

## The Effect of Pyridine Poisoning on the Kinetics of Thiophene Hydrogenolysis and Hexene Hydrogenation

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The kinetics of deactivation of thiophene hydrodesulfurization and hexene hydrogenation by pyridine poisoning was studied in a flow microbalance reactor, which allowed simultaneous measurements of pyridine adsorption and reaction rates. The pyridine adsorption data obeyed a modified Temkin isotherm implying a distribution of adsorption sites. The deactivation kinetics could not be correlated with a reversible (rapid) pyridine adsorption model. A "quasiirreversible" model correlated the data very well. In this model, the rates of adsorption and desorption of pyridine are relatively slow compared to reaction rates. Thus, its effect on catalytic activity is reflected in a "quasipermanent" poisoning of active sites, lowering the reaction rate constant, rather than in a reversible competitive adsorption for active sites. Furthermore, it is deduced that the number of catalytically active sites is small compared to the total adsorption sites. © 1986 Academic Press, Inc.

### INTRODUCTION

The effect of a poison on catalytic activity is generally site specific and may be either reversible or irreversible. Removal of the poison from the feed regenerates the catalytic activity in the former case, whereas a permanent loss in activity remains in the latter case. The kinetics of hydrodesulfurization (HDS) in the presence of a second component which adsorbs on the catalyst but does not undergo reaction itself (which we may call the poison) has generally been treated as a reversible poison. For a truly reversible poison, the amount adsorbed and the (lower) catalytic activity reach steady-state values which depend upon the concentration of poison in the feed. Change in the feed concentration reversibly alters the amount adsorbed and the catalytic activity.

The kinetics of HDS of model compounds, e.g., thiophene, benzothiophene, dibenzothiophene, have often been correlated by use of the Langmuir-Hinshelwood

(LH) treatment (1, 2). In this treatment, reactant and/or product concentrations are included in an inhibition term in the rate expression, reflecting their adsorption on active sites. Invariably, adsorption of these are considered in equilibrium with catalyst sites (or at least very rapid rates of adsorption and desorption) and some surface reaction is assumed to be the slow step in the reaction (rate-limiting step). A reversible poison is then treated as a competitive adsorption in equilibrium and added to the inhibition term. For example, the effect of nitrogen compounds (3, 4) and oxygen compounds (5, 6) on HDS have been so treated. Although this may be valid in many cases, it is not necessarily so in a general sense. Thus, one may envision a reversible poison whose rates of adsorption and desorption are very slow compared to the rate of reaction under consideration. Now, in the time scale of the reaction, the poison can no longer be considered in equilibrium (a basic premise in the L-H treatment), and must be looked at in terms of a "quasiirreversible" adsorbed state at a given concentration of poison. However, the quasiirreversible state is not a true irreversible poisoning, since its extent of adsorption

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TABLE I  
Thiophene Runs with Unpoisoned Catalyst<sup>a</sup>

No <sup>b</sup>	Flow, cm <sup>3</sup> (STP)/min			Conv., % <sup>c</sup>
	F <sub>T</sub> <sup>c</sup>	F <sub>H</sub> <sup>d</sup>	F <sub>S</sub> <sup>e</sup>	
1s	40	40	20	0.423
2	60	20	20	0.396
3	40	30	30	0.404
4	60	30	10	0.426
5	60	10	30	0.379
6s	40	40	20	0.422
7	20	60	20	0.463
8	20	70	10	0.485
9	20	50	30	0.430
10	40	50	10	0.439
11s	40	40	20	0.426
12	40	20	40	0.383
13	60	0	40	0.359
14	20	40	40	0.420

<sup>a</sup> 0.464 g, 350°C, 0.959 atm.

<sup>b</sup> s signifies standard conditions.

<sup>c</sup> H<sub>2</sub> bubbled through thiophene at 0°C (vapor pressure 0.0263 atm).

<sup>d</sup> H<sub>2</sub>.

<sup>e</sup> 10.0% H<sub>2</sub>S in H<sub>2</sub>.

(and effect on catalytic activity) will change with a change in concentration. That is, the poison is in adsorption equilibrium with the catalyst sites, but at the same time is not in rapid equilibrium with respect to the rate of the reaction. In such a case, inclusion of the poison concentration in an inhibition term in the rate equation is no longer valid. Instead, the quasiirreversible (steady state) adsorption should be treated as a quasipermanent loss of active sites unavailable to reactant. The treatment then follows that of a permanent poison, where account is taken in a decrease in the reaction rate constant. However, in contrast to the true irreversible poisoning case, the quasiirreversible poison state will depend on the poison concentration through its slow adsorption-desorption equilibrium.

In a previous study (7), we were unable to correlate the effect of pyridine poisoning on the kinetics of benzothiophene HDS us-

ing L-H kinetics, and have concluded that the failure was due to the slow adsorption-desorption rates of pyridine compared to HDS rates. In the course of investigating the effect of various nitrogen-containing poisons on the HDS of thiophene and hydrogenation of hexene (8), we have accumulated additional results bearing on this question. In the present communication, we present a more detailed analysis demonstrating the validity of the quasiirreversible adsorption treatment for the effect of pyridine adsorption on the kinetics of thiophene HDS and hexene HYD.

#### EXPERIMENTAL

The catalyst used in this study was American Cyanamide 1442A (308 m<sup>2</sup>/g), containing 2.2% Co and 10.4% Mo on an Al<sub>2</sub>O<sub>3</sub> support. Pyridine was of highest purity available (Aldrich). Thiophene (Alpha Products) and 1-hexene (Aldrich) were employed as reactants for HDS and HYD, respectively. Hydrogen was purified with a Deoxo unit followed by 5A molecular sieves. A mixture of 10% H<sub>2</sub>S in H<sub>2</sub> was used for presulfiding the catalyst and addition to the reactant stream.

A stirred, flow microbalance reactor (8) was used for all runs. This reactor has been shown to simulate well a continuous stirred tank reactor (9). The catalyst (20–40 mesh) was presulfided in the reactor at 400°C for 2 h with 60 cm<sup>3</sup>/min flow of H<sub>2</sub>S/H<sub>2</sub> mixture followed by cooling to 350°C. For the kinetic series on the unpoisoned catalyst, H<sub>2</sub> saturated with thiophene via bubblers at 0°C and H<sub>2</sub>S/H<sub>2</sub> were passed over the catalyst for overnight. The next day, runs with varying feed compositions were made according to the schedule of Table 1. Total flow was always held at 100 cm<sup>3</sup>/min and reactor pressure was 0.96 atm.

For the pyridine poisoning experiments with thiophene, another catalyst charge was used. After overnight exposure to thiophene/H<sub>2</sub>/H<sub>2</sub>S mixture, the standard flow conditions were set and a conversion obtained. Following, pyridine in benzene was

TABLE 2  
Parameters for Eq. (1)

	<i>n</i>	
	1	2
$k_T$ , cm <sup>3</sup> /g min atm <sup>2</sup>	278 ± 18	261 ± 13
$K_T$ , atm <sup>-1</sup>	46 ± 10	17 ± 3
$K_S$ , atm <sup>-1</sup>	12 ± 2	5 ± 1
SS/DF × 10 <sup>4</sup>	3.68	3.71

Note. ± Values are 95% CI.

continuously introduced with a syringe pump in step increments, catalyst weight and conversion being determined 3–4 h after each step change. A similar poisoning run with a new catalyst charge was carried out using hexene as the reactant. Under the reaction conditions employed, pyridine did not undergo reaction. Effectiveness factor calculations (10) showed that reaction rates were not influenced by intraparticle diffusion. Further details are given elsewhere (8).

## RESULTS AND DISCUSSION

### 1. Thiophene HDS Runs with Unpoisoned Catalyst

The data obtained at different concentrations of thiophene, H<sub>2</sub>S and H<sub>2</sub> are given in Table 1. The overnight exposure to the thiophene/H<sub>2</sub>S/H<sub>2</sub> mixture was sufficient to obtain a stable catalyst, as judged by the repeat runs at standard conditions. The data were analyzed by a nonlinear regression analysis program (11) to obtain parameters of the L-H rate expression,

$$r_T^0 = \frac{k_T^0 p_T p_H}{(1 + K_T p_T + K_S p_S)^n} \quad (1)$$

where  $r_T$  is the reaction rate,  $k_T$  is the rate constant,  $p$  are partial pressures,  $K$  are adsorption constants, and subscripts T, H, and S represent thiophene, H<sub>2</sub>, and H<sub>2</sub>S, respectively. Similar expressions have been used by others,  $n$  taking on a value of 1 (12) or 2 (13, 14). Parameter values with

95% confidence intervals are given in Table 2 for  $n = 1$  and 2. The goodness of the fits do not permit unequivocal assignment of  $n$ .

### 2. Thiophene HDS Runs with Added Pyridine

Table 3 presents weight pickup, pyridine partial pressure, thiophene conversion and relative activity data. Relative activity,  $A_T$ , is defined as

$$A_T = \frac{x_T/(1 - x_T)}{x_T^0/(1 - x_T^0)} \quad (2)$$

where  $x_T$  is the thiophene conversion of the poisoned catalyst and  $x_T^0$  that of the unpoisoned catalyst.  $A_T$  is a measure of the relative catalyst deactivation due to pyridine poisoning.

For the poisoned catalyst, Eq. (1) can be written as

$$r_T = \frac{k_T p_H p_T^0 (1 - x_T)}{D^n} \quad (3)$$

TABLE 3

Thiophene Runs with Added Pyridine<sup>a</sup>

$W_N^b$ (mmol/g)	$p_N$ (atm × 10 <sup>3</sup> )	Conv., $x_T$	Relative activity, <sup>c</sup> $A_T$
0	0	0.434	1.0
0.042	—	0.286	0.523
0.081	—	0.277	0.499
0.085	0.19	0.260	0.458
0.094	0.27	—	—
0.109	0.38	0.221	0.370
0.143	1.71	0.166	0.260
0.155	2.46	—	—
0.174	3.72	0.127	0.190
0.195	7.53	0.090	0.129
0.216	15.5	0.070	0.098
0.248	32.9	0.056	0.078
0.279	69.7	0.054	0.075

<sup>a</sup> 0.300 g, 350°C, 0.959 atm,  $F_T = 20$  cm<sup>3</sup>/min,  $F_H = 20$  cm<sup>3</sup>/min,  $F_S = 10$  cm<sup>3</sup>/min (see Table 1 for meaning of symbols).

<sup>b</sup> Amount of pyridine added to catalyst under steady-state conditions.

<sup>c</sup> Activity relative to fresh catalyst given by Eq. (2).

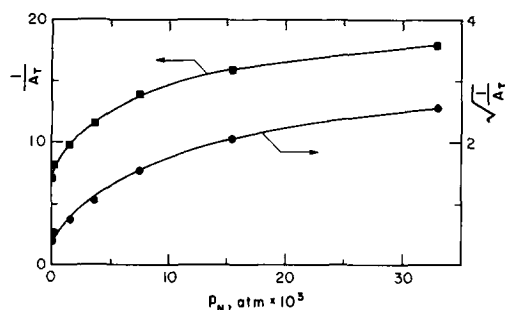


FIG. 1. Test of reversible pyridine adsorption on activity for thiophene reaction according to Eq. (11).

Here  $D$  is the inhibition term for the poisoned catalyst (which may or may not include a term for the pyridine partial pressure). A similar equation for the unpoisoned catalyst is

$$r_T^0 = \frac{k_T^0 p_H p_T^0 (1 - x_T^0)}{(D^0)^n} \quad (4)$$

For a stirred tank reactor, the rates are given by

$$r_T = F_T x_T / W \quad (5)$$

$$r_T^0 = F_T x_T^0 / W \quad (6)$$

where  $F_T$  is the flow rate of thiophene and  $W$  is the weight of catalyst. Combination of Eqs. (2)–(6) gives

$$A_T = \frac{k_T}{k_T^0} \left[ \frac{D^0}{D} \right]^n \quad (7)$$

For fast adsorption–desorption (reversible) of pyridine,  $D$  should include a  $K_N p_N$  term ( $K_N$  is equilibrium adsorption of pyridine) and  $k_T = k_T^0$ ; whereas for slow adsorption–desorption (quasiirreversible) of pyridine (see Introduction),  $D \sim D^0$  (only small differences from different  $x_T$ 's) and  $k_T < k_T^0$ , where  $k_T$  now should account for deactivated sites.

Considering the first option (reversible adsorption of pyridine), rate equation (3) becomes

$$r_T = \frac{k_T^0 p_H p_T}{(1 + K_T p_T + K_S p_S + K_N p_N)^n} \quad (8)$$

Dividing (8) by the analogous equation for the unpoisoned catalyst, and making the substitutions  $p_T = p_T^0(1 - x_T)$  and  $p_S = p_S^0 + p_T^0 x_T$  (where  $p_S^0$  is the partial pressure of added  $H_2S$ ) gives

$$A_T = \left[ \frac{B + C x_T^0}{B + C x_T + K_N p_N} \right]^n \quad (9)$$

where

$$B = 1 + K_T^0 p_T^0 + K_S^0 p_S^0$$

$$C = (K_S - K_T) p_T^0.$$

From the rate parameters of Table 2 and the conversion changes of Table 3, it can be shown that  $B + C x_T^0 \sim B + C x_T$  within 5% for  $n = 1$  and within 10% for  $n = 2$ . Therefore, with this simplification, Eq. (9) becomes

$$A_T = \left[ \frac{G}{G + K_N p_N} \right]^n \quad (10)$$

where  $G = B + C x_T^0$ . Linearization of Eq. (10) yields

$$\sqrt[n]{\frac{1}{A_T}} = 1 + \frac{K_N}{G} p_N \quad (11)$$

Appropriate plots of Eq. (11) for  $n = 1$  and 2 are given in Fig. 1. It is obvious that a suitable correlation is not obtained. The small differences between  $B + C x_T^0$  and  $B + C x_T$  are not sufficient to linearize these plots. The conclusion is that the data do not agree with the assumption of fast, reversible adsorption of pyridine as required by the L-H treatment.

The second option, quasiirreversible adsorption of pyridine, requires a relationship between pyridine adsorbed on active sites and pyridine partial pressure. Thus,  $k_T = k_T^0(1 - \theta_N)$ , where  $\theta_N$  is the coverage of pyridine and  $1 - \theta_N$  represents the residual active sites not poisoned by pyridine. Before devising a test for the deactivation kinetics, an appropriate isotherm needs to be developed.

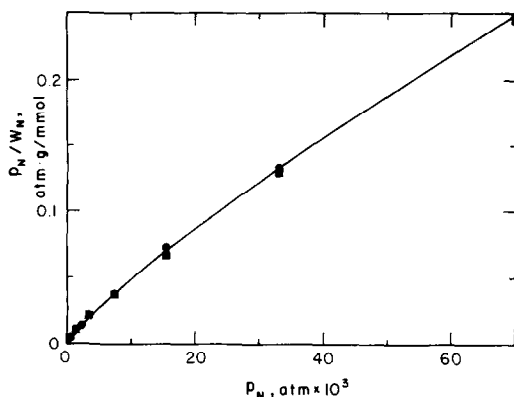


FIG. 2. Langmuir isotherm for pyridine adsorption during thiophene (●) and hexene (■) runs.

### 3. Pyridine Adsorption Isotherms

The pyridine adsorption data of Table 3 were first fitted to a Langmuir isotherm (15), viz.,

$$\theta_N = \frac{W_N}{W_{N,\max}} = \frac{K_N p_N}{1 + K_N p_N} \quad (12)$$

or in linearized form,

$$\frac{p_N}{W_N} = \frac{1}{K_N W_{N,\max}} + \frac{p_N}{W_{N,\max}}$$

where  $W_{N,\max}$  is the total pyridine adsorption at full coverage and  $K_N$  is the adsorption constant. Figure 2 shows that the data do not adequately fit a Langmuir isotherm. On the other hand, the Temkin isotherm (15), viz.,

$$\theta_N = \frac{W_N}{W_{N,\max}} = b \ln(a_0 p_N) \quad (13)$$

or in linearized form,

$$W_N = b W_{N,\max} \ln a_0 + b W_{N,\max} \ln p_N$$

where  $a_0$  and  $b$  are constants, shows a reasonably good linear fit to the data as seen in Fig. 3. The slight curvature in the plot is due to the fact that the Temkin equation is not valid at low and high coverages. Brunauer *et al.* (16) have developed a modified form of the Temkin equation which applies over the entire range of adsorption, viz.,

$$\theta_N = b \ln \frac{1 + a_0 p_N}{1 + a_0 p_N \exp(-1/b)} \quad (14)$$

where  $b = RT/\alpha$ . Equation (14) is based on a distribution of adsorption sites,  $s$ , such that the heat of adsorption,  $q$ , decreases linearly with  $s$ , according to

$$q = q_0 - \alpha s \quad (15)$$

where  $q_0$  is the heat of adsorption on the uncovered surface and  $\alpha$  is a proportionality constant. The parameter,  $a_0$ , is given by

$$a_0 = \frac{k_a}{k_d} e^{q_0/RT} \quad (16)$$

where  $k_a$  and  $k_d$  are adsorption and desorption rate constants.

The adsorption data,  $W_N$ , were correlated with Eq. (14) by a nonlinear regression analysis yielding the parameters  $b W_{N,\max} = 0.032 \pm 0.011$  (95% CI) and  $a_0 = (5.9 \pm 1.1) \times 10^4 \text{ atm}^{-1}$ . The term  $a_0 p_N \exp(-1/b)$  was too small to obtain a reliable value of  $b$ . The fit of the pyridine adsorption data to Eq. (14) is shown by the line in Fig. 3. An excellent fit over the entire range is observed. The consequence of the good correlation of the pyridine adsorption data with the modified Temkin isotherm is that it implies a *dis-*

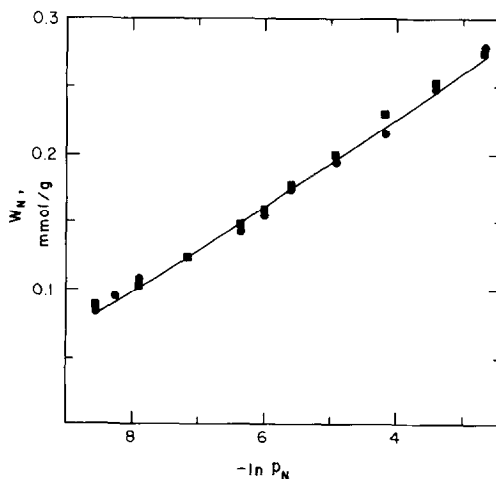


FIG. 3. Modified Temkin isotherm for pyridine adsorption during thiophene (●) and hexene (■) runs. Line is best fit to Eq. (14) for thiophene.

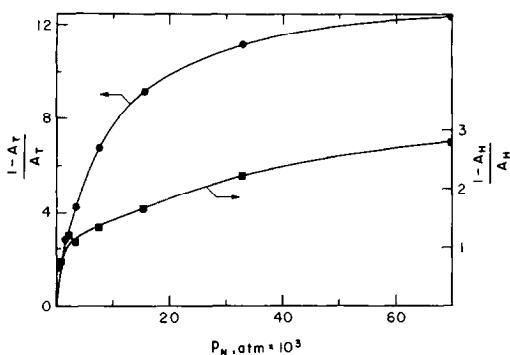


FIG. 4. Test of deactivation with Langmuir isotherm for thiophene (●) and hexene (■) data.

tribution of strengths of adsorption sites on the catalyst.

#### 4. Correlation of Thiophene Deactivation Data

We will now attempt to relate the effect of pyridine on the thiophene activity assuming quasiirreversible adsorption of pyridine (section 2). To simplify analysis, we will assume  $n = 1$  in Eq. (1). Now, the rate constant,  $k_T$ , which includes the number of active sites will decrease linearly with the pyridine adsorbed on active sites,  $\theta'_N$  by

$$k_T = k_T^0(1 - \theta'_N). \quad (17)$$

Introducing  $k_T$  into Eq. (7) gives

$$A_T = (1 - \theta'_N)D^0/D \quad (18)$$

or for  $D \sim D^0$  (less than 5% error over range of  $x_T$ ),

$$1 - A_T = \theta'_N. \quad (19)$$

It is now required to relate  $\theta'_N$  to  $p_N$  through an appropriate isotherm.

It should be mentioned at this point that the fit of the pyridine adsorption data to the modified Temkin isotherm (section 3 above) pertains to the total amount of pyridine adsorbed on the catalyst, which has been shown earlier (8) to consist of catalytically inactive as well as active sites. In this context, we refer to *inactive sites* as those that are catalytically inactive but adsorb pyridine and *active sites* as those that are catalytically active and adsorb pyridine. In-

active sites include sites on the alumina (about 20% of the pyridine adsorbs on the alumina support (8) under our reaction conditions), and possibly adsorption on catalytically inactive CoMo sites. Now, it cannot be assumed *a priori* that the same isotherm will apply to the active sites, especially if they are a small fraction of the total adsorption sites. Accordingly, a simple Langmuir isotherm was first tested for conformance with the activity data. Incorporation of Eq. (12) into (19) and rearranging yields

$$\frac{1 - A_T}{A_T} = K'_N p_N \quad (20)$$

where  $K'_N$  refers to the equilibrium constant for active sites. A plot of Eq. (20), given in Fig. 4, shows that a Langmuir isotherm does not give the expected linear fit to the data.

In view of the failure of the Langmuir isotherm to correlate the activity data, the modified Temkin isotherm was next applied. Incorporation of Eq. (14) into Eq. (19) yields

$$1 - A_T = b' \ln \frac{1 + a'_0 p_N}{1 + a'_0 p_N \exp(-1/b')} \quad (21)$$

where the primes refer to the appropriate parameters of the catalytically active sites. This equation was solved by nonlinear regression analysis to give the best values of the parameters. The parameters obtained are given in Table 4 and the line in Fig. 5 shows the good agreement of the fit to the

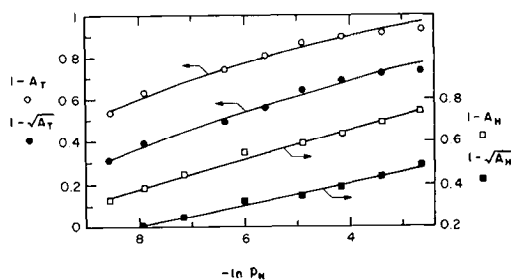


FIG. 5. Test of deactivation with modified Temkin isotherm. Lines are best fits to deactivation Eqs. (21) or (22).

TABLE 4  
Parameters for Activity Correlations According to Eqs. (21) and (22)

Parameter	Thiophene run		Hexene run	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$
$b'$	$0.088 \pm 0.010$	$0.080 \pm 0.007$	$0.068 \pm 0.008$	$0.049 \pm 0.005$
$\alpha$ , kcal/mol	$14.8 \pm 1.7$	$15.5 \pm 1.4$	$18.2 \pm 2.1$	$25.3 \pm 1.0$
$a'_0$ , atm $^{-1} \times 10^{-5}$	$30 \pm 29$	$3.2 \pm 1.8$	$7.7 \pm 6.9$	$2.2 \pm 1.5$

Note.  $\pm$  Values are 95% confidence intervals.

experimental data, despite the large uncertainty in the  $a_0$  value.

For the case of  $n = 2$ , the derivation of Eq. (1) involves a surface reaction involving an adsorbed thiophene molecule and a vacant site (7). Thus, the rate constant includes the square of the active sites, viz,

$$k_T = k_T^0(1 - \theta_N)^2.$$

Assuming negligible changes in the inhibition term  $D$ , the correlating equation analogous to Eq. (21) now becomes

$$1 - \sqrt{A_T} = b' \ln \frac{1 + a'_0 p_N}{1 + a'_0 p_N \exp(-1/b')} \quad (22)$$

Again, a good correlation to the data is obtained as shown in Fig. 5. The dual site mechanism ( $n = 2$ ) shows a better overall data correlation than the single site mechanism as evidenced by lower confidence intervals of the parameters (Table 4).

The good correlation of the activity data with the modified Temkin isotherm equation indicates that *the active sites also have a distribution of strengths of adsorption*. According to Eq. (16), the finding that  $a'_0$  (for active HDS sites) is considerably larger than  $a_0$  (for total adsorption sites) indicates that pyridine adsorption on active HDS sites is stronger than on inactive plus active adsorption sites, a conclusion we had earlier deduced (8).

### 5. Hexene HYD with Unpoisoned Catalyst

The kinetics of hexene hydrogenation were not determined with the American

Cyanamide catalyst. However, it has previously been determined with another catalyst of similar composition and under the same reaction conditions as employed here that the reaction was essentially first order in hexene, i.e., the inhibition terms in hexene and H<sub>2</sub>S were negligible (7). Hence, account of variable inhibition terms in the pyridine poisoning experiments is not necessary in this case.

### 6. Hexene Runs with Added Pyridine

A separate catalyst charge was used to investigate the deactivation of hexene hydrogenation with pyridine. The data are presented in Table 5. Relative HYD activities were less depressed at a given amount of pyridine adsorbed as compared with HDS activities. The pyridine adsorption isotherm during these runs was close to that with thiophene and consequently, the Langmuir isotherm did not correlate the adsorption data (Fig. 2); whereas the modified Temkin isotherm Eq. (21) gave a good fit, with the following constants:  $bW_{N,\max} = 0.034 \pm 0.001$  and  $a_0 = (4.7 \pm 0.8) \times 10^4$  atm $^{-1}$ .

Catalyst deactivation failed to correlate with the Langmuir isotherm (Fig. 4). However, a good correlation was obtained with the modified Temkin isotherm (Fig. 5), and the correlation parameters are given in Table 4. The larger value of  $a'_0$  as compared with  $a_0$  shows that pyridine adsorption on HYD sites is stronger than on inactive plus active sites, as was found for active HDS sites. It is interesting to note that the value

TABLE 5  
Hexene Runs with Added Pyridine<sup>a</sup>

$W_N$ (mmol/g)	$p_N$ (atm $\times 10^3$ )	Conv., $x_H$	Relative activity, <sup>c</sup> $A_H$
0	0	0.349	1.0
0.029	—	0.314	0.855
0.054	—	0.285	0.744
0.072	—	0.270	0.690
0.089	0.19	0.265	0.674
0.102	0.38	0.250	0.621
0.123	0.79	0.229	0.555
0.148	1.71	—	—
0.160	2.46	0.195	0.452
0.177	3.72	0.202	0.472
0.199	7.53	0.184	0.422
0.231	15.5	0.166	0.371
0.252	32.9	0.143	0.312
0.287	69.7	0.122	0.259

<sup>a</sup> Same conditions as in Table 3.

of  $\alpha$ , related to the distribution of active sites [Eq. (15)], is different for HYD and HDS sites. This finding is in line with the supposition that HYD and HDS sites are different on this catalyst (1, 17).

### 7. Estimate of Adsorption Rate versus Reaction Rate

The underlying reason why we consider pyridine poisoning to be quasiirreversible rather than reversible under our reaction conditions is that the attainment of equilibrium at each partial pressure of pyridine was slow compared to the reaction rate of thiophene or hexene. Thus, 3–4 h was required to reach a new steady-state weight and catalytic activity, signifying a slow adsorption–desorption process. Because of the small step changes in pyridine partial pressures used and the attendant small changes in weight adsorbed, it was not possible to accurately assess adsorption rates. However, in the course of this investigation, other N-containing poisons were tested for the purpose of evaluating the effect of strengths of adsorption on HDS and HYD deactivation and the results have been previously published (8). (The data

obtained were not in sufficient detail to include here.) During this work, the rate of adsorption of 3,5-dimethylpyridine was measured during a step change in partial pressure. This experiment was carried out in the presence of the thiophene reaction mixture under the standard conditions and the data are given in Table 6.

From a plot of the amount of pyridine adsorbed versus time, an initial adsorption rate of 0.06 mmol/g h is obtained. Thus, the initial rate of adsorption,  $r_a$ , can be formulated as  $r_a = k_a p_N = 0.06$  where  $k_a$  is the adsorption rate constant. After reaching steady state, the rate of adsorption (equal to the rate of desorption) will be given by

$$r_a^{SS} = k_a p_N f(\theta_N) < 0.06$$

where  $f(\theta_N)$  represents the fractional loss in the number of sites due to adsorbed pyridine and will be less than unity. At steady state, the thiophene conversion was measured and the rate  $r_T$ , calculated to be 0.46 mmol/g h. Thus, the relative rate of adsorption compared to reaction becomes

$$\frac{r_a^{SS}}{r_T} < 0.13$$

demonstrating that the adsorption rate is relatively slow compared to the reaction rate.

TABLE 6  
Rate of Adsorption of 3,5-Lutidine for a Step Change during Thiophene Reaction<sup>a</sup>

Time (h)	$W_N$ (mmol/g)	$x_T$
0	0	0.402
0.45	0.027	0.374
0.93	0.054	0.297
1.42	0.076	0.240
1.90	0.093	0.228
2.40	0.105	0.224
2.89	0.112	0.208
3.37	0.116	0.208
3.86	0.118	0.196

<sup>a</sup> Same conditions as in Table 3. Pyridine step change from 0 to  $1.32 \times 10^{-4}$  atm.



TABLE 7

Effect of Catalyst Exposure to Indole on HDS of Dibenzothiophene and HYD of Naphthalene

	% Conversion	
	HDS	HYD
Before indole	87	69
After indole <sup>a</sup>	64	21
After additional 2 days <sup>b</sup>	80	39

<sup>a</sup> Overnight in dibenzothiophene after indole removed.

<sup>b</sup> Two additional days in dibenzothiophene after indole removed.

Since the pyridine partial pressure in this experiment was rather low, it is instructive to evaluate the steady-state adsorption rates at higher pressures. This can be done by calculating  $k_a$  for the above experiment and using this value to estimate the steady-state adsorption rate at another pressure. Thus,

$$k_a = \frac{r_a}{p_N} = \frac{0.06}{1.32 \times 10^{-4}} = 460 \text{ mmol/g h atm.}$$

Now, at a partial pressure of  $2.6 \times 10^{-3}$  atm, the steady-state adsorption rate becomes

$$r_a^{SS} = 460 \times 2.6 \times 10^{-3} f(\theta_N) < 1.2 \text{ mmol/g h.}$$

Under these conditions, the thiophene HDS rate is estimated (from a multistep experiment) to be 0.2 mmol/g h. Thus, the ratio of adsorption to reaction rates becomes

$$\frac{r_a^{SS}}{r_T} < 6.$$

At higher pyridine pressures then, the steady-state adsorption rate becomes faster than the reaction rate. However, even under those conditions, the adsorption rate is not very much faster as required by the reversible L-H treatment. Furthermore, it should be appreciated that these adsorption calculations pertain to total pyridine ad-

sorbed, i.e., on inactive as well as active adsorption sites. We have argued previously (8) that appreciable adsorption occurs on inactive sites, and in fact the number of active sites can be a small fraction of the total adsorption sites. This, of course, would mean the adsorption rate on active sites would be much lower than indicated in the above calculations. We also note that the slow changes in pyridine adsorption during a step change in pressure are attended by slow changes in catalytic activity over a 4-h period (Table 6), showing that adsorption on active sites is also slow.

### 8. Final Comments

Based on the results presented here, we have demonstrated that N-poisons cannot always be assumed to be in rapid equilibrium. Another example of the slow adsorption-desorption equilibrium with N-compounds comes from elevated pressure runs carried out in this laboratory. Runs on a number of catalysts were made by sequential tests for HDS (using dibenzothiophene), HYD (naphthalene) and HDN (indole) and the results have been reported elsewhere (18). In the course of that investigation, HDS and HYD runs were repeated on one CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst after the HDN run, with the results given in Table 7. The second entries are the individual HDS and HYD conversions after the indole was removed and the catalyst had been exposed to dibenzothiophene for overnight and the third entries are for an additional 2-days exposure to dibenzothiophene. It is obvious that the catalyst has not recovered its initial activity even three days after removal of the indole, although the indications are that it is slowly recovering its initial activity. Modeling the effect of indole on HDS and HYD reaction rates in terms of a fast, reversible equilibrium inhibition in a L-H rate expression is bound to lead to serious difficulties in this case.

We have shown from a lack of fit of the deactivation kinetics to a reversible poisoning model and the good agreement to a

quasiirreversible model, that under our reaction conditions pyridine poisoning can be considered as altering the rate constant of the reaction rather than affecting the rate by reversible competitive adsorption. Implicit in this finding is the requirement that the rate of adsorption on the *active sites* is slower than the rate of reaction. From the analysis of section 7 above, the *total* rate of adsorption can exceed the rate of reaction at higher pressures of pyridine. We conclude from this that the *active sites are actually only a small fraction of the total adsorption sites*. We note that Hall and co-workers (19) based on poisoning studies have concluded that methathesis and hydrogenation reactions over a reduced Mo/Al<sub>2</sub>O<sub>3</sub> catalyst involve only a small fraction of the active surface.

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