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The Catalytic Hydrodesulfurization of Thiophene on the Mo(100) Crystal Surface

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. 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 (250–420°C). The total conversion of thiophene over the course of the reaction was always less than 5%. In all cases the Mo crystal surface was determined to be initially clean by Auger Electron Spectroscopy (AES).

TABLE 1

Product Distribution of the HDS of Thiophene

Product	Fractional yield (%)
Butadiene	5.6
1-Butene	52.8
trans-2-Butene	19.4
cis-2-Butene	13.9
n-Butane	8.1

Note. $C_4H_4S = 2.7t$, $H_2 = 780t$, $T = 340°C$.

TABLE 2

H_2 Pressure Dependence of HDS Product Rates of Appearance

Product	*n*
Butadiene	−0.18
1-Butene	0.54
trans-2-Butene	0.68
cis-2-Butene	0.58
n-Butane	1.10

Note. $C_4H_4S = 2.7t$, $T = 340°C$. $r = A \times (P_{H_2})^n$.

Over the range of experimental condi-

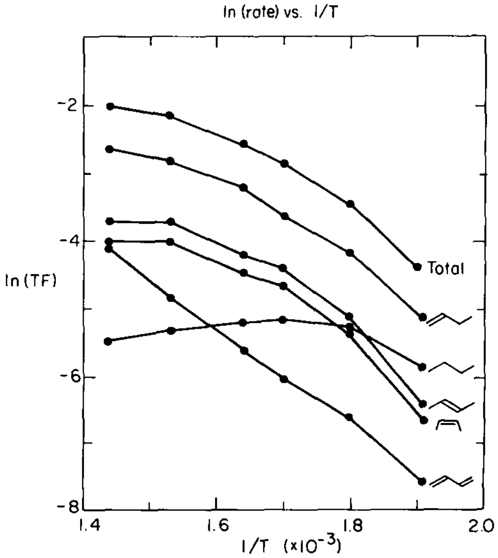

FIG. 1. Arrhenius plot of the temperature dependence of the product appearance rates for the HDS of thiophene. ($C_4H_4S = 2.5t$, $H_2 = 780t$). The activation energy for the production of butadiene is E_a = 14.4 kcal/mole.

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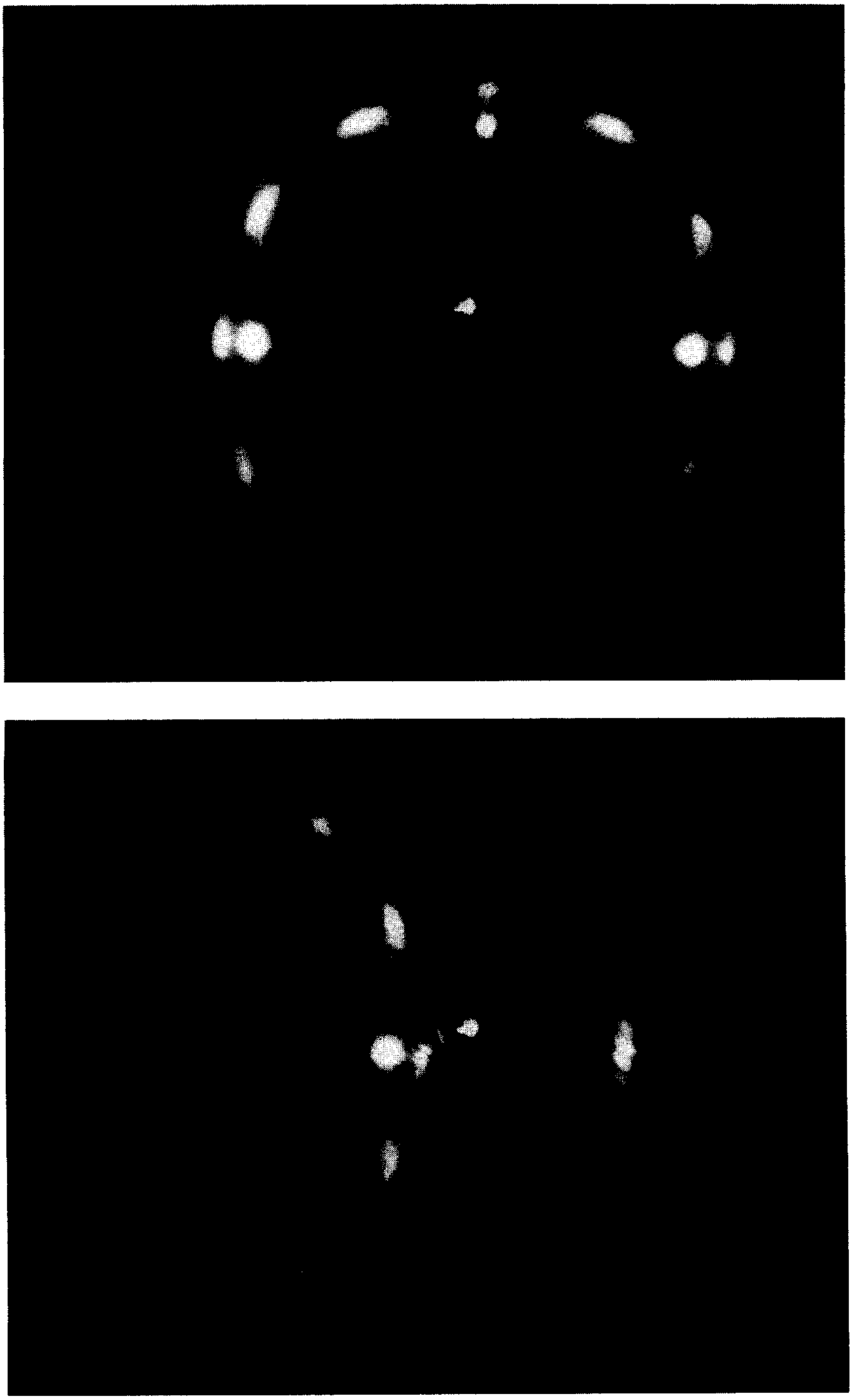

FIG. 2. LEED patterns of the hexagonal sulfur structure taken at normal and off-normal angles of incidence. The diffraction spots due to the Mo(100) substrate form a square lattice. The hexagonal lattice causes the superimposed rings having 12 intensity maxima about the circumference.

tions employed the initial reaction rates have varied from 0.020 to 0.120 turnovers/site/sec assuming that each surface Mo atom is an active site. The reaction proceeds in steady state at these rates for a period of 1–2 hr. and then the activity begins to decline slowly. 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_2 catalyst (*2*). The thiophene pressure dependence appears to be low- or zero-order, suggesting that the surface is saturated with thiophene under these conditions. The hydrogen pressure dependence, displayed in Table 2, is however, more complicated and varies among the products. The data suggests that the hydrogen pressure dependence is zero-order for butadiene, half-order for the butenes, and first-order for butane. The fact that we observe a half-order hydrogen pressure dependence for the butenes indicates that the surface hydrogen concentration is in the low coverage region of the hydrogen adsorption isotherm. The temperature dependence of the rates, shown in Fig. 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 at 700–800°C, after the reaction. On occasion, however, we have observed its presence immediately after the reaction without annealing of the surface, which implies that this structure may be present in all cases but with domain sizes too small to be detectable with LEED. 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 that 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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REFERENCES

1. Farias, M. H., Gellman, A. J., Chianelli, R. R., Liang, K. S., and Somorjai, G. A., submitted for publication.
2. Kolboe, S., *Canad. J. Chem.* **47,** 352 (1969).
3. Furminsky, E., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 31 (1983).
4. Salmeron, M., Chianelli, R. R., and Somorjai, G. A., *Surf. Sci.* **127**(3), 526 (1983).

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