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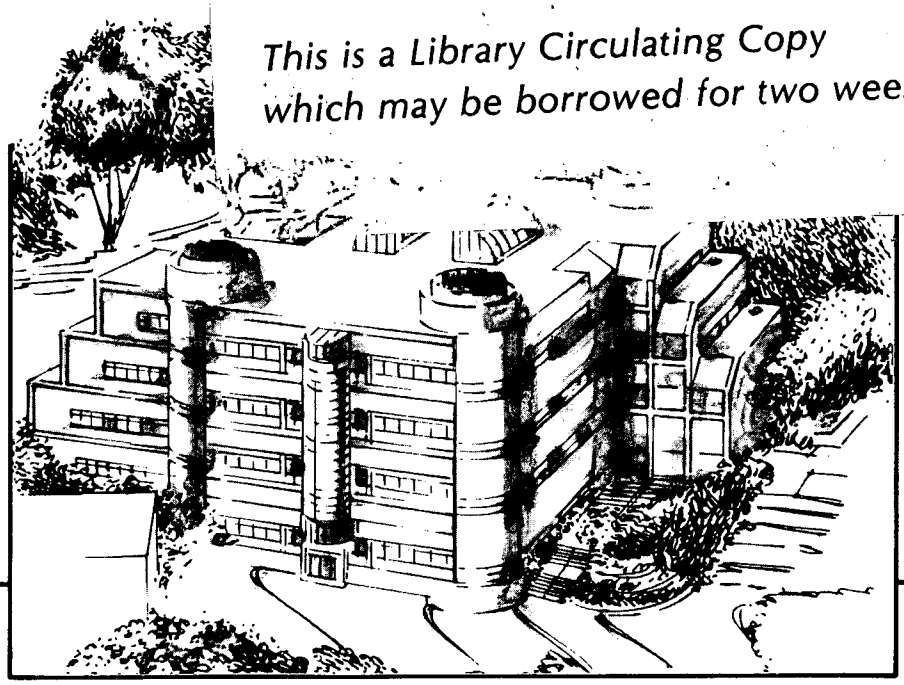

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The Role of Adsorbate Overlayers in Thiophene Hydrodesulfurization over Molybdenum and Rhenium Single Crystals

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Abstract

Thiophene hydrodesulfurization (HDS) has been investigated over model single crystal catalysts of molybdenum and rhenium. Thiophene HDS is a structure sensitive reaction over rhenium and a structure insensitive reaction over molybdenum. Adsorbed sulfur decreases the activity of both Re(0001) and Mo(100) surfaces while adsorbed carbon has distinctly different effects on the catalytic properties of the two metals. Carbon overlayers deactivate the Re(0001) surface but have no effect on the HDS activity of the Mo(100) surface. Radiotracer studies using ^{35}S and ^{14}C indicate that HDS occurs on an adsorbate overlayer on molybdenum comprised primarily of carbon. HDS over rhenium, on the other hand, occurs on the bare metal surface. This difference appears to be responsible for the observed differences in the influence of surface structure on HDS activity.

1 Introduction

Reactions catalyzed by solids can be classified into two types: structure insensitive and structure sensitive, depending upon whether or not their rate and/or product distribution depends upon the surface crystallographic orientation of the metal particles at the catalyst surface [1]. Initial studies of structure sensitivity were carried out by measuring the rate of a reaction over catalysts with different average particle sizes. Over the particle size range of 10-50 Å, the distribution of exposed crystal faces changes considerably and this change can be used to investigate structural effects on a given reaction.

The development of combined ultrahigh vacuum surface analysis/catalytic reactor systems has made possible the investigation of the effects of surface structure on catalytic activity using well characterized metal single crystals [2]. We have recently reported results of thiophene hydrodesulfurization (HDS) experiments over molybdenum and rhenium single crystals in which HDS was found to be structure insensitive over molybdenum and structure sensitive over rhenium [3]. To our

knowledge, this is the first well documented case of a reaction which is structure insensitive over one metal and structure sensitive over another under identical reaction conditions. In this letter we report the results of experiments in which the effects of adsorbed carbon and sulfur overlayers on HDS activity were determined for the the Re(0001) surface. These results are compared with those from a previous study over the Mo(100) surface and a model is put forward to explain the differences in the effect of surface structure on the HDS activities of the rhenium and molybdenum catalysts [4,5].

2 Experimental

The experiments reported were performed in a stainless steel, ultrahigh vacuum chamber (base pressure = 1×10^{-9} Torr) equipped with a high pressure isolation cell for atmospheric pressure reactions and is described in detail elsewhere [6]. The Re(0001) single crystal was approximately 1 cm^2 in area and less than 0.1 cm in thickness. The cleanliness of the single crystal was monitored using AES and LEED. Overlayers of sulfur were formed on the Re(0001) surface using an electrochemical sulfur source which has been described previously [7]. AES calibration of the sulfur coverage was accomplished using the previously observed $(2\sqrt{3}\times2\sqrt{3})$R 30° LEED pattern which occurs at a sulfur coverage of 0.5 monolayer (ML) [8]. AES peak heights were measured for the S(148eV) and Re(177eV) Auger transitions for the sulfur covered and clean Re(0001) surfaces to determine the AES attenuation factor for sulfur. A calibration curve of sulfur coverage versus the AES S(148eV)/Re(177eV) peak height ratio was generated with this attenuation factor and the curve was used to determine all sulfur coverages.

Overlayers of carbon were formed on the Re(0001) surface by dosing with C_2H_4 at room temperature, followed by heating to 800 K. The AES attenuation factor for carbon was determined using the absolute AES intensities for the clean and 0.25 ML covered surface. This latter surface was prepared by saturating the clean Re(0001) surface with C_2H_4 at room temperature followed by annealing to 770 K. This surface

gives a c(4×2) LEED pattern which has been shown previously to correspond to a carbon coverage of 0.25 ML [9]. A calibration curve for carbon coverage versus the AES C(272eV)/Re(177eV) peak height ratio was generated using the carbon attenuation factor in the same manner as for sulfur.

Following preparation of the clean or adsorbate covered Re(0001) surface in UHV, the single crystal was 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 to ensure mixing prior to heating the crystal to a reaction temperature of 613 K. Gas samples were injected into a gas chromatograph at 15 minute intervals and detected with a flame ionization detector. Catalyst activities were calculated using the product accumulation data from the first 90 minutes of reaction. The details of the experiments involving the other single crystals have been described previously [3,4,5].

3 Results and Discussion

The thiophene HDS activities for three low miller index planes of molybdenum and four of rhenium are compared in Figure 1. Surfaces of comparable corrugation were studied for the two metals, yet the rhenium surfaces show a six-fold variation in activity while the molybdenum surfaces exhibit almost identical activities. The surface structure of the single crystals was examined before and after reactions using LEED and was found to be unchanged in all cases. This suggests that neither the molybdenum nor the rhenium single crystals undergo reconstruction under reaction conditions. In order to understand the behavior of the molybdenum and rhenium catalysts, the effects of carbon and sulfur overlayers on the HDS activities of the Mo(100) and Re(0001) surfaces were investigated. Figures 2 and 3 show the influence of these adsorbates on the HDS activity of both the Mo(100) and the Re(0001) single crystals; adsorbed sulfur affects the two catalysts in a similar manner while adsorbed carbon has very different effects on their catalytic activities.

The HDS activity of a Mo(100) single crystal decreases by a factor of two as

the sulfur coverage is increased up to a coverage of about two-thirds monolayer ($\theta_s \approx 0.67$ ML), while further sulfur has very little effect on catalytic activity. Radiotracer studies using ^{35}S on the Mo(100) surface showed that adsorbed sulfur is very stable on this surface; the rate of ^{35}S removal was more than two orders of magnitude slower than the rate of thiophene HDS [5]. Adsorbed sulfur on the Re(0001) surface also blocks active HDS sites as the activity of the rhenium catalysts falls to about two-thirds that of the initially clean surface as the sulfur coverage is increased to 0.5 ML. Atomic sulfur desorbs from the Re(0001) surface with a peak maximum at 1600 K and a shoulder at ~1400 K ($\theta_s > 0.25$ ML) and from the Mo(100) surface in a peak at 1800 K with a shoulder at 1300-1500 K at high coverages ($\theta_s > .67$ ML). The atoms in the Re(0001) surface are more densely packed than the atoms in the Mo(100) surface which is reflected in a lower sulfur coverage at saturation (Re(0001): $\theta_s^{max} = 0.67$ ML, Mo(100): $\theta_s^{max} = 1.0$ ML) [8,10]. The similarity in desorption temperatures for sulfur on the Re and Mo surfaces suggest that sulfur is probably removed from the Re(0001) surface at a rate much slower than the rate of thiophene HDS as well. It appears, therefore, that adsorbed sulfur overlayers modify the Re and Mo catalysts in a similar manner and thus, cannot be responsible for the observed differences in HDS over the two metals.

In contrast to the similar effects caused by sulfiding the Mo and Re single crystals, carburization has distinctly different effects on the catalysts. Adsorbed carbon overlayers deactivate the Re(0001) surface but cause no measureable change in the activity of the Mo(100) surface. Radiotracer ^{14}C and AES studies showed that the initially clean Mo(100) surface becomes covered with ≈ 0.8 ML of carbon from decomposition of thiophene during the initial stages of an HDS reaction [4]. In addition, adsorbed carbon overlayers were found to be removed very slowly from the surface under reaction conditions. Apparently, thiophene decomposition does not occur on the Re(0001) surface under reaction conditions as the initially clean rhenium surface maintains an HDS activity higher than that of a sulfided or carburized Re(0001) surface for the duration of a 90 minute reaction.

Examination of the peakshape of the carbon AES transition for carbonaceous

overlayers on the two single crystal surfaces indicates that adsorbed carbon is carbidic in nature on the Mo(100) surface but more closely resembles graphitic carbon on the Re(0001) surface. The differences in the structure of the carbonaceous overlayers on the two metal surfaces are reflected in the interaction of the carbon covered surfaces with thiophene. Thermal programmed desorption (TPD) studies indicate that at coverages below the saturation value, thiophene adsorbs irreversibly on the clean Re(0001) and Mo(100) surfaces [11,12]. Thiophene decomposes to yield adsorbed carbon and sulfur along with hydrogen which desorbs as H_2. Adsorbed carbon on the Re(0001) surface blocks decomposition sites and thiophene desorbs in two peaks at 180 K and 230 K. Similarly, adsorbed carbon blocks decomposition of thiophene on the Mo(100) surface, but thiophene chemisorbs much more strongly on this surface as attested by its higher desorption temperatures of 300 K and 360 K.

Our results suggest that the structure sensitivity of thiophene HDS over rhenium and structure insensitivity over molybdenum can be traced to the different surface compositions of the metals under reaction conditions. The Re(0001) surface remains free of irreversibly bound deposits of carbon and/or sulfur during reaction, indicating that HDS occurs on the bare metal surface. As a result, the structure of the metal substrate markedly affects its interaction with species involved in the reaction pathway and structure sensitivity is observed. Over the Mo(100) surface, thiophene HDS occurs on a strongly bound overlayer comprised primarily of adsorbed carbon. Thiophene HDS, therefore, is structure insensitive over molybdenum because it occurs on an adsorbate overlayer which blocks the effects of surface structure. Carbonaceous overlayers have also been implicated in the structure insensitivity of ethylene hydrogenation over platinum [13]. In this case, a mechanism has been proposed in which ethylene hydrogenation occurs on top of an ethylidyne overlayer [2].

4 Conclusion

Using model single crystal catalysts, thiophene HDS has been found to be a structure sensitive reaction over rhenium and a structure insensitive reaction over molybdenum. On rhenium, HDS occurs directly on the metal surface while over molybdenum, the reaction occurs on an adsorbate overlayer which moderates the effects of surface structure. Rhenium is more selective toward breaking only the desired C–S bonds in thiophene and remains clean of irreversibly bound adsorbate deposits. Molybdenum becomes covered with a strongly bound adsorbate overlayer during the initial stages of reaction due to indiscriminate breaking of C–S, C–C and C–H bonds. This adsorbate covered surface is the active catalytic surface for thiophene HDS over molybdenum.

Acknowledgements

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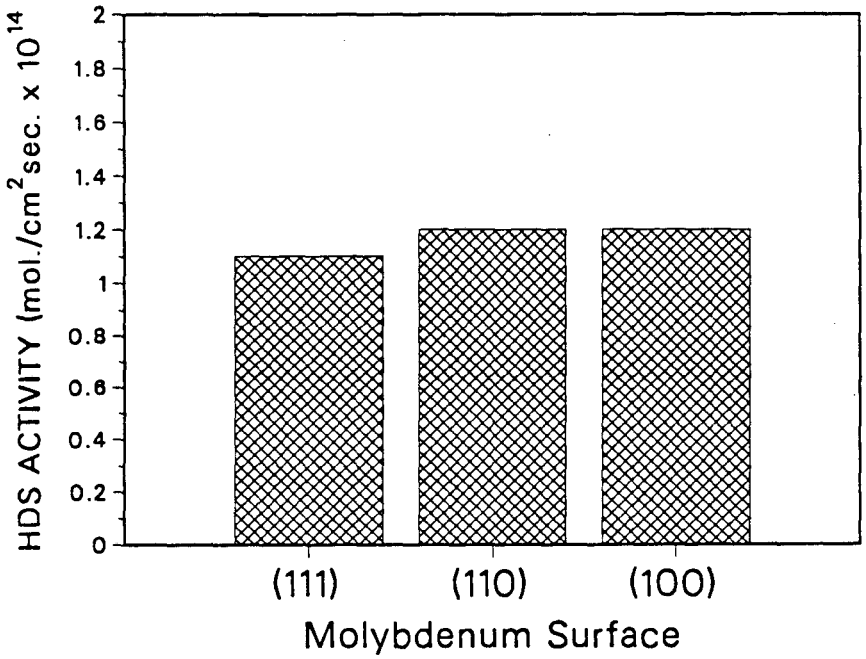
Figure Captions

Figure 1: a) Thiophene HDS activities for three low miller index planes of molybdenum (P_{Th} = 3.0 Torr, P_{H_2} = 780 Torr, T =613 K). b) Thiophene HDS activities for four low miller index planes of rhenium (P_{Th} = 3.0 Torr, P_{H_2} = 780 Torr, T =613 K).

Figure 2: Thiophene HDS activity of a Mo(100) single crystal as a function of the initial sulfur (o) and carbon (•) coverage.

Figure 3: Thiophene HDS activity of a Re(0001) single crystal as a function of the initial sulfur (o) and carbon (•) coverage.

a)



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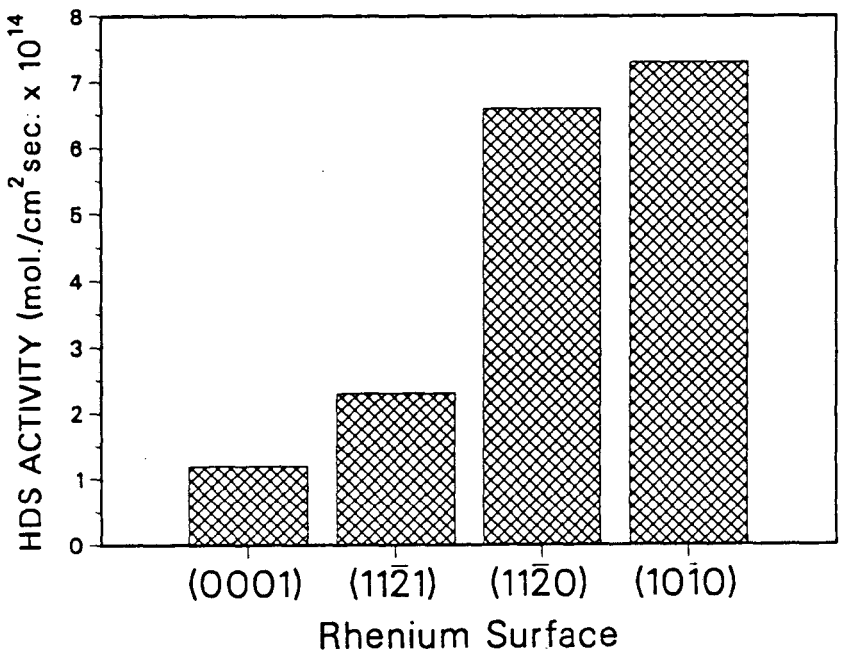

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Fig. 1

Effect of Adsorbates on the HDS Activity of Mo(100)

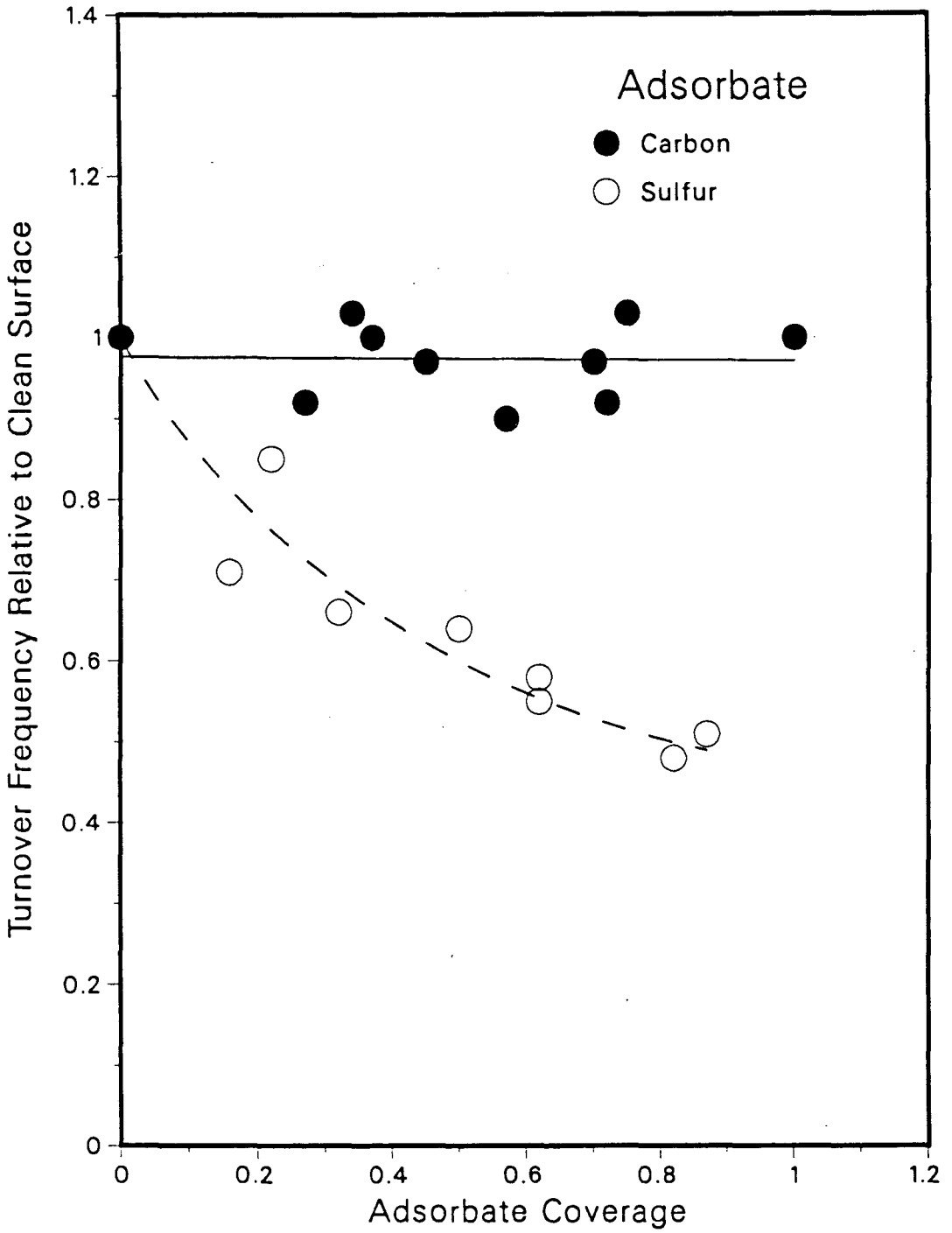

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Fig. 2

Effect of Adsorbates on the HDS Activity of Re(0001)

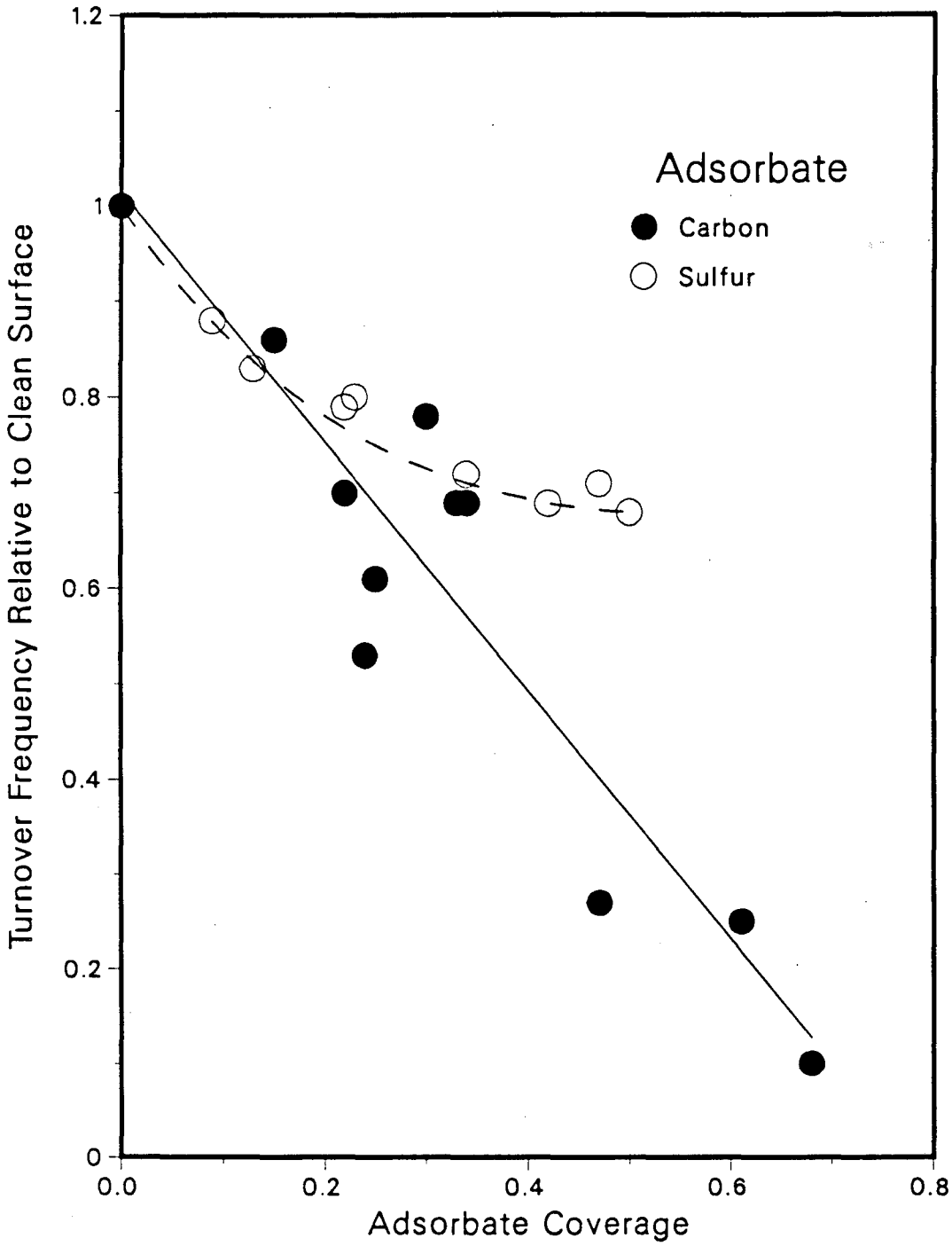

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Fig. 3

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