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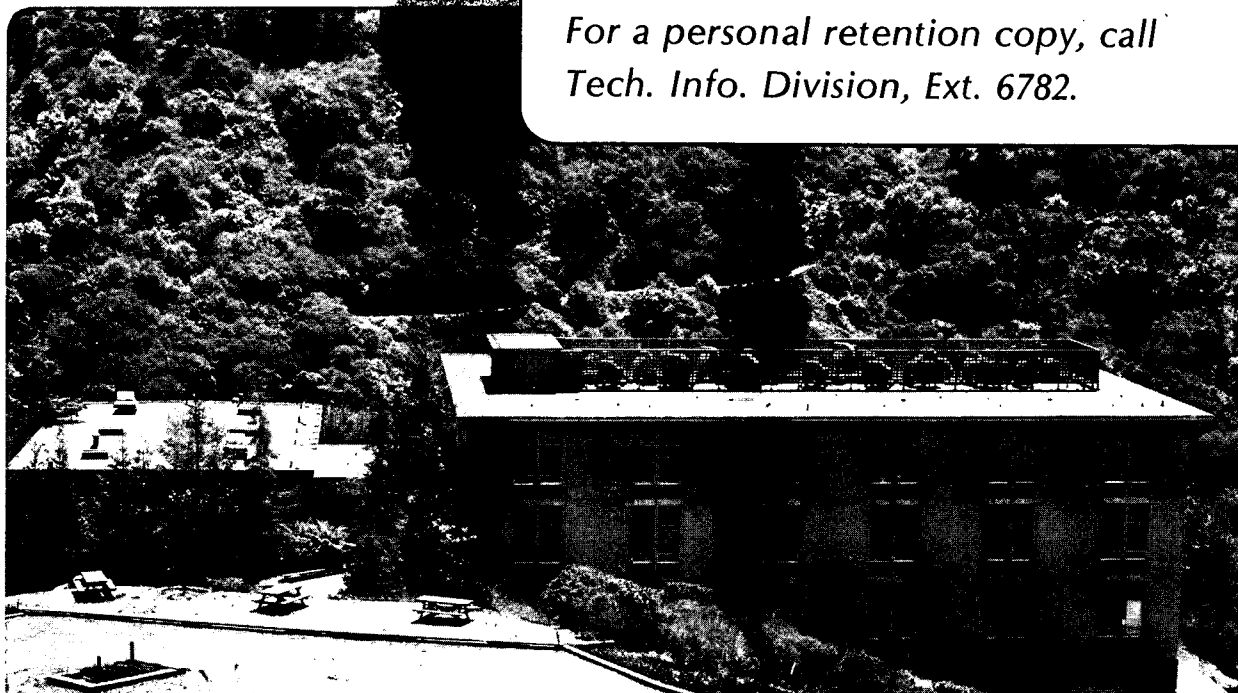
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THE CATALYTIC HYDRODESULFURIZATION OF THIOPHENE ON THE Mo(100) CRYSTAL SURFACE

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In this note we report that the catalytic hydrodesulfurization (HDS) of thiophene can be performed on the Mo(100) single crystal surface. The HDS of thiophene is often used to test the activity of supported molybdenum-sulfur catalysts and, in order to develop improved catalysts for this important process, a molecular level understanding of this reaction is desirable. To this end we are performing a surface science study of this system utilizing both UHV and high pressure techniques.

The experiments described here have been conducted in a UHV chamber equipped with a high pressure cell, described elsewhere. (1) Varying pressures of thiophene (1-5 torr) and hydrogen (100-800 torr) have been mixed and circulated through a loop attached to the cell. Products were analyzed by gas chromatography and reaction rates and product selectivities have been determined as functions of reactant pressures and crystal temperatures (250°C-420°C). In all cases the Mo crystal surface was determined to be initially clean by Auger Electron Spectroscopy (AES).

Over the range of experimental conditions employed the initial reaction rates have varied from .020 - .120 turnovers/site/sec assuming that each surface Mo atom is an active site. Final turnover numbers have been as high as 1500, indicating that the reaction is catalytic. The product distribution displayed in Table 1 is similar to that observed for a MoS<sub>2</sub> catalyst. (2) The thiophene pressure dependence appears to be low order or zero order. The hydrogen pressure dependence, displayed in Table 2, is however, more complicated and varies among the products. The temperature dependence of the rates, shown in Figure 1, also differs among the products and is similar to the temperature dependence of the product distribution

observed for the deoxygenation of tetrahydrofuran. (3) For our HDS reaction, butadiene is the only product showing Arrhenius-like temperature dependence having an activation energy of 14.4 kcal/mole.

The surface after the reaction is covered with sulfur and carbon. The sulfur coverage, in fact, appears to be in excess of one monolayer as determined by our AES calibration. (4) Furthermore, we have identified an ordered sulfur structure on the Mo surface. The LEED pattern of this structure, shown in Fig. 2, indicates a hexagonal overlayer, having a unit cell parameter of 2.7 Å, present on the square lattice of the Mo(100) substrate. In general this structure is difficult to produce and requires the annealing of the surface to a 700-800°C, after the reaction. On occasion, however, we have observed its presence immediately after the reaction without annealing of the surface. More importantly, in the cases in which we have started the reaction with this structure present on the surface it has remained unaltered, indicating that it is stable under reaction conditions. In these cases the initial activity is reduced to about half of the initially clean surface.

The HDS reaction over Mo(100) seems to be similar to that observed over the supported Mo/S catalysts. We are currently conducting detailed studies of the nature of the Mo single crystal surface present under reaction conditions and of the effects of surface composition on reaction rates and product distributions.

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TABLE 1. Product distribution of the HDS of Thiophene ( $C_4H_4S = 2.7t$ ,  $H_2 = 780t$ ,  $T=340^\circ C$ ).

Butadiene	5.6%
1-butene	52.8%
trans-2-butene	19.4%
cis-2-butene	13.9%
n-butane	8.1%

TABLE 2.  $H_2$  pressure dependence of HDS product rates of appearance. ( $C_4H_4S=2.7t$ ,  $T=340^\circ$ ).  $r=A \times (PH_2)^n$

<u>Product</u>	<u>n</u>
butadiene	-0.18
1-butene	0.54
trans-2-butene	0.68
cis-2-butene	0.58
n-butane	1.10

FIGURES

- Figure 1. Arrhenius plot of the temperature dependence of the product appearance rates for the HDS of thiophene. ( $C_4H_4S = 2.5t$ ,  $H_2 = 780t$ ). The activation energy for the production of butadiene is  $E_a = 14.4$  kcal/mole.
- Figure 2. LEED patterns of the hexagonal sulfur structure taken at normal and off-normal angles of incidence. The diffraction spots due to the Mo(100) form a square lattice. The hexagonal lattice causes the superimposed rings having twelve intensity maxima about the circumference.



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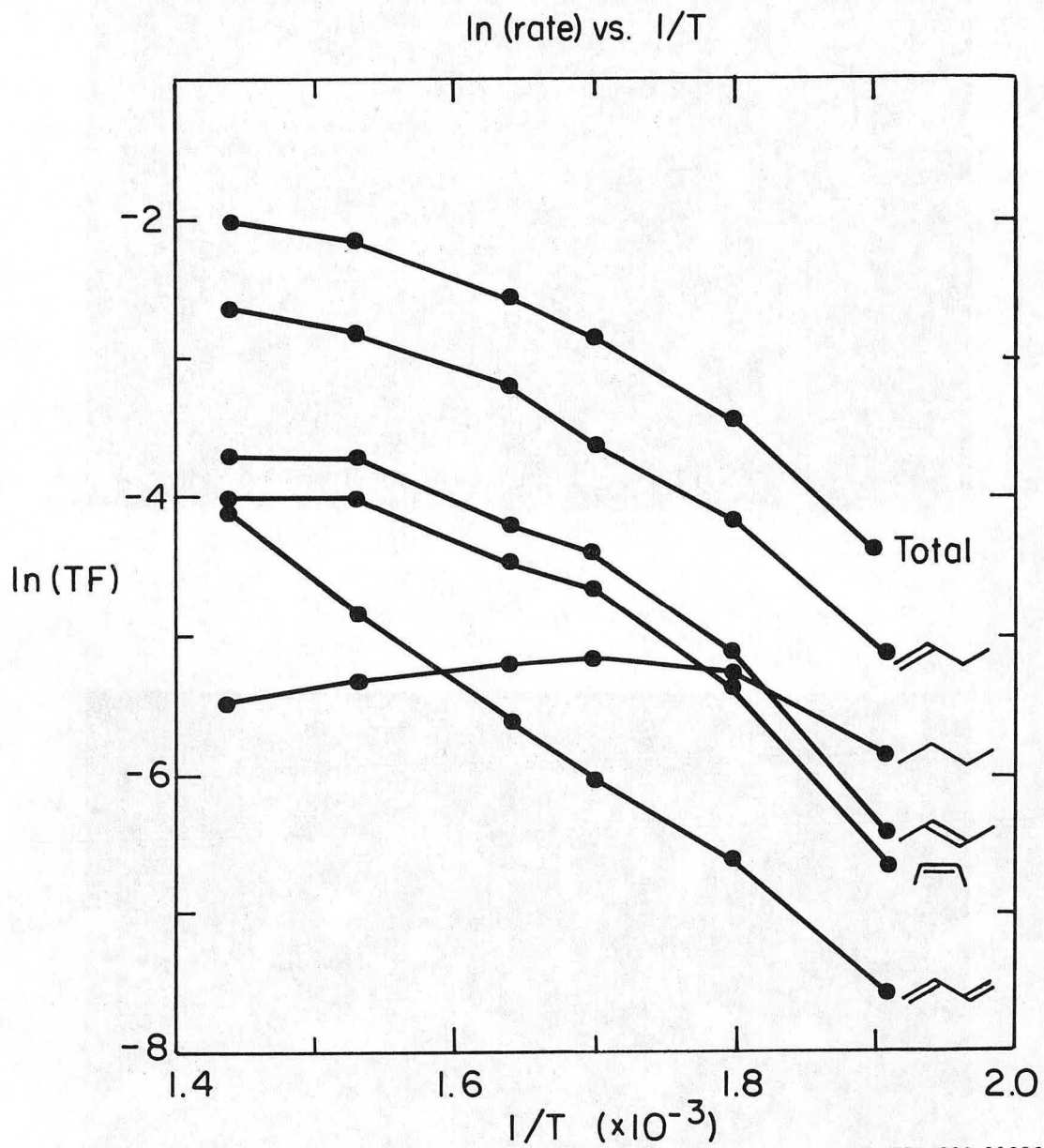
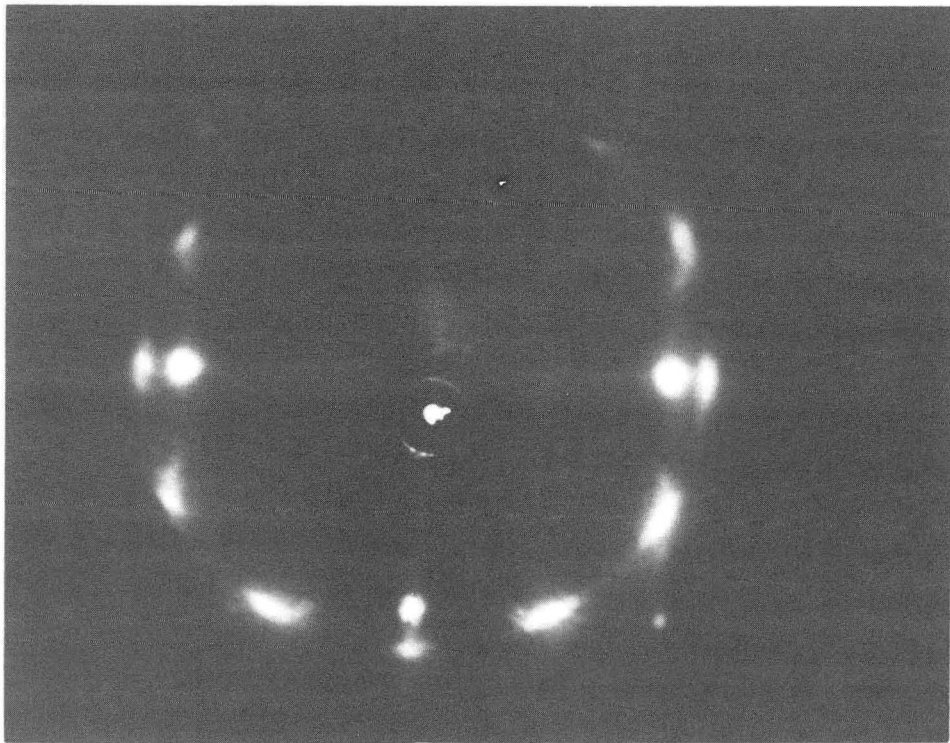
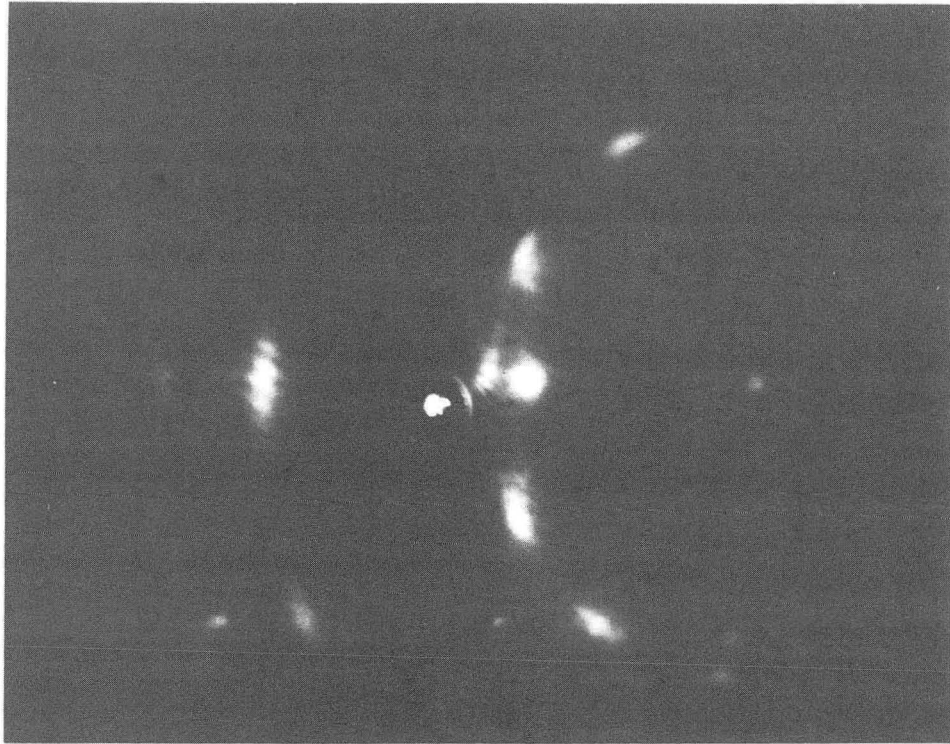


Fig. 1



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Fig. 2

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