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Structural evolution of sulfur overlayers on Pd(1 1 1)

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ABSTRACT

Low energy ion scattering spectroscopy (LEISS) has been used to characterize the evolution of ordered structures of S on the Pd(1 1 1) surface during annealing. During exposure of the Pd(1 1 1) surface to 0.7 L H₂S at 300 K—conditions that produce the S($\sqrt{3} \times \sqrt{3}$)R30 overlayer—the intensity of the Pd LEIS signal decreases and a feature assigned to adsorbed S appears as the adsorbed layer forms. When the surface is held at 300 K after exposure to H₂S is stopped, the LEIS Pd intensity partially recovers and the S signal weakens, presumably as surface S atoms assume their equilibrium positions in the S($\sqrt{3} \times \sqrt{3}$)R30 overlayer. Subsequent annealing of the S($\sqrt{3} \times \sqrt{3}$)R30 structure at 700 K causes it to convert into a S($\sqrt{7} \times \sqrt{7}$)R19 overlayer, whose LEIS spectrum is identical to that of clean Pd(1 1 1). The absence of LEIS evidence for S atoms at the exposed surface of the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer is at odds with published models of a mixed Pd–S top layer. Despite the similarity of the LEIS spectra of Pd(1 1 1) and Pd(1 1 1)–S($\sqrt{7} \times \sqrt{7}$)R19, their activities for dissociative hydrogen adsorption are very different—the former readily adsorbs hydrogen at 100 K, while the latter does not—suggesting that S exerts its influence on surface chemistry from subsurface locations.

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1. Introduction

Palladium is used as a catalyst for a number of important hydrogenation reactions in fine chemicals processing and petroleum refining [1–3] and as a component of dense alloy membranes used for hydrogen purification [4–7]. Exposure to sulfur-containing compounds is well known to deactivate Pd catalysts [8,9] and purification membranes [10,11], and thus, the interaction of sulfur with Pd surfaces has received significant attention from both experimental and computational researchers.

On a Pd(1 1 1) surface, two ordered overlayers of atomic sulfur are commonly formed. A ($\sqrt{3} \times \sqrt{3}$)R30 structure is observed when the Pd(1 1 1) surface is exposed to either H₂S [12–16] or S₂ [17] at approximately room temperature. Experimental [12–14] and computational [18] studies conclude that S atoms in the ($\sqrt{3} \times \sqrt{3}$)R30 structure occupy threefold hollow fcc sites at the surface, with no S atoms in sub-surface layers. The local coverage of S in this layer is 1/3 monolayers. Upon annealing at temperatures in the range 400–700 K, a new ($\sqrt{7} \times \sqrt{7}$)R19 overlayer structure appears [12–14,16]. There have been several proposals for the surface structure of the ($\sqrt{7} \times \sqrt{7}$)R19 overlayer, based on both experiment [12,13,15,16,19] and computational modeling [20]. While there is significant diversity among the details of proposed structures, most reports agree that S does not exist in a simple adsorbed layer.

Instead, S appears to penetrate the metal lattice, causing it to reconstruct to form a mixed Pd–S top-layer, which has sometimes been characterized as a two-dimensional surface sulfide [13]. The models of this structure suggest a local S coverage of either 3/7 [12,13,20] or 2/7 [15] monolayers.

In this work we have used low energy He⁺ ion scattering spectroscopy (LEISS) to characterize the two ordered S structures on the Pd(1 1 1) surface and to monitor their evolution during heating.

2. Experimental procedures

Experiments were performed in a stainless steel ultra-high vacuum chamber with a base pressure of 1×10^{-10} Torr. A Pd(1 1 1) single crystal, ~10 mm diameter \times 1 mm thick, was attached to an x, y, z, θ manipulator by 0.63 mm Ta lead wires spot welded to its edges. The Ta wires provide both mechanical support and electrical/thermal contact to the sample, allowing control of its temperature over the range 80–1100 K. The chamber is equipped with an X-ray source (Thermo VG Scientific), a He⁺ ion gun (Specs IQE 12/38), an energy analyzer (Specs PHOIBOS 150MCD), a mass spectrometer detector for temperature programmed desorption (TPD) experiments, low energy electron diffraction (LEED) optics (Perkin–Elmer 15-120) and an ion gun for sputter cleaning of the sample.

We prepared the surface of the Pd(1 1 1) crystal using cycles of Ar⁺ sputtering (~15 μ A/cm² at 300 K) and annealing (800 K) until S, C and O were no longer detectable by XPS. The final treatment was always a 30 min anneal at 800 K.

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LEED patterns were acquired at ~ 100 K with an electron energy of ~ 140 eV. The XPS experiments used Al $K\alpha$ radiation and an analyzer pass energy of 100 eV. The analyzer collected electrons photoemitted at an angle of 30° from the surface normal. The low energy ion scattering spectroscopy (LEISS) experiments used 750 eV He^+ ions specularly reflected from the sample at an angle of $\sim 50^\circ$ from the surface normal. Low incident ion currents of ~ 50 nA ($\sim 5 \times 10^{12}$ He^+/cm^2 over the course of a single 20 s experiment) were used in order to minimize the damage by incident He^+ .

Atomic S was adsorbed onto the surface of the Pd(1 1 1) crystal, cooled to ~ 100 K, by leaking H_2S into the chamber at 1×10^{-8} Torr for periods chosen to deliver exposures up to 3 L. Adsorbed H_2S was subsequently decomposed by heating the sample to 300 K at a rate of 4 K/s. In a similar manner, H_2 temperature programmed desorption (TPD) experiments were performed by first exposing the crystal to 300 L of H_2 (to guarantee saturation coverage) at ~ 100 K. The crystal was subsequently heated to 500 K at 4 K/s while positioned within 1 mm of the mass spectrometer aperture. The desorption signal at $m/q = 2$ was monitored as a function of temperature during heating.

3. Results and discussion

Fig. 1a shows the (1×1) LEED pattern recorded from the clean Pd(1 1 1) surface. A $S(\sqrt{3} \times \sqrt{3})\text{R}30$ overlayer (Fig. 1b) was generated by exposing the annealed sample to 0.5–1.0 L H_2S at 100 K, followed by heating to 300 K. This result is consistent with other published reports [12–16]. The S/Pd XPS signal intensity ratio that corresponds to this structure is 0.009 ± 0.001 . Additional incremental H_2S exposures up to a total of 2.0 L did not increase the S/Pd ratio as measured by XPS.

Annealing the $S(\sqrt{3} \times \sqrt{3})\text{R}30$ structure at 700 K induces formation of the $S(\sqrt{7} \times \sqrt{7})\text{R}19$ overlayer (Fig. 1c). This result is also consistent with published reports [12–16]. The change in the overlayer structure is not accompanied by a detectable change in the measured S/Pd XPS signal ratio. Incremental exposures of the Pd(1 1 1)– $S(\sqrt{7} \times \sqrt{7})\text{R}19$ surface to H_2S (either at 700 K, or at lower temperatures followed by annealing at 700 K) up to a total exposure of 3 L changed neither the surface composition (as measured by XPS) nor the LEED pattern.

To better understand the evolution of the ordered structures, the clean, annealed Pd(1 1 1) surface was exposed to H_2S at 300 K while measuring the top-layer composition using LEIS. Spectra were collected continuously during H_2S exposure; acquisition time for an individual spectrum was ~ 20 sec. Fig. 2 displays the spectra as a function of (cumulative) H_2S exposure. Each spectrum is dominated by a single feature located at approximately 705 eV, assigned to He^+ scattering from surface Pd atoms. The inset shows an enlargement of the S region of the same spectra, scaled to the

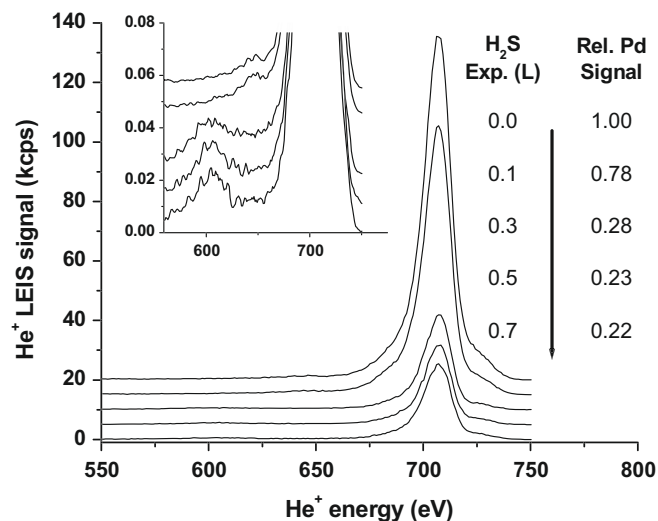


Fig. 2. LEIS spectra of the Pd(1 1 1) surface as a function of H_2S exposure at 300 K. The Pd feature is located at 705 eV; the inset shows an enlargement of S feature at ~ 605 eV. H_2S exposures are, from top to bottom, 0.0 L (clean), 0.1 L, 0.3 L, 0.5 L, and 0.7 L. Pd intensities relative to clean Pd(1 1 1) are shown at the right. As the H_2S exposure increases, the Pd intensity declines and the S intensity increases.

maximum Pd signal for that spectrum. At 0.3 L and higher exposures, a small feature assignable to scattering from S atoms becomes visible at ~ 605 eV. The small size of the S signal likely reflects a low scattering cross-section— He^+ may prefer to neutralize, rather than to scatter, during its collision with S atoms [21]. The appearance of a S signal is accompanied by reduction of the Pd intensity, presumably as surface S atoms screen Pd atoms from incident He^+ . Note that Pd signal attenuation occurs at lower H_2S exposures than that of the first appearance of the S feature, suggesting that Pd scattering intensity is the more sensitive measure of the presence of S atoms at the top surface. At 0.7 L H_2S exposure, key features of the LEIS spectrum—appearance of the S feature at ~ 605 eV and a reduction of Pd intensity to about 20% of the clean surface value—are the same as those observed for surfaces prepared by exposure to H_2S at 100 K followed by heating to 300 K, conditions that yield the $S(\sqrt{3} \times \sqrt{3})\text{R}30$ overlayer, with a S/Pd XPS signal ratio of ~ 0.01 .

At 0.7 L, H_2S exposure was terminated, but the LEIS analysis (at 300 K) was continued for another two minutes to monitor the evolution of the overlayer. The middle three spectra displayed in Fig. 3 were acquired while holding the sample temperature at 300 K; the spectrum obtained immediately following the 0.7 L H_2S exposure from Fig. 2 is included for reference. As time elapses, the S LEIS signal at 605 eV decreases and eventually disappears. Concurrently with the loss of the S LEIS signal, the Pd signal intensity recovers,

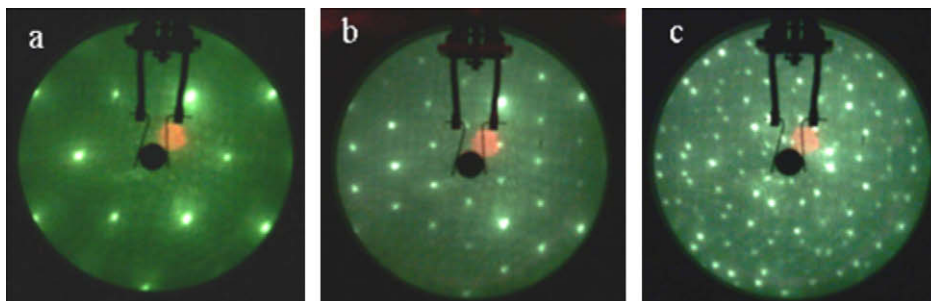


Fig. 1. LEED patterns of (a) Pd(1 1 1), sputter cleaned and annealed at 800 K; (b) the $S(\sqrt{3} \times \sqrt{3})\text{R}30$ overlayer formed on Pd(1 1 1) exposed to ~ 1.0 L H_2S at 100 K, followed heating to 300 K, (c) the $S(\sqrt{7} \times \sqrt{7})\text{R}19$ overlayer formed on the sample from (b) annealed at 700 K for 5 min.

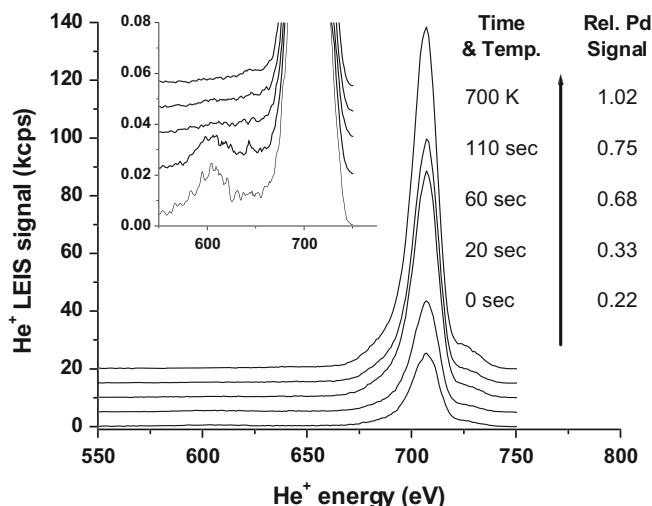


Fig. 3. LEIS spectra of the Pd(1 1 1)-S surface as a function of time at *after* exposure to H₂S at 300 K. The Pd feature is located at 705 eV; the inset shows an enlargement of the S feature at ~605 eV. Starting at the bottom, spectra were acquired at times of 0 (the same spectrum as the bottom of Fig. 2), 20, 60, and 110 s after the H₂S exposure was discontinued. Pd intensities relative to that of clean Pd(1 1 1) are shown at the right. As time increases, the S feature disappears and the Pd feature recovers. The top spectrum was obtained after annealing at 700 K (but returned to 300 K for LEIS analysis).

but only to ~75% of its pre-exposure value. Incomplete recovery of the Pd signal is clear evidence for the presence of top-surface S atoms, and is consistent with experimental and computational characterization of S($\sqrt{3} \times \sqrt{3}$)R30 overlayers. Changes in the LEIS spectra that take place during annealing at 300 K may reflect changes in the surface as adsorbed S atoms assume their equilibrium positions.

After holding the sample temperature at 300 K for 2 min, the sample was annealed at 700 K for 5 min and then returned to 300 K for LEIS analysis. The LEIS spectrum at 300 K (top of Fig. 3) is nearly identical to the LEIS spectrum from the clean Pd(1 1 1) surface (top of Fig. 2): it displays comparable Pd signal at 705 eV and no S signal at 605 eV. Immediately after the LEIS experiments, LEED revealed the presence of the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer, and the S/Pd XPS ratio was 0.010—the same as that observed after 0.5–1.0 L H₂S exposures at 100 K followed by stepwise heating to 300 K (to first generate the S($\sqrt{3} \times \sqrt{3}$)R30 surface structure) and then to 700 K.

We interpret the further increase of Pd LEIS intensity after annealing at 700 K as S leaving an adsorbed layer to penetrate into the sub-surface layer of Pd(1 1 1). Migration of adsorbed sulfur into the Pd(1 1 1) sub-surface is consistent with models of the S($\sqrt{7} \times \sqrt{7}$)R19 surface that have been proposed by several researchers, which suggest a mixed top-surface that consists of both S and Pd atoms [12,13,15,16,19,20]. However, our observation that the LEIS spectra of the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer and the clean Pd(1 1 1) surface are nearly identical is an important—and unexpected—result. Given constant experimental parameters, LEIS signals depend primarily upon the atomic densities of surface species and their scattering cross-sections [22]. Assuming that there is no change in Pd and S scattering cross-sections as a result of adsorption on the surface, our results suggest that the top surface of the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer contains no S atoms—or, at most, S atoms that are well-shielded by neighboring Pd atoms—and that the surface density of Pd atoms is comparable to that of Pd(1 1 1). In other words, we may be observing deeper penetration of S into the Pd matrix than accounted for in the mixed-top layer models of the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer structure.

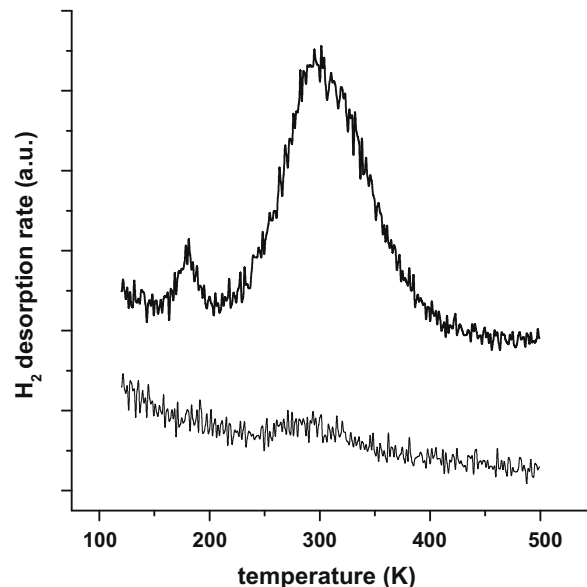


Fig. 4. H₂ TPD from the clean Pd(1 1 1) surface (top) and the Pd(1 1 1)-S($\sqrt{7} \times \sqrt{7}$)R19 surface (bottom), obtained by heating at 4 K/s while monitoring the mass spectrometer signal at $m/q=2$. Exposure of 300 L H₂ at 100 K was sufficient to saturate the clean Pd(1 1 1) surface, but, under the same conditions of exposure, the Pd(1 1 1)-S($\sqrt{7} \times \sqrt{7}$)R19 surface did not adsorb significant H₂.

The view that S atoms on Pd(1 1 1) have been displaced into the immediate sub-surface layer by annealing to 700 K is balanced, at least partially, by the XPS results. The disappearance of LEIS evidence of top-surface S that takes place as the ordered S($\sqrt{3} \times \sqrt{3}$)R30 surface converts to the S($\sqrt{7} \times \sqrt{7}$)R19 structure is not accompanied by a detectable decrease in the XPS S/Pd signal ratio. Thus, XPS suggests that the extent of penetration of S into the near surface is not great enough to cause significant attenuation of the S photoelectron signal by Pd.

The similarity between the LEIS spectra of the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer and the clean Pd(1 1 1) surface also suggests that the two might have similar surface chemistries. We compared TPD spectra of H₂ from the two surfaces; results appear in Fig. 4. As expected [23–26], the clean Pd surface readily adsorbs H₂ at 100 K and, during heating, H₂ subsequently desorbs with a peak maximum in the vicinity of 300 K. The Pd(1 1 1)-S($\sqrt{7} \times \sqrt{7}$)R19 surface, in contrast, does not adsorb H₂ under the same conditions of exposure. This result is consistent with those reported for the Pd(1 1 0) surface, on which the hydrogen adsorption capacity declines linearly with increasing S coverage, resulting in complete deactivation of the surface at a S coverage of $\theta_S = 0.28$ ML [26]. Because the S($\sqrt{7} \times \sqrt{7}$)R19 overlayer adsorbs no H₂, we conclude that either S in the subsurface exerts an electronic effect on the Pd or that structural features of surface sites that are necessary for the dissociative adsorption of H₂ are not adequately probed by LEIS.

4. Conclusions

Exposure of a Pd(1 1 1) surface to H₂S at conditions that produce the S($\sqrt{3} \times \sqrt{3}$)R30 structure—0.5–1.0 L with heating to 300 K—results in decreasing Pd LEIS intensity and appearance of a new feature assigned to surface S. During continued heating at 300 K after exposure to H₂S, the LEIS Pd intensity partially recovers and the S signal disappears, presumably as S atoms assume their equilibrium positions in the S($\sqrt{3} \times \sqrt{3}$)R30 structure. Annealing of the S($\sqrt{3} \times \sqrt{3}$)R30 structure at 700 K causes it to convert into a S($\sqrt{7} \times \sqrt{7}$)R19 overlayer, whose LEIS spectrum is identical to

that of clean Pd(1 1 1). The absence of LEIS evidence for top-surface S in the $S(\sqrt{7} \times \sqrt{7})R19$ overlayer is at odds with published models of a mixed Pd and S top surface.

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