Nanoscale surface chemistry

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We report evidence in several experiments for nanometer-size effects in surface chemistry. The evidence concerns bimetallic systems, monolayer films of Pt or Pd on W(111) surfaces. Pyramidal facets with (211) faces are formed on annealing on physical monolayer of Pt, Pd, on W **float** on the outer surface, whereas multilayer films form alloys on annealing. Acetylene reactions over bimetallic planar and faceted Pd/W surfaces exhibit size effects on the nanometer scale, that is, thermal desorption spectra of reactively formed benzene and ethylene (after acetylene adsorption) change systematically with facet size. In the second case, the decomposition of C2H2 over planar and faceted Ir(210) surfaces also exhibits structure sensitivity; temperature programmed desorption of H2 from C2H2 dissociation depends on the nanoscale surface structure. Finally, we have characterized interactions of Cu with the highly ordered S(4 × 4)/W(111) surface. The substrate is a sulfur-induced nanoscale reconstruction of W(111) with (4 × 4) periodicity, having broad planar terraces (≈30 nm in width). Fractional monolayers of vapor-deposited Cu grow as three-dimensional clusters on the S(4 × 4) surface over a wide coverage range. At low Cu coverage (= 0.1 ML), Cu nanoclusters nucleate preferentially at characteristic 3-fold hollow sites; we find a clear energetic preference for one type of site over others, and evidence for self-limiting growth of nanoclusters.

An important issue in surface chemistry and catalysis is how surface structures and features with nanometer dimensions affect reactivity in heterogeneous systems (1–3). The focus of our work has been on several aspects of nanoscale phenomena that influence surface chemistry, including faceting of metallic and model bimetallic catalyst surfaces, and nucleation of subnanometer metallic clusters on sulfided surfaces. We study atomically rough substrates [bcc (111) surface of W, and fcc (210) surface of Ir] that are morphologically unstable, that is, the initially planar substrate becomes covered with nanoscale facets when covered with monolayer films of gases or other metals, and heated to elevated temperature. Major objectives of this work have been (i) to determine how the surface transition from planar to faceted affects the surface reactivity of metallic and bimetallic systems, and (ii) to characterize the nucleation and growth of metals on sulfided W surfaces. The three main components of this effort are surface structure, surface chemistry, and surface electronic properties.

The importance of bimetallic catalysts based on Pt-group metals has been increasing in recent decades (4, 5). These catalysts display important advantages over classical reforming catalysts, including better stability, as well as improved activity and selectivity. In particular, refractory metals (W, Mo, Re, . . .) in combination with Pt-group metals are active catalysts for hydrogenation and hydrogenolysis reactions (6–9).

Our previous work in the area of bimetallic surfaces is summarized in two review articles (10, 11). In brief, morphologically unstable W(111) and Mo(111) coated with a single physical monolayer (ML) of certain metals or other elements (Pd, Rh, Ir, Pt, Au, O) undergo massive reconstruction from a planar morphology to a microscopically faceted surface on heating to T > 700 K. Three-sided nanometer-sized pyramids form in which the facet sides are mainly film-covered {112} facets. The faceting transition in these systems is believed to be thermodynamically driven but kinetically limited: annealing is needed to achieve sufficient surface atom mobility for mass transport. The overlayer film increases the anisotropy in surface free-energy and enhances the relative stability of the faceted morphology. Striking evidence for structure sensitivity is seen in catalytic hydrogenolysis of butane over planar and faceted Pt/W.

Recent synchrotron radiation studies using soft x-ray photoemission spectroscopy (SXPS) have provided insights into the electronic properties and thermal stability of the bimetallic systems.

In the following paragraphs, we describe recent results and focus on three main aspects of the studies: surface structure and morphology, surface chemistry, and surface electronic properties. We begin with atomistic studies of faceting and reconstruction in bimetallic systems based on W(111) and discuss evidence that acetylene reactions over Pd/W(111) surfaces exhibit size effects on the nanometer scale. We use SXPS to show that interfacial mixing, even at 300 K, is observed for multilayers of Pt, Rh, Ir on W(111), whereas monolayer films are stable at high T. We report the oxygen-induced faceting of Ir(210), and describe structure sensitivity in C2H2 hydrogenation in the overlayer film. WE describe studies of metals on sulfided W(111), including self-limiting growth of Cu nanoclusters on specific surface sites.

This program includes detailed microscopic studies of faceting of metal substrates induced by monolayer overlayer films. We believe the results of these studies are important in understanding the mechanisms of possible dynamic structural rearrangements at the surfaces of high area metallic and bimetallic catalysts under high-temperature operation.

Methods

In this work we have used an array of ultrahigh vacuum surface science methods, including high-resolution scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and
low-energy electron microscopy (LEEM) for structure and morphology; temperature-programmed desorption (TPD) for surface chemistry; and high-resolution SXPS (HRSXPS) using synchrotron radiation for electronic properties.

Results and Discussion

Faceting of W(111) Induced by Ultrathin Metal Films. We have used two microscopic methods to provide insights into the mechanism of metal film-induced faceting of bcc(111) surfaces, and have found evidence for the nucleation and growth of faceted regions (12, 13). LEEM and STM have been used to investigate the faceting of W(111) as induced by Pt. The atomically rough W(111) surface, when fully covered with a monolayer film of Pt and annealed to temperatures higher than ≈750 K, experiences a significant morphological restructuring: the initially planar surface undergoes a faceting transition and forms three-sided pyramids with {211} faces as seen clearly in the STM image of Fig. 1. In complementary studies, LEEM can distinguish between planar and faceted surfaces based on the different types of diffraction of low-energy electrons on surfaces with different morphologies, with up to ≈70 Å lateral resolution. LEEM measurements (12, 13) of Pt/W(111) demonstrate that the transition from planar to faceted structure proceeds through the nucleation and growth of spatially separated faceted regions. The surface remains planar for Pt coverages less than ½ ML (1 ML = 1.7 × 10^{15} atoms per cm^2). As the Pt coverage increases above ½ ML on the heated W surface, local islands of Pt with coverage of 1 ML are able to nucleate, and it is there that facets form. When the entire surface has a coverage of 1 ML, the surface is fully faceted.

STM data (Fig. 2) confirm the LEEM observations that a partially faceted Pt/W surface is a combination of large planar regions with scattered faceted regions. The faceted regions include pyramids of two distinct size distributions (Fig. 2): large individual pyramids or clusters of large pyramids, surrounded by smaller size satellite pyramids. LEEM and STM prove to be excellent complementary microscopic techniques in the study of faceting. STM provides structural information down to atomic scale. Although the resolution of LEEM does not match that of an STM, LEEM has several advantages that make it a most useful tool in studying the kinetics of large scale morphological transformations: it is capable of imaging surfaces at very high temperatures, and the surface is easily observed during metal deposition.

There is ample documentation that the atomically rough W(111) surface develops nanometer-scale facets with W\{211\} orientation when covered by 1 ML films of Pd, Pt, Rh, or Ir, followed by annealing (10, 11). In recent experiments, we have found that the metal film-covered W(211) surface itself may undergo a faceting transition (14). A W(211) surface covered with a thin film (between 0.5 and 1 physical monolayer) of Rh, Pt or Pd is found to exhibit an n × 1 superstructure when annealed above a threshold temperature of ≈900 K (500 K for Pd). The superstructure is observed by using low-energy electron diffraction: phase diagrams have been measured to indicate the coverage range and the temperature threshold where the new structure appears. Scanning tunneling microscopy results indicate that in the case of Pd/W(211) the superstructure phase is caused by missing overlayer rows (Fig. 3), but in the case of Rh/W(211) it is more likely caused by a microfaceting of the surface into \{110\} faces (14). Overlayer coverages >1 ML are thermally unstable, and form ultrathin alloy films on annealing. Alloy formation for thermally annealed multilayers of Rh, Pd, Pt on W(211) is confirmed by synchrotron radiation studies (see below).

To provide guidance for future faceting studies of planar surfaces, we have been collaborating with the group of R. Blaszczyszyn to conduct field-emission microscopy studies (15). In this work, a nearly hemispherical emitter tip, coated with metallic overlayers, develops facets on annealing. The typical
emitter has a diameter of ~200 nm; the shape and dimensions are a good approximation to a single catalyst particle, although a bit larger. Recent studies have focused on ultrathin films of Pt on W, Pt on Ir, and Pd on Mo (16). In general, on annealing the metal film-covered emitter tip, the shape changes from nearly hemispherical to more polyhedral. The faceting effect, i.e., growth of facets, is particularly pronounced for the Pt/W and Pd/Mo systems, and less so for Pt/Ir [consistent with the fact that we have not yet found evidence for metal-induced faceting of planar Ir(210); see below]. The facets that form on bcc W and Mo are {112}, {123} and {178}, whereas {116} and {115} grow on fcc Ir.

**Surface Chemistry of Bimetallic Pd/W.** The surface chemistry of small hydrocarbons on transition metal surfaces is relevant to many important catalytic processes. We focus here on acetylene chemistry, for which reaction pathways are known to be sensitive to surface structure (ref. 17; for a review see ref. 18). Acetylene cyclization, $\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$, is catalyzed by palladium and has been studied extensively on clean and modified surfaces, under ultrahigh vacuum as well as high-pressure conditions. Acetylene cyclization is extremely structure-sensitive, so it is an ideal reaction for probing the effects of surface electronic and geometric structure. Isotopic studies indicate that benzene forms from acetylene in a stepwise fashion on Pd(111) and Cu(110); the reaction proceeds via a C$_6$ intermediate species, and the reactants do not undergo C–C or C–H bond scission (17–19).

Bimetallic systems improve both activity and selectivity. For example, we have shown in a combination high-resolution electron-energy-loss-spectroscopy (HREELS) and TPD study that a single ML of Pd on W(211) decreases the high reactivity of W for C$_2$H$_2$ decomposition, and catalyzes self-hydrogenation of C$_2$H$_2$ to C$_2$H$_4$ and cyclization of C$_2$H$_2$ to C$_6$H$_6$ (20). Evidence for finite size effects in benzene formation has been reported by Goodman et al. (21) for Pd clusters supported on alumina films;

Lambert et al. (22) have shown that there is a minimum ensemble on Pd(111) (~7 atoms) necessary for benzene formation. Although it is clear that electronic structure plays an important role in the cyclization reaction, these studies suggest questions: can electronic structure alone be responsible for these known size effects? What are the effects of geometrical parameters, e.g., size and shape?

Zhdanov and Kasemo (3) have recently performed Monte Carlo analyses on the model catalytic reaction $2\text{A} + 2\text{B} \rightarrow 2\text{AB}$, which indicate that the reaction kinetics on a faceted nanocrystal can be different from those on a single crystal surface. The simulations have identified a kinetic “structure gap” not associated with special electronic effects or properties of small particles, but with their size and shape. They argue that geometric structure alone can play an important role in reaction kinetics. It is this idea that we are testing.

We have found that acetylene reactions over Pd/W(111) surfaces exhibit size effects on the nanometer scale (23). In these studies, we have characterized the self-hydrogenation of C$_2$H$_2$ to form C$_2$H$_4$ and cyclization of C$_2$H$_2$ to form C$_6$H$_6$ on planar and faceted Pd-covered W(111) and on Pd-covered W(112). The substrates ranged from 1 ML of Pd on planar W(211), to faceted Pd/W(111) surfaces containing different facet-size distributions.

The goal is to probe the influence of facet size on reactivity. Below ~700 K annealing temperature, the Pd(111) surface remains planar. Above ~700 K, Pd-covered W(112) facets are formed, which grow in size with increasing annealing temperature. We have measured TPD spectra for self-hydrogenation of adsorbed C$_2$H$_2$ to form C$_2$H$_4$ product (Fig. 4). The ethylene TPD spectra for Pd/W(111) evolve in a systematic fashion as the surface is thermally converted into a faceted substrate, and the facets grow in size. For the largest facets (annealing $T = 1000$ K), the ethylene TPD spectrum is similar to that for C$_2$H$_4$ formation over planar Pd/W(112) (Fig. 4 Upper). Similar facet-size effects are seen for acetylene cyclization to form benzene (Fig. 4 Lower). The data provide clear evidence that size effects at the nanometer scale (3) should be considered in evaluation of reactivity data for faceted bimetallic surfaces.

**Synchrotron Radiation Studies of Metals on W.** During the last several years, we have found that certain ultrathin films (~1 physical ML) on W(111) and Mo(111) substrates can induce facetting (e.g., Rh, Pd, Ir, Pt, Au, as well as O, Cl), whereas others do not [e.g., Ti, Co, Ni, Cu, Ag, Gd (10, 11)]. We noted a correlation, namely, that the elements that cause facetting have Pauling electronegativity >2.0, whereas the elements that do not cause facetting have electronegativities <2.0; W and Mo each have negativity = 1.7. This observation suggested that electronic structure plays a role in faceting. To search experimentally for possible electronic factors that influence facetting, we use HRXSXP based on synchrotron radiation. We study (mainly) the sharp W 4f, Pt 4f, Ir 4f, etc., and measure surface core level shifts (SCLS). Based on an extensive set of measurements, we can draw a number of conclusions.

(i) Although the SCLS is an extremely sensitive and useful indicator of interface formation, there is no clear correlation between Pauling electronegativity and surface or interfacial 4f$_{5/2}$ binding energies (24). This finding was not unexpected, because the Pauling electronegativity is a measure of initial-state charge transfer effects, whereas the measured 4f-binding energies are influenced by a combination of initial and final-state effects.

(ii) Metals with the highest heats of adsorption (e.g., Pt, Pd), and the highest W 4f interfacial binding energies are those which cause faceting (24). This finding is consistent with a first-principles theory that indicates that a higher heat of adsorption provides both a strong thermodynamic driving force for faceting and a lower kinetic barrier to faceting (25, 26).

(iii) For most systems studied [Cu, Ni, Rh, Pd, Ir, Pt, Au on
W(111) and W(112); refs. 27–29], we find evidence that a 1 ML of overlayer metal is thermally stable, and floats on the outer surface without significant alloy formation, for all temperatures up to the onset of desorption. For all systems except Au/W, we find that multilayer films form alloys on annealing: invariably, W atoms from the substrate diffuse into the overlayer film, rather than vice versa. In certain cases (Pt/W, Ir/W) we can measure sharp 4f levels of both overlayer and substrate, and find evidence for alloy formation in multilayer films (Fig. 5). In general, the alloying behavior of the bimetallic systems investigated here is consistent with the known bulk-phase diagrams (e.g., Pt is not soluble in W, but W is soluble in Pt to a maximum of ~60% W).

Moreover, we have used Born–Haber cycles and the equivalent core approximation to extract thermochemical data concerning energetics of adhesion, segregation and alloying in these systems (28).

(iv) We find evidence for intermixing at the interface for multilayer deposition of several metals (Pt, Ir, Rh) on W(111) at room temperature (29) This finding is surprising to those in the thin film community (e.g., for those studying magnetic thin films) who generally believe that thin films of high-melting-temperature materials form abrupt interfaces.

**Faceting and Surface Chemistry of Ir(210).** As part of a larger effort to study the morphological stability of adsorbate covered metallic surfaces, we have investigated the influence of various adsorbates on fcc Ir(210). The structure of the atomically rough Ir(210) surface is similar to that of bcc W(111), but with reduced symmetry (2-fold). Based on studies using LEED and STM, we find that oxygen overlayers induce substantial facets on Ir(210), whereas the metal overlayer studied to date (Au) does not cause faceting.

When Ir(210) is exposed to more than ~0.9 L (1 L = 1 x 10^-6 torr) of oxygen and annealed to T > 600 K, it experiences significant morphological restructuring: nanometer-scale pyramid-like structures (facets) are formed on the initially planar surface (I.E., K.P., and T.E.M., unpublished data.). LEED measurements show that the pyramids have three sides with mirror symmetry (two {311} facets and one {110} facet), and that the faceted surface exhibits a quasi-reversible behavior on annealing to higher temperatures. The surface reverts to its planar state at temperatures above 850 K but, provided the maximum annealing temperature is below the desorption temperature of oxygen, facets reappear on cooling to temperatures below 800 K. Furthermore, we are able to remove the oxygen from the surface by means of catalytic oxidation of CO at ~580 K or by means of the H_2 + O reaction at ~400 K, while preserving the faceted structure. TPD and Auger electron spectroscopy have shown that residual adsorbed O and CO (or H) are negligible after this procedure. The faceted clean surface is stable up to 600 K, but irreversibly reverts to the planar state above 600 K. These experiments indicate that the clean, faceted, metastable Ir(210) surface provides an ideal substrate to study thermal relaxation of nanometer-scale surface features.

In a previous section we reported that C_2H_2 reacts on planar and faceted Pd/W surfaces. In contrast, the clean Ir(210) surface is considerably more aggressive in reacting with C_2H_2 at 100 K onto Pd-covered W (C_2H_2 exposure ~3 x 10^-6 torr). In each case, the metal is precovered with 1 ML of Pd and annealed to the indicated temperature, before deposition of C_2H_2. The sizes of (211) facets increase with annealing temperature >700 K. (Bottom) TPD spectra for C_2H_2 reactively formed after adsorption of C_2H_2 on Pd/W surfaces, as in a.

**Fig. 4.** (a and b) Surface chemistry of acetylene on planar and faceted Pd/W surfaces. (Top) TPD spectra for C_2H_4 reactively formed after desorption of a saturation coverage of C_2H_2 at 100 K onto Pd-covered W (C_2H_2 exposure ~3 x 10^-6 torr). In each case, the metal is precovered with 1 ML of Pd and annealed to the indicated temperature, before deposition of C_2H_2. The sizes of (211) facets increase with annealing temperature >700 K. (Bottom) TPD spectra for C_2H_2 reactively formed after desorption of C_2H_2 on Pd/W surfaces, as in a.

**Fig. 5.** Evidence for formation of interfacial alloy in Pt 4f and W 4f SXPS spectra associated with an annealing sequence for an 8 ML Pt film on W(211). Annealing time is 1 min at each temperature. Features on high binding energy sides of each 4f peak indicate that W atoms diffuse through the interface to form a Pt-W alloy film. [Reproduced with permission from ref. 28 (Copyright 2000, Am. Phys. Soc.).]
dissociating C2H2 than the Pd/W surfaces. We find that adsorption of C2H2 on Ir(210) at either 100 K or 300 K leads to dissociation when the surface is heated, and that the dominant desorption product (>99%) in TPD spectra is H2. Traces of C2H4 are seen at low temperature in TPD.

The observation of unusual growth for a metal on sulfided W(111) is an impetus for further studies of catalytically active metals (Co, Ni) that have direct relevance to the fundamentals of hydrodesulfurization catalysis. Concluding Remarks. The main factor that distinguishes this work from other studies of model bimetallic and sulfide catalysts is our emphasis on atomically rough, high-surface-energy surfaces that may be quite different from those present in the absence of the overlayer metal. We believe that these results are important for understanding dynamic structural rearrangements at the surfaces of high area bimetallic and sulfide catalysts, and in clarifying the role of nanometer-scale size effects in surface reactions.

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