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should have a minimal effect, if any, upon the efficiency of the counter. Rather, it is evident that the added H2O affected the creation of nuclei in the flow reactor.

- (47) Later in the paper an additional, different reaction of OH with SO2 is postulated which results in the concentrations listed in column 4b. However, because of the necessity that the OH concentration must be determined by a steady state of production, the quantities (X) and
- the rate of SO<sub>2</sub> loss are unaffected by the differences in (OH).
  (48) The activity of a substance is the ratio of its vapor pressure to its equilibrium vapor pressure over the pure liquid. It is the generalization of relative humidity.
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# Transfer of Hydrogen by Hydroaromatics. 1. Mechanism of Dehydrogenation/Hydrogenation in Tetralin/Iron Catalyst Systems

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At 400 °C, the gas-phase dehydrogenation of tetralin over iron catalysts is found to result in formation of naphthalene via the reaction of intermediate 1,2-dihydronaphthalene. The kinetic data for these systems were found to follow heterogeneous, first-order rate laws. A mechanism is presented which quantitatively describes the measured tetralin and naphthalene kinetic behavior and successfully predicts the kinetic data observed for the 1,2-dihydronaphthalene intermediate. The rate-limiting reactions in these systems are proposed as involving dehydrogenation/hydrogenation reactions on the surfaces of the catalysts. Based on the data analysis, the rate constants for the surface reactions have values in the  $10^{-4}$ - $10^{-5}$ -s<sup>-1</sup> range. The catalytic surface site populations were found to be in the range  $10^{13}$ - $10^{14}$  molecules cm<sup>-2</sup>.

#### Introduction

The hydrogen-transferring property of hydroaromatics-in particular, tetralin systems-has been the subject of investigation by various researchers.<sup>1-4</sup> These investigations have focused on product identification and the effect of substituents on product composition. The tetralin dehydrogenation/hydrogenation process has been characterized in terms of material balance reaction schemes. Recent investigation of the gas-phase kinetics and the mechanism of tetralin hydrogen-transfer chemistry at 400 °C found the rate-limiting steps to be heterogeneous, zero-order reactions in the absence of added catalysts.<sup>5</sup>

Chemical donation of hydrogen via hydroaromatic molecules such as tetralin to organic molecules undergoing thermal bond cleavage results in formation of lower mo-lecular weight products.<sup>6,7</sup> Such hydrogenation chemistry forms the basis of numerous coal liquefaction processes. Investigation of the mechanisms (both catalytic and noncatalytic) by which hydroaromatics transfer hydrogen is an ongoing effort at this laboratory. The present paper reports the kinetic results obtained when tetralin gas was reacted at 400 °C over iron oxide and iron sulfide catalysts. A general mechanism is presented which quantitatively characterizes these catalytic systems.

### **Experimental Section**

The tetralin, obtained from Aldrich Chemical, was 99.4% pure (the main impurity being 0.4% naphthalene) and was used as received. The iron(III) oxide (Fe<sub>2</sub>O<sub>3</sub>) was from the Baker Chemical Co. The limonite  $(2Fe_2O_3 \cdot 3H_2O)$ , magnetite ( $Fe_3O_4$ ), and pyrite ( $FeS_2$ ) catalysts were purchased from Ward's Scientific Co. The catalysts were ground and sieved such that only those solids which were

 $\sim 44 \ \mu m$  or less were used.

The reaction vessels were 10-cm long quartz tubes (16.0-mm diameter). The catalysts (100 mg unless noted otherwise) were degassed on a vacuum line at room temperature by pumping on the quartz vessel until the system pressure fell below  $10^{-5}$  torr (15–20 min pumping time). Degassed organics (100 µL unless noted otherwise) were then vacuum distilled onto the minerals, and the quartz tubes were sealed. The transfer efficiency for the vacuum distillations was determined to be  $89.9 \pm 0.6\%$ . The vessels were placed in a 400 °C oven for the required period of time, removed, and rapidly chilled to room temperature by plunging into water. The oven interior was a large heat sink (10-kg steel block) with four concentric 18-mm diameter by 12-cm deep chambers for the reaction vessels. The reaction vessel interior reached 400 °C within 5 min and had a 2 °C axial gradient at 400 °C.

The product mixtures were extracted from the vessels by washing with 0.5 mL of analytical grade benzene and analyzed on a Hewlett Packard Model 5750 gas chromatograph by using the flame ionization detector and dual 6-ft Durapak (Carbowax 400-Porasil F) <sup>1</sup>/<sub>8</sub>-in. columns. The GC data were analyzed by using a Hewlett-Packard integrator and are reported as area percent. The tetralin and naphthalene analyses were reproducible to within 1% of the reported area percent values. The 1,2-dihydronaphthalene analysis was not as reproducible (12% of the observed area percent values) because this species eluted on the shoulder of the much larger tetralin peak.

# Results

The gas-chromatographic analyses showed that the main products of the tetralin dehydrogenation were 1,2-di-



**Figure 1.** The extent of reaction (% conversion per 100 mg of catalyst) for ( $\Delta$ ) tetralin dehydrogenation and ( $\Box$ ) naphthalene formation in the (a) Fe<sub>2</sub>O<sub>3</sub>, (b) limonite, (c) magnetite, and (d) pyrite catalyst systems. The solid lines are the calculated fits to the experimental data based on eq 5' and 7'.

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hydronaphthalene and naphthalene. Two other products, 1-methylindane and indane, were observed to be present (less than 1.0%) but represent only minor reaction pathways and are not treated in the present study. The occurrence of the 1-methylindane is significant, however, because it was not found in the previous work done at lower total organic gas densities<sup>5</sup> but is known to be a major product of 400 °C in the tetralin condensed phase system.<sup>8</sup> In the present system, the extent of reaction due to the walls of the quartz vessels is small: after 16 h at 400 °C, the extent of tetralin reaction was only 1.1%. Interestingly, however, the products consisted of an approximately 50/50 mixture of naphthalene and 1methylindane. The organic reactant density per unit surface area appears to be an important parameter in determining the tetralin reaction pathways to naphthalene and 1-methylindane and is a variable that will be investigated further.

Figure 1 shows the tetralin and naphthalene experimental data (% conversion per 100 mg of catalyst) and the mechanistic model fit based on eq 5 and 7. Table I lists the corresponding calculated rate parameters and errors for the proposed reaction mechanism (reactions 1–4). These parameters are obtained from nonlinear least-squares analysis accomplished on a CDC 7600 computer utilizing the resident Dubnal program.<sup>9</sup> Figure 2 shows the measured 1,2-dihydronaphthalene data and calculated fit based on eq 8 where the calculated curves used the rate parameters derived from the tetralin and naphthalene data (Table I).

When naphthalene was heated at 400 °C under 2 atm of hydrogen in these catalytic systems, no reaction was observed for times out to 5 h.

Table II shows the effect of varying the ratio of moles of tetralin to grams of catalyst (i.e., surface area) on the extent of reaction. Table III lists the rate-constant terms for the iron catalyst systems, and Table IV gives some surface populations for reactive species involved in the rate-limiting reactions.

# Discussion

As shown in Table II, doubling the surface area results in a proportionate increase in tetralin dehydrogenation and naphthalene formation. The approximately doubled extents of reaction (C/D ratio of Table II) clearly show that the mechanism is heterogeneous. The 1,2-dihydronaphthalene data in Table II demonstrate the intermediate character of this species. Doubling the surface area does not change the yield of this species because its disproportionation to tetralin and naphthalene<sup>5</sup> is just proportionately increased. Thus the C/D ratio is approximately unity.

These surface area effects indicate that the rate-limiting reactions in the tetralin systems are heterogeneous. The data in Figures 1 and 2 show that the kinetic plots have two characteristic time regimes. During the short, initial stage, the data show curvature that is suggestive of a kinetic system approaching a steady-state condition

$$T \rightleftharpoons D + H_2 \rightleftharpoons N + H_2$$

where T is tetralin, D is 1,2-dihydronaphthalene, and N is naphthalene. Following this brief (on a relative basis) initial stage, the rate-limiting reactions appear to be zero order with respect to the T and N concentrations as shown by the linear form of the plots for times greater than  $\sim 4$  h. Furthermore, the D concentration becomes independent (i.e., constant) of time after the  $\sim 4$ -h initial period. Thus the heterogeneous reaction mechanism must model a complex kinetic behavior.

	(P24') X	- 01	0.002	0.002	0.005	0.008
	$10^{-2}P_{24}^{'}, o($	%/g n-	0.087	0.191	0.086	0.103
	$\sigma(P_{22}) \times (P_{22})$	- <b>N</b> T	0.05	0.08	0.11	0.09
: 1 and 2	$10^{-2}P_{22}',$	11 8/0/	1.93	6.82	0.94	0.59
ves in Figures	(/-	(NV)	0.011	0.01	0.07	0.08
eoretical Cur	A _ h - 1	AN, 11	0.984	1.18	1.44	1.27
Yield the Th	$\sigma(P_{13}) \times 10^{-2}$	ΛT	0.002	0.002	0.010	0.018
and 8' Which	$10^{-2}P_{13}',$	// g II	0.111	0.222	0.193	0.341
for Eq 5', 7',	$\mathfrak{o}(P_{11}) \times \mathfrak{o}_{10-2}$	ΤΛ	0.07	0.10	0.45	0.64
eviations $(\sigma)$	$10^{-2}P_{11}^{11}$	11 8/0/	2.65	8.76	5.41	6.31
Standard De		0(AT)	0.01	0.01	0.11	0.16
ameters and	-1-1	АТ, п	1.16	1.33	2.94	3.48
TABLE I: Rate Par		catalyst	Fe,O,	limonite	magnetite	pyrite



Figure 2. The concentration (% formed per 100 mg of catalyst)/time behavior of 1,2-dlhydronaphthalene in the (a) Fe<sub>2</sub>O<sub>3</sub>, (b) limonite, (c) magnetite, and (d) pyrite catalyst systems. The solid lines are calculated by using eq 8' and the tetralin- and naphthalene-based rate parameters.

TABLE II: Effect of Varying the Surface Area ( $\mu$ L of Tetralin/mg of Catalyst) on the Reactant and Product Yields for the Tetralin/Fe<sub>2</sub>O<sub>3</sub> System at 400 °C

time	C(100 µL/ 200 mg)			D( 1	ratio C/D				
h	T, %	D, %	N, %	T, %	D, %	N, %	$\Delta T$	D	Ν
0.5 1.0 2.9	83.9 72.4 67.9	0.79 0.70 0.54	15.2 26.7 31.4	91.4 85.4 81.5	0.88 0.84 0.45	7.6 13.6 17.8	1.9 1.9 1.8	0.9 0.8 1.2	2.0 2.0 1.8
4.0	61.8	a.04	37.9	76.8	a . 10	22.9	1.7	a a	1.7

<sup>a</sup> Peak partially resolved but not integratable.

The following heterogeneous, first-order mechanism models the experimental observations and quantitatively fits the kinetic data. The adsorption/desorption equilibria, between the organic reactants (T, D, and N) and the catalytic reactive sites for tetralin oxidation/1,2-dihydronaphthalene reduction  $S_n$  and 1,2-dihydronaphthalene oxidation/naphthalene reduction  $S_{n'}$ , which lead to net reactions are

$$T + S_n \rightleftharpoons T/S_n$$
$$D + S_n' \rightleftharpoons D/S_n'$$
$$D + (S/H)_n \rightleftharpoons D/(S/H)_n$$
$$N + (S'/H)_n \rightleftharpoons N/(S'/H)_n$$

where the slant (/) denotes chemisorption and  $(S/H)_n$ denotes a reactive site  $S_n$  which has gained one or more hydrogen atoms (i.e.,  $(S/H)_n$  is a reduced  $S_n$  site). The adsorption-desorption reactions in these equilibria are fast with respect to the rate-limiting surface reactions. Any formation of  $T/(S/H)_n$  and  $N/S_n'$  species does not lead to any significant net reactions for the present system since

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neither reduced tetralin nor oxidized naphthalene products were observed.

The four surface species undergo the following ratelimiting reactions:

$$T/S_n \xrightarrow{\kappa_I} D/(S/H)_n$$
 (I)

$$D/S_n' \xrightarrow{k_n} N/(S'/H)_n$$
 (II)

$$D/(S/H)_n \xrightarrow{k_{III}} T/S_n$$
 (III)

$$N/(S'/H)_n \xrightarrow{R_{IV}} D/S_n'$$
 (IV)

where the reactants in reactions I and II give up two hydrogen atoms to the S<sub>n</sub> and S<sub>n</sub>' sites to form the corresponding oxidized species and vice versa in reactions III and IV. The products of reactions I-IV are released to the gas phase via the adsorption/desorption equilibrium reactions. Fast surface migration redistributes the H species over the surface, resulting in the transfer of H to reductive site, liberation of H from oxidation sites, and the liberation of  $H_2$  gas. The absence of reaction in the naphthalene/ $H_2$ systems is taken as evidence for the nonreversibility of  $H_2$ release under the conditions studied.

For a reaction proceeding via a first-order Langmuir-Hinshelwood mechanism, the rate of reaction will be proportional to the concentration of reactant covered sites. Thus the rate of loss of tetralin concentration [T] for a given quantity of catalyst is proposed to be described by the first-order rate law

$$-\frac{\mathrm{d}[\mathrm{T}]}{\mathrm{d}t} = k_{\mathrm{I}}[\mathrm{T}/\mathrm{S}_{\mathrm{n}}] \tag{1}$$

where the brackets denote concentration and  $[T/S_n]$  is the concentration of the  $S_n$  surface sites covered by tetralin. According to reactions I and III, the rate of loss of  $[T/S_n]$ is given by

$$\frac{\mathrm{d}[\mathrm{T/S_n}]}{\mathrm{d}t} = k_{\mathrm{I}}[\mathrm{T/S_n}] - k_{\mathrm{III}}[\mathrm{D/(S/H)_n}]$$

where the  $T/S_n$  and  $D/(S/H)_n$  surface species constitute the tetralin/1,2-dihydronaphthalene oxidation and reduction sites, respectively. If one constrains the mechanism such that the sum of the concentrations of these two interrelated sights is a constant with respect to time, then one can define this constant  $C_{13}$  as

$$C_{13} \equiv [T/S_n] + [D/(S/H)_n]$$

Under this condition, although the concentration of the fractional surface coverage for tetralin sites  $C_{13}$  is constant during the reaction, there is a competition for these sites involving the  $T/S_n$  and  $D/(S/H)_n$  species. That is, the relative fraction of the  $C_{13}$  sites occupied by tetralin will change as the reaction proceeds. Substituting for [D/  $(S/H)_n$ ]

$$-\frac{d[T/S_n]}{dt} = (k_1 + k_{III})[T/S_n] - k_{III}C_{13}$$
(2)

Integration of this expression yields

$$[T/S_n] = \frac{k_I C_{13} e^{-A_T t} + k_{III} C_{13}}{A_T}$$
(3)

where initially

$$C_{13} = (T/S_n)_{t=0}$$

and we have defined

 $A_{\rm T} \equiv k_{\rm I} + k_{\rm III}$ 

Now substituting eq 3 into eq 1 yields

$$-\frac{d[T]}{dt} = \frac{k_{I}^{2}C_{13}}{A_{T}}e^{-A_{T}t} + \frac{k_{I}k_{III}C_{13}}{A_{T}}$$
(4)

. . .

which upon integration gives the expression for the time dependence of the tetralin concentration

$$[T_0] - [T] = \frac{k_1^2 C_{13}}{A_T^2} (1 - e^{-A_T t}) + \frac{k_T k_{III} C_{13}}{A_T} dt$$

or

$$[T_0] - [T] = \frac{P_{11}}{A_T^2} (1 - e^{-A_T t}) + \frac{P_{13}}{A_T} t$$
 (5)

where  $[T_0]$  is the initial tetralin concentration and the definitions of the P terms are straightforward.

The rate of formation of naphthalene for a given quantity of catalyst is described by the rate law

$$d[N]/dt = k_{II}[D/S_n']$$
(6)

where  $[D/S_n]$  is the concentration of the  $S_n$  surface sites covered by 1,2-dihydronaphthalene. The rate of loss of  $[D/S_n']$ , based on reactions II and IV, is

 $- d[D/S_n']/dt = k_{II}[D/S_n'] - k_{IV}[N/(S'/H)_n]$ 

where the  $D/S_n{}^\prime$  and  $N/(S^\prime/H)_n$  surface species constitute the 1,2-dihydronaphthalene oxidation and naphthalene reduction sites, respectively. Assuming the concentration of the fractional surface coverage of D oxidation sites  $C_{24}$ is constant but subject to relative composition changes involving the  $D/S_n'$  and  $N/(S'/H)_n)$  species, one can define (D/S'/1 + (N/(S'/H)))

$$C_{24} \equiv \left[ \mathbf{D} / \mathbf{S}_{n}^{\prime} \right] + \left[ \mathbf{N} / (\mathbf{S}^{\prime} / \mathbf{H})_{n} \right]$$

Substituting for  $[N/(S'/H)_n]$ 

$$-d[D/S_n']/dt = (k_{II} + k_{IV})[D/S_n'] - k_{IV}C_{24}$$

TABLE III: Rate Constants for Iron Catalyst Systems

			•					
catalyst	$10^4 k_{\rm I}, s^{-1}$	$\sigma(k_{\rm I})  imes 10^4$	$\frac{10^4 k_{\rm II}}{{\rm s}^{-1}},$	$\sigma(k_{\rm II}) \times 10^4$	$\frac{10^{s}k_{\text{III}}}{\text{s}^{-1}},$	$\sigma(k_{\rm III}) \times 10^5$	$\frac{10^{5}k_{\rm IV}}{{\rm s}^{-1}},$	$\sigma(k_{\rm IV}) \times 10^{\rm s}$
Fe <sub>2</sub> O <sub>3</sub> limonite magnetite pyrite	3.08 3.60 7.89 9.17	0.03 0.03 0.36 0.54	2.62 3.19 3.67 3.00	0.04 0.03 0.27 0.38	1.29 0.914 2.81 4.96	0.06 0.026 0.49 0.99	1.18 0.893 3.35 5.2	0.07 0.027 0.75 1.5

TABLE IV: Surface Site Populations for the Ion Oxide Catalytic Systems Where the Ratio of Moles of Reactant per Gram of Catalyst Is in the 10<sup>-2</sup>-10<sup>-3</sup> Range

	surface area		$10^{-13}M$ ,	$\sigma(M)$ ×	$10^{-13}M_{24},$	$\sigma(M) \times$	$10^{-13}M$ ,	$\sigma(M) \times$
catalyst	$\overline{S, m^2/g}$	σ	cm <sup>-2</sup>	10-13	cm <sup>-2</sup>	10 <sup>-13</sup>	cm <sup>-2</sup>	10-13
Fe <sub>2</sub> O <sub>3</sub>	9.76	0.78	9,0	1.2	9.1	1.3	18.1	2.5
limonite	82.68	0.36	2.56	0.08	2,55	0.09	5.11	0.17
magnetite	6.30	0.04	4.36	0.78	3.51	0.99	7.9	1.8
pyrite	2.19	0,11	10.8	3.0	9.4	4.3	20.2	7.3

which integrates to

$$[D/S_{n}'] = \frac{k_{II}C_{24}e^{-A_{N}t} + k_{IV}C_{24}}{A_{N}}$$

where initially

$$C_{24} = [D/S_n']_{t=0}$$

and we have defined

 $A_{\rm N} \equiv k_{\rm II} + k_{\rm IV}$ Now substituting into eq 6 yields

$$\frac{\mathrm{d}[\mathrm{N}]}{\mathrm{d}t} = \frac{k_{\mathrm{II}}^2 C_{24}}{A_{\mathrm{N}}} e^{-A_{\mathrm{N}}t} + \frac{k_{\mathrm{II}} k_{\mathrm{IV}} C_{24}}{A_{\mathrm{N}}}$$

which upon integration gives the expression for the time dependence of the naphthalene concentration

$$[N] = \frac{k_{\rm II}^2 C_{24}}{A_{\rm N}^2} (1 - e^{-A_{\rm N}t}) + \frac{k_{\rm II} k_{\rm IV} C_{24}}{A_{\rm N}} t$$

or

$$[N] = \frac{P_{22}}{A_N^2} (1 - e^{-A_N t}) + \frac{P_{24}}{A_N} t$$
(7)

where the definitions of the P terms are straightforward. The concentration of 1,2-dihydronaphthalene at any

time is

$$[D] = [T_0] - [T] - [N]$$

by mass balance. Substitution of eq 5 and 7 results in the expression for the time dependence of the 1,2-hydronaphthalene concentration

$$[D] = \frac{P_{11}}{A_{\rm T}^2} (1 - e^{-A_{\rm T}t}) - \frac{P_{22}}{A_{\rm N}^2} (1 - e^{-A_{\rm N}t}) + \left(\frac{P_{13}}{A_{\rm T}} - \frac{P_{24}}{A_{\rm N}}\right) t$$
(8)

The forms of the derived eq 5, 7, and 8 which are relevant to the analysis of the data as presented in Table I and Figures 1 and 2 are

$$X_{\rm T} = 100 - \frac{P_{11}'G}{A_{\rm T}^2} (1 - e^{-A_{\rm T}t}) - \frac{P_{13}'G}{A_{\rm T}}t$$
 (5')

$$X_{\rm N} = \frac{P_{22}'G}{A_{\rm N}^2} (1 - e^{-A_{\rm N}t}) + \frac{P_{24}'G}{A_{\rm N}}t \tag{7'}$$

$$X_{\rm D} = \frac{P_{11}'G}{A_{\rm T}^2} (1 - e^{-A_{\rm T}t}) - \frac{P_{22}'G}{A_{\rm N}^2} (1 - e^{-A_{\rm N}t}) + \left(\frac{P_{13}'}{A_{\rm T}} - \frac{P_{24}'}{A_{\rm N}}\right) Gt \quad (8')$$

where

$$X_{\rm T} = \frac{[{\rm T}]}{T_0} 100 \qquad X_{\rm N} = \frac{[{\rm N}]}{T_0} 100 \qquad X_{\rm D} = \frac{[{\rm D}]}{T_0} 100$$
$$P_{11'} = (P_{11}) 10^2 / (T_0 G) \qquad P_{13'} = P_{13} 10^2 / (T_0 G)$$
$$P_{22'} = P_{22} 10^2 / (T_0 G) \qquad P_{24'} = P_{24} 10^2 / (T_0 G)$$

G is the grams of catalyst (i.e., 0.100 g in the present study) and  $T_0$  is the total concentration of organic present in the reaction vessel (i.e.,  $6.81 \times 10^{-4}$  mol in the present study). The analysis of the tetralin and naphthalene data using eq 5' and 7' gives an excellent quantitative fit as shown in Figure 1. As shown in Figure 2, when the parameters obtained from the tetralin and naphthalene analysis are used in eq 8' to calculate the 1,2-dihydronaphthalene percent conversions, one finds that the quantitative fit of the theoretical curves and experimental data generally lies within the system's error limits. The agreement between experiment and theory demonstrates that the proposed mechanism is a reasonable kinetic model for the catalytic systems.

Table III lists the rate-constant terms for the four iron catalysts obtained from the parameters in Table I by using the relationships between  $A_{\rm T}$ ,  $P_{11}$ , and  $P_{13}$ 

$$k_{\rm III} = \frac{A_{\rm T}}{(P_{11}/P_{13}+1)}$$
  
 $k_{\rm I} = A_{\rm T} - k_{\rm III}$ 

and between  $A_N$ ,  $P_{22}$  and  $P_{24}$ 

$$k_{\rm IV} = \frac{A_{\rm N}}{(P_{22}/P_{24}+1)}$$
$$k_{\rm II} = A_{\rm N} - k_{\rm IV}$$

The rate constants for the surface reactions are seen to lie in the range  $10^{-4}-10^{-5}$  s<sup>-1</sup>. Clearly the slow tetralin-tonaphthalene conversion is not a result of slow reactions but is due to the reversibility of the dehydrogenation/ hydrogenations processes. The  $k_{\rm I}$  rate-constant values show that with respect to tetralin dehydrogenation the pyrite sites are the most reactive ( $t_{1/2} = 12.6$  min), followed by the magnetite (14.6 min), limonite (32.1 min), and Fe<sub>2</sub>O<sub>3</sub> (37.5 min) sites. For 1,2-dihydronaphthalene dehydrogenation, the difference between the catalyst site reactivities is less pronounced as shown by the factor between  $k_{\rm II}$ extremum of 1.4 compared to 3.0 for the  $k_{\rm I}$  values. The relative site reactivity between catalysts for the hydrogenation reactions III and IV shows the largest variations with factors of 5.4 and 5.8 between the  $k_{\rm III}$  and  $k_{\rm IV}$  extremum.

Comparison of the net hydrogenation vs. dehydrogenation catalytic activity, as reflected by the ratio  $(k_{\rm III} + k_{\rm IV})/(k_{\rm I} + k_{\rm II})$  for each of the four catalysts, shows that the probability of hydrogenation is three times greater in the pyrite and two times greater in the Fe<sub>2</sub>O<sub>3</sub> and magnetice systems then in the limonite system. This result is consistent with the coal liquefaction literature where it is found that minerals vary in their ability to catalyze conversion, with pyrite being one of the best.<sup>10</sup>

Knowing the values of the rate constants enables one to calculate the fractional surface site populations M since

$$M_{13} = C_{13}/SG = P_{11}/(Sk_1^2G) = P_{13}/(Sk_1k_{III}G)$$

$$M_{24} = C_{24}/SG = P_{22}/(Sk_{\rm II}^2G) = P_{24}/(Sk_{\rm II}k_{\rm IV}G)$$

and one can obtain the total for the fractional surface site population by defining

$$M = M_{13} + M_{24}$$

where S is the surface area of the catalyst. The results of these calculations are given in Table IV. The data were normalized with respect to surface area by utilizing the previously reported<sup>10</sup> surface areas listed in Table IV. These S values were obtained by using argon as the absorbent and are considered a reasonable estimate of the catalyst surface areas. A commonly sited value for surface site<sup>14</sup> populations is  $10^{15}$  molecules cm<sup>-2</sup>. The fraction surface coverages in the present systems are in the  $10^{13}-10^{14}$  range, which is consistent with the observed heterogeneous first-order rate behavior. As shown in Table IV, the pyrite and Fe<sub>2</sub>O<sub>3</sub> systems, on a relative basis, have on the average three times the site population of limonite and magnetite. To within the limits defined by the standard deviations, the populations of the S<sub>n</sub> and S<sub>n</sub>' sites for a given catalyst are equal.

The rate-limiting steps given by eq 1-4 involve dehydrogenation/hydrogenation processes on the surfaces of the catalysts. The nature of these reactive surface sites and adsorbed species is revealed to some extent by the kinetic data and product composition. Only multiple surface site contact processes (n > 1) were considered to result in major reaction pathways. Single-site reactions followed by release of free radicals into the gas phase would result in homogeneous reactions between these radicals and the aromatics. This, in turn, would lead to products whose molecular weight would be greater than tetralin. Experimentation, designed to optimize yields of such products, showed no evidence of high molecular weight molecules.

It is proposed that the minimum number of sites n is three or greater. The reason for a minimum of three adjacent sites for these reactions is based on the fact that only the 1,2-isomer of dihydronaphthalene is observed. No evidence of the other logical intermediate 1,4-dihydronaphthalene was found. This is interpreted to mean that the reactive sites which the ring system occupies on the surface apparently accept only the hydrogens in the 1,2positions. Since the spacings of the 1,2- and 2,3-hydrogens are essentially the same, a third geometric factor must play a role. This is assumed to involve surface interaction with the aromatic ring such that only the 1,2-hydrogens are in the proper configuration. As discussed in a previous paper,<sup>5</sup> evidence of catalytic surface steric constraints have been reported for the closely related 2-methyl and 9-methyl derivatives of decalin and octalin.11,12

Previous work<sup>11-13</sup> on reduced naphthalenes and related methyl derivatives over platinum and palladium catalysts in both the condensed and gaseous states reports results which are relevant to the present study. Polycyclic molecules containing the tetralin moiety were found to dehydrogenate readily when boiled over these catalysts.

Studies with tetralin/catalyst systems showed the reaction rate to be a function of the catalyst. In the vapor phase at 300-350 °C over platinum or palladium, the octalins were found to dehydrogenate. Decalins readily lost H<sub>2</sub> in the vapor phase at 300 °C over these catalysts. These results are consistent with the heterogeneous mechanism proposed for the catalytic systems studied in this work and suggest that a mechanism based on reactions analogous to reactions I-IV may be applicable to decalin and octalin systems.

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# Properties of Oxygen Adsorption on Platinum at 160 K

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Oxygen adsorption on Pt at 160 K has been studied in the presence of preannealed oxygen. Evidence that dissociative adsorption proceeds through a well-defined molecular adsorption state is presented. It is demonstrated that the extent of molecular oxygen adsorption at 160 K is very sensitive to the amount and structure of preadsorbed oxygen atoms. To a lesser degree, carbon monoxide adsorption at 160 K is also sensitive to the oxygen structure.

# Introduction

The adsorption of oxygen on transition metals is important in many catalysis and materials science problems. Its behavior on platinum has been examined frequently on both polycrystalline and single-crystal surfaces. On polycrystalline foils there is general agreement on the following: (a) The initial sticking coefficient is between 0.13 and 0.36 for temperatures between 300 and 800 K.<sup>1-8</sup> (b) Low-temperature ( $T \leq 200$  K) adsorption gives two desorption peaks in thermal desorption spectra (TDS); one is interpreted in terms of molecular adsorption and the other dissociative adsorption. $^{5,8-10}$  (c) Chemisorption is dissociative above 300 K.<sup>2,5,9</sup> (d) The saturation coverage in the dissociative state is  $(4 \pm 2) \times 10^{14}$  atoms cm<sup>-2.6</sup>

Our purpose in this paper is to present experimental evidence that dissociative adsorption proceeds through an adsorbed molecular state at 160 K and that the structure of atomically adsorbed oxygen changes significantly with temperature over the range 170-900 K.

# **Experimental Section**

The experimental apparatus was similar to that described earlier<sup>11</sup> so only a brief description will be presented here. All experiments were carried out in an ultra-highvacuum (UHV) system equipped with an ion gauge and a quadrupole mass spectrometer. The UHV chamber (2.1 L) was pumped by an ion pump through a 1-in. diameter gold sealed valve. The pumping was conductance limited