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H₂S adsorption on chromium, chromia, and gold/chromia surfaces: Photoemission studies

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The reaction of H₂S with chromium, chromia, and Au/chromia films grown on a Pt(111) crystal has been investigated using synchrotron-based high-resolution photoemission spectroscopy. At 300 K, H₂S completely decomposes on polycrystalline chromium producing a chemisorbed layer of S that attenuates the Cr 3d valence features. No evidence was found for the formation of CrS₄ species. The dissociation of H₂S on CrₓOᵧ and Cr₂O₃ films at room temperature produces a decrease of 0.3–0.8 eV in the work function of the surface and significant binding-energy shifts (0.2–0.6 eV) in the Cr 3p core levels and Cr 3d features in the valence region. The rate of dissociation of H₂S increases following the sequence: CrₓOᵧ<Cr₂O₃<Cr. For chromium, the density of states near the Fermi level is large, and these states offer a better match in energy for electron acceptor or donor interactions with the frontier orbitals of H₂S than the valence and conduction bands of the chromium oxides. This leads to a large dissociation probability for H₂S on the metal, and a low dissociation probability for the molecule on the oxides. In the case of CrₓOᵧ and Cr₂O₃, there is a correlation between the size of the band gap in the oxide and its reactivity toward H₂S. The uptake of sulfur by the oxides significantly increases when they are “promoted” with gold. The Au/Cr₂O₃ surfaces exhibit a unique electronic structure in the valence region and a larger ability to dissociate H₂S than polycrystalline Au or pure Cr₂O₃. The results of ab initio SCF calculations for the adsorption of H₂S on AuCrₓOᵧ and AuCr₁₀O₁₅ clusters show a shift of electrons from the gold toward the oxide unit that enhances the strength of the Au(6s)→H₂S(5a₁,2b₁) bonding interactions and facilitates the decomposition of the molecule. © 1997 American Institute of Physics.

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I. INTRODUCTION

One of the most severe poisonings encountered in catalytic systems is that induced by sulfur on metal/oxide catalysts.¹ In industrial applications the life time of a supported metal catalyst can be reduced to only a few months or weeks in the presence of ppm quantities of sulfur contaminants in petroleum-derived feedstreams.¹ Millions of dollars are lost every year in the chemical and oil industries due to the effects of sulfur poisoning on the performance of metal/oxide catalysts.¹ In spite of the importance of this problem, a detailed knowledge of the factors that control the mechanisms of sulfur poisoning at a microscopic level does not exist.¹ This type of fundamental knowledge can provide novel ideas for improving the sulfur tolerance of industrial catalysts.

Model systems generated by vapor depositing a metal onto ultrathin oxide films have recently emerged as a promising way to investigate the behavior of supported metal catalysts.²⁻⁸ These model systems feature many of the advantages of metal single crystals (i.e., they can be characterized by means of surface sensitive techniques where either electrons or ions are used) while still addressing important issues such as the effects of particle size and metal-support interactions.⁵ Exploiting the utility of this approach, we have started a research program aimed at gaining a better understanding of the effects of sulfur on the physical and chemical properties of metal/oxide surfaces.⁹⁻¹¹ In our previous works we have examined the interaction of sulfur with metal/alumina surfaces.⁹,¹⁰ In such systems the large band gap in the oxide support (~9 eV, Ref. 12) leads to very weak sulfur ←alumina interactions, and sulfur attacks mainly the supported metal.⁹,¹⁰ In the present work, we study the adsorption of H₂S on clean and gold “promoted” oxides of chromium. For these systems the band gap of the oxide is relatively small (~5 eV, Ref. 13) and the supported metal, in principle, has a low affinity toward sulfur.¹⁴

Chromia is an active catalyst for the hydrogenation and isomerization of alkenes, methanol synthesis, and the reduction of nitric oxides.¹⁵ Pure and uniform bulk samples of single-crystal chromium oxides are very difficult to prepare. Chromium oxide films offer a convenient and useful route for studying the surface chemistry of chromia.⁶,¹⁶ Recently, the feasibility of growing well-ordered chromium oxide films on Pt(111) with thicknesses ranging from less than a monolayer to more than eight monolayers has been shown.¹⁷ The films were grown by Cr vapor deposition in an O₂ background pressure. The growth mode, structure, and the ther-
nal stability of the resulting overlayers were studied using a combination of ion-scattering spectroscopy, x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and scanning tunneling microscopy (STM). For the first two monolayers, a well-ordered \( p(2 \times 2) \) structure is observed. The overlayer symmetry and core-level XPS data ported on \( \text{Cr}_2 \text{O}_3 \) exhibit a much larger reactivity toward \( \text{H}_2 \text{S} \) than those seen either for the pure oxide or bulk \( \text{Au} \).

II. EXPERIMENT

The experiments were carried out at the U4A beam line of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This beam line is equipped with a 6 m toroidal grating monochromator and an ultrahigh vacuum chamber (base pressure \( < 2 \times 10^{-10} \) Torr) fitted with a hemispherical electron energy analyzer and instrumentation for LEED. The valence spectra were taken with photon energies of 155, 75, and 50 eV, while photon energies of 195 (S 2\( p \) region) and 155 eV (Cr 3\( p \) and Au 4f regions) were used to acquire the core-level spectra. The binding-energy scale in the photoemission spectra was calibrated with respect to the position of the Fermi edge at a given photon energy. There was no problem with sample charging during these studies. The overall instrumental resolution in the photoemission experiments was 0.25–0.30 eV. Work function measurements were made by biasing the sample negatively (\( -14 \) V) and recording the photoemission onset and Fermi edge using a photon energy of 75 eV to excite the electrons.

The Pt(111) substrate, on which the chromia films were grown, was cleaned following standard procedures reported in the literature. The Pt crystal was mounted on a manipulator capable of liquid nitrogen cooling to 100 K and heating to 2000 K. Heating 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 Pt(111) sample for temperature measurements.

Films of chromium oxide were grown on Pt(111) following a methodology described in a previous work. Chromium atoms (generated by heating a W wire wrapped around a high-purity pellet of Cr) were dosed on the platinum substrate at 500–600 K in a background O\(_2\) pressure of \( 2 \times 10^{-6} \) Torr to form the chromium oxide films. This was followed by annealing at 600–700 K for 5 min. The coverage (or thickness) of the chromium oxide films was determined using LEED and the ratio of the Pt 4f and Cr 3p peaks in the photoemission spectra. Gold was vapor deposited on the \( \text{Cr}_2 \text{O}_3/\text{Pt}(111) \) systems at 300 K. The evaporation of gold was achieved by resistively heating a W filament wrapped by an ultrapure wire of Au. The atomic flux from the metal doser was calibrated according to the methodology described in our previous studies for Au/Pt(111). The \( \text{Cr}_2 \text{O}_3 \) and Au/\( \text{Cr}_2 \text{O}_3 \) surfaces were exposed to \( \text{H}_2 \text{S} \) at room temperature. After doing this, the coverage of sulfur was determined by measuring the area under the S 2p peaks, which was scaled to absolute units by comparing to the corresponding area for 0.33 ML of atomic sulfur on Pt(111).

III. RESULTS

A. \( \text{H}_2 \text{S} \) adsorption on chromium

Figure 1 shows S 2p spectra acquired after dosing \( \text{H}_2 \text{S} \) on a polycrystalline chromium film (\( > 10 \) ML) at 300 K. For comparison we also include the corresponding spectrum for 0.33 ML of S on Pt(111). This spectrum shows a well-defined doublet for the S 2p\(_{3/2}\) and 2p\(_{1/2}\) features. Separation of these features is not observed in the case of the \( \text{H}_2 \text{S}/\text{Cr} \) systems, probably due to the roughness of the surface (i.e., more than one adsorption site) or the existence of chemically
The dissociative adsorption of H$_2$S induced a decrease of binding energy of the Cr 3p orbitals of atomic sulfur. In Fig. 1, the uptake of sulfur by the Cr surface is close to 0.8 ML after a dose of 35 L of H$_2$S. At this point the dissociative adsorption of H$_2$S induced a decrease of $\sim 0.3$ eV in the work function of the system. The dissociation of H$_2$S did not lead to significant changes in the binding energy of the Cr 3p features ($\Delta BE \leq 0.1$ eV). This behavior is in contrast with that observed for S$_2$/Cr systems ($\theta_s > 1$ ML),$^{16}$ where the formation of CrS$_2$ produces shifts of $0.4$–$0.6$ eV in the binding energy of the Cr 2p core levels. Thus it is likely that the S atoms created by the decomposi-

tion of H$_2$S remain in a chemisorbed state on top of the Cr surface.

**B. H$_2$S adsorption on Cr$_2$O$_4$**

In this section we describe the results for the reaction of H$_2$S with chromium oxide films that were 1–2 ML thick. These films exhibited a $p(2 \times 2)$ LEED pattern as seen in previous studies.$^{17}$ It has been proposed that the $p(2 \times 2)$ pattern comes from a Cr$_3$O$_4$ overlayer oriented with its (111) surface parallel to the Pt(111) surface.$^{17}$ Because Cr$_3$O$_4$ and Pt have the same underlaying fcc Bravais lattice, the growth of Cr$_3$O$_4$(111) is favored by the metal substrate.$^{17}$ In this configuration, close-packed hexagonal planes of oxygen are separated by cation layers in which Cr$^{2+}$ and Cr$^{3+}$ are present. Indeed, the results of XPS show the presence of Cr$^{2+}$ and Cr$^{3+}$ species in the ultrathin oxide films.$^{17}$ The exact structural geometry of these films is unknown, but photoemission data show that they have the band structure and ‘metallic character’ expected for Cr$_3$O$_4$. In this work, for simplicity, we will refer to these chromium oxide films as ‘1 ML’ and ‘2 ML Cr$_3$O$_4’.

The top panel of Fig. 3 shows a typical S 2p spectrum for the adsorption of H$_2$S on a 2 ML thick Cr$_3$O$_4$ film. A well-defined doublet of peaks is observed for the S 2p$_{1/2}$ and S 2p$_{3/2}$ features. These features appear at binding energies that are very close to those seen after the dissociation of S$_2$ on ZnO,$^{14}$ and lower than those reported for H$_2$S and SH chemisorbed on metals and sulfides (163.5–165 eV).$^{19–21}$ The last difference indicates that H$_2$S undergoes complete dissociation upon adsorption on Cr$_3$O$_4$ at 300 K. This conclusion is also supported by the valence spectra for the H$_2$S/Cr$_3$O$_4$ systems, which showed an absence of the peaks typically associated with adsorbed H$_2$S and HS in the region between 8 and 14 eV. The Cr$_3$O$_4$ films displayed a reactivity toward H$_2$S that was somewhat smaller than that found for polycrystalline Cr. For example, after exposing a 2 ML Cr$_3$O$_4$ film to 55 L of H$_2$S the coverage of sulfur on the surface was close to 0.5 ML, whereas a dose of 35 L of H$_2$S produced a sulfur coverage of $\sim 0.8$ ML on metallic Cr.

The dissociative adsorption of H$_2$S induced a decrease of 0.2–0.4 eV in the work function of the Cr$_3$O$_4$/Pt(111) systems. At the same time, there were positive shifts of 0.4–0.6 eV in the binding energy of the Cr 3p features for the Cr$_3$O$_4$ overlayers (see bottom panel of Fig. 3). Figure 4 displays valence spectra acquired before and after dosing 55 L of H$_2$S to a 2 ML Cr$_3$O$_4$ film. The peaks at 2 and 4 eV are primarily from the oxide layer, while the features between 1 and 0 eV are mostly from the Pt substrate.$^{13}$ The dissociation of H$_2$S leads to a broadening and a binding-energy shift of $\sim +0.5$ eV in the Cr$_3$O$_4$ peak that appears around 2 eV. From these results one can conclude that H$_2$S is able to induce significant changes in the electronic properties of Cr$_3$O$_4$.

**C. H$_2$S adsorption on CrO$_3$**

Cr$_2$O$_3$ is the most common bulk oxide of chromium. In our previous work for CrO$_3$/Pt(111),$^{17}$ it was found that be-

---

**FIG. 2.** Valence spectra acquired after exposing a Cr film ($\theta_s > 10$ ML) to 20 and 35 L of H$_2$S at 300 K (photon energy = 75 eV). In the top spectrum, the hatched area indicates additional intensity not seen for clean Cr.
yond a thickness of two monolayers Cr$_2$O$_3$ appears and grows epitaxially on top of Cr$_3$O$_4$, which wets the substrate. In this section, we will deal with the adsorption of H$_2$S on a Cr$_2$O$_3$ overlayer with a thickness of ~4 ML, and on a relatively thick Cr$_2$O$_3$ film (~6 ML). The thick Cr$_2$O$_3$ film did not show a well-defined pattern in LEED, whereas the 4 ML Cr$_2$O$_3$ film showed a diffuse ($\sqrt{3}\times\sqrt{3}$)R30$^\circ$ pattern. This ($\sqrt{3}\times\sqrt{3}$)R30$^\circ$ structure can be attributed to a Cr$_2$O$_3$ overlayer with its $\{0001\}$ face parallel to Pt$\{111\}$.$^{17}$ Overall, the Cr$_2$O$_3$ systems studied in this work are best described as polycrystalline.

Figure 5 displays the amount of sulfur deposited on the two Cr$_2$O$_3$ films after exposing them to various doses of H$_2$S at 300 K. Among all the systems investigated in our study, the thick Cr$_2$O$_3$ film showed the lowest reactivity toward H$_2$S. For example, a dose of 22 L of H$_2$S on the thick Cr$_2$O$_3$ film at 300 K produced a sulfur coverage of ~0.15 ML, which is much smaller than the sulfur coverages of ~0.4 and 0.7 ML found after dosing 20 L of H$_2$S on 2 ML Cr$_3$O$_4$ and Cr (respectively). For the conditions in Fig. 5, results of photoemission for the S 2$p$ and valence regions indicate that there was a complete decomposition of H$_2$S on the Cr$_2$O$_3$ surfaces. The S 2$p$ spectra showed binding energies that were close to those observed in Fig. 3 for atomic sulfur on Cr$_3$O$_4$, but on the Cr$_2$O$_3$ systems the spectra were broader and there was not a clear separation between the 2$p_{\frac{1}{2}}$ and 2$p_{\frac{3}{2}}$ features (a typical result is shown in the top panel of Fig. 6). This is consistent with the fact that the Cr$_2$O$_3$ surfaces were less ordered (i.e., more rough, with different types of adsorption sites) than the 2 ML Cr$_3$O$_4$ surface, as indicated by LEED.

In the valence spectra for the H$_2$S/Cr$_2$O$_3$ systems, we did not find any peak that indicated the existence of chemisorbed H$_2$S or SH when the H$_2$S exposures were smaller than 50 L. After a H$_2$S dose of 100 L to the thick Cr$_3$O$_4$ film, we observed a new peak at ~9 eV in the valence region (bottom panel of Fig. 6). This peak suggests the presence of SH species on the surface of the oxide, and disappeared upon annealing the sample to 450 K. For the interaction of H$_2$S with metals,$^{19-24}$ it is well known that adsorbed SH is stable only when the very reactive sites of the surface are blocked (or "poisoned") by sulfur atoms. It appears that a

**FIG. 3.** Top: S 2$p$ spectra for 0.33 ML of S on Pt$\{111\}$ and a 2 ML Cr$_3$O$_4$ film exposed to 5 L of H$_2$S at 300 K. The electrons were excited using a photon energy of 195 eV. Bottom: Cr 3$p$ spectra for a clean and H$_2$S exposed 2 ML Cr$_3$O$_4$ film. Photon energy: 155 eV.

**FIG. 4.** Effects of H$_2$S on the valence band of a 2 ML Cr$_3$O$_4$ film. Hydrogen disulfide was dosed at 300 K and the spectra were taken using photon energies of 75 (top) and 155 eV (bottom).
similar phenomenon occurs on the surface of the Cr$_2$O$_3$ oxide.

The interaction with H$_2$S led to substantial changes in the electronic properties of the Cr$_2$O$_3$ films. Upon the deposition of S ($0.1-0.2$ ML), there was a substantial decrease ($0.5-0.8$ eV) in the work function of these systems. This was accompanied by positive binding-energy shifts ($0.3-0.4$ eV) in the Cr 3$p$ core levels.

D. H$_2$S adsorption on Au/Cr$_3$O$_4$ and Au/Cr$_2$O$_3$ surfaces

In a set of experiments we examined the interaction of H$_2$S with a polycrystalline gold film ($>10$ ML) at 300 K. For H$_2$S doses as large as 40 L, we did not find any evidence for the adsorption or dissociation of the molecule on the gold surface. After a dose of 150 L of H$_2$S there was a trace of sulfur ($<0.05$ ML) on the gold, and a dose of 400 L of H$_2$S produced only a small sulfur coverage ($\sim 0.08$ ML). These findings are consistent with previous studies for the H$_2$S/Au(111) and H$_2$S/Au(110) systems, where H$_2$S is adsorbed molecularly (heat of adsorption = 7–10 kcal/mol) and desorbs at temperatures below 250 K. H$_2$S does not dissociate on Au(111) or Au(110). Minor decomposition of the molecule has been observed after producing defect sites on the Au surfaces by sputtering, or after irradiating an adsorbed layer of H$_2$S with electrons.

Figure 7 displays Au 4$f$ and S 2$p$ spectra recorded after depositing 1.5 ML of Au on a 2 ML Cr$_3$O$_4$ film that had been exposed to 5 L of H$_2$S ($\theta_s \sim 0.25$ ML). The intensity observed for the Au 4$f$ peaks is much smaller than those observed for 1 ML of Au on polycrystalline Cr or Pt(111) where Au wets the metal substrate. At the same time, the deposition of Au did not produce any significant reduction in the Cr 3$p$ signal of the oxide film. This indicates that Au is forming three-dimensional (3D) clusters or islands on the H$_2$S/Cr$_3$O$_4$ system, and is also consistent with a migration of S from the oxide to on top of gold, which attenuates the Au 4$f$ signal. Previous studies have shown that Au does not wet well the surfaces of oxides or metal surfaces precoated with sulfur. The deposition of Au on the H$_2$S/Cr$_3$O$_4$ system leads to almost no change in the intensity of the S 2$p$ features, and they shift to lower binding energy to a position near that for sulfur atoms adsorbed on
gold. This behavior suggests that a large fraction of the adsorbed sulfur is migrating from the oxide substrate to on top of the Au clusters. A similar phenomenon has been seen after depositing Au on S/Mo surfaces and is, in part, a consequence of the low surface-free energy of sulfur. In Fig. 7, after exposing the Au/H₂S/Cr₃O₄ system to an additional 10 L of H₂S, one sees a significant increase in the coverage of sulfur. The final sulfur coverage is approximately 0.4 ML. To obtain such a coverage on a clean Cr₃O₄ film, one needs a H₂S dose of 20 L. Thus it appears that the Au/Cr₃O₄ system is somewhat more reactive toward H₂S than clean Cr₃O₄ or bulk Au.

For the interaction of Au with the H₂S/Cr₂O₃ system, the qualitative trends were identical. In all the cases examined the Au 4f signal was small (3D clustering of Au), the S 2p features were not attenuated and they shifted toward lower binding energy on Au deposition (possible migration of S from the oxide substrate of the admetal), and the Au ‘promoted’ surfaces were able to decompose H₂S at 300 K in a relatively easy way. This is best illustrated by the results for the interaction of Au with a thick Cr₂O₃ film (>6 ML). The top panel in Fig. 8 shows a valence spectrum taken after depositing a monolayer of Au on a thick Cr₂O₃ film that had been previously exposed to 40 L of H₂S (θ₂ ~0.2 ML), then ‘promoted’ with 1 ML of Au, and finally exposed to two successive doses of 5 L of H₂S (T = 300 K; photon energy = 195 eV).
Calculations, the H$_2$S molecule was bonded to this Au atom or to the Au


ability, we decided to investigate the effects of chromia on the


The Au/Cr$_2$O$_3$ surfaces is bonded to the admetal. Therefore, it


bottom of Fig. 8 indicates that most of the sulfur present on


FIG. 9. Different views (or projections) of the clusters used to model the

desorption of H$_2$S on Au/Cr$_2$O$_3$ (I–III) and Au (IV). Clusters I, II, and III


have three layers of pure Cr or O atoms. The notation [a:b:c] specifies how


many Cr (small circles) or O atoms (large circles) are in each layer. A gold


atom was deposited on the center of the three-fold hollow site formed by the


oxygen atoms labeled “2” in clusters I, II, and III. In the ab initio SCF


calculations, the H$_2$S molecule was bonded to this Au atom or to the Au


atom labeled “1” in cluster IV.


a unique electronic structure (see above) and a large ability to


adsorb and dissociate H$_2$S.


An analysis of the S 2p positions for the spectra at the bottom of Fig. 8 indicates that most of the sulfur present on the Au/Cr$_2$O$_3$ surfaces is bonded to the admetal. Therefore, it is reasonable to conclude that the active sites for the dissociation of H$_2$S involve Au atoms. The large reactivity of these Au atoms may be a result of electronic perturbations induced by the oxide support. To explore the second possibility, we decided to investigate the effects of chromia on the H$_2$S→Au interactions at a molecular orbital level using ab initio self-consistent-field (SCF) calculations and the clusters shown in Fig. 9. Cluster I (Au+Cr$_4$O$_6$) is a model for an Au atom supported on a defect site of chromia in which the oxygen atoms have a relatively low coordination number. It probably maximizes admetal→oxide interactions. Clusters II (Au+Cr$_4$O$_{12}$) and III (Au+Cr$_{10}$O$_{15}$) were used to study the deposition of Au on a Cr$_2$O$_3$(0001) surface. This surface


produces a ($\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern similar to that observed for some of the Cr$_2$O$_3$ films employed in our work. Cluster IV (Au+Au$_9$) represents an Au atom in contact with a Au(111)-like particle.


For clusters I–III, the Cr–O bond distances were all set equal to 2.0 Å (an average of the distances of 1.97 and 2.02 Å found in Cr$_2$O$_3$, Ref. 36), the O–Cr–O angles were 90°, and the Au–O$_2$ distances were optimized at the ab initio SCF level obtaining values of 2.22–2.26 Å. In cluster IV, the Au–Au bond lengths and angles were set equal to those observed in bulk gold. Figure 10 displays the bonding configuration for H$_2$S when the molecule was adsorbed on a supported gold atom. Spectroscopic evidence shows that hydrogen sulfide is adsorbed on metals making bonds through the sulfur, with its molecular plane either parallel or tilted with respect to the surface normal. For the free H$_2$S molecule, the calculated S–H bond distances (1.35 Å) and H–S–H bond angle (94°) are in excellent agreement with those observed in x-ray diffraction studies for inorganic complexes that contain Au–S bonds. According to the SCF calculations H$_2$S should be adsorbed with its molecular plane slightly tilted (11–18°) with respect to the surface normal, but the difference in bonding energy between perpendicular and tilted adsorption was small (≤1.8 kcal/mol) in all the cases.


For the Cr$_4$O$_6$, Cr$_8$O$_{12}$, and Cr$_{10}$O$_{15}$ clusters, we found that the occupied {O 2p + Cr 3d,4s} states appeared at energies between −6 and −16 eV, with the empty {Cr 3d,4s + O 2p} states located at energies above −1 eV (for a typical result, see Fig. 11). The “band” gap observed in the SCF calculations (6.1–6.8 eV) was somewhat larger than that seen in bulk Cr$_2$O$_3$ (4.8 eV, Ref. 17). Nevertheless, the “band” structure predicted by the SCF calculations for the oxide clusters was in general agreement with that observed for bulk Cr$_2$O$_3$ in first-principles density functional calculations. In Fig. 10, we show a rough picture for the frontier orbitals of H$_2$S. The calculated energies for the 5a$_1$ and 2b$_1$ orbitals are in excellent agreement with the corre-


TABLE I. Theoretical results for the adsorption of H$_2$S on Au and Au/


Cr$_2$O$_3$ clusters.


<table>
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<td>1.33</td>
<td>11°</td>
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<td>2.64</td>
<td>1.34</td>
<td>16°</td>
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<tr>
<td>AuCr$<em>8$O$</em>{12}$</td>
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<td>2.61</td>
<td>1.34</td>
<td>18°</td>
</tr>
<tr>
<td>AuCr$<em>{10}$O$</em>{15}$</td>
<td>10.3</td>
<td>2.61</td>
<td>1.34</td>
<td>18°</td>
</tr>
</tbody>
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$^a$Following the standard convention, positive values denote an exothermic adsorption process.
sponding ionization potentials (13.20 and 10.31 eV, respectively). In principle, the bonding mechanism of H$_2$S to an oxide or metal can involve donation of charge from the ‘‘S lone pairs’’ ($5a_1$ and $2b_1$ orbitals) into the surface and back donation of electrons from the surface into the H$_2$S ($3b_2$) orbital.\textsuperscript{40,41} By comparing the results in Figs. 10 and 11, one can see that the match in energy for an interaction between the molecule ‘‘S lone pairs’’ and the empty bands of Cr$_2$O$_3$, or the occupied bands of Cr$_3$O$_4$, and the LUMO of H$_2$S, is very poor. On the other hand, a gold atom with a half occupied 6$s$ orbital at $-7.7$ eV provides a relatively good match for an electron-acceptor interaction with the $5a_1$ and $2b_1$ orbitals of H$_2$S. We found that a gold atom supported on the clusters of Fig. 9 exhibited positive charges:\textsuperscript{45} 0.32$e$ in AuCr$_3$O$_6$, 0.24$e$ in AuCr$_4$O$_{12}$, 0.27$e$ in Cr$_3$O$_{15}$, and 0.08$e$ in AuAu$_9$. In the AuCr$_3$O$_6$ and AuCr$_{10}$O$_{15}$ systems, there was a significant shift of electrons from the admetal toward the oxide support that increased the stability of the half empty Au(6$s$) orbital by 1.7–2.3 eV and, therefore, facilitated Au(6$s$) $\leftrightarrow$ H$_2$S($5a_1$,2$b_1$) bonding interactions.

In Table I are listed the calculated adsorption energies for H$_2$S on clusters I–IV. Our SCF calculations did not include effects of electron correlation. Thus it is likely that the values listed in Table I underestimate the bonding energy of the molecule on the clusters.\textsuperscript{46,47} This fact explains why the calculated bonding energy for H$_2$S on the AuAu$_9$ cluster (3.4 kcal) is smaller than the adsorption energy of H$_2$S on Au(111) and Au(110) surfaces (7–10 kcal/mol).\textsuperscript{28–38,41} In Table I, one can see a clear increase in the adsorption energy of H$_2$S when Au is supported on the chromium-oxide clusters. These results suggest that the large reactivity seen in the experiments of Fig. 8 for Au/Cr$_2$O$_3$ can be a consequence of electronic perturbations induced by the oxide support on gold.

IV. DISCUSSION

A. H$_2$S adsorption on Cr, Cr$_3$O$_4$, and Cr$_2$O$_3$ systems

The experiments described above indicate that Cr$_2$O$_3$ is much less reactive toward H$_2$S than metallic chromium. The reactivity seen on polycrystalline Cr is comparable to that found for the dissociation of H$_2$S on other early transition metals (W, Ref. 26 and Mo, Refs. 19,22). For chromium, there is a large density of states immediately above or below the Fermi level, and these states offer a better match in energy for electron acceptor or electron donor interactions with the orbitals of H$_2$S than the valence and conduction bands of Cr$_2$O$_3$ (see Fig. 11). This leads to a large dissociation probability for H$_2$S on the metal, and a low dissociation probability for the molecule on the oxide.

The results for the interaction of H$_2$S with the different oxide films show an increase in reactivity that follows the sequence: thick Cr$_2$O$_3$$< 4$ ML Cr$_3$O$_4$$< 2$ ML Cr$_3$O$_4$ (see Fig. 5). This trend cannot be attributed to a rise in the number of defect sites on the oxide surface, since according to LEED the degree of order in the oxide systems also increased following the sequence: thick Cr$_3$O$_4$ (no LEED pattern) $< $4 ML Cr$_2$O$_3$ [diffuse $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern] $< 2$ ML Cr$_3$O$_4$ [clear $(2 \times 2)$ pattern]. The Cr$_2$O$_3$ surfaces are more rough than the 2 ML Cr$_3$O$_4$ surface, and this leads to S $2p$ spectra that are more broad and ill defined (compare Figs. 3 and 6). Thus among the oxide films, the Cr$_3$O$_4$ system exhibits the largest reactivity toward H$_2$S and has the lowest number of defect sites on the surface. First-principles density functional calculations and photoemission experiments show very large differences in the band structures of Cr$_3$O$_4$ and Cr$_2$O$_3$.\textsuperscript{13} The theoretical studies indicate that, in essence, there is no band gap around the Fermi level of Cr$_3$O$_4$.\textsuperscript{13} This oxide exhibits a much larger ‘‘metallic character’’ than Cr$_2$O$_3$, with a high density of states immediately above and below the Fermi level.\textsuperscript{13} The match in energy between the bands of Cr$_3$O$_4$ and the frontier orbitals of H$_2$S is better than for the H$_2$S/Cr$_2$O$_3$ system, and this difference seems to have a direct impact on the reactivity of the oxides toward H$_2$S.

Studies for the S$_2$/Al$_2$O$_3$ (Refs. 9,10) and S$_2$/ZnO (Ref. 11) systems also indicate that there is a correlation between the size of the band gap in an oxide and its reactivity toward S-containing molecules. For example, after exposing films of Al$_2$O$_3$ (bulk band gap $\sim 9$ eV, Ref. 12) to large amounts of S$_2$ (enough to produce AlS$_2$ multilayers on Al), sulfur coverages smaller than 0.1 ML are observed.\textsuperscript{10} However, similar S$_2$ doses on ZnO (bulk band gap $\sim 3.4$ eV, Ref. 48) produce sulfur coverages close to 0.7 ML.\textsuperscript{11} When comparing our results for H$_2$S/Cr$_3$O$_4$ with those previously reported for S$_2$/Al$_2$O$_3$,\textsuperscript{10} one has to keep in mind that S$_2$ is a much more reactive molecule than H$_2$S. Nevertheless, it is easier to generate a sulfur coverage close to 0.1 ML in the H$_2$S/Cr$_3$O$_4$ system than in S$_2$/Al$_2$O$_3$ due to the smaller band gap in Cr$_2$O$_3$ ($\sim 4.8$ eV, Ref. 17).

Thiols (RSH) are common impurities present in oil-derived feedstreams used in the chemical industry.\textsuperscript{49} These species have frontier orbitals similar to those of H$_2$S,\textsuperscript{50,51} and their decomposition reactions (RSH$_{\text{gas}}$ $\rightarrow$ RSH$^-$ + H$_2$; RSH$_{\text{gas}}$ $\rightarrow$ S$_2$ + RH$_{\text{gas}}$) are more exothermic than those of H$_2$S.\textsuperscript{40,50} Our results suggest that oxides with a small band gap (SnO$_2$, ZnO, TiO$_2$, Cr$_2$O$_3$, etc.) should be more susceptible to S poisoning by thiol decomposition than oxides in which the band gap is big (Al$_2$O$_3$, MgO, CaO, etc.).

B. H$_2$S adsorption on Au/chromia surfaces

In previous works, we have examined the interaction of sulfur with metal/alumina surfaces (AM/Al$_2$O$_3$, AM=Cu, Zn, or Ag).\textsuperscript{9,10} In such systems the large band gap in the oxide support leads to very weak sulfur$\rightarrow$alumina interactions, and sulfur attacks mainly the supported metal.\textsuperscript{9,10} The adsorption of sulfur induces drastic changes in the electronic properties of the admetal, and frequently one sees the formation of admetal sulﬁdes (AMS$_x$) that decompose at temperatures above 700 K (which are higher than the temperatures typically used in most catalytic processes).\textsuperscript{9,10} In the Au/chromia systems one is dealing with an oxide support that has a relatively small band gap,\textsuperscript{13} which should enhance S$\leftrightarrow$oxide interactions with respect to S/AM/Al$_2$O$_3$, and Au is
probably the metal with the lowest affinity toward sulfur in the Periodic Table\textsuperscript{14} which should favor S⇌oxide interactions instead of S⇌admetal interactions. In spite of these facts, the S⇌admetal interactions are stronger than the S⇌oxide interactions in the H\textsubscript{2}S/Au/chromia systems. For the deposition of Au on S/chromia surfaces, the results of XPS show shifts in the S 2\textit{p} features and a lack of attenuation in the S signal that suggest a migration of adsorbed S from the oxide substrate to the admetal. The behavior of the Au/S/C\textsubscript{r}O\textsubscript{4} system is particularly interesting because, even when the oxide support has metallic properties,\textsuperscript{13} sulfur prefers to bond to the admetal.

The Au/C\textsubscript{r}O\textsubscript{3} surfaces exhibit a larger ability to dissociate H\textsubscript{2}S than polycrystalline Au or pure C\textsubscript{r}O\textsubscript{3}. This enhancement in reactivity is probably a consequence of the unique electronic structure that the Au/C\textsubscript{r}O\textsubscript{3} surfaces display in their valence spectra (Fig. 8). In principle, three phenomena may be responsible for the large reactivity of Au "promoted" C\textsubscript{r}O\textsubscript{3}: (1) electronic interactions between the admetal and oxide can produce oxide sites that are more chemically active than those in C\textsubscript{r}O\textsubscript{3}; (2) the supported Au clusters can have an intrinsic activity bigger than that of bulk Au; and (3) the oxide support can electronically perturb Au raising its reactivity. The first possibility can be discarded because most of the sulfur adsorbed on the Au/H\textsubscript{2}S/C\textsubscript{r}O\textsubscript{3} systems seems to be bonded to Au and not to the oxide. With respect to the second possibility, it is known that small clusters of noble metals have special structural and electronic properties that can make them very reactive.\textsuperscript{7} Finally, the third possibility is substantiated by the \textit{ab initio} SCF calculations in Sec. III D. These calculations show a shift or polarization of electrons from Au toward the C\textsubscript{r}O\textsubscript{3} substrate that increases the magnitude of the Au(6\textit{s})⇌H\textsubscript{2}S(5\textit{a}_{1},2\textit{b}_{1}) bonding interactions and facilitates the decomposition of the molecule. In the literature a few systems have been reported in which Au becomes chemically active due to bonding with other metals (Au/Ru\textsubscript{001}, Refs. 52–54 and Au/Pd\textsubscript{110}, Ref. 55) or with an oxide (Au/TiO\textsubscript{2}, Ref. 56).

**V. CONCLUSIONS**

(1) Polycrystalline Cr is very reactive toward H\textsubscript{2}S. At 300 K, the molecule completely decomposes producing a chemisorbed layer of sulfur that substantially attenuates the intensity of the Cr 3\textit{d} band near the Fermi level. No evidence was found for the formation of CrS\textsubscript{4} species.

(2) For the adsorption of H\textsubscript{2}S on chromium oxides the rate of dissociation of the molecule increases in the following sequence: C\textsubscript{r}O\textsubscript{3} < C\textsubscript{r}O\textsubscript{4} < Cr. There is a correlation between the "metallic character" (i.e., reduced oxidation state...
of Cr and large density of states at the Fermi level) and the reactivity of an oxide toward $H_2S$. At 300 K, the dissociation of $H_2S$ on Cr$_2$O$_3$ and Cr$_2$O$_3$ surfaces induces a decrease of 0.3–0.8 eV in the work function and significant binding-energy shifts (0.2–0.6 eV) in the Cr 3p core levels.

(3) For the Au/Schormia systems, the Au–S interactions are stronger than the S–oxide interactions. The Au/ Cr$_2$O$_3$ surfaces exhibit a unique electronic structure in the valence region and a larger ability to dissociate H$_2$S than polycrystalline Au or pure Cr$_2$O$_3$. The results of ab initio SCF calculations show a shift or polarization of electrons from Au toward the Cr$_2$O$_3$ substrate that increases the magnitude of the Au(6s)→H$_2$S(5a$_1$,2b$_1$) bonding interactions and facilitates the decomposition of the molecule.

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18. unpublished.

20 D.R. Huntley, Surf. Sci. 240, 13 (1990), and references therein.
33 After dosing 400 L of H$_2$S to an Au film at 300 K ($\theta_S$=0.08 ML), the sulfur adatoms showed a $2p_x$ binding energy of 160.8 eV.
35 (a) The MO calculations were carried out using the HONDO program (Ref. 35b). The nonempirical effective core potentials (ECP’s) of Hay and Wadt (Ref. 35c) were used to describe the inner shells of Cr and Au. The ECP for Au included relativistic effects (Ref. 35c). The 1s electron of O was described through the ECP generated by Stevens, Basch, and Krauss (Ref. 35d). For sulfur and hydrogen, we included all their electrons in the calculations. The molecular orbitals were expanded using Gaussian-type orbitals. The atomic orbitals of S and H were expressed in terms of a double-zeta quality basis set augmented with polarization functions (Refs. 9,35b). A basis set obtained through a (3s2p5d2/1p2d) contraction scheme (Ref. 35e) was used to describe the 4s, 4p, and 3d atomic orbitals of Cr. The 6s, 6p, and 5d atomic orbitals of Au were expressed in terms of a (3s3p4d2/1p2d) basis set (Ref. 35f). Finally, the valence orbitals of O were treated using the basis set recommended by Stevens-Basch-Krauss (Ref. 35d); (b) M. Dupuis, S. Chin, and A. Marquez, in Relativistic and Electron Correlation Effects in Molecules and Clusters, edited by G. L. Malli, NATO ASI Series (Plenum, New York, 1992); (c) P.J. Hay and W.R. Wadt, J. Chem. Phys. 82, 270 (1985); (d) W.J. Stevens, H. Basch, and M. Krauss, ibid. 81, 6026 (1984); (e) L. Zhang, M. Kuhn, U. Dierbold, and J.A. Rodriguez, J. Phys. Chem. B 101, 4588 (1997); (f) J.A. Rodriguez and M. Kuhn, Surf. Sci. 330, L657 (1995).