JOURNAL OF CATALYSIS 154, 355–363 (1995)

The Interaction of Sulfur with Ag/Pt(111) Surfaces: Silver-Promoted Sulfidation of Platinum[1]

Mark Kuhn and José A. Rodriguez[2]

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

Received September 6, 1994; revised February 2, 1995

The coadsorption of sulfur and silver on Pt(111) has been examined using thermal desorption mass spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS), and X-ray excited Auger electron spectroscopy (XAES). The results of XPS and XAES indicate that at temperatures between 300 and 700 K, S_2 gas reacts with Pt(111) producing a chemisorbed layer of sulfur without forming bulk-like platinum sulfides. The sulfidation of platinum occurs after vapor depositing Ag on S/Pt(111) surfaces, or after exposing Ag/Pt(111) surfaces to S_2 gas. At temperatures from 400 to 700 K, the reaction of S_2 gas with Ag/Pt(111) surfaces produces silver sulfides that catalyze the sulfidation of platinum by providing surface sites for the dissociation of S_2, and by favoring the diffusion of S into the bulk of the Pt substrate. The silver and platinum sulfides in the S/Ag/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. At submonolayer coverages of Ag and S on Pt(111), $\theta_{Ag} + \theta_s < 1$ ML, the presence of sulfur significantly weakens the strength of the Pt↔Ag interactions, and the desorption temperature of Ag is ~90 K smaller than on clean Pt(111). The TDS results indicate that a S adatom reduces the ability for bimetallic bonding of several (3–4) platinum surface atoms.

INTRODUCTION

In the petrochemical industry, platinum is widely used as a catalyst in processes that involve the conversion of hydrocarbons (1). The addition of a second metal to a Pt surface can produce dramatic changes in the catalytic properties of the surface. For example, the activity of Pt for C–C hydrogenolysis can be reduced by adding a noble metal (2, 3). In the bimetallic surface, the active (Pt) sites are diluted by the substitutional presence of the inert metal (Cu, Ag, or Au), and therefore the probability of finding large ensembles of free Pt sites is small. In this way, reactions that require a large ensemble or group of active sites like C–C hydrogenolysis are selectively suppressed, without affecting reactions that require a small ensemble of active sites. Bimetallic bonding can also induce significant changes in the electronic properties of Pt (4, 5), enhancing the catalytic activity of the metal (6). On platinum–rhenium surfaces, the rate of ethane hydrogenolysis is much faster than on pure platinum or rhenium catalysts (6).

Due to their superior activity and/or selectivity bimetallic catalysts that contain platinum are frequently used in commercial applications (7, 8). One of the major problems associated with the use of these catalysts is sulfur poisoning (9). The presence of ppm quantities of sulfur contaminants in the reaction mixture can reduce the lifetime of a bimetallic catalysts to only a few months or weeks. This work is part of a research program (10–12) aimed at gaining a better understanding of the effects of sulfur on the structural, electronic, and chemical properties of bimetallic surfaces. In principle, a fundamental knowledge of the mechanisms of sulfur poisoning may provide ideas for the design of new catalysts that are less sensitive to the presence of sulfur in the feedstream. Here, we investigate the interaction of sulfur with Ag/Pt(111) surfaces. These bimetallic surfaces combine a metal that forms stable compounds with sulfur (PtS_2, $\Delta H_f = -108.9$ kJ/mol (13)), and a metal that shows a relatively low affinity toward sulfur (Ag_2S, $\Delta H_f = -32.6$ kJ/mol (13)). The existing data for the Ag/Pt(111) and S/Pt(111) surfaces (14–23) makes S/Ag/Pt(111) an ideal system for studying the effects of sulfur on the properties of a bimetallic surface.

Previous works have examined the properties of silver on Pt(111) in detail using thermal desorption mass spectroscopy (TDS) (14–16), X-ray photoelectron spectroscopy (XPS) (16, 17), low-energy electron diffraction (LEED) (14–16), work function measurements (15, 16), scanning tunneling microscopy (STM) (18), and quantum-mechanical calculations (17, 19). At room temperature, the first monolayer of Ag grows in a $p(1 \times 1)$ fashion (15, 16, 18), with the noble-metal atoms adsorbed on the fcc hollow sites of the Pt substrate (18). Subsequent adlayers

---

[1] The U.S. Government's right to retain a nonexclusive royalty-free license in and to the copyright covering this paper, for governmental purposes, is acknowledged.

[2] To whom correspondence should be addressed.

0021-9517/95 $12.00

adopt lattice structures that are close to that of Ag(111) (15, 18). TDS data (14–16) indicate that for $\theta_{Ag} < 1.0$ ML, Ag desorbs in a single state at ~1050 K with an activation energy of ~290 kJ/mol. For $\theta_{Ag} > 1.0$ ML, a second multilayer desorption peak appears between 900 and 1000 K. Silver adatoms decrease the work function of Pt(111) (15, 16); a phenomenon consistent with a Ag→Pt charge transfer (17, 19). The adsorption of sulfur on Pt(111) has been examined using LEED (20–23), Auger electron spectroscopy (AES) (20), and work function measurements (22). LEED experiments show that sulfur adatoms form $p(2 \times 2)$ ($\theta_s = 0.25$ ML) and $p(\sqrt{3} \times \sqrt{3})$R30° ($\theta_s = 0.33$ ML) structures on Pt(111) (20–23). In the last structure, the S atoms are adsorbed on the fcc hollow sites of the Pt surface (21). Results of AES indicate that at $\theta_s \approx 0.8$ ML, sulfur begins to disappear from the Pt(111) surface around 650 K, with a clean Pt substrate being observed only after heating to 1400 K (20). Work function measurements suggest that the adsorption bond of S on Pt(111) is essentially covalent (22).

Our results for the coadsorption of Ag and S on Pt(111) indicate that the presence of sulfur weakens the strength of the Pt↔Ag interactions. At room temperature, S_2 gas reacts with Ag/Pt(111) surfaces producing silver sulfides and chemisorbed sulfur on top of Pt. The silver sulfides catalyze the sulfidation of platinum at temperatures between 400 and 700 K.

EXPERIMENTAL

The properties of the S/Ag/Pt(111) surfaces were investigated using TDS, XPS, and X-ray excited Auger electron spectroscopy (XAES). The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure lower than 7×10^{-8} Pa. The XPS and XAES spectra were acquired using a Mg$K\alpha$ X-ray source and a hemispherical electron-energy analyzer with multichannel detection. During the photoemission experiments, the elecron-energy analyzer was positioned at 30° from the normal of the surface. For the Ag $3d_{5/2}$ peak of thick Ag multilayers, our instrument gave a full-width at half maximum (FWHM) of 0.85 eV. This Ag FWHM can be taken as the overall instrumental resolution. The binding-energy scale in the photoemission spectra was calibrated by using the Ag $3d_{5/2}$ and Pt $4f_{7/2}$ peaks of pure Ag and pure Pt, which were set at binding energies of 368.0 and 71.2 eV (24), respectively.

The Pt(111) crystal was cleaned following procedures reported in the literature (14, 15). Surface cleanliness was verified by means of XPS. Ag was vapor-deposited on Pt(111) and S/Pt(111) surfaces from a resistively heated W filament wrapped with a high-purity wire of silver. Ag coverages were determined by TDS area analysis (15, 16). A solid-state electrochemical cell (Pt/Ag/AgI/Ag$_2$S/Pt (20, 25)) was used to vapor-deposit sulfur on the Pt(111) and Ag/Pt(111) surfaces. When a voltage was applied across the cell, sulfur evolved as S_n clusters (predominantly S_2). For small doses of gaseous sulfur, 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 to the corresponding area for the saturation coverage of sulfur on Pt(111) at 750 K, which is known to be one third of a monolayer (20, 23). In this work, coverages are reported with respect to the number of Pt(111) surface atoms (1.51×10^{15} atoms/cm^2). One Ag or S adatom per substrate surface atom corresponds to $\theta = 1$ monolayer (ML).

The Pt(111) crystal was mounted in a manipulator capable of resistive heating to 1600 K and liquid nitrogen cooling to 80 K. Temperatures were monitored with a W–5%Re/W–26%Re thermocouple spot-welded to the upper edge of the sample. The thermal desorption spectra were acquired using a heating rate of 5 K/s.

RESULTS

(I) Properties of S/Pt(111) Surfaces

Figure 1 shows S $2p$ XPS spectra acquired after dosing sulfur to a Pt(111) surface at 315 K, with subsequent annealing to 500, 800, and 1200 K. For low coverages of sulfur ($\theta_s < 0.4$ ML), the adatoms are dispersed on the surface and the S ↔ S interactions are minimal (20). At high sulfur coverages ($\theta_s > 0.8$ ML), it is not clear what type of sulfur species are present on the surface. Under these conditions, the sulfur adatoms can agglomerate on the surface forming dimers or trimers (26). LEED experi-

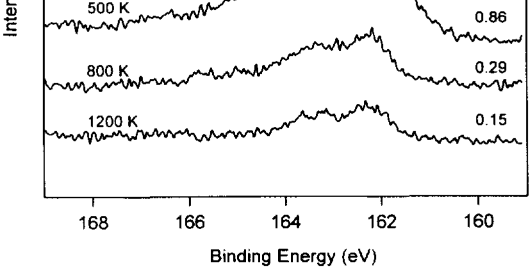

FIG. 1. Sulfur $2p$ XPS spectra taken after depositing 1.06 ML of sulfur on Pt(111) at 315 K, and annealing to 500, 800 and 1200 K.

ments show that the sulfur adlayer is highly disordered (20). The results of Fig. 1 indicate that at $\theta_s > 0.8$ ML more than one type of sulfur is present on the surface.

Figure 2 displays S- and S_2-TDS spectra taken after heating a Pt(111) surface covered by 1.06 ML of sulfur from 325 to 1100 K. During these experiments, we did not detect any significant signal for the desorption of S_3 (mass 96) or S_4 (mass 128). Desorption of S_2 was observed in a small feature at ~380 K and a large sharp peak at ~720 K. For the desorption of S, a sharp peak was seen at ~720 K, with a broad feature appearing between 750 and 950 K. In Fig. 2, after comparing the relative intensities of the S and S_2 signals at 380 K, one can conclude that the S desorption signal at ~720 K is not due to the cracking of S_2 in the mass spectrometer. Previous works have detected the desorption of atomic S from Pt(100) (27) and Ru(001) (28). For sulfur coverages below 0.2 ML, no significant desorption of S_2 or S was detected at temperatures between 325 and 1400 K. In these cases, the sulfur disappeared from the surface by migrating into the bulk of the Pt crystal at temperatures from 1100 to 1400 K (20).

(II) Silver Adsorption on S/Pt(111)

Sulfur adatoms induce a significant reduction in the strength of the Pt–Ag bond. Figure 3 displays Ag-TDS spectra acquired after depositing 1.51 ML of Ag on clean Pt(111) (dotted traces), and after depositing several Ag coverages on a Pt surface precovered with 0.20 ML of S (solid traces). For these experiments, XPS measurements showed that the amount of S present on the surface after taking the TDS spectra was identical to the S coverage seen before the deposition of Ag. (For S/Pt(111), adlayers with $\theta_s \leq 0.2$ ML do not disappear from the surface at temperatures below 1100 K (20)). The spectrum for desorption of Ag from clean Pt(111) shows two well-defined peaks at 1040 (Ag monolayer) and 970 K (Ag multilayer). For a $\{\theta_x = 0.20;\ \theta_{Ag} = 0.29\}$ surface, the Ag-desorption temperature is identical to that of Ag atoms bonded to clean Pt(111), indicating that at these low coverages of S and Ag the presence of sulfur does not affect the strength of the Pt↔Ag interactions. In this case, all the Ag adatoms are able to find Pt sites that are not perturbed by the S adatoms. When the Ag coverage is increased to 0.55 ML, a new Ag-desorption peak appears at ~950 K with a desorption activation energy ~17 kJ/mol smaller than that of Ag bonded to clean Pt(111) (29). This new peak can be attributed to desorption of Ag from Pt sites strongly perturbed by S. On these sites, silver may be forming three-dimensional (3D) clusters before desorbing, leading to a desorption temperature similar to that of Ag multilayers. The clustering of Ag would be occurring at high temperatures. XPS and XAES experiments for $\{\theta_s + \theta_{Ag} < 1\}$ surfaces indicated that at room temperature, immediately after the deposition of Ag, the noble metal was spread out on the substrate, making bonds with Pt and S (see below).

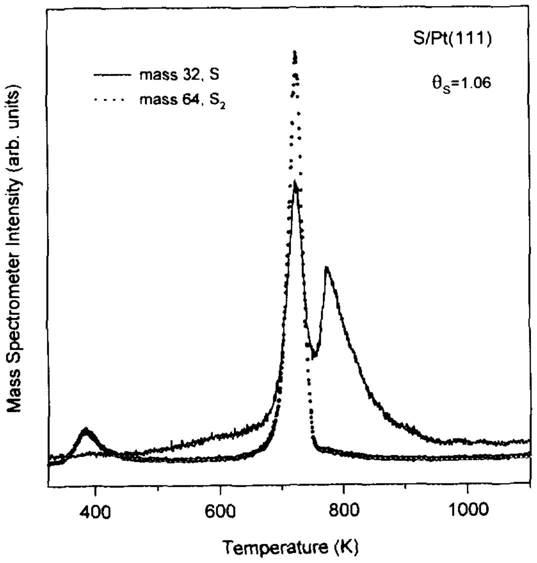

FIG. 2. S- and S_2-thermal desorption spectra acquired after depositing 1.06 ML of sulfur on Pt(111). Heating rate = 5 K/s.

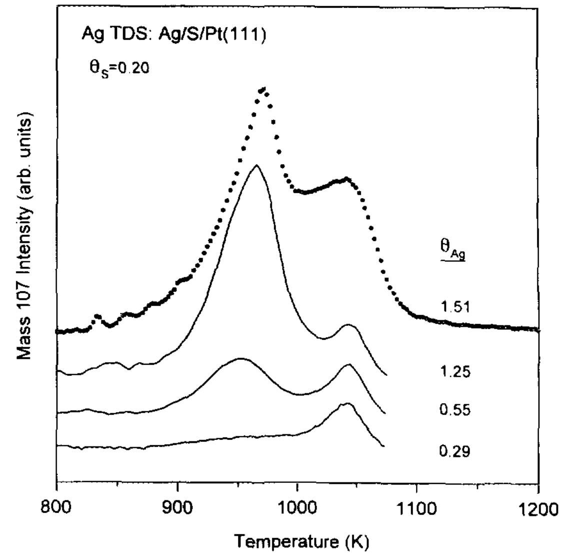

FIG. 3. Silver-thermal desorption spectra for Ag/Pt(111), dotted traces, and Ag/S/Pt(111) surfaces, solid traces. Heating rate = 5 K/s.

Figure 4 shows Ag MVV Auger spectra acquired after dosing small amounts of silver to a Pt(111) surface precovered with 0.20, 0.29 or 0.86 ML of sulfur at 325 K. The Ag MVV Auger transitions are very sensitive to the formation of bonds between Ag and S (30). For bulk Ag_2S, the M_4VV peak is shifted 1.1 eV toward lower kinetic energy with respect to that of metallic Ag (30). The kinetic-energy

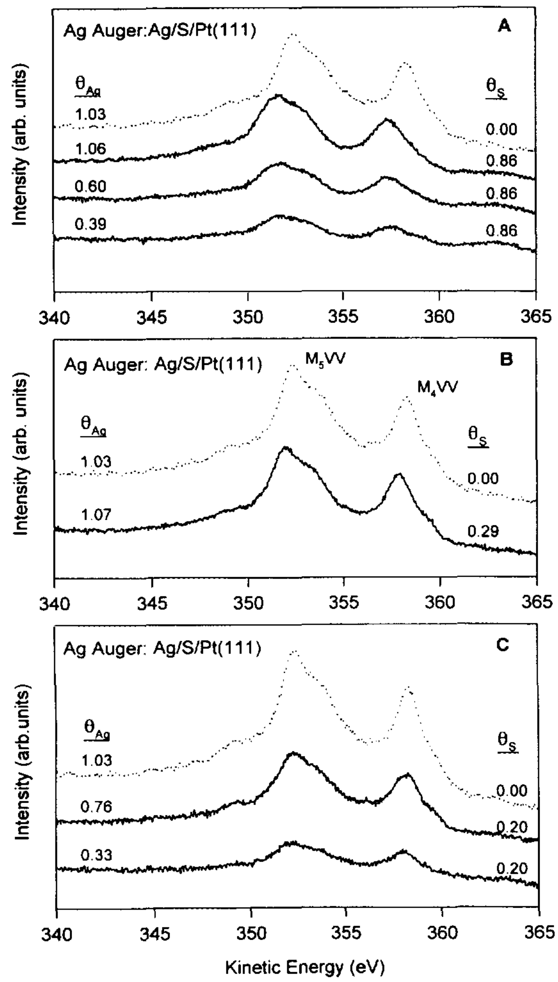

FIG. 4. Ag Auger M_5VV and M_4VV transitions of Ag/Pt(111) and Ag/S/Pt(111) surfaces. The spectra were acquired at 320 K after vapor depositing Ag on clean Pt(111) and Pt(111) precovered with 0.86 (part A), 0.29 (part B), or 0.20 ML (part C) of sulfur. The primary electrons were excited using Mg*Kα* radiation.

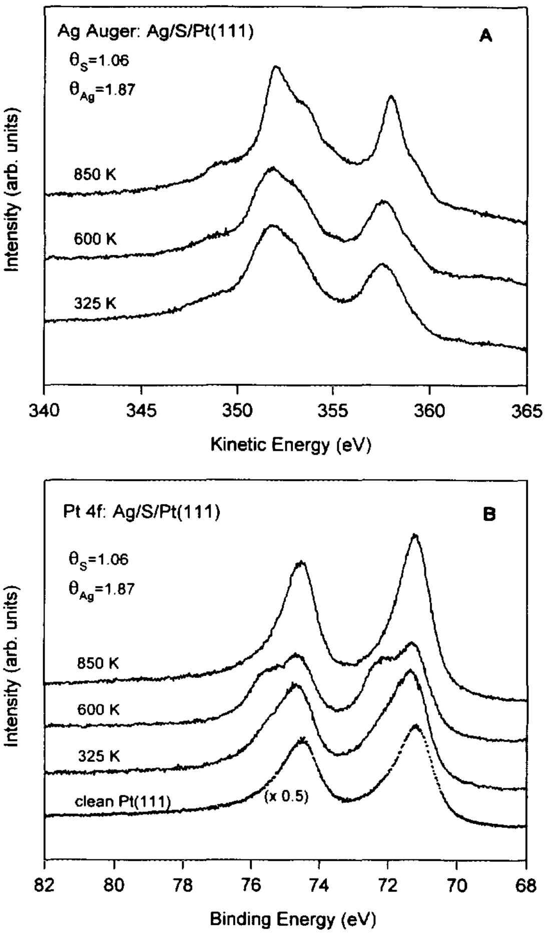

FIG. 5. Ag MVV Auger (part A) and Pt 4*f* XPS (part B) spectra acquired after depositing 1.87 ML of Ag on a Pt(111) surface precovered by 1.06 ML of sulfur at 325 K, and subsequent annealing of this Ag/S/Pt(111) system to 600 and 850 K. In part B, we also include the Pt 4*f* spectrum of clean Pt(111) (dotted traces).

shifts in Fig. 4 indicate the formation of silver sulfides on top of Pt(111).

Figure 5 displays Ag MVV Auger and Pt 4*f* XPS spectra acquired after dosing 1.87 ML of Ag to a Pt(111) surface precovered by 1.06 ML of S. The deposition of Ag was carried out at 325 K, and then, the sample was annealed to 600 and 850 K. At 325 K, the position of the Ag MVV peaks indicates the formation of a silver sulfide (AgS_y). The Pt 4*f* peaks of the Ag/S/Pt(111) system exhibit binding energies and FWHM's slightly larger than those of clean Pt(111) (bottom of Fig. 5B). At this temperature, there is no clear evidence for the formation of a platinum sulfide (31). After annealing the sample from 325 to 600 K, a doublet of peaks is observed for each Pt 4*f* level. This behavior indicates the formation of a platinum sulfide (PtS_x) (31). The Pt $4f_{7/2}$ level of bulk PtS_2 appears shifted 1.8 eV toward higher binding energy relative to that of metallic Pt (31). The annealing from 325 to 600 K produces very minor changes in the Ag MVV Auger features of the Ag/S/Pt(111) system. At 600 K, sulfides of silver and platinum (AgS_y and PtS_x) coexist in the sample. An increase in temperature to 850 K produces the decomposition of these sulfides, with S_2 evolving into gas phase and metallic Ag remaining on a surface that contains a small amount of sulfur ($\theta_s \approx 0.3$ ML).

The top of Fig. 6 shows Pt 4*f* XPS spectra taken after dosing a monolayer of S to Pt(111) at 335 K, and annealing of this S/Pt(111) system to 600 K for 5 min. In this Ag-free system, the annealing at high temperature does not lead to the formation of a significant amount of platinum sulfide and the Pt 4*f* peaks are only slightly broader than in pure Pt(111). On the other hand, when Ag is deposited on the S/Pt(111) surface at 600 K, the formation of a platinum sulfide takes place, and there is an appreciable

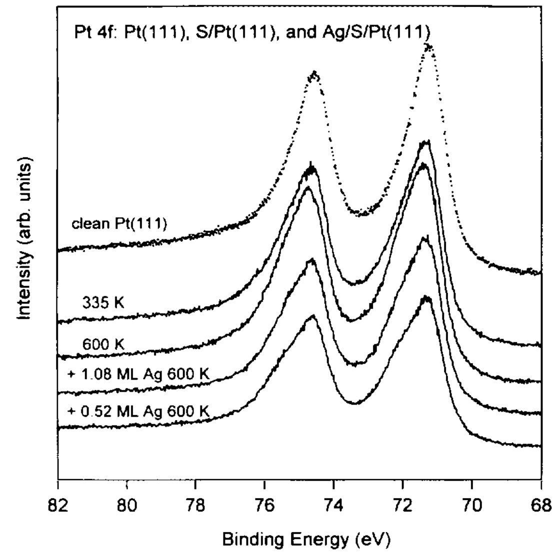

FIG. 6. The two solid curves in the top of the figure correspond to Pt 4*f* XPS spectra taken after dosing a sulfur monolayer to Pt(111) at 335 K, and annealing of this S/Pt(111) system to 600 K for 5 min. This was followed by deposition of Ag at 600 K, and acquisition of the two spectra displayed in the bottom of the figure.

broadening in the FWHM of the Pt 4*f* features. Thus, we can conclude that silver is promoting the formation of platinum sulfides.

Figure 7 displays S-, S_2-, and Ag-thermal desorption spectra for a Ag/S/Pt(111) system. For comparison, we also show the corresponding spectra for a S/Pt(111) surface. The presence of Ag produces drastic changes in the desorption pattern of S and S_2, increasing the relative amount of S_2 that desorbs from the surface. In the Ag/S/Pt(111) system, the desorption of S_2 occurs at higher temperature (~40 K) than in S/Pt(111). In Figs. 7A and 7B, the S and S_2 desorption peaks at ~760 K are a product of the decomposition of silver and platinum sulfides in the Ag/S/Pt(111) system. For this system, most of the Ag desorbs at a temperature similar to that observed for desorption of a Ag multilayer from Pt(111) (16). At 1200 K, only a small amount of S ($\theta_s \approx 0.15$ ML) was present on the Pt(111) surface.

(III) Sulfur Adsorption on Ag/Pt(111)

Adsorption of S_2 on Pt(111) surfaces with submonolayer coverages of Ag at 300 K produced silver sulfides and chemisorbed sulfur. TDS experiments for these systems showed desorption of S_2 in a small peak at ~390 K and a broad feature between 700 and 900 K, with the features for Ag desorption exhibiting peak temperatures and line shapes almost identical to those seen in Fig. 1 for Ag/S/Pt(111) systems.

Figure 8 shows photoemission spectra acquired after dosing sulfur to a Ag film supported on Pt(111). The preparation of the Ag film and the dosing of sulfur were carried out at 325 K, with a subsequent annealing of the sample to 600 and 850 K. The adsorption of S_2 on Ag(111) at 300 K leads to the fast formation of a Ag_2S film (32). In Fig. 8A, bonding between S and Ag at 325 K induces a large decrease (~1.1 eV) in the kinetic energy of the Ag M_4VV transition. This is consistent with the formation of Ag_2S (30). An analysis of the corresponding Pt 4*f* spectrum (see Fig. 8B) reveals that no platinum sulfide has been formed at 325 K. Annealing to 600 K induces the appearance of new peaks in the Pt 4*f* spectrum. These peaks are shifted ~1.4 eV with respect to those of metallic Pt. They indicate the formation of a platinum sulfide (PtS_x) (31). The annealing to 600 K also produces changes in the morphology of the silver sulfide film. These structural changes "uncover" part of the Pt substrate, increasing the Pt 4*f* signal.

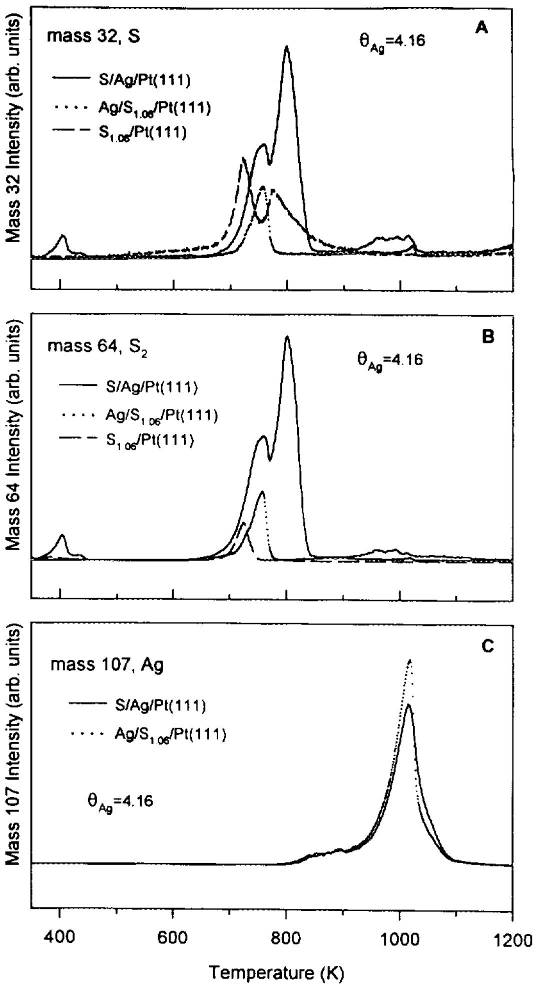

FIG. 7. S-, S_2-, and Ag-thermal desorption spectra for S/Pt(111) {θ_s = 1.06 ML}, Ag/S/Pt(111) {θ_s = 1.06 ML, θ_{Ag} = 4.16 ML}, and S/Ag/Pt(111) {θ_{Ag} = 4.16 ML} surfaces. Heating rate = 5 K/s.

For the S/Ag/Pt(111) system of Fig. 8, an increase in temperature from 600 to 850 K caused the decomposition

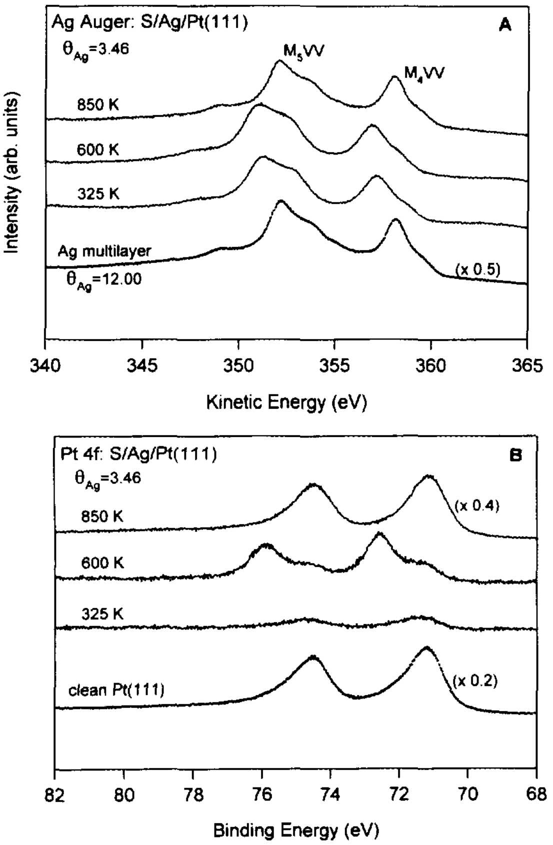

FIG. 8. Ag MVV Auger and Pt 4*f* XPS spectra acquired after preparing a thick Ag_2S film on Pt(111) at 325 K, with subsequent annealing of this system to 600 and 850 K.

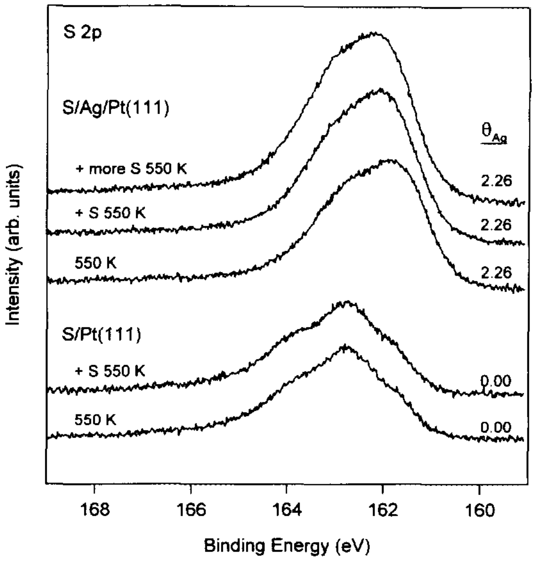

FIG. 9. The three S 2*p* XPS spectra in the top of the figure correspond to S/Ag/Pt(111) systems. In the first step, a Ag_2S film was prepared on Pt(111) at 320 K and heated to 550 K (third spectrum from the top). Then, this system was exposed to gaseous sulfur at a temperature of 550 K. The two spectra in the bottom of the figure correspond to a S/Pt(111) surface {θ_S = 0.85 ML} annealed to 550 K, and exposed to large amounts of gaseous sulfur at this temperature.

of the silver and platinum sulfides, with most of the sulfur evolving into gas phase. Figure 7 shows S-, S_2-, and Ag-TDS spectra acquired after heating a S/Ag/Pt(111) system prepared following the same methodology used to "synthesize" the system that provided the XPS data in Fig. 8. The decomposition of the silver and platinum sulfides produces desorption of S_2 at 800 and 760 K, with most of the silver desorbing from the surface around 1000 K. At 1200 K, only a small amount of sulfur was present on the Pt(111) surface.

We examined the effects of silver sulfide on the reactivity of metallic platinum toward S_2 gas at 550 K using XPS. Representative S 2*p* and Pt 4*f* spectra are shown in the top of Figs. 9 and 10. In the first step, a Ag_2S film was prepared on Pt(111) at 320 K and heated to 550 K. Then, the sample was exposed to gaseous sulfur at 550 K. After dosing sulfur at 550 K, there was an appreciable increase in the amount of sulfur adsorbed on the S/Ag/Pt(111) system (top of Fig. 9). In addition, the Pt 4*f* signal for platinum sulfide increased, while the corresponding signal for metallic platinum decreased (top of Fig. 10). On the other hand, when a Ag-free Pt(111) surface partially covered by 0.85 ML of sulfur was exposed to large amounts of S_2 gas at 550 K, no extra adsorption of sulfur was detected (bottom of Fig. 9) and the amount of platinum sulfide formed was insignificant (bottom of Fig. 10). Thus, it appears that silver *catalyzes* the formation of platinum sulfide.

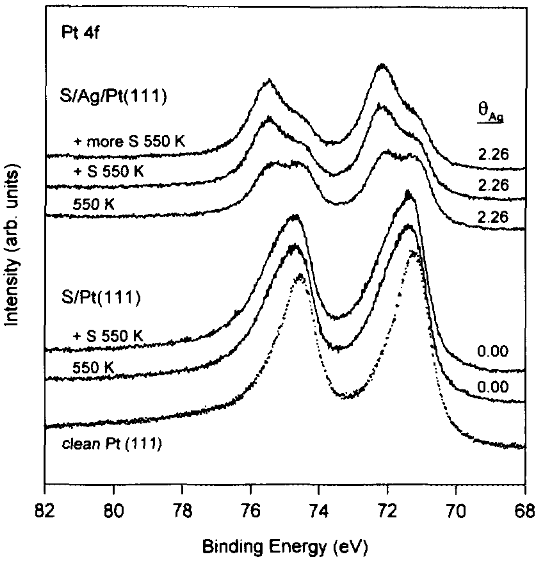

FIG. 10. Pt 4*f* XPS spectra acquired in the same set of experiments that led to the data in Fig. 9.

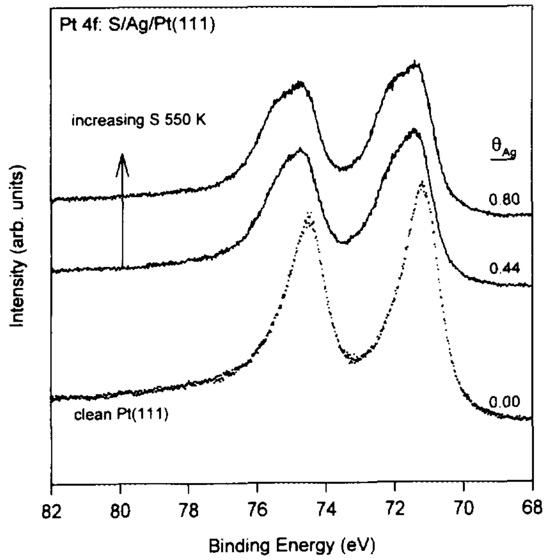

FIG. 11. Pt $4f$ XPS spectra acquired after exposing Ag/Pt(111) surfaces (θ_{Ag} = 0.44 or 0.80 ML) to gaseous sulfur at 550 K.

The results in Fig. 11 illustrate that submonolayer coverages of silver sulfide also promote the reaction between S_2 gas and metallic Pt at 550 K. For the surface with 0.8 ML of silver, we estimate that at least two layers of the Pt substrate have been transformed into platinum sulfide.

DISCUSSION

(I) Sulfur-Induced Destabilization of the Pt–Ag Bond

At 300 K, silver atoms in contact with Pt(111) react with sulfur to form sulfides that decompose at high temperatures. Coadsorption with sulfur substantially decreases the bonding energy of silver on Pt(111). At $\theta_s \geq$ 0.2 ML, the activation energy for desorption of silver is reduced by ~17 kJ/mol (29). Under these conditions, the weakening of the Pt–Ag bonds is so large that the noble-metal adatoms form 3D clusters on the Pt(111) surface after the breaking of the Ag–S bonds at high temperatures. The TDS results of Fig. 3 indicate that a sulfur adatom reduces the bonding ability of several (3–4) platinum surface atoms. At θ_s = 0.20 ML, most of the Pt sites show strong perturbations in their chemical properties. At the present time, it is not clear how sulfur weakens the strength of the Pt–Ag bonds. Work function measurements indicate that the adsorption bond of S on Pt(111) is essentially covalent (22). A S adatom could reduce the bonding ability of adjacent surface sites by changing the stability of the Pt valence levels that have the appropriate symmetry to hybridize with the Ag orbitals. A similar phenomenon has been observed in the "poisoning" of CO chemisorption on Rh(100) by sulfur (35).

Previous works for S/X/Ru(001) (X = Cu, Ag, Au, or Zn) surfaces have shown that in the presence of sulfur there is a significant weakening in the strength of the Ru–Zn and Ru-noble metal bonds (10–12). By comparing the TDS data for Ag/S/Pt(111) with results reported for Ag/S/Ru(001) (12) and Co/S/Mo(100) (36) surfaces, one finds two different extremes in the types of phenomena that can occur when S interacts with a bimetallic system. On Pt(111) and Ru(001), the presence of sulfur leads to an appreciable decrease (70–90 K) in the desorption temperature of the Ag adatoms. In contrast, the $\{\theta_s = 0.5, \theta_{Co} = 1.0\}$/Mo(100) system shows a cobalt-desorption temperature (1326 K) larger than that of a cobalt monolayer supported on Mo(100) (1313 K). In this case, cooperative interactions between the Co–S and Co–Mo bonds increase the thermal stability of Co on the surface (36). For Ag/S/Pt(111) and Ag/S/Ru(001) surfaces, bonding between the admetal and sulfur occurs, but the Ag–S bonds break at high temperature producing S and noble-metal adatoms that compete for making bonds with the Pt or Ru substrate.

(II) Silver-Promoted Sulfidation of Platinum

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 of the system (37)

$$S_2(\text{gas}) + 2\text{Pt(solid)} \rightarrow 2\text{PtS(solid)}, \quad \Delta G = -232.5 \text{ kJ/mol} \quad [1]$$

$$S_2(\text{gas}) + \text{Pt(solid)} \rightarrow \text{PtS}_2\text{(solid)}, \quad \Delta G = -179.8 \text{ kJ/mol.} \quad [2]$$

Thus, from a thermochemical viewpoint, the formation of PtS or PtS_2 should occur spontaneously at room temperature. However, the kinetic barrier for the penetration of S into Pt(111) is large, and only a layer of chemisorbed S is formed on top of the Pt surface. This sulfur layer "passivates" the metal toward further adsorption of S_2. For the S/Pt(111) systems, two factors make difficult the penetration of S into the bulk of the sample at temperatures below 700 K. First, the surface free energy of sulfur (0.08 J m^{-2} (38)) is much lower than that of platinum (2.69 J m^{-2} (38)). Second, the cohesive energy of metallic Pt is relatively large (564 kJ/mol (39)). If the influence of these factors is somehow suppressed, then, the formation of platinum sulfides should take place.

Our results indicate that at temperatures between 400 and 700 K the sulfidation of platinum occurs after dosing Ag to S/Pt(111) surfaces, and after exposing Ag/Pt(111) surfaces to S_2 gas. Silver has a relative low surface free energy (1.30 J m^{-2} (38)), and its presence on the Pt surface probably frees sulfur for migration into the bulk of the sample. In addition, silver sulfides can promote the forma-

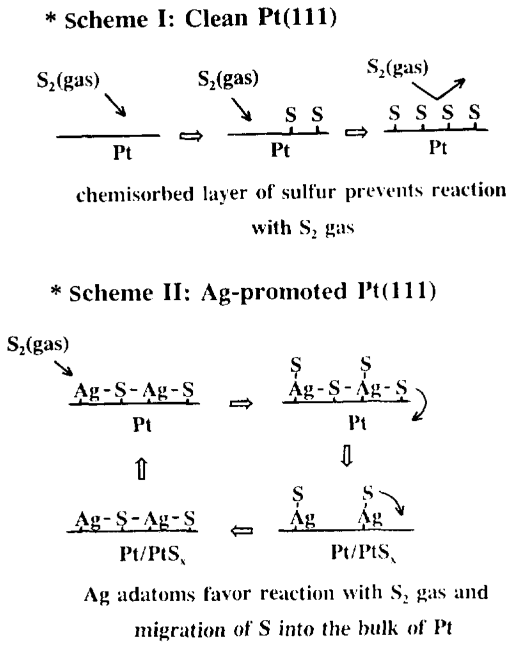

FIG. 12. Schemes for the reaction of S_2 gas with clean and Ag-promoted Pt(111).

tion of platinum sulfides by inducing changes in the structural geometry of the surface that enhance the diffusion of S into the lattice of metallic Pt. For the adsorption of S_2 on AgS_x/Pt(111) surfaces, we propose the reaction scheme displayed in the bottom of Fig. 12. The Ag adatoms provide surface sites on which S_2 can dissociate. Once sulfur is adsorbed on Ag, the large difference between the thermochemical stabilities of the Ag–S and Pt–S bonds (40) favors the migration of sulfur to form platinum sulfides.

In our previous studies dealing with the adsorption of S_2 on Ag/Ru(001) surfaces (12), we saw no experimental evidence for a Ag-promoted sulfidation of the Ru substrate. On these surfaces, the adsorption of sulfur at 300 K produced silver sulfides and chemisorbed sulfur on top of ruthenium. Annealing to high temperature induced desorption of sulfur without the formation of ruthenium sulfides, although the heat of formation of RuS_2 (−196.8 kJ/mol (13)) is much larger than that of PtS_2 (−108.9 kJ/mol (13)) or PtS (−81.6 kJ/mol (13)). The key to the difference in the behavior of the S/Ag/Pt(111) and S/Ag/Ru(001) systems may be in the difference between the cohesive energies of metallic Pt (564 kJ/mol (39)) and metallic Ru (650 kJ/mol (39)). On a ruthenium surface, the "promotional effect" of silver may not be able to overcome the large activation barrier associated with the migration of sulfur into the bulk of ruthenium. To test this hypothesis, it would be interesting to examine the coadsorption of silver and sulfur on metal substrates that have cohesive energies smaller (Fe, Ni, Pd, and Rh) or bigger (Mo, Re, Os, and Ir) than Pt and are frequently used in catalytic processes.

In another set of experiments (41), we investigated the interaction between S_2 and Cu/Pt(111) surfaces (θ_{Cu} = 0.4–3.8 ML) at 500–600 K. The Pt 4*f* XPS data indicated that Cu promotes (or catalyzes) the formation of several layers of platinum sulfide (PtS_x). The "mechanisms" proposed above to explain the promotional effect of Ag on the sulfidation of Pt can also explain the promotional effect of Cu on this reaction (41). The Ag/Pt(111) and Cu/Pt(111) systems have the following characteristics: (1) Ag and Cu form sulfides that are less stable than those formed by Pt (13), and (2) the admetals have a surface free energy that is smaller than that of Pt (38). These properties facilitate the migration of S from the surface into the bulk of the Pt substrate.

CONCLUSIONS

Our results indicate that sulfur can affect the properties of Ag/Pt catalysts by weakening the Pt↔Ag interactions (segregation of Pt and Ag into separate domains), and by forming sulfides with both metals (modification of the chemical properties of Pt and Ag).

At 300 K, the coadsorption of silver and sulfur atoms on Pt(111) leads to the formation of silver sulfides. These sulfides decompose at high temperature (800–900 K) producing Ag and S adatoms that compete for making bonds with the Pt substrate. A S adatom reduces the ability for bimetallic bonding of several (3–4) platinum surface atoms. At $\theta_s \geq 0.2$ ML, the weakening of the Pt–Ag bonds is very large, and the Ag adatoms form 3D clusters on the Pt(111) surface before desorbing at ~1000 K.

At temperatures between 300 and 700 K, S_2 gas reacts with Pt(111) producing a chemisorbed layer of sulfur, without forming bulk-like platinum sulfides. The sulfidation of platinum occurs after vapor depositing Ag on S/Pt(111) surfaces, or after exposing Ag/Pt(111) surfaces to S_2 gas. Silver promotes the formation of platinum sulfides by favoring the migration of sulfur from the surface into the lattice of the Pt substrate. These platinum sulfides are stable up to temperatures around 800 K, where they dissociate into S_2 gas, chemisorbed sulfur, and metallic Pt.

ACKNOWLEDGMENTS

The authors thank J. Hrbek for many valuable comments. This work was carried out at Brookhaven National Laboratory and supported by the U.S. Department of Energy (DE-AC02-76CH00016), Office of Basic Energy Sciences, Chemical Science Division.

REFERENCES

1. (a). Somorjai, G. A., "Introduction to Surface Chemistry and Catalysis." Wiley, New York, 1994; (b). Gates, B. C., "Catalytic Chemistry." Wiley, New York, 1992.
2. Vogelzang, M. W., Botman, M. J. P., and Ponec, V., *Discuss. Faraday Soc.* **72,** 33 (1982).
3. Sachtler, J. W. A., and Somorjai, G. A., *J. Catal.* **81,** 77 (1983).
4. Alnot, M., Gorodetskii, V., Cassuto, A., and Ehrhardt, J. J., *Thin Solid Films* **151,** 251 (1987).
5. (a). Rodriguez, J. A., and Kuhn, M., *J. Chem. Phys.*, **102,** 4279 (1995); (b). Rodriguez, J. A., *Surf. Sci.* **318,** 253 (1994); (c) Rodriguez, J. A., and Kuhn, M., *Chem. Phys. Lett.* in press.
6. Godbey, D. J., Garin, F., and Somorjai, G. A., *J. Catal.* **117,** 144 (1989).
7. (a). Clarke, J. K. A., *Chem. Rev.* **75,** 291 (1975). (b). Sinfelt, J. H., Via, G. H., and Lytle, F. W., *Catal. Rev.-Sci. Eng.* **26,** 81 (1984).
8. Sinfelt, J. H., "Bimetallic Catalysts." Wiley, New York, 1983.
9. Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R., *Adv. Catal.* **31,** 135 (1982).
10. Kuhn, M., Rodriguez, J. A., and Hrbek, J., *Surf. Sci.* **314,** L897 (1994).
11. Kuhn, M., and Rodriguez, J. A., *Chem. Phys. Lett.* **231,** 199 (1994).
12. Kuhn, M., and Rodriguez, J. A., *J. Phys. Chem.* **98,** 12059 (1994).
13. Dean, J. A., "Lange's Handbook of Chemistry." 13th ed., pp. 9–21, 9–42, 9–50, 9–53 and 9–59. McGraw-Hill, New York, 1985.
14. Davies, P. W., Quinlan, M. A., and Somorjai, G. A., *Surf. Sci.* **121,** 290 (1982).
15. Paffett, M. T., Campbell, C. T., and Taylor, T. N., *Langmuir* **1,** 741 (1985).
16. (a). Härtel, T., Strüber, U., and Küppers, J., *Thin Solid Films* **229,** 163 (1993); (b). Strüber, U., and Küppers, J., *Surf. Sci.* **294,** L924 (1993).
17. Rodriguez, J. A., and Kuhn, M., *J. Phys. Chem.* **98,** 11251 (1994).
18. (a). Brune, H., Röder, H., Boragno, C., and Kern, K., *Phys. Rev. B* **49,** 2997 (1994); (b). Brune, H., Romainczyk, C., Röder, H., and Kern, K., *Nature* **369,** 469 (1994).
19. Feibelman, P. J., *Surf. Sci.* **313,** L801 (1994).
20. Heegemann, W., Meister, K. H., Bechtold, E., and Hayek, K., *Surf. Sci.* **49,** 161 (1975).
21. Hayek, K., Glassl, H., Gutmann, A., Leonhard, H., Prutton, M., Tear, S. P., and Welton-Cook, M. R., *Surf. Sci.* **152/153,** 419 (1985).
22. Billy, J., and Abon, M., *Surf. Sci.* **146,** L525 (1984).
23. Koestner, R. J., Salmeron, M., Kollin, E. B., and Gland, J. L., *Surf. Sci.* **172,** 668 (1986).
24. Williams, G. P., "Electron Binding Energies of the Elements." National Synchrotron Light Source, Brookhaven National Laboratory, Version II, January 1992.
25. Xu, G.-Q., and Hrbek, J., *Catal. Lett.* **2,** 35 (1989).
26. Dunphy, J. C., McIntyre, B. J., Gomez, J., Ogletree, D. F., Somorjai, G. A., and Salmeron, M. B., *J. Chem. Phys.* **100,** 6092 (1994).
27. Gutleben, H., and Bechtold, E., *Surf. Sci.* **191,** 157 (1987).
28. Kelemen, S. R., and Fischer, T. E., *Surf. Sci.* **87,** 53 (1979).
29. The new Ag-desorption peak appears at a temperature that is 90 K smaller than the corresponding one for Ag atoms bonded to clean Pt(111), and very similar to that of Ag multilayers (15). The difference between the desorption activation energies of the monolayer and multilayer states in Ag/Pt(111) is ~17 kJ/mol (15).
30. Kaushik, V. K., *J. Electron Spectrosc. Relat. Phenom.* **56,** 273 (1991).
31. Jaegermann, W., and Schmeisser, D., *Surf. Sci.* **165,** 143 (1986).
32. Schwaha, K., Spencer, N. D., and Lambert, R. M., *Surf. Sci.* **81,** 273 (1979).
33. The large decrease in the Ag 3*d* signal was not produced by desorption of silver. This type of phenomenon has been seen before in studies for metal overlayers (34), and is caused by the formation of 3D islands (cluster crystallites) of the admetal.
34. (a). Houston, J. E., Peden, C. H. F., Blair, D. S., and Goodman, D. W., *Surf. Sci.* **167,** 427 (1986); (b). Rodriguez, J. A., Campbell, R. A., and Goodman, D. W., *J. Phys. Chem.* **95,** 2477 (1991).
35. Feibelman, P. J., and Hamann, D. R., *Surf. Sci.* **149,** 48 (1985).
36. Knight, C. C., and Somorjai, G. A., *Surf. Sci.* **240,** 101 (1990).
37. The changes in Gibbs free energy (ΔG) for reactions (1) and (2) were calculated using values reported in ref. [13] for the Gibbs-free energy of formation of S_2, Pt, PtS and PtS_2 at 298.15 K.
38. Mezey, L. Z., and Giber, J. *Jpn. J. Appl. Phys.* **21,** 1569 (1982).
39. Kittel, C., "Introduction to Solid State Physics," 6th ed., p 55. Wiley, New York, 1986.
40. The heats of formation of PtS_2 (−108.9 kJ/mol (13)) and PtS (−81.6 kJ/mol (13)) are much larger than that of Ag_sS (−32.6 kJ/mol (13)).
41. Kuhn, M., and Rodriguez, J. A., *Catal. Lett.*, in press.