JOURNAL OF CATALYSIS **107**, 92–102 (1987)

Catalytic Hydrodesulfurization over the Mo(100) Single Crystal Surface

I. Kinetics and Overall Mechanism

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Received August 19, 1986; revised February 16, 1987

The hydrodesulfurization of thiophene is catalyzed by the Mo(100) crystal surface at atmospheric pressures. The product distribution is similar to that detected over a high-surface-area powdered MoS_2 catalyst. Detailed kinetic studies have been performed in the 1 atm pressure regime and in the temperature range of 250–425°C. The initial reaction steps involve the desulfurization of thiophene to produce butadiene with an activation energy of 14.4 kcal/mole. Butenes and butane are produced via the subsequent hydrogenation of butadiene. The catalytic surface is predominantly covered with the partially hydrogenated hydrocarbon intermediates in the hydrogenation pathway. The hydrogen coverage on the other hand is very low and varies in proportion to $P^{1/2}(H_2)$.

1. INTRODUCTION

Although the hydrodesulfurization (HDS) process has been the object of catalytic studies for many years, the need to refine petroleum feedstocks with ever increasing sulfur contents has generated renewed interest in these reactions. These studies either consist primarily of kinetic and mechanistic investigations or are aimed at catalyst characterization. The catalyst most commonly used is molybdenum sulfide supported on a high-surface-area alumina and often promoted with cobalt. More recently surface science methods using single crystal surfaces have been utilized (*1–6*) to elucidate the elementary steps of this reaction. The work reported here describes combined ultrahigh vacuum (UHV) surface science and atmospheric pressure catalytic studies of the hydrodesulfurization of thiophene over single crystal surfaces of molybdenum.

The kinetic studies of HDS over dispersed Mo catalysts have been recently reviewed by Vrinat (*7*). For the most part these have been performed over high-surface-area, Co-promoted catalysts supported on γ-Al_2O_3. Variation of the reactant pressures has yielded rates that can be fitted to Langmuir–Hinshelwood type rate expressions while the temperature dependence of the rates is used to determine the Arrhenius parameters. This general approach to the study of these reactions has not as yet yielded a complete consensus, as can be seen from Vrinat's review which tabulates seven different rate expressions that have been successfully fitted to experimental data. The reported Arrhenius activation energies range from 3.7 to 26 kcal/mole. The exact source of the discrepancies is uncertain but it is clear that when working with poorly characterized and complex catalysts, minor differences in preparative procedures can result in different catalytic

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0021-9517/87 $3.00

behavior. Furthermore, the complexity of such catalysts makes interpretation of results very difficult since the reactions can take place on a variety of active sites within the catalyst. For example, H_2S was found to inhibit desulfurization activity but not hydrogenation activity. Therefore, it has been suggested that these two reactions occur on two distinct catalytic sites (*8*, *9*). Changes in product distribution with the addition of a support suggest that this complicates the situation either through reactions occurring on the support or by modifying the nature of the catalytically active sites (*10*).

The rate expressions that have been proposed for thiophene HDS have a general form:

$$r = \frac{kK_TP_TK_HP_H}{(1 + K_TP_T + K_SP_S)^2}.$$

Here k is the rate constant; K_i are equilibrium constants; P_i are pressure values; and the subscripts T, H, S refer to thiophene, hydrogen, and H_2S, respectively. This expression implies first-order adsorption of both thiophene and hydrogen and adsorption inhibition by thiophene and H_2S. The product distribution over supported catalysts consists primarily of the three isomers of butene with a small fraction of butane and in some cases butadiene. The fact that small amounts of butadiene have been observed while no tetrahydrothiophene has been produced has led to the conclusion that butadiene is an intermediate in the reaction and that hydrogenation of C–S bonds occurs prior to the hydrogenation of C–C bonds (*9*).

Our investigation has been performed over Mo single crystal surfaces that have been well characterized in terms of both, structure and composition. The results have been divided into two papers. This, the first, discusses the nature of the catalytic reaction and its kinetics over initially clean Mo surfaces. The second paper discusses the role of adsorbed sulfur in the reaction and the details of the initial desulfurization step. The first experiments were aimed at determining whether or not it is possible to catalyze the HDS of thiophene over a metal surface and what similarities this reaction may have to that performed over an industrial catalyst. Following this a series of kinetic experiments were performed over the Mo(100) surface to measure the effects of variations in reaction parameters. No detailed fitting of rate expressions has been performed although a model is proposed that is consistent with the observed kinetic parameters. It should be noted that this reaction is complicated, involving the scission of two C–S bonds, the dissociation of H_2, and the formation of two S–H bonds and between two and six C–H bonds. The proposal of a detailed mechanism and the fitting of rates to obtain kinetic constants based purely on kinetic observations would be extremely difficult and of questionable value. It is also worth noting that the kinetic studies performed to date over supported catalysts have all focused on the overall reaction rate, as measured by the disappearance of thiophene or the appearance of C_4 hydrocarbon products. In this study it has been very useful to examine the kinetics of formation of each of the products, as not all are identical.

2. EXPERIMENTAL

The characterization of the catalytic single crystal surfaces before and after reaction was performed in a stainless steel chamber pumped to a pressure of 1×10^{-9} Torr. This chamber was equipped with a four-grid, retarding field, electron energy analyzer used for both Auger Electron Spectroscopy (AES) and Low-Energy Electron Diffraction (LEED). The AES and LEED characterization of the clean and sulfided Mo(100) surface has been described elsewhere (*12*, *13*) with the details of sample preparation and cleaning.

The UHV chamber in which the sample characterization was performed was equipped with an atmospheric pressure isolation cell that could be enclosed over the sample and pressurized to 1 atm without any degradation of the vacuum in the chamber. This cell was part of a closed loop batch reactor through which reactant gases were circulated. The general procedure for performing an atmospheric pressure catalytic reaction was as follows. Having prepared and characterized its surface under UHV conditions the Mo single crystal was enclosed in the cell. Thiophene vapor was then leaked into the loop to the desired pressure (0.1–5 Torr) followed by pressurizing with hydrogen (100–800 Torr). This gas mixture was then circulated through the reactor loop for 30 min to ensure complete mixing. Following this the crystal was resistively heated to the desired temperature to initiate the reaction. The crystal temperature was measured using a Pt–Pt/Rh 10% thermocouple spot-welded to its edge and was maintained using a Eurotherm temperature controller. While the crystal was hot the gas mixture in the reactor was periodically analyzed by injection of samples into a gas chromatograph via a sampling valve. The reactants and products were separated on a 19% picric acid on Carbowax column and detected using a flame ionization detector. Following a reaction the crystal was allowed to cool in the gas mixture which was then pumped out of the loop via a mechanical pump for 2 hr before opening to expose the crystal to UHV conditions.

The crystal was mounted on the manipulator by spot-welding between two thick (0.125-in.) Ta posts allowing resistive heating of the sample without simultaneous heating of the supports. This configuration had to be repaired periodically as the crystal would become dismounted. Some fluctuations in the absolute reaction rate under a given set of conditions were observed from one mounting to the next and these are the major source of error in the reported value of the absolute rate. The exact cause of these fluctuations is unknown but may arise from small changes in the heating characteristics of the crystal from one mounting to the next. Severe hot-spots were easily detectable during the reactions by high rates of thiophene hydrogenolysis and methane production. During a series of experiments in which a number of reactions were performed to measure some kinetic parameter, remounting of the crystal was avoided to minimize the error in the parameter value.

3. RESULTS

3.1. The Thiophene HDS Reaction over a Mo(100) Single Crystal Catalyst: Comparison with a High-Surface-Area MoS_2 Catalyst

The catalytic hydrodesulfurization of thiophene over a Mo(100) surface can be readily performed (*2*). It is useful to compare this reaction on the single crystal metal surface with that over a powdered MoS_2 catalyst to illustrate the similarities between the two. Under typical conditions $P(H_2)$ = 780 Torr, $P(Th)$ = 2.5 Torr, T = 340°C, the reaction proceeds at a steady-state rate of 0.11 ± 0.03 molecules/site/sec for periods up to 90 min. We define a site as a single surface atom. A comparison of the absolute reaction rates shows that the single crystal is much more active than the MoS_2 powder. The single crystal gives a turnover rate of 3.2×10^{-2} molecules/site/sec or 5.3×10^{-7} mole/m^2/sec (at 280°C) while the MoS_2 catalyst with a BET surface area of 67 m^2/g, had an activity of 2.3×10^{-9} mole/m^2/sec (*11*). This difference in activity is not particularly surprising since it is not clear that the BET measurement is sensitive only to the active surface and the MoS_2 powder probably has a large fraction of inactive surface area composed of the sulfided basal planes of MoS_2 crystallites. Several studies have shown that there is no correlation between the BET surface area and HDS activity for a number of sulfided Mo catalysts (*14*). A comparison of activity per unit weight of metal shows a similar discrepancy with the single crystal having an activity of 3.4×10^{-4} mole/g/sec as compared with 2.5 × 10^{-7} mole/g/sec for the high-surface-area catalyst. Apparently only a small fraction of the metal atoms in the MoS_2 are active. Again this is not surprising since a large fraction of Mo atoms lie sandwiched between the sulfided planes of MoS_2 crystallites and are probably not exposed to the reactant mixture.

The reaction product distribution is shown in Fig. 1 compared with that obtained over the MoS_2 catalyst (*11*). In addition to the breaking of C–S bonds leading to the C_4 hydrocarbon products, there is some breaking of C–C bonds, leading to smaller hydrocarbons. The rate of this reaction, however, is always <5% of the total rate. It is clear from the comparison of the C_4 product distributions that the two are almost identical, suggesting that the reaction over the Mo(100) surface proceeds via the same mechanism as that over the MoS_2 powder.

3.2. Hydrodesulfurization of Tetrahydrothiophene

In an attempt to determine whether the hydrogenation reactions precede or follow the C–S bond breaking we have studied the HDS of tetrahydrothiophene (C_4H_8S). Reaction conditions were $P(H_2) = 780$ Torr, $P(\text{THTh}) = 2.5$ Torr, and $T = 340°C$, and

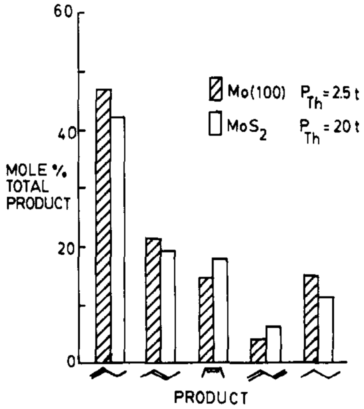

FIG. 1. Comparison of the product distributions from thiophene HDS over the clean Mo(100) surface and powdered MoS_2.

resulted in a total reaction rate of 0.49 molecules/site/sec. In addition to HDS, a simple dehydrogenation reaction produces thiophene at a rate of 0.02 molecules/site/sec. The most striking feature of the product distribution is the very large fraction of propylene produced, not apparent in the thiophene HDS product distribution. In all cases of thiophene HDS, the rate of hydrogenolysis of C–C bonds was less than 5% of the total reaction rate. In the case of tetrahydrothiophene HDS, propylene is the primary product (65% of total yield). Clearly, tetrahydrothiophene is not a likely intermediate in the thiophene HDS reaction.

The tetrahydrothiophene HDS reaction is interesting in its own right. The production of propylene implies breaking of C–C bonds but is not accompanied by the simultaneous production of methane. No products other than C_3 and C_4 hydrocarbons have been detected. Auger analysis of the surface after the reaction shows no anomalous buildup of carbon to account for the nonstoichiometric reaction, nor is there any apparent contamination of the bulk of the crystal with dissolved carbon. The flame ionization detector used in this work is sensitive only to carbon atoms in a reduced form and so, such possible carbon-containing products as CS_2 would not be detectable. The fate of the remaining carbon atom is still under investigation.

One study of the HDS of tetrahydrothiophene over a powdered MoS_2 catalyst reports the production of C_3 hydrocarbons, although in this case the product was allene (C_3H_4) rather than propylene (*20*). The discrepancy here may lie in the fact that the hydrogen pressure used was 10 Torr vs the 780 Torr used in the present study, suggesting that in our case allene is an intermediate that is hydrogenated to propylene. Again, no products containing only one carbon atom were detected and the remaining atom was assumed to be left adsorbed on the catalyst. Propylene has been observed as a product of the hydrodeoxygenation (HDO) of furan (*16*) and once again the fourth carbon atom from the ring was assumed to be remaining on the catalyst. In this case, however, our own investigation over Mo foils showed that during the HDO of both furan and tetrahydrofuran the production of propylene was accompanied by the appearance of CO (*17*).

The product distribution of tetrahydrothiophene HDS is quite different from that of thiophene HDS, indicating that thiophene is not hydrogenated to tetrahydrothiophene as an initial step in the HDS process. We have also compared the distribution of butenes and butane produced by butadiene hydrogenation with their distribution from thiophene HDS. The two are quite similar. These results together support a proposed mechanistic pathway in which thiophene is initially desulfurized to butadiene which is subsequently hydrogenated to yield the butenes and butane.

3.3. *The Kinetics of Thiophene HDS*

This section presents the results of kinetic measurements of thiophene HDS made over the initially clean Mo(100) surface. Description of a model consistent with both these and other results will be reserved for the discussion section. An Arrhenius plot of the appearance rates of each of the products is shown in Fig. 2. The rate of butadiene production is the only curve that shows Arrhenius-type temperature dependence with an activation energy of 14.4 ± 2 kcal/mole. The Arrhenius plots for the butenes have a negative curvature, all having similar temperature dependences. The rate of butane production has a strongly non-Arrhenius-type temperature dependence showing a decrease in rate with increasing temperature and a maximum at about 320°C. A comparison of the reaction rates in a D_2 atmosphere shows no significant change in the reaction rates except at the highest temperature (420°C). The isotope effect that might be expected for a reaction whose rate-limiting step is hydrogenation is not apparent. An Arrhenius plot of the reaction rates in D_2 shows the same general behavior as that for the reaction in H_2. Since the butenes are the primary product, the total rate of reaction follows their temperature dependence and shows the same non-Arrhenius-type behavior.

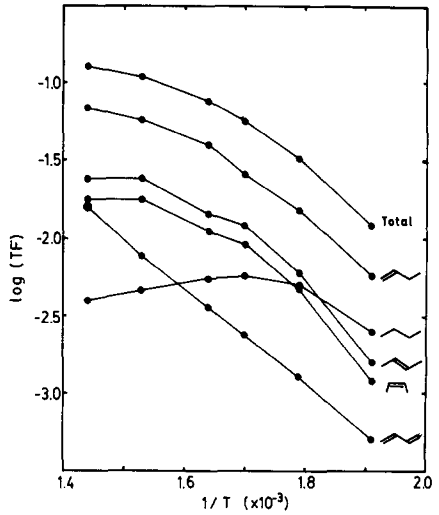

FIG. 2. Arrhenius plot of the rates of product appearance during thiophene HDS over the clean Mo(100) surface. $P(H_2)$ = 780 Torr, $P(Th)$ = 2.5 Torr.

Figures 3 and 4 are order plots illustrating the dependence of the reaction rates for butadiene, the butenes, and butane on both hydrogen and thiophene pressures. The dependence among the three butene isomers shows very little variation. The rate dependence on hydrogen pressure is roughly 0, $\frac{1}{2}$, and 1 for butadiene, the butenes, and butane, respectively, with the measured values listed in the figure. The rate of butadiene production has a first-order dependence in thiophene pressure while the hydrogenated products show only very weak dependence. Again, exact values are listed in the figure.

4. DISCUSSION

We have shown that the catalytic hydrodesulfurization of thiophene in hydrogen can be carried out over the Mo(100) surface and that this reaction has a very similar product distribution to that over a powdered MoS_2 catalyst. The reaction over the

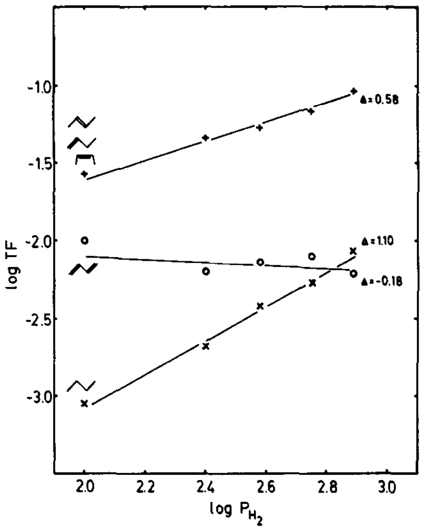

FIG. 3. Hydrogen pressure dependence of the product rates of appearance during thiophene HDS over the clean Mo(100) surface. $P(\mathrm{Th})$ = 2.7 Torr, T = 340°C.

initially clean surface proceeds with a turnover frequency of 0.11 ± 0.03 at a temperature of 340°C and reactant pressures of 2.5 Torr of thiophene and 780 Torr of hydrogen. The activity of the catalyst is constant over a period of about 90 min after which a deactivation process becomes apparent. This deactivation is discussed in the companion to this paper. Comparison of the product distribution with that of tetrahydrothiophene HDS suggests that the reaction proceeds via initial desulfurization, possibly yielding butadiene that is subsequently hydrogenated to the butene and butane products.

4.1. The Temperature Dependence of Thiophene HDS

The kinetic parameters of the reaction over the initially clean Mo(100) surface suggest a fairly complex reaction scheme. The first point of interest is the dependence of the reaction rates on the crystal temperature. Arrhenius-type kinetic behavior requires reactant concentrations to be independent of temperature. In the case of surface-catalyzed reactions, however, although gas phase reactant pressures may be independent of temperature the critical surfaces coverages need not be. The non-Arrhenius temperature dependence of the butene and butane products and, in particular, the maximum in the rate of butane production suggest a depletion of the surface of one of the reactant species with increasing temperature. Such an effect occurs because the observed rate constant in a surface reaction can often be composed of both true rate constants and adsorption equilibrium constants (*19*). The details of such considerations are given in Appendix A.

In the present case the depletion of the surface in hydrogen can explain the observed Arrhenius plots. Since the production of butadiene is independent of hydrogen pressure it is expected that, if this is the case, its rate of appearance will obey Arrhenius-type kinetics; $r_{\mathrm{B0}} = k_{\mathrm{B0}}$. Here

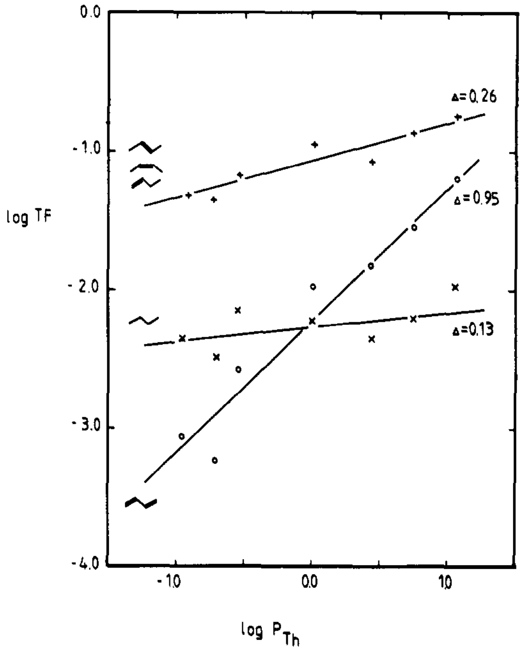

FIG. 4. Thiophene pressure dependence of the product rates of appearance during thiophene HDS over the clean Mo(100) surface. $P(H_2)$ = 780 Torr, T = 340°C.

r_{B0} is the rate of butadiene production and k_{B0} is a rate constant that contains any dependence on thiophene coverage but, nevertheless, results in Arrhenius kinetics. The fact that the butenes all have approximately half-order dependence on hydrogen pressure means that they should each have similar temperature dependences, having rate expressions of the form $r_{B1} = k_{B1}\theta_H$ at a given temperature. The term for the hydrogen coverage θ_H, however, does depend on the temperature. The butane production rate, being first order in hydrogen pressure, is expected to have a stronger dependence on hydrogen coverage, having a rate expression of the form $r_{B2} = k_{B2}\theta_H^2$. Hence, if the rate of butene production shows non-Arrhenius temperature dependence the rate of butane production will deviate to an even greater extent.

The pressure dependence of the reaction rates was measured at 340°C ($1/T = 1.63 \times 10^{-3}$ K^{-1}). The fact that the rate of butene production has a half-order dependence on the hydrogen pressure suggests that at this temperature the adsorption equilibrium is in the low-coverage regime of the hydrogen adsorption isotherm. Since adsorption is dissociative the coverage (θ_H) is proportional to the square root of the hydrogen pressure.

4.2. The Pressure Dependences of the HDS Product Appearance Rates

Having discussed the temperature dependence of the thiophene HDS reaction and presented arguments concerning the behavior of the hydrogen coverage it is necessary to discuss the overall mechanism leading from adsorbed thiophene to the reaction products. The detailed kinetic expressions are given in Appendix B while in this section we summarize the results and their implications.

In examining the kinetics of the HDS reaction the first product of interest is butadiene. Its rate of appearance is independent of hydrogen pressure in spite of the fact that its formation requires the creation of at least two C–H bonds. This might be used to argue that the surface is saturated with hydrogen. The fact that its rate of hydrogenation to butene is dependent on hydrogen pressure, however, rules out the possibility of a hydrogen-saturated surface. The other possible reason for a zero-order hydrogen pressure dependence is that the surface is saturated with butadiene and that the reaction is rate-limited by its desorption. This can be eliminated based upon the fact that the rate of butadiene production has a first-order dependence on the thiophene pressure.

The butadiene formation kinetics can be explained by a reaction mechanism in which the rate-limiting step occurs prior to hydrogenation and the subsequent hydrogenation and butadiene desorption steps are fast.

$$\mathrm{Th_g} \xrightarrow{k_1} \mathrm{T_a} \xrightarrow[\mathrm{H}]{k_2} \mathrm{T_1} \xrightarrow[\mathrm{H}]{k_3} \mathrm{T_2} \xrightarrow[\mathrm{H}]{k_4}$$

$$\mathrm{T_3} \xrightarrow[\mathrm{H}]{k_5} \text{butadiene}_\mathrm{a} \xrightarrow{k_6} \text{butadiene}_\mathrm{g}$$

Here $\mathrm{Th_g}$ represents gas phase thiophene, $\mathrm{T_a}$ a species resulting from thiophene adsorption that has not been hydrogenated by surface hydrogen, and $\mathrm{T_1}$, $\mathrm{T_2}$ and $\mathrm{T_3}$ are partially hydrogenated intermediates in the reaction pathway leading from $\mathrm{T_a}$ to adsorbed butadiene. The rate-limiting step could be adsorption of thiophene or a reaction step leading to the species $\mathrm{T_a}$ that is then hydrogenated to butadiene. If thiophene adsorption is the rate-limiting step, it is difficult to understand the origin of the 14.4 kcal/mole activation energy since this represents an unusually high barrier for a molecular absorption process.

The point in the reaction path at which sulfur is extracted from the ring and desorbs as H_2S cannot be determined. A possible rate-limiting step might be the breaking of C–S bonds to form a metal–sulfur species and a hydrocarbon fragment, both of which can be subsequently hydrogenated. The second of this pair of papers describes direct measurements of the rates of hydrogenation of the Mo–S species using a ^{35}S isotope. These have shown that the formation of an Mo–S intermediate is not a step in the HDS mechanism of thiophene. A final alternative that has been proposed in the literature is an intramolecular desulfurization reaction leading to H_2S and a diacetylene-like species that must be hydrogenated to yield butadiene (*11*, *20*). This mechanism, originally proposed by Kolboe (*11*), is consistent with our kinetic data. At present the rate-limiting step cannot be defined in any greater detail other than to reiterate that it must occur prior to any of the hydrogenation steps.

The second sequence of reaction steps involve the hydrogenation of butadiene to butene and butane. These exhibit roughly half-order and first-order dependence on hydrogen pressure, respectively, and are only weakly dependent on thiophene pressure. The hydrogen pressure dependences must be reconciled with the fact that the hydrogenation of butadiene to butene requires two hydrogen atoms while its hydrogenation to butane requires four. Our analysis of the kinetic data suggest the presence of two partially hydrogenated hydrocarbon species labeled BH and BH_2 that are ultimately hydrogenated to butene and butane respectively. These exist in equilibrium with adsorbed hydrogen and butadiene and are close to saturating their available adsorption sites, resulting in the independence of thiophene pressure.

The nature of this hydrocarbon species is undetermined at this point. Our study of the effects of adsorbed sulfur on the HDS reaction, however, shows that sulfur blocks the formation of butene and butane but not butadiene. These results are discussed in detail in the companion to this paper. Briefly, this suggests that the species BH and BH_2 are adsorbed in the same binding site as the sulfur atom which, on the Mo(100) surface, is the fourfold hollow site (*13*, *18*, *22*).

The above analysis of the kinetics of thiophene HDS has yielded a mechanistic pathway that conforms to the observed behavior and is outlined in Fig. 5. Needless to say, such a pathway cannot be shown to be unique in explaining our results. Nevertheless, it does embody three conclusions that would be difficult to avoid in any interpretation of the data. First, the hydrogen coverage of the catalytic surface varies, under our conditions, in the temperature range 250–425°C resulting in non-Arrhenius-type temperature dependences for the rates of production of butane and butene. At a temperature of 340°C the coverage is at the low end of the hydrogen adsorption isotherm and thus varies as the half-order power of the hydrogen pressure. Second, the rate-determining step in the production of butadiene occurs prior to any hydrogenation steps. This results in the observed first-order dependence on thiophene pressure and apparent independence of hydrogen pressure. Finally, the hydrogenated products are produced via an intermediate whose coverage saturates its available adsorption sites, resulting in an independence of thiophene pressure.

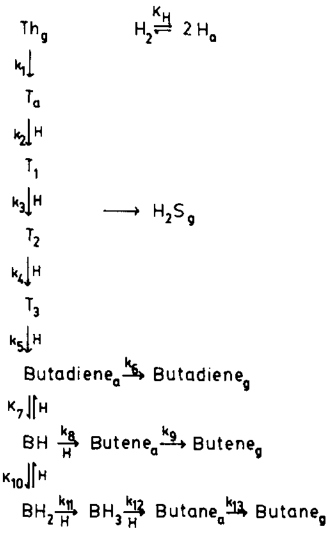

FIG. 5. A mechanistic pathway for thiophene HDS that is consistent with the observed kinetics.

6. SUMMARY

The thiophene HDS reaction over Mo single crystal catalysts appears to proceed via initial desulfurization to yield butadiene followed by hydrogenation reactions producing butenes and butane. The kinetics of butadiene formation suggest that the rate-limiting step occurs prior to any hydrogenation steps with an activation energy of 14.4 ± 2 kcal/mole. These results are consistent with the Kolboe mechanism in which the desulfurization step occurs via an intramolecular dehydrodesulfurization step in which the sulfur atom is hydrogenated by atoms originating from the thiophene molecule (*11*).

The kinetics of hydrogenation suggest that under the conditions employed the catalytic surface is deficient in hydrogen, i.e., in the low-coverage regime of the hydrogen adsorption isotherm. Hydrogenation of the butadiene intermediate to butenes and butane occurs via partially hydrogenated intermediates designated BH and BH_2, respectively, that are in equilibrium with adsorbed butadiene and hydrogen. These species appear to saturate their available binding sites on the surface. The fact that sulfur, adsorbed in the fourfold hollows, blocks adsorption sites for these species suggests that they are also bound in the fourfold hollows. Butadiene production is unaffected by adsorbed sulfur, suggesting that the thiophene and butadiene adsorption sites or configurations are different from those of the partially hydrogenated intermediates.

APPENDIX A

The intent of this section is to give a detailed account of the hydrogen adsorption/desorption kinetics that lead to non-Arrhenius reaction kinetics. These will be related to the observed temperature dependences of butene and butane production which suggest that the surface becomes depleted of one of the reactants at high temperatures.

Consider a unimolecular reaction in which a gas phase molecule (A_g) is in equilibrium with its adsorbed counterpart (A_a), and $A_a \rightarrow B_a$ with B_a desorbing immediately.

$$\begin{array}{lll} A_g \leftrightarrows A_a & K_A = A\exp(\Delta H_A/RT) & \\ A_a \rightarrow B_a & k_r = A'\exp(-E_a/RT) & \\ B_a \rightarrow B_g & k_d & (k_d \gg k_r) \end{array}$$

The surface coverage of A_a will be given by

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A}$$

and thus the reaction rate is given by

$$r_A = \frac{k_r K_A P_A}{1 + K_A P_A}.$$

The Arrhenius plot yields an apparent activation energy of

$$E_A = \frac{d\ \ln(r)}{d(-1/RT)}$$
$$= E_a - \Delta H_A + \frac{\Delta H_A K_A P_A}{1 + K_A P_A}.$$

At low temperatures θ_A will be ≈ 1 and fairly independent of temperature and the slope of the plot will give the correct activation energy of E_a. At high temperatures $K_A P_A$ will become very small and the apparent activation energy will be $E_a - \Delta H_A$ which can be negative if $\Delta H_A > E_a$.

In the case of thiophene HDS, it is the hydrogen coverage that is temperature-dependent. The rate of butene production is given by the expression

$$r_{B1} = \frac{k_{B1} K_H^{1/2} P_H^{1/2}}{1 + K_H^{1/2} P_H^{1/2}} = k_{B1}\theta_H(T)$$

with k_{B1} depending upon the butene isomer and θ_H(T) being the hydrogen adsorption isotherm at a given pressure. The butane production rate, being first order in hydrogen pressure, is expected to have a stronger dependence on hydrogen coverage and should have a rate expression given by

$$r_{B2} = \frac{k_{B2}(K_H^{1/2} P_H^{1/2})^2}{(1 + K_H^{1/2} P_H^{1/2})^2} = k_{B2}\theta_H^2(\mathrm{T}).$$

If this analysis is correct and sufficient to explain the non-Arrhenius behavior of the rates, the ratio r_{B1}^2/r_{B2} should have the form

$$\frac{r_{B1}^2}{r_{B2}} = \frac{k_{B1}^2}{k_{B2}}.$$

The constants k_{B1} and k_{B2} are products of rate constants and the coverages of the surface species being hydrogenated to yield butenes and butane, respectively. If, over the temperature range investigated, these take the form of just a rate constant, or possibly the product of a rate constant and an equilibrium constant, then the plot $\ln(r_{B1}^2/r_{B2})$ vs $1/T$ should be linear. This plot is shown in Fig. 6 and, in fact, is linear through all but the highest temperatures.

APPENDIX B

The intention of this section is to present the analysis of the kinetics of the hydrogenation reactions that lead from butadiene to the butenes and butane.

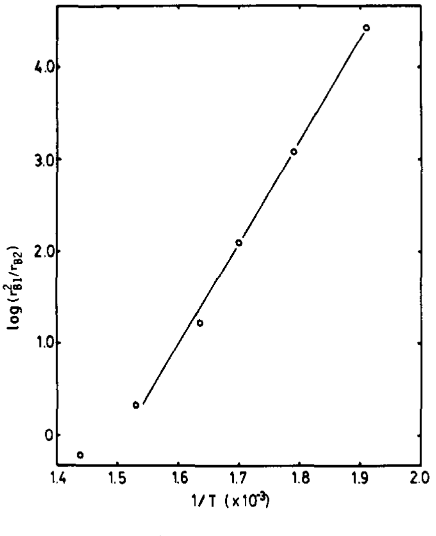

FIG. 6. Plot of (r_{B1}^2/r_{B2}) vs $1/T$. r_{B1} is the rate of butene production and r_{B2} the rate of butane production during thiophene HDS. $P(H_2)$ = 780 Torr, $P(Th)$ = 2.5 Torr.

The rates of appearance of the hydrogenated products are dependent upon hydrogen pressure and almost independent of thiophene pressure. These kinetics suggest an intermediate in the hydrogenation pathway that is saturating its available adsorption sites. If such a species were present in equilibrium with butadiene, or any of the precusors to butadiene, the equilibrium expression for its coverage would be

$$K_7 \cdot \theta_B \cdot \theta_H(1 - \theta_{BH}) = \theta_{BH}(1 - \theta_H),$$

where θ_B is the coverage of butadiene or the precursor to butadiene that, when hydrogenated yields the species BH. θ_{BH} is the coverage of this intermediate that will lead to butene and butane production. Note that the above expression does not include competition for binding sites between butadiene and BH or between hydrogen and hydrocarbons. The lack of competition between butadiene and the partially hydrogenated intermediate might result from differences in their bonding to the surface. The noncompetitive coadsorption of hydrogen and hydrocarbons has also been observed in a related study of the hydrogenation of butadiene over Pt(110) surfaces (*21*). Given that the hydrogen coverage is low the equilibrium coverage of BH is given by

$$\theta_{BH} = \frac{K_7\theta_B\theta_H}{1 + K_7\theta_B\theta_H},$$

which, for a large value of the equilibrium constant, will be approximately unity, independent of the pressure of either reactant. A subsequent hydrogenation step to yield butene would have a rate expression of

$$r_{B1} = k_8\theta_{BH}\theta_H \approx k_8\theta_H$$

which would be independent of thiophene pressure and have a half-order dependence on hydrogen pressure, as observed.

The first-order dependence of the butane production in hydrogen pressure implies a second equilibrium step involving hydrogen, before the final hydrogenation steps. If the above-mentioned intermediate BH is in equilibrium with a second species BH_2 that ultimately leads to butane production then the equilibrium expressions become

$$K_7\theta_B\theta_H(1 - \theta_{BH} - \theta_{BH_2}) = \theta_{BH}(1 - \theta_H)$$

and

$$K_{10}\theta_{BH}\theta_H = \theta_{BH_2}(1 - \theta_H)$$

and the final coverages of each are given by

$$\theta_{BH} = \frac{K_7\theta_B\theta_H}{1 + K_7\theta_B\theta_H + K_7K_{10}\theta_B\theta_H^2}$$

$$\theta_{BH_2} = \frac{K_7K_{10}\theta_B\theta_H^2}{1 + K_7\theta_B\theta_H + K_7K_{10}\theta_B\theta_H^2}.$$

The denominator is still dominated by the term $K_7\theta_B\theta_H$, if K_{10} is not large, because θ_H^2 is small. The coverages are

$$\theta_{BH} \approx 1$$

$$\theta_{BH_2} \approx K_{10}\theta_H,$$

not affecting the butene production kinetics. The hydrogenation of the BH_2 species to butane will have a rate given by

$$\theta_{B2} = k_{11}K_{10}\theta_H^2,$$

which will be first-order in hydrogen pressure and independent of thiophene pressure, as observed. The suggestion that K_{10} is not large is consistent with the fact that butene production is much greater than butane production. The apparent rate constants k_{B1} and k_{B2}, introduced in our earlier analysis of the temperature dependence of the reaction rates, are exactly equivalent to k_8 and $k_{11}K_{10}$, respectively.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

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