Interaction of Sulfur with Au/Pt(111) and Ag/Pt(111) Surfaces: Photoemission Studies

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Interaction of Sulfur with Au/Pt(111) and Ag/Pt(111) Surfaces: Photoemission Studies

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The reaction of sulfur with Au/Pt(111) and Ag/Pt(111) surfaces has been investigated using high-resolution photoemission spectroscopy with synchrotron radiation. The valence spectra of S/Au/Pt(111) and S/Ag/Pt-(111) surfaces display weak signals at binding energies between 1.8 and 0 eV. The adsorption of S induces a large decrease in the density of states displayed by the bimetallic surfaces around the Fermi level. This phenomenon may be responsible for the decrease in chemical and catalytic activity that accompanies sulfur poisoning. In S/Au/Pt(111) surfaces, sulfur does *not* form compounds with Au or Pt. Au forms three-dimensional clusters, while S segregates into two-dimensional islands of high local coverage where it is bonded to hollow and bridge sites of the Pt substrate. In S/Ag/Pt(111) surfaces, silver *reacts* with sulfur and *promotes* the synthesis of platinum sulfides. The formation of silver and platinum sulfides makes possible the adsorption of large amounts of sulfur on Ag/Pt(111) surfaces. The S/Au/Pt(111) and S/Ag/Pt(111) systems illustrate different extremes of the phenomena that can occur when sulfur is present on a bimetallic surface. The differences in the behavior of the S/Au/Pt(111) and S/Ag/Pt(111) surfaces arise from variations in the nature of the admetal ↔ S and admetal ↔ Pt interactions.

I. Introduction

In recent years, the interaction between sulfur and well-defined bimetallic surfaces has been the subject of a large series of studies.[1−14] In part, this interest is motivated by the important role that sulfur plays in several areas of heterogeneous catalysis.[15,16] Catalysts that combine noble and late-transition metals are very sensitive to sulfur poisoning,[15] and there is a general desire to improve the sulfur tolerance of these systems. In addition, Mo- and W-based bimetallic sulfides are frequently used for hydrodesulfurization (HDS) processes in the petroleum industry,[16] and there is a clear need to enhance the activity of these catalysts. A fundamental understanding of the factors that control the interaction of sulfur and bimetallic systems can provide novel ideas for improving existing industrial catalysts and serve as the foundation for the development of new ones.

Depending on the nature of the metal ↔ sulfur and metal ↔ metal interactions, several phenomena can occur when sulfur reacts with a bimetallic surface.[1] For some systems,[4,5,6b,13,17] the interaction between sulfur and one of the metals (M1) is repulsive, with sulfur and the metal showing a tendency to segregate into separate domains or regions of the surface. In many of these cases, sulfur and the metal (M1) compete for making bonds with the second metal,[4] and there is a weakening in the strength of the bimetallic bonds that leads to a reduction in the degree of "mixing" of the metals.[4,5,17] In another type of bimetallic system,[8,10,14] metal−metal bonding largely increases the reactivity of one of the metals toward sulfur. For example, in the reaction of sulfur with admetal/Mo(110) surfaces (admetal = Zn, Ag, Cu, Fe, Co, or Ni), the admetals promote Mo ↔ S interactions and the formation of several layers of molybdenum sulfide.[8,14,18] Co and Ni exhibit a unique ability to promote Mo ↔ S interactions that can be attributed to electronic effects induced by the formation of bimetallic bonds.[14]

In this work, we investigate the properties of S/Au/Pt(111) and S/Ag/Pt(111) surfaces using high-resolution photoemission spectroscopy with synchrotron radiation. Pt-based catalysts are

widely used in oil refineries and are very sensitive to sulfur poisoning.[15,19] By adding a noble metal like Au or Ag to a Pt reforming catalyst, one can increase the selectivity of the catalyst for the isomerization of hydrocarbons.[20−22] The lifetime of these bimetallic catalysts can be reduced to a few months or weeks in the presence of ppm levels of sulfur contaminants in the oil-derived feedstream.[15] Our photoemission results for the adsorption of sulfur on Au/Pt(111) and Ag/Pt(111) show a large decrease in the density of states displayed by the bimetallic surfaces around the Fermi level. This change in the band structure of the metals modifies the chemical properties of the surfaces. Important differences are observed in the interactions between sulfur and the noble metals on top of Pt(111). Au reduces the adsorption energy of sulfur on Pt(111), whereas Ag promotes the formation of platinum sulfides.

II. Experimental Method

The experiments were carried out at the U3C beam line of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This beam line is equipped with a grasshopper monochromator and an ultrahigh vacuum chamber (base pressure $< 1 \times 10^{-10}$ Torr) fitted with a double-pass cylindrical mirror electron-energy analyzer and a quadrupole mass spectrometer. The valence spectra were taken with a photon energy of 70 eV, while a photon energy of 250 eV was used to acquire the S 2p, Pt 4f, and Au 4f core-level spectra. The overall instrumental resolution in the photoemission experiments was 0.3−0.4 eV.

The Pt(111) crystal was cleaned following methodologies reported in the literature.[23] Au and Ag were deposited by sublimation from high-purity wires of gold and silver which were heated by tungsten filaments. The metal dosers were outgassed thoroughly prior to vapor deposition. The Ag coverages were determined by TDS area analysis,[23] while the Au coverages were determined by calibrating the atomic flux of the doser with a Au 4f and Pt 4f core-level intensity analysis.[24] A solid-state electrochemical cell (Pt/Ag/AgI/Ag$_2$S/Pt)[25,26] was used to vapor-deposit sulfur on the Pt(111) surface. When a voltage was applied across the cell, sulfur evolved as

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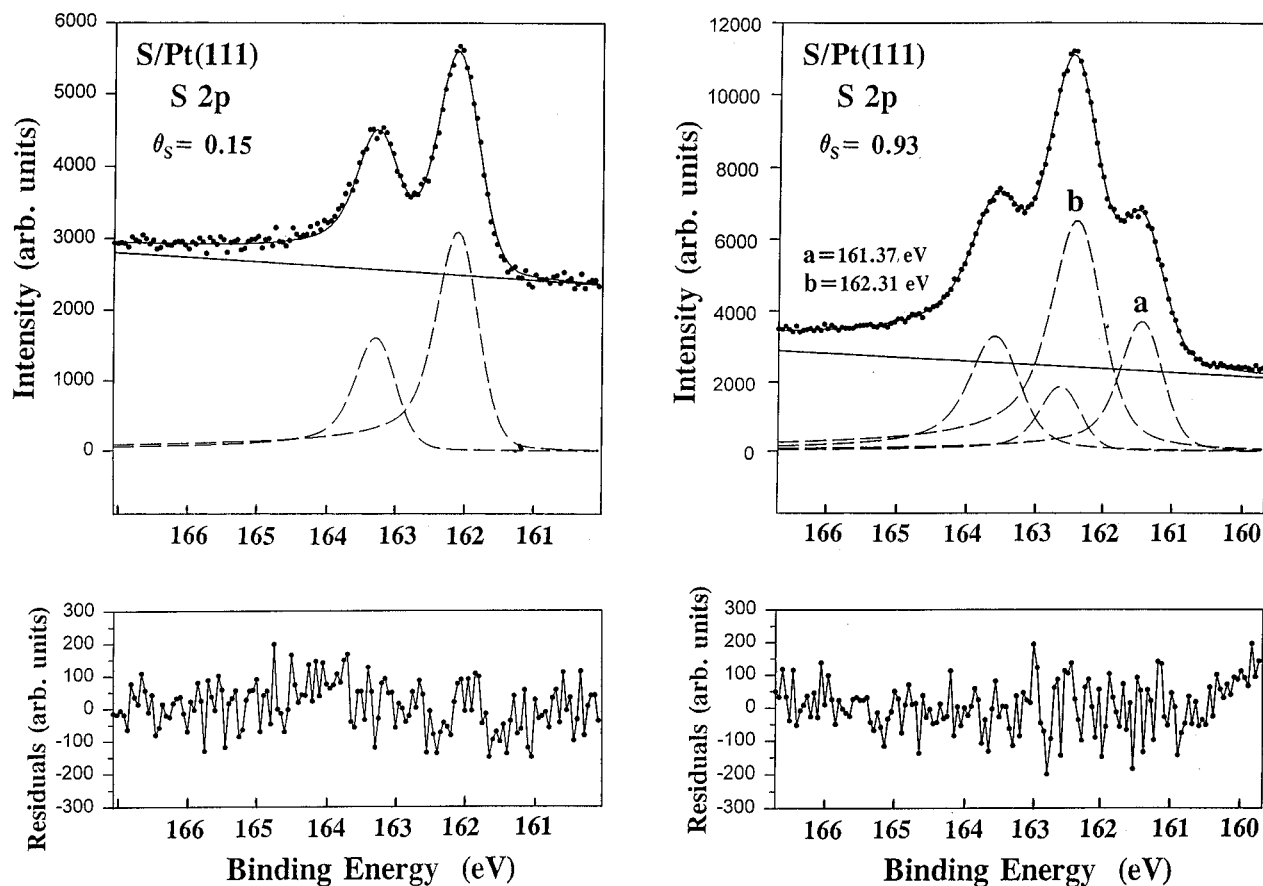
Figure 1. S 2p spectra acquired after dosing S_2 to Pt(111) at 300 K. The spectra were taken using a photon energy of 250 eV. The S 2p features were fitted using a many-body line shape (Doniach−Šunjić[29]) convoluted with a Gaussian function to account for instrumental resolution. A linear background subtraction was performed before each fit.

S_n clusters (predominantly S_2).[26] The coverage of sulfur on the sample was determined by measuring the area under the S 2p peaks, which was scaled to absolute units by comparing them to the corresponding area for the saturation coverage of sulfur on Pt(111) known to be close to a full monolayer.[25] In this work, coverages are reported with respect to the number of Pt-(111) surface atoms, i.e., 1.51×10^{15} atoms/cm^2 corresponds to one monolayer (ML).

III. Results

III.1 Interaction of Sulfur and Pt(111). Before examining the coadsorption of sulfur and gold or silver on top of Pt(111), we will focus our attention on the photoemission results for sulfur on Pt(111). LEED experiments show that sulfur atoms form p(2 × 2) (θ_S = 0.25 ML) and ($\sqrt{3} \times \sqrt{3}$)R30° (θ_S = 0.33 ML) superstructures when adsorbed on Pt(111).[25,27,28] In the last structure, the S atoms are bonded to the fcc hollow sites of the Pt surface.[27] Figure 1 shows S 2p spectra acquired after the deposition of 0.15 and 0.93 ML of sulfur on Pt(111). For the $S_{0.15}$/Pt(111) system, excellent agreement is observed after fitting the S $2p_{1/2}$ and $2p_{3/2}$ features with two peaks (i.e., one doublet). The separation between these two peaks is close to the expected $2p_{1/2}-2p_{3/2}$ spin−orbit splitting of 1.2 eV,[30] with the S $2p_{3/2}$ level appearing at 162.14 eV. At sulfur coverages below 0.35 ML, we observed only a well-defined doublet of peaks in the S 2p spectrum (the S $2p_{3/2}$ binding energy decreased by ~0.2 eV when θ_S was raised from 0.15 to 0.32 ML). These photoemission features can be attributed to S adsorbed on the hollow sites of the Pt(111) substrate.[27]

A set of two doublets is necessary to fit the S 2p spectrum of the $S_{0.93}$/Pt(111) system in Figure 1. At this relatively large sulfur coverage, no LEED pattern is observed[25] and two kinds

of adatoms are present on the surface which exhibit a difference of 0.94 eV in their S $2p_{3/2}$ binding energies. A similar result was observed in photoemission results for S/W(100) surfaces,[30] with the S $2p_{3/2}$ peaks corresponding to S adsorbed on hollow (peak at higher binding energy) and bridge sites (peak at lower binding energy) of the W substrate. We propose an identical assignment for the S 2p features of the $S_{0.93}$/Pt(111) surface. In general, the S $2p_{3/2}$ peak at ~161.4 eV was seen only at sulfur coverages above 0.4 ML, while the peak at 162.3−161.9 eV was present in all the S/Pt(111) surfaces examined (0.10 ML < θ_S < 0.95 ML).

Figure 2 displays Pt 4f spectra for a series of S/Pt(111) surfaces. A system with 0.93 ML of S exhibits Pt 4f features at ~71.5 and 74.8 eV that are at higher binding energy (0.4−0.7 eV) than those seen for the bulk and surface atoms of Pt-(111).[31] The direction of the Pt 4f shift induced by S on the S/Pt(111) surfaces is similar to that seen for the formation of bulk PtS_2,[32] but the magnitude is much smaller. As can be seen in the valence-band spectra in Figure 2, the adsorption of sulfur induces a large reduction in the density of states that the Pt-(111) substrate exhibits around the Fermi level. The Pt 5d feature that appears at ~0.8 eV attenuates and shifts toward a higher binding energy when the S coverage is raised. Surfaces covered with 0.15, 0.30, and 0.90 ML of S display shifts of ~0.4, 0.5, and 0.9 eV (respectively) in the first peak of the Pt 5d band. Previous photoemission results for S/W(100)[30] and theoretical calculations for S/Rh(100),[33] S/Rh(111),[4b] S/Mo-(110),[4b] and S/Pt(111)[34] show a S-induced decrease in the density of states that the metal substrates display around the Fermi level. In the valence spectra of Figure 2, electron emissions from the S 3p levels appear between 4.5 and 6 eV[30,35] and overlap with one of the main features of the Pt 5d band.
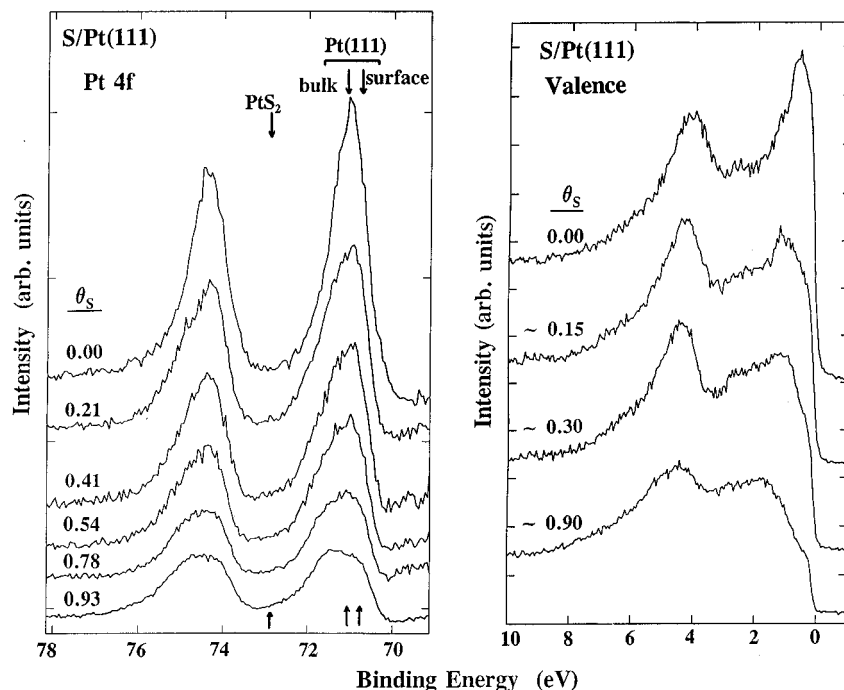
Figure 2. Left: Pt 4f spectra for Pt(111) and S/Pt(111) surfaces. The spectra were taken using a photon energy of 250 eV. The vertical arrows indicate the Pt $4f_{7/2}$ binding energies reported for the bulk and surface atoms of Pt(111)[31] and the bulk atoms of PtS$_2$.[32] Right: valence photoemission spectra acquired after dosing S$_2$ to Pt(111). The electrons were excited with a photon energy of 70 eV.
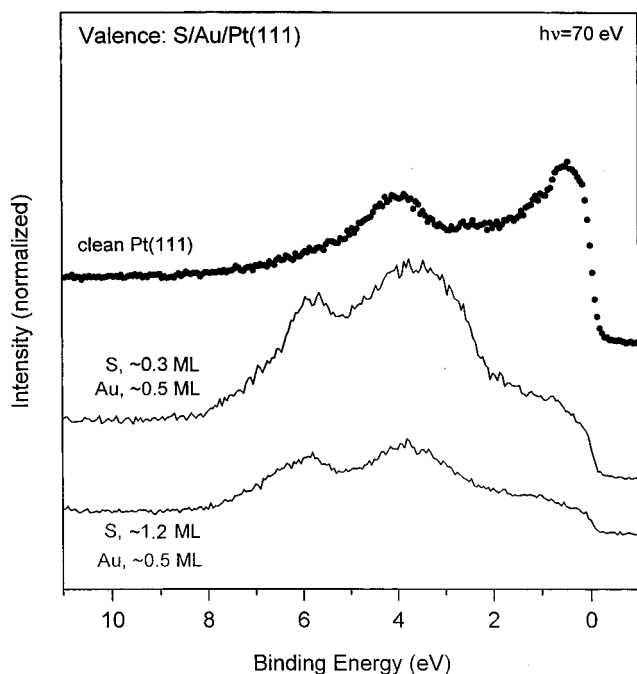

Figure 3. Valence photoemission spectra for clean Pt(111) and S/Au/Pt(111) surfaces. S$_2$ was dosed to a Au$_{0.5}$/Pt(111) surface at 300 K. Then, the spectra were acquired using a photon energy of 70 eV.

III.2 Interaction of Sulfur and Au/Pt(111). Previous studies indicate that the growth mode of Au on Pt(111) proceeds via a Stranski–Krastanov mechanism at 300 K.[24] At submonolayer coverages, the Au adatoms form two-dimensional (2D) islands on the Pt substrate, while the formation of 3D clusters is observed at Au coverages above 1 ML.

Figure 3 shows valence photoemission spectra for Pt(111) and S/Au/Pt(111) surfaces acquired using a photon energy of 70 eV. At this photon energy the corresponding spectra for bulk Au and Au multilayers[36] exhibit strong electron emissions from the Au 5d band around 5.8 (5d$_{3/2}$ component) and 3.5 eV (5d$_{5/2}$ component), with weak emissions from the Au 6s and 6p bands appearing between 2 and 0 eV. The cross section of

the Au 5d band in photoemission is much larger than that of the Pt 5d band.[36] In Figure 3, the spectrum for the S$_{0.3}$/Au$_{0.5}$/Pt(111) surface displays intense features at 5.8 (Au 5d$_{3/2}$ band) and 3.6 eV (mostly Au 5d$_{5/2}$ band, with some signals from the Pt 5d band and S 3p levels), plus the spectrum displays weak features from 2 to 0 eV as a consequence of the formation of S–Pt bonds and a subsequent attenuation of emissions from the Pt 5d band in this region. After saturating the system with sulfur at 300 K, S$_{1.2}$/Au$_{0.5}$/Pt(111) surface, one sees a large decrease in the intensity of the Au 5d and Pt 5d features with very weak emissions around the Fermi level. In general, the adsorption of sulfur on Au$_{\leq 1.8}$/Pt(111) surfaces led to a large depletion in the density of states that the bimetallic system showed near the Fermi level. This was accompanied by an attenuation of the signal for the Au 5d band without significant changes in the separation of the 5d$_{3/2}$ and 5d$_{5/2}$ components. This type of behavior indicates that there may be chemisorption of S on top of the Au adlayers, but there is no compound formation between S and the noble metal (the formation of AuS$_x$ would produce a substantial narrowing in the width of the Au 5d band[36]).

In Figure 4 are displayed Au 4f and Pt 4f spectra which were acquired after dosing ~0.8 ML of sulfur to a Au$_{0.7}$/Pt(111) surface at 300 K, followed by annealing to 550 K. For the Au$_{0.7}$/Pt(111) surface, the Au 4f$_{7/2}$ peak appears at 83.84 eV, a value located in between the Au 4f$_{7/2}$ positions reported for the bulk (83.99 eV) and surface atoms (83.64 eV) of Au(111).[37] The adsorption of sulfur at 300 K induces an increase of ~0.15 eV in the Au 4f$_{7/2}$ binding energy of the Au$_{0.7}$/Pt(111) system. After annealing the S–Au complexes to 550 K, one can see a significant reduction in the intensity of the Au 4f features and an enhancement in the Pt 4f signal. This phenomenon has to be attributed to the formation of 3D clusters of Au on the surface, since at these relatively low temperatures (300–550 K) Au does not desorb or form alloys with the Pt substrate.[24] The S$_{0.8}$/Au$_{0.7}$/Pt(111) system annealed to 550 K exhibits Pt features very similar to those seen for S$_{0.6-0.8}$/Pt(111) surfaces (Figure 2). Thus, upon dosing sulfur at 300 K, one sees that most of the sulfur atoms probably adsorb on top of the Au layer,
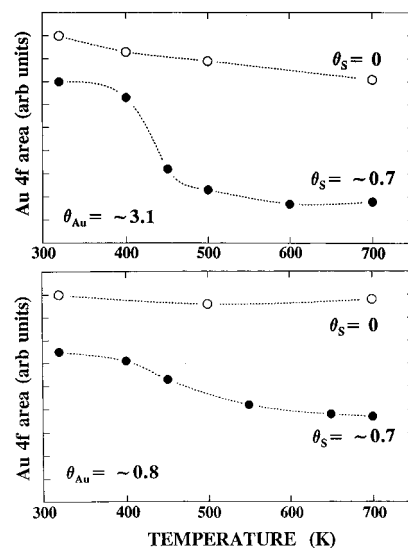
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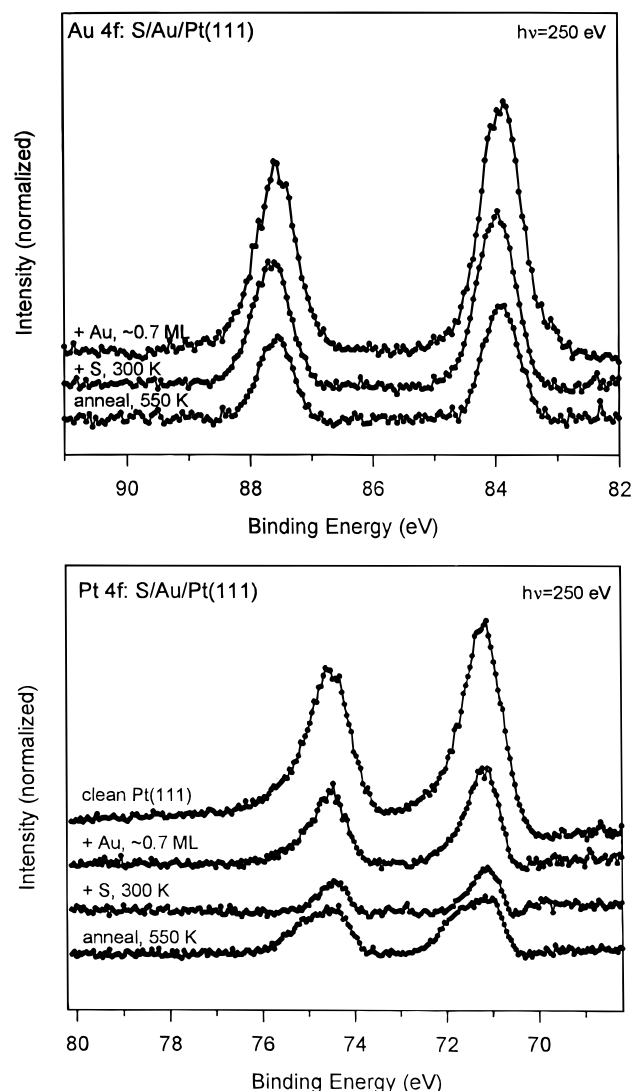
Figure 4. Au 4f (top) and Pt 4f (bottom) spectra acquired after depositing 0.8 ML of sulfur on a $Au_{0.7}/Pt(111)$ at 300 K and subsequent annealing to 550 K.

Figure 5. Effects of annealing on the Au 4f signals of Au/Pt(111), empty circles, and S/Au/Pt(111) surfaces, filled circles. Top: results for $Au_{3.1}/Pt(111)$ and $S_{0.7}/Au_{3.1}/Pt(111)$. Bottom: results for $Au_{0.8}/Pt(111)$ and $S_{0.7}/Au_{0.8}/Pt(111)$. Sulfur was deposited on the Au/Pt(111) surfaces at 320 K, followed by annealing at the indicated temperatures for 60 s.

Figure 6. S_2- and S-thermal desorption spectra for S/Pt(111) and S/Au/Pt(111) surfaces ($\theta_S = 0.7$ ML; $\theta_{Au} = 0.0$, 0.8 or 3.1 ML). The S/Au/Pt(111) systems were prepared by dosing S_2 to Au/Pt(111) at 320 K. Heating rate = 5 K/s.
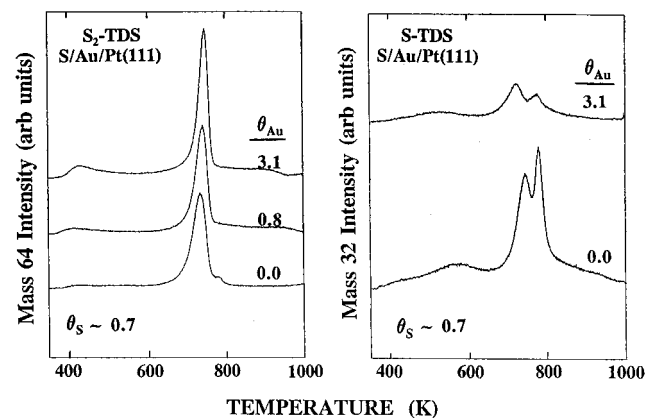
and after annealing they migrate toward the Pt substrate inducing the formation of 3D clusters of Au.

The results in Figure 5 illustrate how the morphology of the Au overlayer changes in Au/Pt(111) and S/Au/Pt(111) systems as a function of annealing temperature. In these experiments, there was no desorption of Au. For a $Au_{0.8}/Pt(111)$ surface, the 2D islands of Au always wet the Pt substrate,[24] and there is no substantial change in the Au 4f intensity when the temperature is raised from 300 to 700 K. After depositing 0.7 ML of S on the $Au_{0.8}/Pt(111)$ surface at 320 K and increasing the temperature, one sees that 3D clustering of Au occurs between 400 and 600 K. For the $Au_{3.1}/Pt(111)$ system, the small decrease in Au 4f intensity from 300 to 700 K indicates the transformation of part of the Au multilayer into large 3D clusters.[24] More pronounced changes in the morphology of the $Au_{3.1}/Pt(111)$ system are seen upon the deposition of sulfur, with the "balling-up" of the Au film occurring again at temperatures between 400 and 600 K.

Figure 6 shows S_2-TDS and S-TDS spectra for S/Au/Pt(111) surfaces with coverages identical to those of the systems in Figure 5. No desorption of Au was detected. Most of the sulfur desorbs at temperatures above 700 K. For a $S_{0.7}/Pt(111)$ surface (spectra at the bottom of Figure 6), there are simultaneous desorptions of S_2 and S at 730 K, and S at 780 K.[10a] Au causes an increase in the S_2 desorption signal and a reduction in the

amount of S that desorbs from the surface. After the TDS experiments for the $S_{0.7}/Au_{3.1}/Pt(111)$ system, the amount of sulfur left on the surface at 1000 K was ~0.04 ML. In contrast, for the $S_{0.7}/Pt(111)$ system, we found a sulfur coverage of ~0.25 ML after the sample was heated to 1000 K.

In a set of experiments, we investigated the interaction between S_2 and Au/Pt(111) surfaces ($\theta_{Au} < 4$ ML) at 550 K. Typical results are shown in Figure 7. After exposing a $Au_{0.7}/Pt(111)$ surface to S_2 at 550 K, one finds a sulfur saturation coverage of ~1.2 ML. The Au $4f_{7/2}$ peak displays a shift of ~+0.4 eV probably as a consequence of the chemisorption of S on Au.[4a] The Pt 4f features are very similar to those of $S_{0.8-0.9}/Pt(111)$ surfaces, offering no clear evidence for the formation of significant amounts of platinum sulfide in the system. This result is valid for all the S/Au/Pt(111) surfaces examined.

Our photoemission data for the deposition of Au on S/Pt-(111) surfaces show large Au-induced changes in the morphology of the S overlayers. This phenomenon is illustrated by the S 2p spectra in Figure 8. In a $S_{0.3}/Pt(111)$ system, the S overlayer exhibits a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern,[25,27] with the S atoms adsorbed on fcc hollow sites of the Pt substrate[27] and a well-defined doublet of peaks in the S 2p spectrum.
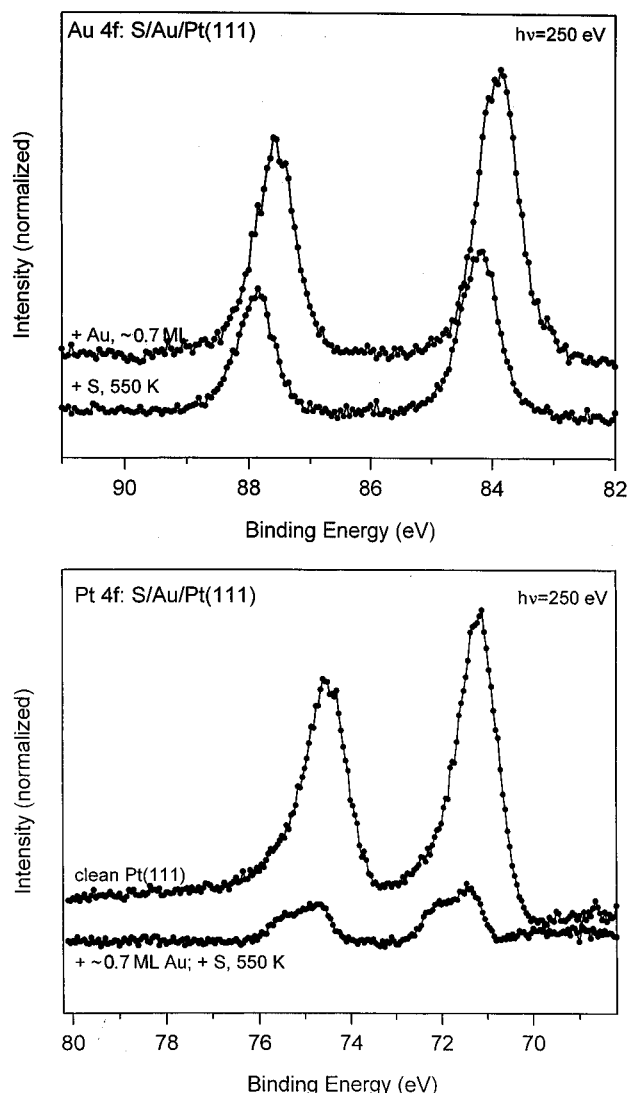
Figure 7. Au 4f (top) and Pt 4f (bottom) spectra for Au$_{0.7}$/Pt(111) and S$_{1.2}$/Au$_{0.7}$/Pt(111) surfaces. Sulfur was dosed at 550 K.

When Au is added to the S$_{0.3}$/Pt(111) surface, a new feature appears at ~161.3 eV in the S 2p region. The intensity of this feature increases as the amount of deposited Au is raised. The S 2p spectrum of the Au$_{0.6}$/S$_{0.3}$/Pt(111) surface is fitted by a set of two doublets, which display peak positions that match those seen for S$_{0.60-0.95}$/Pt(111) surfaces (Figure 1). The corresponding Au 4f spectrum (Figure 9) shows no evidence for the formation of Au−S bonds, as indicated by a Au 4f$_{7/2}$ peak position that is very close to that of bulk and Pt-bonded gold. Thus, it is likely that Au compresses the ($\sqrt{3} \times \sqrt{3}$)-R30° S overlayer into islands of high local coverage, in which sulfur occupies hollow and bridge sites of the Pt substrate.

The compression of the S overlayer by Au (which implies Au ↔ S repulsive interactions) does not force the migration of S into the bulk of the Pt substrate, and the Pt 4f spectra for the Au$_{0.2-0.6}$/S$_{0.3}$/Pt(111) surfaces (Figure 9) indicate that no platinum sulfide is formed in these systems. However, the compression of the sulfur overlayer modifies the reaction pathways for the removal of sulfur from the sample. For a S$_{0.3}$/Pt(111) system one sees desorption of S from 780 to 1000 K and no evolution of S$_2$. On the other hand, Au$_{0.5-1.4}$/S$_{0.3}$/Pt(111) surfaces show desorption of S$_2$ and S from 750 to 1000 K. Au also reduces the thermal stability of S on Pt(111). For example, in Figure 10 TDS results for a Au$_{2.0}$/S$_{0.2}$/Pt(111) surface show evolution of S$_2$ and S from 800 to 1000 K, and at 1000 K the amount of S left on the system is ~0.05 ML. In

contrast, after heating a S$_{0.2}$/Pt(111) surface from 300 to 1000 K, one observes no desorption of S$_2$ or S, and the system is stable up to ~1100 K when the removal of S from the surface begins.[25] All these results are consistent with a model in which gold compresses the sulfur overlayer into islands of high local coverage, reducing in this way its stability and favoring the "pairing" of sulfur atoms and desorption of S$_2$.

After comparing the behavior of S$_{<1}$/Au/Pt(111) and Au/S$_{<1}$/Pt(111) surfaces, we found that at ~500 K all these systems have the same configuration in which Pt-bonded sulfur coexists with 3D clusters (or islands) of Au.

III.3 Interaction of Sulfur and Ag/Pt(111). In a previous work we investigated the coadsorption of sulfur and silver on Pt(111) using TDS and Auger electron spectroscopy.[10a] After depositing silver on S$_{0.25-1.1}$/Pt(111) surfaces, one sees Ag MVV Auger spectra that are typical of silver sulfides.[10a] The silver sulfides in the Ag/S/Pt(111) systems decompose at temperatures between 750 and 850 K, with S$_2$ and S evolving into gas phase and metallic Ag remaining on top of a Pt(111) substrate partially covered by chemisorbed S.[10a] The deposition of Ag on S$_{<0.25}$/Pt(111) does not affect the stability of sulfur on the surface, with silver desorbing at temperatures below 1050 K and sulfur at temperatures above 1100 K.[10a] This pattern of behavior contrasts with that observed for the Au/S/Pt(111) surfaces, where there are repulsive interactions between the adsorbates and no indication of compound formation between gold and sulfur. These differences in the behavior of the Ag/S/Pt(111) and Au/S/Pt(111) surfaces probably arise from differences in the reactivity of the noble metal adlayers toward sulfur. After dosing S$_2$ to Au multilayers at 300 K, we see the formation of only a chemisorbed layer of sulfur. On the other hand, the reaction of S$_2$ with Ag multilayers[6] or Ag(111)[38] at 300 K produces films of silver sulfides.

In this work we study the interaction between S$_2$ and Ag/Pt-(111) surfaces using synchrotron-based photoemission experiments. Our experimental setup provides the high resolution necessary to examine in detail the valence region and core levels (S 2p, Pt 4f) of a series of S/Ag/Pt(111) surfaces. Figure 11 shows Pt 4f spectra taken after dosing S$_2$ to Ag/Pt(111) surfaces (θ_{Ag} = 1.16 an 3.28 ML) at 325 and 550 K. At 325 K the Ag and S overlayers in the S/Ag$_{3.28}$/ Pt(111) system completely attenuate the Pt 4f signal. The S/Ag$_{1.16}$/ Pt(111) surface exhibits Pt 4f features with a line shape and binding energy very similar to those of S$_{0.6-0.8}$/Pt(111) surfaces, indicating that part of the adsorbed sulfur is able to penetrate through the Ag overlayer and reach the Pt substrate. After dosing S$_2$ at 550 K, one sees an enhancement in the Pt 4f signal that suggests the balling-up of the Ag adlayers. This is accompanied by a shift toward higher binding energy in the peak positions. Under these conditions the S/Ag/Pt(111) systems have Pt 4f binding energies that are 0.6−1.1 eV larger than those of bulk Pt. This indicates the formation of platinum sulfides.[32] By comparing the results for the reaction of S$_2$ with Pt(111) and Ag/Pt(111) surfaces at 550 K, we conclude that Ag promotes the sulfidation of platinum.

Figure 12 shows S 2p spectra acquired during the experiments in Figure 11. After dosing S$_2$ to a Ag$_{1.16}$/Pt(111) surface at 325 K, one sees a sulfur saturation coverage that is close to 1.3 ML. The corresponding S 2p spectrum is a convolution of spectra observed for S/Pt(111) (Figure 1) and S/Ag surfaces,[6b] which show S 2p features covering the range from 165 to 161 eV. At 550 K, the sulfur uptake of the Ag$_{1.16}$/Pt(111) surface is much greater than at 325 K. This difference is a consequence of the formation of PtS$_x$ compounds at 550 K.
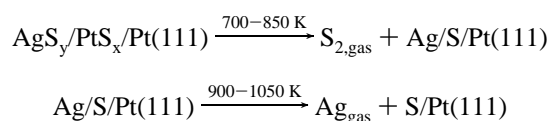
Figure 13 displays photoemission data for the valence region of Ag/Pt(111) surfaces. The features associated with the Ag

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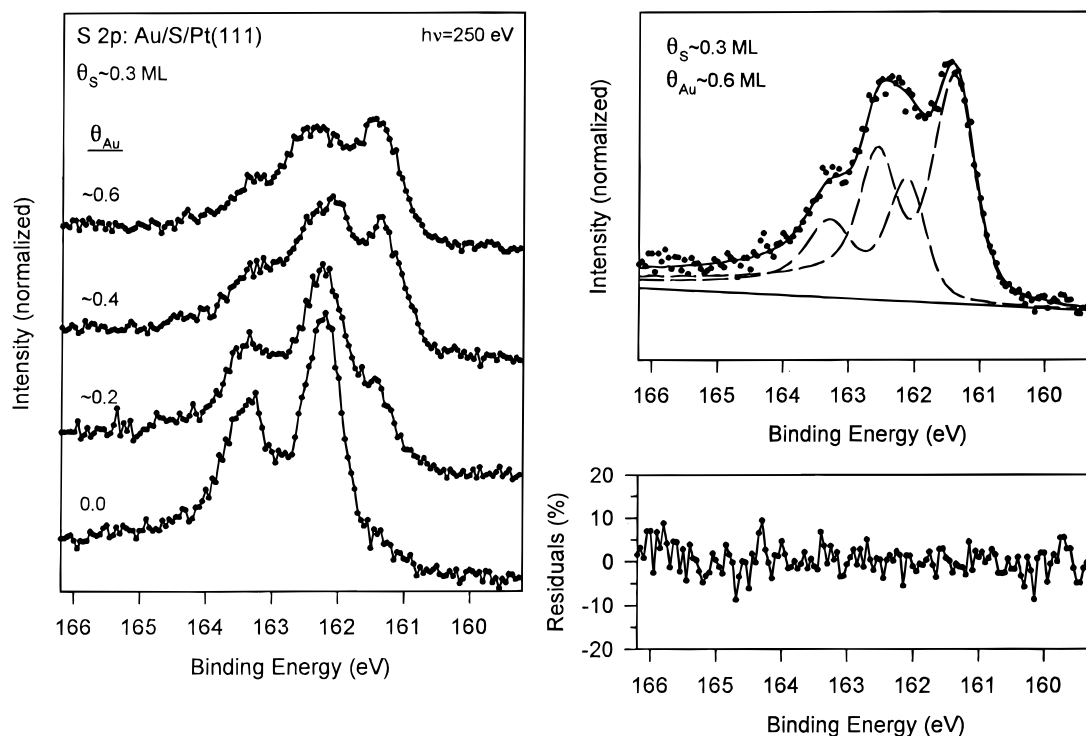
Figure 8. S 2p spectra acquired after depositing Au (0.2−0.6 ML) on a $S_{0.3}$/Pt(111) surface at 300 K. The S 2p features of the $Au_{0.6}$/$S_{0.3}$/Pt(111) system were fitted using a many-body line shape (Doniach-Šunjić[29]) convoluted with a Gaussian function to account for instrumental resolution. A linear background subtraction was performed before the fit.

4d band appear between 8 and 4 eV.[6] The deposition of sulfur produces a large reduction in the width of the Ag 4d features (30−50%) as a consequence of the formation of silver sulfides.[6] Perhaps the most important change induced by sulfur on the band structure of the Ag/Pt(111) surfaces is a big depletion in the density of states for the region between 1.8 and 0 eV.

The results of TDS and photoemission indicate that the AgS_y/PtS_x/Pt(111) systems dissociate in a sequential way:

$$AgS_y/PtS_x/Pt(111) \xrightarrow{700-850\ K} S_{2,gas} + Ag/S/Pt(111)$$

$$Ag/S/Pt(111) \xrightarrow{900-1050\ K} Ag_{gas} + S/Pt(111)$$

Thus, the platinum and silver sulfides formed by "sulfur poisoning" are stable up to temperatures that are higher than those typically used in chemical processes catalyzed by Ag/Pt surfaces.

IV. Discussion

The valence photoemission spectra of S/Au/Pt(111) and S/Ag/Pt(111) surfaces display relatively weak signals at binding energies between 1.8 and 0 eV. The adsorption of sulfur induces a large decrease (50−80%) in the density of states displayed by the bimetallic surfaces around the Fermi level. This change in the band structure of the metals reduces the ability of the surfaces to respond to the presence of adsorbates, and we argue that it is responsible for the decrease in catalytic activity that accompanies sulfur poisoning.[15] We found that several S/Au/Pt(111) and S/Ag/Pt(111) surfaces (θ_{Au} = 0.3−0.4, θ_S = 0.3; θ_{Ag} = 0.3, θ_S = 0.3−0.5; θ_{Ag} = 0.6−1.3, θ_S = 0.3) were not able to adsorb CO at room temperature. In contrast, $Au_{<0.8}$/Pt(111) and $Ag_{<0.8}$/Pt(111) surfaces adsorb CO at 300 K and the molecule desorbs at around 420 K.[24] The lack of reaction between CO and the S/Au/Pt(111) and S/Ag/Pt(111) systems probably reflects a poor π-back-donation of electrons from the surfaces toward CO.

Previous studies indicate that Au and Ag affect the chemical (or catalytic) properties of Pt surfaces in a similar way.[20−22,24] For example, in CO/$Au_{<0.8}$/Pt(111) and CO/$Ag_{<0.8}$/Pt(111) surfaces, the presence of Au or Ag does not alter the CO binding energy to the Pt substrate, and the CO desorption features for these systems are always very similar.[24] However, for the S/Au/Pt(111) and S/Ag/Pt(111) surfaces, one finds important differences in the interactions between sulfur and the noble metals. The Au ↔ S interactions are clearly repulsive with gold reducing the adsorption energy of sulfur on Pt(111). On the other hand, silver reacts with sulfur and promotes the sulfidation of platinum.

The thermochemical stability of bulk compounds that contain gold and sulfur is very small.[39] Thus, in the Au/S/Pt(111) systems, there is no effective bonding between gold and sulfur and the adsorbates compete for making bonds with the Pt substrate. The electronic perturbations induced by Au on Pt are relatively small.[40] In contrast, S significantly decreases the density of states of Pt around the Fermi level (Figure 2), diminishing its ability to form bimetallic bonds. In some cases, the weakening in the bimetallic bonds is so large that the Au adatoms ball up on the surface. Studies of scanning tunneling microscopy (STM) for Au/S/Mo(100)[5] and Au/S/Ru(001)[17] surfaces show the segregation of Au and S into separate domains, with Au forming 3D clusters on the surface instead of "wetting" the transition-metal substrate as probably happens in the case of Au/S/Pt(111). Our results suggest that S can alter the performance of Au/Pt catalysts by inducing a reduction in the degree of mixing of the metals.

In order to minimize through-space and through-substrate Au ↔ S interactions, the Au/S/Pt(111) surfaces adopt a configuration in which sulfur segregates into islands of high local coverage where it is bonded to hollow and bridge sites of the Pt substrate. The data in Figure 8 prove that the S 2p region of the photoemission spectrum is very useful for studying changes in the structure of sulfur overlayers. When a S overlayer is compressed into islands of high local coverage by Au, there is a displacement of the S atoms from their optimal
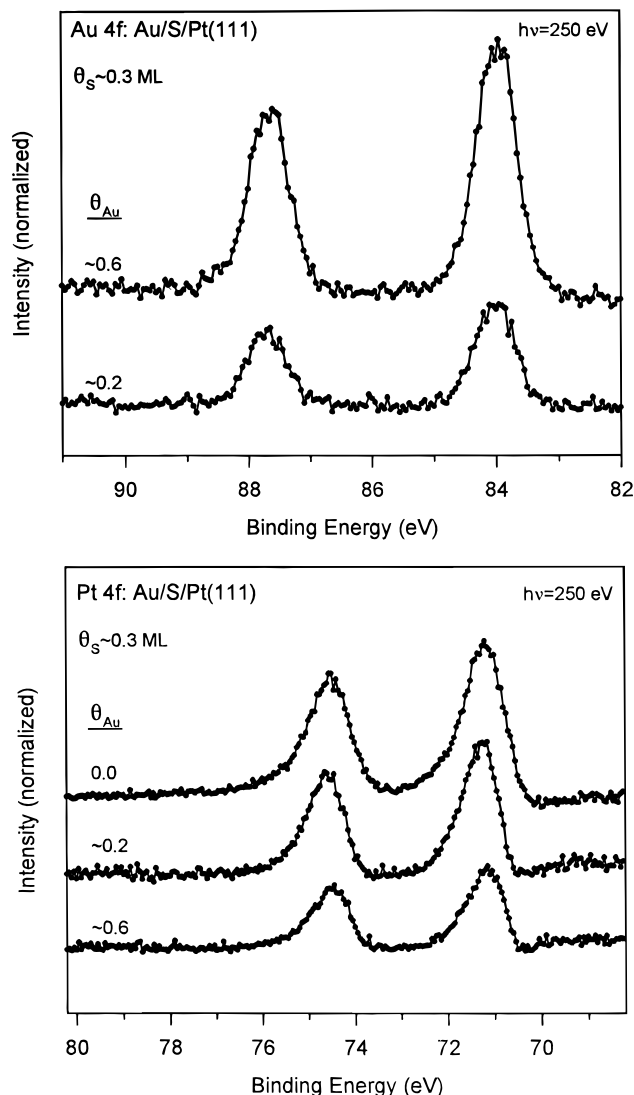
Figure 9. Au 4f (top) and Pt 4f (bottom) spectra taken after depositing Au (0.2−0.6 ML) on a $S_{0.3}$/Pt(111) surface at 300 K.
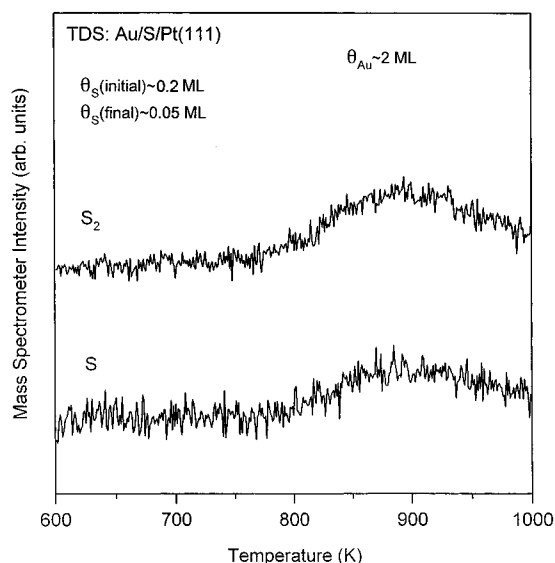
Figure 10. S_2- and S-thermal desorption spectra acquired after depositing 2 ML of Au on a $S_{0.2}$/Pt(111) surface at 300 K. No desorption of Au was detected. Heating rate = 5 K/s.

adsorption sites and a decrease in the S−S separation. This opens the possibility for new reaction channels for the removal of S from the Pt substrate. In the Au/S/Pt(111) surfaces, Au
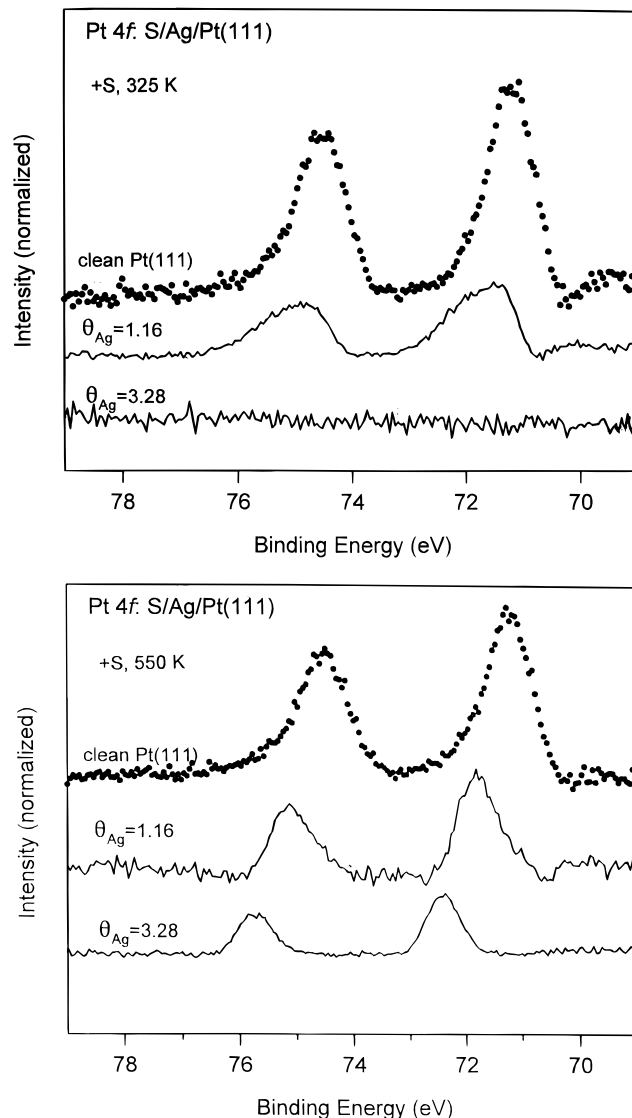

Figure 11. Pt 4f spectra acquired after exposing Ag$_{1.16}$/Pt(111) and Ag$_{3.28}$/Pt(111) surfaces to S_2 at 325 (top part) and 550 K (bottom part). A photon energy of 250 eV was used in these experiments.

substantially decreases the thermal stability of adsorbed sulfur, forcing the desorption of S_2 at temperatures between 700 and 1000 K.

Silver forms compounds with sulfur that are more stable than those formed by gold.[39] In the Ag/S/Pt(111) systems, the formation of silver and platinum sulfides makes possible the adsorption of large amounts of sulfur on the sample. Silver is much more effective than Au at promoting the synthesis of platinum sulfides. In principle the formation of PtS_x from metallic Pt and S_2 should occur spontaneously ($\Delta G = -180$ to -230 kJ/mol[41]), but there is a large kinetic barrier for the penetration of S into the bulk of the sample. An admetal can promote the sulfidation of Pt by facilitating the migration of S from the surface into the Pt lattice, or by increasing the reactivity of Pt toward S through metal−metal bonding. Three factors make Ag a much better promoter than Au. First, Ag is more effective at dissociating S_2 than Au.[42] Second, Ag has a surface free energy (1.30 J m^{-2} [43]) smaller than that of Au (1.63 J m^{-2} [43]) or Pt (2.69 J m^{-2} [43]). In the S/Pt(111) system, the large difference between the surface free energies of S (0.08 J m^{-2} [43]) and Pt makes difficult the diffusion of sulfur into the Pt lattice. Therefore, the presence of Ag on the Pt surface probably frees sulfur for migration into the bulk of the sample. Third, the charge transfer within the Au−Pt(111) bond is negligible,[40a] whereas in the Ag−Pt(111) bond there is a significant shift of

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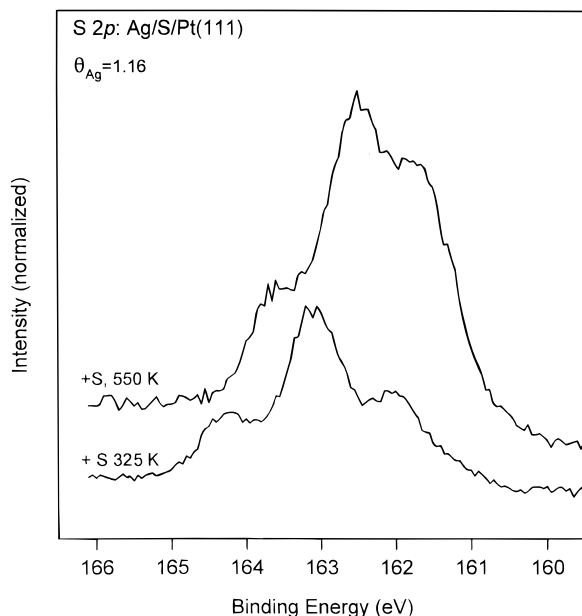
Figure 12. S 2p spectra taken after exposing a $Ag_{1.16}$/Pt(111) surface to S_2 at 325 and 500 K. The S 2p electrons were excited using a photon energy of 250 eV.
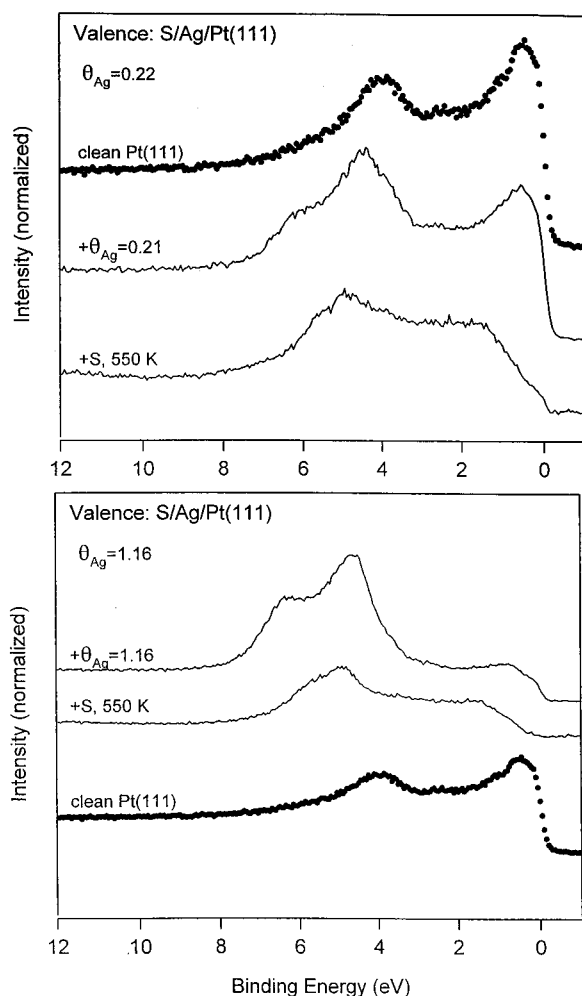
Figure 13. Valence photoemission data for Pt(111), Ag/Pt(111), and S/Ag/Pt(111) surfaces. Silver was vapor-deposited at ~300 K, and the Ag/Pt(111) surfaces were annealed to 550 K before dosing S_2 at this temperature. The spectra were acquired using a photon energy of 70 eV.

electrons from the admetal toward the metal substrate[44,45] that favors the formation Pt → S dative bonds.

The results presented in this paper illustrate how admetals that enhance the performance of Pt reforming catalysts in a very similar way can lead to mechanisms for sulfur poisoning that are very different.

V. Conclusions

(1) The adsorption of sulfur on Au/Pt(111) and Ag/Pt(111) induces a large depletion in the density of states displayed by the bimetallic surfaces around the Fermi level. This change in the band structure of the metals may be responsible for the decrease in chemical and catalytic activity that accompanies sulfur poisoning.

(2) On Pt(111), the Au ↔ S interactions are repulsive. Au forms 3D clusters, while S segregates into islands of high local coverage where it is bonded to hollow and bridge sites of the Pt substrate. Au substantially decreases the thermal stability of adsorbed sulfur on Pt(111), forcing the desorption of S_2 at temperatures between 700 and 1000 K.

(3) On Pt(111), silver reacts with sulfur and promotes the synthesis of platinum sulfides. The formation of silver and platinum sulfides makes possible the adsorption of large amounts of sulfur on Ag/Pt(111) surfaces. The sulfides decompose at high temperatures (700−850 K), with S_2 evolving into the gas phase and metallic Ag remaining on top of a Pt(111) substrate partially covered by chemisorbed sulfur.

(4) The differences in the behavior of the Au/S/Pt(111) and Ag/S/Pt(111) surfaces arise from variations in the nature of the admetal ↔ S and admetal ↔ Pt interactions. Au and S show a weak tendency to form bonds between them and compete for making bonds with the Pt substrate. On the other hand, Ag forms bonds with S, and in addition, a charge transfer from Ag to Pt favors the formation of Pt−S bonds. The Au/S/Pt(111) and Ag/S/Pt(111) systems illustrate different extremes of the phenomena that can occur when sulfur is present on a bimetallic surface.

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(41) The reaction of S_2 gas with metallic Pt to produce PtS or PtS_2 leads to a large decrease in the Gibbs free energy (ΔG) of the system; S_2(gas) + 2Pt(solid) → 2PtS(solid), $\Delta G = -232.5$ kJ/mol or S_2(gas) + Pt(solid) → PtS_2(solid), $\Delta G = -179.8$ kJ/mol. The changes in free energy for these reactions were calculated using values reported in ref 39 for the Gibbs free energy of formation of S_2, Pt, PtS, and PtS_2 at 298.15 K.

(42) During the reaction of S_2 with Au multilayers at 300 K, only a chemisorbed layer of sulfur is formed. On the other hand, when Ag multilayers are exposed to S_2 at 300 K, one sees the fast formation of films of silver sulfides.

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