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The interaction of sulfur with Cu/Pt(111) and Zn/Pt(111) surfaces: copper-promoted sulfidation of platinum

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The interaction of sulfur with Pt(111), Zn/Pt(111) and Cu/Pt(111) has been examined using X-ray photoelectron spectroscopy (XPS), X-ray excited Auger electron spectroscopy (XAES), and thermal desorption mass spectroscopy (TDS). At temperatures between 300 and 600 K, the exposure of Pt(111) to S_2 gas produces a chemisorbed layer of sulfur *without* the formation of bulk sulfides. Exposure of S_2 to a Zn/Pt(111) alloy, at room temperature, results in a breakdown of the alloy and formation of a zinc-sulfide film on Pt(111). Further S_2 exposure at 550 K sulfidizes the remaining metallic zinc *without* affecting platinum. For the Cu/Pt(111) surface alloy, on the other hand, exposure to S_2 at 550 K leads to sulfidation of the platinum. Platinum can effectively compete for sulfur atoms bonded to copper but not for those bonded to zinc. The reaction of S_2 gas with Cu/Pt(111) surfaces produces copper sulfides that *promote* the sulfidation of Pt by providing surface sites for the dissociation of S_2, and by favoring the diffusion of S into the bulk of the system.

Keywords: S poisoning; Pt sulfidation; Cu/Pt and Zn/Pt catalysts

1. Introduction

Platinum is widely used in the petrochemical industry as a catalyst for the conversion of hydrocarbons [1,2]. It has been shown that the addition of a second metallic component can dramatically change the properties associated with a Pt catalyst [3–9]. For example, the addition of a noble metal modifies to a large extent the ability of Pt to isomerize alkanes [2,5,8].

One of the most serious problems that these bimetallic catalysts face is sulfur poisoning [10,11]. This work reflects an ongoing research program probing the effects of sulfur on the physical and chemical properties of bimetallic systems that contain platinum. Recently, we have discovered that the presence of silver on a Pt(111) surface promotes the formation of several layers of platinum sulfide [12], changing

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the chemical properties of the Pt atoms. The cause of this promotional effect is unclear at the present time. To explore if other admetals can induce the sulfidation of platinum, here we examine the interaction of sulfur with Zn/Pt(111) and Cu/Pt(111) surfaces. These bimetallic systems contain admetals that can form sulfides exhibiting a large range of thermal stabilities. Zinc forms very stable compounds with sulfur (ZnS, $\Delta H_f = -49$ kcal mol^{-1}). In contrast, compounds that contain copper and sulfur (CuS, $\Delta H_f = -13$ kcal mol^{-1}) are less stable than platinum sulfides (PtS, $\Delta H_f = -20$ kcal mol^{-1}).

Both zinc and copper interact strongly with the Pt(111) surface [13–16]. At room temperature both admetals adsorb as films on top of the Pt(111) surface. Upon annealing (> 500 K) they diffuse into the Pt(111) surface to form Zn–Pt and Cu–Pt alloys [13,14,16]. Zn desorbs at temperatures between 750 and 1050 K [16]. For Cu, on the other hand, no desorption is observed at temperatures as high as 1300 K. Sulfur also interacts strongly with the Pt(111) surface. For high coverages of sulfur ($\theta_S > 0.3$ ML) sharp desorption features are seen between 700 and 800 K [12]. Low coverages desorb as a broad band from 1000–1500 K [12]. At temperatures between 300 and 600 K, the exposure of Pt(111) to S_2 gas produces a chemisorbed layer of sulfur ($\theta_S \approx 1$ ML) without the formation of bulk sulfides [12].

2. Experimental

Experiments were carried out in an ultrahigh vacuum system (base pressure $\approx 4 \times 10^{-10}$ Torr) equipped with a quadrupole mass spectrometer for thermal desorption mass spectroscopy (TDS) and a hemispherical electron-energy analyzer with multichannel detection for photoemission and Auger studies. An unmonochromatized Mg Kα anode was used as the photon source. The sample was positioned with a take-off angle of 30°. Binding energies were calibrated using the Zn $2p_{1/2}$, Cu $2p_{3/2}$, and Pt $4f_{7/2}$ peaks of the pure metals, which were set at 1044.9, 932.5, and 71.2 eV, respectively [18].

The Pt(111) crystal was mounted on a manipulator capable of resistive heating to 1600 K and liquid nitrogen cooling to 80 K. Cleaning involved neon ion sputtering (2 kV and 20 mA emission) for 30 min followed by roasting in 5×10^{-8} Torr of oxygen at 800 K for 5 min. This was followed by a flash to 1300 K. Cleanliness was verified by the lack of a signal from sulfur, oxygen and carbon in the XPS spectrum.

Both Zn and Cu were deposited by resistively heating a W filament wrapped by a high purity wire of the respective metal. Coverage calibration of both Cu and Zn has been described elsewhere [13,14,16]. Coverages are reported with respect to the number of Pt surface atoms. Sulfur was vapor-deposited using a solid-state electrochemical cell: Pt/Ag/AgI/Ag_2S/Pt [17]. When a voltage is applied across the cell, sulfur evolves as S_n clusters (predominantly S_2) [17,19].

3. Results and discussion

3.1. ADSORPTION OF SULFUR ON PLATINUM ZINC SURFACES

We will first examine the results for sulfur adsorption on Zn/Pt(111) systems. We have dosed S_2 to two different types of Zn/Pt(111) systems; chemisorbed multilayers prepared by vapor deposition at 320 K, and zinc platinum alloys prepared by annealing a supported Zn multilayer to 550 K.

Fig. 1 shows the Zn $LM_{45}M_{45}$ XAES results (top) and Pt 4f XPS results (bottom) for S_2 exposure of a $Zn_{2.4}$/Pt(111) system. In fig. 1A, we note that upon S_2 exposure at 320 K, a new Auger feature emerges at about 3 eV lower kinetic energy as com-

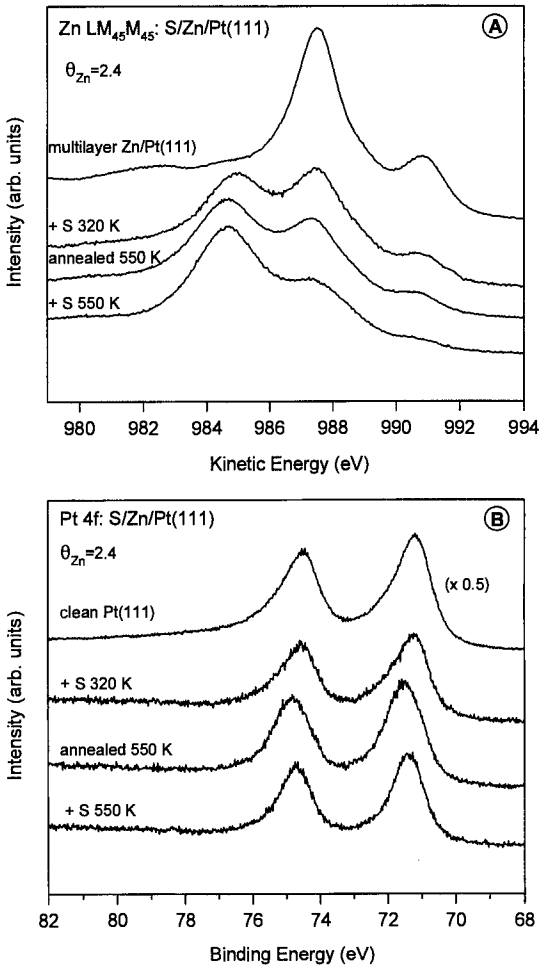

Fig. 1. Zn $LM_{45}M_{45}$ XAES (top) and Pt 4f XPS (bottom) spectra acquired after dosing S_2 to a Zn multilayer (θ_{Zn} = 2.4 ML) supported on Pt(111). The system was exposed to S_2 at 320 K, annealed to 550 K, and finally exposed again to S_2 at 550 K.

pared to that of the clean $Zn_{2.4}/Pt(111)$. This Auger feature shows the presence of zinc sulfide [20]. No change is observed in the Pt 4f core levels. After annealing to 550 K the zinc sulfide Auger feature grows with a continued shift to lower kinetic energy and the metallic zinc Auger feature is somewhat smaller. The Pt 4f core levels show a small shift ($\sim$ 0.2 eV) toward higher binding energy. This indicates that the metallic zinc, at the interface of the zinc-sulfide film and Pt(111) surface, has formed a zinc–platinum alloy [16]. Subsequent S_2 exposure at 550 K results in a further increase in the zinc-sulfide Auger signal at the expense of the metallic zinc with the Pt 4f core levels shifting back to lower binding energy. This indicates the breakdown of the zinc–platinum alloy and transformation of the metallic zinc into zinc sulfide.

In fig. 2 the Zn $LM_{45}M_{45}$ XAES results (top) and Pt 4f XPS results (bottom)

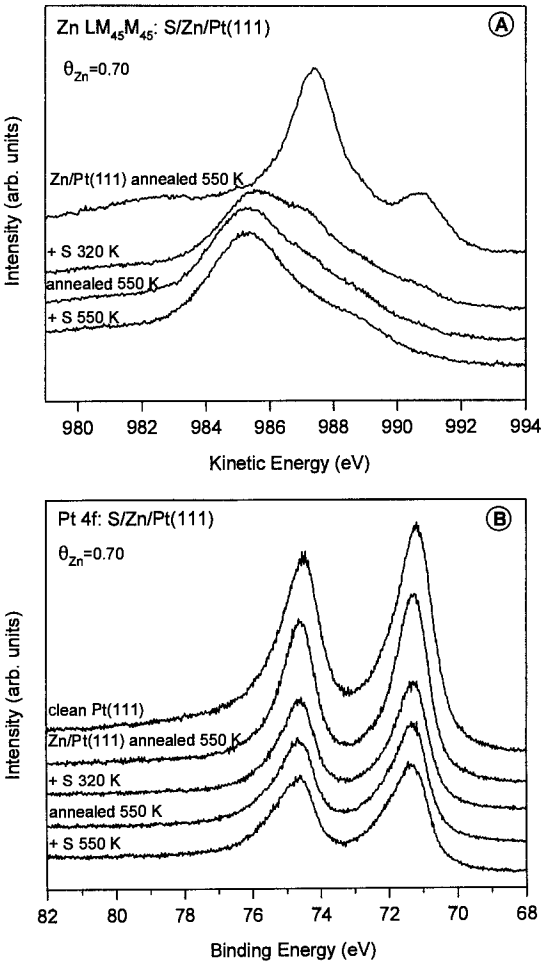

Fig. 2. Zn $LM_{45}M_{45}$ XAES (top) and Pt 4f XPS (bottom) results for a $Zn_{0.70}/Pt(111)$ alloy. Exposure to S_2 was carried out at 320 and 550 K.

are shown for S_2 exposure of a $Zn_{0.70}/Pt(111)$ surface alloy. (In this alloy, most of the zinc is in the surface layer and exhibits a Zn $2p_{1/2}$ binding energy that is $\sim$ 0.5 eV smaller than that of metallic Zn [16].) We see that, upon initial exposure to S_2 at 320 K, most of metallic zinc is transformed into zinc sulfide as shown by the distinctive zinc-sulfide Auger feature [20]. Annealing and subsequent S_2 exposure at 550 K results in an increase in the zinc-sulfide Auger feature and in the complete loss of the metallic zinc Auger feature. The remaining metallic zinc alloyed with platinum has been converted to zinc sulfide. The Pt 4f core levels (fig. 2B) show only a small shift ($\sim$ 0.05 eV) to higher binding energy as we compare the clean Pt(111) substrate with the Zn/Pt(111) alloy (spectra in the top of fig. 2B). This shift disappears after the adsorption of sulfur, and no extra features are observed that indicate the formation of bulk-like platinum sulfides [21].

Next, we will briefly examine the XPS results for the S 2p core levels in fig. 3A.

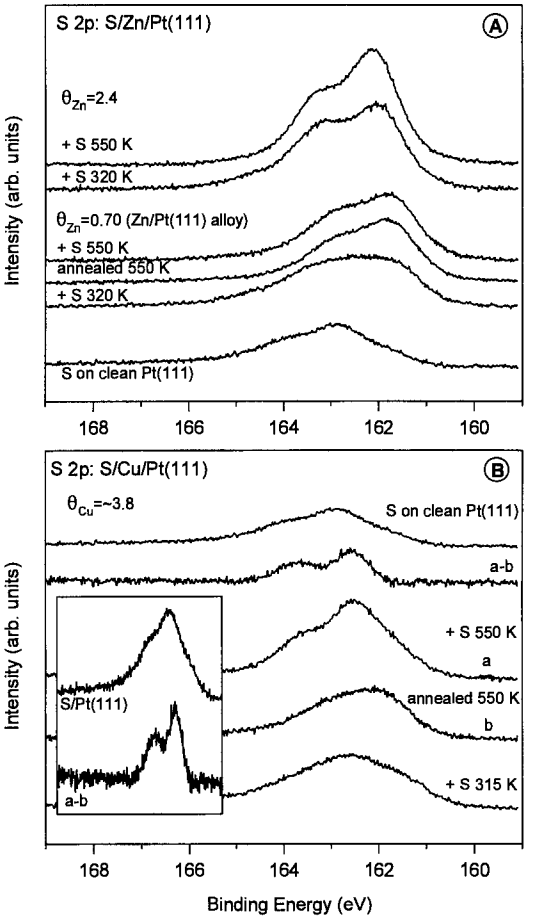

Fig. 3. S 2p XPS results for the S/Zn/Pt(111) systems described in figs. 1 and 2 (top) and exposure of S_2 to a chemisorbed $Cu_{3.8}/Pt(111)$ system (bottom). The inset compares a S/Pt(111) system with the difference spectra shown in the main graph as a–b.

A saturation coverage ($\theta_S \approx 1$) on Pt(111) is compared to the chemisorbed and alloyed zinc which had been exposed to S_2 at 320 and 550 K. In all cases, a shift of ~ 1.0 eV toward lower binding energy was experienced. The binding energy positions for the S $2p_{3/2}$ core level of the S/Zn/Pt systems correspond well to that measured for thick zinc-sulfide films supported on Ru(001) [20]. The S 2p intensity (area) is much higher than that for a saturated Pt(111) surface ($\theta_S \approx 1$ ML [12,17]) and it is clear from comparison of the chemisorbed and alloyed zinc that the greater the amount of available zinc the more sulfur that is adsorbed. The S signal around 161.5 eV increases as the Pt-bonded sulfur is converted to zinc sulfide (see data for the Zn/Pt(111) alloy system at 320 and 550 K).

In summary, we have observed that exposure of S_2 to either a chemisorbed or alloyed Zn/Pt(111) system leads to formation of zinc sulfide with a *breakdown* of any Zn/Pt(111) alloy and with no evident sulfidation of bulk platinum. Thermal desorption experiments for the ZnS_x/Pt(111) systems showed evolution of zinc and sulfur into the gas phase at temperatures between 700 and 950 K. At 950 K, only a small amount of sulfur ($\theta_S \approx 0.25$ ML) remained on the Pt(111) substrate. The temperature range in which the zinc sulfides of the ZnS_x/Pt(111) systems decomposed (750–950 K) is similar to that observed for the decomposition of zinc-sulfide films supported on Ru(001) [20].

3.2. ADSORPTION OF SULFUR ON PLATINUM COPPER SURFACES

Next we will examine the results for sulfur exposure to a Cu multilayer supported on Pt(111). Fig. 4 shows the Cu $2p_{3/2}$ XPS results (top) and Pt 4f XPS results (bottom) for a $Cu_{3.8}$/Pt(111) system which has been exposed to S_2, first at 315 K and subsequently at 550 K. In fig. 4A the Cu core levels shift to lower binding energy upon S_2 exposure and shift back upon annealing to 550 K. This indicates the formation of a Cu_xS film ($x \approx 1$) followed by transformation of this film into the more stable Cu_xS ($x \approx 2$) [22,24]. During this process the Pt core levels (fig. 4B) show the emergence of a new feature at ~ 0.9 eV higher binding energy which dominates the spectrum after exposure of S_2 at 550 K. The alloying of Pt and Cu induces a maximum shift of only +0.4 eV in the Pt $4f_{7/2}$ core level [23], and therefore we assign the new peak to be due to emission from platinum sulfide [21] formed in the reaction: $CuS/Pt \rightarrow Cu_2S/PtS_x/Pt$.

From the behavior of the S 2p core levels (fig. 3B), we arrive at the same conclusions as those derived from the behavior of the Cu and Pt core levels. Upon S_2 exposure at 315 K (spectrum at the bottom of fig. 3B), the centroid of the S 2p features is shifted toward lower binding energy as compared to chemisorbed sulfur on Pt(111) (spectrum at the top of fig. 3B). After annealing to 550 K, the centroid is shifted to even lower binding energy, indicative of the initial formation of a "CuS" film which is transformed into the more stable "Cu_2S" film [22,24]. A similar centroid position and similar behavior of the S 2p core levels have been observed

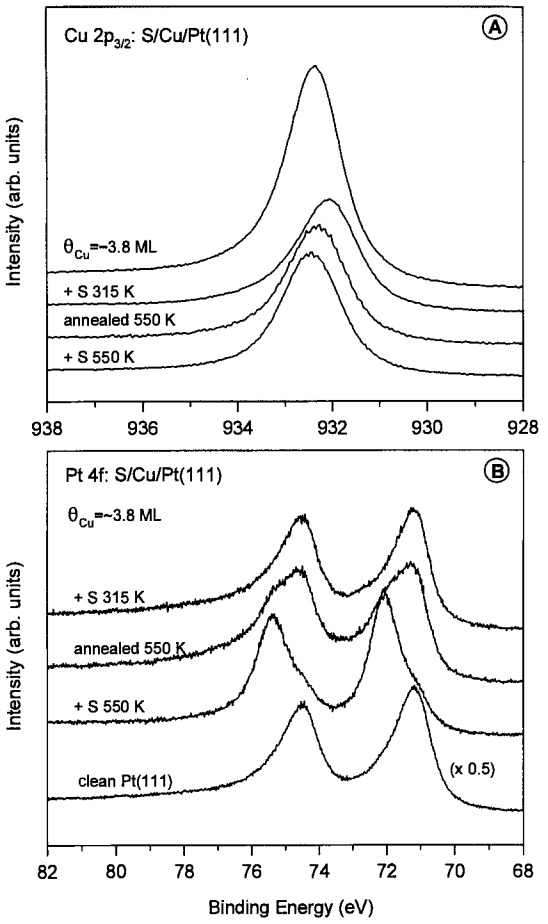

Fig. 4. Cu $2p_{3/2}$ (top) and Pt 4f (bottom) XPS spectra acquired after dosing S to a Cu multilayer (θ_{Cu} = 3.8 ML) supported on Pt(111). The system was exposed to S_2 at 315 K, annealed to 550 K, and finally exposed again to S_2 at 550 K.

for copper-sulfide films prepared on a Ru(001) substrate [24]. After S_2 exposure at 550 K, the centroid shifts to higher binding energy. Subtraction of the S 2p feature due to emission from "Cu_2S" (plot b in fig. 3B) from this feature (plot a in fig. 3B) distinctly reveals a single sulfur species (inset fig. 3B). The position exhibited by this sulfur species indicates that it cannot be due to emission from "Cu_2S" or "CuS" [22,24], and therefore must be due to increased formation of platinum sulfide. Since there is no attenuation present (a – b inset) in the region for emission from "Cu_2S", it is clear that the "Cu_2S" film is stable under these conditions. The system consists of a mixture of copper and platinum sulfides on top of metallic platinum.

Fig. 5 displays Pt 4f spectra acquired after exposing a Pt(111) surface with 0.41 ML of Cu to S_2 gas, first at room temperature and subsequently at 500 K. A

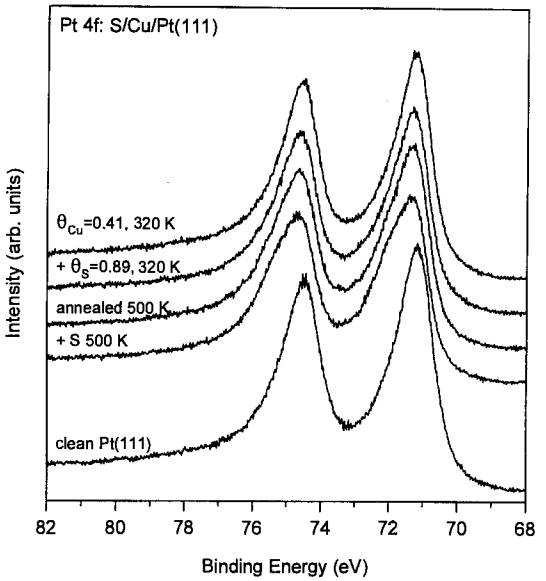

Fig. 5. Pt 4f spectra of submonolayer depositions of Cu and S on Pt(111). This system was annealed and further exposed to S_2 at 500 K.

significant broadening of the Pt 4f core levels (to the higher binding energy side) is evident after S_2 exposure at 500 K, indicating the formation of a platinum sulfide [21]. Annealing of a S/Pt(111) surface ($\theta_S \approx 1$ ML) to 600 K or exposure of Pt(111) to a similar dose of S_2 at 550 K did not produce an increase in the FWHM or position of the Pt 4f core levels [12]. Thus, it appears that the presence of copper *promotes* the formation of platinum sulfides. This phenomenon was observed after dosing S_2 gas to copper films supported on Pt or copper platinum alloys. The sulfides in the S/Cu/Pt systems decomposed at temperatures in the range between 600 and 800 K, producing S_2 gas, and chemisorbed sulfur on top of a copper platinum alloy.

In fig. 6 we compare Pt 4f spectra acquired after dosing the same amount of sulfur to clean Pt(111), three-dimensional Ag_xS clusters supported on Pt(111) [12], and alloys of platinum with copper or zinc. (The bimetallic systems contained the equivalent of 2.3, 3.8, and 2.4 monolayers of Ag, Cu, and Zn, respectively.) A dose of S_2 to a clean Pt(111) surface leads to a small broadening of the Pt 4f core levels with the extra emission occurring on the higher binding energy side. A similar S_2 exposure to systems containing silver or copper leads to bulk platinum-sulfide formation as indicated by the large Pt 4f feature located $\sim$ 0.9 eV toward higher binding energy. For the system containing zinc, on the other hand, no bulk sulfidation is detected. In this case, the Pt 4f core levels are actually narrower than that of clean Pt. This is a consequence of the fact that the surface contribution in clean platinum has been eliminated by the formation of the zinc-sulfide film and that there are no Pt–S bonds which would broaden the peak toward higher binding energy.

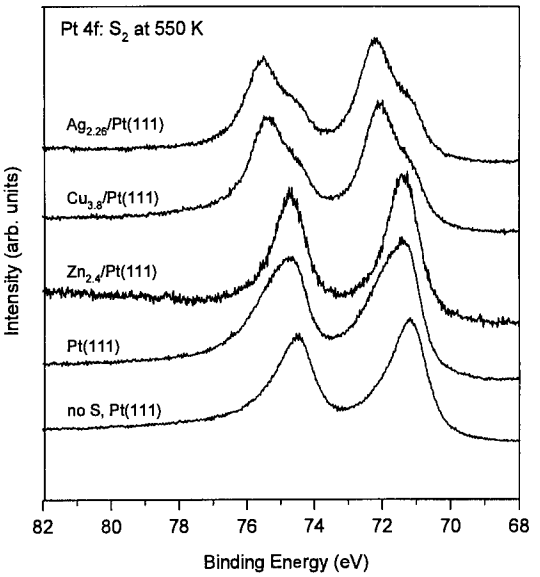

Fig. 6. Pt 4f XPS results comparing clean Pt(111) with a series of X/Pt(111) systems (X = Zn, Cu, and Ag) which have been exposed to S_2 at 550 K (see text).

The results in fig. 6 indicate that Cu and Ag increase the rate of formation of platinum sulfides, whereas Zn does not. When sulfur is adsorbed on a pure platinum surface, the large difference between the surface free energies of Pt (2.69 J m^{-2} [25]) and S (0.08 J m^{-2} [25]) prevents the migration of sulfur into the bulk of the sample, and only a layer of chemisorbed S is formed. The surface free energies of Cu (1.93 J m^{-2} [25]) and Ag (1.30 J m^{-2} [25]) are smaller than that of Pt. In principle, the presence of Cu or Ag in/on the surface frees sulfur for migration into the bulk of the sample. The Cu and Ag atoms provide surface sites on which S_2 can dissociate. Once sulfur is adsorbed on Cu or Ag, the large difference between the thermochemical stabilities of the S–noble metal and S–Pt bonds [26] favors migration of sulfur to form bulk-like platinum sulfides. Zn also has a smaller surface free energy (0.94 J m^{-2} [25]) than Pt, but the Zn–S bond is much stronger than the Pt–S bond [26], prohibiting the migration of sulfur from the surface into the bulk of Pt.

From the behavior observed for the S/Cu/Pt(111) and S/Ag/Pt(111) surfaces, one can expect that in bimetallic systems that contain Pt, the second metal will promote the formation of platinum sulfides if it has a surface free energy smaller than that of Pt *and* forms sulfides that are less stable than those formed by Pt. If one extrapolates these results, one can also expect that Cu and Ag would promote the sulfidation of metals that exhibit a cohesive energy (which makes the penetration of S an "uphill process") and an affinity toward sulfur (which makes the penetration of S a "downhill process") comparable to those of Pt. For example, this will apply to bimetallic catalysts that combine Cu or Ag and transition metals like Fe, Ni and Pd [26].

4. Summary and conclusions

Our results show that Cu increases the rate of formation of platinum sulfides, whereas Zn does not. At 300 K, exposure of sulfur to a chemisorbed Zn multilayer on Pt(111) or a Zn/Pt(111) alloy leads to formation of a zinc-sulfide film. Upon annealing, and further exposure to sulfur at elevated temperatures (450–600 K), no sulfidation of the platinum substrate is observed. Exposure of sulfur to a chemisorbed Cu multilayer on Pt(111) also leads to formation of a sulfide but with annealing and subsequent exposure to sulfur, at elevated temperatures, the copper sulfide promotes the sulfidation of the platinum substrate. This is analogous to the behavior observed for silver films on Pt(111) [12]. The order for the heats of formation is ZnS >> PtS > CuS > AgS [26], pointing out the fact that Pt can effectively compete for sulfur atoms bonded to both Cu and Ag but not for those bonded to Zn. In bimetallic catalysts that contain Pt, the relative stability of the sulfides dictates if the second metal will promote the rate of sulfidation of Pt.

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