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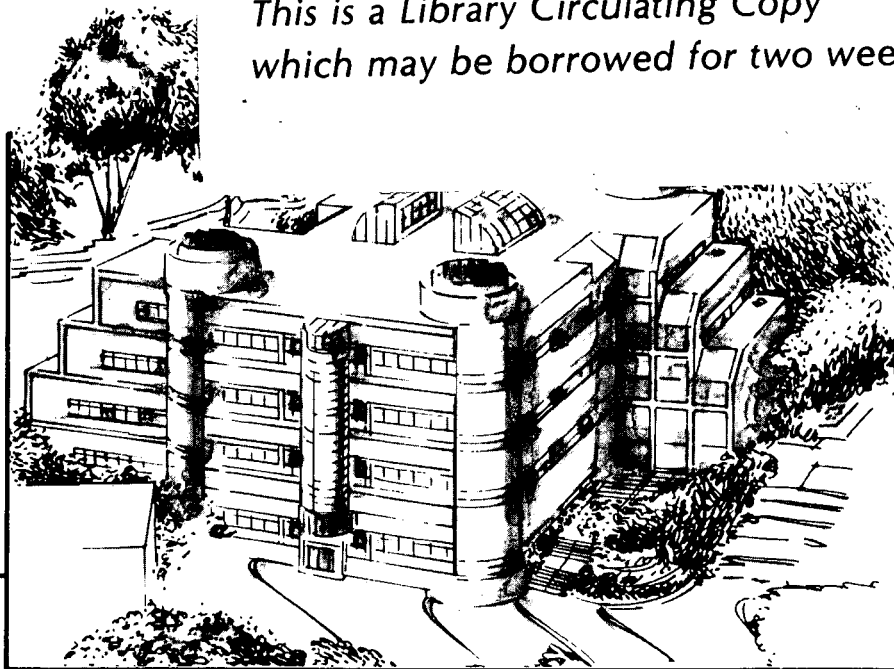
Thiophene Hydrodesulfurization over Rhenium Surfaces: The Effects of Structure and Adsorbates (C and S)

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Thiophene Hydrodesulfurization over Rhenium Surfaces: The Effects of Structure and Adsorbates (C and S)

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ABSTRACT

Thiophene Hydrodesulfurization (HDS) has been investigated over rhenium single crystals and polycrystalline foils and was found to be a structure sensitive reaction over these surfaces. Rhenium single crystals are one to six times more active than molybdenum single crystals which is in agreement with previous studies using rhenium disulfide and molybdenum disulfide catalysts. Adsorbed carbon and sulfur overlayers decrease the activity of the rhenium single crystals, suggesting that the catalyst surfaces remain free of strongly bound deposits of carbon and/or sulfur. The trend in HDS activity measured for the Re catalysts can be explained by considering the difference in coordination of the top layer rhenium atoms in the single crystals surfaces.

1 INTRODUCTION

For over fifty years, removal of sulfur from crude oil has been accomplished by the hydrodesulfurization (HDS) process in which the petroleum feedstock is treated with hydrogen over Co-Mo/Al₂O₃ catalysts. In order to understand and improve the catalysts employed, numerous investigations of the hydrodesulfurization of thiophene and other model compounds such as dibenzothiophene have been carried out over Co-Mo and other transition metal catalysts.

Pecoraro and Chianelli measured the activities of unsupported sulfides of the transition metals for HDS of dibenzothiophene [1]. The first row sulfides were found to be relatively inactive, while the second and third row transition metal sulfides showed variations in activities of three orders of magnitude and volcano type dependence of the activities upon periodic position. Similar trends were observed by Ledoux et al. for the HDS of thiophene over transition metal sulfides supported on activated carbon [2]. Theoretical calculations by Harris and Chianelli indicate that the variation in HDS activity is due to electronic differences in the sulfides [3]. Their calculations show that the HDS activity of the sulfides correlates with a parameter

which takes into account the number of d electrons in the highest occupied molecular orbital (HOMO) of the sulfide as well as the strength and degree of covalency of the metal-sulfur bond. However, in considering the results of these studies, it should be pointed out that it is very difficult to measure the "active" surface area of sulfide catalysts and, therefore, the turnover frequency. HDS studies by Tauster over MoS₂, for example, indicate that the basal plane is inactive and that the active sites are located at sulfur vacancies at the edges of MoS₂ crystallites [4]. The HDS activity of the MoS₂ catalysts did not correlate with their BET surface areas but did vary linearly with their O₂ chemisorption capacities. However, the relationship between O₂ chemisorption and the active HDS sites is not well understood and to our knowledge the O₂ chemisorption studies have not been extended to other transition metal sulfides. Pecoraro and Chianelli note that the HDS activities of the sulfides do not correlate with their BET surface areas and instead normalize their HDS activities per millimole or gram of metal. It is far from obvious that either of these quantities accurately measures the active surface area of a catalyst. In their work, Ledoux and coworkers assume unit dispersion of the metal on the carbon support and that the dispersion remains constant during the presulfidation process. The similarity of the volcano type curves obtained in the two studies indicate that the relative trends in activity are most likely correct, but it is not clear that quantitative comparisons between the activities of different sulfides can be made.

Our approach has been to study hydrodesulfurization using model, single crystal catalysts for which the surface structure and composition can be characterized at the molecular level, and for which the surface area can be accurately measured. These studies were initiated by investigating the adsorption and bonding of thiophene and its desulfurization products on MoS₂ and clean, sulfided and carbided Mo(100) single crystals [5,6,7,8]. The basal plane of MoS₂ was found to be chemically inert towards chemisorption of thiophene, butene and H₂S which agrees with the catalytic results described above in which the basal plane was found to be inactive. Unfortunately, it is very difficult to prepare MoS₂ single crystals which expose large numbers of the catalytically active edge sites, so this material is inappropriate

for single crystal studies of thiophene HDS. As a result, we have focused on the use of transition metal single crystals for model studies of thiophene hydrodesulfurization. Preliminary studies using a Mo(100) single crystal showed HDS of thiophene to be a catalytic reaction over this surface and that the product distribution is similar to that over a MoS₂ catalyst [6]. These results led us to extend our studies to include examination of the effects of surface structure and composition on thiophene HDS over molybdenum single crystals. Adsorbed sulfur on the Mo(100) surface was found to decrease the activity of the catalyst by a factor of two, while adsorbed carbon (carbide) had no effect on the catalyst's activity [7,8]. Radio-tracer ¹⁴C and ³⁵S studies showed that both adsorbed carbon and sulfur are stable on the metal surface under reaction conditions, and that an initially clean Mo(100) single crystal becomes covered primarily with adsorbed carbon ($\theta_c \approx 0.8$, $\theta_s \approx 0.2$) during the initial stages of the reaction [8,7]. Consistent with this result, thiophene HDS was found to be structure insensitive over molybdenum surfaces ((100), (110), (111)), suggesting that the reaction occurs on an adsorbate overlayer which blocks the influence of the metal's surface structure on catalyst activity [9].

To determine the effect of periodic position on the surface chemistry of the HDS reaction, we have undertaken parallel HDS studies using rhenium single crystal catalysts. Chianelli and Pecoraro found rhenium disulfide (ReS₂) to be about four times more active than MoS₂ while Ledoux and coworkers found ReS₂ supported on carbon to be about two times more active than MoS₂ on the same support [1,2]. Rhenium was chosen for this study because of the significantly higher activity of ReS₂ and because of the similarity in structure of the two sulfides. Both ReS₂ and MoS₂ have lamellar structures and it is expected that differences in their HDS activities are primarily due to electronic differences. To this end, the HDS activities of four initially clean rhenium single crystals of different crystallographic orientation ((0001), (10 $\bar{1}$ 0), (11 $\bar{2}$ 0), (11 $\bar{2}$ 1)) have been measured and the effects of adsorbed overlayers of carbon and sulfur determined for the least active (Re(0001)) and most active (Re(10 $\bar{1}$ 0)) surfaces.

2 EXPERIMENTAL

The experiments reported were performed in a stainless-steel ultrahigh vacuum (UHV) chamber equipped with an atmospheric pressure isolation cell for catalytic reactions. A stainless-steel reaction loop is connected via an inlet and outlet to the isolation cell and is outfitted with a gas circulation pump and a sampling valve connected to a gas chromatograph. The ultrahigh vacuum/catalytic reactor system is described in detail elsewhere [10]. The UHV chamber is pumped with both ion and diffusion pumps (ultimate chamber pressure, 1×10^{-9} Torr) and is equipped with a four grid, retarding field analyzer for Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Four different rhenium single crystals were used in this study: Re(0001), Re(10 $\bar{1}$ 0), Re(11 $\bar{2}$ 0) and Re(11 $\bar{2}$ 1), as well as a polycrystalline rhenium foil. The single crystals were on average 1 cm² in area and less than 0.1 cm thick and were cut and polished to within 1° using standard metallurgical techniques. The single crystals were mounted on the sample manipulator between two 0.020 in. tantalum wires spot-welded to two 0.125 in. tantalum rods, and were heated resistively over the temperature range 300-1900 K. The polycrystalline foil was 1 cm² in area and 0.025 cm. thick. The foil was spot-welded to two 0.020 in. rhenium wires which were in turn spot-welded to two 0.125 in. thick tantalum rods. The sample temperature was measured with a platinum-platinum 10 % rhodium thermocouple spot-welded to the edge of the crystal or the polycrystalline foil.

The major impurities in the single crystals were found to be carbon and sulfur. Carbon was removed by treatment with oxygen (1×10^{-7} Torr O₂, 1100 K) while sulfur and residual oxygen were removed by annealing the crystals to 1900 K. Surface cleanliness was monitored using AES and LEED. Overlayers of sulfur were formed on the Re(0001) and Re(10 $\bar{1}$ 0) surfaces using an electrochemical sulfur source which has been described previously [11]. With the single crystals at room temperature, it was possible to deposit sulfur coverages up to and including 0.5 ML and 1.0 ML on the Re(0001) and Re(10 $\bar{1}$ 0) surfaces respectively. Lower sulfur coverages were produced

by annealing the sulfur covered surfaces to desorb a fraction of the adsorbed sulfur. AES calibration of the sulfur coverage was accomplished using previously observed LEED patterns which correspond to known sulfur coverages [12]. A $(2\sqrt{3}\times 2\sqrt{3})R$ 30° LEED pattern and a $p(2\times 2)$ LEED pattern are observed from the $\text{Re}(0001)$ and $\text{Re}(10\bar{1}0)$ surfaces respectively at a sulfur coverage of 0.5 monolayer (ML). AES peak heights were measured for the $\text{S}(148\text{eV})$ and $\text{Re}(177\text{eV})$ Auger transitions for the sulfur covered and clean rhenium surfaces to determine the AES attenuation factors for sulfur on rhenium. Calibration curves of sulfur coverage versus the AES ($\text{S}(148\text{eV})/\text{Re}(177\text{eV})$) peak height ratio were generated using these attenuation factors and the curves were used to determine all sulfur coverages.

Overlayers of carbon were formed on the $\text{Re}(0001)$ and $\text{Re}(10\bar{1}0)$ surfaces by dosing with C_2H_4 at room temperature, followed by heating to 800 K. This procedure was sufficient to produce carbon coverages up to 0.25 and 0.6 ML on the $\text{Re}(0001)$ and $\text{Re}(10\bar{1}0)$ surfaces respectively. To obtain higher coverages, the surfaces were dosed with C_2H_4 at 800 K. Carbon coverages were determined on both surfaces using calibration curves of carbon coverage versus the AES ($\text{C}(272\text{eV})/\text{Re}(177\text{eV})$) peak height ratio. For the $\text{Re}(0001)$ surface, the AES attenuation factor for carbon on rhenium was determined using the absolute AES intensities for the clean and 0.25 ML carbon covered ($\theta_c = 0.25$) $\text{Re}(0001)$ surfaces. This latter surface is prepared by saturating the clean surface with C_2H_4 at room temperature followed by annealing to 770 K. This surface gives a $c(4\times 2)$ LEED pattern which has been shown previously to correspond to a carbon coverage of 0.25 ML [13]. On the $\text{Re}(10\bar{1}0)$ surface, the AES attenuation factor for carbon was determined in the following manner. The surface was dosed with thiophene at room temperature to saturation coverage and then annealed to 700 K. Using the AES calibration curve for sulfur on the $\text{Re}(10\bar{1}0)$ surface, the sulfur coverage was determined to be 0.1 ML ($\theta_s = 0.1$). Thiophene decomposes completely on the clean $\text{Re}(10\bar{1}0)$ surface with desorption of H_2 only, indicating that the carbon coverage is 0.4 ML ($\theta_c = 0.4$). The $\text{C}(272\text{eV})$ and $\text{Re}(177\text{eV})$ AES peak heights were measured for this surface and the clean surface and were used to calculate the AES attenuation factor for carbon. This

procedure does not take into account attenuation of the Re(177eV) peak by the coadsorbed sulfur from the thiophene, but carbon coverages using this calibration are believed to be accurate within 15 % [14].

Following preparation and characterization of the catalyst surfaces in UHV, the samples were enclosed in the atmospheric pressure cell and the reactor loop pressurized with thiophene and hydrogen ($P_{Th} = 3.0$ Torr, $P_{H_2} = 780$ Torr). The reactant gases were circulated for 30 minutes prior to heating the catalyst to reaction temperature to ensure mixing. Gas samples were injected into a gas chromatograph during reaction and were separated on a 19 % picric acid on carbowax column and detected using a flame ionization detector. Catalyst activities were calculated using the product accumulation data from the first 90 min. of reaction.

3 RESULTS

3.1 Thiophene HDS over Initially Clean Rhenium Surfaces

Thiophene HDS activities were measured for four different rhenium single crystals and a polycrystalline foil and they are compared in Figure 1. Idealized drawings of the single crystal surfaces are shown in Figure 2. The HDS of thiophene is a structure sensitive reaction over rhenium with a six-fold variation in activity for the single crystal surfaces studied. Product accumulation curves for the HDS of thiophene over the Re(0001) surface are shown in Figure 3 and the product distribution obtained over this same surface is shown in Table 1. The accumulation curves and product distribution are similar to those observed for the other rhenium surfaces. Small amounts of C_1 to C_3 hydrocarbons were produced by hydrogenolysis but their contribution to the product distribution was always less than 5 %. The deactivation of the rhenium catalysts in the closed loop batch reactor was studied using a rhenium foil catalyst. The HDS activity of the polycrystalline Re foil was found to be constant for the first three hours of reaction but then to decline steadily with complete deactivation occurring after 9-12 hours (10-15 % conversion). The role

of product poisoning in deactivation of the rhenium catalysts was therefore examined by including hydrogen sulfide and cis-2-butene in the initial reaction mixture at partial pressures corresponding to 5-15 % thiophene conversion. Cis-2-butene had no effect on the activity of a rhenium polycrystalline foil while H₂S strongly decreased the activity of the catalyst as shown in Figure 4.

Following a 90 min. reaction and evacuation of the reaction cell, AES showed the single crystal catalysts to be covered with substantial quantities of sulfur (Re(0001): $\theta_s = 0.5$, Re(10 $\bar{1}$ 0): $\theta_s = 0.7$) but only small amounts of adsorbed carbon. However, this sulfur probably adsorbs during evacuation of the high pressure cell as the high activity of the catalysts after 90 min. of reaction indicates that they are not covered with irreversibly bound sulfur. The temperature dependence of thiophene HDS was measured for a Re(10 $\bar{1}$ 0) single crystal and a polycrystalline foil over the temperature range 493-653 K and the data is plotted in Figure 5. Identical activation energies of 9.4 kcal/mole were measured for the two rhenium surfaces. At reaction temperatures of 673 K and above, the temperature dependence of thiophene HDS becomes non-Arrhenius and the activity of the rhenium catalysts actually decreases. AES analysis of the Re foil surface after reactions at temperatures above 673 K shows the catalyst surface to be covered with an overlayer of graphitic carbon.

3.2 The Effects of Adsorbed Carbon and Sulfur on the HDS Activity of the Re(0001) and Re(10 $\bar{1}$ 0) Single Crystal Surfaces

In Figures 6 and 7, the effects of pre-adsorbed carbon and sulfur on the HDS activity of the least active (Re(0001)) and most active (Re(10 $\bar{1}$ 0)) of those rhenium surfaces studied are shown. Adsorbed sulfur decreases the activity of both single crystal surfaces compared to the initially clean single crystals. The activity of the (0001) surface is markedly decreased at low sulfur coverages ($\theta_s \leq 0.25$), while additional sulfur is a much weaker poison of HDS activity. At a sulfur coverage of 0.5 ML, close to the saturation coverage of 0.6-0.7 ML, the HDS activity is about 70 % of that of the initially clean surface. On the more active Re(10 $\bar{1}$ 0) surface, adsorbed sulfur is

a stronger poison; at a sulfur coverage of 0.75 ML, the HDS activity is about 40 % of the initially clean surface value. As with the (0001) surface, adsorbed sulfur at high coverages ($\theta_s > 0.6$) is a weaker poison of active HDS sites.

On both rhenium single crystal surfaces, adsorbed carbon decreases their HDS activity as well. Indeed, carbon is a stronger poison than sulfur. The decrease in activity is linear as a function of carbon coverage and the curves tend to zero activity at the full monolayer coverage. These results indicate that each adsorbed carbon atom blocks an active HDS site on the catalysts, in contrast to adsorbed sulfur for which this is true only at low coverages.

3.3 Form of Adsorbed Carbon on Re(0001) and Re(10 $\bar{1}$ 0) and its Effect on HDS Activity

The structure and bonding of adsorbed carbon overlayers on transition metal surfaces has been shown to change as a function of temperature [15]. Auger electron spectroscopy has been used in combination with other surface science techniques to determine the form of adsorbed carbon overlayers [16]. Figure 8a shows the carbon Auger spectrum as a function of annealing temperature for ethylene on the Re(0001) surface. The carbon AES peak shape for annealing temperatures below 900 K most closely resembles that of amorphous and graphitic carbon. This suggests that at these temperatures the surface is primarily covered with carbonaceous species containing C-C bonds. Following heating above 900 K, the carbon AES peak shape more closely resembles that of a transition metal carbide, suggesting that the predominant carbon species on the surface is atomic carbon bonded to rhenium. Similar carbon AES peak shapes were observed for adsorbed carbon on the Re(10 $\bar{1}$ 0) surface; two representative spectra are shown in Figure 8b.

Thiophene HDS reactions were carried out for carbon covered surfaces annealed at 800 K and 1100 K, and the resulting activities are compared in Figure 9 for the Re(0001) surface. For both this and the (10 $\bar{1}$ 0) surface, the annealing temperature of the carbon covered surfaces had no effect on the HDS activity of the catalysts. The initial state of the carbon does not, therefore, appear to be an important factor.

4 DISCUSSION

In this study we have found rhenium single crystals and polycrystalline foils to be active catalysts for the hydrodesulfurization of thiophene. The most important results of this work are the following:

I. Rhenium is a more active HDS catalyst than molybdenum, in agreement with previous studies using sulfide catalysts [1,2].

II. Adsorbed sulfur and carbon overlayers decrease the activity of rhenium single crystal catalysts towards thiophene HDS.

III. Thiophene HDS is a structure sensitive reaction over rhenium single crystals.

4.1 Activity and Poisoning of Model Rhenium HDS Catalysts

The lack of reliable techniques for the measurement of catalyst surface areas to distinguish between active and inactive adsorption sites on metal sulfide catalysts has hampered the ability of researchers to compare reaction rates of different catalysts with confidence. The use of single crystals as catalysts allows one to measure the turnover frequencies of catalysts per unit area of the active metal, and therefore facilitates direct comparison of activities for different transition metal catalysts. The results of this study, in conjunction with previous work in our laboratory, show that rhenium single crystal catalysts are up to six times more active for thiophene HDS than molybdenum single crystals, depending on the crystallographic orientation of the rhenium single crystals [9]. This difference in HDS activities is similar to that measured for unsupported as well as supported molybdenum and rhenium disulfide catalysts. As mentioned in the introduction, Pecoraro and Chianelli found unsupported ReS_2 to be about four times more active than MoS_2 while Ledoux et al. found ReS_2 supported on carbon to be approximately two times more active than MoS_2 supported on this same material [1,2]. The similarity of these results is significant because it indicates that the HDS activities measured in the studies described above are suitably normalized to reflect the activity per unit of active

surface area and most importantly that metal single crystals can indeed be used as model catalysts to study the surface chemistry of the hydrodesulfurization process.

The product distribution obtained for thiophene HDS over the rhenium catalysts, shown in Table 1 for Re(0001), was found to be independent of the crystallographic orientation of the rhenium surface. The product distributions from thiophene HDS over the Mo(100) surface and from butadiene hydrogenation over a rhenium film are also shown in Table 1 and are almost identical to that for thiophene HDS over the rhenium surfaces [6,17]. The reaction is clearly kinetically controlled as thermodynamics predicts that under the conditions used the products should consist almost entirely of butane. The similarity of the three product distributions leads us to conclude that the HDS pathway is essentially the same over Re and Mo surfaces and that butadiene is an intermediate in the reaction. This suggests that thiophene is desulfurized on the catalyst surface prior to hydrogenation of its ring as tetrahydrothiophene HDS produces a different product distribution over Mo(100) [6]. Apparently, desulfurization of thiophene on the catalyst surface yields adsorbed butadiene and its hydrogenation then determines the product distribution.

The similarity of the product distributions over the different rhenium single crystal surfaces studied indicates that the reaction mechanism is the same on the various crystal faces, despite differences in surface structure. It might have been expected that the adsorption geometry of thiophene is different on surfaces of dissimilar structure which could possibly lead to different reaction mechanisms. This, however, does not appear to be the case. Similar behavior has been observed by Lang and Masel on platinum surfaces [18]. They investigated the desulfurization of thiophene in UHV on the Pt(100), Pt(111) and Pt(210) surfaces using TPD, EELS and XPS and found the desulfurization of thiophene to be identical on the three surfaces. Thiophene adsorbs in a parallel configuration at 170 K, but assumes a tilted geometry at higher temperatures due to the developing Pt-S bond. Desulfurization is complete by 350 K, leaving a tilted butadiene-like species on the platinum surfaces. This ultrahigh vacuum work is consistent with our catalytic results which suggest that thiophene is desulfurized to produce butadiene on the rhenium surfaces

studied with subsequent hydrogenation to give butenes and butane.

The temperature dependence studies of thiophene HDS over the $\text{Re}(10\bar{1}0)$ surface and a polycrystalline rhenium foil also support the conclusion that the reaction mechanism is the same over the different Re surfaces (i.e. the mechanism is insensitive to the catalyst surface structure). Identical activation energies of 9.4 kcal/mole were measured for the two surfaces. A Re foil has been shown to consist of primarily crystallites of the thermodynamically most stable (0001) face following high temperature annealing [13]. The low HDS activity of the rhenium foil indicates that this is the case. The similarity of the activation energies over a $\text{Re}(10\bar{1}0)$ single crystal and a rhenium foil provides further evidence that the reaction mechanism is the same over the different rhenium surfaces.

The deactivation of a polycrystalline foil was investigated by including the products H_2S and cis-2-butene in the initial HDS gas mixtures. Hydrogen sulfide was previously found to poison the $\text{Mo}(100)$ surface while cis-2-butene had no effect on catalyst activity, both results being consistent with HDS studies over industrial Co/Mo catalysts [8]. At H_2S and cis-2-butene partial pressures corresponding to 5-15 % thiophene conversion, H_2S strongly decreases the activity of a Re foil catalyst while the effect of cis-2-butene is negligible. As in the case of a $\text{Mo}(100)$ single crystal catalyst, the poisoning of a Re foil is largely reversible as the activity of the catalyst could be restored to a value close to the initially clean surface activity by removing the H_2S from the reactor. This indicates that the rate of H_2S dissociation to give strongly bound sulfur on the $\text{Re}(0001)$ surface is very slow when compared to the rate of thiophene HDS. As will be discussed shortly, strongly bound sulfur on the $\text{Re}(0001)$ and $\text{Re}(10\bar{1}0)$ surfaces irreversibly poisons the catalysts. Some irreversible poisoning occurs during long reactions (9-12 hours) which reduces the activity of the catalyst to approximately 60-70 % of the clean surface value and is probably associated with adsorption of strongly bound sulfur and carbon on the rhenium surface. It should be noted, however, that this irreversible deactivation process occurs on a timescale much longer than the reversible deactivation caused by adsorption of H_2S on the active HDS sites.

4.2 Effect of Adsorbed Sulfur on HDS Activity

Overlayers of sulfur adsorbed on the Re(0001) and Re(10 $\bar{1}$ 0) single crystal surfaces decrease the thiophene HDS activity of the catalysts. Kelly et al. have investigated the UHV chemisorption of thiophene on the clean and sulfur covered Re(0001) and Mo(100) surfaces using temperature programmed desorption (TPD) [19,20]. On the clean single crystal surfaces, the major reaction pathway for adsorbed thiophene is decomposition to yield adsorbed carbon, sulfur and hydrogen, with the latter desorbing into the vacuum as H₂. Adsorbed sulfur on these surfaces was found to decrease their reactivity towards thiophene decomposition; as the coverage of sulfur is increased, the fraction of adsorbed thiophene that decomposes on the surface decreases. Instead, thiophene interacts very weakly with the sulfur covered surfaces and desorbs at temperatures below 200 K, indicative of physical adsorption. Clearly, the addition of sulfur to the Re(0001) and Mo(100) single crystal surfaces weakens their interaction with thiophene in the UHV environment to the extent that thiophene desorption is favored over bond cleavage. Our catalytic results also indicate that adsorbed sulfur weakens the interaction between thiophene and the single crystal surfaces. Adsorbed sulfur blocks active HDS sites on the rhenium surfaces and as a result, the HDS activities of the sulfur covered surfaces are lower.

The poisoning effect of sulfur is not transient but instead remains constant for the entire reaction, strongly suggesting that the sulfur overlayer is stable under reaction conditions. However, sulfur adsorbed at low coverages (Re(0001): $\theta_s \leq 0.25$, Re(10 $\bar{1}$ 0): $\theta_s \leq 0.6$) appears better able to block active sites than the additional sulfur at higher coverages. This suggests that the high coverage sulfur is removed from the catalyst surface under reaction conditions. This data can be usefully compared with the HDS behavior of Mo(100) surfaces [7]. Adsorbed sulfur on the Mo(100) surface blocks active sites at coverages $\theta_s \leq 0.67$ ML. TPD, XPS and UPS studies of sulfur on the Mo(100) surface indicate that at sulfur coverages above 0.67 ML, the additional sulfur populates weaker binding sites on the surface [21,22]. This sulfur may occupy new adsorption sites (e.g. two-fold bridge sites) or simply be

more weakly bound due to repulsive interactions with neighboring sulfur atoms. A recent scanning tunneling microscopy (STM) study indicates that at high coverages all sulfur atoms occupy identical sites suggesting that repulsive interactions between sulfur atoms are responsible for the reduction in sulfur binding strength [23]. Radiotracer ^{35}S experiments showed that the rate of hydrogenation of the high coverage sulfur ($\theta_s > 0.67$) is faster than that of the low coverage species [7]. Apparently, the high coverage sulfur does not decrease the HDS activity of the Mo(100) surface because it is removed from the catalyst surface under reaction conditions.

TPD studies of sulfur adsorbed on the Re(0001) and Re(10 $\bar{1}$ 0) surfaces and our catalytic results indicate similar phenomena for these surfaces as for the Mo(100) surface [12]. On the Re(0001) surface, adsorbed sulfur at low coverages ($\theta_s \leq 0.25$) desorbs in a single peak at 1600 K. As the coverage is increased, low temperature shoulders appear in the TPD spectrum at 1400 K ($\theta_s > 0.3$) and 900 K ($\theta_s > 0.5$). On the more open Re(10 $\bar{1}$ 0) surface, sulfur desorbs at 1700 K at low coverages ($\theta_s \leq 0.5$) and a low temperature shoulder at 1500-1600 K appears above 0.5 ML. The coverages at which sulfur begins to populate the more weakly bonding adsorption sites corresponds approximately to the coverages above which the effectiveness of sulfur in poisoning the HDS process on Re surfaces is decreased. As mentioned above, this is consistent with previous results on the Mo(100) surface for which the coverage at which a low temperature shoulder appeared in the TPD spectrum coincided with the coverage above which additional sulfur did not affect the HDS activity. Radiotracer ^{35}S studies verified that this more weakly bound sulfur could be removed from the catalyst under reaction conditions, suggesting that only the strongly bound sulfur remains on the catalyst surface during reaction [7].

It is important to note that during HDS reactions over the rhenium single crystal catalysts, sulfur is not deposited into the strong binding sites populated when sulfur is pre-adsorbed on the single crystals in UHV. Sulfur bonded in these adsorption sites lowers the HDS activity of the catalyst, while the initially clean single crystals maintain high catalytic activities for up to three hours. Well over 1000 thiophene molecules are desulfurized per surface rhenium atom in three hours; yet if sulfur was

deposited in these strong binding sites during reaction, the surface would become covered with sulfur in a few seconds and the HDS activity would fall to that of a sulfur covered surface. The high catalyst activities of the initially clean single crystals indicate that this is not the case. The results suggest, as was concluded in an earlier paper, that the thiophene HDS mechanism does not include a step in which the C-S bonds are cleaved to give a hydrocarbon and a sulfur atom directly bonded to the metal surface [7].

4.3 Effect of Adsorbed Carbon on HDS Activity

Overlayers of adsorbed carbon on the Re(0001) and Re(10 $\bar{1}$ 0) surfaces strongly decrease the HDS activity of the single crystal catalysts. As discussed in section 3.2, the linearity of the plots of HDS activity versus carbon coverage indicates that each adsorbed carbon atom blocks an active HDS site on the catalyst surfaces. These results are distinctly different from those for the Mo(100) surface; adsorbed carbon had no effect on the HDS activity of this surface [8]. Previous work using ^{14}C showed that carbon overlayers were stable on the Mo(100) surface and that decomposition of thiophene on the initially clean Mo(100) surface in the reactor resulted in the catalyst surface being covered with predominantly adsorbed carbon under reaction conditions [8]. Therefore, we concluded that the active catalyst surface is covered with an overlayer of carbon.

In both the Mo(100) study and our present work with rhenium, the form of the adsorbed carbon overlayers was investigated using Auger electron spectroscopy. Numerous studies have been made which show that the lineshape of the carbon AES transition is different for carbon in a metal carbide, graphite, and amorphous carbon [24]. On the Mo(100) surface, carbon overlayers produced by adsorption of ethylene on the single crystal and heating to $T > 500$ K give AES lineshapes characteristic of carbidic carbon [25]. Ion scattering studies of the carbon covered Mo(100) surface indicate that carbon is adsorbed in four-fold hollow sites [26]. This study and preliminary dynamical LEED calculations in our group suggest that the carbon overlayer extends $< 0.6 \text{ \AA}$ above the metal surface [14]. This is consistent

with the results of Jona et al. for carbidic type carbon on the Fe(100) surface [27]. Their dynamical LEED calculations indicate that the adsorbed carbon overlayer sits $< 0.5 \text{ \AA}$ above the metal plane.

For the Re(0001) and Re(10 $\bar{1}$ 0) surfaces, carbon overlayers formed in the same manner as described for molybdenum and annealed $< 900 \text{ K}$ give AES lineshapes which resemble those of graphite and amorphous carbon (see Figs. 8a and 8b). For a graphitic or amorphous carbon overlayer, the interaction between the overlayer and the metal substrate is considerably weaker than for a carbide overlayer as strong bonds are formed between neighboring carbon atoms and not with metal atoms in the substrate. This is reflected in the increased height of the carbon overlayer above the metal plane. Using surface extended energy loss fine structure spectroscopy (SEELFS), Rosei et al. determined that a graphitic overlayer sits $2.8 \pm 0.08 \text{ \AA}$ above the Ni(111) surface [28]. The Re(0001) face is also a close packed surface and the Re(10 $\bar{1}$ 0) surface has only a weak corrugation, so it is expected that a graphitic or amorphous carbon overlayer would extend well above these surfaces as well.

The differences in the structure of the carbon overlayers on the Mo(100) and Re(0001) surfaces are reflected in how they influence thiophene chemisorption. As mentioned earlier, adsorbed carbon on the Mo(100) surface blocks thiophene decomposition and creates new molecular adsorption states from which thiophene desorbs at 310 K and 360 K [19]. On the (0001) face of rhenium, adsorbed carbon also blocks thiophene decomposition, but thiophene interacts much more weakly with this surface giving rise to molecular desorption peaks at 180 K and 230 K [20]. Theoretical calculations by Maclaren et al. also suggest that the height of an adsorbate above the metal surface influences its poisoning effect [29]. They calculated the local density of states (LDOS), often used as a theoretical measure of catalyst activity, for different adsorption heights of carbon on the Ni(100) surface. They found that as the height of an adsorbed carbon atom was increased from 0.4 \AA to 1.3 \AA , the LDOS at the surface, and therefore the predicted catalytic activity, decreased strongly. This provides further evidence that carbon's poisoning effect is dependent upon its overlayer structure.

As shown in Figures 8a and 8b, the AES line shapes for carbon on the Re(0001) and Re(10 $\bar{1}$ 0) surfaces change with temperature. The lineshape evolves from one resembling most closely graphitic and amorphous carbon at low annealing temperatures to a peak shape most similar to carbon in a metal carbide after annealing above 900 K. These changes suggest that the form of the carbon overlayers becomes more carbidic in nature following annealing at high temperatures. On the basis of the preceding discussion, this change would be expected to coincide with a higher thiophene HDS activity. The HDS activities compared in Figure 9 show that this is not the case as carbon covered surfaces annealed at 800 K and 1100 K were found to have similar turnover frequencies for HDS.

The interaction of carbon with rhenium surfaces has also been investigated by other researchers. Ducros et al. studied ethylene decomposition on the Re(0001) surface and found that dehydrogenation of ethylene is complete by 700 K and that C-C bond cleavage occurs by 800 K [13]. This latter conclusion is based upon observation of a c(4 \times 2) LEED pattern following heating of an ethylene saturated surface to 770 K. TPD of ethylene indicates that the carbon coverage is 0.25 ML, hence the spacing between carbon atoms in the unit cell requires that scission of the C-C bonds has occurred. Our AES studies, however, indicate that the structure of the carbon overlayers is graphitic-like up to 900 K, above which it resembles carbidic-type carbon. Gall and coworkers used AES and TPD to study the interaction of carbon with a polycrystalline rhenium ribbon and report carbon AES line shapes similar to those shown in Figures 8a and 8b [30]. In addition, they observed a stable rhenium carbon surface phase formed at $T \geq 1500$ K which persisted to $T \geq 2600$ K. Although the rhenium-carbon phase diagram shows no carbide phases, the authors believe the stable phase observed is a surface carbide. The reactivity of the carbon covered rhenium surfaces was probed using the UHV dissociation of CsCl as a test reaction. Clean rhenium, the surface carbide and carbon covered surfaces annealed between 800-1100 K were found to be active towards CsCl dissociation while a graphite covered surface was inactive.

In this work, AES indicates that carbon overlayers annealed to 800 K are more

graphitic in nature while overlayers annealed to 1100 K are more carbidic-like. The work of Gall et al. suggests that the carbon overlayers produced on the Re(0001) and Re(10 $\bar{1}$ 0) surfaces at 1100 K are probably intermediary between a surface carbide and an overlayer of graphite. The most important point, however, is that the carbon species produced at the two annealing temperatures are both strong poisons of HDS activity. This suggests that the carbon overlayers sit well above the rhenium metal plane and therefore block active sites for HDS. This is in contrast to the Mo(100) surface for which adsorbed carbon sits in the plane of the metal and does not decrease the activity of the catalyst.

4.4 Explanation of the Structure Sensitivity

Re(0001) and Re(10 $\bar{1}$ 0) surfaces maintain higher HDS activities when they are initially clean than when they are covered with predeposited overlayers of sulfur or carbon. This indicates that the initially clean rhenium single crystals do not become covered with strongly bound overlayers of sulfur or carbon under reaction conditions. Instead the single crystal surfaces are apparently covered with only reversibly bound species which either desorb into the gas phase or are hydrogenated to products. This suggests that HDS of thiophene does indeed occur directly on the metal surface and not on an adsorbate overlayer, in contrast to the Mo(100) surface for which it was found previously that thiophene HDS occurred on an overlayer composed primarily of adsorbed carbon [8]. Consequently, thiophene's interaction with the rhenium surfaces is not moderated by an adsorbate overlayer and the structure of the different crystal faces influences their HDS activity.

As discussed in a previous publication, the large size of the thiophene molecule probably limits its interaction with the rhenium surfaces to the top layer rhenium atoms. It was also noted that the HDS activity of the rhenium surfaces did not correlate with surface openness, but instead could be related to the coordination numbers of the top layer rhenium atoms. In Figure 10, the HDS activity of the rhenium single crystal catalysts is plotted as a function of the coordination number of the top layer rhenium atoms (see Figure 2). The "volcano" shaped curve shown in

Figure 10 is common throughout heterogeneous catalysis and can be understood by relating the catalytic activity to the chemisorption energy of species involved in the reaction [31]. If we assume that the active sites for thiophene HDS on the rhenium surfaces are composed of the top layer rhenium atoms, the trend in activity can be explained. On the left side of the curve, a C_6 surface atom is the most coordinately unsaturated compared to the other top layer surface atoms and would be expected to bind species involved in the reaction the most strongly. Although the coverage of reactant and intermediate species will be high, the species may be so stable that they do not decompose into products, therefore causing the $\text{Re}(11\bar{2}1)$ surface to have a relatively low activity. In addition, this surface is the most likely to experience product inhibition due to strong binding of product molecules on the active sites. At the other extreme, a C_9 surface atom is the most coordinately saturated and will therefore be expected to interact the weakest with species involved in the reaction. As a result, the coverage of reactant and intermediate species will be lower and the surface will be less able to "activate" thiophene molecules. Therefore the turnover frequency of the $\text{Re}(0001)$ surface would also be expected to be low. In addition, the close-packed structure of this surface may sterically hinder adsorption of reactant species. The most active surfaces, the $\text{Re}(10\bar{1}0)$ and $\text{Re}(10\bar{2}0)$ surfaces, are those which have top layer atoms with coordination numbers (C_7, C_8) intermediary between the two extremes described above. Unfortunately, it is not possible to directly determine the chemisorption energies of thiophene on the different surfaces as thiophene decomposes to carbon, sulfur and hydrogen instead of desorbing molecularly. However, desorption energies have been determined for sulfur on the $\text{Re}(0001)$ and $\text{Re}(10\bar{1}0)$ surfaces. At low coverages, sulfur desorbs from $\text{Re}(0001)$ at 1600 K ($E_d = 98$ kcal/mole) and from $\text{Re}(10\bar{1}0)$ at 1700 K ($E_d = 104$ kcal/mole) [12]. Sulfur is believed to be adsorbed on three-fold sites formed between three C_9 atoms on the $\text{Re}(0001)$ surface and on three-fold sites formed between two top layer C_8 atoms and one second layer C_{10} atom on the $\text{Re}(10\bar{1}0)$ surface. Clearly, sulfur chemisorbs more strongly on $\text{Re}(10\bar{1}0)$ which may indicate that thiophene and other species in the reaction pathway also bind more strongly to this surface.

5 CONCLUSION

We have shown that rhenium single crystals and polycrystalline foils are active catalysts for the hydrodesulfurization of thiophene. Both adsorbed sulfur and carbon block active HDS sites on the rhenium surfaces, indicating that the active catalyst surfaces are free of strongly bound deposits of sulfur and/or carbon. Thiophene HDS is a structure sensitive reaction over rhenium in contrast to earlier work over molybdenum for which the reaction was found to be structure insensitive. The rhenium single crystals studied were found to be one to six times more active than low miller index planes of molybdenum ((100), (110), (111)) which may be due to their ability to remain free of irreversibly bound deposits of sulfur and carbon while HDS over the molybdenum catalysts occurs on a strongly bound overlayer composed primarily of adsorbed carbon.

ACKNOWLEDGEMENTS

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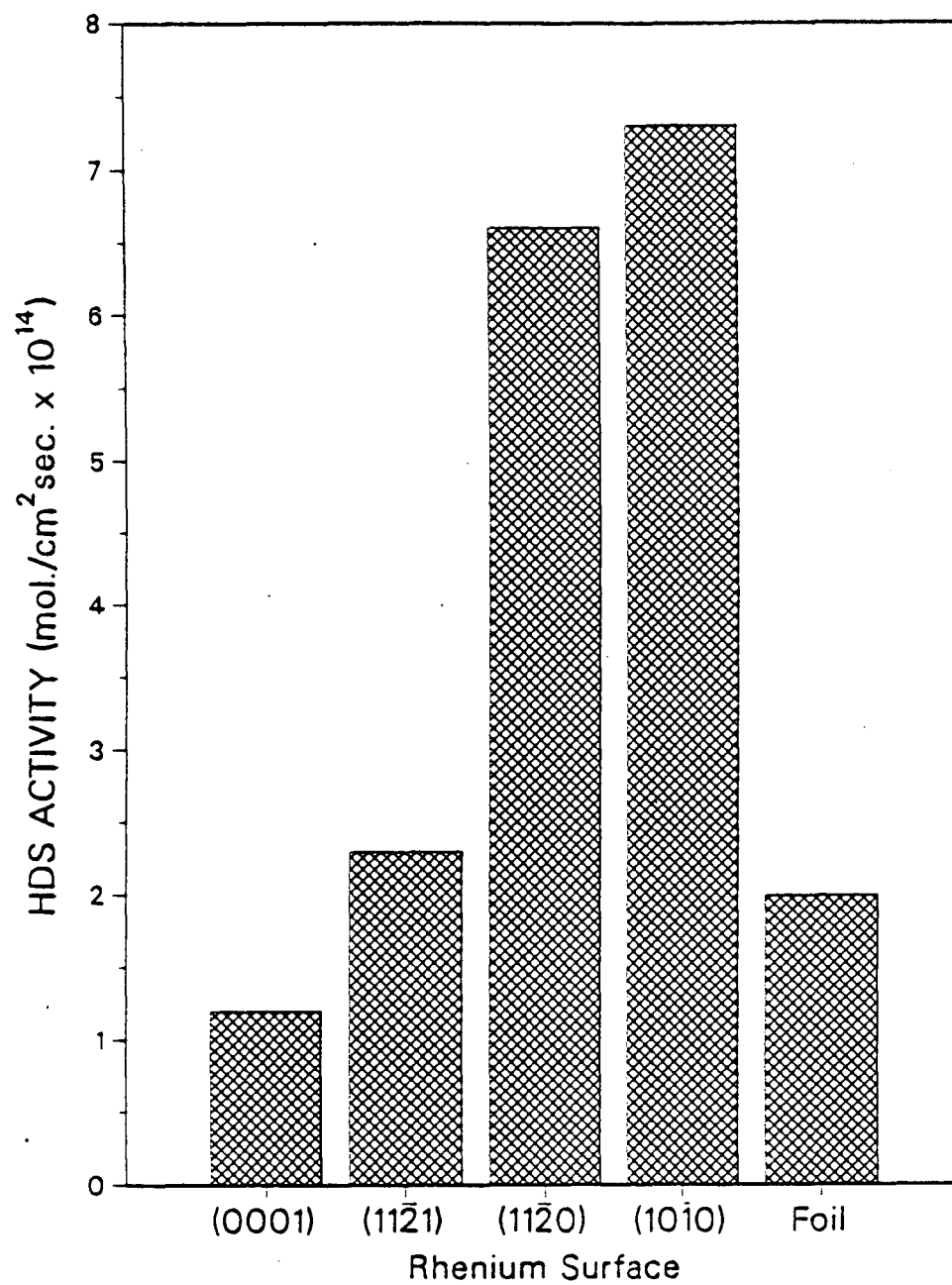
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Table 1: Comparison of Product Distributions

Product	Fractional Yield (%)		
	Thiophene HDS		Butadiene + H ₂
	Re(0001)	Mo(100)	Re Film
Butadiene	4.4	5.6	—
1-Butene	49.7	52.8	49
trans-2-Butene	23.5	19.4	31
cis-2-Butene	13.9	13.9	11
Butane	4.4	8.1	9

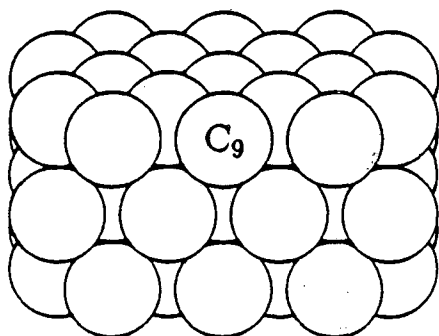
Table 1: Comparison of product distributions for thiophene HDS and butadiene hydrogenation. The Mo(100) data is from ref. [6] and the butadiene hydrogenation data is from ref. [17].



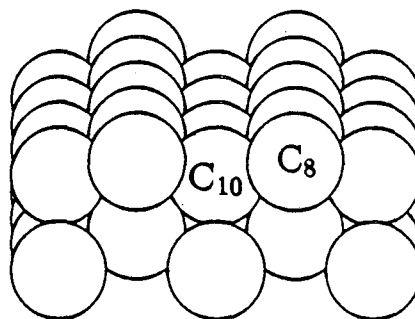
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Figure 1.

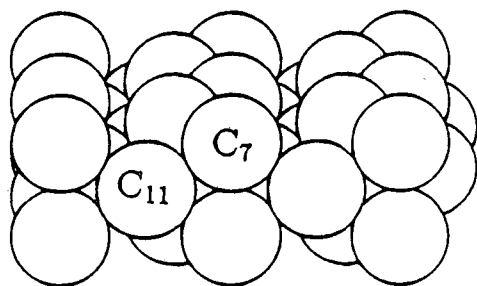
Re(0001)



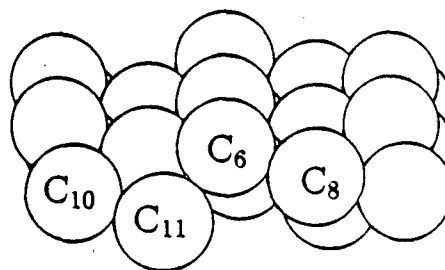
Re(10 $\bar{1}$ 0)



Re(11 $\bar{2}$ 0)

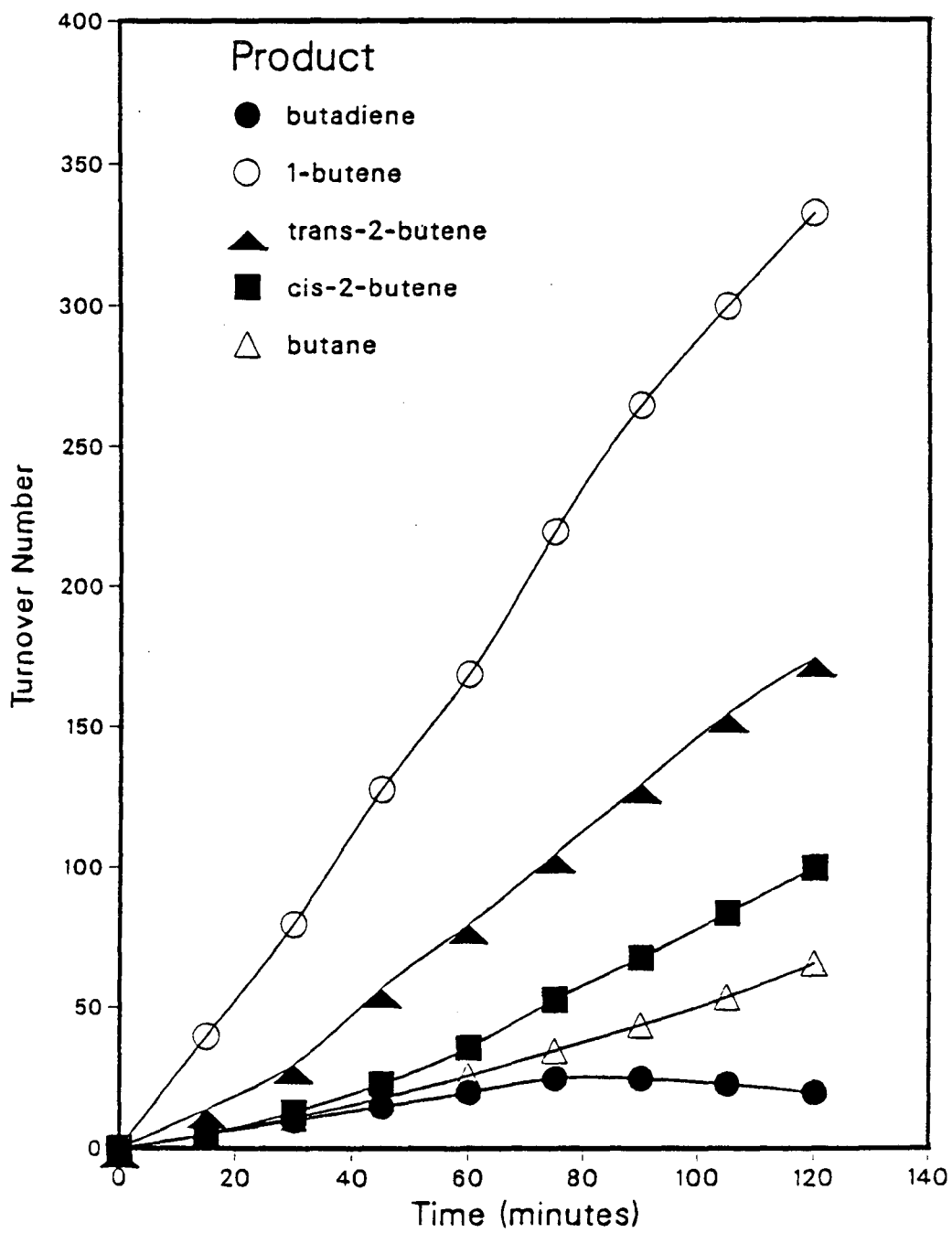


Re(11 $\bar{2}$ 1)



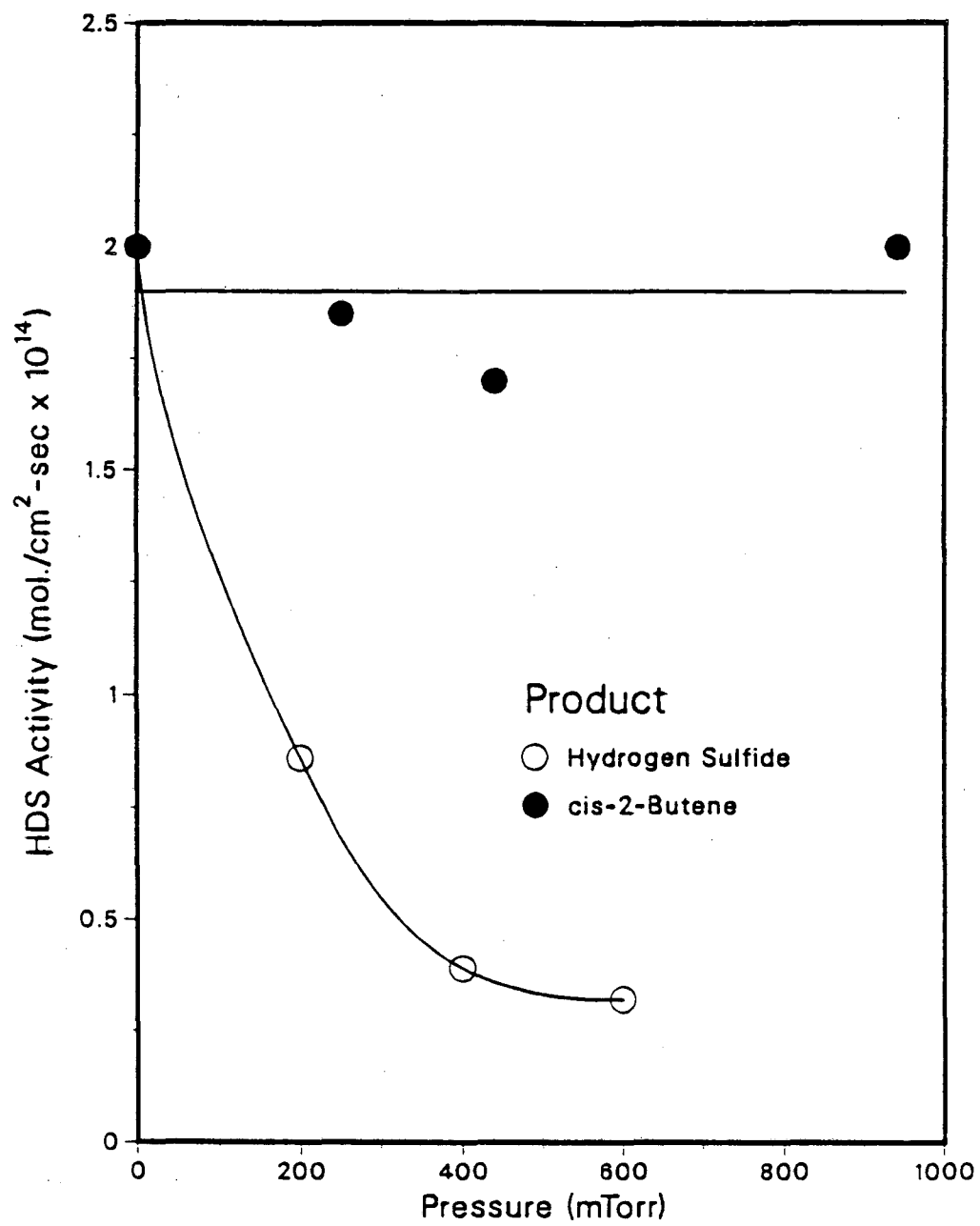
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Figure 2.



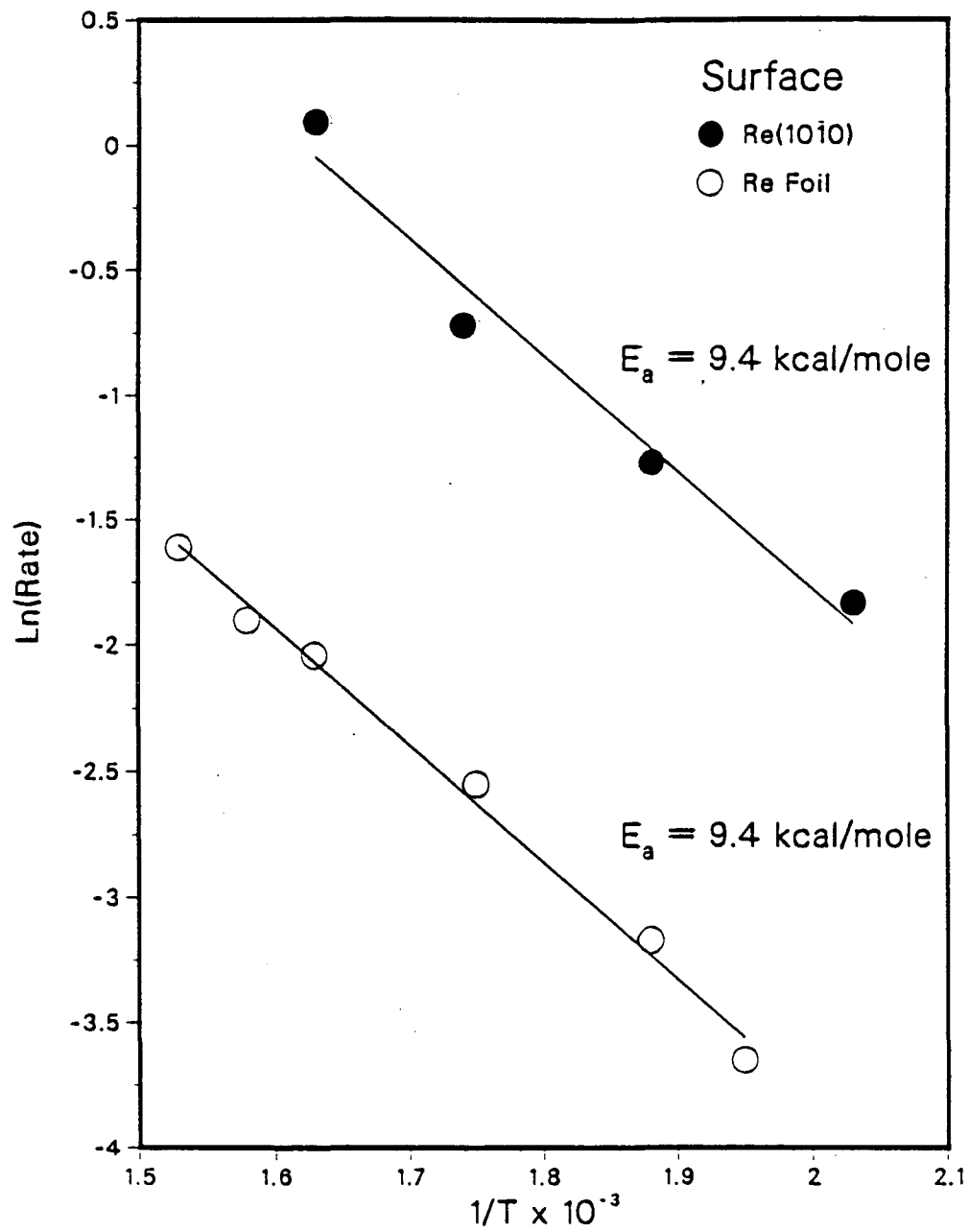
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Figure 3.



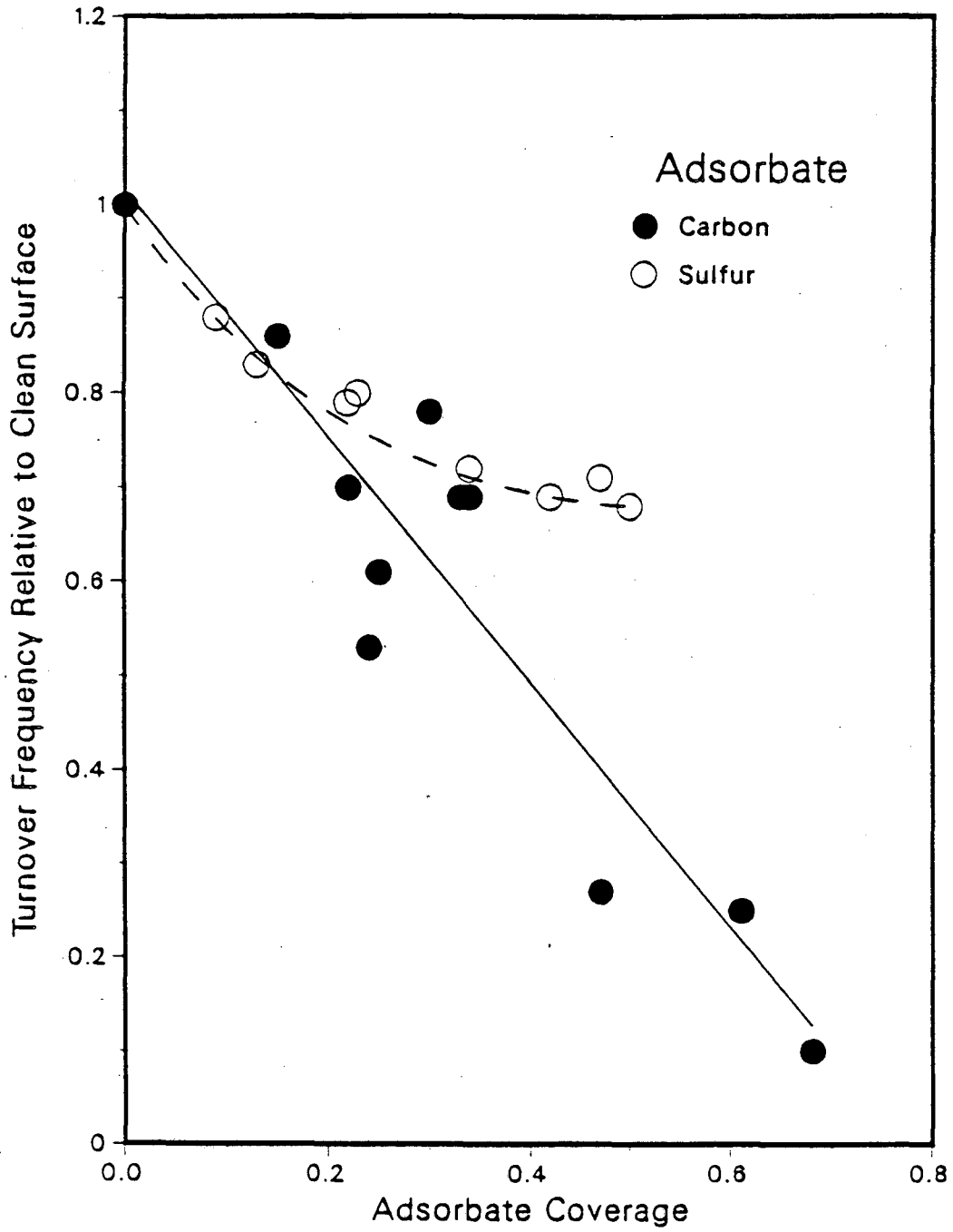
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Figure 4.



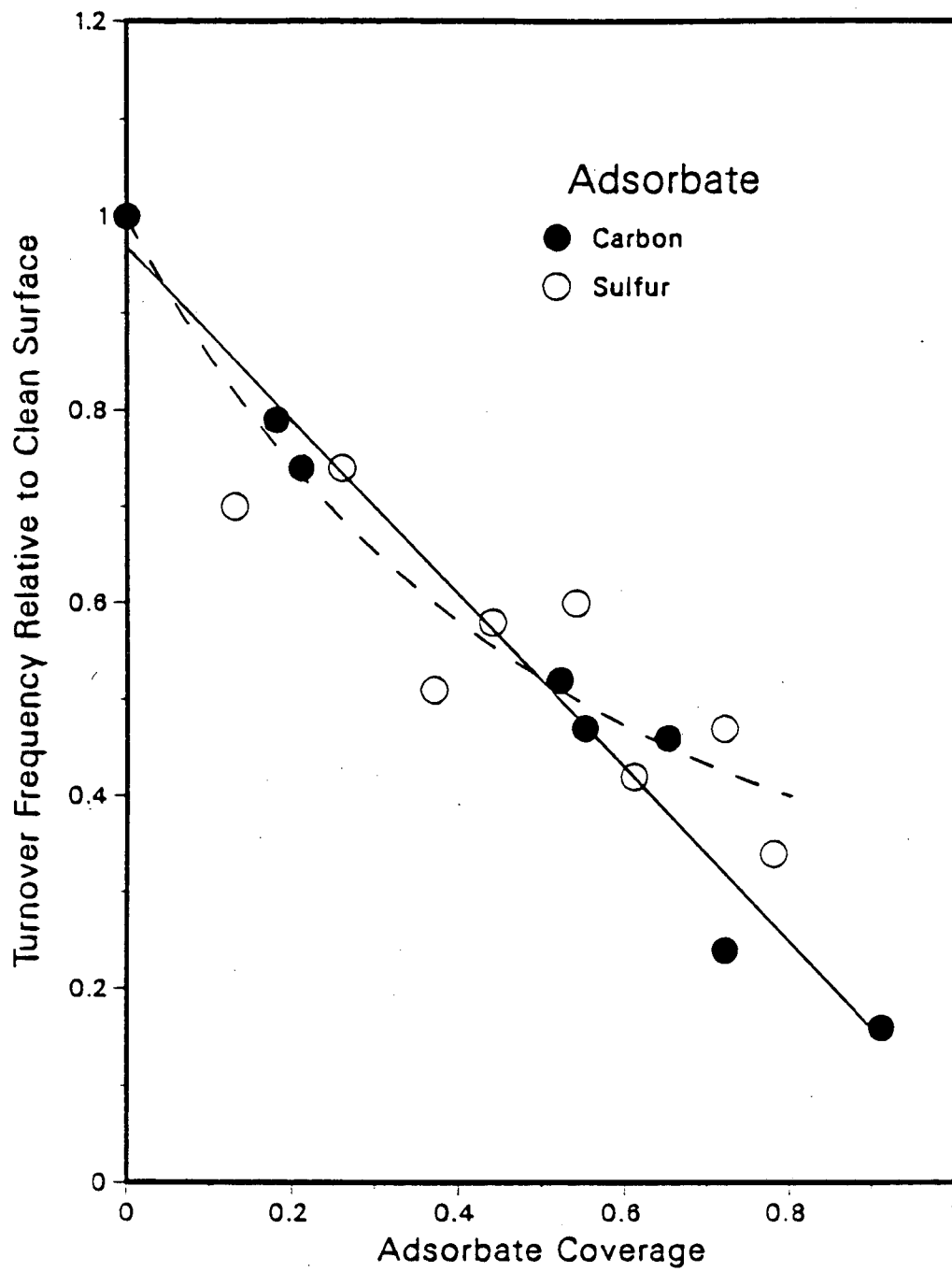
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Figure 5.



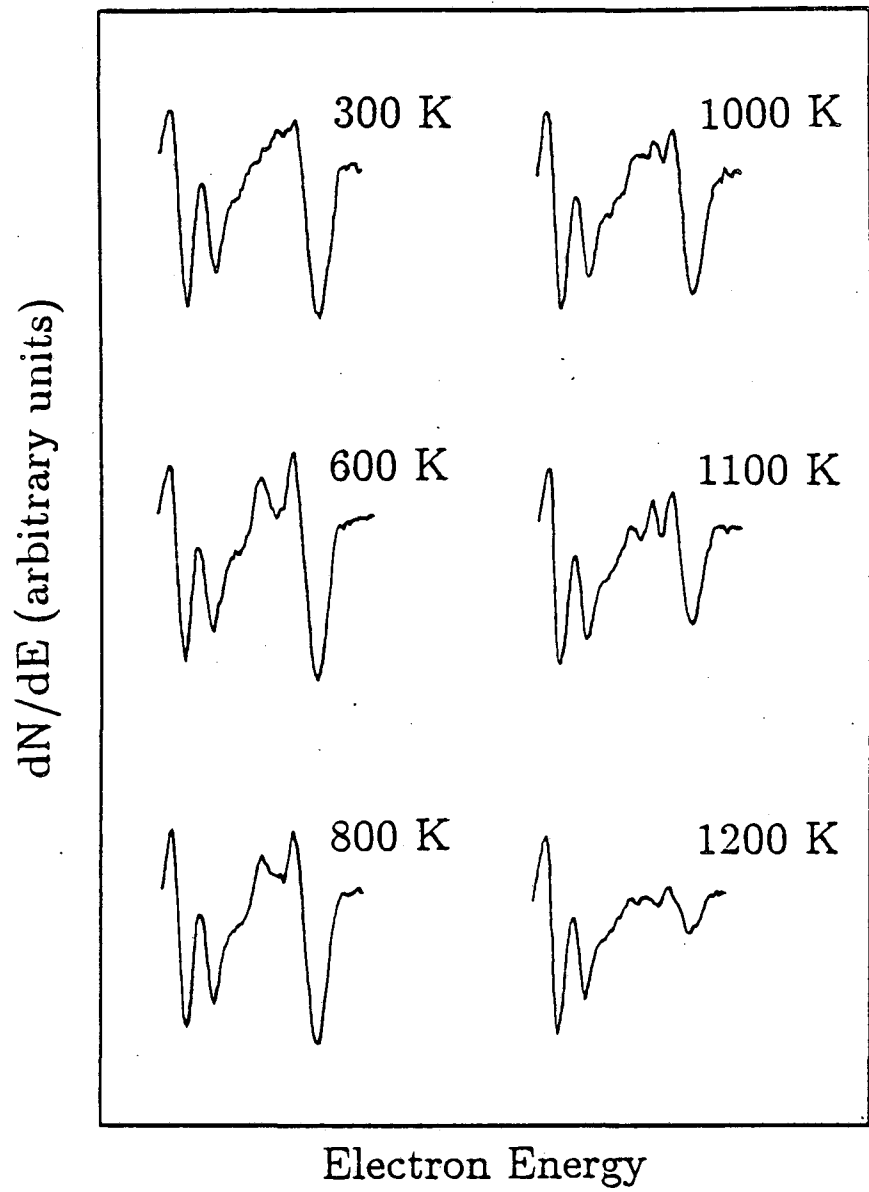
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Figure 6.



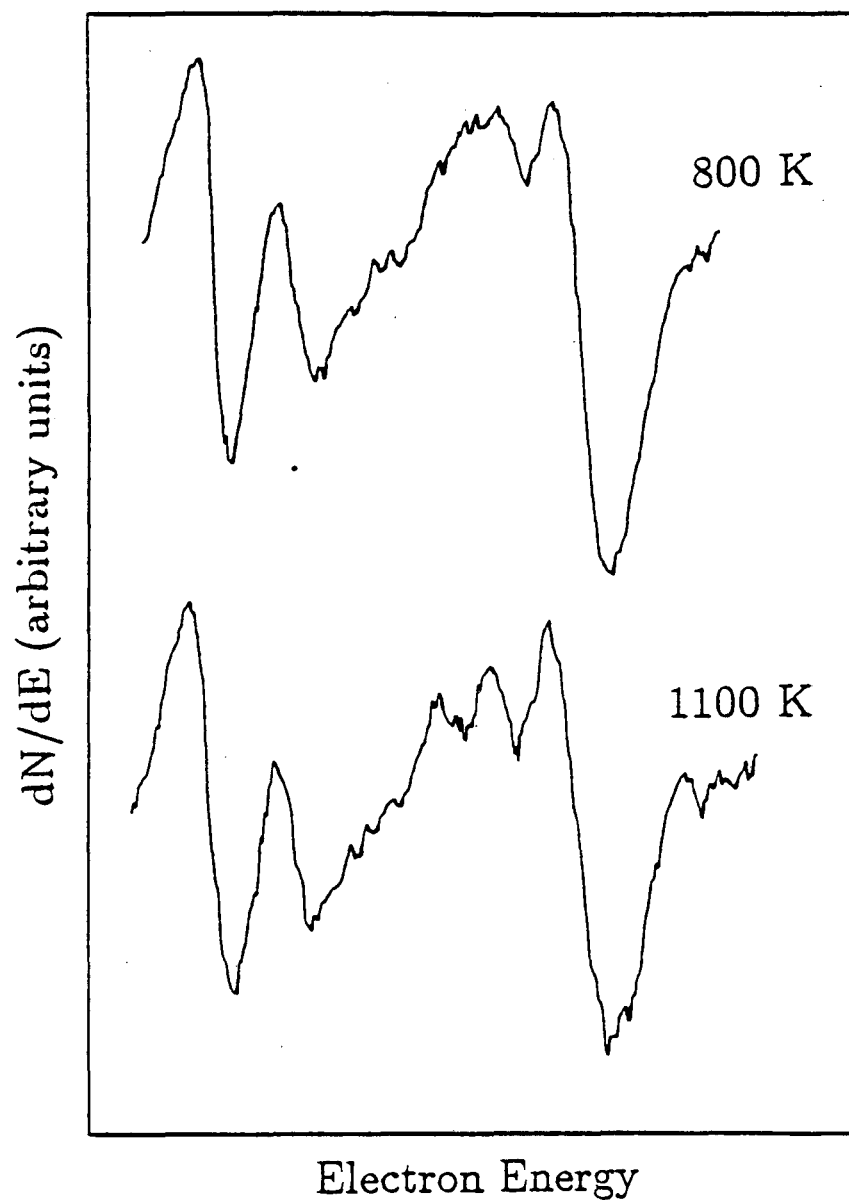
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Figure 7.



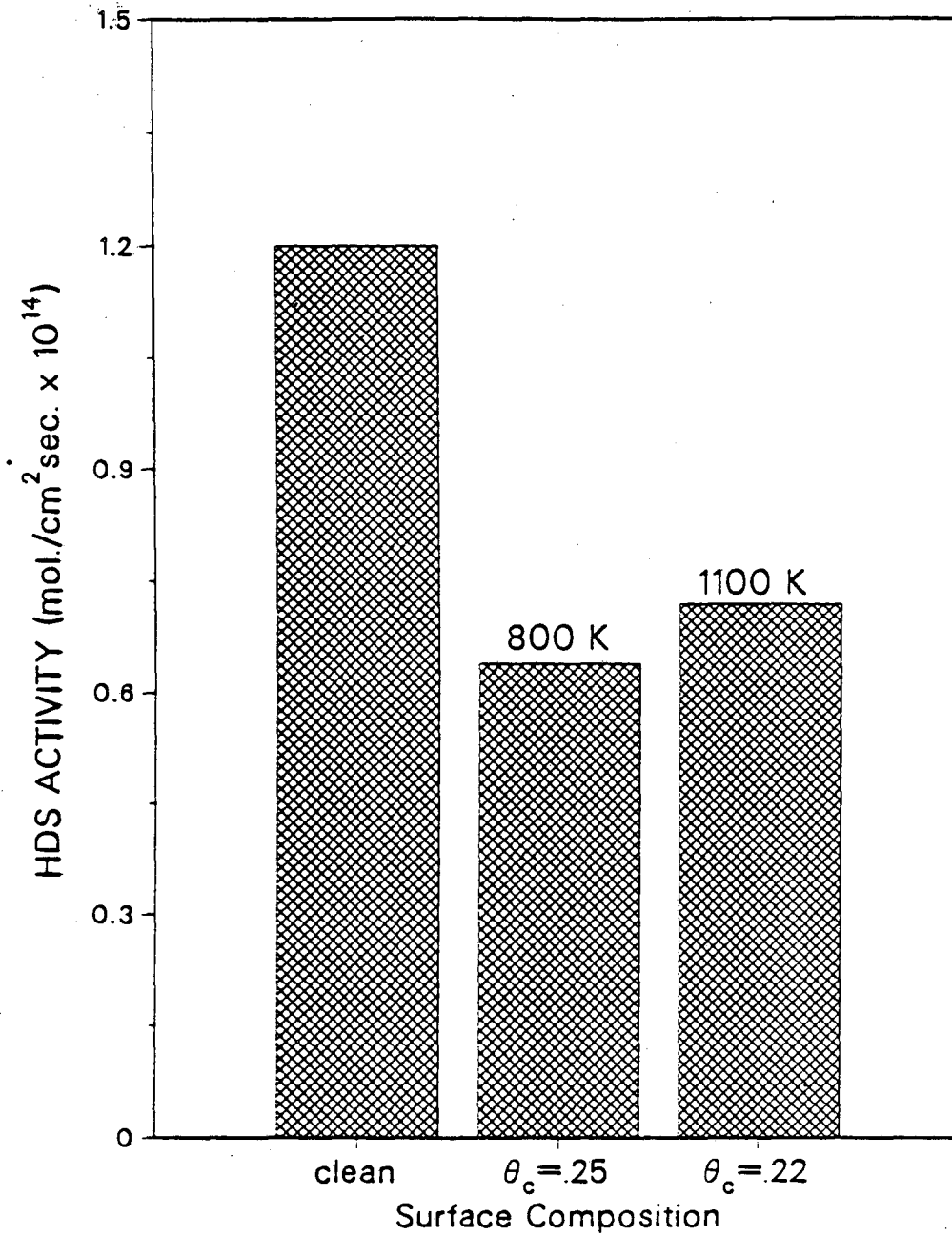
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Figure 8a.



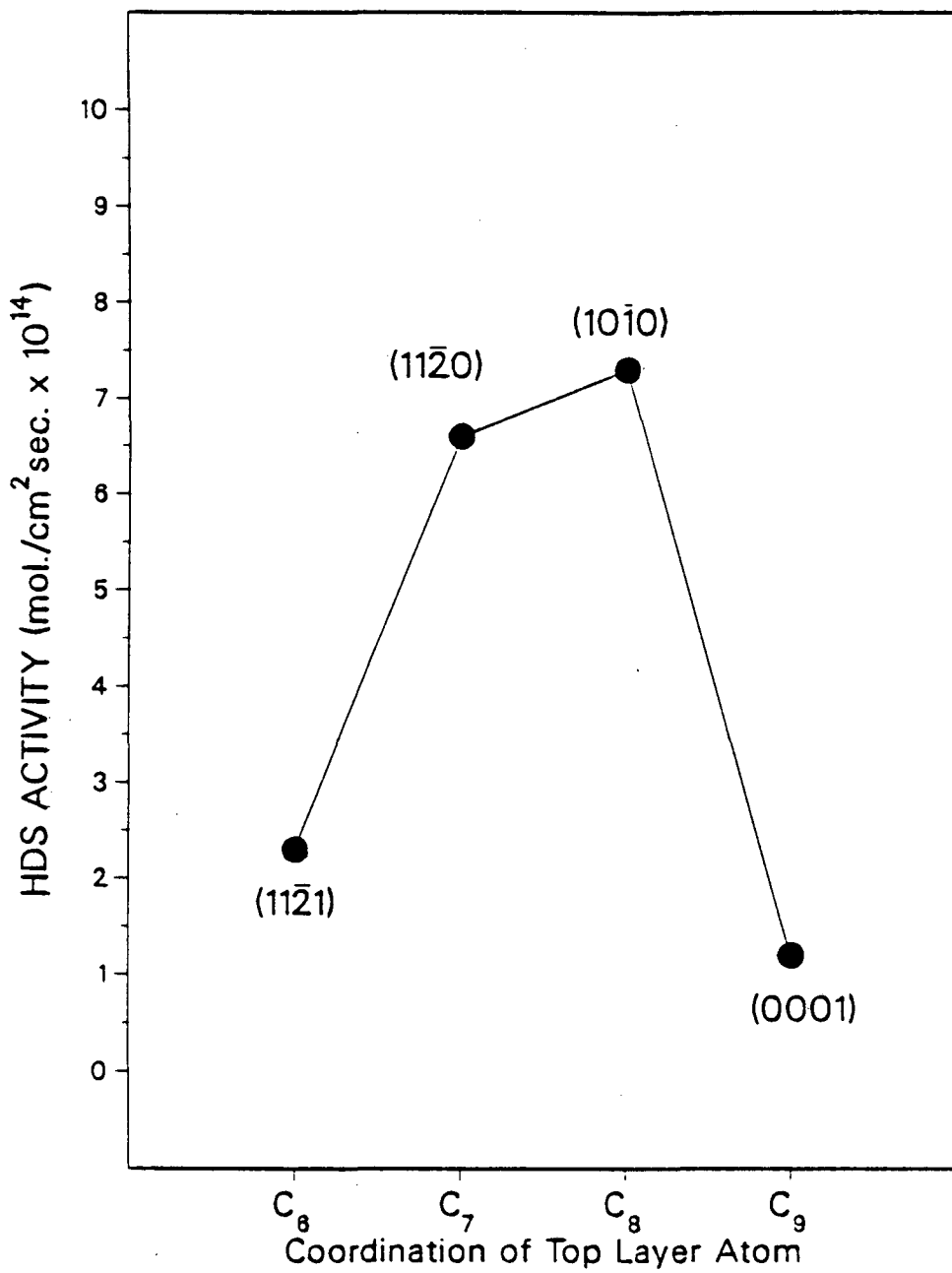
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Figure 8b.



XBL 884-1377

Figure 9.



XBL 879-3761

Figure 10.

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