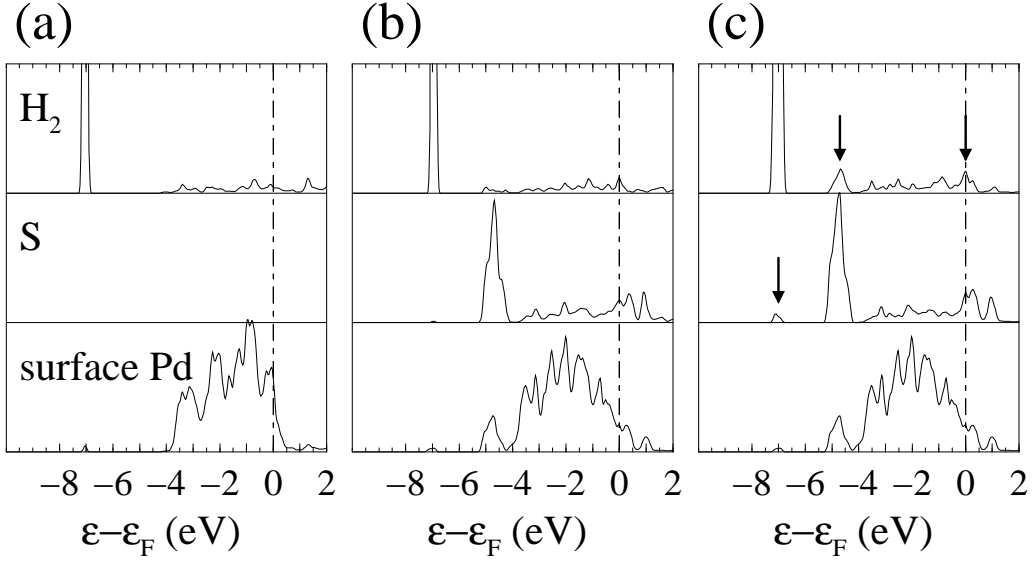


FIG. 3. Density of states (DOS) for a  $\text{H}_2$  molecule situated over a hollow site at clean Pd(100) (a) and over the hollow sites  $\mathbf{h}_1$  (b) and  $\mathbf{h}_2$  (c) at  $(2 \times 2)$  S covered Pd(100). The Figure corresponds to a particular point ( $Z=1.6 \text{ \AA}$ ,  $d_{\text{H-H}}=0.79 \text{ \AA}$ ) along the reaction pathways shown in Fig. 2. Given is the local DOS at the H atoms, the S adatom, and the surface Pd atoms within the respective muffin-tin sphere.