ULTRATHIN METALS FILMS ON W(221): STRUCTURE, ELECTRONIC PROPERTIES AND REACTIVITY

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Abstract

Nanoscale pyramidal facets with (211) faces are formed when W(111) surface is covered by monolayer film of certain metals (including Pt, Pd and Au) and annealed to $T \geq 750$ K. In the present work, we focus on the structure, electronic properties and reactivity of planar W(211) covered by ultrathin films of platinum and palladium. The measurements include soft X-ray photoelectron spectroscopy using synchrotron radiation, Auger electron spectroscopy, low energy electron diffraction (LEED) and thermal desorption spectroscopy. The metal film growth and evolution during annealing has been investigated for coverages ranging from 0 to 8 monolayers. The films grow initially in a layer-by-layer mode at 300 K. LEED, Auger, and Surface Core Level Shift (SCLS) measurements reveal that for coverages of one monolayer, the films are stable up to temperatures at which desorption occurs. In contrast, at higher coverages, SCLS data indicate that surface alloys are formed upon annealing films of Pt and Pd; surface alloy formation is not seen for Au overlayers. These findings are discussed in terms of structural and electronic properties of these bimetallic systems. Relevance to catalytic properties for acetylene cyclization over Pd/W(211) is also discussed.

1. Introduction

Recently, bimetallic systems have drawn significant attention because of their interesting properties, which lead to applications in fields such as novel materials, catalysis, and microelectronics. Bimetallic systems (thin films and alloys) are important catalysts for hydrocarbon reactions. Their selectivity and activity may be tuned by changing concentrations, exposed crystallographic faces and thermal treatment [1-4]. Despite their importance, the experimental data

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on these systems is rather scarce, and even general trends across the periodic table have not yet been established [5].

Bimetallic systems are rather complex and their experimental description requires a multitechnique approach to obtain information on electronic structure, geometry and defects, as well as adsorption and dissolution energies. Soft X-ray Photoelectron Spectroscopy (SXPS) is a particularly suitable technique for characterization of the electronic properties of such materials. Moreover, the utilization of high resolution synchrotron radiation as an excitation source allows one to measure such subtle effects as surface core level shifts (SCLS) and interface core level shifts, which recently have been topics of many theoretical studies [6–8]. It is believed that core level binding energy shifts provide a probe of the changes in the electronic structure of atoms in different chemical environments; this is supported by arguing that core levels associated with compact orbitals lie entirely within the valence shells, which are changed due to chemical interaction. Thus, the electrostatic potential in the space occupied by the core shells is changed uniformly. Nonetheless, interpretation of photoelectron spectra is not easy, as—apart from a simple charge exchange effect—they may be influenced by a number of other effects related to changes in final state screening, changes in the reference level (Fermi energy) and intra-atomic charge transfer [9]. Other complementary techniques, such as Temperature Programmed Desorption (TPD), Auger Electron Spectroscopy (AES) or Low Energy Electron Diffraction (LEED), are necessary to measure adsorption/desorption energies, and to diagnose the geometric structure and overall chemical composition in bimetallic systems.

In the present work, we study transition and noble metals (Pd, Pt, Au) on a tungsten (211) substrate. Tungsten has the cubic body centered lattice structure and its (211) face is composed of parallel rows and troughs, which run along the <1\(\frac{1}{2}\)1> crystallographic direction. There are two inequivalent sites for tungsten atoms on this surface, which, together with bulk atom sites, produce a three component XPS spectrum (see Sec. 3 A). During adsorption of metals onto W(211), it is expected that the trough sites are filled first, then the sites above the substrate atom rows. The electronic properties of transition bimetals are determined mostly by the distribution of their d electrons and the interplay between d and non-d (s,p) conduction bands [10,11].

It has been shown recently that the W(111) surface undergoes massive reconstruction upon adsorbing a single monolayer of certain metals (including Au, Pt and Pd) and annealing. The resulting surface is covered completely by three-sided pyramidal facets, whose sides are {211} planes [12].
In the present work, we report on the growth, thermal stability, structure, electronic properties and surface reactivity of metallic films (Pd, Pt, Au) on a W(211) substrate. Film thicknesses are in the range 0–8 monolayers. Most of the data are shown for Pd on W(211), although Pt films have a very similar behaviour. Of particular interest is the observation, using SXPS, that an alloy is formed in the surface region upon heating multilayers of Pd or Pt to temperatures higher than 700 K. In contrast, Au does not form an alloy with W. An unusual enhancement of chemical activity for acetylene cyclization over the annealed Pd/W alloy surface is found, in comparison with a monolayer or multilayer of Pd.

2. Experimental

Experiments have been performed in two stainless steel ultrahigh vacuum chambers at Rutgers University and at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory, on beamline U4A. The chambers have base pressures of \( \leq 1 \times 10^{-10} \) Torr. The Rutgers setup is equipped with an Auger spectrometer, LEED optics, quadrupole mass spectrometer (QMS) and a quartz crystal microbalance. The NSLS setup is connected to the UV storage ring via a 6-meter toroidal grating monochromator providing light in the range 10–200 eV. Photoelectron spectra have been measured with a 100 mm VSW hemi-spherical analyser. The total spectral resolution is about 0.2 eV at 150 eV, and below 0.1 eV at 80 eV photon energy. The excitation X-ray beam is incident at 45 degrees with respect to the surface normal and the light polarization vector does not coincide with any low index crystallographic directions of our sample. Both setups also contain several metal dosers used for deposition of platinum, palladium and gold. The (211) tungsten substrate is prepared by repetitive heating in oxygen \( (1 \times 10^{-7} \text{ Torr}) \) at 1300 K, followed by an abrupt increase of substrate temperature to 2300 K for a few seconds. The cycle is repeated until no traces of carbon can be found in AES spectra. Following this treatment, the tungsten sample rarely needs oxygen treatment, and it can be cleaned by high temperature flashes only. Metal dosers are constructed by wrapping thin metal wires \( (0.1–0.25 \text{ mm}; \text{ Pt, Au, Pd}) \) around a resistively heated tungsten filament or by spot-welding a piece of foil (Pt) to a tungsten wire. Special care is taken to outgas the dosers before their use. Dosers are shielded during operation by cooled surfaces. The background pressure during dosing does not exceed \( 2 \times 10^{-10} \) Torr.

A variety of techniques is used throughout the present experiments to estimate surface coverages. As discussed below, calibration of sources is based on a quartz crystal microbalance
technique (QCM), Auger uptake curves, SXPS admetal peak shapes, quenching of substrate surface features, and TPD curves.

The only absolute technique employed in this work for determining surface coverage is the measurement using the QCM. The QCM allows determination of 1 physical monolayer (ML) to an accuracy of ±15% (corresponding to 1.63 × 10¹⁵ atoms/cm², the coverage for which all the substrate W atoms in the rows and troughs are covered by overlayer metal atoms). We use the QCM data to compare with Auger peak-to-peak intensities and TPD spectra in the same vacuum chamber. The Auger and TPD measurements are used as “transfer” standards for coverage determination in other vacuum chambers, and other indicators for identification of 1 physical ML are also developed. For example, in a SXPS experiment, several different approaches are employed to identify formation of 1 ML, including (a) quenching of surface core level features in W(211) spectra, (b) monitoring changes in 4f admetal core level spectra with increasing coverage (for Au and Pt) [13], and (c) the change of photoelectron work function. In the following sections, more information is given about the various methods for coverage determination.

In order to investigate thermally activated processes occurring on overlayer films and at the interface, stepwise annealing to increasingly higher temperatures is used: after metal deposition the sample is annealed in a sequence of increasing temperatures ranging from 400 to 2300 K. After each step the sample is cooled down, and depending on the experiment, XPS, AES and LEED data are recorded. TPD spectra are measured at 10 K/sec heating rate. Photoelectric work function changes are recorded by the low energy spectrometer cutoff signal with a bias voltage −5 V on the target. Sample temperature is measured by a W5%Re–W26%Re thermocouple spot-welded to a side of the W crystal.

3. Results and Discussion

A. Film growth and thickness calibration

For deposition of Pt onto W(211) at 300 K, the Auger peak-to-peak amplitude has been measured as a function of deposition time. Straight line segments with distinct breaks at regular intervals are observed (cf. Fig. 1). Each break may be associated with completion of one physical ML, as verified with QCM and TPD measurements (sec Sec. 3 B). Evidence for layer growth is observed to ≥ 3 ML.
Fig. 1. Auger peak-to-peak intensity (at 64 eV) during deposition of Pt with incident electron energy of 3 keV.

A variation in the intensity of substrate photoelectron peaks has been measured in SXPS of W 4f$_{7/2}$ intensities vs. deposition time for Pt, Pd, and Au. See, for example, Fig. 2, for deposition of Pd. The upper curve is the W 4f$_{7/2}$ spectrum for a clean W(211); the two peaks at lower binding energy (31.1 and 31.3 eV) are surface features, and are associated with photoemission from row and trough atoms respectively. The third peak at higher binding energy (31.5 eV) is due to bulk W. As the dosing time increases (cf. Fig. 2), the W surface atoms are buried beneath Pd atoms, and the surface peaks are attenuated. The coverage, at which the surface peaks disappear completely, is identified as one physical monolayer of Pd. Similar behavior is seen for attenuation of surface peaks by monolayers of Pt and Au on W(211).

Figure 3 shows two series of LEED patterns for films of Pt and Pd “as deposited” at 300 K. The persistence of (1 × 1) LEED patterns indicates that overlayer growth is pseudomorphic for the first two layers. As film thickness increases, e.g., for Pd/W(211) (not shown here), the images exhibit well defined periodicity along the $<111>$ direction, however, they are streaked and more diffuse along $<0\bar{1}1>$ (across rows). This suggest that the surface is composed of atomic chains running parallel to substrate rows. However, these chains (with well-defined atomic periodicity along them) are randomly terminated and, thus, no distinct periodicity in the direction perpendicular to the rows can be seen.
Rows on W(211) surface form channels, along which admetal atoms can diffuse easily. For example, for palladium the activation energy for a single jump along the row is 0.32 eV [15]. This value is low enough to allow efficient diffusion along rows even at temperatures well below the room temperature. In contrast, diffusion of a single admetal atom across the row-trough substrate structures is inhibited by a higher energy barrier, and has low probability at room temperature [16]. Note also that Pd and Pt have metallic radii very close to the W substrate and, thus, pseudomorphic growth may proceed with little stress of the film lattice. The remaining LEED patterns in Fig. 3 are discussed below.

B. Thermally activated processes and annealing behaviour of admetal films

TPD spectroscopy provides insights into the overlayer coverages and desorption energies. Three components can be seen in the TPD spectra of palladium on W(211) (cf. Fig. 4). At low coverages, up to ~0.5 ML, only a single peak is seen at ~1600 K. As Pd coverage increases, a second peak develops (~1400 K) and saturates with increasing dose. Using the QCM, we identify
Fig. 3. LEED images for $\sim 2$ ML Pt on W(211) shown in the left column: (a) as dosed, (b) annealed to 700 K, and (c) annealed to 1400 K. LEED images for $\sim 2$ ML Pd on W(211) shown in the right column: (d) as dosed, (e) annealed to 700 K, and (f) annealed to 1050 K.
Fig. 4. TPD spectra of Pd desorbed from W(211) for a few different coverages. Heating rate is 10 K/s.

The coverage corresponding to saturation of the two peaks at 1400 K and 1600 K as one physical monolayer (corresponding to $1.63 \times 10^{15}$ atoms/cm$^2$). The first peak (at lowest temperature) is attributed to bulk Pd sublimation, while the peaks at 1400 K and 1600 K with Pd atoms adsorbed on row and trough sites on W(211). The desorption behavior of platinum is similar, however, the desorption temperatures are higher, and the lower temperature monolayer peak coincides with the bulk TPD peak. Detailed results will appear elsewhere [17].

By looking at the sample with SXPS (cf. Figs. 2 and 5), one can study the adsorption and desorption of Pd from the perspective of the W surface. On the "as dosed" surface, a single Pd monolayer leads to suppression of the surface core level (W4f_{7/2}) features (cf. Fig. 2). Upon heating the Pd monolayer (cf. Fig. 5), the desorption onset can be seen starting at 1300 K. Further annealing steps uncover (at 1400 K) the row tungsten atoms (cf. Fig. 5). Continued heating to increasingly higher temperatures produces the clean-tungsten three-component spectrum at about 1650 K. The two results (TPD and SXPS) are quite consistent.

For temperatures below 1100 K for palladium, and 1700 K for platinum, the desorption rate is insignificant. However, it is clear from AES and SXPS that there are substantial changes that take place in the surface and interfacial layers. We describe now the processes occurring on overlayers due to annealing, as studied with LEED, AES and SXPS.
Fig. 5. W 4f photoelectron energy spectra from 1 ML Pd on W(211) (annealing sequence). Photon energy is 85 eV.

The sequences of LEED images (cf. Fig. 3a to 3c and 3d to 3f), taken for ~2 ML films of Pd and Pt, show that the pseudomorphic structure of the overlayers is not changed by thermal treatment. Although LEED images become sharper with higher contrast when annealing temperature is increased, there is no qualitative change in LEED patterns up to the desorption temperatures. (The case of submonolayer coverages, where various surface reconstructions occur, is discussed in [17].) The Auger annealing curves (cf. Fig. 6) show stable Auger signal ratios for Pd/W, for thicknesses of one monolayer and below. This stability (seen also for Pt) has been assigned to the strong interaction of Pt and Pd atoms with the tungsten substrate, and to the fact that Pt-group metals have smaller surface free energies than W; the low energy state in these cases is comprised of a wetting layer, where a single monolayer film stays on top of the substrate [12,18].

For thicker films (2 and 5 ML), there is a substantial drop in the values of Auger ratios between 500 K and 700 K for palladium, and between 800 K and 1100 K for platinum, well below the temperature, at which desorption begins to be observed. Such changes have been observed previously for Pt and Pd films on W(111) and W(110) surfaces [19–21] and were attributed to the agglomeration into clusters of the overlayer material in excess of one monolayer. As discussed in Sec. 3 C, this explanation does not appear to be consistent in the present case.
Fig. 6. The ratio of Auger peak-to-peak intensities at 330 eV and 169 eV for Pd and W, respectively, as a function of annealing temperature for a few different coverages. Electron energy is 3 keV.

Similar to the AES results, photoelectron spectroscopy shows evidence for stable single monolayer films. The annealing sequence for one monolayer coverage is shown in Fig 5. As can be seen, the chemical state of tungsten interface atoms remains the same for all temperatures below the desorption onset.

C. Evidence for formation of an alloy film

As shown in Fig. 6 and discussed above, there are considerable changes in AES intensities for multilayer films, at temperatures well below the onset of desorption. We also find that a new feature appears in SXPS spectra when multilayer Pd or Pt films are annealed above ~700 K (cf. Fig. 7). This new peak is shifted ~1 eV towards higher binding energies with respect to the bulk W4f7/2 peak. Moreover, it can be seen that the tungsten substrate peak does not change significantly in intensity up to 1100 K for Pd. This stability indicates that the palladium deposit on (211) surface remains flat and does not break into clusters. If clusters were forming at temperatures below 1100 K, one would expect significant increase of the substrate peak intensity. (The bulk W peak attenuated by a 5 ML palladium film has less than 10% of the intensity, which we would expect for tungsten covered with single monolayer of palladium. Based on a simple
calculation, if only 10% of the surface were uncovered due to the cluster formation, the intensity of the tungsten peak should increase at least by a factor of two upon annealing. If 30% of the surface were uncovered, the peak should increase at least by a factor of four.) Thus, the apparent absence of Pd cluster formation leads to another explanation for the appearance of the new peak at 32.4 eV binding energy (W4f_{7/2}), namely, that tungsten atoms diffuse from the interface into the overlayer film. This indicates the formation of a palladium-tungsten (or platinum-tungsten) alloy. The content of tungsten in the overlayer alloy increases with annealing temperature; up to 850 K, the tungsten alloy peak remains at fixed position but its intensity increases. This indicates that there is a single chemical state of W atoms in the Pd lattice. Under this conditions, the alloy is very likely dilute, and tungsten atoms are surrounded by host atoms only.

Fig. 7. W 4f photoelectron spectra for 5 ML Pd on W (211) (annealing sequence). Photon energy is 145 eV.

Above 850 K, the alloy peak in Fig. 7 shifts to lower binding energy and broadens. The 4f photoemission peaks for W atoms in the Pd host are shifted (as compared to bulk W) due to chemical interactions. It is expected that a W atom surrounded completely by unlike atoms will experience the maximum core level shift, while for configurations with both like and unlike nearest neighbour atoms, the resulting core level binding energy should be somewhere between
that of the tungsten bulk and the tungsten impurity in a palladium host. Different possible nearest neighbor configurations cause broadening of W 4f photoelectron peaks due to disorder and Madelung-type effects [22].

In the simplest view, charge transfer between the valence levels of atoms in an alloy uniformly changes the electrostatic potential in the space occupied by core levels; this causes chemical shifts of core electron binding energies. However, in most cases of binary alloys, this simplistic attitude is not sufficient, and even a condition that the shift should be in opposite directions for the two alloy components is not fulfilled [9]. There seems to be a general trend in early-d–late-d transition bimetals, that upon bond formation, the chemical shifts are in same direction—to higher binding energies—for both constituents [10]. Indeed, we have found that the Pt–W system follows this trend [13]. Corresponding data for Pd core levels in the Pd–W system cannot be measured with our monochromator (the 3d Pd levels are beyond our photon energy range, while 4s and 4p levels are broad and not suitable for SCLS), however, we expect that Pd should follow the same trend for its 3d shallow core level. In fact, such a shift (to higher binding energy) was observed by Campbell et al. for an annealed 4.5 ML film of Pd on W(110), but it was attributed to effects other than alloying [18].

The work function changes for 8 ML Pd/W(211) (see Fig. 8) are correlated with the SXPS results of Fig. 7. The work function value does not change substantially up to \( \sim 800 \) K. In the region \( 800–1100 \) K, the work function drops by 0.4 eV; this drop coincides with alloy formation. There is a plateau in work function between \( 1100 \) K and \( 1200 \) K, whereas the W 4f\(_{7/2}\) substrate peak intensity increases substantially within this range. This may be attributed to slow desorption of Pd from the alloy, with simultaneous segregation of excess tungsten to the interfacial region, so the surface itself remains unchanged. (The limiting concentration of W in the Pd host cannot be exceeded; see discussion below.) The plateau is followed by another significant drop of 0.2 eV, with a simultaneous dramatic increase of tungsten signal, which is caused by desorption of the multilayer palladium deposit. The work function then reaches a local minimum, which also has been observed during growth of Pd and Pt, and has been attributed to the single physical monolayer coverage. The work function value returns to the value characteristic for clean W(211) surface after annealing to \( 1550 \) K. The changes in W 4f\(_{7/2}\) spectra associated with desorption of a single Pd monolayer are shown in Fig. 5.

Inspection of the Pd–W alloy phase diagram [23] reveals that the solubility of Pd in a solid W host is rather insignificant: below 2 at.%. On the other hand, W shows significant solubility in a Pd host. The solubility limit is about 22 at.% and is nearly independent of temperature.
(The limiting value, however, may be different in our case, as we possibly have an artificial bcc palladium lattice due to pseudomorphic growth.) For platinum, the overall character of the phase diagram is similar, but the solubility limit for W in a Pt host is about 60 at.%. Our SXPS data for monolayers and multilayers of Pt and Pd on W(211) are consistent with the diagrams. We have found that one monolayer of Pd on W and of Pt on W is stable with no evidence for intermixing. Upon annealing multilayers of Pd (Pt) on W(211), the data can be interpreted to indicate that tungsten atoms diffuse into palladium and platinum lattices. Independent studies show that a Pd (Pt) monolayer film remains on the outer surface to cover the surface alloy [24].

![Graph](image)

**Fig. 8.** Work function changes on 8 ML Pd/W(211) sample (circles) and photoelectron signal intensity at the W substrate peak position (squares) as a function of annealing temperature.

For gold on W(211), no evidence for alloying is found. On a heavily dosed W(211) sample, gold tends to form clusters at rather low temperatures (∼500 K), as suggested by a significant increase in W peak intensity starting at this annealing temperature. Simultaneously, the intensity of Au 4f photoelectron peak decreases, and an additional peak attributed to a single monolayer appears. Apart from the Au 4f monolayer peak, no chemical shifts for gold films on W(211) have been observed.
Valence band spectra for 5 ML Pd/W(211) are presented in Fig. 9a. Both the “as dosed” and the annealed films (to 700 K) exhibit an intense peak just below the Fermi level and a broader and less intense one about 3 eV below $E_F$. Upon annealing to 1050 K to form an alloy (annealing was done twice to check for saturation), a significant change appears. The intensity of the peak just below $E_F$ dramatically decreases. In Fig. 9b, we show a hypothetical spectrum of a homogeneous “mechanical” 22 at.% W + 78 at.% Pd mixture (obtained by a linear combination of pure Pd and pure W spectra), and compare it with measured W–Pd alloy spectrum. As can be seen, due to the alloying process intensity is transferred from the region 0–2 eV below $E_F$ to the region 2–6 eV below $E_F$. Due to the prevailing content of Pd in the alloy, and the rather weak W signal, we expect that the recorded valence band spectra reflect mostly the palladium band structure.

![Fig. 9](image)

**Fig. 9.** (a) Valence band SXPS spectra at 85 eV photon energy for a 5 ML Pd/W(211) sample. (b) Comparison of a hypothetical “mechanical” mixture 22at.% W + 78 at.% Pd spectrum (dashed line) with Pd–W saturated alloy spectrum (solid line). Photon energy is 85 eV.

Electronic structure of palladium has been the subject of intensive theoretical and experimental studies [11,25]. Pd is characterized by a system of d-like bands cut through by a broad s,p-like band. The Fermi level is situated nearly at the edge of the d band system. In general,
the total density of states (DOS) is dominated by the d-like states. At the Fermi level and in
the region just below $E_F$, the DOS is almost purely d-like, but in the region 2–7 eV below the
Fermi level, there is a noticeable admixture of s,p-like DOS. Based on differences in electroneg-
ativity (1.7 for tungsten and 2.2 for palladium), one might expect a charge transfer to tungsten
atoms upon alloying. Bzowski and Sham [10] investigated a chemically similar early-d–late-d
transition alloy (Pd–Ti) by XPS and XANES. They found that alloying causes rehybridization of
the palladium valence band structure. As a result of this process, Pd gains s,p electrons and
loses d electrons. The net charge transfer onto the Pd site is negative, so the electronegativity
condition is fulfilled; nevertheless, the Pd 3d core level energy shift is in the direction opposite to
the simplistic prediction of the charge transfer model. The depletion of intensity in the valence
band spectrum upon alloying strongly suggests a similar behaviour of the Pd–W system.

A sophisticated local density formalism has been applied by Wu and Freeman [26] to study
interaction of palladium monolayers on different early transition metals (Ta, W, Re). They find
that electron density is depleted from around outer regions of substrate atoms and from the
central regions of palladium atoms, which is in line with the s,p $\rightarrow$ d rehybridisation process.

D. Catalytic properties of Pd/W(211)

To understand the structure-reactivity relationship on bimetallic surfaces, acetylene cyclization
to form benzene, a known structure-sensitive reaction, is of particular interest [27,28]. TPD
results exhibit negligible amounts of benzene formation on a clean W(211). A single monolayer
of Pd on W(211) decreases the high reactivity towards acetylene decomposition and increases the
propensity towards benzene product formation (see Fig. 10). Increasing the Pd film thickness
to $\approx$ 6 ML causes large changes in benzene product distributions formed from 3 L of acetylene
(1 L = 1×10$^{-6}$ Torr·s). The integrated benzene yield decreases by more than 50%, in comparison
to the 1 ML Pd covered surface. A more detailed discussion of C$_2$H$_2$ reactions on these two
surfaces is presented elsewhere [29].

In contrast to the above, heating a 6 ML Pd/W surface to 1050 K results in a surprising
five-fold increase in benzene yield from acetylene cyclization, as compared to the 1 ML Pd/W
surface (cf. Fig. 10). As shown in Figs. 9a and 9b, annealing a multilayer Pd/W(211) surface
causes a striking change in surface electronic structure due to surface alloy formation. Whereas
annealing of multilayer Pd/W leads to alloy formation, a single monolayer of Pd/W(211) does
not form a surface alloy. The lower desorption temperatures of benzene (150 K, 180 K, and 270 K) and the five-fold increased benzene yields on the 1050 K preannealed 6 ML Pd/W(211) surface, apparently result from the Pd–W alloy formed at the Pd/W interface.

Fig. 10. TPD spectra of reactively formed benzene on a surface of 1 ML and 6 ML Pd on W(211) model catalyst.

4. Conclusions

The bimetallic systems Pd–W, Pt–W, and Au–W have been studied with LEED, AES, TPD, and SXPS. The admetal form pseudomorphic films on W(211). Single monolayers of these admetals are very stable against thermally activated rearrangement. This may be attributed to minimization of surface free energy upon formation of the monolayer and strong chemical interactions between early-d–late-d transition metal atoms. Thick (2–8 ML) films of Pd and Pt undergo alloying with the W substrate during annealing. In accordance with alloy phase diagrams, it appears that tungsten atoms diffuse into the overlayer. A substantial rearrangement of the valence band of Pd, consistent with the core level shifts of W and Pt, has been observed. This suggests charge transfer from W to Pd/Pt, accompanied by rehybridization of the valence bands, and intra-atomic s,p → d charge transfer in Pt group metal atoms. No evidence for clustering of Pt or Pd films has been found. On the contrary, in Au–W system no alloying
is found, but cluster formation occurs upon annealing. A Pd–W model catalyst, composed of multilayer Pd supported by W(211), has shown greatly increased reactivity towards acetylene tricyclization when annealed to 1050 K. This effect is attributed to the chemical activity of a W–Pd saturated alloy.

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References