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Citation: The Journal of Chemical Physics **108**, 3064 (1998); doi: 10.1063/1.475697 View online: http://dx.doi.org/10.1063/1.475697 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/108/7?ver=pdfcov Published by the AIP Publishing

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The adsorption of sulfur on Rh(111) and Cu/Rh(111) surfaces

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(Received 25 September 1997; accepted 10 November 1997)

The reaction of S_2 with Rh(111) and Cu/Rh(111) surfaces has been investigated using synchrotron-based high-resolution photoemission, thermal desorption mass spectroscopy and ab *initio* self-consistent-field calculations. At 100 K, the adsorption of S_2 on Rh(111) produces multilayers of S_n species (n=2-8) that desorb between 300 and 400 K, leaving a film of RhS_x on the sample. S₂ dissociates upon adsorption on clean Rh(111) at 300 K. An adsorption complex in which S_2 is bridge bonded to two adjacent Rh atoms (Rh–S–S–Rh) is probably the precursor state for the dissociation of the molecule. The larger the electron transfer from Rh(111) into the S₂($2\pi_a$) orbitals, the bigger the adsorption energy of the molecule and the easier the cleavage of the S-Sbond. On Rh(111) at 300 K, chemisorbed S is bonded to two dissimilar adsorption sites (hollow and probably bridge) that show well separated S 2p binding energies and different bonding interactions. Adsorption on bridge sites is observed only at S coverages above 0.5 ML, and precedes the formation of RhS_x films. The bonding of S to Rh(111) induces a substantial decrease in the density of d states that the metal exhibits near the Fermi level, but the electronic perturbations are not as large as those found for S/Pt(111) and S/Pd(111). Cu adatoms significantly enhance the rate of sulfidation of Rh(111) through indirect Cu \leftrightarrow Rh \leftrightarrow S₂ and direct Cu \leftrightarrow S–S \leftrightarrow Rh interactions. In the presence of Cu there is an increase in the thermal stability of sulfur on Rh(111). The adsorption of S_2 on Cu/Rh(111) surfaces produces CuS_y and RhS_x species that exhibit a distinctive band structure and decompose at temperatures between 900 and 1100 K: $CuS_v/RhS_r/Rh(111) \rightarrow S_2(gas)$ +Cu(gas)+S/Rh(111). © 1998 American Institute of Physics. [S0021-9606(98)00207-4]

I. INTRODUCTION

catalyzed oxidation of CO O_2 The by $(2CO+O_2\rightarrow 2CO_2)$ or NO $(2CO+2NO\rightarrow 2CO_2+N_2)$ is an important process in the pollution control of combustion products.¹⁻³ Currently, the removal of CO and NO from automobile exhaust is accomplished by catalytic converters which contain Rh, Pt, or Pd, or a combination of these metals.^{1,2} A relatively high activity and selectivity for NO reduction to N₂, coupled with the ability to withstand a harsh operating environment, make rhodium the crucial ingredient in the so-called three-way catalyst frequently used in automotive converters.² This type of catalyst is deactivated by sulfur-containing compounds that are present in all commercial gasoline.¹ Several studies document the inhibiting effect of sulfur on the NO_x reduction performance of rhodium.¹⁻³ In order to improve the sulfur tolerance of automotive catalysts, one must have a fundamental understanding of how sulfur interacts with Rh surfaces.¹

The interaction of S₂ with Rh(111) at 300 K has been previously studied using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and thermal desorption mass spectroscopy (TDS).⁴ At this temperature, the S₂ molecule dissociates on the surface, and the results of LEED show $(\sqrt{3} \times \sqrt{3})R30^\circ$ and $c(4 \times 2)$ superstructures when the S coverage is raised from 0.33 to 0.5 ML.⁴ At higher sulfur coverages, the formation of Rh₂S₃ probably occurs.⁴ In this article, we examine the electronic properties of a series of S₂/Rh(111) systems using synchrotron-based high-resolution photoemission spectroscopy. The adsorption and dissociation of the S₂ molecule are studied using *ab initio* self-consistentfield (SCF) calculations. Our results indicate that the bonding interactions between the S adatoms and Rh(111) substrate lead to a substantial decrease in the density of *d* states that the metal centers exhibit around the Fermi level, but these electronic perturbations are not as large as those found after depositing sulfur on the other two metals commonly used in automotive exhaust catalysts (Pt and Pd). Remarkable correlations are found when comparing the magnitude of the electronic and chemical perturbations that the metal surfaces display in S₂/Rh(111), S₂/Pt(111),⁵ and S₂/Pd(111).⁶

In addition, we examine the reaction of S₂ with Cu/ Rh(111). Cu/Rh catalysts are used for hydrocarbon reforming and are very sensitive to sulfur poisoning.^{7–9} For Cu/Rh surfaces, one finds large core-level shifts¹⁰ and changes in the CO-chemisorption properties of the metals^{10,11} as a product of strong Cu \leftrightarrow Rh interactions. Recent results of firstprinciples density functional calculations for the Cu/Rh(100) and Cu/Rh(111) systems show an important redistribution of charge around the Cu and Rh atoms.¹² Thus, the Cu/Rh(111) surface is ideal for studying how metal–metal bonding can affect the reactivity of rhodium toward sulfur.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Instrumentation

The experiments were performed at the U7A end station of the National Synchrotron Light Source (NSLS) at

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to TP: 216.165.95.75 On: Mon. 24 Nov 2014 01:01:42 Brookhaven National Laboratory. This beamline is equipped with a toroidal-spherical grating monochromator and an ultrahigh vacuum chamber (UHV) fitted with a hemispherical electron energy analyzer, a Mg $K\alpha$ x-ray source, and instrumentation for LEED and TDS. The valence and S 2*p* spectra were acquired using a photon energy of 240 eV. The binding energy scale in these spectra was calibrated by the position of the Fermi edge in the valence region. Unmonochromatized Mg $K\alpha$ radiation was used to take the Cu 2*p*_{3/2} and Rh 3*d* spectra.¹³

The Rh(111) crystal was mounted in a manipulator capable of resistive heating to \sim 1400 K and liquid nitrogen cooling to 80 K. Heating to 2000 K was achieved by electron bombardment from behind the sample. A W-5%Re/W-26%Re thermocouple was spot welded to the edge of the sample for temperature measurements. The Rh(111) surface was cleaned following procedures reported in the literature.^{10,11,13}

S2 gas was generated inside the UHV chamber by decomposing Ag₂S in a solid-state electrochemical cell: Pt/Ag/AgI/Ag₂S/Pt.^{13,14} After applying a voltage across the cell, sulfur evolved predominantly as S_2 with a minor "contamination" of S_n clusters.^{14(b)} 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 0.5 monolayer (ML) of S on Rh(111) $[c(4 \times 2)]$ LEED superstructure⁴]. Copper was vapor deposited from a resistively heated W filament wrapped with a high purity wire of the noble metal.^{10,11} The Cu coverages were determined mainly by TDS area analysis,^{10,11} and in some cases by the relative intensity of the Cu $2p_{3/2}$ core level $(\theta_{Cu} \le 1 \text{ ML})$. In this work, coverages are reported with respect to the number of Rh(111) surface atoms (1.6 $\times 10^{15}$ atoms cm⁻²). One S or Cu adatom per substrate surface atom corresponds to $\theta = 1$ ML.

B. Molecular orbital calculations

The interactions between S_2 and a series of Rh_n and CuRh_n clusters were investigated at the *ab initio* SCF level. The molecular orbital (MO) calculations were performed using the HONDO program.¹⁵ Since the systems under consideration contain a large number of heavy atoms, sulfur was the only element for which we included all its electrons in the calculations. The nonempirical effective core potentials of Hay and Wadt were used to describe the inner shells of Rh and Cu.¹⁶ The MO's were expanded using Gaussian-type orbitals (GTO's). The atomic orbitals of S were expressed in terms of a double-zeta quality basis set augmented with polarization functions: 15,17 12s, 8p, and 1d primitive GTO's contracted to 6s, 4p, and 1d (12s8p1d/6s4p1d). A basis set obtained through a (3s3p4d/2s1p2d) contraction scheme was used to describe the 5s, 5p, and 4d atomic orbitals of Rh.¹³ The 4s, 4p, and 3d atomic orbitals of Cu were expressed in terms of a $(3s_2p_5d/2s_1p_2d)$ basis set.¹⁸ Previous experience indicates that these basis sets provide satisfactory results for adsorption geometries. On the other hand, the energetics derived from these SCF calculations for adsorption reactions are not quantitative and simply provide



FIG. 1. S 2p and valence spectra collected after depositing a sulfur multilayer on Rh (111) at 100 and annealing to 400 K. In the bottom panel of the figure, for comparison, we also show the valence spectrum of clean Rh (111).

a guide for the interpretation of experimental results. The size of the basis set, the use of finite clusters, and the lack of electron correlation introduce uncertainty in the computed bonding energies.¹⁹ In spite of this limitation, the use of *ab initio* SCF methods with cluster models has proved to be a very useful approach for studying a large variety of surface phenomena.^{19,20}

III. RESULTS

A. Reaction of S₂ with Rh(111)

Previous studies have shown that at 100 K, S₂ reacts and forms multilayers of S_n species (n=2-8) on Mo(110), Ru(001), and Cu(111).²¹ The sulfur multilayers desorb from these metal surfaces at temperatures between 300 and 400 K.^{21,22} Figure 1 displays S 2p and valence spectra acquired after depositing a thick (>10 ML) sulfur film on Rh(111) at 100 K. The spectra are in excellent agreement with those reported for multilayers of S_n species.^{21,22} Heating to 400 K induces the desorption of the majority of the sulfur film, leaving a S 2p spectrum that is complex (at least two types of S present) and has an area approximately five times larger than that measured for 0.5 ML S/Rh(111). This S 2p spectrum can be assigned to a rhodium sulfide (RhS_x). At this point the valence region shows a line shape that is very different from that of clean Rh(111) (see bottom of Fig. 1). The most important change is a large drop in the density of states immediately below the Fermi level. The valence spectrum for RhS_x shows the most intense feature at a binding energy



FIG. 2. S₂-thermal desorption spectra for RhS_x/Rh(111), $\theta_s > 3$ ML, and S/Rh(111), $\theta_s = 0.5$ and 0.7 ML. Heating rate=5 K/s.

of ~2.5 eV, while on clean Rh(111) the maximum of the 4*d* band appears at ~0.7 eV. The RhS_x/Rh(111) system did not show any trace of a clear LEED pattern, which is consistent with a large change in the structure of the metal substrate and the formation of an amorphous film of RhS_x.

After heating $RhS_x/Rh(111)$ surfaces ($\theta_s > 1.5$ ML) to high temperature, we observed desorption of S₂ in a broad range of temperatures (500–1000 K). A typical TDS spectrum is shown in Fig. 2. Minor S₂ desorption features are seen between 500 and 800 K. At ~900 K, most of the RhS_x decomposes and there is a very intense S₂ desorption peak. After heating the RhS_x/Rh(111) systems to 1000 K, the results of photoemission showed sulfur coverages of 0.3–0.4 ML on the Rh substrate and S 2*p* line shapes that are typical of chemisorbed S (see below).

Figure 3 displays S 2p spectra taken after dosing S₂ to Rh(111) at 300 K to avoid the formation of S_n species and to induce the dissociation of S_2 .^{21,22} At coverages between 0.05 (spectrum "a" at the bottom) and 0.45 ML, only a single doublet of peaks is observed in the S 2p region. The separation between the two peaks is close to the expected $2p_{1/2}-2p_{3/2}$ spin-orbit splitting of 1.2 eV,^{5,23} with the binding energy for the peak positions increasing by $\sim 0.2 \text{ eV}$ when θ_s is raised. At these low coverages ($\theta_s < 0.5$ ML), S is adsorbed on the hollow sites of the Rh(111) surfaces²⁴ and there is no desorption of S₂ at temperatures below 900 K (Fig. 2 and Ref. 4). For $\theta_s > 0.5$ ML (spectra "d" and "e"), the complex line shape of the S 2p features indicates that more than one type of S species is present on the Rh(111)surface. Spectrum "e" can be fitted²⁵ in a reasonable way by a set of three doublets (see Fig. 4). The S $2p_{3/2}$ peak at ~163.2 eV probably indicates the presence of S_n species on the metal surface.^{21,22} Most of these species were transformed into atomic sulfur upon annealing to 400 K.

In Fig. 4, one sees a drastic change in the line shape of the S 2*p* spectra when heating the sulfur/Rh(111) surface from 300 to 500 or 700 K. At 500 K the sulfur coverage is close to 1 ML and the S 2*p* spectrum ("f") can be well fitted with a set of two doublets that exhibit a difference of ~0.95 eV in their S 2*p*_{3/2} binding energies. A similar result was observed for S/Pt(111)⁵ and S/W(100),²³ with the S



FIG. 3. S 2p spectra acquired after dosing S₂ to Rh(111) at 300 K and annealing to the indicated temperatures for 30 sec.

 $2p_{3/2}$ peaks corresponding to S adsorbed on hollow (peak at higher binding energy) and bridge sites (peak at lower binding energy) of the metal substrates. We propose an identical assignment for the S 2p features of the S/Rh(111) surface annealed to 500 K. As we will see below, this assignment is consistent with the negative charges found in MO calculations for S atoms adsorbed on Rh(111) (hollow<bridge). In Fig. 4, the S 2p spectrum at 700 K ("g") also represents the convolution of two doublets, but these components display binding energies and relative intensities that are very different from those of the two doublets that produce the spectrum at 500 K. The S $2p_{3/2}$ peak at 162.5 eV in spectrum "g" can be assigned to RhS_x , since it matches very well the main peak position observed for the sulfide in Fig. 1. This peak disappeared after heating the sample to 900 K $[RhS_x \rightarrow S_2 + S/Rh(111)]$. At this point ~0.5 ML of S remained on the Rh surface and the S 2p region displayed a single and well defined doublet (see top of Fig. 3).

The chemisorption of sulfur on Rh(111) did not produce significant changes in the peak position ($\Delta BE \leq 0.1 \text{ eV}$) or line shape of the Rh 3*d* core levels. Figure 5 shows valence spectra for a series of S/Rh(111) surfaces. The adsorption of sulfur induces a clear reduction in the density of states in the region between 0 and 2 eV. The deposition of 0.4 and 0.9 ML of S leads to decreases of 38% and 53%, respectively, in the intensity of the main Rh 4*d* feature. The surface with 0.9 ML of S exhibits a valence spectrum similar to that of RhS_x in Fig. 1, with the most intense feature around 2.5 eV.

The bonding interactions between Rh(111) and S or S_2 were investigated using *ab initio* SCF calculations. The top of Fig. 6 shows the 12-atom cluster used to model the metal surface. A S atom was set above one of the following ad-





FIG. 4. Results for the deconvolution of spectra "e", "f", and "g" from Fig. 3. The raw data are plotted using dots, whereas solid and dashed lines are used to plot the results of the curve fitting (Ref. 25). Two S 2p doublets are necessary for fitting spectra "g" and "f," whereas the fitting of spectrum "e" requires a set of three doublets.

sorption sites: the center of the face-centered-cubic (fcc) hollow site formed by the atoms labeled A and B (ABB), the middle of a bridge site between the A atom and one of the B atoms (AB), or atop atom A (A). In the bottom of Fig. 6 are displayed the adsorption configurations for S₂ on atop and bridge sites of the cluster. Strictly speaking, the S/Rh₁₂ and S₂/Rh₁₂ systems model adsorbate \leftrightarrow substrate interactions at the limit of low coverages of sulfur. In all the cases studied, the Rh–Rh separations were set equal to 2.69 Å as in bulk rhodium.²⁶ The S–Rh nearest-neighbor distances were optimized at the *ab initio* SCF level and the calculated values are listed in Tables I and II. The predicted values are within the range of S–Rh distances found in LEED studies for S/Rh surfaces (2.18–2.39 Å^{24,27}) and in x-ray diffraction studies for coordination complexes (2.23–2.40 Å²⁸).

We will examine first the theoretical results for the S/Rh₁₂ cluster. On the hollow ABB site, the adsorption energy of S was 6 and 10 kcal/mol larger than on the bridge AB and top A sites, respectively. For a $(\sqrt{3} \times \sqrt{3})R30^\circ$ – S/Rh(111) surface, a quantitative LEED analysis indicates that the S atoms are adsorbed on fcc hollow sites,²⁴ in agreement with the prediction of the SCF calculations. Table I shows calculated charges²⁹ and atomic orbital populations for different conformations of the S/Rh₁₂ cluster. Sulfur behaves as an electron acceptor when bonded to Rh(111): S^{\delta}, δ =0.3–0.4 e. This is consistent with the large

FIG. 5. Valence spectra acquired after depositing sub-monolayer coverages of sulfur on Rh(111) at 300 K. In the final step, the sample was annealed to 900 K.

difference between the electronegativities of Rh and S,³⁰ and with the increase observed in the work function of Rh(111)upon the adsorption of S.⁴ The results of first-principles density functional calculations for S on Rh(100) also show a net $Rh \rightarrow S$ charge transfer.³¹ In the S/Rh₁₂ system, the negative charge on the adatom is mainly a consequence of a $Rh(4d,5s) \rightarrow S(3p)$ electron transfer. On the hollow ABB site, the negative charge on S is smaller than on the bridge AB or atop A site. For hollow adsorption, the S adatoms are forced to make bonds through their occupied 3s and 3porbitals. This leads to a more covalent adsorption bond, in which part of the charge that is transferred from the surface into the vacant S(3p) orbitals is compensated by a charge transfer from the occupied S(3s,3p) orbitals into the empty bands of the Rh substrate. The trend in the theoretical calculations is consistent with the results of photoemission data where S atoms on bridge sites exhibit S 2p binding energies lower than those of S atoms on hollow sites.^{5,23} According to a simple electrostatic model,³² the larger the negative charge on a S adatom, the lower the binding energies of its core levels.

Now, we will focus our attention on the results for the S_2/Rh_{12} system in Table II. For the free S_2 molecule, the calculated S–S bond length (1.88 Å) agrees very well with the reported experimental value of 1.89 Å.³³ The adsorption of the molecule induced a substantial increase (0.10–0.23 Å) in the S–S separation. The ground ${}^{3}\Sigma_{g}^{-}$ state of S_2 arises from a $4\sigma_{g}^{2}4\sigma_{u}^{2}5\sigma_{g}^{2}2\pi_{u}^{4}2\pi_{g}^{2}$ electronic configuration. The $2\pi_{g}$ orbitals are only half occupied. The bonding mechanism of S_2 to Rh(111) involves a donation of charge from the S–S bonding $2\pi_{u}$ and $5\sigma_{g}$ orbitals into the surface, and back donation of electrons from the surface into the S–S antibond-





ABB site of the Rh_{12} cluster. Bottom: Geometries investigated for the absorption of S_2 on the Rh_{12} cluster. The S_2 molecule was adsorbed on top of the Rh atom labeled "A" (end-on and side-on orientations), on the short bridge site formed by the atoms labeled "B," and on the long bridge (or pseudohollow) site formed by the atoms labeled "A" and "C." We also studied the adsorption of two S atoms on the fcc hollow sites labeled "1."

ing $2\pi_g$ orbitals. The combination of these two phenomena leads to a substantial weakening and elongation of the S–S bond. Overall, S₂ acts as a net electron acceptor on Rh(111). The negative charges on the adsorbed molecule (0.1–0.2 e) are smaller than those found for S adatoms (0.3–0.4 e). This again is consistent with the results of photoemission, where the S 2*p* features of adsorbed S_n species appear at higher binding energy than the corresponding features for S adatoms (Figs. 1 and 4).

In Table II are listed calculated adsorption energies for S_2 on atop and bridge sites of Rh(111). In previous works we

TABLE I. $\ensuremath{\mathsf{S/Rh}}\xspace_{12}$ cluster: Atomic orbital populations and charges (electrons).

| | Rh-S bond | Rh (A) ^a populations | | | Sulfur |
|--------------|-----------|---------------------------------|--------|--------|--------|
| S on | (Å) | 4d | 5s, 5p | charge | charge |
| Hollow (ABB) | 2.27 | 7.88 | 1.05 | 0.07 | -0.28 |
| Bridge (AB) | 2.26 | 7.82 | 1.02 | 0.16 | -0.39 |
| A-top (A) | 2.22 | 7.78 | 0.91 | 0.31 | -0.43 |
| no S | | 7.92 | 1.11 | -0.03 | |

^aThe values listed are for the Rh atom labeled "A" in Fig. 6.

TABLE II. Adsorption of S₂ on Rh₁₂ and Cu/Rh₁₂.

| | Rh-S bond (Å) | S-S bond (Å) | Charge on S ₂ (e) | Adsorption energy (kcal/mol) ^a |
|-------------------------------------|------------------|-----------------|---------------------------------|--|
| Free S ₂ | | 1.88 | | |
| On Rh ₁₂ | | | | |
| End-on (A) | 2.31 | 1.98 | -0.13 | 18 |
| Side-on (A) | 2.37 | 2.01 | -0.14 | 21 |
| Bridge 1 (B,B) | 2.35 | 2.08 | -0.20 | 26 |
| Bridge 2 (A,C) | 2.38 | 2.11 | -0.19 | 27 |
| 2 S atoms (1,1) | 2.27 | | -0.62^{b} | 55 |
| On Cu/Rh ₁₂ ^c | | | | |
| 2 S atoms (1,1) | 2.28 | | -0.68^{b} | 59 |
| 2 S atoms (Cu,1) | 2.27 | | -0.63^{b} | 62 |

^aA positive value denotes an exothermic adsorption process. The adsorption energy was calculated using the S_2 molecule and the isolated cluster (Rh₂ or Cu/Rh₁₂) as reference state.

^bSum of the charge on the two S adatoms.

 $^{\rm c}{\rm The}$ Cu atom was adsorbed on the center of the ABB hollow site of the Rh_{12} cluster.

have found that the type of SCF approach used here typically predicts adsorption energies that are 35%-60% lower than the experimental values.^{17,34,36} This deficiency is in part a consequence of the lack of electron correlation in the calculations.¹⁹ When dealing with adsorption energies, we will pay more attention to qualitative trends than to quantitative results. On the Rh₁₂ cluster, the S₂ molecule is more stable when both S atoms are simultaneously bonded to the metal substrate. The larger the charge transfer from Rh into the $S_2(2\pi_a)$ orbital, the bigger the adsorption energy and the elongation of the S-S bond. Bonding configurations in which S₂ bridges two rhodium atoms ("bridge 1" and "bridge 2" in Fig. 6) are probable precursors for the dissociation of the molecule. In the SCF calculations, we found that two separate sulfur adatoms were much more stable on the Rh₁₂ cluster than S₂ bonded in end-on, side-on, or bridge conformations. Therefore, it is not surprising that S₂ dissociates when adsorbed on clean Rh(111).

B. $\textbf{Cu}{\leftrightarrow}\textbf{S}$ interactions and the formation of copper sulfides

Before studying the reaction of S₂ with Cu/Rh(111) surfaces, we will examine how sulfur interacts with copper. Figure 7 shows S 2*p* and valence spectra acquired after depositing Cu on a thick (>10 ML) sulfur film at 100 K, followed by annealing to 400 and 750 K. Initially, the deposition of Cu induces the appearance of an "extra" feature around 162.5 eV in the S 2*p* region. This feature grows in intensity when the Cu coverage increases and becomes dominant upon annealing to 400 K for inducing the desorption of the pure (or unreacted) sulfur. At this point the S 2*p* spectrum shows a line shape that is characteristic of CuS_x (0.6 < x < 1).³⁷ Further annealing to 750 K produces the desorption of part of the sulfur, leaving a S 2*p* spectrum identical to that expected for Cu₂S.³⁷

For the Cu/S_n systems at 100 K, one sees Cu 3d bands that are very narrow when compared to the 3d band of pure metallic Cu. Thus, it appears that the Cu(3d) \leftrightarrow S(3s,3p) interactions are significantly weaker than the Cu(3d)

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FIG. 7. S 2p (left panel) and valence (right panel) spectra for the deposition of Cu on a sulfur multilayer (>20 Å) at 100 K and subsequent annealing to 400 and 750 K for 30 sec. In the bottom of the right panel, for comparison, we show the valence spectrum of metallic Cu.

 \leftrightarrow Cu(3*d*) interactions. The valence spectra at 400 and 750 K exhibit 3*d* bands centered at more than 3 eV below the Fermi level. At 2.5 eV, where metallic Cu shows its maximum 3*d* intensity, one finds relatively weak electron emissions in the spectra for CuS_x and Cu₂S. Sulfur shifts the *d* band of the metal away from the Fermi level, as happened in the case of S/Rh(111). The results in Fig. 7 indicate that Cu₂S has very distinctive features in the S 2*p* and valence regions.

C. Reaction of S₂ with Cu/Rh(111) surfaces

LEED, x-ray photoelectron spectroscopy (XPS), and TDS have been employed to examine the interaction of Cu with Rh(111).³⁸ The first Cu monolayer is pseudomorphic to the Rh substrate. This behavior is identical to that found for Cu/Rh(100),¹¹ Cu/Ru(001),³⁹ and Cu/Mo(110).⁴⁰ Cu atoms bonded to Rh(111) have Cu $2p_{3/2}$ binding energies that are ~0.5 eV lower than that of bulk Cu.³⁸ A similar result has been reported for the Cu/Rh(100) system.¹⁰ The results of first-principles density functional calculations for the Cu/ Rh(111) and Cu/Rh(100) systems show an important redistribution of charge around the Cu and Rh atoms.¹² Previous studies have shown that these electronic perturbations can affect the chemical properties of the metals.^{10,11,41}

Figure 8 compares the sulfur uptakes at 300 K of Rh(111), Cu/Rh(111) surfaces with admetal coverages of 0.4 and 0.8 ML, and a Cu multilayer. The reactivity of these systems toward sulfur increases in the following sequence: Rh(111)<Cu/Rh(111)<Cu multilayer. Three factors contribute to the large sulfur uptake of the Cu multilayer: (1) the roughness of the surface favors dissociation of S₂; (2) the relative low cohesive energy of Cu²⁶ facilitates the penetration of sulfur into the "bulk" of the sample; and (3) the thermodynamic stability of copper sulfides.⁴² Rhodium also

forms stable sulfides, but the smoothness of the Rh(111) face and its relatively large cohesive energy²⁶ make the sulfidation of this system difficult.

When Rh(111) is "promoted" with 0.4 and 0.8 ML of Cu, there is a large increase in the rate of sulfur adsorption. For example, the surface with 0.4 ML of Cu reaches a S



FIG. 8. Variation of the S(2p)-integrated signal with S_2 exposure for Rh(111) (\bullet), Cu_{0.4}/Rh(111) (\blacksquare), Cu_{0.8}/Rh(111) (\blacktriangle), and a Cu film (∇). S₂ was dosed at 300 K.



FIG. 9. S 2p (left panel) and valence (right panel) spectra for the deposition of sulfur on a Cu/Rh(111) surface ($\theta_{Cu}=0.8$ ML) at 300 K. In the final step, the S₂/Cu/Rh(111) system was annealed to 500 K.

coverage of 1 ML almost twice as soon as pure Rh(111). And the sulfur uptake is even faster in the case of $Cu_{0.8}/Rh(111)$. In principle, the enhancement in the rate of sulfur adsorption could be a consequence of the following phenomena: (1) an increase in surface roughness due to the presence of Cu adatoms; (2) direct Cu-S bonding; and (3) an increase in the reactivity of rhodium toward sulfur as a result of the electronic perturbations associated with the Cu-Rh bond.¹⁰⁻¹² The increase in the roughness of the surface may not be a dominant factor, because the Cu_{0.8}/Rh(111) surface (which should not be very rough due to pseudomorphic growth of the admetal³⁸) adsorbs sulfur much faster than the $Cu_{0.4}/Rh(111)$ surface (which contains a medium-sized coverage of the admetal and should be very rough). Direct Cu-S bonding has a clear and important effect on the enhancement of the rate of sulfur adsorption, but after reaching S coverages that are enough to saturate the Cu adatoms $[\theta_s]$ = 0.4 ML in Cu_{0.4}/Rh(111), 0.8 ML in Cu_{0.8}/Rh(111)], one still finds rates in the sulfur uptake that are significantly larger than those seen on clean Rh(111). Thus, it appears that the Cu adatoms increase the reactivity of rhodium toward sulfur. This conclusion is also supported by the results of theoretical calculations. In Table II, the energy liberated by the dissociation of S₂ on two Rh sites of a Cu/Rh₁₂ cluster (hollow sites labeled "1" in Fig. 6) is 4 kcal/mol larger than the energy released by the dissociation of the molecule on the same sites of a pure Rh₂ cluster. Furthermore, for the dissociation of S2 on Cu/Rh12 with one S bonded to the Cu atom and the other on a hollow "1" site of the Rh substrate, one finds a dissociation energy that is 7-9 kcal/mol more exothermic than those found on adsorption sites of Rh₁₂. Thus, Cu facilitates the sulfidation of Rh through indirect $Cu \leftrightarrow Rh \leftrightarrow S_2$ and direct $Cu \leftrightarrow S-S \leftrightarrow Rh$ interactions.

Figure 9 shows S 2*p* and valence spectra collected after dosing S₂ to a $Cu_{0.8}/Rh(111)$ surface at 300 K. Spectra "a" correspond to the deposition of 0.45 ML of S on the bime-

tallic system. At this point, the S 2p region shows a well defined doublet of peaks with binding energies that match those of Cu₂S (Fig. 7) and S/Rh(111) (Fig. 3). The corresponding valence spectrum displays a substantial attenuation of the Cu 3d signal around 3.5 eV and the Rh 4d signal near the Fermi level. Thus, at this relatively low θ_s , sulfur is bonded to copper and rhodium sites of the surface (i.e., no preferential bonding to Cu). When the S coverage is raised, new features appear in the S 2p region (165–163 eV), and in the valence spectra there is a narrowing of the Cu 3d band (indicative of the formation of copper sulfides, see Fig. 7) and a large reduction in the Rh 4d signal immediately below the Fermi level. This is the dominant characteristic of spectrum "e" ($\theta_s \approx 2.5$ ML). At this point, the system under study probably contains adsorbed S_n species, plus CuS_x and RhS_x . Upon annealing to 500 K, there is a large decrease in the S 2p signal as a result of sulfur desorption. Only 1.3 ML of S are left on the surface and the valence spectrum exhibits a Cu 3d band with a line shape and centroid position very similar to those of Cu_2S (Fig. 7). At the same time, the Rh 4d features near the Fermi level and the S 2p spectrum show line shapes typical of RhS_x (Fig. 1).

Figure 10 displays S₂- and Cu-TDS spectra for two different CuS_y/RhS_x/Rh(111) systems. The spectra in the top panel were acquired after dosing S₂ ($\theta_s = 1.6$ ML) to a Cu_{1.2}/Rh(111) surface at 300 K. The spectra in the bottom panel were taken after depositing 1.1 ML of Cu on a S_{0.9}/Rh(111) surface at room temperature. Upon heating these systems to 1200 K, only a small amount of S (0.2–0.3 ML) remained on the Rh(111) crystal. For a pure S_{0.9}/Rh(111) surface one can expect a strong S₂ desorption peak at ~900 K (see Fig. 2). In contrast, the Cu_{1.1}/S_{0.9}/Rh(111) system shows the main S₂ desorption feature above 1000 K. Thus, the presence of Cu increases the thermal stability of sulfur on the surface. The S_{1.6}/Cu_{1.2}/Rh(111) system shows weak S₂ desorption peaks



FIG. 10. Cu- and S_2 -TDS spectra for $S_{1.6}/Cu_{1.2}/Rh(111)$ and $Cu_{1.1}/S_{0.9}/Rh(111)$ surfaces. Copper and sulfur were deposited on Rh(111) at 300 K. Heating rate=5 K/s.

between 400 and 500 K and strong peaks from 900 to 1100 K. The main S₂ desorption peak appears at ~1050 K, whereas in $RhS_x/Rh(111)$ most of the sulfur desorbs around 900 K (Fig. 2). Again, copper raises the thermal stability of sulfur on the surface.

In Fig. 10 the most intense S₂ desorption peaks occur immediately before the desorption of Cu. Copper evolves into gas phase at temperatures between 1000 and 1100 K. TDS data for Cu/Rh(111) show desorption of the Cu monolayer at \sim 1240 K, with the onset for desorption of the multilayer appearing around 1020 K (top of Fig. 11). The sulfur adatoms induce a significant weakening in the strength of the Rh-Cu bonds. Figure 11 shows Cu-TDS spectra collected after depositing Cu on $S_{0.2}/Rh(111)$, center panel, and $S_{0.5}/Rh(111)$, bottom panel, at 300 K. For Cu/ $S_{0.2}/Rh(111)$, there was no desorption of sulfur at temperatures below 1300 K. In the case of $Cu/S_{0.5}/Rh(111)$, sulfur desorbed at temperatures above 950 K, and in each TDS experiment a "fresh" $S_{0.5}/Rh(111)$ surface was prepared before depositing Cu at room temperature. In these Cu/S/Rh(111) systems, bonding between the admetal and sulfur can occur at low temperature, but the Cu-S bonds break at high temperature, producing S and Cu adatoms that compete for making bonds with the Rh substrate. This leads to lower Cu desorption temperatures than seen for Cu atoms bonded to clean Rh(111). The Cu/S_{0.5}/Rh(111) surfaces are particularly interesting since Cu desorbs at temperatures that are close to those of Cu multilayers in Cu/Rh(111). In these cases, however, the line shape of the Cu desorption that peaks at $\theta_{Cu} < 1$ ML is different from that expected for zero-order desorption kinetics, indicating that the Cu atoms were "wetting" the S/Rh(111) surface when the desorption process started. From the decreases in Cu desorption temperature observed in Fig. 11 (70–150 K), one can estimate⁴³ that sulfur induces a reduction of 5-10 kcal/mol in the adsorption energy of copper.



FIG. 11. Cu-thermal desorption spectra for Cu/Rh(111), top, $Cu/S_{0.9}/Rh(111)$, center, and $Cu/S_{0.5}/Rh(111)$, bottom. Cu was vapor deposited on the Rh(111) and S/Rh(111) surfaces at 300 K. Heating rate=5 K/s.

IV. DISCUSSION

A. Interaction of sulfur with Rh(111)

The photoemission results in Sec. III A show that sulfur induces a substantial reduction in the density of states (DOS) of Rh(111) near the Fermi level. A similar trend is observed in photoemission data for S/Pt(111),⁵ S/Pd(111),⁶ and S/W(100).²³ For the S/Rh(100) system, first-principles density functional calculations predict that S-bonded Rh atoms will have a limited contribution to the DOS around the Fermi level of the system.³¹ This prediction is consistent with experimental results for the decomposition of H₂S on Rh(100).⁴⁴

It is worthwhile to examine in detail how sulfur affects the bands of the three metals most frequently used in automotive exhaust catalysts (Rh, Pt, and Pd).^{1,2} The top panel in Fig. 12 compares the decreases induced by sulfur on the intensity of the metal *d* features that appear 0–1 eV immediately below the Fermi level in S_{0.4}/Rh(111), S_{0.3}/Pt(111),⁵ and S_{0.3}/Pd(111).⁶ In a S_{0.4}/Rh(111) surface, sulfur produces a reduction of ~25% in the DOS near the Fermi level (Fig. 5), whereas in S_{0.3}/Pd(111) the corresponding reduction is as large as 58%.⁶

The results of *ab initio* SCF calculations indicate that sulfur also produces decreases in the valence *d* populations of the metals (Table I and Refs. 5 and 6) as a result of metal \rightarrow S charge transfers and a rehybridization of the *d* and *s*, *p* orbitals in the metals. The bottom panel in Fig. 12 compares the *d*-population reduction calculated for an A



FIG. 12. Top panel: Results of photoemission (PE) measurements for $S_{0.4}/Rh(111)$, $S_{0.3}/Pt(111)$ (Ref. 5), and $S_{0.3}/Pd(111)$ (Ref. 6). The graph displays the percentage decrease induced by sulfur on the intensity of the main peak (located at 0–1 eV below the Fermi edge) in the Rh 4*d*, Pt 5*d*, and Pd 4*d* bands. Bottom panel: Results of *ab initio* SCF calculations for S/Rh₁₂ (Table I), S/Pt₁₂ (Refs. 5 and 6), and S/Pd₁₂ (Ref. 6) clusters. The graph shows the reduction in the valence *d* population of the A atom in Fig. 6 upon the adsorption of S on atop (empty bars) and hollow ABB (hatched bars) sites.

atom (see Fig. 6) in S/Rh₁₂ (Table I), S/Pt₁₂,^{5,6} and S/Pd₁₂⁶ when the sulfur is above the A atom or on the hollow ABB site. In the S/M₁₂ clusters, the tendency of a metal to lose *d* electrons increases in the following order: Rh<Pt<Pd. This sequence agrees well with the relative occupancy of the *d* shell in the isolated elements: Rh, d^8s^1 <Pt, d^9s^1 <Pd, $d^{10}s^{0.45}$ L_{2,3}-edge XANES (x-ray absorption near-edge structure) measurements for a large series of bulk compounds have shown that Pd exhibits a bigger tendency to lose *d* electrons than Pt.⁴⁶ By comparing the trends in Fig. 12, a clear correlation is seen between the change in the *d* population of a metal and the attenuation in its DOS near the Fermi level. Pd shows the biggest drop in the *d* population and the largest attenuation in the DOS. On the other hand, Rh exhibits the weakest electronic perturbations.

The modifications induced by sulfur on the *d* bands of Rh, Pt, and Pd introduce the possibility for new and unique chemical properties. In general, one can expect a decrease in the activity of the metals for adsorption reactions that involve donation of electrons to the adsorbate. It is well established now that sulfur inhibits the chemisorption of CO and the dissociation of NO on metal surfaces.^{44,47–51} The electronic perturbations shown in Fig. 12 indicate that Pd should be more affected by sulfur than Rh. Indeed, automotive ex-

haust catalysts based on Pd are more sensitive to sulfur poisoning than catalysts based on Rh.¹

Many industrial catalysts consist of Rh particles dispersed on an alumina support.^{1,2,7,8} In a previous work, we found that alumina surfaces are not very reactive toward sulfur.¹⁷ When comparing the sulfur uptake for Rh(111) in Fig. 8 with that previously reported for alumina,¹⁷ one finds that the sticking coefficient of sulfur on the metal at 300 K is almost one order of magnitude larger than on the oxide. For example, a 10 min dose of S₂ produces a sulfur coverage \sim 0.08 ML on alumina,¹⁷ whereas on Rh(111) the sulfur coverage is close to 1.1 ML (Fig. 8). In the S₂/Al₂O₃ system, there is an energy mismatch between the orbitals of the molecule and the bands of the oxide, and the reactivity of S₂ on pure alumina is very low.¹⁷ For Rh/Al₂O₃ surfaces, the Rh adatoms provide a large number of electronic levels that can be very efficient for interactions with sulfur (Sec. III A). Thus, on Rh/Al₂O₃ catalysts, sulfur should attack mainly the supported metal.

B. Interaction of sulfur with Cu/Rh(111) surfaces

The results in Sec. III B indicate that copper promotes $Rh \leftrightarrow S$ interactions. To the best of our knowledge, this is the first time that it has been shown that a second metal can enhance the rate of sulfidation of rhodium. In our previous study for the coadsorption of gold and sulfur on Rh(111),¹³ we saw no evidence for an increase in the strength of the interactions between Rh and S. Instead, gold reduced the adsorption energy of sulfur on Rh(111).¹³ By adding a noble metal like Cu or Au to a Rh reforming catalyst, one can the activity of the catalyst for C-C control hydrogenolysis.^{3,7–9} These Cu/Rh and Au/Rh catalysts show a behavior that is similar in many aspects.^{3,7-9} However, Au is probably a better choice than Cu when trying to minimize the sensitivity of the Rh reforming catalyst toward sulfur poisoning.

When comparing the results for the $S_2/Cu/Rh(111)$ surfaces with those previously reported for $S_2/Cu/Mo(110)^{52}$ and $S_2/Cu/Pt(111)$,⁵³ one finds that in all these systems copper promotes the sulfidation of the metal substrate. This seems to be a general property of copper, since the phenomenon has been observed on late and early transition-metal substrates, and with elements in which the strength of the metal-sulfur bond varies widely.^{42,54} For the Cu/Mo(110) and Cu/Rh(111) systems, the results of first-principles density functional calculations show that the admetal induces a substantial modification in the spatial distribution of electrons around the Mo and Rh atoms.12 These electronic changes probably lead to stronger $Mo \leftrightarrow S_2$ and $Rh \leftrightarrow S_2$ interactions. In the case of S₂/Cu/Rh(111), the ab initio SCF calculations in Sec. III C indicate that Cu also facilitates the sulfidation of Rh through direct $Cu \leftrightarrow S - S \leftrightarrow Rh$ interactions.

V. CONCLUSIONS

The dosing of S_2 to Rh(111) at 100 K produces multilayers of S_n species (n=2-8) that desorb between 300 and 400 K, leaving a film of RhS_x on the sample. Most of the RhS_x decomposes around 900 K. S₂ dissociates upon adsorption on clean Rh(111) at 300 K. An adsorption complex in which S₂ is bridge bonded to two adjacent Rh atoms (Rh-S-S-Rh) is probably the precursor state for the dissociation of the molecule. The larger the electron transfer from Rh(111) into the S₂($2\pi_{g}$) orbitals, the bigger the adsorption energy of the molecule and the easier the cleavage of the S-S bond. On Rh(111) at 300 K, chemisorbed S is bonded to two dissimilar adsorption sites (hollow and probably bridge) that show well separated S 2p binding energies and different bonding interactions. At S coverages below 0.5 ML, S is adsorbed only on hollow sites and desorbs from the surface as S₂ in a broad feature at temperatures above 900 K. At S coverages larger than 0.5 ML, bridge-bonded S appears on the surface and, at the same time, a new and sharp S₂ desorption peak is observed at ~ 900 K. The bonding interactions between S and Rh(111) induce a substantial decrease in the density of d states that the metal exhibits near the Fermi level, but the electronic perturbations are not as large as those found for S/Pt(111) and S/Pd(111).

Cu adatoms significantly enhance the rate of sulfidation of Rh(111) through indirect $Cu \leftrightarrow Rh \leftrightarrow S_2$ and direct $Cu \leftrightarrow S-S \leftrightarrow Rh$ interactions. In the presence of Cu there is an increase in the thermal stability of sulfur on Rh(111). At 300 K, the reaction of S₂ with Cu/Rh(111) surface produces CuS_y (0.5 < y < 1) and RhS_x species. The CuS_y transforms into Cu₂S upon annealing to 500 K, with S₂ evolving into gas phase. At this point, the mixed metal sulfides exhibit a distinctive band structure with a relatively weak density of states near the Fermi level. The Cu₂S/RhS_x/Rh(111) systems decompose at temperatures between 900 and 1100 K: Cu₂S/RhS_x/Rh(111) \rightarrow S₂(gas)+Cu(gas)+S/Rh(111).

ACKNOWLEDGMENTS

This work was carried out at Brookhaven National Laboratory and supported by the U.S. Department of Energy (Contract No. DE-AC02-76CH00016), Office of Basic Energy Sciences, Chemical Science Division. The NSLS is supported by the divisions of Materials and Chemical Sciences of the U.S. Department of Energy.

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