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Use of Alkali Metal Poisons in the Elucidation of Cracking Catalyzed by Silica-Alumina

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Information concerning the silica-alumina sites active in cumene cracking has been obtained from an analysis of results of cumene cracking using catalysts with and without alkali metal poison. A combination of kinetic studies with absolute rate theory suggests there are 10^7–10^8 sites cm^{-2} in a commercial co-gelled silica-alumina catalyst, several orders of magnitude less than is usually supposed. The data are consistent with the assumption that active sites are associated with a very small fraction of the surface aluminum which exchanges with alkali metal ion. Different alkali metal salts vary in their ion-exchanging ability, but for the same amount of removed aluminum these salts poison the catalyst to the same extent. K_A/K_I, where K_A and K_I are the equilibrium quotients for ion exchange with active and inactive aluminum, respectively, is greater than unity, is approximately constant over the whole concentration range, and is approximately independent of salt. K_I decreases with increasing amounts of exchange. These results suggest that under cracking conditions the active sites are a very narrow band of the most energetic sites in a spectrum of sites (all associated with aluminum) of varying energies, and that this situation is parallel to the ion exchange reaction. Acid both removes aluminum and activates some of the remaining aluminum. The catalytic properties of several silica-alumina catalysts impregnated by other methods or compounds confirm this model. To validate further the kinetic scheme used to count active sites, studies on the effect of temperature and poison in the reactor charge are reported. It is shown that there cannot be a temperature of maximum rate in catalyzed unimolecular decomposition unless the heat of desorption from active sites is greater than the cracking-step heat of activation of the adsorbed molecule. This condition is not met in the cumene-silica-alumina system.

INTRODUCTION

Recently the rate law and the density of active sites in silica-alumina-catalyzed cracking of isopropylbenzene ("cumene") have been investigated (*1–3*). Others noticed that pretreatment of the catalyst with alkali metal salt (*4–7*) or acid (*8*) affects the activity of the catalyst. In addition, treatment with aqueous alkali metal salt or acid effects an ion exchange with surface aluminum (*9, 10*). We therefore in the present work bring together these various experiments by pretreating with aqueous alkali metal salt or acid the same catalysts upon which we carry out kinetic studies. By measuring the extent of ion exchange thus brought about in each catalyst we are able to gain some information concerning the relationship between the ion exchange and catalytic properties of the surface.

In earlier work (*2*) it was found, and it is confirmed here, that the density of active cracking sites in unpoisoned silica-alumina (involving no ion exchange) is extremely low, i.e., ~10^7–10^8 sites cm^{-2}. The relationship between ion exchange and activity which we develop here is not only consistent with a low site density, but it also tends to confirm the low value. Because the site density conclusion is so striking, we discuss in the last section the results of others concerning the site densities of several catalysts.

We use the Prater-Lago (*1*) reaction scheme,

$$S + A \underset{k_2}{\overset{k_1}{\rightleftarrows}} SA \xrightarrow{k_3} \text{products} \qquad (1)$$

where S represents cumene; A, active site; SA, adsorbed cumene; and the products are benzene and propylene. The steady state rate law for this reaction is (*1*)

$$v = k_3B[P_s/(P_s + G)] \qquad (2)$$

where B is the concentration (mole g^{-1}) of active sites, P_s is the partial pressure of cumene, and $G = (k_2 + k_3)/k_1$. Equation (2) holds when conversion is low ($<\sim 2\%$), allowing the reverse of the k_3 step to be neglected.

EXPERIMENTAL

Materials

Silica-alumina. The surface areas (BET), pore volumes (water), and percent Al_2O_3 of the catalysts supplied by the Houdry Process Corporation (S-90, 4 × 4 mm pellets) and the Socony Mobil Oil Company (S-M, beads) are, respectively, as follows: 440, 393 m^2 g^{-1}; 0.74, 0.47 ml g^{-1}; 12.4, 10.0%. These are the same co-gelled catalysts which were used earlier (*9*).

Hydrocarbons. Pure grade cumene (Phillips Petroleum) was passed through an alternate-layer N.F. kaolin (J. T. Baker)-silica gel (Davison, 28–200 mesh, Grade H) column, stored under nitrogen, and used within 1 week. Longer storage was difficult because of the easy formation of peroxide from oxygen traces, bringing about poisoning of the catalyst (*11*). Each cumene batch was given a standard catalytic test carried out at 420° and $P_s = 1$ atm (see below for further procedural details). Only batches whose test rates were between 2.00 and 2.40×10^{-4} mole g^{-1} sec^{-1} were accepted. Before purification the test rate was $\sim 0.3 \times 10^{-4}$ mole g^{-1} sec^{-1}. Pure grade cyclopentane (Phillips Petroleum) was used with and without further purification (see Results and Discussion section). The purification procedure was the same as the one used for cumene. Once purified, poison accumulation was not the problem it was with cumene.

Other. Reagent salts and acids were used in impregnation and analysis.

Procedure

Impregnation. Beads and pellets of S-M and S-90 catalysts were impregnated as they were earlier (*9*), except where otherwise noted. In the S-M preparations 35 ml of solution was mixed with 25 g of catalyst; with S-90, 50 ml was mixed with 30 g. The contact time was always at least 2 days. A summary of the impregnation data, including the amount of Al^{3+} exchanged, is given in Table 1. A distinction is made between n_r, the amount of metal ion reacted with the surface, and n_d, the amount of metal ion dissolved in the pore-volume liquid, but not reacted with the surface, at the time drying begins. The method of determining n_r and n_d is given in Ref. (*9*). (For convenience, n_r and n_d are also used to denote the equivalent amount of Al^{3+}; hence, n_r expressed as mmole g^{-1} is one-third n_r expressed as meq g^{-1}; cf. Table 1 and Figs. 1–4.)

Certain S-90 catalysts in which Al^{3+} was released by NaCl impregnation were reimpregnated, using $Al(NO_3)_3$, in order that the amount of Al^{3+} lost in the first step was made up in the reimpregnation step. The reimpregnation was carried out by adding to the calcined product of the first step a volume of solution (containing the required amount of Al^{3+}) slightly less than the pore volume of the silica-alumina sample, thus ensuring that all the Al^{3+} added—the amount lost in the first step—actually entered the pores.

In another group of S-90 catalysts the Al^{3+} released from the surface was kept in the pore volume by impregnating initially with a volume of NaCl solution slightly less than the pore volume of the sample. From the known effect of NaCl, at various concentrations, on S-90 from other impregnation experiments the amount of Al^{3+} released from the surface was calculated. Doubtless some parts of the surface remained unpoisoned, while others received an excess of Na^+: some of the catalysts prepared in this

TABLE 1
CATALYSTS AND ACTIVITIES

Electrolyte	C_i[a] (M)	$C_f(M^+)$[b] (M)	$[Al^{3+}]$ $(M \times 10^2)$[c]	n_r (mmole g^{-1} $\times 10^2$)	n_d (mmole g^{-1} $\times 10^2$)	v (mole g^{-1} sec^{-1} $\times 10^4$)			
						T(°C): 390°	420°	450°	480°
S-M Catalysts									
None	0	0	0	0	0	1.03	2.14	3.85	—
NaCl	0.033	0.0506	0.228	0.260	0.634	0.800	1.30	1.79	3.30
NaCl	0.124	0.114	0.555	0.647	1.60	0.594	1.06	2.10	—
NaCl	0.210	0.183	0.941	1.10	2.97	0.307	0.505	0.990	2.09
LiCl	0.695	0.710	2.23	2.60	2.47	0.111	0.228	0.329	—
LiCl	0.953	0.980	2.62	3.05	3.33	0.054	0.115	0.210	—
KCl	0.054	0.0426	0.710	0.827	0.350	—	0.986	—	—
KCl	0.129	0.0998	1.21	1.41	1.45	—	0.477	—	—
KCl	0.218	0.170	1.83	2.20	3.52	—	0.242	—	—
KCl	0.271	0.182	3.32	3.87	2.55	0.051	0.095	0.183	—
KNO_3	0.050	0.0311	0.621	0.723	0.537	—	1.05	—	—
KNO_3	0.120	0.0593	1.34	1.56	1.35	—	0.502	—	—
KNO_3	0.200	0.137	2.06	2.40	2.32	—	0.158	—	—
K_2SO_4	0.050	0.0656	1.14	1.33	0.330	—	0.440	—	—
K_2SO_4	0.120	0.165	2.18	2.55	1.01	—	0.106	—	—
K_2SO_4	0.200	0.308	3.59	4.19	1.71	—	~0	—	—
NH_4Cl	0.472	2.84	4.81	2.90	5.98	—	2.87	—	—
NH_4Cl	0.912	2.44	4.90	3.87	12.1	—	2.38	—	—
NH_4Cl	2.06	1.94	3.84	4.65	29.6	—	2.30	—	—
NH_4Cl	1.48	1.40	3.94	4.77	21.2	—	2.65	—	—
NH_4Cl	2.94	0.857	3.17	5.93	36.7	—	2.21	—	—
NH_4Cl	2.53	0.424	2.39	5.83	43.5	—	1.92	—	—
S-90 Catalysts									
None	0	0	0	0	0	1.20	2.61	4.69	6.99
NaCl	0.593	0.460	4.44	4.67	11.7	—	0.147	—	—
NaCl	0.750	0.604	4.86	5.10	15.2	—	0.079	—	—
NaCl[d]	0.096	0.0607	1.24	1.70	1.77	—	1.06	—	—
NaCl[d]	0.185	0.141	1.53	2.10	2.83	—	0.545	—	—
NaCl[d]	0.460	0.400	2.57	3.53	9.67	—	0.135	—	—
NaCl[d]	0.929	0.832	3.92	5.37	21.7	—	0.025	—	—
HCl	0.0045	3.8[e]	0.278	1.02	~0	—	2.94	—	—
HCl	0.0085	3.8[e]	0.560	2.05	~0	—	1.69	—	—
HCl	0.0433	3.7[e]	0.242	8.88	~0	—	2.44	—	—
HCl	0.0905	3.35[e]	4.57	16.8	~0	—	2.34	—	—
HCl	0.149	3.12[e]	6.88	24.5	~0	—	2.24	—	—

[a] C_i, initial electrolyte concentration.

[b] C_f, equilibrium concentration of cation other than aluminum.

[c] $[Al^{3+}]$, equilibrium concentration of aluminum.

[d] These catalysts were those used to produce additional catalysts (not shown in table) by $Al(NO_3)_3$ impregnation. Also not shown: three NaCl catalysts in which there was no equilibrium solution. See text and Fig. 4.

[e] pH, not C_f.

way exhibited higher activities than would be expected, comparing them with others in the group and those prepared using conventional procedures.

Rate studies. The all-glass reactor was essentially the same as that used earlier (*2*). This is a "differential" reactor, in which conversion is <2%, usually <1%. Ten to twenty-five milligrams of $-100 + 200$ catalyst was used, with rates calculated from the benzene content of weighed 2-min samples of product stream. The liquid flow rate was about 0.7 ml min^{-1}, corresponding to an LHSV of 1500–5000. The reported rate for an experiment is the average of the rates determined from three 2-min samples taken between 40 and 70 min after cumene flow began. It was shown in the present and also in earlier work that a constant rate is attained before there is flow for 40 min. The total pressure was atmospheric pressure, close enough to 1 atm to warrant the assumption that 1 atm was the total pressure. The slight variation in atmospheric pressure was neglected in order that there be possible a comparison between different experiments.

Impregnated catalysts were dried at about 200° for 18 hr, calcined at 450° in flowing oxygen for 2 hr, and stored dry. Before use a catalyst was ground to $-100 + 200$ mesh. On the day it was used it was heated for 1 hr in flowing nitrogen at 450°; in the reactor it was heated at 480°, the highest temperature of use, in flowing nitrogen for 20 min prior to the beginning of cumene flow at the temperature of interest.

The drying–calcining history of the catalyst is important. Many [e.g., see ref. (*12*)] postulate an active site incorporating water. Several have shown that small amounts of water enhance cracking activity (*13–15*). Prater and Lago (*13*) also showed that the time necessary to achieve a constant rate is a function of the water content. Even though water is important, all studies indicate that a catalyst is defined once the predrying history is specified, and for this reason all catalysts were treated alike.

There was more scatter in the rates than in the earlier work (*2*, *11*, *16*) because in the present work a higher cumene purity level was attained: consequently, small absolute fluctuations in the poison level were more important in the present work. The thermal rate, found to be $<0.05\%$ conversion between 390° and 450° and $\sim 0.07\%$ conversion at 480°, was small enough to be neglected.

The test used for diffusion limitation within the catalyst particle is that of Weisz and Prater (*17*), who showed that if $(R^2/D_{\text{eff}})(v_v/c)$ is less than unity (where R is the particle radius; D_{eff} the diffusion coefficient of the reactant gas of concentration c; and v_v, the reaction rate per unit catalyst volume), there is no particle diffusion limitation. Our highest rate was $<4 \times 10^{-4}$ mole $\text{g}^{-1}\ \text{sec}^{-1}$, or $\sim 4 \times 10^{-4}$ mole $\text{ml}^{-1}\ \text{sec}^{-1}$; assuming D_{eff} for cumene at 480° to be $\sim 0.27\ \text{cm}^2\ \text{sec}^{-1}$, R (100 mesh) to be $\sim 1.3 \times 10^{-2}$ cm, and c ($P_s = 1$ atm, $T = 480°$) to be 1.62×10^{-5} mole ml^{-1}, the indicated product is less than 2×10^{-5}, indicating there is no particle diffusion limitation.

To obtain cumene partial pressures less than one, the reactor feed was in some cases diluted with cyclopentane. Most of these runs were with two NaCl-poisoned catalysts; some were carried out on the S-M catalyst to confirm earlier results (*2*).

Analytical

The benzene:cumene mole ratio in a weighed sample, taken from the product stream, was determined on an Aerograph 90-P Gas Chromatograph, using either a 15% Benton 34-Chromosorb W (60–80 mesh) or a 20% SF 96-Chromosorb R (60–80 mesh) column (both supplied by Wilkens Instrument), with the latter always used when cyclopentane was present.

Aluminum analyses were carried out with a $ZnCl_2$ back-titration of excess EDTA. Chloride was analyzed using $AgNO_3$, with dichlorofluorescein the indicator.

RESULTS AND DISCUSSION

Effect of Metal Poison

An analysis of the effect of metal poison on the reaction rate yields information about the nature of the catalytically active site. Certain aspects of the surface model so developed are confirmed by the results of the HCl and NH_4Cl experiments, and these are described in the next section. The development of the model rests partially on the idea that there are very few active sites per unit area. This idea stems from earlier work and from new work, reported

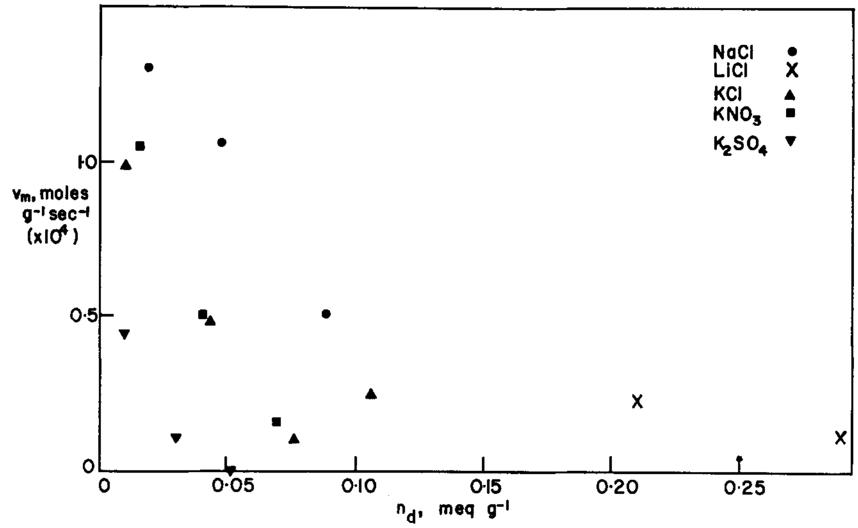

FIG. 1. Rates at 420°; v_m vs. n_d for poisoned S-M catalysts; v_m is activity of poisoned catalyst.

in the sections on the determination of rate parameters and site densities.

All the reaction rates, except for those used only in connection with parameter calculation, are given in Table 1.

Distinction between reacted and unreacted alkali metal ion. The difference between the two kinds of salt in the pores, given by n_d and n_r in Table 1, is readily seen by comparing Figs. 1 and 2. The reaction rate for the poisoned catalyst is evidently no function of n_d (Fig. 1), but it does depend upon n_r in a regular manner (Fig. 2), even though 15 different poisoned S-M catalysts, using five different salts, were used. (There is of course no correlation of v_m with the total concentration of alkali metal salt in the pores, $n_r + n_d$.) Topchieva (*4d*) stated that the effect of alkali metal cation upon this system depends upon the

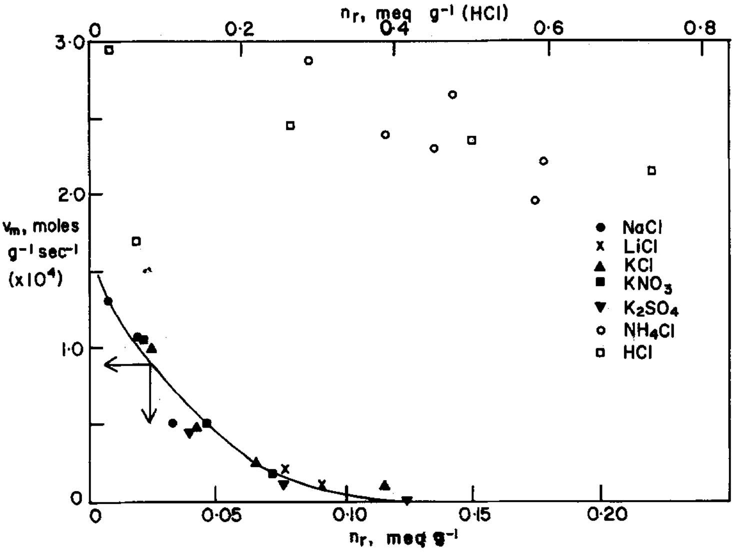

FIG. 2. Rates at 420°; v_m vs. n_r, HCl on S-90, with n_r on upper abscissa; all others on S-M, with n_r on lower abscissa.

cation; a comparison of Figs. 1 and 2 indicates the difference to be in the varying tendencies of the alkali metal ion to react with the surface, not in any difference between alkali metal cations once there has been reaction. When using a *single* electrolyte, Topchieva and Moskovskaya (*4a*) and Wang and Wu (*7*) have understandably found the rate to be a smooth function of poison concentration.

Several have suggested that the alkali metal ion is a poison because it reacts with surface hydrogen, and that this surface hydrogen is in some way associated with aluminum to make an active site. Evidence offered has been the pH drop in the equilibrating solution. This pH change is, however, accounted for by considering the amount of hydrolysis of liberated Al^{3+}. In addition, Hall and co-workers (*18*) showed by another method that K^+ and Ba^{2+} do not replace surface hydrogen in silica-alumina. The HCl-silica-alumina results, discussed in the next section, indicate that the action of the alkali metal ion is not one of first reacting with surface hydrogen, with the released hydrogen then exchanging with aluminum.

Fate of the salt during drying. Why does not *all* the alkali metal ion in the pores (i.e., $n_r + n_d$) remove Al^{3+}, since the salt in solution must become very concentrated during drying? If the high alkali metal ion concentration achieved during drying were the concentration at which Al^{3+} is removed, all activities would be zero or near zero.

The explanation is probably related to a phenomenon which depends upon the nonuniformity of pore size. During drying the smallest pores empty last and while there is some liquid still present the nonvolatile solute moves to these pores (*19*). Thus the salt becomes concentrated (limited chiefly by its solubility) in a small fraction of the pore volume. Even if the rate of exchange is rapid, drying will cause the maximum amount of Al^{3+} exchange to occur in only a very small part of the total surface when these highly soluble salts are used.

Suggested model of the cumene-silica-alumina system. We shall show that the shape of the curve of Fig. 2 (and similar curves using other v_m values of Table 1) and the equivalence of the various salts are consistent with a simple model of the system. As a result, there is some elucidation of the nature of the catalytic site and the relation between this site and other surface sites.

A basic assumption of the model is that alkali metal ions exchange simultaneously with Al^{3+} associated with active sites [A(s)] and with Al^{3+} associated with inactive sites [I(s)]

$$3M^+(aq) + A(s) \overset{K_A}{\rightleftarrows} Al^{3+}(aq) + M_3A(s) \quad (3)$$

$$3M^+(aq) + I(s) \overset{K_I}{\rightleftarrows} Al^{3+}(aq) + M_3I(s) \quad (4)$$

We may write

$$K_A = \frac{[Al^{3+}(aq)][M_3A(s)]}{[M^+(aq)]^3[A(s)]} \quad (5)$$

$$K_I = \frac{[Al^{3+}(aq)][M_3I(s)]}{[M^+(aq)]^3[I(s)]} \quad (6)$$

where $[M_3A(s)]/[A(s)]$ and $[M_3I(s)]/[I(s)]$ are molar ratios and are equal to the corresponding mole fraction ratios. We allow for heterogeneity in both A(s) and I(s), and we therefore consider the K's to be equilibrium quotients rather than equilibrium constants.

Equations (2), (5), and (6) are combined to give

$$\frac{v_m^2B}{v} + \frac{v_m}{\alpha - 1}(\alpha U - \alpha D + B + D) + \frac{v}{\alpha - 1}(n_r - D) + v_m n_r = 0, \quad (7)$$

where $\alpha = K_A/K_I$, v is the reaction rate for the unpoisoned catalyst, U is the concentration (per gram) of inactive sites in the unpoisoned catalyst, and $D = B + U$; v and v_m are determined at $P_s = 1$ atm.

The value chosen for D is the value of n_r at which v_m becomes zero. In some cases (*9*) the maximum amount of aluminum released is greater. Nevertheless, D is defined in this way because all the active sites are included in this population, the active sites being those which have been removed when $v_m = 0$. In principle an error can be introduced by defining D in this way. Suppose D' moles (per gram) of Al^{3+} ions can be removed by alkali metal ion of a sufficiently high concentration, where $D' > D$. Then, for a value of n_r in Fig. 2 such that $n_r < D$, there is the possibility that *some* of the Al^{3+} released from the surface is in the $(D' - D)$ population, the population not of interest. Fortunately, this error is minimal because K_I decreases significantly with increasing n_r (shown below), and therefore n_r need not be corrected to subtract out this additional Al^{3+}.

It is shown in the third section that B, the site density, is very small. When the actual numbers are considered, it is seen that the first term of Eq. (7) can be neglected and that B is small enough (with respect to D) so that B can be neglected in the second term. Thus, Eq. (7) can be used with confidence even though B has not been determined accurately.

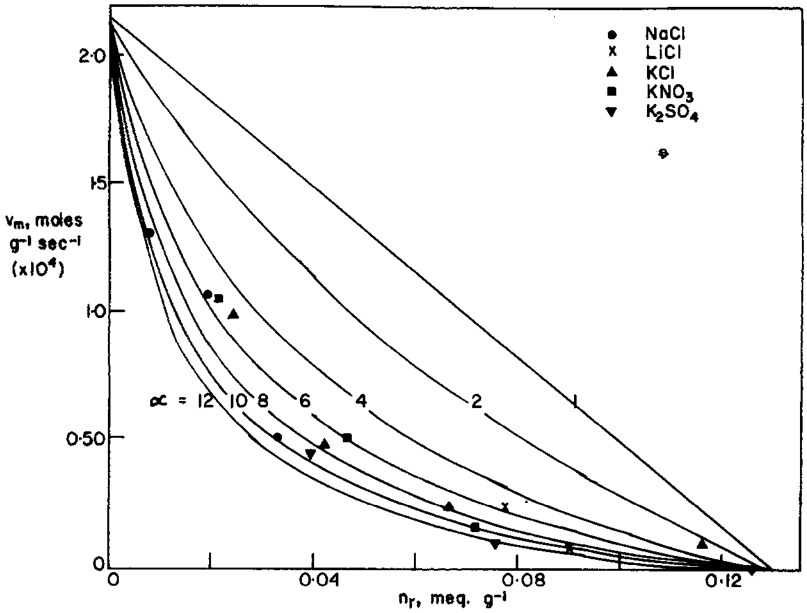

FIG. 3. Rates at 420°; v_m vs. n_r for poisoned S-M catalysts. Curves calculated for values of α indicated.

Using Eq. (7), v_m vs. n_r curves can be calculated for various assumed values of α, and a family of such curves is shown in Fig. 3 along with the experimental points of Fig. 2. While the K's were taken to be only equilibrium quotients, the figure indicates α to be about seven over the whole concentration range. Thus K_A and K_I have about the same dependence upon n_r.

Equation (7) is also solved for α for each poisoned catalyst, and for each temperature at which v_m was determined. In addition, since $B \ll D$, it is possible to calculate an approximate value of K_I (approximate since hydrolysis effects were neglected), assuming in the solution equilibria that Eq. (3) is unimportant. Table 2 gives a summary of α, K_I, and K'_I (calculated where D', not D, must be used) values.

We conclude from Table 2: (a) α is approximately constant, regardless of the salt, salt concentration, or temperature of the catalytic experiment. The mean of the 14 values is 7.5, with a standard deviation of 2.7. Omitting the two with the largest deviation, the mean and standard deviation of the six lowest and six highest n_r values are, respectively, 7.4 ± 2.1 and 7.4 ± 1.5, suggesting α is independent of concentration. (b) K_A is about seven times as large as K_I at a given n_r value, since $\alpha \pm K_A/K_I$. (c) K_I or K'_I decreases significantly with an increasing amount of aluminum removed. Therefore, since α is approximately constant, K_A also decreases.

The point of view taken here is that the active sites constitute a very small group (as shown in the third section), and that the energy needed for Al^{3+} removal varies just as much within this group as it does in any segment of comparable size in the larger group of inactive but exchangeable surface aluminum ions. The smallness of the active group ensures effective homogeneity, justifying one of the Langmuir assumptions underlying the development of the rate law of Eq. (2). The active sites are thus taken to be associated with the most-easily-removable Al^{3+}, with the energy of Al^{3+} removal varying (with fraction removed) the same within each of the two groups. These two groups also differ in that there is a difference in the activation energy for the cracking step, such that the inactive group is defined as that group in which this activation energy is so large that the sites are not "seen" catalytically. Thus it is suggested that the only difference between active and inactive sites associated with Al^{3+} is a quantitative one. The energy difference between active and inactive sites in the exchange reaction is only of the order of 1 kcal; surely for the model to be valid the catalytic activation energy difference would be at least several kilocalories. Such a magnification of the difference between the exchangeable aluminum ions during the catalyst activation process is quite reasonable.

We note also that (a) α is not a function of the temperature of the catalytic reaction, and (b) α is essentially the same for the different salts. The first must hold: while α is determined using rate data, it is defined in terms of quantities which have no relation to the conditions of the catalytic experiment. Statement (b) is also consistent with the model proposed. For, the more likely a given kind of ion will react with an active site, the more likely it will react with an inactive site, if it is indeed true that the difference between active and inactive sites is only a quantitative one. In sum, the model presented thus accounts in a natural way for the shape of the v_m vs. n_r curve (concave upward, because $\alpha > 1$) and also for the equivalence of the various salts, and this has been accomplished using only a few reasonable assumptions.

TABLE 2

K_I (or K'_I) AND α VALUES FOR S-M CATALYSTS

Salt	n_r (mmole g^{-1} $\times 10^2$)	K_I[a]	K'_I[b]	α		
				T(°C): 390°	420°	450°
NaCl	0.260	—	0.903	4.50	10.0	15.9
NaCl	0.647	—	0.518	4.18	5.79	4.74
NaCl	1.10	—	0.398	6.97	9.53	8.51
LiCl	2.60	0.092	—	5.55	5.61	7.17
LiCl	3.05	0.066	—	7.70	7.42	7.31
KCl	0.827	—	9.65	—	4.95	—
KCl	1.41	—	2.38	—	7.19	—
KCl	2.20	—	1.27	—	7.57	—
KCl	3.87	—	4.40	2.27	2.59	2.42
KNO_3	0.723	—	—	—	7.32	—
KNO_3	1.56	—	—	—	5.79	—
KNO_3	2.40	—	—	—	10.1	—
K_2SO_4	1.33	—	—	—	8.72	—
K_2SO_4	2.55	—	—	—	13.5	—
K_2SO_4	4.19	—	—	—	[c]	—

[a] For K_I, $D = 0.0433$ mmole g^{-1}.

[b] For K'_I, $D' = 0.0533$ mmole g^{-1} for NaCl and 0.0867 mmole g^{-1} for KCl. [See Ref. (*9*)].

[c] Not calculable because rate is, within experimental error, zero.

A confirmation of the model. An experiment was carried out in which the Al^{3+} released by the poison in four NaCl-poisoned catalysts was replaced by impregnation with $Al(NO_3)_3$. In a second experiment NaCl

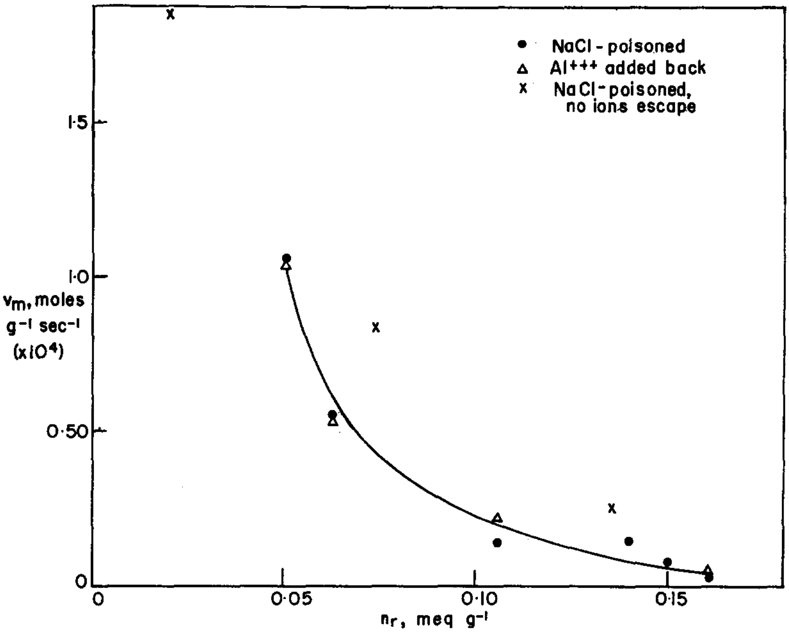

FIG. 4. Rates at 420°, Houdry catalyst; v_m vs. n_r for NaCl-poisoned S-90 catalysts; ●, poisoned in usual way; △, $Al(NO_3)_3$ added back to catalyst of same n_r value; ×, poisoned without external solution at equilibrium.

poisoning was carried out (on three catalysts) so that the entire NaCl solution just about filled the catalyst pore volume. In this way no exchanged Al^{3+} could leave the pores. Thus in both sets of experiments the amount of surface aluminum in the calcined catalyst was the same as it would have been had there been no poisoning.

The results for these seven catalysts, plus six poisoned by NaCl in the normal manner, are given in Table 1 and Fig. 4. The general conclusion, with two possible exceptions (probably due to the difficulty of poisoning uniformly without an excess of solution), is that active aluminum once removed is not easily replaced. This is as expected. Since α is greater than one, a disproportionate amount of active aluminum leaves the surface when NaCl is added. Yet the fraction of exchangeable Al^{3+} which is catalytically active is (in the model) very small. In these experiments, where there is readdition of Al^{3+} to the surface, the ratio of the number of the active to the number of the inactive sites in the added Al^{3+} is very small, perhaps just as small as it was on the original surface. There has thus been a net destruction of almost as many sites as were removed by the poison initially. [Horton and Maatman (*2*) showed that the fraction of Al^{3+} which is active in $Al(NO_3)_3$-impregnated silica gel is almost as low as in co-gelled silica-alumina.]

Effect of Acid Treatment

It has been sufficiently well proved by others that both surface aluminum and some kind of surface acidity are associated with the catalytic activity of silica-alumina. Therefore, it is particularly interesting that removal of Al^{3+} by means of an acidic solution leads to a result quite different from that obtained using alkali metal ion solutions of approximately neutral pH.

The S-90-HCl and S-M-NH_4Cl activities given in Table 1 and Fig. 2 are seen, if anything, to be *higher* than the activities of the corresponding untreated S-90 and S-M catalysts given in Table 1. The larger scatter in the HCl points undoubtedly occurs because HCl treatment is not easily reproducible, since this acid is matrix-destroying (*8*, *9*, *20*). We conclude that since large amounts of Al^{3+} are removed, active sites are indeed destroyed. In addition, it seems that the acid produces new sites. Both Bronsted and Lewis acidity have been postulated for the finished catalyst; it is certainly conceivable that either kind of acidity could be the result of drying and calcining a surface initially covered with a proton acid.

One question concerning the mechanism of alkali metal poisoning can be answered by combining the acid and metal ion data of Fig. 2. (The difference between the S-90 and S-M bases is slight and does not bear upon this argument.) What has been deduced is that it is Al^{3+} removal, and not H^+ removal, that is the poisoning action of alkali metal ion. The question concerns the mechanism whereby M^+–Al^{3+} exchange is effected. A possible mechanism is (a) exchange of alkali metal with surface hydrogen (presumably H^+ of an $=AlOH$ complex), followed by (b) exchange of H^+ so produced with surface aluminum. Consumption of the amount of hydrogen necessarily involved in postulated step (a) in the HCl experiments (it is seen in Table 1 that the acid is consumed, leaving an equilibrium solution no more acid than with M^+–Al^{3+} exchange), leads, however, to very high activities. Thus, were step (a) actually involved in metal ion reaction, the resultant activity would be high enough to produce the drastic effect observed with HCl. The similarity between HCl and NH_4Cl suggests that the higher pH of the NH_4Cl solutions is compensated for by the capacity to produce H^+ by hydrolysis.

Use of the Rate Law

Part of the above development depends upon the assumption that the active site density is low. This assumption is consistent with the results discussed, and in addition it can be independently derived from the rate law study which was made. In this section certain parameters of the Prater-Lago rate law (*1*), Eq. (2), are evaluated; some of these results are used in the next section to determine site densities. Along with parameter evaluation we investigated the consequences of the presence of catalyst poison if it is present in the reactant gas stream.

Temperature dependence. In order to evaluate the parameters of Eq. (2) it is important to differentiate between "appar-

TABLE 3
CRACKING RATES WITH CYCLOPENTANE DILUTION

Catalyst[a]	Cyclo-pentane[b]	P_s (atm)	v (mole g^{-1} sec^{-1} $\times 10^4$) T(°C): 390°	420°	450°	480°
S-M	P	0.669	1.11	2.22	—	—
S-M	P	0.403	0.616	1.77	—	—
S-M	P	0.189	0.444	0.791	—	—
S-M	U	0.669	0.835	1.74	—	—
S-M	U	0.403	0.499	0.894	—	—
S-M	U	0.189	0.217	0.395	—	—
S-90	U	0.669	0.690	1.97	—	—
S-90	U	0.403	0.377	1.19	—	—
S-90	U	0.189	0.221	0.560	—	—
S-M-1	P	0.669	0.643	1.20	1.67	2.62
S-M-1	P	0.403	0.472	0.813	1.29	1.84
S-M-1	P	0.189	0.235	0.445	0.614	0.819
S-M-2	P	0.669	0.246	0.490	0.826	—
S-M-2	P	0.403	0.185	0.387	0.555	—
S-M-2	P	0.189	—	0.175	0.282	—

[a] S-M, unpoisoned S-M; S-90, unpoisoned S-90; S-M-1, NaCl-poisoned (n_r = 0.260 × 10^{-2} mmole g^{-1}) S-M; S-M-2, NaCl-poisoned (n_r = 1.10 × 10^{-2} mmole g^{-1}) S-M.

[b] P, purified; U, unpurified.

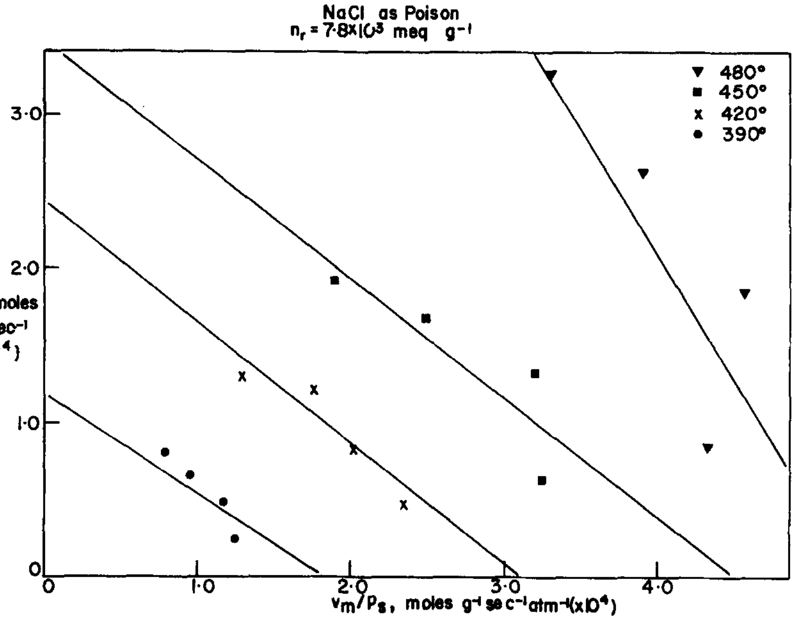

FIG. 5. Rate parameters; v_m vs. v_m/P_s for NaCl-poisoned ($n_r = 7.8 \times 10^{-3}$ meq g^{-1}) S-M catalyst.

ent" and "true" activation energies. The apparent value is that which is associated with k in an assumed rate law of $v = kP_s^n$, where n is a constant, while the true value is associated with k_3 of Eqs. (1) and (2). Since G is a function of temperature, we do not use the apparent activation energy. When G is temperature-dependent, it is in principle possible for the Arrhenius plot to be nonlinear, whereupon the apparent activation energy is a function of temperature. It is even possible for a *maximum* to exist in an Arrhenius plot. No curvature, much less a maximum, was detected in the present work for any catalyst. It can be shown (see the Appendix) what the condition is for a maximum to appear. Cumene cracking over silica-alumina does not even come close to meeting this condition and it is therefore not surprising that there is no curvature in any Arrhenius plot.

Determination of constants. Studies were made on three catalysts, the S-M catalyst and two NaCl-poisoned S-M catalysts. To obtain a partial pressure of cumene less than 1 atm, cyclopentane was used as diluent. The rate data are in Table 3 and are used in conjunction with the relevant $P_s = 1$ atm data of Table 1.

In order that the constants be determined, Eq. (2) is rearranged,

$$v = -G(v/P_s) + k_3B \qquad (8)$$

where v_m and b can be used for a metal-poisoned catalyst. Typical least-mean-square plots of v_m vs. v_m/P_s at various temperatures are given in Fig. 5 for one of the NaCl-poisoned S-M catalysts. Values of G and k_3B from the slope and intercept, respectively, are given for the catalysts for various temperatures in Table 4. If B is temperature-independent, the activation energy of the k_3 step, Q_3, can be obtained from the slope of a plot of ln k_3B vs. $1/T$, as in Fig. 6. Similarly, the heat of desorption of cumene from active sites, $(Q_2 - Q_1)$, is obtained from plots of ln G vs. $1/T$. Values of Q_3 and $(Q_2 - Q_1)$ are given in Table 5.

With respect to these constants, there is apparently no important difference between the NaCl-poisoned catalysts and the unpoisoned catalyst. The unpoisoned catalyst was not studied extensively in the present work, since the results for it are in essential agreement with the silica-alumina results of Pansing and Malloy (*3*), Prater and Lago (*13*), and Horton and Maatman (*2*). There were in these four studies, including the

TABLE 4

G AND k_3B VALUES FOR THREE S-M CATALYSTS

n_r (mmole g^{-1} × 10^2)	G (atm^{-1}) T(°C): 390°	420°	450°	480°	k_3B (moles g^{-1} sec^{-1} × 10^4) 390°	420°	450°	480°
0	0.398[a]	0.407[a]	—	—	1.46	3.17	—	—
0.260[b]	0.616	0.790	0.762	1.63	1.50	2.14	2.84	7.17
1.10[b]	0.666	1.17	1.56	—	0.480	1.39	2.69	—

[a] Values too close to use in $(Q_2 - Q_1)$ calculation of Table 5.

[b] NaCl-poisoned S-M catalyst.

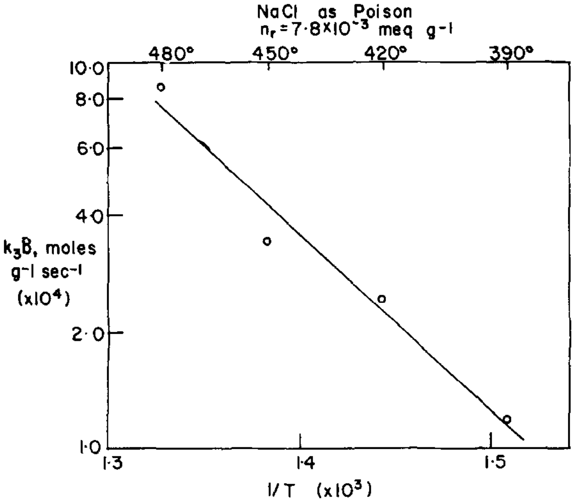

FIG. 6. Rate parameters; ln k_3B vs. $1/T$ for catalyst of Fig. 5.

present one, significant variations in the catalyst, the reactor, experimental conditions, and cumene purity. These differences thus seem not to be fundamental and the values in Tables 4 and 5 are probably not far from being correct. It is not readily evident that cumene purity can change while essentially the same values of these constants are obtained. We show in the remainder of this section that there are indeed situations in which charge impurity is very important, and that it is possible to ascertain when the level of purity does not confuse the issue.

TABLE 5

Q VALUES AND SITE DENSITIES

n_r (mmole g^{-1} × 10^2)	$Q_2 - Q_1$ (kcal mole^{-1})	Q_3 (kcal mole^{-1})	B (sites cm^{-2} × 10^7)[a]
0	9.5[b]	23.6	9.44
0.260[c]	9.4 ± 1.8[d]	20.9 ± 2.6[d]	0.928[e]
1.10[c]	13.5 ± 2.1[d]	27.4 ± 1.5[d]	59.0[f]

[a] Calculated for 420°C.

[b] Taken from Ref. (*2*); see footnote a of Table 4.

[c] NaCl-poisoned S-M catalyst.

[d] Standard deviations in slopes of Arrhenius plots, such as in Fig. 6.

[e] Standard deviation in log B = 0.47.

[f] Standard deviation in log B = 0.54.

Poison introduced via cumene. Cumene accumulates peroxide-type poisons very easily, and consequently the cumene-cyclopentane mixtures used can contain poison. The rate when poison is present, v_p, becomes (*11*)

$$v_p = k_3B \frac{P_s}{P_s + G(1 + K_pP_p)} \qquad (9)$$

where P_p is the partial pressure of the poison and K_p is the equilibrium constant for poison adsorption on active sites. Rearranging, to give an equation analogous to Eq. (8), we have

$$v_p = -G(1 + K_pP_p)(v_p/P_s) + k_3B \quad (10)$$

The cumene purity was not the same in the four studies cited. At 420° and $P_s = 1$ atm, with the S-M catalyst v is 2.14×10^{-4} mole g^{-1} sec^{-1} in the present work and it was 0.958×10^{-4} mole g^{-1} sec^{-1} in the work of Horton and Maatman (*2*), who used a different purification procedure. (We have produced occasional cumene batches whose test value was $\sim 3 \times 10^{-4}$ mole g^{-1} sec^{-1}; no such batch was used.) Prater and Lago (*13*), using a similar catalyst, obtained a test value of $\sim 2.0 \times 10^{-4}$ mole g^{-1} sec^{-1}. For two reasons it appears that these differences do not cause trouble if within one study a constant purity level is maintained.

First, inspection of Eq. (10) reveals that decreasing P_s should, if poison is present, decrease the apparent G [i.e., $G(1 + K_pP_p)$], since P_p is proportional to P_s if cumene, not cyclopentane, is the poison source. In Fig. 5 and in a similar figure of Horton and Maatman (*2*) the scatter is obviously greater than any curvature caused by this poison effect.

Second, the apparent G values, the values determined, are near unity. If the actual poison level were high the true G value would necessarily be very small, and accidental fluctuations in the observed cracking rate than those which were observed. This effect of accidental fluctuation would become more important as the poison level decreases, and this is probably the chief reason the scatter was larger in the present work than it was in that of Horton and Maatman (*2*). The value of G at 420° in the present work is lower, indicating less poison, than those reported by Prater and Lago ($G \approx 5$) and Pansing and Malloy ($G \approx 2.5$, for another catalyst, obtained by extrapolation to 420°).

If, in spite of these considerations, the values of G reported here are in error because of poison, the true value of G is then lower, and k_3B is even lower than reported. If such were the case, the site densities are even lower than the strikingly low ones we calculate, and our conclusions are, if anything, made stronger.

Poison introduced via the diluent. The poison effect (on curves such as those in Fig. 5) if cumene is the poison source is not the same as it is when the poison source is the diluent, in this case cyclopentane. In the latter instance, the poison partial pressure in the gas mixture contacting the catalyst is, at a total pressure of 1 atm

$$P_p = k(1 - P_s) \quad (11)$$

where k is a constant for a given cyclopentane batch, and is proportional to the concentration of poision in the cyclopentane. Eliminating P_p between Eqs. (9) and (11) and rearranging, we have

$$v_p = -\frac{v_p}{P_s}\left[\frac{G + GK_pk}{1 - GK_pk}\right] + \frac{k_3B}{1 - GK_pk} \quad (12)$$

Thus, in a plot of v_p vs. v_p/P_s there can be a negative, infinite, or positive slope, depending upon the value of K_pk.

The effect of changing slope is shown in Fig. 7, where v_p vs. v_p/P_s plots are given for S-90 and S-M catalysts using unpurified cyclopentane; for comparison there are given two of the curves of Fig. 5, where purified cyclopentane was used. Evidently $GK_pk \approx 1$ in the unpurified cyclopentane experiments, and the slope is consequently very large.

The Density of Active Sites

There has been interest in recent years in the site density of silica-alumina in various reactions, some of which are reactions in which the solid acts as catalyst. The surface site is a reactant, and it is of obvious interest to know the reactant concentration. In our work this density is needed in order that the effect of metal ions be understood. In addition, the density is of intrinsic interest because the value found is extremely small.

Method of calculation. The site density, B, one of the constants of Eq. (2), is not obtained directly, but rather it is obtained by applying absolute rate theory to values of k_3B (*21*). We have

$$k_3B = B\kappa(kT/h) \exp(S_3/R) \exp(-Q_3/RT) \quad (13)$$

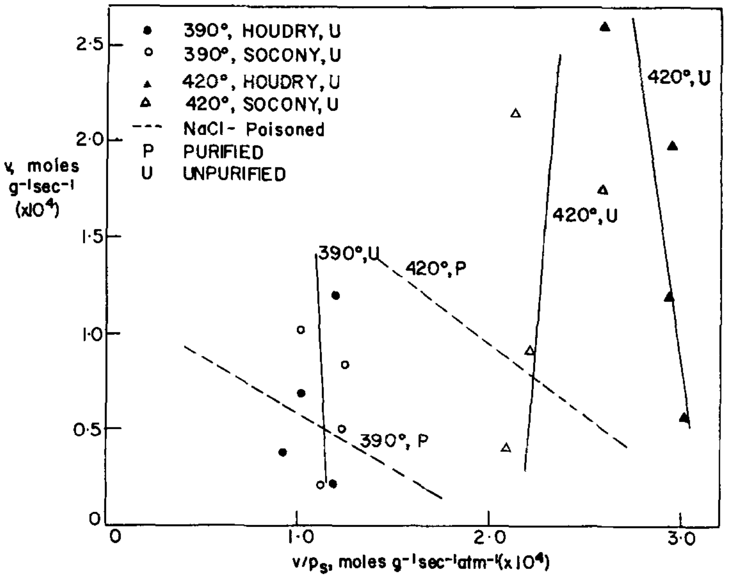

FIG. 7. Effect of cyclopentane purification; v vs. v/P_s, ●, 390°, S-90; ○, 390°, S-M; ▲, 420°, S-90; △, 420°, S-M. Solid curves with points and for unpurified (U) cyclopentane. Dashed curves are the lower two curves of Fig. 5, with purified (P) cyclopentane.

where κ is the transmission coefficient, k and h are the Boltzman and Planck constants, and S_3 is the entropy of activation of the k_3 step. If we assume that $\kappa \approx 1$ and that S_3 is small (since both reactant and activated complex are adsorbed), B can be calculated. The results are in Table 5.

Possible sources of error. These site densities are much lower than what is usually assumed to be the case. Possible sources of error should therefore be discussed. First, the question of the validity of the kinetic scheme, particularly the matter of site uniformity, arises. Almost any reaction model, however, calls for sites having a narrow band of energies. Second, were experimental error to account for the low values, the error would have to be so large as to render rate measurements meaningless, a rather unlikely situation. In addition, the experimental results of other workers (Table 6, discussed below) lead to the same low-density conclusion. Third, in the use of the absolute rate theory the transmission coefficient is assumed to be unity. For this assumption to be the reason for a low density the coefficient would have to be several orders of magnitude smaller, which again is highly unlikely. Fourth, to the extent S_3 is actually negative and not zero, as assumed, the calculated site density would be higher. If a factor of 10^5 were to be gained in B, S_3 would be -23 e.u. This is roughly one-half the translational entropy of cumene at 420°, and yet S_3 refers merely to the activation of the *adsorbed* molecule, surely accompanied by only a relatively small entropy change.

Other site densities. It is instructive to compare the low site densities found in this work, 10^7–10^8 cm^{-2}, corresponding to an average distance of $\sim 10^4$ Å between sites, with other site densities. Representative densities, with different methods used for determination, for different reactions and solids, are given in Table 6. As expected from the essential agreement of our kinetic results (as summarized in Tables 4 and 5) with the results of others, the site densities are also in good agreement. This "agreement" is obviously no better than within an order of magnitude, and it may be concluded that the true value is known only approximately.

Using absolute rate theory in this way could perhaps be questioned. In Table 6 it is

TABLE 6
OTHER SITE DENSITIES

Solid	Reaction[a]	Method[b]	Sites cm^{-2}	Reference
SiO_2-Al_2O_3	C.C.	A*	2×10^8	*13*
SiO_2-Al_2O_3	C.C.	A*	2×10^7[c]	*3*
SiO_2-Al_2O_3	C.C.	A	6×10^7	*2*
SiO_2-Al_2O_3[d]	C.C.	A	2×10^8	*2*
Cr-Si-Al[e]	C_2H_4 P.	A	3×10^{10}[f]	*22*
Ni	Des. H_2	A	$\sim 10^8$	*23*
Au	Des. H_2	A	$\sim 10^{13}$	*24*
W	NH_3 Dec.	A	$\sim 10^{15}$	[g]
W	NH_3 Dec.	A	$\sim 10^{15}$	[g]
Mo	NH_3 Dec.	A	$\sim 10^{15}$	[g]
Au	HI Dec.	A	$\sim 10^{10}$[h]	[g]
SiO_2-Al_2O_3	C. C_3H_6	Y	$<1 \times 10^{12}$[i]	*25*
SiO_2-Al_2O_3	P.C.F.	ESR	2×10^{12}	*26, 27*
SiO_2-Al_2O_3	Ads. NH_3	S.T.	5×10^{13}	*28*
SiO_2-Al_2O_3	KI ox.	C	9×10^{11}	*29*
SiO_2-Al_2O_3	Ex. Al	C	$\sim 10^{13}$	*9*

[a] C.C., crack cumene; C_2H_4 P., C_2H_4 polymerization; Des. H_2, desorb H_2; NH_3 Dec., NH_3 decomposition; HI Dec., HI decomposition; C. C_3H_6, crack cyclopropane; P.C.F., perylene cation formation; ads. NH_3, adsorb NH_3; KI ox., KI oxidation; Ex. Al, exchange Al^{3+} with alkali metal or alkaline earth salt.

[b] Asterisk indicates calculation not made in cited reference. A, absolute rate; Y, from yield; ESR, electron spin resonance; S.T., surface titration; C, chemical analysis of system.

[c] Obtained by extrapolating to 420°C.

[d] Average of four catalysts made by impregnating SiO_2 gel with $Al(NO_3)_3$.

[e] The mixed oxide.

[f] Authors indicate value could be larger, with ΔS of this step equal to 4 e.u.

[g] Quoted and calculated in Ref. (*21*).

[h] Indicated in Ref. (*21*) that product poisoning probably causes low value.

[i] Calculation holds only if active sites are Bronsted sites.

seen that this theory gives a broad spectrum of site densities when systems quite different from ours are included. Thus, low densities are not inherent in the theory; nor are low densities limited to systems similar to ours. On the other hand, various *reactions with* the surface (e.g., perylene cation formation), as distinguished from *reactions catalyzed by* the surface, are characterized by high site densities.

These results are consistent with the concept of site heterogeneity, even when only one kind of site (e.g., exchangeable Al^{3+}) is considered. Catalytic reactions can be very sensitive to such heterogeneity, while adsorption, exchange, etc., would in general be expected to be insensitive. There are numerous examples of site heterogeneity on the same catalyst and between similar catalysts. For example, Weisz and Miale have shown that the rate of *n*-hexane cracking is 10^4 times greater using as catalyst certain crystalline aluminosilicates, than with other similar catalysts, even though the apparent (and almost certainly the true) activation energies are the same (*30*). The major difference in the rate constants thus lies in the pre-exponential factor. Even if there were 10^{13} sites cm^{-2} in the most active catalyst, the site density in the least active approaches the very low values we report. Therefore, the nature of the site varies going from catalyst to catalyst in this series.

Other examples of heterogeneity, with only the most active sites "seen" in a given catalytic reaction are as follows: (a) Parahydrogen conversion catalyzed by PdH decreases by a factor of 10^7 when a very small number of high-energy sites is destroyed (*31*). (b) The activation energy of the k_3 step in the cumene-silica-alumina system is 4–6 kcal larger when silica gel impregnated with $Al(NO_3)_3$ is the catalyst, as compared to co-gelled silica-alumina (*2*). (c) The activation energy of formic acid decomposition catalyzed by silver varies from 12 to 35 kcal, depending on surface coverage (*32*). (d) The data for positive-ion radical formation and pivaldehyde decomposition in the presence of silica-alumina catalyst suggest a spectrum of oxidation sites, with different types of electron transfer at different sites (*33*). (e) With KI oxidation in the presence of silica-alumina (Table 6) the number of oxidation sites is only $\sim 5\%$ of the number of I^- adsorption sites (*29*).

General Conclusion

Our results and these considerations indicate it is highly probable that the site density is extremely low, corresponding to concentrations equivalent to a low impurity level. We have shown that in spite of this low density it is possible, in our case by studying the exchange of metal ions with the surface, to make certain deductions concerning the nature of the active site. Even so, since there is a real possibility in any catalytic system that the site density is very low, extreme caution should be used in making deductions from macroscopic properties of the catalyst about the nature of the site.

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APPENDIX

Conditions Required for the Existence of a Temperature of Maximum Rate

To ascertain this condition for a system obeying Eq. (1), we express k_1, k_2, and k_3 each in exponential form, giving in place of Eq. (2),

$$v = \frac{BP_s c_3 \exp(-Q_3/RT)}{P_s + \dfrac{c_2 \exp(-Q_2/RT) + c_3 \exp(-Q_3/RT)}{c_1 \exp(-Q_1/RT)}} \tag{14}$$

where c_i and Q_i are the pre-exponential factor and activation energy, respectively, of the k_i step. Rearranging,

$$\frac{1}{v} = \frac{1}{Bc_3} \exp\left(+\frac{Q_3}{RT}\right) + \frac{c_2}{P_s B c_1 c_3} \exp\left[\frac{(-Q_2 + Q_1 + Q_3)}{RT}\right] + \frac{1}{P_s B c_1} \exp\left(+\frac{Q_1}{RT}\right) \tag{15}$$

Differentiating with respect to T,

$$\begin{aligned}\frac{d(1/v)}{dt} = &-\left(\frac{Q_3}{Bc_3 RT^2}\right) \exp\left(+\frac{Q_3}{RT}\right) + \left(\frac{c_2}{P_s B c_1 c_3 RT^2}\right) \\ &\times (Q_2 - Q_1 - Q_3) \exp\left[\frac{(-Q_2 + Q_1 + Q_3)}{RT}\right] - \left(\frac{Q_1}{P_s B c_1 RT^2}\right) \exp\left(+\frac{Q_1}{RT}\right)\end{aligned} \tag{16}$$

If there is a temperature of maximum rate, T_m, there is a minimum in $1/v$ at T_m, whence $d(1/v)/dT = 0$. At T_m Eq. (16) becomes, after each term is multiplied by BRT_m^2,

$$\begin{aligned}-\left(\frac{Q_3}{c_3}\right) \exp\left(\frac{+Q_3}{RT_m}\right) + \left(\frac{c_2}{P_s c_1 c_3}\right) (Q_2 - Q_1 - Q_3) \exp\left[\frac{(-Q_2 + Q_1 + Q_3)}{RT_m}\right] \\ - \left(\frac{Q_1}{P_s c_1}\right) \exp\left(\frac{+Q_1}{RT_m}\right) = 0\end{aligned} \tag{17}$$

Using $k_i = c_i \exp(-Q_i/RT_m)$ and rearranging,

$$\frac{k_3}{k_2}\left[\frac{k_1 Q_3}{k_3} + \frac{Q_1}{P_s}\right] = Q_2 - Q_1 - Q_3 \tag{18}$$

Since every quantity in Eq. (18) is positive,

$$Q_2 > Q_1 + Q_3 \tag{19}$$

But $(Q_2 - Q_1)$ is the heat of desorption from active sites, the temperature coefficient of G. Therefore, the condition that there be a temperature of maximum rate is

Heat of desorption from active sites > true activation energy (20)

In the cumene-silica-alumina system this condition is not approached, since $(Q_2 - Q_1)$ is about one-half of Q_3. Obviously the condition expressed by Eq. (20) is a very stringent one.

Since the reactant molecules for the k_2 and k_3 steps are the same, the relative rates depend upon the activation energies. If Eq. (20) holds, the activation energy for the k_2 step is greater than that for the k_3 step, and therefore $k_2 < k_3$. Thus, wherever $k_3 < k_2$, as in the cumene-silica-alumina system, Eq. (20) cannot hold and there cannot be a temperature of maximum rate.