A Novel Surface Structure: Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P

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Received August 7, 1995

The interactions of electronegative species with transition metal surfaces can yield a wide range of structural arrangements, and the methods of surface structure determination, especially low-energy electron diffraction (LEED), are giving important new information.[1] Structures with the ($\sqrt{7}\times\sqrt{7}$)R19.1° translational symmetry are providing considerable interest, in part because they represent the upper end of complexity for current structural analyses, when no other information is available, and they can show distinctive chemistries compared with simpler systems. Examples include the $\sqrt{7}$ structures formed by I on Pt(111) and S on Ru(0001) which have been indicated respectively by scanning tunneling microscopy[2] and LEED crystallography[3] to have simple chemisorption arrangements without substantial modifications to the metallic structures; but in contrast the $\sqrt{7}$ structures formed by S on Pd(111),[4] Cu(111),[5] and Ag(111)[6] appear much more challenging. There have been frequent suggestions that the latter systems involve mixed sulfur−metal overlayers and, in particular, that the structures for the S/Cu(111) and S/Ag(111) cases relate to the (111) plane of the bulk compounds Cu_2S and Ag_2S,[5,6] but confirmation has proven hard to obtain. Another case in point is the Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P surface, which is highly stable and the work here shows that it has a novel structural arrangement. Discussions of this structure, its implications for other $\sqrt{7}$ systems, and possible links between this structural type and chemical properties provide the subject of this communication.

The Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P surface was prepared under ultrahigh-vacuum conditions (base pressure 2×10^{-10} Torr) by exposing a clean, well-ordered single-crystal of rhodium in the (111) orientation to approximately 4.8 (1 L = 10^{-6} Torr s) PH_3 at room temperature, followed by a flash annealing to 1000 °C. The surface was assessed with standard surface science procedures, including Auger electron spectroscopy, throughout the cleaning and preparation steps. A sharp LEED pattern is obtained from this surface, and its high stability is shown by a number of observations including its persistence over long periods (weeks) in the vacuum chamber, as well as the difficulty of its removal under typical ion bombardment conditions. Intensity-versus-energy ($I(E)$) curves were measured with a video system for 12 inequivalent diffracted beams with appropriate beam averaging, smoothing, and normalization for normal incidence and for energies up to 252 eV (total energy range 1438 eV). The analysis was done with multiple-scattering calculations in the context of tensor LEED[7] using the R-factor (R_P) introduced by Pendry;[8] the potential of the solid was approximated with the muffin-tin model with the electron scattering by the Rh and P cores described by phase shifts (l_{max} = 7) as used in another study.[9] Over 50 structural types consistent with the $\sqrt{7}$ translational symmetry were tested,[10] but only the model type shown in Figure 1 yielded a satisfactory correspondence between the experimental and calculated $I(E)$ curves. In fact the optimized R_P value of 0.235 can be seen as a high level of correspondence for such a relatively complex surface structure, and the specific $I(E)$ curves comparisons are in Figure 2.

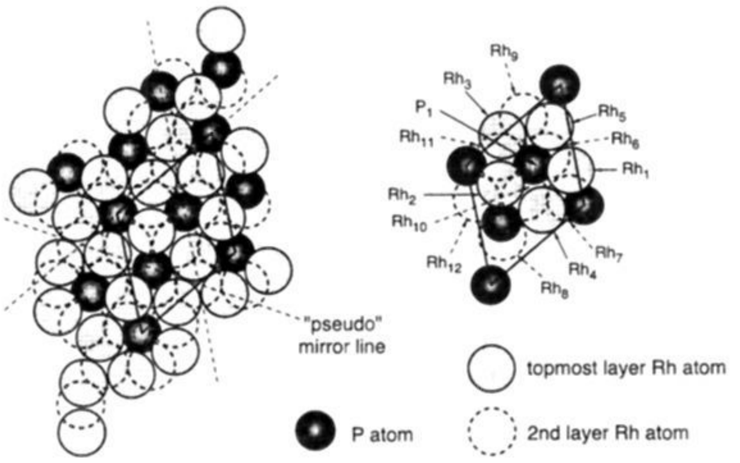

Figure 1. The Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P surface structure with an indication of atom designations used in the text. The 3-fold rotation axes are located at the centers of atoms Rh_1, Rh_2, and Rh_9.

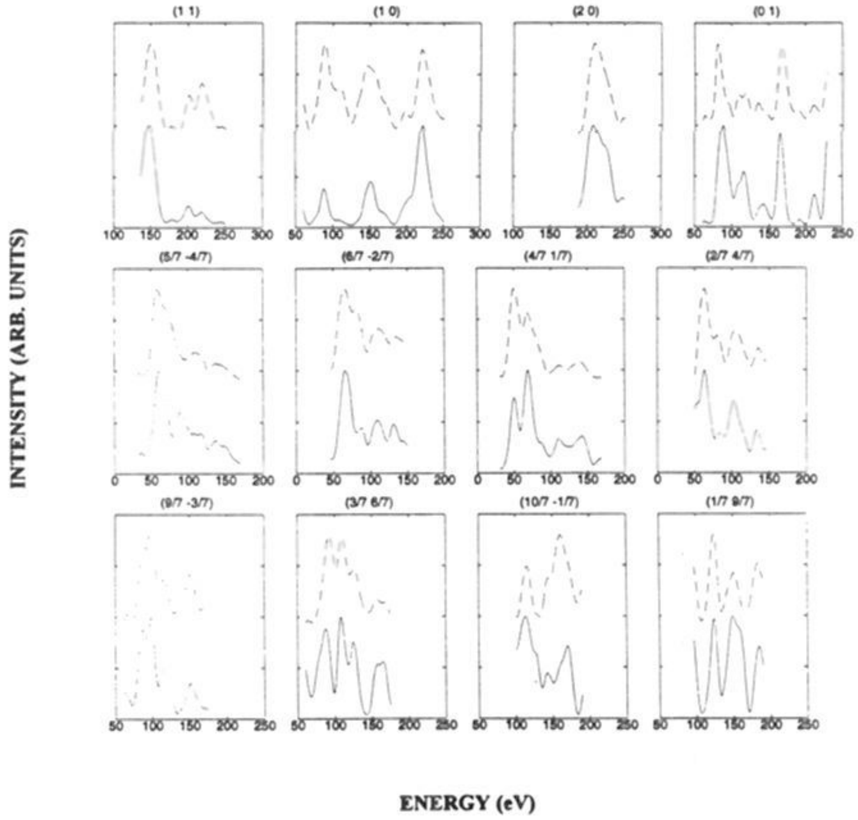

Figure 2. Comparison of experimental $I(E)$ curves (dot-dashed lines) with those calculated (solid lines) for the favored geometry.

The structural features for the Rh(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°-P surface as indicated by this tensor LEED analysis (Figure 1) are summarized in the following: (i) The structure has 3-fold rotational symmetry axes, and the P coverage corresponds to 3 atoms per unit mesh. (ii) Each P atom occupies an identical site created by the reconstructed Rh structure and is within the bonding distance of eight Rh atoms (Table 1). (iii) The topmost Rh layer is characterized by a packed arrangement of pentagons and triangles at a density of 5 Rh atoms per unit mesh (those designated Rh_1, Rh_3, Rh_4, and Rh_5 remain close to their bulk-like fcc hollow sites with respect to the lower layers, while Rh_2

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0002-7863/95/1517-12344$09.00/0

Table 1. Some Important Bond Lengths (Å) for the First- and Second-Layer Rh and P Atoms[a]

P_1-Rh_1	2.17	Rh_1-P	2.17 (×3)	Rh_1-Rh	2.81 (×6)
P_1-Rh_2	2.22	Rh_2-P	2.22 (×3)	Rh_2-Rh	2.85 (×6)
P_1-Rh_3	2.48	Rh_3-P	2.53 (×3)	Rh_3-Rh	2.77 (×7)
P_1-Rh_4	2.71	Rh_6-P	2.30 (×1)	Rh_6-Rh	2.71 (×11)
P_1-Rh_5	2.40	$Rh_{10}-P$	2.95 (×2)	Rh_9-Rh	2.68 (×12)
P_1-Rh_6	2.30			$Rh_{10}-Rh$	2.69 (×11)
P_1-Rh_{10}	2.93				
P_1-Rh_{11}	2.97				

[a] Bond lengths given for Rh atoms are averaged over neighboring bonds (the number of such neighbors is indicated in parentheses in each case). Due to the 3-fold rotational symmetry, Rh_4 and Rh_5 have bonding situations equivalent to that of Rh_3; similarly for the (Rh_6, Rh_7, Rh_8) and (Rh_{10}, Rh_{11}, Rh_{12}) groups.

is at a hcp hollow site), so that the densely-packed Rh−P mixed layer (with a P atom incorporated into the center of each pentagon) consists of 8 surface atoms per 7 for the Rh(111) substrate. (iv) Relaxations occur which are much more significant laterally than vertically (the largest lateral displacements from the "ideal" 3-fold symmetrical sites are about 0.66 Å for P atoms and about 0.28 Å for Rh atoms, while vertical displacements among the top three layers are 0.08 Å or less). Without relaxations, a "first-approximation" estimate of first-layer Rh atoms in 3-fold sites would require an irregular pentagon with a 15% variation in side lengths, but the structure from the tensor LEED analysis shows that this variation is reduced to less than 3%. (v) Vertically, the topmost Rh atoms are almost coplanar (the rumpling is 0.06 Å) with P sitting 0.13 Å below the center-of-gravity plane for the first Rh layer, but 2.15 Å above the second Rh layer. The Rh−Rh interlayer spacings are only slightly changed from the bulk value of 2.196 Å (the percentage changes correspond to +3.7, −1.3 and +0.7 for the first, second and third spacings, respectively). (vi) The P−Rh distances range from 2.17 to 2.97 Å (Table 1); for each P atom there are two short (2.17−2.22 Å), three medium (2.30−2.48 Å), and three longer (2.71−2.97 Å) bonds to the neighboring Rh atoms. (vii) "Pseudo" mirror lines are indicated in Figure 1 for the topmost Rh−P layer; the determined atomic positions show an approach to a mirror symmetry within this layer, although this is not required by the overall symmetry.

This structure shows a completely new bonding arrangement for P at a transition metal surface. The eight-coordination for P matches the situation in bulk Rh_2P (*anti*-fluorite),[11] although other details differ. For example, the average P−Rh bond length in Rh(111)-($\sqrt{7}\times\sqrt{7}$)*R*19.1°-P (2.52 Å) is slightly longer than the distance in Rh_2P (2.38 Å); in part this increase arises from the limited "free valencies" available for the neighboring Rh atoms, given that they are themselves each bonding to between 6 and 11 other Rh atoms (and sometimes other P atoms as well). Additionally this structure is constrained by the need to maintain an appropriate local coordination around P while simultaneously maintaining the diperiodicity to match the substrate. The high density of the topmost Rh−P layer, its flatness, and its possibilities for maintaining high total bonding by P appear as major factors contributing to the generally high stability of this surface. We consider it very likely that the $\sqrt{7}$ structures formed by S on Cu(111), Ag(111), and Pd (111) have similar structures given that they have also been reported to have mixed S−metal overlayers[4−6] and the fact that they all form cubic bulk compounds (i.e., Cu_2S, Ag_2S, and Pd_4S)[11] in which the S atoms are eight-coordinate.[12] In particular, the $\sqrt{7}$ S/Pd(111) surface is also reported to have very high stability and to be flat with a S coverage of 3/7 ML.[4] Indeed STM images taken on this surface match exactly with the structural model in Figure 1 if the bright spots are interpreted as metal atoms.[4b,c]

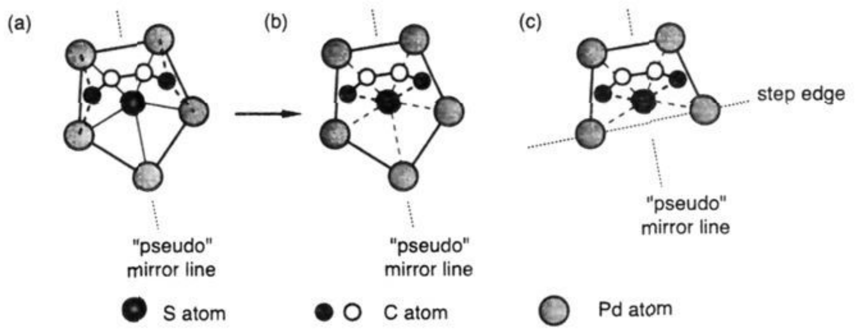

Figure 3. Schematic indication of a possible route for the formation of thiophene from the cyclization of acetylene on Pd(111)-($\sqrt{7}\times\sqrt{7}$)-*R*19.1°-S structures: a and b are for a flat terrace, and c is for a step edge. The small circles represent C atoms of the C_4H_4 intermediate; the open ones are expected to be tilted away from the surface, while the filled circles are closer and bond initially with surface Pd atoms as indicated (the H atoms are not shown, but one bonds to each C atom).

That the Pd(111)-($\sqrt{7}\times\sqrt{7}$)*R*19.1°-S surface is likely to have a different structural arrangement from the lower-coverage ($\sqrt{3}\times\sqrt{3}$)*R*30° form has been indicated by chemical reactivities.[13] For the cyclization reaction of acetylene to thiophene, carried out on these two sulfided Pd(111) surfaces, the former (after heating to 1050 K) appears approximately five times more effective than the more-regular $\sqrt{3}$ chemisorption structure,[4d] a factor that has already been alluded to by Gellman.[13a] With the probability that the $\sqrt{7}$ structure for S/Pd(111) is analogous to that in Figure 1, the reaction scheme outlined in Figure 3 suggests how the novel arrangement of S, nearly coplanar with the pentagonally-arranged neighboring Pd atoms, may help accelerate the reaction compared with that in the $\sqrt{3}$ form, where S is held above the regular Pd(111) surface. Like the conversion of C_2H_2 to C_6H_6 on the clean Pd(111) surface,[14] the formation of thiophene may also proceed through the C_4H_4 intermediate (Figure 3a), and Figure 3b indicates how the cyclization to thiophene may be facilitated by a neighboring S atom bound to the center of a Pd pentagon. Indeed with the expected tilting,[14c,d] the C_4 unit could approach coplanarity with the S. Figure 3c outlines an extension of this situation to a step edge where the S is bound to a smaller number of Pd atoms and, hence, should be more easily removed. In summary, it seems that while the pentagonal reconstruction for the topmost layer encourages the formation of thiophene, the presence of steps helps the desorption; together these points indicate a rationalization of observations that the yield of desorbed thiophene increases with the step density for the $\sqrt{7}$ structure.[4b]

As well as introducing a completely new surface structure, this communication indicates how modern surface structure determinations can help add insight for surface stability and reactivity. The interest in establishing such structure−reactivity relationships has been alluded to for many years,[15] but it is clear that the recent rapid developments in LEED crystallography are now strengthening such efforts in relation to significant catalytic processes.[1]

Acknowledgment. We are grateful for the support of this research provided by the Natural Sciences and Engineering Research Council of Canada. Also we thank the University of British Columbia for a graduate fellowship to W.L. and Dr. M. A. Van Hove (University of California, Berkeley) for supplying the tensor LEED computer codes.

JA952645I

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(12) This argument is also supported by the constancy in the ratio of M−S (or P) distance in these bulk compounds to the neighboring M−M distance on the metal (111) surfaces. All examples fit within 0.92 ± 0.05, but the combinations P/Rh and S/Pd are particularly close (both 0.88), as are S/Cu and S/Ag (0.97 and 0.95, respectively).

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