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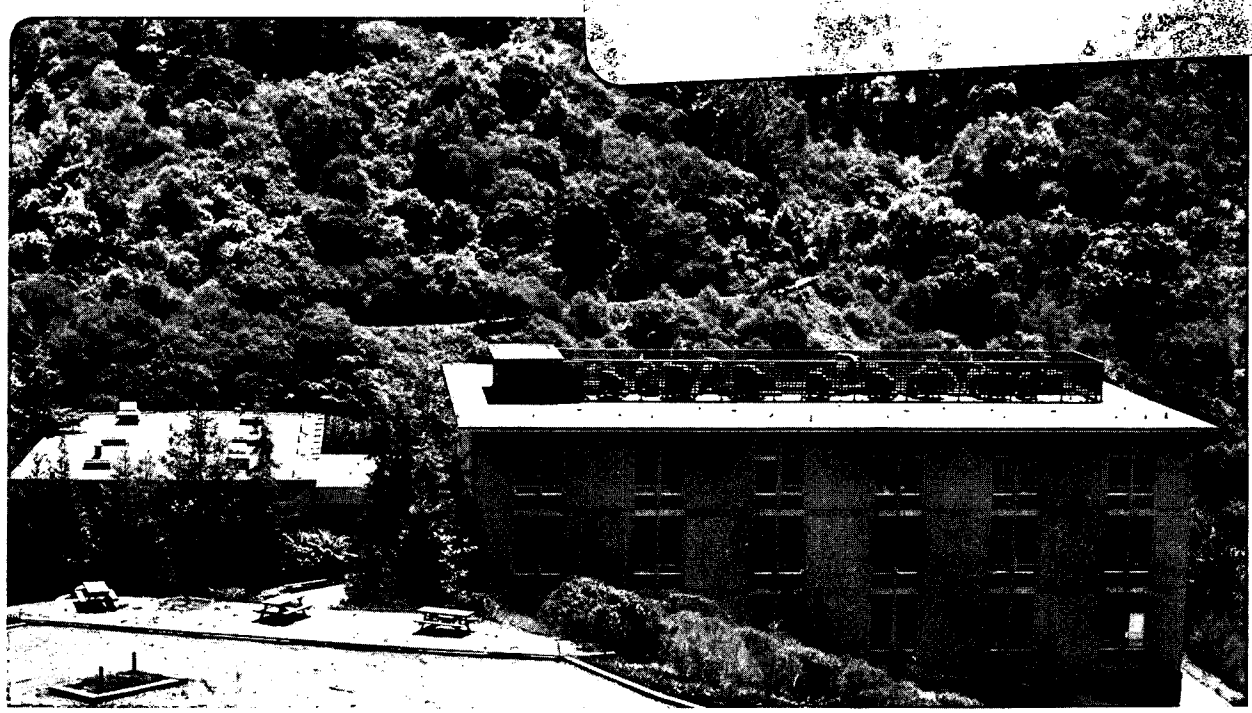

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A RADIOTRACER (^{14}C) AND CATALYTIC STUDY OF THIOPHENE HYDRODESULFURIZATION ON THE CLEAN AND CARBIDED Mo(1OO) SINGLE CRYSTAL SURFACE

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ABSTRACT

The role of adsorbed carbon overlayers and possible product poisoning (H_2S and cis-2-butene) in the thiophene hydrodesulfurization (HDS) reaction over Mo(1OO) single crystal surfaces was investigated. Using the β^- emitting ^{14}C isotope, it was shown that adsorbed carbon remains on the Mo(1OO) surface after many thiophene turnovers (TN $\approx 10^3$). HDS activities measured for carbided surfaces were found to be identical to that of initially clean Mo(1OO) single crystals, suggesting that the active catalyst surface is carbon covered. Deactivation of the single crystal catalysts was caused by adsorption of H_2S onto the active HDS sites. Removal of the H_2S by evacuation of the reaction mixture readily regenerated the catalyst's activity towards a fresh mixture of thiophene and hydrogen. The product cis-2-butene had no effect on the activity of the catalysts.

1 INTRODUCTION

Treatment of crude oil with hydrogen over Co-Mo/Al_2O_3 catalysts to remove sulfur impurities has been an important process in the petroleum industry for over fifty years, yet the complexity of these catalysts has made it difficult to understand the surface chemistry of the hydrodesulfurization (HDS) reaction. The aim of our research is to gain a molecular level understanding of HDS by investigating thiophene hydrodesulfurization over molybdenum single crystal surfaces. Previous work in our laboratory has looked at the structure and bonding of thiophene and C_4 hydrocarbons on clean, sulfided, and carbided Mo(1OO) single crystals[1,2] and catalytic HDS of thiophene over clean and sulfided Mo(1OO) surfaces.[3,4] The product distribuition for thiophene HDS over a Mo(100) single crystal was found to be similar to that over a powdered MoS_2 catalyst. This suggests that a Mo(100) single crystal catalyst can be used to model the active sites on an MoS_2 based catalyst, believed to be anion vacancies at the edges of MoS_2 crystallites. The role of adsorbed sulfur in thiophene HDS was explored using overlayers of radiotracer ^{35}S on the Mo(1OO)

surface.[5] It was found that atomic sulfur adsorbed on the Mo(1OO) surface in ultrahigh vacuum (UHV) lowered the rate of thiophene HDS relative to an initially clean surface. Furthermore, the rate of removal of sulfur from the Mo(1OO) surface during thiophene HDS was measured to be two orders of magnitude lower than the thiophene turnover frequency. These results show that sulfur removed from thiophene during desulfurization is not deposited in the same binding sites as sulfur adsorbed on the surface in UHV. Dynamical LEED analysis of a Mo(1OO) surface covered with one-half monolayer of sulfur indicates that sulfur atoms are adsorbed in four-fold hollow sites at this coverage.[6] Apparently, the adsorption of sulfur in four-fold hollow sites during thiophene HDS does not occur, and the initially clean surface maintains an activity higher than the sulfur covered surfaces prepared in ultrahigh vacuum. Thermal desorption,[7] XPS and UPS,[8] and radiotracer ^{35}S studies[5] show that as sulfur coverage exceeds two-thirds of a monolayer, sulfur atoms begin to occupy lower energy binding sites, believed to be bridge sites. Sulfur adsorbed at coverages above two-thirds monolayer does not further decrease the HDS activity of the catalyst suggesting that it is removed from the surface during reaction. However, the rate of hydrogenation of sulfur adsorbed in bridge sites is still too slow for deposition of sulfur into these sites to be an intermediate step in thiophene HDS.

High resolution electron energy loss spectroscopy experiments[9] investigating thiophene adsorption on clean Mo(1OO) surfaces show that decomposition and dehydrogenation occurs by 69OK, leaving adsorbed sulfur and carbon on the surface. This suggests that the surface of the Mo(1OO) catalyst is covered with a mixed monolayer of adsorbed carbon, hydrocarbon fragments (C_xH_y) and adsorbed sulfur atoms. Angularly resolved ion scattering from a carbided Mo(1OO) surface indicates that carbon atoms adsorb in four-fold hollow sites[1O]. Only recently has work been initiated to investigate carburized molybdenum catalysts; a catalytic study of thiophene HDS over an unsupported molybdenum carbide powder showed that this catalyst and a sulfided Mo/Al_2O_3 catalyst had almost identical initial activities.[11] The activity of the Mo_2C catalyst decreased steadily over a six hour period. Following reaction, the catalyst was treated with hydrogen at 77OK after

which the catalyst was found to contain an amount of sulfur corresponding to one-half the total Mo surface atoms. This tightly bound sulfur may be responsible for the decreasing activity of the catalyst as was observed in our single crystal studies.

The results described above motivated the research reported here in which thiophene HDS over initially clean and carbon covered Mo(100) single crystal surfaces was investigated. Experiments were preformed to measure HDS turnover frequencies for surfaces with different initial carbon coverages and to determine the residence time for carbon adsorbed on Mo(100) single crystals in pure hydrogen, butadiene and hydrogen, and in the thiophene HDS mixture. The residence time of adsorbed carbon on the Mo(100) surface was measured using the β^- emitting ^{14}C isotope which was deposited on the clean surface by decomposition of $^{14}C_2H_4$. Lastly, the influence of adsorbed sulfur and the products H_2S and cis-2-butene on thiophene HDS activity was determined to help understand the mechanism of catalyst deactivation.

2 EXPERIMENTAL

The experiments reported were performed in a stainless steel, ultrahigh vacuum chamber equipped with a high pressure isolation cell for catalytic reactions, and is described in detail elsewhere.[1] The system was pumped with an ion pump and a base pressure of 1.0×10^{-9} Torr (1 Torr = 133.3 N/m^2) was achieved after bake-out. The chamber is outfitted with a four grid, retarding field analyzer for Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The Mo(100) single crystal of thickness 0.5 mm was cut by spark erosion from a molybdenum rod obtained from the Materials Research Corporation. It was oriented to within 1° using Laue back diffraction and polished to a mirror finish using standard metallurgical techniques. The crystal temperature was measured using a platinum-platinum 10% rhodium thermocouple spotwelded to the edge of the crystal. The crystal was mounted between 0.125 inch tantalum rods and heated resistively over the temperature range 300-1900K. The surface was characterized in UHV before reactions

using AES and LEED. Overlayers of carbon were prepared by dosing the surface at room temperature with C_2H_4 through a stainless steel leak valve, followed by heating to 700K. A dosing tube extends from the leak valve to the sample and a dose of 1×10^{-8} Torr of C_2H_4 for sixty seconds was sufficient to give a carbon coverage of about 0.85 monolayer (θ_c = 0.85 ML). To obtain higher coverages, it was necessary to thermally decompose C_2H_4 on the surface and this was achieved by dosing at 1×10^{-8} Torr C_2H_4 for 30 seconds at 1100K. Carbon coverage was determined using the previously observed LEED patterns for carbon on the Mo(100) surface: c(2×2), $\left|\begin{smallmatrix} 2 & \bar{1} \\ 1 & 1 \end{smallmatrix}\right|$, and p(1×1) at respective coverages of 0.50, 0.67, and 1.0 monolayer.[12] The peak heights of the AES transitions C(272) and Mo(221) were measured at each coverage and a curve drawn through a plot of carbon coverage versus the AES peak height ratio C(272)/Mo(221). All carbon coverages were determined using this plot and are believed to be accurate within 15% of a monolayer. The carbidic nature of the carbon was confirmed by the low energy fine structure of the carbon 272 volt AES peak.[13] After determining the carbon coverage, the Mo single crystal was enclosed in the high pressure isolation cell, the reactor loop pressurized with reactant gases (P_{Th} = 1-5 Torr, P_{H2} = 100-780 Torr) and the gases circulated for thirty minutes to insure mixing. When the influence of products (H_2S, cis-2-butene) on initial catalyst activity was investigated, the product was leaked into the reactor loop prior to pressurizing with thiophene and hydrogen. Several experiments were also performed on sulfur covered Mo(100) surfaces and surfaces in which sulfur was deposited on top of a carburized Mo(100) single crystal. Sulfur was deposited on the single crystal using an electrochemical sulfur source described elsewhere.[14] The sulfur covered surfaces were prepared by depositing approximately 1 ML of sulfur onto the clean Mo(100) surface followed by annealling to 1250K to produce the c(4×2) LEED pattern which has been shown to correspond to a sulfur coverage of 0.75 ML.[15] The sulfur on carburized Mo(100) surfaces were prepared by first thermally cracking C_2H_4 as described earlier to produce a p(1×1) Mo(100)-C LEED pattern (θ_c = 1.0 ML), followed by deposition of sulfur onto this surface and annealling to 613K. The sulfur coverage of 0.75 ML is approximate and was

determined using the AES calibration for sulfur on the Mo(100) surface. The reactor loop consists of one-quarter inch stainless steel tube and is connected through an inlet and outlet to the isolation cell. Gases are circulated in the reactor loop using a small micropump. Gas samples were injected into a gas chromatograph at 15 minute intervals during reaction and the products separated on a 19% picric acid on carbowax column and detected with a flame ionization detector. Catalyst activities were calculated using the product accumulation data from the first two hours of reaction.

To determine the composition of initially clean Mo(100) surfaces during thiophene HDS reactions, AES spectra were recorded of the catalyst surface after annealling the single crystal to 613K in the reaction mixture, and, after 90 minutes of reaction at 613K. In each case the isolation cell was evacuated for two hours before opening to the UHV environment. It is possible that the surface composition of the catalyst changes during pump-down due to adsorption of molecules from the gas phase onto the surface.

The ultrahigh vacuum system was equipped with a solid state β^- detector for measuring β^- emission from ^{14}C adsorbed on the surface of the Mo(100) single crystal. The detector and the data collection system have been described previously.[16] The detection system consists of an Ortec silicon surface barrier detector recessed in a liquid nitrogen cooled copper jacket and connected to a rotatable feedthrough. The detector is located in the center of the chamber and could be reproducibly positioned in front of the Mo(100) single crystal for counting ^{14}C β^- emission, or rotated away from the crystal for AES and LEED experiments as well as reactions performed in the high pressure isolation cell. A schematic diagram of the β^- detector and counting system is shown in Figure 1. Overlayers of ^{14}C were prepared by decomposition of $^{14}C_2H_4$ on the clean Mo(100) crystal. The labelled ethylene was purchased from the Amersham Corporation and had a specific activity of 100 mCi/mmole and a radiochemical purity of 98.7%. Coverages of ^{14}C up to 0.85 monolayer were prepared by dosing at room temperature (1×10^{-8} Torr, 60 sec.) followed by a flash to 700K. The single crystal was not heated above

700K to minimize diffusion of ^{14}C into the bulk of the crystal. Following characterization of the ^{14}C overlayer with AES and LEED, the initial ^{14}C coverage was determined by measuring the β^- emission from the crystal surface. The single crystal was enclosed in the high pressure isolation cell and the reaction loop was pressurized with gases as described before. The crystal was heated to the reaction temperature for an interval of 5-60 minutes and then cooled to room temperature in the presence of the gas mixture. The isolation cell was evacuated to a pressure $\leq 10^{-3}$ Torr prior to opening to the UHV environment. Upon opening the isolation cell, the ^{14}C coverage was determined and the reaction procedure repeated with either the existing surface or a newly prepared surface.

3 RESULTS

3.1 Thiophene HDS over initially clean and carbided Mo(100) Surfaces

A steady state thiophene HDS rate of 0.13 ± 0.02 molecules/site·sec was measured for the initially clean Mo(100) surface under the following conditions: $P_{Th} = 3.0$ Torr, $P_{H2} = 780$ Torr, T = 613K. This turnover frequency agrees within experimental uncertainty with results reported earlier.[4] An AES spectrum of a clean Mo(100) surface exposed to the reaction mixture at reaction temperature showed the surface to be covered with predominantly carbon ($\theta_c \approx 0.8$ ML, $\theta_s \approx 0.2$ ML). The fine structure of the c(272) peak indicates that the carbon is carbidic. After a 90 minute reaction, the carbon coverage is high ($\theta_c \approx 0.7$ ML) and the sulfur coverage has increased to $\theta_s \approx 0.9$ ML. This sulfur does not block active HDS sites suggesting that it is weakly adsorbed or adsorbs after reaction during evacuation of the isolation cell .

Figure 2 is a plot of thiophene HDS activity as a function of initial carbon coverage. As will be discussed shortly, carbon adsorbed on the Mo(100) surface in UHV remains on the surface during HDS. Adsorbed carbon atoms, bound to

the metal in four-fold hollow sites, do not block the HDS activity of the Mo(100) catalyst. The product distribution for thiophene HDS over carbided Mo(100) surfaces is similar to the distribution obtained over an initially clean surface which has been reported earlier.[4] Deactivation of the carbided catalysts occurred at similar conversions as for the initially clean surface as well. In a closed loop batch reactor, deactivation of an initially clean Mo(100) single crystal begins after approximately 90 minutes and is complete after about 12 hours.

3.2 Hydrogenation of Adsorbed Carbon on Mo(100) Surfaces

Figure 3 shows the decrease in ^{14}C coverage as a function of reaction time in hydrogen at two temperatures. Reactions were not carried out to times longer than fifteen minutes in pure hydrogen due to the gradual adsorption of sulfur and carbon onto the Mo single crystal from the reactor loop. After 15 minutes of reaction at 613K, the carbon coverage was reduced to 65% of its initial value of 0.85 ML. The time scale for carbon hydrogenation is much longer than for thiophene HDS over the carbided M(100) surface; over 100 thiophene molecules are desulfurized per surface Mo atom in 15 minutes at this temperature. The hydrogenation of adsorbed carbon on the Mo(100) surface was found to be independent of hydrogen pressure over the range 100-780 Torr.

3.3 Removal of ^{14}C during Thiophene HDS and Butadiene Hydrogenation on the Mo(100) Surface

In order to show that adsorbed carbon does not affect the HDS activity of a Mo(100) catalyst relative to an initially clean single crystal, it is necessary to show that carbon remains on the catalyst surface during reaction. The removal of adsorbed ^{14}C from the Mo(100) surface was measured in typical HDS conditions (P_{Th} = 3.0 Torr, P_{H2} = 780 Torr, T = 613K). Following an initial drop in ^{14}C

coverage from 0.80 ML to 0.68 ML, the ^{14}C coverage decreases very slowly to 0.63 ML after 90 minutes of reaction. Over a 90 minute reaction period, the thiophene turnover number is in excess of 700. Clearly, carbon adsorbed on the Mo(100) surface in UHV remains on the surface during reaction, but does not block the active thiophene HDS sites.

Butadiene has been shown to be an intermediate in thiophene HDS over the Mo(100) surface.[4] It is of interest to investigate the influence of the hydrocarbons produced in thiophene HDS on the removal of adsorbed carbon in the absence of sulfur. Figure 4 compares the removal of ^{14}C in a butadiene/hydrogen mixture, in the HDS gas mixture and also in pure hydrogen at a temperature of 573K. The decrease in ^{14}C coverage in the butadiene hydrogenation mixture is very similar to that observed in pure hydrogen, and greater than in the case of the thiophene HDS mixture. Apparently, butadiene and the hydrogenated products produced (butenes, butane) have no effect on the rate or extent of ^{14}C removal, while thiophene (and/or the H_2S produced) decreases the rate and amount of adsorbed carbon which is removed from the Mo(100) catalyst.

3.4 Effect of adsorbed Sulfur on the HDS activity of Clean and Carbided Mo(100) Surfaces

Sulfur was deposited onto a p(1×1) Mo(100)-C surface at room temperature to a coverage of 0.75 ML. No observable change was apparent in the LEED pattern. Annealling to 613K for one minute caused the (1×1) spots to become blurred with faint streaks between spots. An HDS reaction was performed over this surface and an activity of 0.076 molecules/site·sec measured. As mentioned in the introduction, carbon atoms adsorbed on the Mo(100) surface are bound in four-fold hollow sites. Therefore, sulfur deposited onto the carbon covered surface must occupy different binding sites. The decreased HDS activity of this surface indicates that sulfur atoms need not be adsorbed in four-fold hollow sites to block active HDS sites. For comparison, the HDS turnover frequencies of the sulfur covered carbide

surface, a sulfur covered Mo(100) surface, a carbided surface and the initially clean Mo(100) surface are shown together in Figure 5. As discussed in the introduction, sulfur atoms adsorbed at a coverage of 0.5 ML occupy four-fold hollow sites on the Mo(100) surface. At the coverage used in this experiment (θ_s = 0.75 ML), sulfur atoms occupy both four-fold hollow and bridge sites.

3.5 The Influence of Products (H_2S, cis-2-butene) on HDS Activity of the Mo(100) Surface

Figure 6 shows the effect of H_2S and cis-2-butene on thiophene HDS activity. The partial pressures used were chosen to correspond to the pressures of H_2S and C_4 hydrocarbon present when catalyst deactivation occurs (5-10% conversion). Cis-2-butene has a very small influence on the HDS activity of the catalyst; we do not believe the increase in activity observed is significant. Hydrogen sulfide strongly decreases the activity of the catalyst. At a partial pressure of 300 mTorr of H_2S, an HDS turnover frequency of 0.053 molecules/site·sec, less than one-half the activity in the absence of H_2S. After pumping the reaction loop to a pressure of $\leq 10^{-3}$ Torr, the reactor loop was repressurized with a fresh mixture of thiophene (3.0 Torr) and Hydrogen (780 Torr). The activity of the catalyst was measured to be 0.12 molecules/site·sec showing that the inhibition of HDS activity by H_2S is reversible. This indicates that it is molecular H_2S which blocks active HDS sites instead of a species which decomposes to form strongly bound sulfur that cannot be removed by evacuation.

4 DISCUSSION

There are three primary points which can be made that help to understand the surface chemistry of thiophene HDS over the Mo(100) surface.

I. Carbon adsorbed on the Mo(100) surface remains on the surface during HDS

but does not block the active thiophene HDS sites, while adsorbed sulfur decreases the activity of the catalyst.

II. The active catalytic surface is covered with adsorbed carbon. An initially clean Mo(1OO) single crystal catalyst becomes covered with predominantly carbon from thiophene decomposition. Deposition of atomic sulfur onto either the metal or carbon covered surface does not occur during thiophene HDS.

III. Deactivation of the Mo(1OO) catalyst in a batch reactor occurs by reversible adsorption of H_2S onto the active catalytic sites. The hydrocarbon product cis-2-butene does not significantly alter the activity of the catalyst.

4.1 Structure of C and S Overlayers and their Effects on the Reactivity of the Mo(1OO) Surface

Both sulfur ($\theta_s \leq$ O.67 ML) and carbon atoms ($\theta_c \leq$ 1.O ML) bond to the Mo(1OO) surface in high coordination four-fold hollow sites. The different sizes of the two adsorbates, however, suggest that the amount of exposed molybdenum on the adsorbate covered surfaces is quite different. Using published values for the atomic radii of molybdenum[17] sulfur and carbon[18] of 1.36, 1.O4 and O.77 Å respectively, as well as the relaxation value for the molybdenum atoms at the Mo(1OO) surface (top layer 11.5%[19]), the surface structures of the adsorbate covered surfaces can be modelled as shown in Figure 7. Carbon's smaller size makes it possible for it to adsorb in a four-fold hollow without extending above the top layer molybdenum atoms, while sulfur, on the other hand, extends above the surface Mo atoms when adsorbed in a four-fold hollow. In fact, due to its larger size, a sulfur atom experiences repulsive interactions with neighboring sulfur atoms which force some sulfur atoms to occupy weaker binding sites, believed to be bridge sites, instead of the higher coordination four-fold hollow sites at high coverages ($\theta_s \geq$ O.67 ML).

An experimental and theoretical study of CO chemisorption on sulfur, oxygen and carbon covered Fe(1OO) surfaces by Benziger and Madix[2O] indicates that sulfur attenuates the reactivity of the metal surface more than carbon because of its larger

size. Carbon and sulfur have similar electronegativities and should cause similar shifts in the Fermi level of the metal. The authors' calculations indicate that sulfur is a stronger poison for CO chemisorption because sulfur atoms sit high above the plane of the metal and therefore interact strongly with CO molecules (decreasing CO chemisorption). Carbon, however, sits in the plane of the surface, and CO interactions with carbon atoms are much less than with sulfur.

The difference in site blocking potential of sulfur and carbon is reflected in the interactions of sulfur and carbon covered surfaces with thiophene and hydrogen. Kelly et al showed that adsorbed sulfur on the Mo(1OO) surface blocks thiophene decomposition and that no molecular adsorption states other than the physisorbed state exist on this surface.[2] Carbon adsorbed on the Mo(1OO) surface blocks thiophene decomposition as well, but this surface also has new molecular chemisorption states for thiophene. Thiophene desorbs from the carbided Mo(1OO) surface at temperatures of 3OOK and 36OK, well above the temperature of 17OK as observed on the sulfided Mo(1OO) surface.

Zaera and coworkers have investigated hydrogen chemisorption on the clean and sulfided Mo(1OO) surface.[21] They suggest that hydrogen adsorbs at bridge sites and find that hydrogen dissociative adsorption is blocked at a sulfur coverage of O.5 ML. At this coverage there are sulfur atoms adjacent to all of the bridge sites, suggesting that sulfur in four-fold hollows can block dissociative adsorption of hydrogen at bridge sites. Adsorbed carbon also blocks dissociative adsorption of hydrogen but total suppression does not occur until the carbon monolayer is complete.[22] These results show that the interaction of thiophene and hydrogen is greater on the carbided than the sulfided surfaces, suggesting that the carbided Mo(1OO) surface may be a better HDS catalyst.

4.2 Thiophene HDS over the Mo(1OO) Surface: Evidence that the Active Surface is Covered with Adsorbed Carbon

To prove that the active Mo(100) surface is carbon covered it is necessary to show that adsorbed carbon remains on the Mo(100) surface during thiophene HDS and that carbided surfaces are active for thiophene HDS. Using the β^- emitter ^{14}C, it was found that 80% of a carbidic overlayer prepared in UHV remained on the surface following 90 minutes of thiophene HDS in typical reaction conditions (P_{Th} = 3.0 Torr, P_{H2} = 780 Torr, T = 613K). There are two mechanisms by which ^{14}C can be removed from the Mo(100) surface during thiophene HDS: 1) exchange with carbon atoms from thiophene and/or hydrocarbon products, and 2) direct hydrogenation (discussed in detail below). The former process causes no net change in the carbon coverage while the latter will result in a decrease in carbon coverage. The ^{14}C coverages measured represent a lower bound for the actual carbon coverage on the Mo(100) surface during HDS. Our results show that adsorbed carbon remains on the Mo(100) surface during thiophene hydrodesulfurization.

The HDS activity measured for carbon covered Mo(100) surfaces was found to be the same as for initially clean Mo(100) single crystals. The identical turnover frequencies and product distributions for thiophene HDS over initially clean and carbon covered Mo(100) surfaces indicate that the steady state surface composition for the surfaces is similar during reaction. The fact that adsorbed carbon remains on the surface in reaction conditions suggests that the active surface is covered with a carbidic overlayer. Decomposition of thiophene occurs on the clean surface upon heating to reaction temperature, producing a surface which is covered primarily with adsorbed carbon. AES of a Mo(100) surface following thermal desorption of a saturated monolayer of thiophene shows the surface to be covered with sulfur and carbon from thiophene decomposition. Zaera and coworkers have found the saturation thiophene coverage in UHV to be 0.3 thiophene molecules per surface Mo atom which gave a sulfur coverage of 0.3 ML following thermal decomposition of thiophene.[9] No desulfurized hydrocarbon products desorb from the thiophene saturated surface upon heating,[2] indicating that carbon coverage must be high as each thiophene molecule has four carbon atoms. In this work, thiophene decomposition on the clean Mo(100) surface at 613K in the typical HDS gas mix-

ture (P_{Th} = 3.0 Torr, P_{H2} = 780 Torr) gave a surface composition of $\theta_c \approx 0.8$ ML of carbidic carbon and ≈ 0.2 ML of coadsorbed sulfur following evacuation of the reactant gases. This indicates that the initially clean Mo(100) catalyst is covered with predominantly adsorbed carbon at the beginning of a thiophene HDS reaction. After 90 minutes of reaction, the carbon coverage remains high ($\theta_c \approx 0.7$ ML), while the amount of coadsorbed sulfur has increased to $\theta_s \approx 0.9$ ML. This coadsorbed sulfur does not block active HDS sites suggesting that it is weakly bound to the surface or adsorbs onto the catalyst surface during evacuation of the isolation cell. Clearly, it is not bound to the surface in the strong binding sites populated when sulfur is adsorbed onto the clean or carbided Mo(100) surface in UHV, as this sulfur decreases the activity of the catalyst.

4.3 Hydrogenation of Adsorbed Carbon on the Mo(1OO) Surface: The Effect of Butadiene and Thiophene

Hydrogenation of adsorbed carbon on metal surfaces has been the subject of surface science investigation in the past. Carbon hydrogenation on the Pt(111) surface was studied by Davis and coworkers in our laboratory[24] and Krebs and Bonzel[25] investigated carbon hydrogenation on an iron foil. For both the Pt and Fe surfaces there are two stages of reaction: an initial stage in which adsorbed carbon is hydrogenated rapidly, followed by a second phase in which hydrogenation is much slower. This two stage behavior has been attributed to two kinds of carbon adsorbed on the surfaces: 1) carbidic carbon and 2) graphitic carbon. Both Davis and Krebs concluded that the former type of carbon is reactive and rapidly hydrogenated, while graphitic carbon is quite stable under the hydrogenation conditions investigated. In the case of the Mo(1OO) surface, hydrogenation of the ^{14}C overlayer does not show a clear break in the ^{14}C coverage versus reaction time curves which would suggest two kinds of carbon on the surface. This result is supported by AES studies which showed the adsorbed carbon to be carbidic in nature.

Introduction of butadiene into the hydrogen atmosphere has no effect on the rate

of ^{14}C hydrogenation on the Mo(100) surface. Apparently, butadiene and the hydrogenated products (butenes, butane) do not alter the bonding of adsorbed carbon or significantly change the amount of adsorbed hydrogen available for ^{14}C hydrogenation. Thiophene, on the other hand, does influence the removal of adsorbed carbon from the surface. Including thiophene in the gas mixture decreases the rate and extent of ^{14}C removal from the crystal surface. Adsorbed thiophene may decrease the hydrogen coverage by blocking hydrogen dissociation sites or simply compete with the carbidic overlayer for available hydrogen on the surface. Previously published results from our laboratory indicate that the hydrogen coverage is low during thiophene HDS while the work reported here suggests that hydrogen saturates a carbon covered surface in a pure hydrogen atmosphere.

A radiotracer ^{35}S study of sulfur hydrogenation on the Mo(100) surface[5] showed that thiophene enhanced ^{35}S removal by a factor of approximately 30 compared to a pure hydrogen atmosphere. Repulsive interactions between adsorbed thiophene molecules and ^{35}S atoms may decrease the Mo-^{35}S bond strength, making adsorbed sulfur more labile to hydrogenation. This effect would be expected for adsorbed sulfur which extends well above the metal surface and to a lesser extent for carbon which does not extend above the top layer Mo atoms. As discussed earlier, sulfur more effectively blocks hydrogen dissociation than does carbon and, in fact, a positive hydrogen pressure dependence of 0.34 for sulfur hydrogenation suggests that the sulfur covered surface is not saturated in hydrogen under reaction conditions (P_{H2} = 780 Torr). Thiophene, or surface intermediates, might increase sulfur hydrogenation by providing an additional source of hydrogen or by acting as a hydrogen transfer agent.

4.4 Effect of Adsorbed Sulfur, cis-2-butene, and H_2S on the HDS Activity of Mo(100) Surfaces

Atomic sulfur adsorbed on clean and carbided Mo(100) surfaces decreases the activity of the catalysts to about 60% of the activity of the initially clean surface.

As discussed earlier, sulfur adsorbed on the Mo(100) surface blocks decomposition of thiophene and no chemisorption of thiophene occurs on the sulfur covered surface. The decreased activity of the sulfur covered surfaces for thiophene HDS reflects the attenuation of the reactivity of the surface towards thiophene in UHV. The observation that sulfur deposited onto the carbon covered Mo surface also decreases the catalyst's activity allows the following conclusions to be made. Bonding interactions between sulfur and the carbided surface stabilize the sulfur such that it is not hydrogenated from the surface during reaction. Sulfur atoms must occupy lower coordination sites on the carbided surface as carbon atoms are adsorbed in the four-fold hollows, yet the decreased catalyst activity indicates that the sulfur remains on the surface and blocks HDS activity. This excludes the possibility that adsorbed carbon keeps the Mo(100) surface active by blocking sulfur deposition into strong binding adsorption sites. Adsorption sites for sulfur exist on the carbon covered surface from which sulfur is not removed in the reaction conditions used. This allows us to conclusively rule out a thiophene desulfurization mechanism in which atomic sulfur is deposited into binding sites on the metal or carbide surface. It also allows us to rule out deposition of atomic sulfur onto the catalyst as the pathway by which catalyst deactivation occurs as deactivation has been found to be reversible; atomic sulfur does not desorb from the surface upon evacuation. Likewise, carbon deposition from thiophene decomposition is not involved in deactivating the catalyst as adsorbed carbon does not affect catalyst activity.

Deactivation of the Mo(100) surface is caused by reversible adsorption of molecular H_2S on the catalyst surface. Catalyst activity begins to fall after about 5% conversion and complete deactivation occurs by a conversion of approximately 10% under normal HDS conditions (P_{Th} = 3.0 Torr, P_{H2} = 780 Torr, T = 613 K). This deactivation is reversible as catalyst activity can be restored to close to its initial value by replacing the gases in the reactor with a fresh mixture of thiophene and hydrogen. We believe that this adsorption site, in which H_2S is weakly bound to the catalyst surface, is the site in which thiophene desulfurization occurs. Hydrogenation of the thiophenic sulfur takes place in the initial steps of the reaction, prior to

or simultaneously with the cleavage of the C-S bonds to give butadiene and molecular H_2S. Hydrogen sulfide desorbs from the surface freeing the site for adsorption of another thiophene molecule. The key feature of this mechanism, proposed in an earlier paper from our laboratory[5], is that sulfur is never present atomically on the catalyst surface. Atomic sulfur on the metal surface and the carbon covered surface is strongly bound and blocks active HDS sites. In the hydrogenated state (H_2S), the bonding of sulfur to the catalyst surface is moderated and catalyst activity is maintained as H_2S desorbs from the surface following scission of the C-S bonds.

These results allow us to rule out high symmetry metal sites, four-fold hollows and bridge sites, as the active sites for thiophene HDS as these sites dissociate H_2S and bind atomic sulfur very strongly to the metal surface. We believe the active HDS site is a mixed molybdenum-carbon site on which decomposition of H_2S to atomic sulfur and hydrogen does not occur. This mechanism is in contrast to the mechanism proposed by Lipsch and Schuit.[25] They propose that the sulfur containing molecule adsorbs onto the catalyst through the sulfur atom,and, following C-S bond cleavage, the sulfur atom is hydrogenated to H_2S which desorbs from the catalyst surface. The C_4 hydrocarbons produced during thiophene HDS do not compete with thiophene for adsorption sites as indicated by cis-2-butene having no effect on catalyst activity. Hydrogenation of butadiene and butenes apparently occurs on different sites than the desulfurization sites. The inhibitory effect of H_2S and the insignificant effect of butenes on thiophene HDS activity has been observed previously.[26,27] In both cases the catalysts employed were industrial cobalt molybdate catalysts. The similar effect of products on the activity of a Mo(1OO) single crystal and industrial HDS catalysts suggests that the active sites on the two catalysts are the same.

5 CONCLUSION

We have shown that the active catalytic surface of a Mo(1OO) single crystal during thiophene HDS is covered with adsorbed carbon from thiophene decompo-

sition. Deposition of atomic sulfur onto the catalyst surface does not occur during desulfurization of thiophene. Rather, hydrogenation of the thiophenic sulfur occurs prior to or simultaneously with C-S bond cleavage. Hydrogenation of butadiene and butene occurs on different sites than desulfurization. Deactivation of the Mo(1OO) catalyst in a batch reactor is caused by reversible adsorption of H_2S onto the active thiophene HDS sites and occurs at conversions of 5-1O% in the conditions investigated. Two products of thiophene HDS: H_2S and cis-2-butene, were found to have the same effect on catalyst activity for a Mo(100) single crystal as for an industrial cobalt molybdate catalyst. This indicates that investigation of the surface chemistry of thiophene over single crystal catalysts gives useful insights for understanding HDS over industrial catalysts.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. A schematic diagram of the detection and counting system for beta emission from ^{14}C adsorbed on the Mo(1OO) single crystal surface.

Figure 2. Rate of thiophene HDS as a function of initial carbon coverage on the Mo(1OO) surface. Carbon is adsorbed onto the surface in UHV prior to reaction in the high pressure reactor.

Figure 3. ^{14}C coverage on the Mo(1OO) surface as a function of reaction time in pure hydrogen.

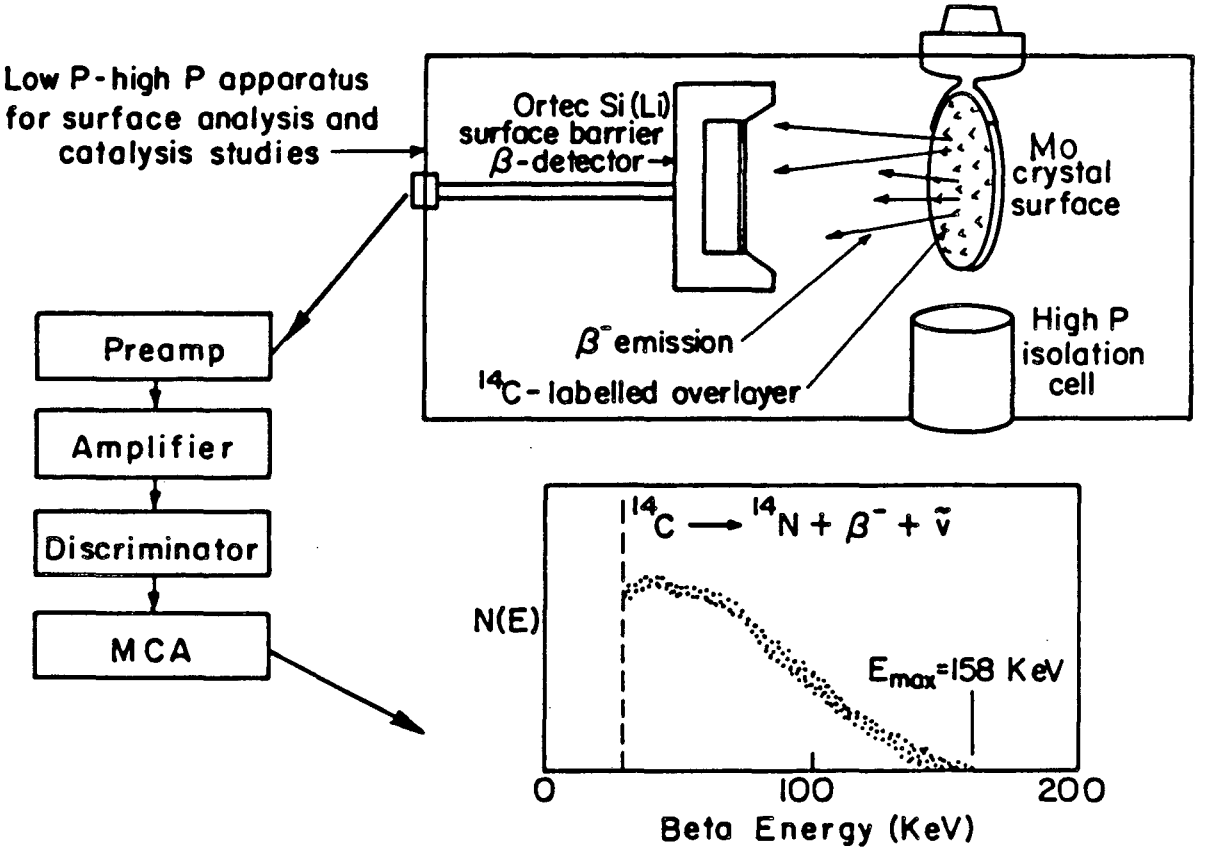
Figure 4. ^{14}C coverage on the Mo(1OO) surface a function of reaction time in thiophene and hydrogen, butadiene and hydrogen, and in pure hydrogen.

Figure 5. Thiophene HDS activity of Mo(1OO) catalysts with different initial surface compositions. The last surface was prepared by depositing O.75 ML of sulfur on a carbided Mo(1OO) surface.

Figure 6. HDS activity of an initially clean Mo(1OO) single crystal as a function of partial pressure of product (H2S or cis-2- butene) in the gas mixture.

Figure 7. Schematic diagram of carbon (a) and sulfur (b) adsorbed on the Mo(1OO) surface. Covalent radii were used for carbon and sul- fur and the metallic radius for molybdenum.

^{14}C Radiotracer Studies of Adsorbed Carbon on Molybdenum



XBL 868-2963

Fig. 1

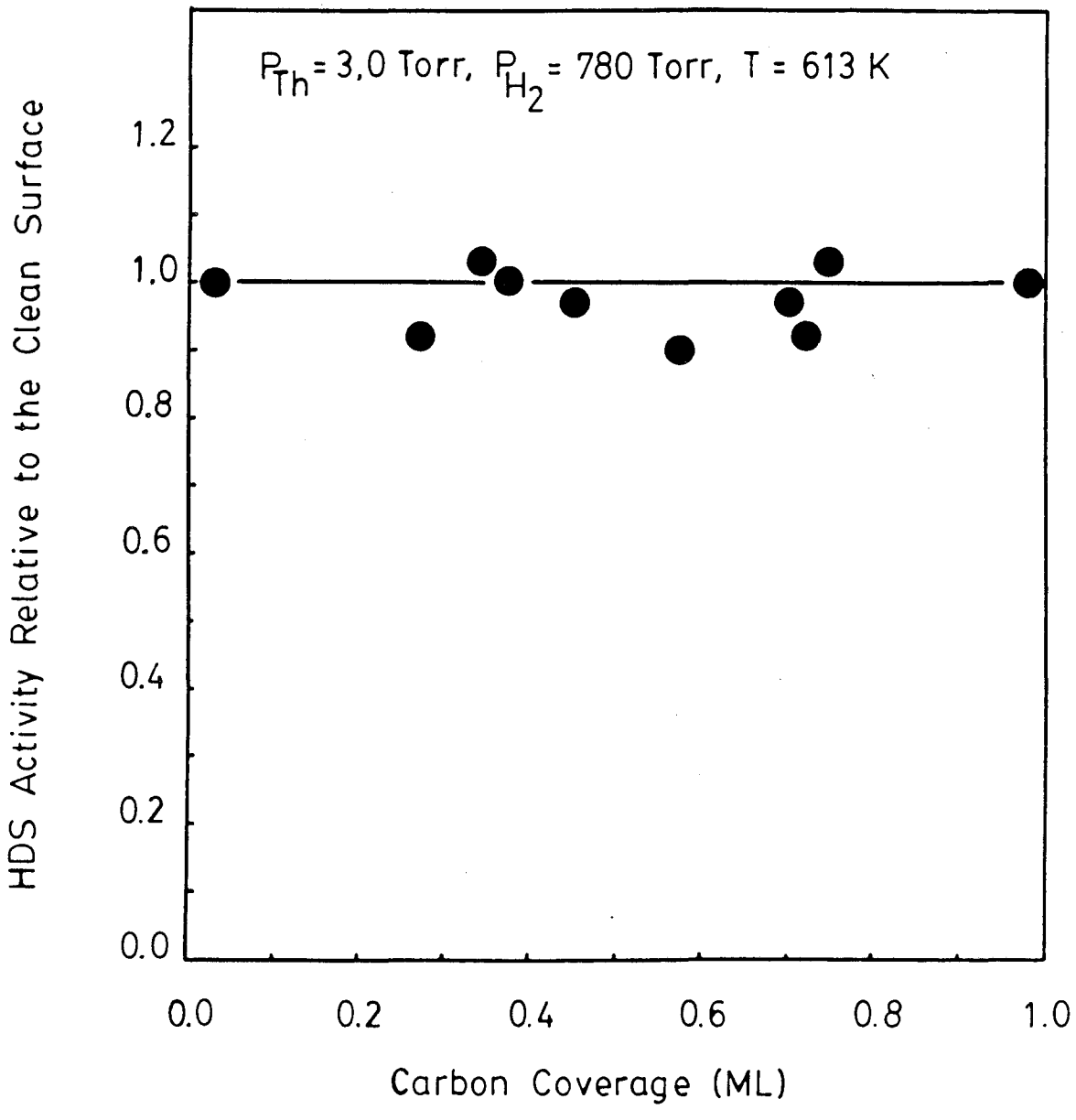


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Fig. 2

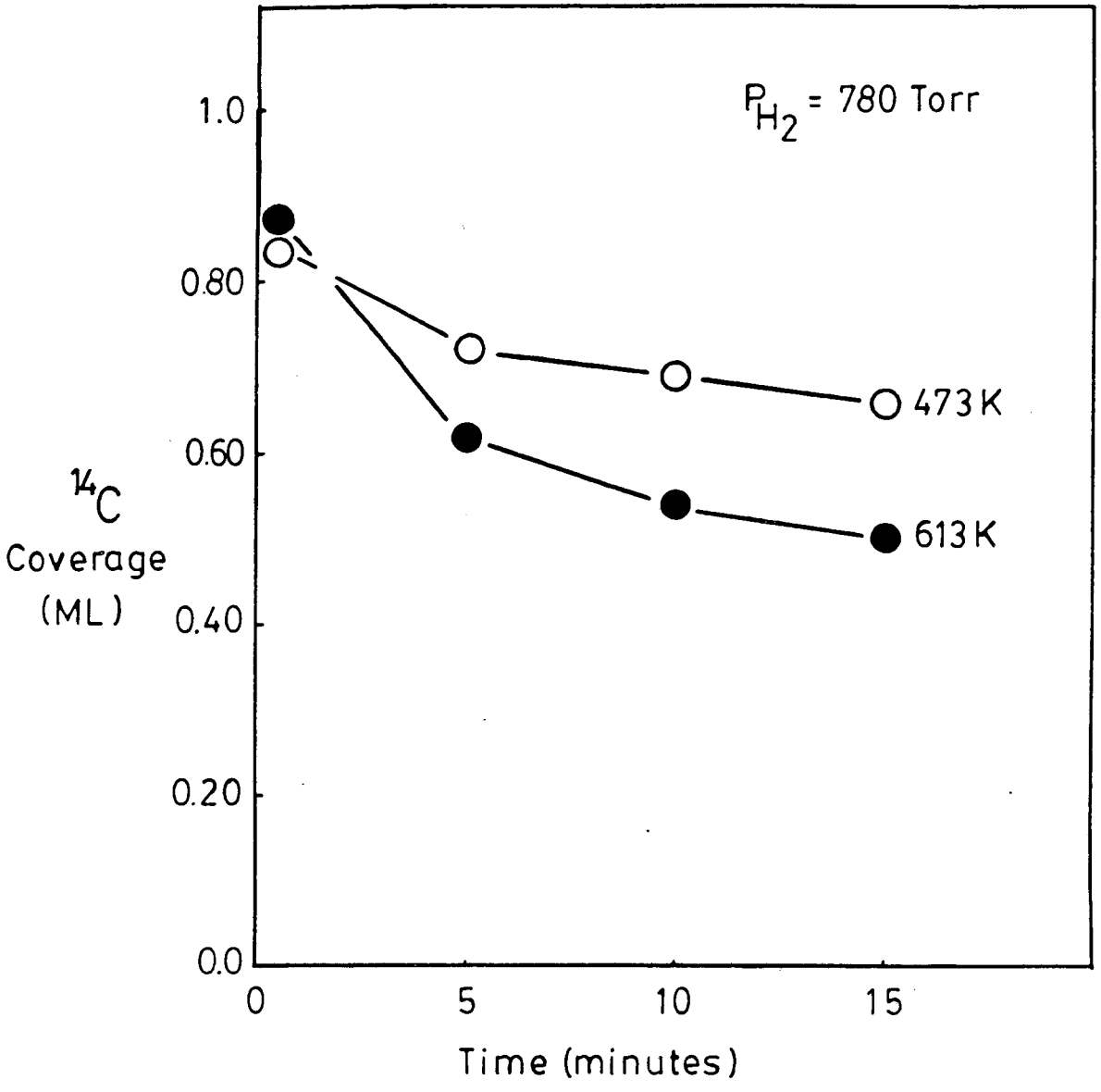

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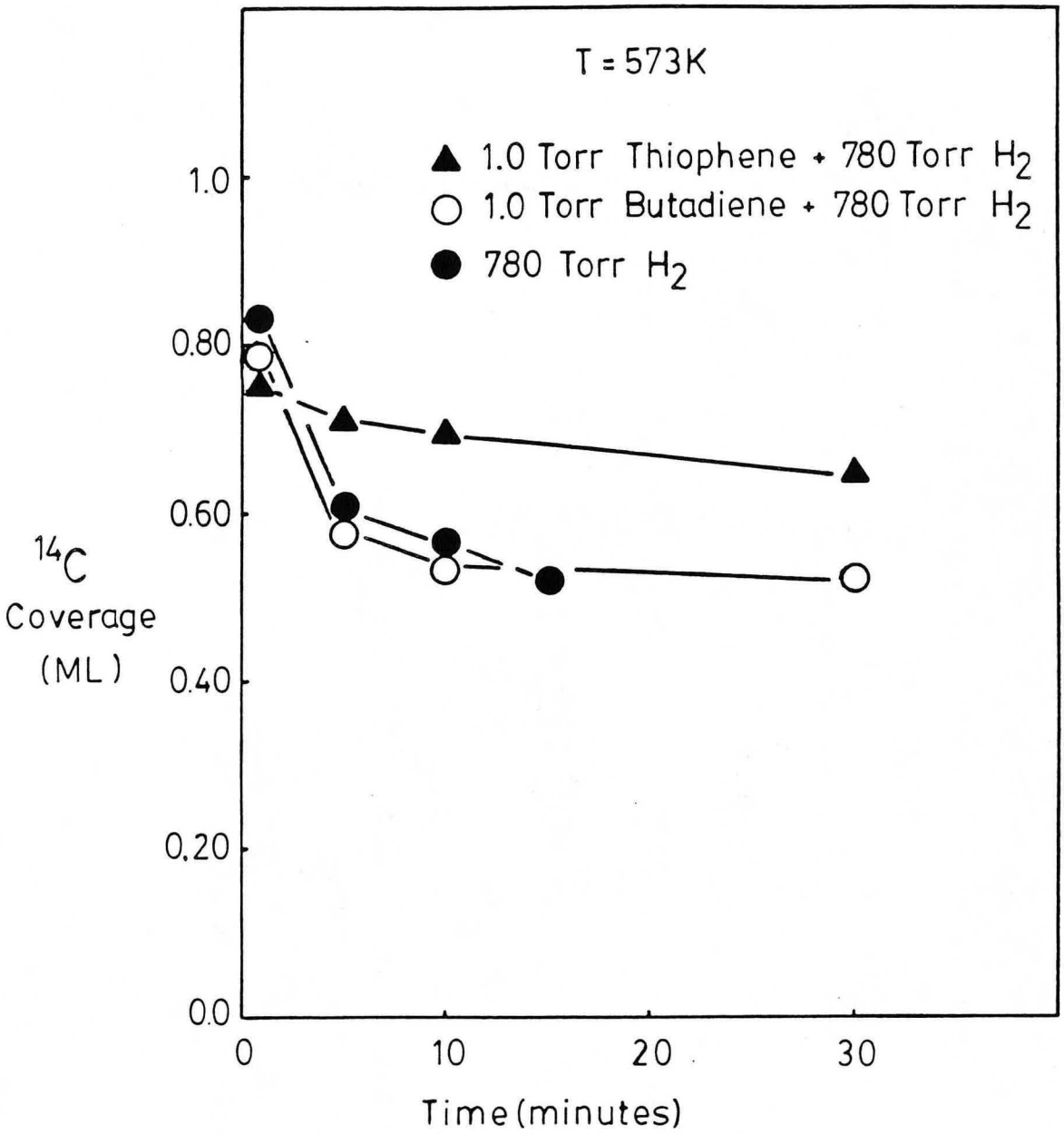
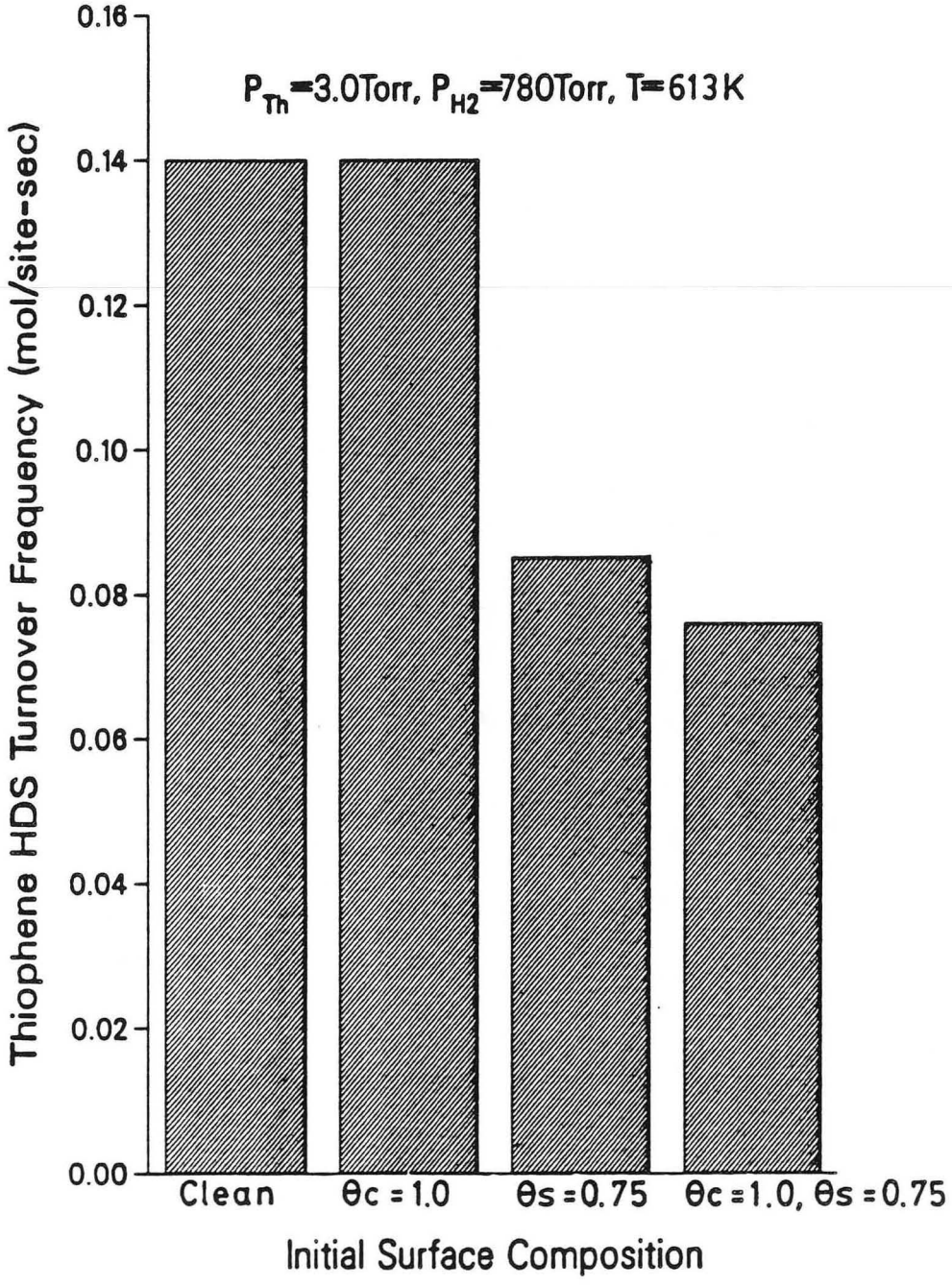
Fig. 3



XBL 869-3469

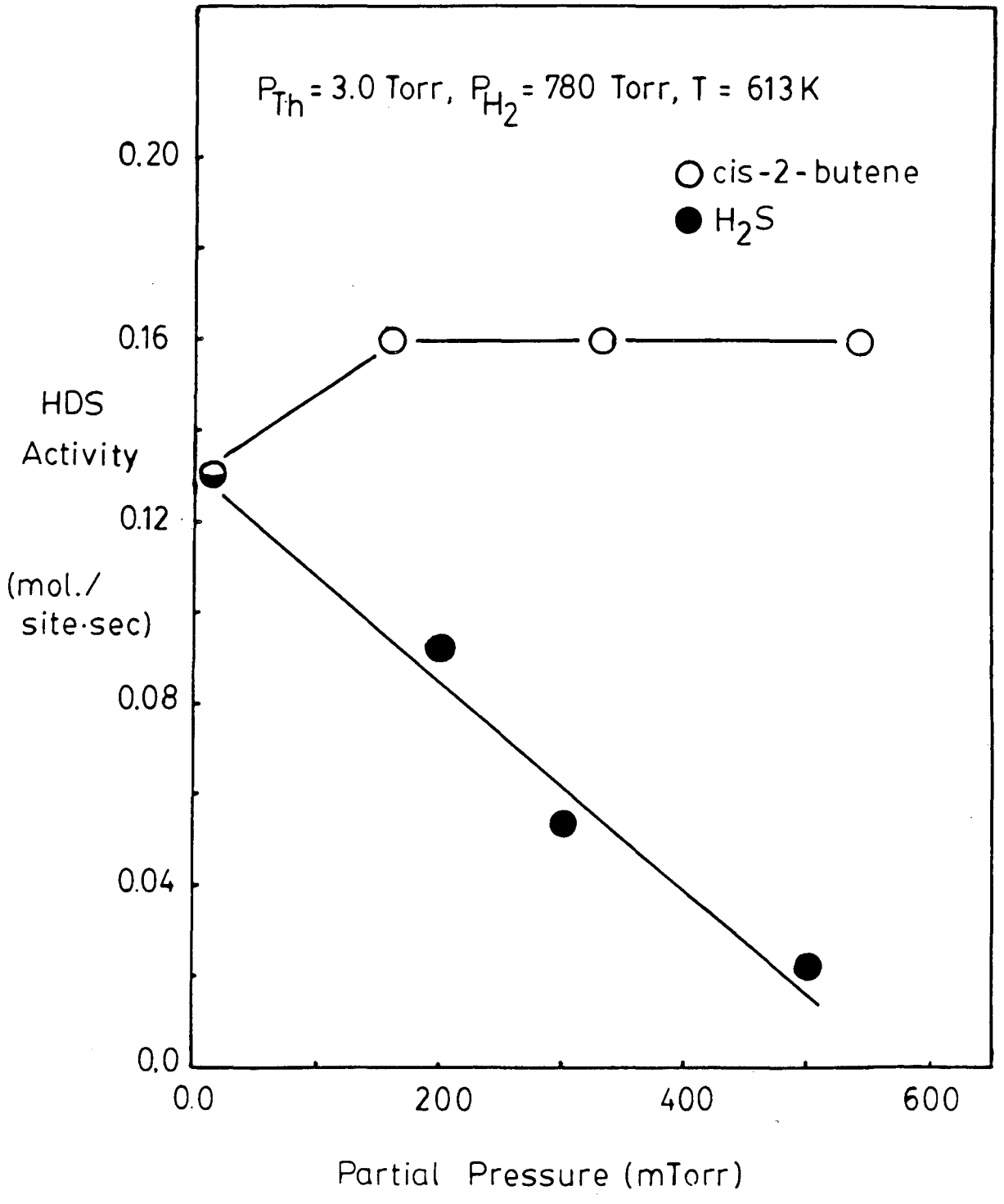
Fig. 4

Effect of Adsorbed Sulfur and Carbon on Thiophene HDS Activity



XBL 868-2958

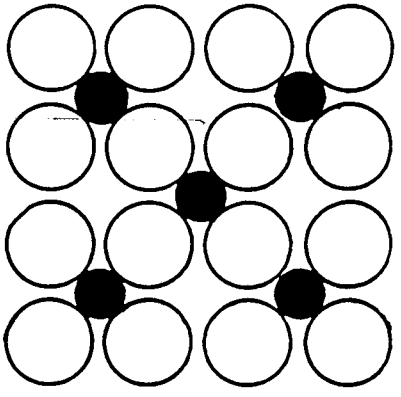
Fig. 5



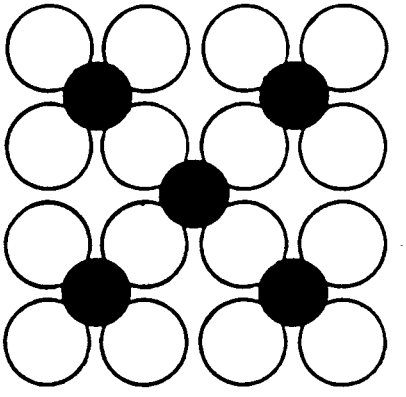
XBL 869-3470

Fig. 6

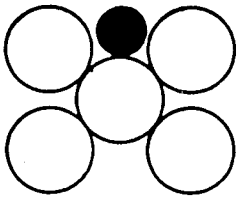
Adsorbed Carbon and Sulfur on the Mo(100) Surface



$\theta_C = 0.50$ ML

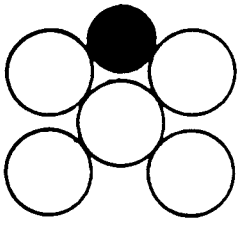


$\theta_S = 0.50$ ML



Carbon

(a)



Sulfur

(b)

XBL 868-2965

Fig. 7

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