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Studies of Molybdena–Alumina Catalysts

VI. Kinetics of Thiophene Hydrogenolysis

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The kinetics of thiophene hydrogenolysis over a presulfided $Mo/\gamma\text{–}Al_2O_3$ catalyst was determined using a stirred microbalance reactor. Steady state conversions as well as attendant catalyst weight changes were measured. Separate adsorption studies were made of reversible H_2S adsorption over the sulfided catalyst. The hydrogenolysis rate was found to be first order in thiophene and first order in H_2, with appreciable inhibition in thiophene, H_2S and H_2. Mechanisms are considered which give good correlation with the kinetic data.

Based on these results and other information, it was concluded that the slow step in thiophene reaction was due to a surface reaction and involved dual sites, one upon which thiophene and H_2S competitively adsorbed and one upon which H_2 adsorbed. The former was associated with vacancies on the catalyst under thiophene-reaction conditions, and the latter with terminal sulfide anion sites. The active hydrogen specie was judged to be reversibly adsorbed, but it could not be unequivocally established whether the H_2 was molecularly or atomically adsorbed.

NOMENCLATURE

b	constant in Eq. (4)
D	butadiene
F_T	flow rate of TP
k_i	rate constant for i-th step
k_T	overall rate constant
K_H	equilibrium constant for H_2 adsorption
K_S	equilibrium constant for H_2S adsorption
K_T	equilibrium constant for TP adsorption
$K_{i \text{ or } j}$	equilibrium constant for adsorption of i-th or j-th specie
L_1	sites for TP and H_2S adsorption
L_2	sites for H_2 adsorption
m	power coefficient
M_i	molecular weight of i-th specie
n	power coefficient
N	number of data points in Eqs. (8) and (11)
p	power coefficient
p_H	partial pressure of H_2
$p_{i \text{ or } j}$	partial pressure of i-th or j-th specie
p_s	partial pressure of H_2S
p_T	partial pressure of TP
q	power coefficient
r_T	rate of TP reaction
s_1	unoccupied L_1 sites
s_2	unoccupied L_2 sites
TP	abbreviation for thiophene
TS	thiophene molecule in mechanisms
v	variance defined by Eqs. (8) and (11)
W	combined weight of adsorbed TP and H_2S
W_C	weight of catalyst
W_i	weight of adsorbed specie i
W_S	weight of adsorbed H_2S
W_T	weight of adsorbed TP
X_T	thiophene conversion

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Y	activity parameter defined by Eq. (7) or (10)
$\bar{Y}$	average of Y values
Y^*	value of Y calculated from regression fit

INTRODUCTION

In the previous paper (*1*) in this series, an attempt was made to relate the thiophene (TP) hydrodesulfurization activity over a molybdena catalyst with its sulfided state under operating conditions. Catalyst activity was shown to correlate with catalyst vacancy concentration, as determined by stoichiometric measurements defined therein, and with sulfur level in a complex manner. The present paper deals with the kinetics of the hydrodesulfurization reaction of thiophene over the presulfided catalyst.

The literature is replete with numerous kinetic studies of the hydrodesulfurization process. Many model compounds have been used for the purpose, the most popular being thiophene. The favorite catalyst has been "cobalt molybdate" supported on an activated alumina. In some studies, catalysts were prereduced or presulfided; in others, no pretreatment was given. Virtually no definitive kinetic studies have been made using Mo/Al_2O_3 despite the fact that Mo is the source of the desulfurization activity, insofar as added promoters (such as Ni or Co) have small intrinsic desulfurization activity by themselves

The results of kinetic studies of thiophene hydrogenolysis over $CoMo/Al_2O_3$ have been at some variance (*2*). All, however, display a common theme, namely, reaction is first order in thiophene and inhibited by reactant and/or products. Few studies investigated the order in hydrogen. From these studies, a generalized rate expression may be written as:

$$r_T = \frac{k_T p_T p_H{}^m}{(1 + K_T p_T + K_S p_S)^n}, \qquad (1)$$

where r_T is the rate of disappearance of thiophene (TP); p_T, p_H and p_S are the partial pressures of TP, H_2 and H_2S, respectively; k_T is the reaction rate constant; K_T and K_S are the dynamic adsorption equilibrium constants for TP and H_2S. Inhibition by-product butenes or butane appears not to be important. Values of m have generally been assumed to be 0, $\frac{1}{2}$ or 1, and of n to be 1 or 2.

EXPERIMENTAL METHODS

The catalyst was the same as used previously (*1*), namely, 8.1% Mo on Ketjen γ-Al_2O_3. Catalyst particle sizes of 20 to 40 mesh were used. Calculations of effectiveness factors as outlined by Satterfield and Sherwood (*3*), using typical reaction rates obtained in the present study, revealed that intraparticle diffusional effects should be nil.

A specially constructed, stirred flow microbalance reactor was used to simultaneously obtain catalyst weight changes and activities. Details of the apparatus are given elsewhere (*4*). The reactor operates as a constant stirred tank reactor; consequently, rate data are obtained directly. A Pt wire-screen bucket containing the catalyst was suspended in the reactor by means of thin quartz rods attached to the microbalance (Cahn, R. G.). A squirrel-cage stirrer, magnetically operated from below the reactor, provided for gas mixing and gas–catalyst contact. Gas feed mixtures were made up by metering with calibrated rotometers. A small portion of the feed, whose rate was kept constant by a mass flow controller (Matheson), was diverted to the reactor, the balance being vented. Thiophene was added by saturating a separate H_2 stream; the H_2 first passed through a bubbler containing thiophene at room temperature, then through one maintained at 13°C by means of a refrigerated bath. Effluent gas samples were analyzed by gas chromatography for thiophene conversion to products as before (*1*).

A catalyst charge of 200 mg was used. Presulfiding was accomplished *in situ* by exposing the oxidized catalyst to a 1 H_2S/10 H_2 mixture at 400°C for 2 hr, followed by a 1-hr N_2 purge. After presulfiding, the catalyst was exposed to a thiophene/H_2 stream at 400°C for an overnight period to assure attainment of a lined-out activity, since preliminary runs had shown a gradual decrease in catalyst activity over several hours. In order to be able to delineate the various partial pressure effects on the reaction rate, a series of runs was made containing TP, H_2, H_2S and N_2 at varying inlet concentrations. The entire series was run in 1 day. Run details are presented in Table 1. A stirring rate of about 500 rpm was used throughout. Quartz particles in place of catalyst gave no reaction.

Reversible adsorption of H_2S on the sulfided catalyst was determined gravimetrically employing a Cahn R-100 vacuum microbalance in conjunction with a conventional glass vacuum, circulating system. The catalyst was presulfided at 400°C at atmospheric pressure in a flow of H_2S/H_2. Following an N_2 purge, the catalyst was evacuated, then exposed to several H_2S/H_2 ratios at various subatmospheric pressures. Pressures were measured with a Baratron capacitance manometer, employing a corrosion-resistant sensor. Calibration of the manometer was checked against a secondary Heise pressure gage standard, which had been calibrated with a deadweight test meter.

TREATMENT OF DATA

Kinetics of Thiophene Hydrogenolysis

By design and operation, the stirred microbalance reactor fulfills the criteria of a constant stirred tank reactor (*4*). At steady state, the rate of thiophene conversion, r_T, is given by,

$$r_T = \frac{F_T X_T}{W_C}, \tag{2}$$

where F_T is the TP flow rate, X_T is the TP conversion defined as ΣC_4 products/(unreacted TP + ΣC_4 products), and W_C is the catalyst weight.

TABLE 1

Conversion Data for Reaction of Thiophene over Sulfided Mo/γ-Al_2O_3 Catalyst[a]

Run[b]	1	2	3	4	5	6	7
p_T^0 (atm)	0.0266	0.0266	0.0135	0.0135	0.0135	0.0266	0.0266
p_H^0 (atm)	0.99	0.95	0.60	0.97	0.56	0.59	0.99
p_N^0 (atm)	0	0	0.40	0	0.40	0.40	0
p_S^0 (atm)	0	0.036	0	0.036	0.036	0	0
p_A (atm)	0.0007	0.0004	0.0003	0.0002	0.0001	0.0005	0.0008
p_B (atm)	0.0024	0.0140	0.0012	0.0008	0.0006	0.0020	0.0026
p_T (atm)	0.0237	0.0249	0.0120	0.0125	0.0128	0.0242	0.0234
p_S (atm)	0.0031	0.0376	0.0153	0.0372	0.0368	0.0025	0.0034
p_H (atm)	0.99	0.95	0.60	0.96	0.56	0.59	0.99
C (mole fraction)	0.115	0.068	0.113	0.074	0.052	0.095	0.125
r_T (cm^3/min g)	0.716	0.423	0.358	0.233	0.163	0.590	0.782
ΔW (mg)	0.30	0.75	0.50	0.70	0.80	0.60	0.55

[a] Catalyst charge: 200 mg; presulfiding conditions: 400°C; $H_2S/H_2 = 1/10$; 1 atm; 2 hr; thiophene reaction conditions: 400°C; 47.5 cm^3 (STP)/min; 1 atm.

[b] Subscripts represent: A, butane; B, butenes; H, hydrogen; N, nitrogen; S, hydrogen sulfide; T, thiophene.

Rate expressions tried in data correlation were of the type given in Eq. (1). These were linearized in the form,

$$\left(\frac{p_T p_H{}^m}{r_T}\right)^{1/n} = \frac{1}{(k_T)^{1/n}}(1 + K_T p_T + K_S p_S) \quad (3)$$

and solved for chosen values of m and n by least squares linear regression analysis for the parameters k_T, K_T and K_S.

Reversible Adsorption

The stirred microbalance reactor allows continuous monitoring of catalyst weight changes attending catalytic reaction at various fixed vapor-phase compositions. If gas–solid equilibrium is achieved, catalyst weights should reflect reversibly adsorbed species.

Assuming equilibrium is adequately described by Langmuir isotherms, the weight of an adsorbed specie, W_i, in competitive adsorption with other species is given by,

$$W_i = \frac{bM_iK_ip_i}{(1 + K_ip_i + \Sigma K_jp_j)^n}, \quad (4)$$

where p_i is the partial pressure; M_i, the molecular weight; and K_i, the adsorption constant of the i-th specie; p_j and K_j are the partial pressures and adsorption constants of the j species; b is a constant proportional to the total number of active adsorption sites and the sample weight; and n is the order in the adsorption term.

For the reactions under consideration, only adsorption of TP and H_2S are important, since the weight of adsorbed H_2 is negligible. Thus, the total weight adsorbed becomes,

$$W = W_T + W_S = \frac{b(M_TK_Tp_T + M_SK_Sp_S)}{(1 + K_Tp_T + K_Sp_S)^n}. \quad (5)$$

Since this equation contains four unknowns, n, b, K_T and K_S, accurate data over a wide range of conditions are needed. In addition, solution for the unknowns requires a nonlinear, least squares analysis technique.

RESULTS

Kinetics of Thiophene Hydrogenolysis

The data for these runs are given in Table 1. At each run condition, reaction was continued until a new steady state was achieved as evidenced by constancy in conversion and weight change (about 1 hr). Partial pressures of reactants and products in the reactor were then calculated for each run condition from the appropriate conversion and inlet feed compositions. Run 1 was omitted in the kinetic analysis since it appeared not to be lined-out as judged by lower conversion and weight gain compared to run 7.

The results are graphically displayed in Fig. 1, in terms of TP conversion and catalyst weight change versus run sequence. The lower scale shows qualitatively the reactor inlet compositions for each run, 0 indicating the absence and + the presence of the compound, and H and L referring to a high or low level of TP. It should be appreciated, that since the reactor operated in a continuous stirred tank mode, the results reflect gas compositions in the reactor, which are somewhat different from but related to the inlet compositions.

The presence of H_2S (in considerable excess over that which is generated in the reaction) caused an appreciable drop in conversion and concomitant gain in weight. When N_2 was present, H_2 partial pressure was lower, and this resulted in a lowering in conversion, as can be seen by comparing the last two runs in the series, and also the fourth and fifth runs. The effect of thiophene level is less obvious, since it

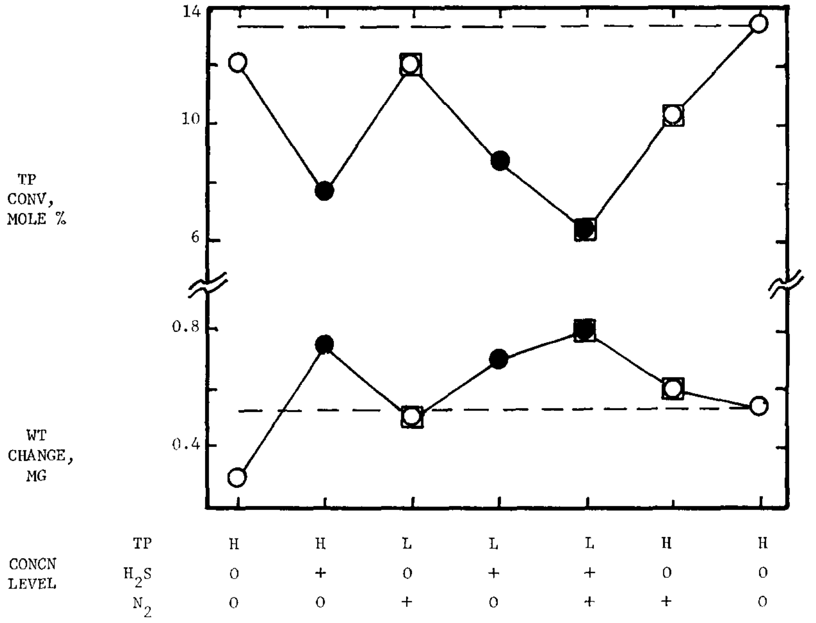

FIG. 1. Effect of reaction conditions on thiophene conversion and catalyst weight change. 400°C, 200 mg catalyst. (H) high level; (L) low level; (+) present; (0) absent. (●) H_2S present; (□) N_2 present; (○) neither present.

is confounded with other effects in the series.

Detailed kinetic analysis of the data according to Eq. (3) gave only a fair correlation. The rate was first order in TP and H_2, and was inhibited by TP and H_2S. However, the data were not of sufficient accuracy to distinguish between a first or second order inhibition term ($n = 1$ or 2). Both the kinetic analysis, and a separate run in which excess 1-butene was added to the inlet feed showed that butene had no effect on the thiophene rate.

Further analysis revealed certain inconsistencies in the data fit. Specifically, the H_2 partial pressure was not entirely satisfied. A much superior correlation was obtained when an H_2 inhibition term was added to the rate expression, for example, as in the form,

$$r_T = \frac{k_T p_T p_H}{(1+K_T p_T + K_S p_S)(1+K_H p_H)}. \quad (6)$$

In order to test other expressions of this general nature, Eq. (6) was generalized and cast in a linear form, viz,

$$Y_A = \left(\frac{p_T p_H{}^m}{r_T[1 + (K_H p_H)^{1/p}]^q}\right)^{1/n}$$
$$= \frac{1}{(k_T)^{1/n}}(1 + K_T p_T + K_s p_s). \quad (7)$$

Linear regression analyses were carried out on Eq. (7) for various values of K_H and a given set of exponent values of m, n, p, and q. For each combination of exponents chosen, the best fit was taken for that K_H giving the lowest variance function defined by (*5*),

$$v_A = \frac{\Sigma(Y_A - Y_A{}^*)^2}{(N-3)} \times \frac{(N-1)}{\Sigma(Y_A - \bar{Y}_A)}, \quad (8)$$

where Y_A is the experimental value of the middle term in Eq. (7), $\bar{Y}_A$ is the average of the Y values, $Y_A{}^*$ is the value calculated from the regression fit values of k_T, K_T and K_S, and N is the number of experimental points. The number 3 in the denominator represents the three correlating parameters.

The above expressions derive from kinetic considerations assuming a dual site mechanism for reaction (see Kinetics section). Considering a single site mechanism, the corresponding equations become,

$$r_T = \frac{k_T p_T p_H}{(1 + K_T p_T + K_S p_S + K_H p_H)}, \quad (9)$$

for the simplest case, and for the linearized general case,

$$Y_B = \left(\frac{p_T {p_H}^m}{r_T}\right)^{1/q} = \frac{1}{(k_T)^{1/q}} \times [1 + K_T p_T + K_S p_S + (K_H p_H)^{1/p}] \quad (10)$$

Again, linear regression analyzes were carried out on Eq. (10) for various sets of m, p and q values. Now K_H is obtained explicitly in the analysis. Goodness of fit was assessed by the variance function given by,

$$v_B = \frac{\Sigma(Y_B - Y_B^*)^2}{(N-4)} \times \frac{(N-1)}{\Sigma(Y_B - \bar{Y}_B)^2}. \quad (11)$$

TABLE 2

Results of Data Correlations[a]

Case A	n	m	p	q	$V \times 10^3$
Dual site[b]					
1	1	1	1	1	0.88
2	1	1	2	2	0.91
3	1	2	1	1	55
4	1	$\frac{1}{2}$	2	1	36
5	1	1	2	1	0.93
6	2	1	1	1	Negative coefficient
7	2	1	2	2	4.4
Case B					
Single site[c]					
1		1	1	2	1.26
2		$\frac{1}{2}$	2	2	Negative coefficient
3		1	2	2	1.82
4		1	1	1	9.1

[a] V = variance as defined by Eq. (8) or (11).

[b] $r_T = \dfrac{k_T p_T {p_H}^m}{(1 + K_T p_T + K_S p_S)^n [1 + (K_H p_H)^{1/p}]^q}$

[c] $r_T = \dfrac{k_T p_T {p_H}^m}{[1 + K_T p_T + K_S p_S + (K_H p_H)^{1/p}]^q}$

TABLE 3

Parameter Values for Best Fits

Case	k_T (cm^3/min g atm)	K_H (atm^{-1})	K_T (atm^{-1})	K_S (atm^{-1})
A-1	84	0.55	20	45
A-2	121	0.24	19	44
A-5	149	3.0	19	44
A-7	112	0.26	6.4	14
B-1	90	0.38	8.0	18
B-3	175	0.94	10.9	26

Table 2 presents the results of these correlations. Forms represented by Cases A-1, 2, 5, and B-1 and 3 showed satisfactory correlations, whereas the others did not. Parameter values for the best correlations are given in Table 3. All expressions in which K_H was not included gave significantly poorer fits.

A postrun analysis of the stoichiometry of the catalyst according to the method outlined in the previous article (*1*) gave the results shown in Table 4. Of major concern here is the calculated vacancy concentration, especially the value corrected for coke. The latter value of 0.23 mmol/mmol Mo is equivalent to 0.19 mmol/g catalyst for the catalyst used in this study.

TABLE 4

Postrun Stoichiometry Analysis[a]

ΔW_{OT}, overall wt gain (mg/g)	23.4
W_S, sulfur added (mg/g)	45.9
W_C, carbon added (assumed) (mg/g)	4.5
S, sulfide content (mmol/mmol Mo)	1.70
O_T, active oxide content (mmol/mmol Mo)	0.96
$\square_T$, vacancies (mmol/mmol Mo)	0.34
$(\square_T)_1$, vacancies minus coke (mmol/mmol Mo)	0.23

[a] See Ref. (*1*) for symbols used and details of analysis.

Equilibrium Constants from Weight Change Data

a. H_2S adsorption on sulfided catalyst. Because of the small weight changes obtained in the thiophene kinetic runs and due to the weight relationships to the adsorption coefficients, as exemplified by Eq. (5), involving solution of four unknown parameters, it was decided to determine the H_2S equilibrium constant, K_S, separately in the absence of thiophene. To this end, an adsorption isotherm at reaction temperature of 400°C, was determined on a separate catalyst presulfided under conditions similar to those employed in the kinetic studies.

The adsorption isotherm data are given in Fig. 2. Points were obtained at three H_2S/H_2 ratios. Adsorption was rapid, but desorption slower. A slight hysteresis was observed, accounting for the scatter in the data. Absolute weights were calculated from weight changes and extrapolation of the curve to $p_s = 0$.

The parameters K_S and b were determined by a trial-and-error difference fitting of the data to Eq. (5), with the TP terms omitted and $n = 1$. Although the calculated values of the parameters are subject to some error, a satisfactory fit to the data was obtained with $K_S = 45$ atm^{-1} and $b = 0.08$ mmol/g, as seen by the solid curve in Fig. 2. The lower value of b obtained here for the sulfided catalyst is not inconsistent with the higher value obtained above for the thiophene-reacted catalyst. Thus, taking b to be a measure of vacancies, it was shown previously (*1*) that the vacancy concentration of the sulfided catalyst increases as a result of reaction with thiophene. The value of K_s should be independent of the value of b.

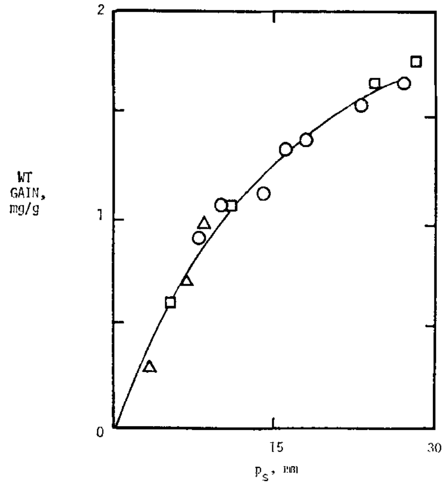

FIG. 2. Adsorption isotherm for H_2S/H_2 over sulfided catalyst. 400°C. (○) 9%; (□) 4.6%; (△) 2.2% H_2S.

TABLE 5

Adsorption Constants for Thiophene Hydrogenolysis over Sulfided Mo/γ-Al_2O_3 Catalyst

Source	b (mmol/g)	K_T (atm^{-1})	K_S (atm^{-1})
H_2S adsorption[a]	0.08	—	45
Kinetic analysis[b]	—	20	45
Wt change			
Method 1	0.15[c]	15	36
Method 2	0.15[c]	14	45
Postrun analysis	0.19[d]	—	—

[a] On separate sulfided catalyst.
[b] For Case A-1.
[c] Total adsorption sites for thiophene and H_2S.
[d] Vacancies calculated from stoichiometry (see Table 4).

b. Thiophene adsorption on sulfided catalyst. The adsorption constant for thiophene cannot be directly determined at reaction temperature owing to the H_2S formed by reaction, which product also adsorbs. Therefore, it was necessary to consider the simultaneous adsorption of both, using the weight change data obtained in the kinetic runs. Equation (5) was employed for this purpose with $n = 1$. Adsorption of butene is ignored since its contribution was negligible on catalyst weight changes due to its low partial pressure. Furthermore, addition of excess butene in a separate run showed no change in catalyst weight.

Since the weight data were neither numerous nor highly accurate, a nonlinear least squares analysis for the three parameters b, K_T and K_S was unsuccessful. Two other approaches were tried. In the one, the K_S/K_T ratio found from the kinetic analysis was used to eliminate one of the unknown parameters. In the other, the value of K_S obtained from the H_2S adsorption isotherm was used to eliminate one parameter. The calculated values obtained by these analyses, given in Table 5, gave results reasonably consistent with the kinetic studies for Case A-1.

DISCUSSION

Kinetics

There can be little doubt that the thiophene hydrogenolysis reaction is complex. The reaction rate is apparently first order in both TP and H_2, but no less than three inhibition terms were needed to obtain a satisfactory data fit. Rate expressions of the form given in Table 2 which gave good correlations can be derived from standard Langmuir–Hinshelwood treatments. Two cases need to be considered, viz, dual site and single site mechanisms. In the dual site mechanisms, TP and H_2S are assumed to adsorb on one site and H_2 on another; whereas, in the single site mechanism, all three are assumed to adsorb on the same site. Surface reaction of adsorbed species is taken to be the rate limiting step; other rate-controlling steps did not give agreement with the experimental rate form obtained. In these mechanisms, it is assumed that the primary hydrocarbon product is butadiene, which then subsequently undergoes hydrogenation to butenes and butane (*6*).

Lipsch and Schuit (*7*) have presented a general mechanism for thiophene hydrogenolysis over Mo/Al_2O_3 catalysts. In this mechanism, dual sites are invoked; anion vacancies for thiophene adsorption and neighboring oxide or sulfide anions for hydrogen adsorption. Reaction occurs by transfer of hydrogen to the adsorbed molecule with concomitant C–S bond cleavage, resulting in formation and desorption of butadiene. The absorbed sulfur residue is then removed as hydrogen sulfide by a subsequent hydrogenation step. In the previous paper (*1*), we have satisfactorily correlated our conversion results with this mechanism; however, it was necessary to modify some details of the surface species present during reaction.

The simplest reaction sequences consistent with Lipsch and Schuit's mechanism (*7*) and the kinetic results found here are presented in Table 6. For the molecular hydrogen mechanism, either step

TABLE 6

Possible Thiophene Reaction Mechanisms[a]

Molecular hydrogen mechanism

$$\mathrm{TS} + \mathrm{s}_1 \rightleftarrows \mathrm{TSs}_1 \qquad (1A)$$

$$\mathrm{H}_2 + \mathrm{s}_2 \rightleftarrows \mathrm{H}_2\mathrm{s}_2 \qquad (2A)$$

$$\mathrm{TSs}_1 + \mathrm{H}_2\mathrm{s}_2 \rightarrow \mathrm{HTSHs}_1 + \mathrm{s}_2 \qquad (3A)$$

$$\mathrm{HTSHs}_1 + \mathrm{H}_2\mathrm{s}_2 \rightarrow \mathrm{D} + \mathrm{H}_2\mathrm{Ss}_1 + \mathrm{s}_2 \qquad (4A)$$

$$\mathrm{H}_2\mathrm{S} + \mathrm{s}_1 \rightleftarrows \mathrm{H}_2\mathrm{Ss}_1 \qquad (5A)$$

$$r_T = \frac{(k_3 L_1 L_2 K_T K_H) p_T p_H}{(1 + K_X p_T + K_S p_S)(1 + K_H p_H)} \qquad \text{(Case A-1)}$$

$K_X = K_T$, for 3A slow step

$K_X = K_T(1 + k_3/k_4)$, for 4A slow step

Atomic hydrogen mechanism

$$\mathrm{TS} + \mathrm{s}_1 \rightleftarrows \mathrm{TSs}_1 \qquad (1B)$$

$$\mathrm{H}_2 + 2\mathrm{s}_2 \rightleftarrows 2\mathrm{Hs}_2 \qquad (2B)$$

$$\mathrm{TSs}_1 + \mathrm{Hs}_2 \rightarrow \mathrm{HTSs}_1 + \mathrm{s}_2 \qquad (3B)$$

$$\mathrm{HTSs}_1 + \mathrm{Hs}_2 \rightarrow \mathrm{D} + \mathrm{Ss}_1 + \mathrm{s}_2 \qquad (4B)$$

$$\mathrm{Ss}_1 + \mathrm{H}_2 \rightarrow \mathrm{H}_2\mathrm{Ss}_1 \qquad (5B)$$

$$\mathrm{H}_2\mathrm{S} + \mathrm{s}_1 \rightleftarrows \mathrm{H}_2\mathrm{Ss}_1 \qquad (6B)$$

$$r_T = \frac{(k_3 L_1 L_2^2 K_T K_H) p_T p_H}{(1 + K_T p_T + K_S p_S)[1 + (K_H p_H)^{\frac{1}{2}}]^2} \qquad \text{(Case A-2)}$$

[a] L_1 = thiophene + H_2S adsorption sites; L_2 = H_2 or H adsorption sites; TS = thiophene; D = butadiene.

(3A) or step (4A) as the rate limiting step (RLS) leads to Case A-1 of Table 2. Step (3A) in equilibrium gives Case A-3. In the atomic hydrogen mechanism, either step (3B) or (4B) as RLS gives Case A-4, while equilibrium in step (3B) leads to Case A-5. Case A-2 is obtained when steps (3B) and (4B) occur simultaneously, i.e., a concerted reaction involving $TSs_1 + 2Hs_2$. Of these, the data correlated satisfactorily only with Cases A-1, A-2, and A-5.

Similar reaction sequences as above can be derived for single site mechanisms. Thus, a sequence analogous to steps (1A)–(5A) of Table 6, but with only one common active site, leads to Case B-1 of Table 2 for either steps (3A) or (4A) as RLS. Likewise, Case B-3 can be derived from the analogous equations (1B)–(6B) if step (3B) is at equilibrium. These are the only two cases which agreed with the data. Satterfield and Roberts (*8*) reported a kinetic study with a sulfided CoMo/Al_2O_3 catalyst in which the best fit for TP hydrogenolysis was given by,

$$r_T = \frac{k p_T p_H}{(1 + K_T p_T + K_S p_S)^2}. \quad (12)$$

This form is a simplified version of Case A-6 or A-7 of Table 2. Since they did not vary the hydrogen partial pressure appreciably in their experiments, any inhibition term in p_H was approximately constant. Our kinetic analysis showed these forms to be inferior in data fit. Also, the value for K_S derived from Case A-7 (Table 3) did not agree with that obtained in the H_2S adsorption experiment (45 atm^{-1}). Therefore, we conclude that the Roberts and Satterfield rate model does not apply to the Mo/Al_2O_3 catalyst under our reaction conditions.

a. Dual site vs single site. Kinetic analyses of the reaction data do not permit distinguishing between mechanisms involving dual or single sites.[1] The subject arises from the finding that a hydrogen partial pressure term was needed in the denominator of the rate expression to obtain good data correlation. Previous work had not investigated the hydrogen effect sufficiently to detect this. Thus, early work had assumed a simple first-order or fractional order dependence in hydrogen pressure. In such a case, discussion of dual vs single sites becomes kinetically meaningless. In those few cases where a hydrogen inhibition term was found, a dual site was generally assumed, e.g., a form similar to Case A-1 of Table 2 was used to fit the data. It is probable that in those cases, a single site form of the type given in Case B-1 would also fit as well within the experimental error. Quite accurate data over a wide range of hydrogen partial pressures are required to unequivocally distinguish between these two cases.

Previous work (*9*) had shown that the sulfided catalyst contained anion vacancies. Considering these to be active sites for TP adsorption, it was shown that catalytic activity could not be correlated with vacancy concentration alone (*1*). In fact, satisfactory correlation with catalyst activity required a second active site. This latter site appeared to be related to the surface anion concentration. Correlation of catalytic activity required both types of sites. The dual site mechanisms considered here assume the same types of sites, namely, one for TP adsorption (L_1) and another for H_2 adsorption (L_2) without specifying their nature. Therefore, the dual site mechanism is consistent with the earlier findings.

The single site mechanisms, in which H_2 competitively adsorbs on TP sites, are not in accord with these earlier findings

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[1] Dual sites in the sense used here should not be confused with separate sites for hydrogenolysis of TP and for hydrogenation of butadiene or butene, as discussed by Amberg (*6*).

if vacancies are the active sites. Single site mechanisms based on surface or Rideal-type reactions should correlate directly with vacancies, contrary to these earlier results. Furthermore, the values of K_S derived from these forms do not agree with the independently derived value of 45 atm^{-1} from the H_2S adsorption studies (cf. Table 3).

b. Vacancies as active sites. We have no direct proof that TP adsorbs at vacancies. However, NH_3 chemisorption studies (*9*) showed that NH_3 adsorption on reduced and sulfided catalysts was directly proportional to vacancy concentration. These anion vacancies can be considered to have Lewis acid character in the sense that electron-pair donor molecules can be strongly chemisorbed. Thus, it is reasonable to presume that TP would act similarly by attachment through the free electron pair on the sulfur atom of thiophene.

Other evidence comes from a comparison of catalyst stoichiometry with dynamic weight change measurements. Table 5 shows that vacancy concentration calculated on the TP-reacted catalyst was 0.19 mmol/g catalyst compared to a value of 0.15 for dynamic adsorption sites for TP and H_2S derived from analysis of weight changes during the kinetic runs. This good agreement strongly suggests that TP adsorption sites and vacancies are indeed one and the same.

Inhibition of TP reactivity by H_2S is most likely due to reversible, competitive adsorption for vacancy sites. The good agreement between K_S values calculated from the adsorption experiment, kinetic analysis and weight change analysis supports this viewpoint.

c. Mode of H_2 adsorption. There is little information to bear on the question as to whether H_2 is adsorbed associately or dissociatively. Kinetic analysis could distinguish between these modes of adsorption in principle, but the data at hand are not sufficiently accurate to make this distinction. For molecular H_2 adsorption, good data correlation is obtained for step (3A) or step (4A) as the RLS, since both yield the same kinetic form (Table 6). However, for atomic H_2 adsorption, a distinction can be made. Now only step (4B) as the RLS fits the data, and that only with (3B) reversible.

The special case of concerted reaction involving dissociatively adsorbed H_2 reverts to Case A-2, and therefore, cannot be ruled out on kinetic grounds. Kabe and Todo (*10*) use this formulation in correlating their thiophene data over an Mo/Al_2O_3 catalyst. (Their correlating equation does not include adsorbed TP, as does ours.) It is doubtful whether their data could unequivocally distinguish between this mechanism and the others found to give good correlations with our data.

d. The rate limiting step. All the equations which correlated the kinetic data involve surface reaction of adsorbed species as the RLS. The various rate expressions encountered in the literature are invariably based on the same precept. Desikan and Amberg (*11*), based on comparative rates of methyl-substituted thiophenes, concluded that the slow step is likely a "surface reaction such as C–S bond fission on the catalyst surface."

Limiting the discussion to dual site mechanisms, we will first consider molecular hydrogen adsorption (Reactions (1A)–(5A) of Table 6). As discussed above, either step (3A) or (4A) could be the slow step. Smith *et al.* (*12*), have shown by deuterium exchange experiments that thiophene adsorbed on Mo/Al_2O_3 preferentially exchanged at α C–H positions on the thiophene molecule. This could only occur in the reaction mechanism shown if step (3A) were reversible. Further, they found that the exchange rate was appreciably faster than the thiophene hydrogenolysis reaction rate. Assuming then that step (3A) is in equilibrium and step (4A) is the RLS, the resulting expression is equivalent to Case A-3 of Table 2, which did not adequately fit the data. It appears, therefore, that both the kinetics and the exchange data cannot be reconciled to a mechanism involving molecularly adsorbed H_2. Of course, if the exchange reaction occurs by a different path from the thiophene reaction (see below), then this argument becomes invalid.

Turning now to atomically adsorbed H_2, a similar argument can be applied. Now, step (4B) of Table 6 as the RLS with step (3B) in equilibrium fits the kinetic data (Case A-5 of Table 2). Since step (3B) is in equilibrium (or at least $k_3 \gg k_4$ and $k_3' \gg k_4$), D_2 exchange will occur more rapidly than TP hydrogenolysis. Hence, this mechanism is in accord with both the kinetic results and the exchange results. Accepting this viewpoint, the reversibly adsorbed H_2 active in the hydrogenolysis reaction must be atomically adsorbed.

Based on recent exchange studies, Cowley (*13*) has proposed a mechanism for thiophene exchange with is different from that for hydrogenolysis. Briefly, his explanation entails a π-bonded thiophene adsorbed specie which readily undergoes D_2 exchange. This specie can then transform to an σ-bonded thiophene adsorbed through the sulfur atom but at a slower rate. The latter specie is considered the intermediate in the hydrogenolysis reaction. If in our mechanism schemes, the adsorbed specie written as TSs is in fact his σ-bonded specie, then exchange need not be explained by reversibility of step (3). If this view is correct, we must conclude that we cannot determine at present whether molecular or atomic H_2 is the adsorbed specie involved in the thiophene hydrogenolysis reaction, or even which step is the RLS if the former case applies.

Active Sites for Hydrogenolysis

From the results of this investigation and prior findings (*1*), we associate TP adsorption sites with catalyst vacancies (L_1) and H_2 adsorption sites with surface sulfide anions (L_2) in the sulfided catalyst. Since some hydrogen was found to be strongly (in fact, irreversibly) adsorbed on the sulfided catalyst (*9*), it was assumed that this source was the hydrogen which took part in the reaction, it being rapidly replenished by H_2 in the gas phase. A problem now arises with this mechanism due to the fact that the kinetic analysis shows the hydrogen to be reversibly adsorbed. Numerous attempts at mechanisms in which irreversible H_2 was assumed to be directly involved in the C–S bond cleavage step, with gas-phase H_2 replacing the consumed irreversible H_2 either directly or through a reversibly adsorbed specie, failed to yield rate expressions consistent with the experimentally determined form.

Evidence of reversibly as well as irreversibly adsorbed H_2 has been given for reduced Mo/Al_2O_3 catalysts (*14*). Evidence of reversibly adsorbed H_2 has also been reported by Owens and Amberg (*15*) for a sulfided $CoMo/Al_2O_3$ catalyst. These same authors state that loosely bound hydrogen is necessary for TP reaction over the $CoMo/Al_2O_3$ catalyst. If the same holds true for the Mo/Al_2O_3 catalyst of the present study, then it may be surmised that indeed reversibly adsorbed and not irreversibly adsorbed hydrogen is the active agent in TP hydrogenolysis.

Secondary Hydrogenation

In our mechanism considerations, we have ignored the fate of the hydrocarbon products of the TP hydrogenolysis. The work of Amberg (*6*) has demonstrated that the primary reaction product is butadiene. However, its reactivity towards hydrogenation is so great, that it is only observed at low conversions or under special conditions. Under normal reaction conditions, only the hydrogenated products, *n*-butenes and *n*-butane are obtained. These secondary hydrogenation reactions are only important to our discussion of the TP reaction if they involve identical sites.

The preponderance of evidence seems to indicate that hydrogenation of butene (and presumably butadiene) occurs on different sites from that of TP hydrogenolysis (*2*). To this we add our own observation that addition of an eightfold excess of butene over that produced in the TP reaction had no effect on the TP conversion. The nature of the sites responsible for hydrogenation is only vaguely known at present. We intend to report on the kinetics of this reaction at a later date. Suffice it to say, we need not be concerned with the influence of this reaction on the primary TP hydrogenolysis reaction.

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