JOURNAL OF CATALYSIS 47, 300–315 (1977)

Studies of Molybdena–Alumina Catalysts

V. Relation between Catalyst Sulfided State and Activity for Thiophene Hydrodesulfurization

F. E. MASSOTH

Department of Mining, Metallurgical and Fuels Engineering, University of Utah, Salt Lake City, Utah 84112

AND

C. L. KIBBY

Pittsburgh Energy Research Center, ERDA, Pittsburgh, Pennsylvania 15213

Received August 4, 1976; revised February 17, 1977

Sulfiding of a molybdena–alumina catalyst with thiophene/H_2 mixtures was studied by a gravimetric technique. Thiophene conversions were separately measured using a catalytic microreactor. Simultaneous measurements of catalyst changes and reactivity were also carried out in a stirred, microbalance reactor. Runs were made on oxidized, prereduced and presulfided catalysts.

The results of sulfiding the catalyst with thiophene were similar to those previously obtained with H_2S. The predominant reaction was exchange of reactive O for S, with some anion vacancies also being formed. Prereduced catalysts sulfided to a lesser extent than the oxidized catalyst. Thiophene conversion varied with catalyst pretreatment and time on stream.

A correlation between catalyst activity and catalyst surface concentrations is proposed based on dual sites consisting of anion vacancies and surface sulfide–oxide sites. It is supposed that the former are sites for thiophene adsorption and the latter for hydrogen adsorption and transfer.

NOMENCLATURE[1]

a	proportionality constant in Eq. (6) (sec g/mmol)
b	conversion constant in Eq. (15) $(g/mmol)^2$
C	fractional thiophene conversion [1]
C_4	coke on thiophene-reacted catalyst [2]
D	adsorption term in Eq. (4) [1]
k_o, k_s	surface rate constants (mmol/sec g)
k_T	global rate constant for thiophene reaction (mmol/sec g)
L_o, L_s, L_v	number of surface sites given by Eq. (12) (mmol/g)
O	active oxygen remaining [2]
O_s	surface oxygen given by Eq. (7) [2]
p_H	partial pressure of hydrogen in reactor (atm)
p_T	partial pressure of thiophene in reactor (atm)
r_T	global rate of thiophene reaction (mmol/sec g)
S	total sulfur on catalyst [2]
S_E	exchange sulfur on catalyst [2]

---

[1] [1] dimensionless; [2] mmol/mmol Mo; [3] mg/g; g = grams of catalyst.

ISSN 0021-9517

S_I	sulfur incorporated as irreversibly adsorbed hydrogen sulfide [2]
S_I^*	defined by Eq. (3) [2]
S_s	surface sulfur given by Eq. (8) [2]
W_{cat}	weight of catalyst (mg)
W_{CH}	weight of coke on catalyst [3]
W_M	weight of molybdenum on catalyst [3]
W_S	weight of total sulfur on catalyst [3]
ΔW_{OR}	weight loss in reduction of oxidized catalyst [3]
ΔW_{OS}	weight gain in sulfidation of oxidized catalyst [3]
ΔW_{OT}	weight gain in thiophene reaction of oxidized catalyst [3]
Y	activity parameter defined by Eq. (6) [1]
$\square$	anion vacancies [2]
$(\square_T)_i$	effective anion vacancies present after thiophene reaction as defined in Eq. (10) [2]
$\theta_{H,O}$	fraction of surface oxygen covered by adsorbed hydrogen [1]
$\theta_{H,S}$	fraction of surface sulfur covered by adsorbed hydrogen [1]
θ_T	fraction of vacancies covered by adsorbed thiophene [1]

Subscripts

R	value after reduction
S	value after sulfidation
s	surface species
T	value after thiophene reaction

INTRODUCTION

Previous papers in this series have been concerned with characterization of reduced (*1–3*) and sulfided (*4*) states of molybdena–alumina catalysts. The present paper attempts to relate these studies to catalyst activity for thiophene hydrogenolysis. Specifically, we report on changes in the state of the catalyst under thiophene reaction conditions and attendant catalytic activity.

Thiophene undergoes hydrogenolysis at moderate temperatures over an Mo/ or $CoMo/Al_2O_3$ catalyst in the presence of hydrogen to give as principal products: butenes, butane and hydrogen sulfide. Butadiene (*5*) and ethane (*6*) have occasionally been reported in minor amounts. Possible mechanisms for thiophene desulfurization have been reviewed by Mitchell (*7*). Early workers held the view that hydrogenation to tetrahydrothiophene preceded C–S bond cleavage. Amberg and co-workers (*8*) later presented evidence that C–S bond splitting preceded hydrogenation. In their scheme, butadiene was a primary product (but not generally observed because of its rapid subsequent hydrogenation to butene).

A detailed mechanism scheme, based on Amberg and co-workers' results, has been advanced by Lipsch and Schuit (*9*). Briefly, this entails adsorption of thiophene on a vacancy in the molybdena layer created by prereduction of the catalyst. An essential feature of this scheme is that the reduced catalyst contains OH groups neighboring the vacancy. Recent results have verified the reasonableness of this postulate (*3*). Two H's are then transferred to the carbon positions of the adsorbed thiophene molecule. Following C–S bond cleavage, butadiene desorbs (or becomes further hydrogenated), leaving an S anion at the vacancy. Subsequent action by hydrogen removes the S as H_2S and restores the catalyst to its original reduced state. Presumably, terminal SH groups can partake of the reaction as well as OH groups. Essentially, the mechanism involves a surface redox cycle, the reduced catalyst becoming oxidized, then reduced again, similar to (but the reverse of) those proposed for oxidation mechanisms (*10*). The redox nature is manifested in apparent changes in Mo valence of the cations involved.

Our original intent was not to check the validity of this mechanism. However, it eventually became apparent in our characterization studies of the reduced and sulfided catalyst, that we had developed a method to measure the surface concentration of vacancies, and thus were able to assess this or other mechanisms involving surface catalyst concentrations. What was required for this purpose was to extend the previously developed method to enable characterization of the catalyst under reaction conditions, at the same time that catalyst activity is monitored.

EXPERIMENTAL METHODS

The catalyst employed in these studies was an 8.1% Mo supported on γ-Al_2O_3, prepared by impregnation of a Ketjen thermally stabilized γ-Al_2O_3 with ammonium paramolybdate solution, followed by calcination in air at 540°C for 16 hr. This same catalyst had been used in the previous studies (*3*, *4*). A standard pore size distribution determination using N_2 gave the following values: surface area, 185 m^2/g; pore volume, 0.42 cm^3/g and average pore radius, 4.59 nm. Catalyst particle sizes of 20–40 mesh were used throughout.

Thiophene (Aldrich) was of 99+% purity and gave only a single peak by gas chromatographic (gc) analysis. Air, N_2 and H_2 were predried by passing through 4A molecular sieves. N_2 was passed through hot copper turnings and H_2 through a Deoxo unit prior to the sieves. H_2S was used from a prepared mixture containing 9 vol% H_2S in H_2.

Catalysts were generally heated to constant weight in an airflow for several hours or overnight at 500°C. Following an N_2 purge, the temperature was lowered to that of the pretreatment or run condition. Pretreatments consisted of either a reduction in H_2 or a sulfidation in H_2S/H_2.

Determination of catalyst changes accompanying prereduction, presulfidation and reaction with thiophene were carried out in the flow microbalance apparatus previously described (*2*, *4*). After the appropriate treatment, the catalyst was purged in N_2 to constant weight (about 1 hr). The catalyst was subsequently analyzed for sulfur and carbon by standard oxidation analyses. The sulfur analysis was good to ±0.05 wt% S. However, the carbon analysis gave inconsistent and irreproducible results (probably because the limit of accuracy of the method was being approached due to the low carbon content of the samples). A gas chromatographic method, in which CO_2, SO_2, and H_2O products from a 1 hr, 538°C air oxidation were analyzed after separation, gave good results, but only a few of the samples from runs reported here were analyzed in that way because most had been exhausted by the standard analyses. The carbon values averaged 0.45 wt% for 2 hr runs in thiophene/H_2 (1:40) at 1 atm and 343°C; this value was adopted for all such runs reported here. For runs of 2 hr at 300°C a slightly lower value, 0.40 wt% carbon, was used. An error of 0.1 wt% in the carbon values is equivalent to an error of 0.08 oxygen atoms or vacancies per molybdenum. Since the better carbon analyses gave values ranging from 0.3 to 0.6 wt% carbon, adopting the average value should lead to less than an error of ±0.12 in the values for oxygen and vacancy concentrations (per Mo). Adding uncertainties due to sulfur analysis and retained hydrogen, the overall error should be within ±0.15 for oxygen/Mo and vacancies/Mo.

Preliminary catalyst reactivity studies were carried out in a microcatalytic reactor under continuous flow conditions. Analysis of reaction products was accomplished by gc, using an *n*-octane on Porasil C (Durapak) column at 72°C. Butadiene was not observed in the products in any of the runs although a small amount of ethane was sometimes obtained, especially at the start of a run.

For simultaneous measurement of catalyst weight changes and activity, the flow microbalance was modified to simulate a constant stirred tank reactor by deadending the bottom and top of the reactor space and inserting a stirring blade for gas agitation. The catalyst charge was contained in a shallow quartz bucket above the fan blade. The latter was connected through a quartz shaft and Teflon bearing to a laboratory stirrer, rotating at about 300 rpm. The reactive gas mixture entered at the bottom, passing up the stirrer shaft to the reactor. Reactant and products exited at the top of the reactor volume (about 50 ml). Gas-mixing tests were not made on this reactor, but later studies in a similar type of flow microbalance reactor (*11*) lead us to believe that the results obtained in the current reactor were valid within the scope of the reaction conditions employed.

TREATMENT OF DATA[2]

Catalyst Stoichiometries

Catalyst stoichiometries were determined on catalysts which had been exposed to a thiophene–H_2 mixture in the flow microbalance reactor. Oxidized, prereduced or presulfided catalysts were run. Data analysis basically consists of a material balance on catalyst oxygen, sulfur and carbon, after reaching a constant weight in an N_2 purge. Therefore, the analyses pertain to the final stable catalyst state, exclusive of readily desorbed reactants or products.

The following general assumptions are made:

1. The only active O is that associated with the Mo in the catalyst and is in the ratio of O/Mo = 3 for the oxidized catalyst, i.e., Mo valence is +6.
2. Sulfur added is associated with the Mo.
3. The sulfur valence is always −2.
4. Hydrogen is retained only in adsorbed H_2S and in coke (as CH_1).
5. Adsorbed water remaining from reaction is negligible after the N_2 purge.

The validity of these assumptions has been previously discussed (*4*).

a. *Pretreatment.* Catalyst pretreatments prior to reaction with thiophene consisted of a reduction with H_2 or a sulfidation with H_2S/H_2. Reduction removes surface oxide ions associated with the Mo phase of the catalyst in the form of H_2O. This creates anion vacancies which can be calculated directly from the loss in weight of the catalyst (*4*). Table 1 presents the appropriate equations.

In presulfiding an oxidized catalyst, active oxide anions are partly exchanged by sulfide anions and some vacancies are created. It was shown earlier (*4*) that two types of sulfur can exist on the sulfided catalyst. These are exchanged sulfur, S_E, which replaces catalyst oxygen directly, and incorporated sulfur, S_I, which is taken to be H_2S irreversibly adsorbed on vacancies. A material balance in this case yields (*4*):

$$\square_S = \frac{96}{16W_M}\left(\tfrac{1}{2}W_S - \Delta W_{OS}\right) + \tfrac{1}{8}S_I. \qquad (1)$$

TABLE 1

Equations Used to Calculate Catalyst Stoichiometries

Reduced state

$$\square_R = \frac{96\Delta W_{OR}}{16\ W_M} \qquad (1A)$$

$$O_R = 3 - \square_R \qquad (2A)$$

Sulfided state

$$\square_S = \frac{96}{15W_M}\left(\tfrac{1}{2}W_S - \Delta W_{OS}\right) \qquad (3A)$$

$$S = \frac{96W_S}{32W_M} \quad (4A) \quad \begin{cases} S_I = \square_S/2 & (4A\text{-}1) \\ S_E = S - S_I & (4A\text{-}2) \end{cases}$$

$$O_S = 3 - S - \square_S \qquad (5A)$$

Thiophene-reacted state

$$\square_T = \frac{96}{15W_M}\left(\tfrac{1}{2}W_S - \Delta W_{OT} + W_{CH}\right) \qquad (6A)$$

S, S_I, S_E and O same as above, unless $\square_T > 2S$, then $S_I = S$, $S_E = 0$, and

$$\square_T = \frac{96}{16W_M}\left(\tfrac{1}{2}\ W_S - \Delta W_{OT} + W_{CH}\right) + \frac{S}{8} \qquad (7A)$$

---

[2] Complete derivations of equations given here and in Table 1 are available from the authors.

In order to solve Eq. (1) another relationship for S_I is needed. Recourse is made to a previous correlation between S_I and vacancies [see Fig. 5 of Ref. (*4*)] which showed that one H_2S was irreversibly adsorbed per three vacancies. In terms of the sulfided catalyst, this becomes,

$$S_I = \Box s/2. \tag{2}$$

Combination of Eqs. (1) and (2) gives the expression listed in Table 1 for the vacancy concentration.

The equations in Table 1 allow calculation of the stoichiometry of the sulfided catalyst from the experimentally measured weight change and sulfur content. It should be noted that only the value of S is obtained directly from the experimental data, the other values requiring the correlation of Eq. (2). However, the variation in $\Box$ and O is not large if other values of S_I are assumed.

b. *Reaction with thiophene.* Three cases must be considered: (a) direct reaction with the oxidized catalyst, (b) reaction with a prereduced catalyst and (c) reaction with a presulfided catalyst. In all cases, thiophene is passed over the catalyst at temperatures in which appreciable reaction occurs. The concern here is the effect of such reaction on the catalyst stoichiometry.

For simplicity of treatment, all three cases are treated the same by considering the overall change from the original oxidized state to the final thiophene-reacted state. This avoids three separate analyses based on original, prereduced and presulfided states. This is partly predicted on the fact that the presulfided state and the thiophene-reacted state cannot both be determined in the same run since a sulfur analysis is required for each, and we are most interested in the latter state in this study.

The following overall catalyst changes may occur in going from the oxidized to the thiophene-reacted states:

1. Exchange of active oxygen for sulfur.
2. Loss of additional active oxygen with formation of vacancies.
3. Irreversible adsorption of H_2S.
4. Irreversible adsorption of coke (sulfur free).
5. Irreversible adsorption of thiophene.
6. Irreversible adsorption of hydrocarbon products from the thiophene hydrogenolysis.

In order to make the analysis tenable, further simplifications are required. We arbitrarily omit step (5) from consideration since there is no analytic way that it can be separately distinguished from a combination of (4) and catalyst sulfur. Reasons for choosing this rather than omitting (4) are discussed more fully below. We also omit (6) from separate consideration as it is indistinguishable from (4) and thus (4) can be considered to include (6) under the term coke. We further assume coke has the empirical formula CH_1.

Material balance analysis similar to that given above for the presulfided case yields the expression given in Table 1. Again, the relationship of Eq. (2), which also appears to be valid for thiophene reaction (see below), was employed.

RESULTS

1. Catalyst Stoichiometries

a. Prereduced catalysts. A number of catalysts, which had been prereduced in H_2 at various conditions, were subsequently exposed to a thiophene–H_2 stream at 300°C. In Table 2, data are presented for a constant thiophene reaction time at varying degrees of prereduction. Exposure to thiophene resulted in appreciable sulfiding of the catalysts. Sulfiding decreased with increasing extent of reduction, whereas the oxygen content went through a maximum; both results are similar to those obtained with H_2S/H_2 in earlier work (*4*). These

TABLE 2

Effect of Prereduction on Stoichiometry of Thiophene-Reacted Catalysts[a]

Pretreatment						
Temp (°C)	300	400	450	500	600	650
Time (hr)	$\frac{1}{4}$	$\frac{1}{4}$	1	1	2	18
O_R	2.97	2.85	2.60	2.48	1.84	1.23
$\square_R$	0.03	0.15	0.40	0.52	1.16	1.77
Thiophene reaction[b]						
W_S (mg/g)	21.0	17.3	15.3	15.1	10.0	7.1
ΔW_{OT} (mg/g)	10.5	11.9	8.5	6.4	−1.4	−13.2
S	0.78	0.64	0.57	0.56	0.37	0.26
O_T	1.88	2.27	2.16	2.01	1.78	1.15
$\square_T$	0.34	0.09	0.27	0.43	0.85	1.59
$\square_R - \square_T (= S_I^*)$	—	0.06	0.12	0.09	0.31	0.18
S_I	0.17	0.04	0.14	0.21	0.37	0.26
S_E	0.61	0.60	0.43	0.35	0	0

[a] All values in mmol/mmol Mo unless otherwise specified. Carbon = 0.40 wt% assumed for each run.
[b] 0.025 atm thiophene in H_2 at 1 atm, 300°C, 2 hr.

effects are more clearly illustrated in Fig. 1, where catalyst stoichiometries are plotted as a function of degree of prereduction, $\square_R$. The diagonal, broken line represents the reactive oxygen content, O_R, left after the appropriate prereduction, but prior to thiophene reaction. Vacancy concentrations after reaction, $\square_T$, were somewhat lower than before, $\square_R$, mainly due to irreversible H_2S adsorption.

In order to estimate the amount of irreversible H_2S (S_I) on the catalyst, it was assumed that no additional reduction of the prereduced catalysts occurred in reaction with the thiophene since the latter was carried out at a temperature below that employed in the prereductions. Thus,

$$S_I^* = \square_R - \square_T, \qquad (3)$$

where S_I^* is the value of S_I when no additional reduction occurs. In Fig. 2, S_I^* values are plotted versus $\square_R$. The broken line in Fig. 2 represents the correlation obtained previously for sulfiding of prereduced catalysts (*4*). The agreement of the S_I^* values with the previous correlation indicates the same relationship obtained in both cases. An exception is the highly reduced catalyst where the total amount of sulfur added to the catalyst is much lower than predicted. Evidently, the correlation only holds up to about $\square_R = 1$.

Referring to Fig. 1, it is seen that at low prereduction, sulfur was added mainly via exchange with catalyst active oxygen,

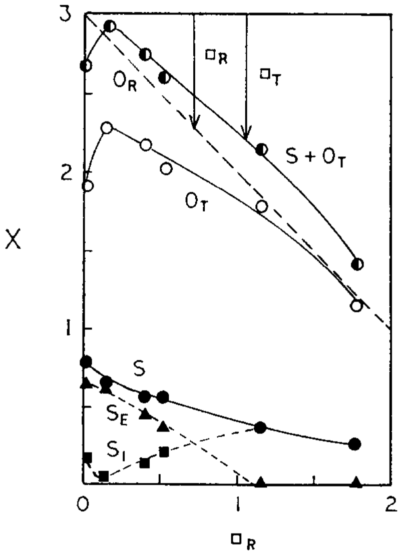

FIG. 1. Variation in thiophene-reacted catalyst stoichiometry with prereduction. Conditions given in Table 2. X represents the species shown on the curves.

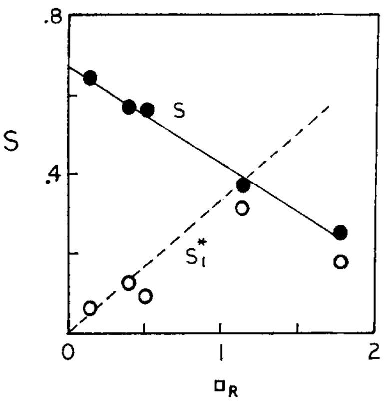

FIG. 2. Variation in catalyst sulfur species with prereduction. Conditions in Table 2.

whereas this reaction decreased with increasing extent of prereduction. Irreversibly adsorbed H_2S showed the opposite effect.

It is interesting to note that after reaction the oxidized catalyst (extreme left data points of Fig. 1) exhibited a larger vacancy concentration than the mildly prereduced catalyst, showing that catalyst reduction, i.e., loss of anion sites, occurred as well as exchange with thiophene–H_2 reactant. As shown below, this has important ramifications for catalytic activity. Account is not taken at this point of possible coverage of vacancies of coke.

b. Presulfided catalysts. The effect of thiophene reaction on presulfided catalysts was also studied. It was not possible to analyze presulfidation states in the same run that subsequent thiophene reaction was undertaken since a separate sulfur analysis is required on the presulfided catalyst. Hence, companion runs were employed, in one stopping and analyzing the catalyst after presulfiding, and in the other continuing with the thiophene reaction and analyzing the catalyst at the end. Data for such a series at several temperatures are given in Table 3.

As expected, the results show very little additional sulfur was added to the presulfided catalyst due to subsequent reaction with thiophene except for the 300°C presulfiding treatment which was lower than the thiophene reaction temperature. However, reaction with thiophene resulted in appreciable loss in active oxygen with consequent catalyst reduction, i.e., increase in vacancy concentration. This result is most likely due to the higher partial pressure of H_2 in the thiophene reaction and the higher temperature employed (compared to results of Table 2). The last entry in Table 3 shows that post-H_2 reduction of a sulfided catalyst gave similar results.

2. Catalyst Activities

Since it was established that catalyst stoichiometry undergoes appreciable changes in the presence of thiophene, it was of interest to determine catalyst activities during this transition. The microcatalytic reactor was used for this purpose. Products of reaction were identical to those reported by many workers, viz, *n*-butane and *n*-butenes. Isomerization was limited to double-bond migration, no skeletal isomerization being detected. By-product H_2S

TABLE 3

Effect of Presulfidation on the Stoichiometry of Thiophene-Reacted Catalysts[a]

Pretreatment[b] Temp (°C)	400	343		300	400[c]
S	1.83	1.76		1.65	1.56
O_S	0.86	1.22		1.25	1.18
$\square_S$	0.31	0.02		0.11	0.26
Thiophene reaction[d]					
S	1.86	1.79[e]	1.70	1.74	1.58[f]
O_T	0.34	0.82	0.71	0.78	0.89[f]
$\square_T$	0.80	0.39	0.59	0.48	0.53[f]

[a] All values in mmol/mmol Mo unless otherwise specified.

[b] 0.09 atm H_2S in H_2 at 1 atm, 2 hr.

[c] 8.5% Mo/η-Al_2O_3 catalyst used.

[d] 0.025 atm thiophene in H_2 at 1 atm, 343°C, 2 hr.

[e] This run was continued for 10 hr.

[f] This catalyst was reduced in H_2 at 1 atm, 400°C, 2 hr after sulfiding, in place of the thiophene reaction.

and H_2O were obtained, their concentrations depending upon the degree of sulfiding of the catalyst. Thus, oxidized or mildly reduced catalysts gave much H_2O initially and later H_2S almost exclusively in line with the catalyst stoichiometry results reported above.

The variations in thiophene conversion obtained with onstream time for three prereduced catalysts are shown in Fig. 3. Large differences in initial conversion were obtained for the three catalysts; conversion increased with extent of reduction. However, activities converged with continued reaction time and then crossed over. Lined-out conversions showed the opposite trend to the initial conversion; now, the least reduced catalyst was the most active. The most active catalysts after line-out were those with the greatest sulfur levels.

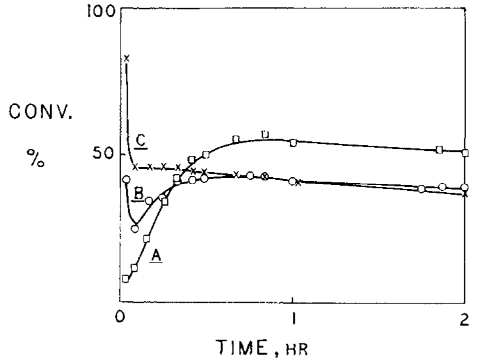

Fig. 3. Thiophene conversion vs on-stream time for prereduced catalysts. Reaction conditions: 300°C, 250 mg catalyst, 2.8 μl (liquid) thiophene/min, 50 cm^3 (STP) H_2/min. Prereduction conditions: H_2 for 2 hr at (A) 300°C, (B) 500°C and (C) 600°C. Initial reduction states as $\square_R/Mo$ were (A) 0.12, (B) 0.55 and (C) 1.15.

3. Catalyst Activity and Stoichiometry

In order to follow changes in catalyst activity and state simultaneously, the stirred microbalance reactor was used. For oxidized catalysts, the initial conversion was low, but as the catalyst gained weight the conversion increased rapidly and then declined slowly. Reduced catalysts showed the behavior exhibited in the fixed bed reactor, viz, an initially high activity and subsequent decay, with the lined-out conversion lower than that for the oxidized catalysts due to less sulfur being added. The stirred microbalance reactor gave results in complete accord with those obtained separately with the flow microbalance and microreactor.

The run shown in Fig. 4 was made to check for catalyst stability towards changes in reactive gases and the effect of the relative amounts of adsorbed species on conversions. After 45 min, the thiophene was turned off, leaving only H_2 passing over the catalyst. A small, gradual weight loss ensued. Upon readmitting thiophene, the weight was quickly regained, but significantly, the catalyst activity was higher. However, the activity slowly decayed back to the projected line-out condition. The catalyst was next subjected to a 9% H_2S/91% H_2 stream, whereupon the catalyst picked up additional weight due to further sulfiding. When the thiophene/H_2 stream was readmitted, the catalyst activity was initially low, showing that adsorbed H_2S strongly inhibited reaction. After the excess H_2S desorbed (weight loss), catalyst activity returned to normal.

The results of this run demonstrated a complex interaction between catalyst and reactant/product gases occurred, which changes also affected catalyst conversion. The following phenomena may be inferred: (a) reversibly adsorbed species can be detected by weight changes, (b) reactant and/or product show some reversible inhibition on the reaction rate, (c) specifically H_2S reversibly inhibits the rate, and (d) excess H_2S results in some irreversible weight gain. The latter phenomenon is undoubtedly due to additional catalyst sulfiding.

From a number of runs carried out in the flow microbalance reactor under identical reaction conditions, but with varying pretreatments and/or run times, an attempt

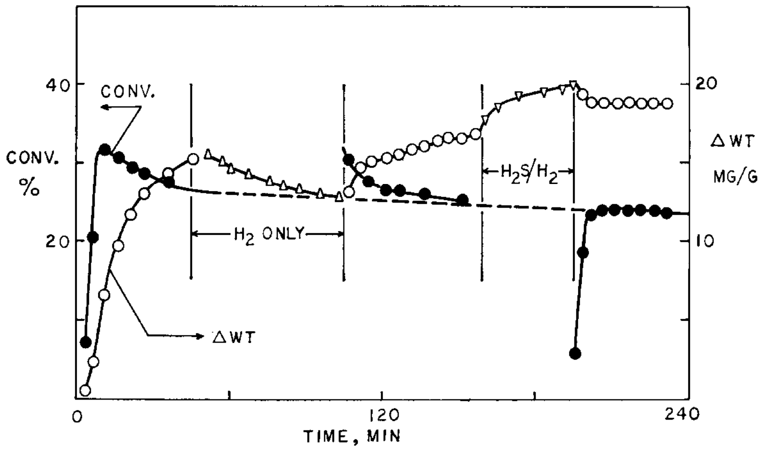

FIG. 4. Thiophene hydrogenolysis over oxidized Mo/Al_2O_3, 343°C.

was made to relate lined-out catalyst activities with catalyst stoichiometries. The latter were calculated for catalysts purged in N_2 for about 1 hr after reaction (at reaction temperature). Consequently, the stoichiometries pertain to actual catalyst states, exclusive of reversibly adsorbed species, at the time the final conversion was measured. Data for these runs are presented in Table 4. The number of vacancies per Mo was less than one for all but the highly reduced catalyst (next to last column). Therefore, the correlation of Fig. 2 was assumed to be valid and values for S_E and S_I were calculated according to Eqs. (4A-1) and (4A-2). The entries in Table 4 are discussed below. It should be noted that presulfided catalysts gave lower steady state conversions (at 2 hr) than either the oxidized or prereduced catalysts. De Beer *et al.* (*12*) found a similar trend for their Mo/γ-Al_2O_3 catalysts.

Relationships between lined-out conversions and catalyst stoichiometries are given in Fig. 5. (Included for comparison, although it was not lined out, is a run over an oxidized catalyst, in which the thiophene flow was stopped when the activity was near its maximum value.) The correlation with sulfur level gives a maximum near $S = 1$, with conversions decreasing rapidly as S approaches 2 (presulfided catalysts) or 0 (severely prereduced catalyst). The validity of the left curve (broken) is confirmed by the microcatalytic data. There is a rough correlation with the remaining oxygen, although the data are scattered. A more serious reservation with this correlation is that the third (remaining) oxygen associated with Mo is believed to reside in the second surface layer and thus, be unavailable as a catalyst site (*4*). Furthermore, bulk MoS_2 is a well-known catalyst for hydrodesulfurization and it presumably contains no oxygen under HDS conditions. There is no apparent correlation with the vacancy concentration.

DEVELOPMENT OF A CATALYST CORRELATION

No single catalyst property correlated directly with catalyst activity. This is not surprising in view of the complexity of the hydrogenolysis reaction. Carbon–sulfur bond scission and hydrogen transfer must both operate for sustained reaction to occur. Thus, it is not unreasonable to presume a dual site, one for adsorbed thiophene and another for adsorbed hydrogen, would be required. There is already sufficient evidence that at least two active sites are present on the catalyst (*8*). In developing a model we will presume that both sites are needed.

TABLE 4

Catalyst Stoichiometries and Activities for Thiophene Hydrogenolysis at Steady State 8% Mo/γ-Al_2O_3[a]

	S	S	S	S	S	O	O	O	O	R	R	O[b]
Pretreatment temp (°C)												
Calcination	500	343	500	500	500	343	343	500	500	500	600	500
Reduction	—	—	—	—	—	—	—	—	—	400	600	—
Sulfidation	400	343	343	343[c]	300	—	—	—	—	—	—	—
Thiophene reaction, 343°C												
Time (hr)	2	10	2	2	2	2	2.5[d]	2	0.25[e]	2	2	2
Final conversion, C	0.14	0.10	0.13	0.17	0.13	0.23	0.24	0.20	0.36	0.25	0.1	0
Final sulfur, W_s (mg/g)	50.1	48.4	45.9	44.2	47.1	37.0	39.7	37.8	22.0	32.2	13.2	1.0
Wt change, ΔW_{OT} (mg/g)	19.8	24.1	20.4	16.7	22.3	15.6	19.4	20.8	10.0	11.4	−14.2	5.9
Final catalyst stoichiometries (mmol/mmol Mo)[c]												
Active oxygen, O_T	0.34	0.82	0.71	0.56	0.78	1.02	1.11	1.36	1.88	1.05	0.60	—
Sulfur, S	1.86	1.79	1.70	1.63[f]	1.74	1.37	1.47	1.40	0.81	1.19	0.49	—
Vacancies, $\square_T$	0.80	0.39	0.59	0.81	0.48	0.61	0.42	0.24	0.31	0.76	1.91	—
Adsorbed H_2S, S_I	0.40	0.20	0.30	0.41	0.24	0.31	0.21	0.12	—	0.38	—[g]	—
Exchanged sulfur, S_E	1.46	1.59	1.40	1.22	1.50	1.06	1.26	1.28	—	0.81	—	—
Coke, as C_4H_4, C_4	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	—	0.11	0.11	—
Net vacancies, $(\square_T)_1$	0.69	0.28	0.48	0.70	0.37	0.50	0.31	0.13	—	0.65	1.80	—
Surface oxygen, O_S	0	0	0	0	0	0.02	0.11	0.36	—	0.05	0	—
Surface sulfur, S_S												
A. S_I inactive	0.80	1.41	1.11	0.79	1.28	1.06	1.26	1.28	—	0.81	—	—
B. S_I active	1.20	1.61	1.41	1.19	1.52	1.37	1.47	1.40	—	1.19	—	—

[a] S = sulfidation, R = reduction, O = calcination (in air) only.

[b] Pure γ-Al_2O_3 support.

[c] Average percentage C value of 0.45% used.

[d] This sample was treated briefly with 9% H_2S/91% H_2 during the run so has more sulfur than other oxide catalysts.

[e] This run was stopped at the approximate time that maximum conversion was reached, so it was not at steady state but is included for comparison.

[f] This sample was sulfided in 2% H_2S/98% H_2 so has less sulfur than other sulfided catalysts.

[g] Reduction was so extensive in this run that it is outside the range for which S_I, S_E, and S_s can be calculated.

We base our model of the active center on the mechanism earlier proposed by Lipsch and Schuit (*9*) (see Introduction). We identify vacancies as sites for thiophene adsorption and terminal surface anions as sites for hydrogen adsorption. Further, we

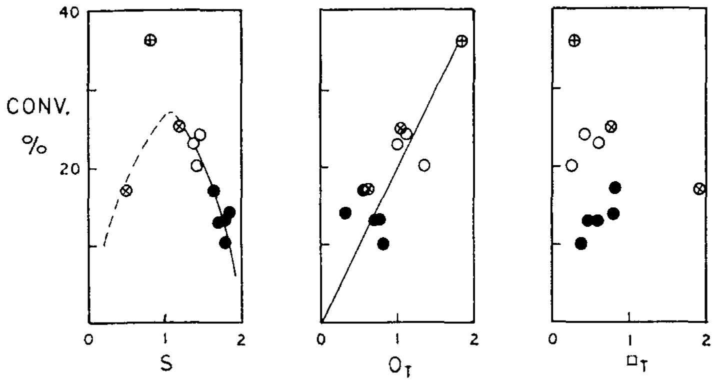

FIG. 5. Thiophene conversion vs catalyst stoichiometry. Catalysts were prereduced or presulfided under various conditions (Table 4). (○) oxidized; (⊗) prereduced; (●) presulfided; (⊕) short time run.

assume that the slow step in the reaction is a surface reaction between adsorbed species on these sites.

Our task now is to relate catalyst activities to catalyst surface concentrations. This involves proper analysis of the rate data and a model of the catalyst surface.

1. Reaction Rate Analysis

We wish to relate thiophene conversions obtained over the various catalysts in the stirred microbalance reactor to basic reaction rate constants. Although the literature (*6*) is not in agreement on the precise form of the rate expression, for our purposes a generalized form can be used, viz,

$$r_T = \frac{k_T p_T p_H}{D}, \tag{4}$$

where r_T is the desulfurization rate, k_T is a global rate constant, p_T and p_H are the partial pressures of thiophene and hydrogen, and D is an adsorption term. The latter term may contain partial pressures of thiophene, hydrogen sulfide and hydrogen, together with their appropriate adsorption constants (*6*). Detailed kinetic studies on the same catalyst [see following article (*16*)] confirmed the reasonableness of Eq. (4) for sulfided catalysts. Since the stirred microbalance reactor operates kinetically as a constant stirred tank reactor (*11*), the rate is given by:

$$r_T = \frac{F_T C}{W_{cat}}, \tag{5}$$

where F_T is the thiophene flowrate, C is the conversion, and W_{cat} is the catalyst weight. Since all catalysts were run under identical reaction conditions, and H_2 was in excess, the following relationship can be derived,

$$\frac{C}{1 - C} = Y = ak_T, \tag{6}$$

where a is a constant which depends only on reaction conditions. Implicit in this derivation is the assumption that the adsorption constants are the same for all catalysts at the lined-out state.

2. Catalyst Surface Concentrations

We wish to estimate surface concentrations that may be involved in the reaction from measured catalyst stoichiometries. It is necessary to invoke a specific model of the surface of the catalyst for this purpose. We will use one previously proposed from earlier studies on the sulfided catalyst (*4*).

Briefly, this model consists of an epitaxial monolayer of Mo and O extended over the Al_2O_3 substrate such that only two O's per Mo are terminal, the third residing in the Al layer [cf. Fig. 7 of Ref. (*4*)]. The terminal O's are reactive towards reduction (forming vacancies) and sulfidation (S exchange for terminal O), whereas the underlying O's are much less reactive. Further, the MoO_2 terminal groupings are in essentially one-dimensional or chainlike structures rather than two-dimensional patches. This model only applies for one-half or less surface coverage of the Al_2O_3 support.

Vacancies are assumed to be only possible at the surface, and we will limit the correlation to catalysts with no more than 1 vacancy/Mo. Sulfur exchange for catalyst active oxygen occurs preferentially on terminal oxide anions; however, sulfur exchange in highly sulfided catalysts can also occur in the second O layer, i.e., when $O_T < 1$. The chainlike structure allows this deep sulfiding without serious disruption of the surface structure, whereas a two-dimensional structure would require extensive reorientation of the surface due to the much larger ionic radius for S^{2-} as compared to O^{2-}.

Only anions residing in the terminal layer are considered possible active catalyst sites for hydrogen adsorption and transfer. We assume both terminal S or O anions apply here, recognizing that their intrinsic activity may be different. Calculation of these surface sites involves two cases as follows:

$$\begin{array}{ll} \underline{\text{Case I}: \mathrm{O_T} > 1} & \underline{\text{Case II}: \mathrm{O_T} < 1} \\ \mathrm{O_s = O_T - 1} & \mathrm{O_s = 0} \qquad (7) \\ \mathrm{S_s = S}_E & \mathrm{S_s = S}_E - (1 - \mathrm{O_T}), \quad (8) \end{array}$$

where the subscript "s" refers to surface layer. In Case I, all sulfur exchanged is at the surface and some surface oxygen remains. In Case II, all O on the surface has been removed (as vacancies or exchanged S) and some additional O in the second layer has also been exchanged.

In the above treatment, irreversibly adsorbed H_2S has not been accounted for. It is assumed to adsorb at vacancies (thus reducing vacancy concentration) but remain inactive as a hydrogen site. However, it is possible that S_I could also function as an active site. In that case, the above equations will still apply but with S_E replaced by S.

3. Effect of Coke

Before making our final correlation, we must take into account the coke found on all catalysts after reaction with thiophene. If the coke covers some active sites, they will presumably become inactive. It seems most likely that small amounts of coke will be adsorbed at vacancies. We will assume coke to have the composition of butadiene, i.e., C_4H_4, although other H/C ratios will not noticeably affect our analysis. The coke concentration, C_4, in mmol/mmol Mo is then given by,

$$\mathrm{C_4} = \frac{96W_{\mathrm{CH}}}{52W_{\mathrm{M}}}. \qquad (9)$$

Correction of vacancy concentration for coke can then be made according to,

$$(\square)_i = \square - i\mathrm{C_4}, \qquad (10)$$

where i represents the number of vacancies covered per coke molecule, and $(\square)_i$ is the effective vacancy concentration.

4. Relationship between Reaction Rate Constants and Catalyst Surface Concentrations

We are now ready to make our final correlation. We assume thiophene adsorbs on vacancies and hydrogen on either surface sulfide or oxide anion sites. For surface reaction between adsorbed thiophene and adsorbed hydrogen, the rate is given by,

$$r_{\mathrm{T}} = k_{\mathrm{s}}\theta_{\mathrm{T}}\theta_{\mathrm{H,S}} + k_{\mathrm{o}}\theta_{\mathrm{T}}\theta_{\mathrm{H,O}}, \qquad (11)$$

where k_{s} and k_{o} are the intrinsic surface reaction rate constants for reaction between adsorbed thiophene and adsorbed hydrogen on a sulfide site or on an oxide site, respectively, θ_{T} is the fraction of vacancies covered by thiophene, and $\theta_{\mathrm{H,S}}$ and $\theta_{\mathrm{H,O}}$ are the fraction of surface sulfide and oxide sites covered by hydrogen. Conventional treatment gives

$$r_{\mathrm{T}} = \frac{k_{\mathrm{s}}L_{\mathrm{V}}p_{\mathrm{T}}L_{\mathrm{s}}p_{\mathrm{H}}}{D} + \frac{k_{\mathrm{o}}L_{\mathrm{V}}p_{\mathrm{T}}L_{\mathrm{o}}p_{\mathrm{H}}}{D} \qquad (12)$$

$$= \left(\frac{k_{\mathrm{s}}L_{\mathrm{V}}L_{\mathrm{s}} + k_{\mathrm{o}}L_{\mathrm{V}}L_{\mathrm{o}}}{D}\right)p_{\mathrm{T}}p_{\mathrm{H}}, \qquad (13)$$

where L_{V} is the total number of active vacancies, and L_{s} and L_{o} are the total numbers of surface sulfide and oxide sites. Comparison to Eq. (4) shows that,

$$k_{\mathrm{T}} = k_{\mathrm{s}}L_{\mathrm{V}}L_{\mathrm{s}} + k_{\mathrm{o}}L_{\mathrm{V}}L_{\mathrm{o}}. \qquad (14)$$

Replacing L_{V}, L_{s} and L_{o} by $(\square)_i$, $\mathrm{S_s}$ and $\mathrm{O_s}$ from earlier terminology gives,

$$k_{\mathrm{T}} = bk_{\mathrm{s}}(\square_{\mathrm{T}})_i\mathrm{S_s} + bk_{\mathrm{o}}(\square_{\mathrm{T}})_i\mathrm{O_s}, \qquad (15)$$

where b is a constant equal to $(M_{\mathrm{M}}/W_{\mathrm{M}})^2$. Incorporating the relationship between Y and k_{T} given by Eq. (6) and casting into linear form gives,

$$\frac{Y}{(\square_{\mathrm{T}})_i\mathrm{S_s}} = abk_{\mathrm{s}} + abk_{\mathrm{o}}\left(\frac{\mathrm{O_s}}{\mathrm{S_s}}\right). \qquad (16)$$

When $O_s = 0$, Eq. (16) simplifies to,

$$\frac{Y}{S_s} = abk_s(\square_T)_i. \qquad (17)$$

Equations (16) and (17) provide convenient forms to check the proposed model with the experimental data.

5. *Correlation Tests of Data*

Values needed to test Eqs. (16) and (17) are given in Table 4. The value for C_4 is based on an average carbon content for all runs. Values of $(\square_T)_i$ for $i > 2$ are unrealistic as some negative values were obtained. Values of S_s are given for two cases, viz, Case A-S_I inactive site, in which S_E is used to calculate S_s in Eq. (8); and Case B-S_I active site, in which S is used in Eq. (8).

Figure 6 displays the correlations obtained for the case in which all surface sulfur was assumed to be active, and $i = 1$. Equally good fits were obtained for the case in which S_I was assumed inactive and $i = 1$. Both gave a ratio of k_o/k_s of about 20, indicating that oxygen sites are considerably more reactive than sulfur sites. Correlations using $i = 0$ or 2 gave poor fits; in these cases, the intercepts of $Y/S_s(\square_T)_i$ versus O_s/S_s did not equal the slope of Y/S_s versus $(\square_T)_i$ as it should according to Eqs. (16) and (17).

DISCUSSION

1. *Reaction of Thiophene with the Catalyst*

Thiophene (with H_2) is a good sulfiding agent for the Mo/Al_2O_3 catalyst, whether the latter is in an oxidized or prereduced state. Analysis of the results indicates that the major reaction is replacement of catalyst active oxide by sulfide. Since catalytic hydrogenolysis of the thiophene occurs, we cannot be sure whether sulfiding takes place directly with permanent attachment of the sulfur atom or through a secondary sulfiding from the H_2S produced in the hydrogenolysis reaction.

Partial pressure considerations may be invoked to explain the additional reduction obtained upon reacting presulfided catalysts with thiophene–H_2 mixture. In the latter case, the H_2 partial pressure was greater than that employed during the presulfiding and a separate experiment demonstrated that postreduction of a presulfided catalyst can indeed cause additional reduction (Table 3). It is interesting to note that this extra reduction is not due to sulfur loss, but rather to additional oxygen loss.

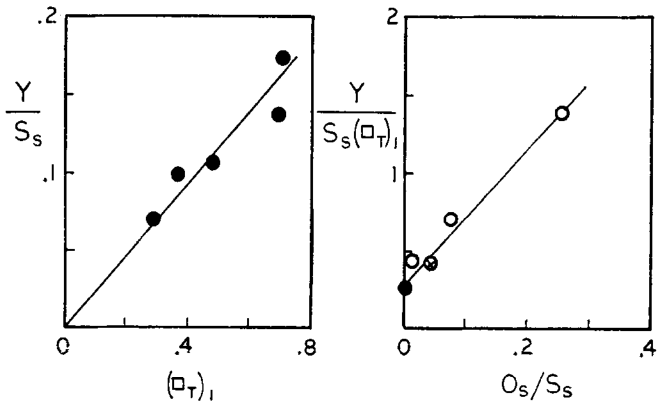

FIG. 6. Catalyst activity correlations with surface concentrations for Case B-S_I active site. Symbols same as for Fig. 5.

The finding that the catalyst undergoes significant changes in stoichiometry and surface concentrations as a result of exposure to thiophene–H_2 mixture has important consequences with respect to changes in catalyst activity. The importance of such catalyst changes to a basic understanding of the catalysis involved lies in the interaction between catalyst kinetics and reaction kinetics (*13*). Basic reaction kinetics must account for catalyst changes to have fundamental significance.

2. Effect of Coke

Although carbon analyses were rather inaccurate and inconsistent, there is no doubt that small amounts of coke were present on the catalyst in all runs with thiophene. Since no trends could be discerned between carbon content and catalyst properties, average values were used.

The nature and location of this coke is important insofar as it may be adsorbed on vacancies. First, we must consider whether it is predominantly present as irreversibly adsorbed thiophene or as coke. Little data are available to bear on this question as material balance calculations cannot distinguish unequivocally between the two possibilities. Several circumstantial facts seem to mitigate against coke being exclusively absorbed thiophene.

1. Coke alone decreased catalytic activity. In a separate experiment, after a catalyst steady state was obtained, the catalyst was exposed to a butene–N_2 mixture, whereupon an irreversible weight gain due to coke was obtained. Upon re-establishing the former reaction conditions, thiophene conversion was appreciably lower than before coking. This demonstrates that simple coke adsorbs on active sites causing lower conversion, although a similar phenomenon due to irreversibly adsorbed thiophene is not necessarily ruled out.

2. Coke formation is usually a slow process, whereas irreversible thiophene adsorption would be expected to be reasonably fast. The gradual catalyst activity decay observed in reaching a steady state would thus seem to be indicative of a slow coking process.

3. Presulfided catalysts did not show increased sulfur levels after reaction with thiophene. The average coke level obtained would be equivalent to about 0.12 mmol TP/mmol Mo if due to irreversibly adsorbed thiophene alone. Thus, the sulfur content of the presulfided catalyst should have increased by this amount, contrary to the results of Table 3.

Second, since the coke does affect catalyst activity, its location and form are important to catalyst correlations. It seems reasonable to assume that it adsorbs at free anion vacancies. It could adsorb and affect activity on surface sulfide/oxide sites, but activity correlations based on this latter possibility were unsuccessful.

Coke is generally considered to form from olefinic structures that are too strongly adsorbed to be saturated by hydrogenation. The mode and mechanism of formation, especially the relatively long time periods involved, are not well understood. In order to reduce the problem to manageable proportions, we have arbitrarily assumed a localized molecular structure equivalent to C_4H_4, i.e., butadiene-like. Butadiene is known to be strongly absorbed and could well be the coke precursor present on the catalyst. Larger coke deposits and/or longer reaction times could cause the coke to recrystallize into a more graphic type (*14*). We presume at the low levels of coke obtained in our experiments and the relatively short reaction period that this has not yet occurred. The fairly constant values obtained for coke may be due to a small, constant number of superactive sites (vacancies), on which the coke precursor (butadiene) is strongly adsorbed, neither desorbing nor hydrogenating.

Finally, based on the assumptions that all the coke is involved in catalyst deactivation and is of the molecular form equivalent to C_4H_4, our correlation shows one vacancy occupied per molecule. Adsorption on dual vacancies gave an unsatisfactory correlation. This is not unexpected since the number of dual vacancies would be statistically low due to the low vacancy concentrations present, and could not accommodate all the coke obtained. When dual vacancies were considered to be the only sites available for coke, which deactivated them (any excess coke not causing deactivation), correlation using the remaining single vacancy sites did not give a satisfactory fit to the data.

3. Identification of Active Sites

The salient features of the Schuit mechanism in terms of our proposed catalyst surface stoichiometry for highly sulfided catalysts are depicted in Fig. 7. According to this mechanism, thiophene adsorbs on surface vacancies and hydrogen on neighboring sulfide sites. First-stage hydrogen transfer is kinetically equivalent to reaction between the two adsorbed species. If thiophene and hydrogen are in equilibrium with their respective adsorbed species, then reaction should be proportional to the product of the active sites, viz, vacancies times sulfide sites (or oxide sites, if present). This holds whether the first-stage hydrogenation is rate determining or whether the first-stage transfer is in equilibrium and the second-stage transfer is rate determining (*15*). We cannot distinguish between transfer of one H in each step, to form butadiene +S (as shown), or transfer of two H's in each step to form butadiene $+H_2S$. Also, the timing of C–S bond rupture is uncertain. The irreversibility of the second-stage hydrogen transfer reaction seems reasonable since butadiene is not known to form thiophene over the sulfided catalyst under normal hydrogenolysis conditions.

In order to obtain catalyst activity correlations according to this mechanism, it was necessary to correct for vacancy poisoning by coke. This may be viewed as subsequent adsorption of butadiene on particular vacancies which form strong chemisorptive bonding with the butadiene. Some vacancies are also occupied by strongly chemisorbed hydrogen sulfide, converting vacancy sites to potential hydrogen sites. The correlations do not permit establishing whether the latter sites are active or not.

Since all surface sulfide sites are assumed to be active in our correlation, it is necessary to postulate that they all are active

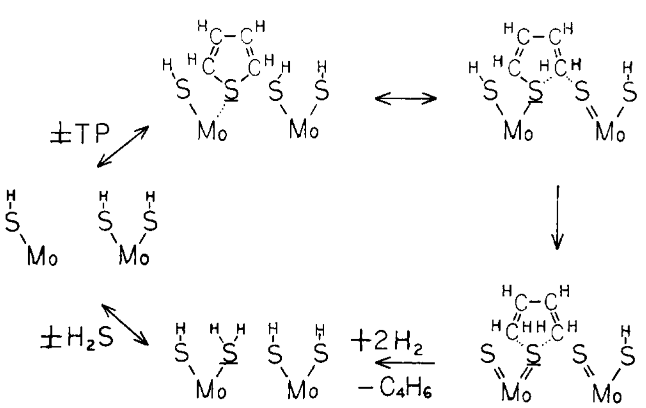

FIG. 7. Proposed steps in thiophene reaction.

sites for hydrogen adsorption. Although this situation does not apply to reduced catalysts (*3*), where it appears that only two H's per vacancy are adsorbed (irreversibly), it does apply to sulfided catalysts (*4*), where essentially all the sulfide has the equivalent of 1 hydrogen.

4. Initial and Transient Activities

Since the catalyst state changes rapidly upon exposure to thiophene/H_2, it is not surprising to find that its activity also undergoes changes during this initial stage. The oxidized catalyst was initially inactive, rapidly became activated and then gradually lost activity with time. During this process, sulfur was added and some vacancies were produced. The prereduced catalyst, on the other hand, started off with a very high activity which rapidly diminished to a lined-out stage. During this process, sulfur was also added but the vacancy concentration did not change much.

The correlation developed for the steady state catalyst can qualitatively account for initial and transient activities. Consider first the prereduced catalyst. Depending upon extent of reduction, this catalyst contains some vacancies and adsorbed H. Upon exposure to thiophene the initial rate constant in this case will be according to Eq. (15),

$$k_T = bk_o(\Box_R)O_s. \tag{18}$$

Since k_o is some 20 times larger than k_s, k_T will be larger than under steady state sulfided conditions and consequently initial activity will be high. However, catalyst sulfiding will begin with exchange of surface O for S, and some product H_2S and coke will adsorb on vacancies. Thus, catalyst surface concentrations will rapidly change and k_T will now be given by the complete expression of Eq. (15), where the $k_o(\Box_T)_iO_s$ term decreases and the $k_s(\Box_T)_iS_s$ term increases with time.

The case of the oxidized catalyst is also explicable in terms of our correlation. Since no vacancies are present, initial catalyst activity will be nil. From sulfiding studies with H_2S/H_2 (*4*), it has been shown that slight partial reduction of the catalyst occurs prior to sulfiding. A similar response may be expected with thiophene/H_2. Vacancies should be rapidly formed, resulting in the rapid rise in catalytic activity observed in Fig. 3. Now however, sulfur exchange and H_2S and coke poisoning as described above for the reduced catalyst take over, with the resultant drop in activity to steady state.

ACKNOWLEDGMENTS

The experimental work reported herein was carried out while the authors were employed at Gulf Research and Development Co., whom they wish to acknowledge. Thanks also go to Mr. W. E. Faust for excellent technical assistance.

REFERENCES

1. Seshadri, K. S., and Petrakis, L., *J. Catal.* **30,** 195 (1973).
2. Massoth, F. E., *J. Catal.* **30,** 204 (1973).
3. Hall, W. K., and Massoth, F. E., *J. Catal.* **34,** 41 (1974).
4. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
5. Koboe, S., and Amberg, C. H., *Canad. J. Chem.* **44,** 2623 (1966).
6. Weisser, O., and Landa, S., "Sulfide Catalysts, Their Properties and Applications," Pergamon, New York, 1973.
7. Mitchell, P. C. H., "The Chemistry of Some Hydrodesulfurization Catalysts Containing Molybdenum," Climax Molybdenum Co., Ltd., London, 1967.
8. Owens, P. J., and Amberg, C. H., *Advan. Chem., Ser.* **33,** 182 (1961); Desikan, P., and Amberg, C. H., *Canad. J. Chem.* **42,** 843 (1964).
9. Lipsch, J. M. J. G., and Schuit, G. C. A., *J. Catal.* **15,** 179 (1969).
10. Margolis, L., *Catal. Rev.* **8,** 241 (1974).
11. Massoth, F. E., and Cowley, S. W., *Ind. Eng. Chem. Fundam.* **15,** 218 (1976).
12. DeBeer, V. H. J., Van Sint Fiet, T. H. M., Van Der Steen, G. H. A. M., Zwaga, A. C., and Schuit, G. C. A., *J. Catal.* **35,** 297 (1974).
13. Frye, C. G., Pickering, H. L., and Eckstrom, H. C., *J. Phys. Chem.* **68,** 1508 (1958).
14. Appleby, W. G., Gibson, J. W., and Good, G. M., *Ind. Eng. Chem., Process Design Develop.* **1,** 102 (1962).
15. Boudart, M., *AIChE J.* **18,** 465 (1972).
16. Massoth, F. E., *J. Catal.* **47,** 316 (1977).