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March 1990

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Surface Science Studies of Cobalt Overlayers on
Clean and Sulfur Covered Mo(100) Single
Crystal Surfaces

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Abstract

The interaction of cobalt with clean and sulfur covered Mo(100) surfaces was investigated with Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Temperature Programmed Desorption (TPD). On the clean surface, the deposition and subsequent annealing of one monolayer of cobalt resulted in the formation of an ordered overlayer with (1 x 1) surface structure. When cobalt was deposited on sulfur covered Mo(100) surfaces, after annealing the sulfur overlayer migrated on top of the cobalt layer. This topmost sulfur overlayer did not significantly affect the thermal desorption of cobalt from the Mo(100) surface. Various ordered structures of sulfur, cobalt and coadsorbed sulfur and cobalt were observed by LEED. A new surface structure showing (3 x 1) symmetry was observed when at least one monolayer of cobalt was deposited and annealed at 870 K on an ordered monolayer of sulfur on the Mo(100) surface. This surface structure was stable in ultrahigh vacuum up to 940 K.

1 Introduction

Cobalt promoted molybdenum disulfide hydrodesulfurization (HDS) catalysts are used in virtually every refinery in the world [1]. Molybdenum disulfide can itself be used as a catalyst but the addition of cobalt can increase the turnover frequency of this catalyst by a factor of 10 -30. Many different proposals have been offered to explain this promotional effect of cobalt [2]. Briefly, some of these suggestions include 1) an interaction of cobalt with the edges of the molybdenum disulfide crystallites to form the so called Co-Mo-S structure which has a higher turnover frequency [3 - 5], 2) an electronic interaction between cobalt and molybdenum resulting in an increased electron density in the Highest Occupied Molecular Orbital (HOMO) of molybdenum that beneficially influences the catalytic activity [1], and 3) an increased dispersion of Co₉S₈ (proposed to be the phase responsible for the higher turnover frequency) by molybdenum disulfide (proposed in this model to act as a support) [6]. In order to understand the effect of cobalt, it is necessary to explore the chemical and bonding

interactions between cobalt, molybdenum and sulfur.

It has been shown by infrared and volumetric studies of NO adsorption, that in cobalt promoted molybdenum disulfide catalysts, cobalt is located on the edges of the molybdenum disulfide crystallites. The higher turnover frequencies measured for these catalysts were attributed to the presence of cobalt on these molybdenum disulfide edges in so called Co-Mo-S structures [3]. Mössbauer Emission Spectroscopy has also been used to show the presence of other cobalt phases [4, 5]. Although there have been several studies on complex cobalt promoted molybdenum disulfide catalysts, there have been very few studies aimed at understanding the effect of cobalt on the more tractable model single crystal catalysts. For a review of recent catalytic studies, the reader is referred to reference [2].

Chianelli and others has shown by Scanning Auger Microscopy that when low levels of cobalt are incorporated into molybdenum disulfide single crystals, the cobalt tends to surface segregate onto edge planes, although some cobalt is present throughout the crystal [7]. These authors have also shown that the addition of cobalt increases the length of the edge planes or step height, though it decreases the number of edge planes compared to undoped molybdenum disulfide single crystals. Molybdenum single crystals have been shown to be extremely useful and appropriate as model catalysts for thiophene hydrodesulfurization [8 - 11]. However, there has been no previously reported studies of either the structural, electronic or catalytic effects of cobalt overlayers deposited on molybdenum single crystal surfaces.

In this study, the surface interactions between cobalt and/ or sulfur overlayers on a Mo(100) single crystal were investigated by condensing known amounts of cobalt and sulfur respectively on the molybdenum surface from the vapor phase. The growth of cobalt overlayers on the (100) face of molybdenum was studied with AES. The migration of sulfur on top of cobalt overlayers was also monitored with AES. The different symmetries of cobalt and/ or sulfur overlayers at different coverages were probed using LEED. TPD was used to determine the activation energy of desorption of cobalt from the clean and sulfur covered Mo(100) surfaces. Thiophene HDS reactions performed over these different surfaces to correlate the surface structure and

composition with the measured catalytic activity will be described in a later paper.

2 Experimental

Experiments were performed in an ultrahigh vacuum chamber equipped with a four grid retarding field analyser for AES and LEED. There was also a quadrupole mass spectrometer which was used for TPD as well as for monitoring the composition of the background gases in the chamber. The chamber also contained a high pressure isolation cell which could be pressurized with one atmosphere of reactant gases for in situ study of thiophene HDS over single crystal catalysts [8 - 11]. The residual gas pressure was 1×10^{-9} Torr. The Mo(100) single crystals had dimensions of about one square centimeter and were oriented to within 1° using Laue backscattering and polished using standard metallurgical techniques.

The crystal was spotwelded between two short pieces of twenty mil rhenium wires which were in turn spotwelded to 125 mil tantalum rods. The crystal was heated resistively up to 1900 K. The temperature of the crystal was monitored using a Platinum-Platinum 10% Rhodium thermocouple spotwelded to the top edge of the crystal. The major impurity in a new crystal was carbon which could be removed from the near surface region by repeated heating in 5×10^{-7} Torr of oxygen at 1600 K. The oxygen was then pumped away and the crystal was rapidly heated to 1900 K to remove surface oxygen. For subsequent removal of surface carbon and sulfur, 1×10^{-7} Torr of oxygen was used. Cobalt could be removed from the crystal by heating the sample to 1900 K.

Sulfur was deposited on the crystal using an electrochemical cell described previously [12]. Briefly, this electrochemical cell is composed of a solid silver iodide electrolyte sandwiched between silver and silver sulfide electrodes which form the cathode and anode respectively. The cell is heated to about 420 K to increase the conductivity of the solid electrolyte, and a voltage of 1.5 V is applied to cause the electrolytic decomposition of silver sulfide to S_2 . The sulfur source was positioned such that the sulfur beam was condensed on the molybdenum crystal surface.

Cobalt was deposited on the crystal using a source which consisted of a one millimeter wide strip of five mil cobalt foil wrapped around twenty mil tantalum wire. The source was heated by a DC power supply. The cobalt source was enclosed in a tantalum cone and equipped with a shutter which could be opened or closed to allow or prevent the vapor from reaching the crystal. The temperature of the cobalt vapor leaving the source was between 1150 and 1250 K. At these temperatures the vapor pressure of cobalt is in the 10^{-10} - 10^{-9} Torr region. As a result the chamber pressure did not rise noticeably during cobalt deposition. The cobalt source was degassed for several days using the current just below that required for sublimation. Before each use, the source was heated with the operating current for at least one hour. This allowed reproducible doses of cobalt to be evaporated and condensed on the surface of the crystal.

In order to determine coverages, the intensities of the molybdenum (MNN) 186 eV, sulfur (LMM) 152 eV, and cobalt (LMM) 775 eV Auger transitions were recorded using a primary voltage of 2 kV and a crystal current of 10 μ A. In the TPD experiments, a linear heating rate of 35 K/sec was used. The ionizer of the mass spectrometer was enclosed in a gold collimator. The orifice of the collimator was five millimeters in diameter which is smaller than the diameter of the samples used. The mass spectrometer was mounted on bellows and the orifice of the collimator was brought to within three millimeters of the center of the single crystal to minimize the detection of gases desorbing from the support wires or other parts of the manipulator.

3 The Structure of the Clean and Sulfur Covered Mo(100) Crystal Surface

Dynamical LEED analysis by Clarke [13] of the clean (100) face of molybdenum indicates that there is a surface layer contraction of $9.5 \pm 2.0\%$ and a contraction of 1% in the second interlayer spacing relative to the bulk interlayer spacings. In this dynamical LEED analysis neither lateral displacements nor interlayer relaxations beyond the second interlayer were allowed. A more recent dynamical LEED study

was conducted by Kelly et al in which both lateral displacements and relaxations up to the third interlayer were allowed [14]. These authors have suggested that atoms in the topmost layer are displaced $0.13 \pm .05$ Å away from the centers of the fourfold hollow sites of the second molybdenum layer. This asymmetric displacement destroys the perfect (1 x 1) symmetry of the clean surface. These authors have also found that the first three interlayer spacings of the clean Mo(100) surface have relaxations of $-6 \pm 1.5\%$, $2 \pm 2\%$ and $0.5 \pm 3\%$ relative to the bulk interlayer spacing.

The LEED structures of sulfur on the Mo(100) face have received considerable attention [15 -19]. The four commonly seen patterns are assigned to structures with sulfur coverages of 0.5 , 0.67 , 0.75 and 1.0 monolayer, but more realistically according to Gellman [20] are seen at coverages between 0.15 -0.55 , 0.65 -0.7 , 0.75 -0.9 , 0.99 -1.05 monolayers respectively. These structures show $c(2 \times 2)$, $\begin{vmatrix} 2 & -1 \\ 1 & 1 \end{vmatrix}$, $c(4 \times 2)$ and $p(2 \times 1)$ symmetry with respect to the underlying Mo(100) surface. With the exception of the LEED pattern for the overlayer with $c(2 \times 2)$ symmetry, in which only one domain is present, the other LEED patterns are due to contributions from two perpendicular domains. Only the lowest coverage sulfur structure has been solved by dynamical LEED analysis. According to Clarke [16], in the $c(2 \times 2)$ structure, sulfur atoms are adsorbed in the highly symmetric fourfold hollow sites on the Mo(100) surface, while according to Kelly and coworkers [14], the sulfur atoms are randomly displaced by 0.2 Å away from fourfold hollow sites and towards bridge sites.

A Scanning Tunneling Microscopy study of the high coverage (one monolayer) $p(2 \times 1)$ surface structure indicated that the sulfur atoms were adsorbed in asymmetric sites halfway between the fourfold hollow and bridge sites [21]. These results contrast with total energy calculations for one monolayer of sulfur on Mo(100). Total energy calculations favor a $p(2 \times 1)$ structure in which the sulfur atoms are adsorbed in highly symmetric bridge and hollow sites [22].

Gellman [20] has studied the thermal desorption of sulfur from a Mo(100) crystal surface. At sulfur coverages less than one monolayer only one desorption peak is seen from which the binding strength of sulfur on Mo(100) is estimated to be about 110 kcal/mol. At higher sulfur coverages, ie. at sulfur coverages greater than 0.67

monolayer, a poorly resolved peak between 1300 -1500 K appears as a shoulder on the main desorption peak at 1800 K. Therefore in the case of the higher sulfur covered structures, in addition to the high binding energy peak there is a lower binding energy peak in the range of 75 -90 kcal/mol.

In these experiments, disordered layers of sulfur were deposited on the crystal surface using the electrochemical sulfur source described in the experimental section, and the crystal was heated to varying temperatures to desorb a fraction of the sulfur and order the remaining sulfur. Coverages of 1 , 0.75 , 0.67 and 0.5 monolayer of sulfur were ordered on the Mo(100) surface by annealing at approximately 970, 1220, 1370 and 1620 K respectively. The LEED structures seen in this study as functions of sulfur coverage and annealing temperature agreed with those observed in the previous works mentioned.

4 Results

4.1 Characterization of the Surface Composition of Cobalt Overlayers on the Clean and Sulfur Covered Mo(100) Surface

4.1.1 Auger Studies of Cobalt Deposited on the Clean Mo(100) Surface

The cobalt coverage on a clean Mo(100) single crystal was determined by evaporating cobalt on the crystal at 300 K followed by annealing the crystal at 870 K for one minute. Cobalt grew in a dispersed and disordered fashion on the Mo(100) surface at 300 K and a diffuse background was observed by LEED. Upon annealing at 870 K an ordered (1 x 1) surface structure was observed by LEED and the first monolayer appeared to grow in a layer by layer fashion as documented by a break in the Auger uptake curve. From Fig.[1], the monolayer coverage is chosen to be where the rate of change in both the cobalt and molybdenum Auger ratios decrease significantly with increasing evaporation of cobalt. For cobalt coverages greater than one monolayer, the cobalt/ molybdenum Auger ratio decreased significantly after annealing. This decrease in the cobalt Auger intensity after annealing cobalt coverages

greater than one monolayer is attributed chiefly to the formation of three-dimensional cobalt islands at higher cobalt coverages (ie. $\Theta_{Co} \geq 1$ monolayer). Berlowitz and Goodman [23] have studied the growth of nickel overlayers on tungsten single crystals, a system reasonably similar to cobalt overlayers on molybdenum single crystals. They observed that only the first monolayer grew in a two-dimensional fashion on W(100) and W(110) surfaces following the deposition of nickel and subsequent annealing at 1200 K for one to two minutes. However, these authors found that above 1.3 monolayers, the nickel/ tungsten ratio decreased significantly upon annealing at 1200 K, but remained relatively constant with increasing deposition of nickel. This was attributed to the formation of three-dimensional nickel islands. Other workers [24 - 27] have also reported that for strained metal overlayer systems above a certain annealing temperature and one or two monolayer coverage three-dimensional growth occurs.

4.1.2 The Growth of Cobalt Overlayers on Mo(100)-c(4 x 2)S

The adsorption of different cobalt coverages on Mo(100)-c(4 x 2)S was studied. After the evaporation of more than three monolayers of cobalt at room temperature, the sulfur Auger intensity was decreased by less than 25 %. Observation of the LEED patterns showed that the unannealed surfaces were disordered. The crystal was then annealed at 870 K for one minute. Fig.[2] shows the sulfur, cobalt and molybdenum Auger ratios after annealing. From Fig.[2], it can be seen that with increasing cobalt coverage, the sulfur intensity after annealing has not appreciably decreased from the sulfur intensity before any cobalt was deposited on the surface. This indicates that either sulfur is migrating on top of the deposited cobalt overlayers or that cobalt is diffusing through the sulfur. In either case, the fact that the Auger intensity of the sulfur LMM transition does not decrease strongly indicates that sulfur remains in the topmost layer. The small decrease in the molybdenum Auger intensity is consistent with the decaying signal caused by adsorption of second and subsequent overlayers. The LEED pattern observed after annealing throughout the entire range of cobalt coverages studied indicated that a surface structure with (3 x 1) symmetry

was formed. This surface structure will be discussed in Sections 4.2.3 and 4.2.4.

4.2 The Structure of Cobalt Overlayers on Sulfur Covered Mo(100) as Determined by LEED

4.2.1 Cobalt Overlayers on Mo(100)-c(2 x 2)S

The adsorption of cobalt on Mo(100)-c(2 x 2)S was studied. From Fig.[3], it can be seen that the overlayer kept this symmetry even after evaporation of about four monolayers of cobalt. With increasing cobalt coverage, the intensity of the background increased somewhat, but the spots still remained fairly sharp. Even though the exact arrangement of cobalt and sulfur atoms on the Mo(100) surface cannot be determined from the LEED pattern, it is clear that ordered overlayers are formed.

4.2.2 Cobalt Overlayers on Mo(100)-c(4 x 2)S and Mo(100)-p(2 x 1)S

The adsorption of cobalt on Mo(100)-c(4 x 2)S and Mo(100)-p(2 x 1)S was studied. One monolayer of cobalt was evaporated on these sulfur covered surfaces and annealed at 870 K for one minute. Surface structures were formed showing (3 x 1) symmetry in both cases. Up to 4 monolayers of cobalt was evaporated on these surfaces and the overlayer formed maintained (3 x 1) symmetry. These LEED patterns are shown in Fig.[4, 5] With increasing coverage, the background intensity increased somewhat, but still the overlayer spots remained clearly visible. This indicates that above a certain sulfur coverage (approximately 0.75 monolayer) the subsequent deposition of cobalt followed by annealing causes the formation of a surface structure which has (3 x 1) symmetry.

4.2.3 Effect of Cobalt and Sulfur Coverage, Annealing Temperature and Air Exposure on the (3 x 1) Surface Structure

To form the surface structure which shows (3 x 1) symmetry at least one monolayer of cobalt had to be deposited on a Mo(100) single crystal covered with at least 0.75

monolayer of ordered sulfur. When less than one monolayer of cobalt was deposited and annealed on these higher sulfur covered surfaces, only structures showing diffuse (1×1) symmetry were observed by LEED. When cobalt was deposited first and the surface annealed at 870 K to order the cobalt, and then sulfur was deposited again only (1×1) spots in a diffuse background were observed.

A study of the effect of annealing temperature on this structure showed that the (3×1) spots started to appear dimly by 720 K. Using an annealing temperature of 770 K, the (3×1) spots became clearly visible and by 870 K, the annealing temperature generally used the (3×1) spots were about their sharpest. This implies that by 870 K, the surface structure showing (3×1) symmetry is well ordered. However, annealing at 940 K and higher, caused the disappearance of the (3×1) spots. Above 940 K, only (1×1) spots were observed. This indicates that the surface structure showing (3×1) symmetry is not stable above 940 K.

The stability of this surface structure to air exposure supports our claim that the topmost layer is composed of sulfur. Very little carbon and oxygen accumulated on the surface after exposure to one Torr of air at 300 K for sixteen hours in the high pressure cell. The Auger spectra before and after air exposure are shown in Fig. [6]. There was no noticeable decrease in the intensity or sharpness of the LEED spots after air exposure. After similar exposure of either the clean Mo(100) or a cobalt covered Mo(100) surface to air, significant amounts of graphite and oxygen are detected by Auger on these surfaces. It has been shown that when surfaces consisting of an ordered monolayer of sulfur on Mo(100) or an ordered half of a monolayer of sulfur on Re(0001) [28] are exposed to air, very little carbon and oxygen accumulated on these surfaces. This is because high coverages of sulfur passivate the (100) and (0001) surfaces of molybdenum and rhenium respectively. After exposure, the LEED patterns of these surfaces also remained sharp.

4.3 Temperature Programmed Desorption Studies of Cobalt Overlayers on Clean Mo(100) and Mo(100)-c(2 x 2)S

On the clean Mo(100) surface, the first monolayer of cobalt desorbed with first order kinetics as shown in Fig.[7]. The binding energy of cobalt on Mo(100) was determined to be about 87.5 kcal/mol. Above one monolayer, the temperature at the maximum rate of desorption of cobalt (T_p) increased and zero order kinetics were observed. On a Mo(100) surface covered with 0.5 monolayer of sulfur, the desorption characteristics of cobalt were only slightly different. At submonolayer coverages, the temperature at the maximum rate of desorption decreased slightly from 1326 K at a cobalt coverage of 0.3 monolayer, to 1309 K at a cobalt coverage of 0.5 monolayer. Then T_p increased to 1326 K at a full monolayer coverage of cobalt. This is shown in Fig.[8]. Using the value for the temperature at the maximum rate of desorption at a cobalt coverage of one-third of a monolayer, the activation energy of desorption of cobalt from the sulfur covered Mo(100) surface is calculated to be about 88.4 kcal/mol. Again, above one monolayer coverage of cobalt, the temperature at the maximum rate of desorption increased with increasing cobalt coverage in a very similar manner to the clean surface. At two monolayers of cobalt the temperature at the maximum rate of desorption was 1348 K on the clean surface while it was 1346 K on the sulfur covered surface. This difference is considered to be within experimental error.

Unfortunately, the interaction of cobalt with the structurally more interesting high sulfur covered surfaces, where the (3 x 1) surface structure is formed, could not be studied using TPD because as stated in Section 3.1, at sulfur coverages greater than two-thirds of a monolayer, sulfur begins to desorb from Mo(100) at a lower temperature than cobalt desorbs. Therefore in the process of heating to desorb the cobalt some sulfur would desorb decreasing the sulfur coverage on the surface.

5 Discussion

The important experimental findings of this work that shed light on the interaction of cobalt with the clean and sulfur covered Mo(100) surface are the following:

- 1) Upon annealing at 870 K, the first monolayer of cobalt grew with (1×1) surface symmetry on the Mo(100) substrate. At higher cobalt coverages, three-dimensional islands were formed upon annealing.
- 2) The structure and symmetry of the ordered overlayer formed when cobalt was deposited on ordered sulfur covered Mo(100) surfaces depended on the initial sulfur coverage. Sulfur was always present in the topmost layer.

5.1 The Growth of Cobalt Overlayers on the Clean Mo(100) Surface

The deposition of atomic cobalt on the clean molybdenum surface at room temperature resulted in a disordered overlayer as observed by LEED. This indicated that at room temperature there was insufficient mobility for the surface diffusion and subsequent ordering of cobalt into a strained overlayer. After annealing at 870 K for one minute, a surface structure with (1×1) symmetry was observed with LEED. If the molybdenum surface is considered to be unreconstructed, this growth pattern would suggest a substantial strain in the first cobalt monolayer, and a cobalt monolayer density that is about 36 % less than the corresponding monolayer density for either the Co(100) or Co(111) crystal faces. A detailed LEED I(V) analysis will be performed to determine the structure of the first cobalt monolayer on the Mo(100) surface. The additional deposition and annealing of cobalt overlayers on the surface resulted in the formation of three-dimensional islands.

It has been seen that for strained overlayers, layer-by-layer growth can occur up to a certain critical thickness. Beyond that thickness, interfacial misfit dislocations appear which result in cluster formation [29]. Bauer [30] has also demonstrated that if the deposited overlayer has a larger surface free energy than the substrate, the overlayer will tend to grow in a three-dimensional fashion. However if the deposited overlayer has a lower surface free energy, then layer-by-layer growth is favored. The reported surface free energy of cobalt at the melting point is lower than the surface free energy of molybdenum at the melting point [31]. This suggest that it is likely

that cobalt will grow in a layer-by-layer fashion on molybdenum, and this is indeed what we find on the (100) surface.

The growth of face-centered cubic metals on body-centered cubic substrates has been studied previously. Wang and coworkers [32] found by LEED intensity analysis that metastable, highly defective copper films grew with body-centered cubic symmetry on the Fe(001) surface at room temperature. The films had nearly the same lattice parameter as the Fe(001) surface.

As mentioned in Section 4.1.1, we have found that the growth of cobalt overlayers on the Mo(100) surface has similarities to the growth of nickel overlayers on tungsten single crystals that Berlowitz and Goodman observed. It has been found [33] that when copper was deposited on Ru(0001) at 100 K, the copper overlayer was dispersed and disordered. However upon annealing at 300 K, ordered two-dimensional islands pseudomorphic with the substrate formed. Novel copper-ruthenium interface and copper surface states were identified using angle-resolved photoemission studies. The dehydrogenation reaction of cyclohexane was increased by about ten-fold at a copper coverage close to three-quarters of a monolayer on the Ru(0001) surface. It is clear that strained metal overlayer systems can have markedly different chemical and structural properties. The effect of strained cobalt overlayers on the thiophene hydrodesulfurization reactivity over molybdenum single crystals is currently being investigated in our laboratory.

5.2 The Growth of Cobalt Overlayers on Sulfur Covered Mo(100) Surfaces

We have found that ordered surface structures were formed when cobalt was deposited and annealed on sulfur covered Mo(100) surfaces. The sulfur Auger intensity did not decrease significantly after the deposition of multilayers of cobalt at room temperature. This indicated that even at room temperature there was sufficient mobility for cobalt to diffuse under the sulfur overlayer. After annealing to form an ordered surface structure, the sulfur Auger intensity was identical within experimental error (15 %) to the sulfur Auger intensity before the deposition of cobalt. At

the annealing temperature of 870 K used, cobalt did not desorb from the sample. The fact that ordered structures were seen after multilayers of cobalt were deposited on the sulfur covered molybdenum surface may indicate that the underlying cobalt overlayers were also well ordered. This contrasts with the clean Mo(100) surface in which case cobalt multilayers clearly formed three-dimensional clusters.

The activation energies of desorption obtained from TPD studies indicate that at sulfur coverages lower than two-thirds of a monolayer, the molybdenum-sulfur bond is stronger than the molybdenum-cobalt bond. At higher sulfur coverages, the activation energies of desorption of cobalt and sulfur are comparable. Therefore it is difficult to explain the surface migration of sulfur using bond strength arguments. However, the surface free energy of sulfur is lower than that of either cobalt or molybdenum and so a structure in which sulfur is in the topmost layer is compatible with surface free energy considerations.

6 Conclusion

We have shown that: 1) A surface structure with $p(1 \times 1)$ symmetry was formed by the deposition and annealing of the first cobalt monolayer on the Mo(100) surface. 2) When cobalt was deposited on Mo(100)- $c(2 \times 2)$ S and the crystal was annealed, the $c(2 \times 2)$ symmetry persisted up to the deposition of four monolayers of cobalt. 3) When cobalt was deposited and annealed on a surface covered with 0.75 or 1.0 monolayer of sulfur, the symmetry of the surface structure was changed from $c(4 \times 2)$ and $p(2 \times 1)$ respectively to (3×1) . This surface structure was stable in vacuum up to 940 K. 4) In the overlayer structures mentioned above, following annealing, sulfur was located in the topmost layer and was responsible for the stability of the (3×1) surface structure towards air exposure. 5) Finally, this topmost sulfur overlayer did not significantly affect the thermal desorption of cobalt from the molybdenum(100) surface.

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Figure Captions

Figure 1. Uptake Curve of cobalt on Mo(100). After each deposition the crystal was annealed at 870 K for one minute.

Figure 2. Intensities of Mo (MNN) 186 eV, S (LMM) 152 eV, and Co (LMM) 775 eV Auger transitions vs cobalt deposition time. After each deposition the crystal was annealed at 870 K for one minute. This plot shows that the sulfur intensity does not decrease after deposition and annealing of the cobalt overlayers indicating that sulfur is migrating on top of the cobalt layers.

Figure 3. LEED patterns of cobalt on Mo(100) covered with an ordered one-half monolayer of sulfur (annealed at 870 K).

Figure 4. LEED patterns of cobalt on sulfur covered Mo(100), ($\Theta_S = 0.75$ ML), showing that upon evaporation of cobalt the symmetry of the overlayer is changed from $c(4 \times 2)$ to (3×1) (annealed at 870 K).

Figure 5. LEED patterns of cobalt on sulfur covered Mo(100), ($\Theta_S = 1.0$ ML) (annealed at 870 K).

Figure 6. Auger Spectra of Surface Structure with (3×1) Symmetry before and after air exposure. The spectra shows that little carbon and oxygen have accumulated on the surface.

Figure 7. TPD spectra of cobalt from the Mo(100) surface showing that the first monolayer of cobalt desorbs with first order kinetics.

Figure 8. TPD spectra of cobalt from sulfur covered Mo(100), ($\Theta_S = 0.5$ ML).

Uptake Curve of Cobalt on Mo(100)

Deposition of Cobalt on Sulfur Covered Mo(100), $\Theta_S = 0.75\text{ML}$

Fig. 1

XBL 907-2341

Fig. 2

LEED Structure Formed by the Interaction of
Cobalt With 0.5 ML of Sulfur on Mo(100)

Mo(100) + S
 $\Theta_S \approx 0.5$ ML
140 eV

Mo(100) + S + Co
 $\Theta_S \approx 0.5$ ML
 $\Theta_{Co} \approx 1$ ML (deposited)
140 eV

$\Theta_S \approx 0.5$ ML
 $\Theta_{Co} \approx 4$ ML (deposited)
140 eV

Fig. 3

LEED Structure Formed by the Interaction of
Cobalt With 0.75 ML of Sulfur on Mo(100)

Mo(100) + S
 $\Theta_S \approx 0.75$ ML S
120 eV

Mo(100) + S + Co
 $\Theta_S \approx 0.75$ ML
 $\Theta_{Co} \approx 1.0$ ML (*deposited*)
100 eV

Fig. 4

LEED Structure Formed by the Interaction of
Cobalt With 1.0 ML of Sulfur on Mo(100)

Mo(100) + S
 $\Theta_S \approx 1.0$ ML
115 eV

Mo(100) + S + Co
 $\Theta_S \approx 1.0$ ML
 $\Theta_{Co} \approx 1.0$ ML
115 eV

Fig. 5

Auger Spectra of (3 x 1) Surface Structure Before and After Air Exposure

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Fig. 6

Fig. 7

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Fig. 8

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