**Final Report for DoE Grant #DE-FG02-08ER46546
The Pennsylvania State University**

**Atomic-Scale Chemical, Physical and Electronic Properties of the
Subsurface Hydride of Palladium**

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We employed low-temperature, extreme-high vacuum scanning tunneling microscopy (STM) to investigate the roles of subsurface hydride (H) and deuteride (D) in the surface reconstruction and surface reactivity of Pd{110}. Specifically, we gained the ability to tailor the surface structure of Pd{110} both by preparation method and by deposition of deuterium from the gas phase. We observed thiophene at low coverage on Pd{110} to determine its adsorption orientation and electronic structure through scanning tunneling spectroscopy (STS) – namely, conductance spectroscopy and differential conductance imaging. We developed the methods necessary to coadsorb D adatoms with thiophene molecules, and to induce the reaction of individual molecules with predefined subsurface H or D features. In the case of Pd{110}, we found a much more pronounced effect from subsurface D, as it is influenced by the surface directionality. These experiments facilitate an understanding of the role of surface and subsurface H and D in heterogeneous catalytic processes, specifically in the hydrodesulfurization (HDS) of thiophene, an important and ubiquitous component found to be detrimental to petroleum refining.

In the D/Pd{110}-(1 × 2) system, D-induced surface reconstruction¹ is followed by unprecedented local faceting of (1 × 1) Pd atomic structure induced by tunneling electrons in the presence of adsorbed thiophene. Figure 1 shows a topographic STM image (Figure 1a) demonstrating the row-pairing of the Pd atoms after exposure to D. The inset is a model indicating the directionality of this surface. A line scan (Figure 1b) highlights the surface corrugation. We use these data to calibrate STM images, and to show that there is negligible contamination by subsurface impurities.²⁻⁴

Figure 1. a) D-induced Pd{110}-(1 × 2) surface reconstruction. (a) Atomically resolved STM image ($V_s = 0.01$ V; $I_t = 1.4$ nA; $22 \text{ Å} \times 22 \text{ Å}$) with model structure (inset) of the (1 × 2) phase. (b) Apparent height profile acquired along the dashed line in (a).

After obtaining the reconstructed Pd surface, we deposited thiophene to investigate local and long-range structural and electronic perturbations. The topographic STM image in Figure 2a shows surface morphology after deposition of thiophene at 4 K. We note that

thiophene is imaged with two distinct apparent heights, which we attribute to two separate bonding orientations. Two distinct bonding orientations were also observed in our previous work on thiophene on Ni{110}.⁵ Additionally, we observe thiophene preferring to adsorb between rows (green arrow in Figure 2a) and a small amount of sulfur impurities (white arrow in Figure 2A). Furthermore, we were able to deconvolve the physical and electronic structure of individual thiophene molecules by employing differential conductance imaging. The molecule in Figure 2b (topography) is the same as that of Figure 2c (differential conductance), as these images were acquired simultaneously. Because we image in constant-current mode with positive sample bias, the lobes apparent in Figure 2c are attributed to the π^* orbitals of thiophene, which is indicative of those observed in the STM simulations of thiophene on Pd{111}.⁶

Figure 2. Thiophene adsorption on D/Pd{110}-(1 × 2) and on clean Pd{110}-(1 × 1). (a) Topographic STM image ($V_s = -0.015$ V; $I_t = 0.2$ nA; $73 \text{ Å} \times 73 \text{ Å}$) of thiophene on a D-reconstructed Pd{110} surface. Thiophene molecules appear as protrusions with two distinct apparent heights. (b and c) Topographic and differential conductance, respectively, STM images ($V_s = 0.1$ V; $I_t = 0.9$ nA; $22 \text{ Å} \times 22 \text{ Å}$) acquired simultaneously. At positive sample bias, we observe lobes attributed to empty states.

We also deconstructed the adsorption characteristics of thiophene on Pd{110} with respect to surface-state mediated interactions (SMI). These interactions are known to occur on noble and near-noble metal surfaces, where the electronic surface structure presents oscillatory behavior resulting from the electrons' confinement as a two-dimensional electron gas.⁷⁻¹¹ Preliminary data suggest that there may be competition between the structural singularity of the surface (driven by the corrugation of the Pd{110} surface) and the SMIs. Figure 3 shows results from Pd{110} with a higher density of thiophene molecules. In this case, the surface was not pretreated with D, thus, the surface has adopted the primary (1 × 1) structure. Figure 3a represents a single topographic STM image displaying the typical thiophene density for this system. The thiophene molecules image as protrusions, and the directionality of the corrugation is evident by the labeled white arrows. From more than 50 of these images acquired over non-overlapping regions, we were able to index and to measure the distances between each local maximum (*i.e.*, the thiophene molecules). The histogram in Figure 3b displays these data as the probability of finding a thiophene molecule at a

particular distance away from another thiophene molecule. This type of measurement is sufficient for isotropic surfaces (*i.e.*, fcc {111} noble metals), however, the anisotropy of this system necessitates a more accurate measurement that is angle dependent. Figure 3c shows this data set in a polar coordinate form. Here, the color scale indicates the probability of finding a thiophene molecule at a given distance *and* angle away from a neighboring thiophene molecule. In this light, we should be able to extract the SMI component of adsorption from the surface potential energy landscape as dictated solely by the surface physical structure (*i.e.*, the (1×1) corrugation). We note that thiophene adsorbs with preferred separations (representative model given in Figure 2b, red curve) and we label these distances for further analysis. The corrugation in the $\langle 001 \rangle$ direction ($3.98 \text{ \AA}$) dominates due to the surface morphology of $\text{Pd}\{110\}$.

Figure 3. Determining the effects of surface physical structure and surface electronic structure on the adsorption of thiophene on $\text{Pd}\{110\}$ -(1×1) at 4 K. (a) Topographic STM image ($V_s = 0.1 \text{ V}$; $I_t = 0.9 \text{ nA}$; $400 \text{ \AA} \times 400 \text{ \AA}$) of thiophene deposited from room temperature onto a $\text{Pd}\{110\}$ single crystal held at 4 K. The surface directionality is given by the labeled white arrows. (b) Histogram of the probability of finding a thiophene molecule at a given distance from another thiophene molecule, compiled from more than fifty non-overlapping STM images like that in (a). (c) Polar histogram of the data in (b) where the color scale represents the probability of finding a molecule at a given distance and angle from another thiophene molecule (red = high probability; blue = low probability).

On the D-reconstructed (1×2) $\text{Pd}\{110\}$ surface, we observed the phenomenon of directional local faceting that occurs only when both thiophene *and* tunneling electrons of sufficient energy are present. With repeated imaging at high bias voltages (*ca.* $\pm 1 \text{ V}$) we are able to create new faceted steps (Figure 4a) that propagate along the $\langle 1\bar{1}0 \rangle$ direction with a plane that is incommensurate with the plane of the underlying substrate. Step edges are known to be more catalytically active sites due to the charge dipole across the step and higher coordination.¹²⁻¹⁴ Here, we posit that the proximity of adsorbed thiophene to these active sites favors the bias voltage-driven faceting. After creating the faceted steps, we were able to discern between regions where the surface remained unaffected and where the surface Pd atoms relaxed outward. This observation is apparent in Figure 4a, where the unaffected region is denoted α and the faceted region is denoted β . Height profiles obtained over topography in this area revealed that the faceted plane is at $3.2 \pm 0.8^\circ$ grade off the substrate plane. In Figure 4b we have normalized the plane of the β region to demonstrate that the angle of the facets are self-consistent. The inset of Figure 4b is a high resolution STM image showing that the Pd atoms revert back to the (1×1) phase on the β region.

Figure 4. Adsorbate-promoted tunneling electron-induced faceting of D/Pd{110}-(1 × 2). (a) Topographic STM image ($V_s = 0.05$ V; $I_t = 0.05$ nA; $348 \text{ Å} \times 348 \text{ Å}$) highlighting the deviation of the facet planes (β) from the underlying substrate plane (α). (b) Topographic STM image ($V_s = 0.05$ V; $I_t = 0.05$ nA; $260 \text{ Å} \times 260 \text{ Å}$) of region β in (a), self-consistently plane subtracted. The inset is a high resolution STM topographic image ($V_s = 0.01$ V; $I_t = 1.4$ nA, $22 \text{ Å} \times 22 \text{ Å}$) acquired over the region denoted by the black box. Here, the (1×1) Pd structure has returned. (c) Representative $I(V)$ spectrum taken over Pd in the α region. The red curve represents the forward sweep and the blue curve represents the reverse sweep. The dashed line marks the experimentally obtained onset value (0.38 ± 0.02 eV) from an average of 45 spectra. Note: $I(V)$ spectroscopy was acquired in constant-height mode.

Conductance spectroscopy over the α region has allowed us to determine the onset voltage for D migration to the subsurface layer. The spectra in Figure 4c represent a typical conductance measurement of the faceting process. Initially appearing like a hysteretic anomaly, closer inspection reveals that since D is drawn to the subsurface region, outward relaxation of the Pd lattice occurs, thus, physically decreasing the tip-sample separation. Because of the exponential dependence of current, I , on the tip-sample separation, this surface relaxation is observed in real time as a steep onset in I response (dashed line in Figure 4c). Since only a finite amount of subsurface D could be drawn up beneath the probe, we were able to acquire only one spectrum in each location. From 45 such spectra, we have determined the onset to drawing subsurface D to be 0.38 ± 0.8 eV. This conductance signature is not observed over the (1×1) β regions, suggesting complete population of the subsurface sites.

The microscopes used in this work have been moved to UCLA and are being used in further DoE-supported work imaging buried interfaces.

Supported Personnel

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Mr. Adam Kurland, Graduate Student (now a Research Scientist at Science Instruments)

Mr. John Thomas, Graduate Student

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Publications

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“Heads *and* Tails: Simultaneous Exposed and Buried Interface Imaging of Monolayers,” P. Han, A. R. Kurland, A. N. Giordano, S. U. Nanayakkara, M. M. Blake, C. M. Pochas, and P. S. Weiss, *ACS Nano*, **3**, 3115-3121 (2009).

“Scanning Tunneling Microscopy and Spectroscopy of Nanoscale Assemblies,” M. M. Blake, Ph.D. Thesis, Department of Chemistry, The Pennsylvania State University, University Park, PA, USA (2010).

“Adsorbate-Promoted Tunneling-Electron-Induced Microfaceting of D/Pd{110}-(1×2),” A. R. Kurland, P. Han, J. C. Thomas, A. N. Giordano, and P. S. Weiss, *Journal of Physical Chemistry Letters* **1**, 2288 (2010).

“Atomic-Scale Studies of Heterogeneous Catalysis, Substrate-Mediated Interactions, and Interface Structures,” A. R. Kurland, Ph.D. Thesis, Department of Chemistry, The Pennsylvania State University, University Park, PA, USA (2010).

Awards

IEEE, Senior Member, 2009

National Chemical Laboratory, Prof. J. W. McBain Memorial Lecture, Pune, India, 2009

Hong Kong University of Science and Technology Institute of Advanced Study Distinguished Lecture, 2010

Thomas Jefferson University, William Potter Lecture, 2010

American Chemical Society, Elected Fellow (2010)

Chinese Academy of Sciences and Chinese Chemical Society, Molecular Science Forum Lecture Professorship (2010)

Chinese Chemical Society, Honorary Fellow (2010)