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Poisoning of Pd(100) for the dissociation of H_2: a theoretical study of co-adsorption of hydrogen and sulphur

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Abstract

The presence of sulphur adatoms on Pd(100) is known to hinder the dissociative adsorption of hydrogen. Using density-functional theory we studied the adsorption of hydrogen on clean and sulphur precovered Pd(100) surfaces. The results show that the poisoning effect of sulphur is not caused by a strict blocking of hydrogen adsorption sites in the vicinity of S adatoms. For a (2×2) sulphur adlayer (coverage $\theta_S = 1/4$) hydrogen adsorption remains an exothermic process for all surface hollow sites not occupied by sulphur. The blocking of hydrogen adsorption happens only for higher sulphur coverages. We conclude that the poisoning of Pd(100) is a combined effect of the formation of energy barriers hampering the H_2 dissociation *and* a modest decrease of the adsorption energy in the vicinity of the sulphur adatoms.

Keywords: Hydrogen; Palladium; Sulphur

Adsorbates will often modify the chemical reactivity of metal surfaces. In particular group Vb and VIb elements, such as phosphorus, sulphur, and oxygen are known to poison transition metal surfaces for many catalytic processes [1–3]. Although the facts are known for decades, the microscopic understanding of the poisoning action is still grossly incomplete. A benchmark system for the poisoning of transition metal surfaces is the adsorption of sulphur on Pd(100) and its influence on the dissociative adsorption of H_2.

At the clean Pd(100) surface H_2 dissociates spontaneously [4–7], i.e., dissociation is not hampered by an energy barrier. In order to explain the dependence of the initial sticking probability [6] of an H_2 beam on the angle of incidence and the molecules kinetic energy, and to explain the observed vibrational heat of desorbing H_2 molecules [8] it has been assumed that in addition to non-activated reaction pathways also activated reaction pathways with an energy barrier are present already at the clean surface [6,8]. In view of the fact that the relevant potential energy surface (PES) is six-dimensional, this idea is indeed plausible.

A density-functional study of Feibelman [9] of a H_2 molecule at different heights in front of Rh(100) obtained significant variations of the total energy with the orientation of the molecule in the surface unit cell, and indicated the possibility of non-activated dissociation pathways.

When the surface is covered with sulphur the description of the interaction with H_2 is even qualitatively unclear. Based on different experimental studies competing explanations have been suggested. Molecular beam studies show that the initial sticking prob-

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ability of H_2 molecules scattered at Pd(100) strongly decreases with increasing coverage of preadsorbed sulphur [6,7]. This is in particular so for low beam energies, at which the sticking is most sensitive to the presence of non-activated reaction pathways. These results were interpreted as such that with increasing sulphur coverage the character of the dissociative adsorption process shifts towards that of an activated reaction [6] in which the dissociation process of H_2 is governed by energy barriers in front of the surface.

Adsorption studies at $T = 110$ K showed that the hydrogen saturation coverage decreases linearly with the amount of preadsorbed sulphur [7]. Furthermore, the analysis of the thermal adsorption of hydrogen shows that the initial sticking probability (averaged over the thermal distribution of H_2 gas phase molecules at $T = 110$ K) also decreases linearly with the sulphur coverage. In contrast to the above mentioned molecular beam scattering these results were explained in terms of a blocking of surface hollow sites neighboring sulphur adatoms. The term "blocking" refers to a substantial reduction of the adatom total energy, making those sites unstable against associative desorption of hydrogen [7]. Sulphur adatoms occupy the same surface hollow adsorption sites as hydrogen [4,10,11] and make at least one hollow site inaccessible for hydrogen adsorption; but it was suggested [7] that the actual surface area deactivated per sulphur adatom is larger comprising about four hydrogen adsorption sites.

A somewhat similar model was proposed by Comsa et al. [5] who suggested that sulphur atoms strongly decrease the hydrogen adsorption energy E_{ad} in their surrounding and that the occurrence of desorbing deuterium molecules with higher kinetic energies is due to a desorption and association of atoms leaving directly from subsurface sites. We note that the latter process may well be a result of their special experimental conditions (deuterium permeation).

In order to determine the S-induced change of the hydrogen adsorption energy and to achieve a better understanding of the poisoning action of sulphur for hydrogen dissociation we performed density-functional calculations of the adsorption energy and geometry of hydrogen at different adsorption sites on clean Pd(100) and on Pd(100) precovered with a (2×2) and c(2×2) sulphur adlayer. The calculations were performed using the full-potential linear augmented-plane wave method (FP-LAPW) [12], which has been enhanced by the calculation of forces [13]. By this the atomic positions of stable and metastable geometries can be calculated efficiently. A proper description of H_2 bonding and dissociation requires the application of the generalized gradient approximation (GGA) [14] for the exchange-correlation functional [15–17]. However, for the description of chemisorbed hydrogen, due to the more delocalized H-metal wave functions, already the local-density approximation gives reliable results. This is confirmed by our calculations which show that energy differences for hydrogen adsorption into hollow and subsurface sites on the clean surface agree within 0.04 eV for the LDA [18] and GGA. For the below reported adsorption geometries and energies we used the LDA, and for the calculations of the free molecule and the PES we employed the GGA. The FP-LAPW wave functions in the interstitial region are represented using a plane wave expansion up to $E_{cut} = 11.6$ Ry, and for the potential representation it is necessary to take into account plane waves up to $\tilde{E}_{cut} = 121$ Ry. Inside the muffin-tin spheres the wave functions are expanded in spherical harmonics with $l_{max} = 10$, and non-spherical components of the density and potential are included up to $\tilde{l}_{max} = 3$. Taking into account the components up to $\tilde{l}_{max} = 4$ changes the adsorption energies by only 10 meV. For the k-integration we used 64 uniformly spaced points in the two-dimensional Brillouin zone corresponding to the c(2×2) surface unit cell. All calculations were performed non-relativistically. The metal substrate is modeled by five layers separated by a 10 Å thick vacuum region. Increasing the substrate thickness to seven layers changes the total energy results by less than 50 meV. Hydrogen and sulphur atoms are adsorbed at both sides of the slab. Typically we allowed all adatoms and the top metal layer to relax. Only for the calculated PES we used a rigid substrate because due to the large mass ratio between Pd and H the substrate will not change during the scattering event. For the PES calculation we employed a super cell with a c(2×2) surface structure and a three layer thick substrate slab. Tests showed that increasing the surface cell or the substrate thickness changes the H_2 potential energies by less than 50 meV.

Fig. 1 displays a two-dimensional cut through the six-dimensional PES of H_2 dissociation and adsorption on clean Pd(100). The center of the molecule is taken

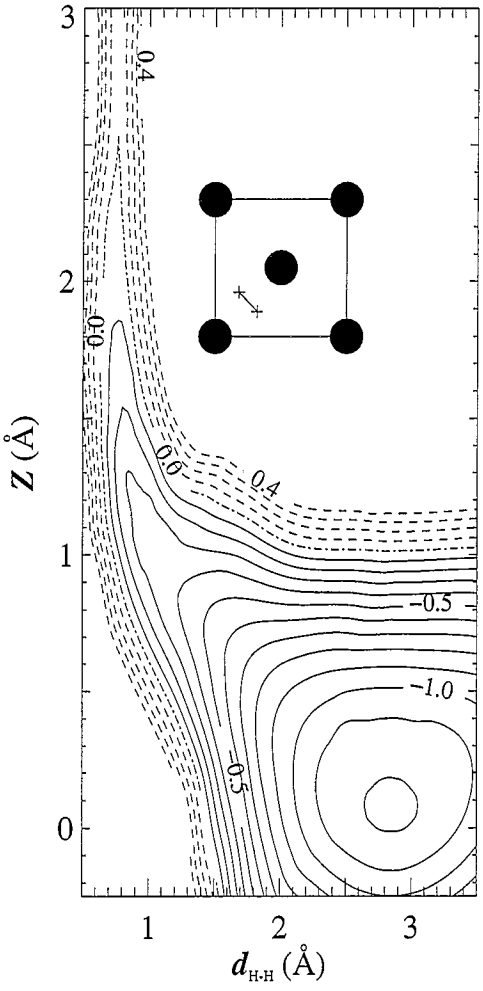

Fig. 1. Cut through the six-dimensional potential energy surface (PES) of a H_2 molecule in front of Pd(100). We display an "elbow plot" where Z is the height of the H_2 center of mass over the surface, and d_{H-H} is the distance between the two hydrogen atoms. The cut is defined by keeping the molecule parallel to the surface at an azimuthal orientation shown in the inset. The units are eV and the interval between adjacent contour lines is 0.1 eV.

over the bridge sites and the molecular axis is parallel to the surface.

The figure confirms that the dissociation of H_2 is non-activated, i.e., the potential energy of the H_2 molecule decreases monotonously along the reaction pathway when approaching the surface. Our more detailed analysis [19] shows that the six-dimensional PES of H_2 dissociation exhibits several, geometrically different non-activated dissociative adsorption channels, but pathways of activated adsorption exist as well. The number of H_2 molecules that proceed via those non-activated dissociative adsorption channels is determined by the capability of the molecules to reorientate and to follow such a pathway. As a consequence, the initial sticking probability is expected to depend sensitively on the H_2 initial energy which is consistent with the experimental results [6].

Adsorption of sulphur will modify the PES of Fig. 1. In view of the above discussion of experimentally derived ideas on the poisoning action of sulphur there might be two limiting possibilities: (*i*) sulphur will mainly modify the PES in the region of the H adsorption geometry (Z = 0.11 Å, d_{H-H} = 2.85 Å), and (*ii*) sulphur will change the reaction path and/or its energetics. If the first case were dominant this would reflect that the *bonding properties* of H *atoms* are changed by the presence of sulphur. Whereas, when (*ii*) were dominant the *dissociation* of H_2 *molecules* becomes hindered by an energy barrier. This barrier may arise from the Pauli repulsion of the tails of the substrate s-waves with the H_2 orbitals [20] or by a reduced bonding character of the covalent coupling between the orbitals of the impinging H_2 molecule and the d-states of the surface metal atoms [21]. Indeed, our calculations show that sulphur adsorption reduces the contribution of d-states to the surface density of states (DOS) at the Fermi level which enhances the importance of both mentioned effects. The reduction of the DOS at the Fermi level is a result of the strong S–Pd interaction and the formation of bonding and antibonding states which are situated below and above E_F, respectively. Qualitatively the same result has been obtained for sulphur adsorption on Rh(100) in a study of Feibelman and Hamann [22] who for the first time related the poisoning effect of sulphur to the S induced change of the magnitude and the spatial distribution of the DOS at E_F.

We calculated the hydrogen adsorption energy at Pd(100) covered by sulphur with θ_S= 0.25 and 0.5 in order to determine the importance of mechanism (*i*), and to explain the above mentioned experimental results. Obviously, such an analysis and the comparison with experimental results enables us to draw conclusion about the importance of mechanisms (*ii*).

For the (2×2) sulphur overlayer on Pd(100) the calculated adatom height is h_0(S) = 1.25 Å above the center of the top substrate layer and the relaxation of the topmost metal layer is +1.8% of the bulk interlayer distance d_0. Note that the clean surface has a −0.8% d_0 inward relaxation. The work function in-

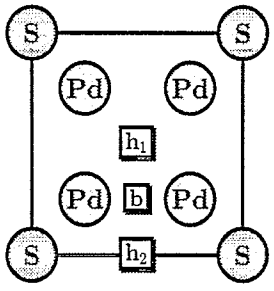

Fig. 2. Surface geometry of (2×2)S on Pd(100) with the two different hollow sites indicated by "h_1" and "h_2" and the bridge site "b".

creases from 5.35 eV at the clean surface by 0.24 eV to 5.59 eV. If the sulphur coverage is increased to $\theta_S = 1/2$ [(c(2 × 2) S adlayer)] the sulphur adsorption energy decreases by 0.31 eV. Thus we find that the S–S interaction is repulsive which prevents at low coverages the formation of sulphur islands and which is in agreement with experiment [7,10]. In the c(2 × 2) structure the sulphur adsorption height is increased to $h_0(S) = 1.31$ Å. This calculated value is in close agreement with the 1.3 ± 0.05 Å obtained by a LEED analysis [11]. The outward relaxation of the topmost metal layer increases to $+2.2\% d_0$. The higher c(2 × 2) sulphur coverage is found to induce a small decrease of the work function by 0.03 meV compared to the(2×2) S layer . This reflects a strong depolarization interaction between sulphur adatoms which is also consistent with the reduction of the sulphur adsorption energy.

The calculated hydrogen adsorption energies [23], $E_{ad}(H)$, for different adsorption positions of hydrogen at clean and sulphur covered Pd(100) surfaces are compiled in Table 1. The absolute value of the hydrogen adsorption energy at the clean surface $E_{ad}(H) = 0.61$ eV has been calculated using the GGA [14] approximation. It includes the calculated adsorption induced change of the vibrational zero point energy which is only 0.03 eV per H atom. The larger value of the calculated adsorption energy in comparison to the experimental result of 0.53 eV [4] results mainly from the difference between the experimental total energy of H_2 and that obtained within the GGA [14]. In the case that a (2×2) sulphur overlayer is adsorbed on the Pd(100) surface two different kinds of surface hollow sites are available to a subsequent hydrogen adsorption (see Fig. 2). One of them, indicated by "$\mathbf{h_2}$" in Fig. 2, has two sulphur atoms at nearest neighbor hollow sites. The central hollow site ("$\mathbf{h_1}$" in Fig. 2) has no nearest neighbor sulphur atoms but four sulphur atoms occupying next nearest neighbor positions. We find that the hollow site"$\mathbf{h_1}$" is energetically most favorable, the adsorption energy of hydrogen at this site is reduced by 0.1 eV in comparison to the clean Pd(100) surface.

A significantly larger decrease of the adsorption energy of 0.28 eV is obtained for the hollow site "$\mathbf{h_2}$". The absolute value decreases to $E_{ad} = 0.33$ eV (0.25 eV if the experimental result is inserted for the adsorption energy at the clean surface) but adsorption remains exothermic. The occupation of all empty hollow sites with hydrogen ($\theta_H = 0.75$) gives an adsorption energy per hydrogen atom of $E_{ad} = 0.38$ eV, close to the weighted average of the exclusive occupation of only one kind of hollow sites (see Table 1), which reflects that the H–H interaction is rather weak. Concerning the interaction between H and S atoms at the surface the theoretical results show that this is repulsive: The interaction energy is 0.1 eV for H at the "$\mathbf{h_1}$" sites which are more distant to S adatoms, and it is 0.28 eV for the closer "$\mathbf{h_2}$" sites. The magnitude of the H–S repulsion found at Pd(100) is consistent with the 0.17 eV decrease of the hydrogen adsorption energy calculated by Feibelman [24] for an H–S pair on Rh(100) in comparison to the isolated H adatom.

At the clean Pd(100) surface the adsorption energy of hydrogen at hollow and bridge sites differ by about 0.3 eV (see also Ref. [25]). We checked whether

Table 1
Calculated H_2 adsorption energy $E_{ad}(H)$ per hydrogen atom for different adsorption positions of hydrogen at clean and sulphur covered Pd(100) surfaces

Sulphur adlayer	Sulphur coverage	Hydrogen adsorption site	Hydrogen coverage	$E_{ad}(H)$ (eV)
–	0.0	Hollow	0.5	0.61
–	0.0	Bridge	0.25	0.29
–	0.0	Subsurface	1	0.28
(2×2)	0.25	Hollow "h_1"	0.25	0.51
(2×2)	0.25	Hollow "h_2"	0.25	0.33
(2×2)	0.25	Hollow "h_1"+2× "h_2"	0.75	0.38
(2×2)	0.25	Bridge "b"	0.25	0.14
c(2×2)	0.5	Hollow	0.5	0.02
c(2×2)	0.5	Subsurface O_h	1	0.22

The positions "h_1", "h_2", and "b" are explained in Fig. 2.

preadsorbed S may change the adsorption site of hydrogen and calculated the adsorption energy of hydrogen placed into bridge sites (denoted as "**b**" in Fig. 2) with a coverage $\theta_S = 0.25$ and $\theta_H = 0.25$. This adsorption site is found to have a 0.2 eV lower adsorption energy than the less favorable hollow site "$\mathbf{h}_2$". Thus, hydrogen adatoms at bridge sites can be ruled out.

A different situation is obtained for hydrogen adsorption into the empty hollow sites of the Pd(100) surface covered with a c(2×2) sulphur adlayer ($\theta_S = 0.5$). In this structure every available surface hollow site is surrounded by four sulphur atoms at nearest neighbor hollow positions. The hydrogen adsorption energy in surface hollow sites is only 0.02 eV, which implies that hydrogen will not adsorb at normal temperatures. Sulphur adsorption, however, has only little influence on the energy of H atoms in the subsurface O_h sites. The adsorption energy of a monolayer of hydrogen placed into subsurface O_h position below c(2×2)S/Pd(100) decreases only by 0.06 eV in comparison to the clean surface. Consequently, in the case of the c(2×2) sulphur adlayer surface sites are blocked and O_h subsurface and bulk sites become the energetically preferred sites for hydrogen atoms.

In conclusion, our DFT calculations show that the poisoning of Pd(100) for H_2 dissociation by sulphur is not governed by a decrease of the adsorption energy alone at least for sulphur coverages up to $\theta_S \leq 0.25$. The presence of sulphur at the surface reduces the hydrogen adsorption energy at sites close to sulphur but in the case of a (2×2)S overlayer on Pd(100) hydrogen adsorption into all hollow sites not occupied by sulphur remains an exothermic process. However, the decrease of the adsorption energy, makes the occupation of sites close to the sulphur adatoms energetically less favorable than that of more distant sites.

Only at very high sulphur coverages ($\theta_S = 0.5$) the strong repulsive H–S interaction strictly blocks the adsorption of hydrogen in the vicinity of the sulphur adatoms.

In order to explain the experimental observed reduction of the initial sticking probability of H_2 with sulphur coverage [6,7] and the inhibition of non-activated dissociative adsorption at $\theta_S \approx 0.25$ we conclude that in addition to a modest decrease of the hydrogen adsorption energy the dissociation process is hampered by the formation of energy barriers. This is consistent with the study of Feibelman and Hamann [22] which shows that the sulphur induced changes of the *total* electron density are rapidly screened out with increasing distance from the S adatoms, but the reduction of the surface DOS close to the Fermi level is significantly longer ranged.

The investigation of the PES of H_2 dissociation over clean Pd(100) shows that several reaction pathways of dissociative adsorption exist. We expect that adsorbed sulphur changes the PES noticeably not only in the region of the adsorption geometry but also at distances further away from the surfaces, giving rise to different reaction pathways and energy barriers which hinder the H_2 dissociation. As a consequence, the presence of sulphur adatoms reduces the number of approachable reaction pathways without an energy barrier and, hence, the initial sticking probability decreases.

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