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The Preparation of Pt–Alumina Catalyst and Its Role in Cyclohexane Dehydrogenation

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The reactions of aqueous H_2PtCl_6 with alumina in the preparation of Pt–alumina catalyst, and some of the catalytic properties of the product, were investigated. The H^+ of H_2PtCl_6, a strong acid, reacts much more with alumina (to release an aluminum species to the solution) than does $PtCl_6^{2-}$. The two reactions are apparently independent of each other, and the Pt reaction is probably irreversible. The activities of a large number of Pt–alumina catalysts in the dehydrogenation of cyclohexane at 150°C, without added hydrogen, were measured. Activity depends upon Pt concentration, but not upon the mode of the preparation of the catalyst. For a given Pt concentration, reproducible Pt surfaces are not easily obtained. Even for the 130–150°C temperature range, where the equilibrium mixture contains only $\sim 1\%$ benzene, it is possible to eliminate the effect of the back reaction in order that the rate of dehydrogenation be obtained. Dehydrogenation was shown to be zero order, indicating a fully covered surface, at atmospheric pressure and 150°C. Therefore, the Arrhenius plots of the 130–150°C activities for several catalysts can be used to calculate the true activation energies. The number of active sites per unit area, calculated using these data in connection with transition-state rate theory, radically differs from the number determined using another method. From the discrepancy between the two methods of counting sites, it is deduced that benzene desorption is not the slow step and that cyclohexene and/or cyclodiene are probably intermediates in the dehydrogenation reaction.

INTRODUCTION

The widespread use of Pt–alumina as a catalyst has been responsible for interest in the nature of the catalyst and the detailed mechanism of the reactions it catalyzes. Concerning the nature of the catalyst, we report here the results of attempts to elucidate the reaction of aqueous H_2PtCl_6 (frequently used in preparing platinum catalysts) with the alumina surface under the conditions usually used in catalyst preparation. We have been interested in this surface reaction because we found earlier—in cracking (*1*), dehydrogenation (*2*), and dehydration (*3*)—that certain conclusions can sometimes be made about the catalytic reaction itself if the sequence of events in prior catalyst impregnation is understood. In the present case, however, we conclude (in agreement with the conclusions others have made recently) that the events which take place as H_2PtCl_6 reacts with alumina are related to the catalytic reaction of interest here, the dehydrogenation of cyclohexane without added hydrogen, only to the extent that these events determine the number of exposed Pt atoms in the finished catalyst.

In a recent publication (*4*) we showed it to be highly probable that less than 0.01% of the surface is active in many catalysts. It was, therefore, suggested that the active fraction, or site density, should be ascertained in catalytic studies wherever possible. By following this procedure in the present work, we have obtained an unexpected result and perhaps an insight into the nature of the reaction. We attempted to count the number of sites on the surface of Pt supported on alumina which are active in the dehydrogenation of cyclohexane. The number obtained does not agree with the number (reported elsewhere (*5*)) obtained using another method. The latter number, a large value, we accepted in our earlier work (*4*) and there is not reason to doubt it. Thus, as we show below, the conflict between the two values leads us to conclude that the reaction is not simple, and that benzene desorption is not the rate-limiting step.

EXPERIMENTAL METHODS

The bases used were Houdry 100S and 200S alumina pellets, whose pore volumes (water absorption) are, respectively, 0.45 and 0.32 ml g^{-1}, and whose BET surface areas (manufacturer's data) are, respectively, 75–85 and 150–180 m^2 g^{-1}. (All the activity measurements and all but a few impregnations, which are indicated, were carried out using 100S alumina.) The cyclohexane was Phillips' Research Grade, and the other chemicals were reagent grade. To minimize the non-uniform distribution of Pt which arises because H_2PtCl_6 reacts with and deposits on the first part of the particle it encounters (*6*, *7*), the alumina was ground to $-100 + 200$ mesh, dried in an oxygen stream at 500°C for 1 hr, and kept dry until it was impregnated.

Impregnation of the alumina powder was carried out by mixing an excess of H_2PtCl_6 solution with a weighed powder sample. After a contact period of the required length (see below), the solution was removed for analysis. The catalyst was prepared as follows: As much liquid as possible was drained off, and the still wet particles were contacted with absorbent paper until the superficial liquid was removed. The powder was dried at 120°C for 18 hr in air, calcined at 500°C in N_2 (20 min) and H_2 (2 hr), and resized to $-100 + 200$ mesh when cool.

The concentration of Pt in the solid was determined by analysis of the "equilibrium" and stock solutions. The method used was that of Ayres and Meyer (*8*), in which the concentration of the reaction product of $SnCl_2$ and H_2PtCl_6 is measured spectrophotometrically. The amount of Al^{3+} released by the solid upon reaction with solutions was determined by EDTA–$ZnCl_2$ titration of an aliquot, using Eriochrome Black T as indicator.

Catalytic activities were measured in two differential reactors, Reactors A and B, similar to those which were described earlier (*2*, *3*). Catalytic measurements were made at 150°C in Reactor A except where noted. In both reactors clock-driven syringes fed cyclohexane at the rate of 6.54 ml hr^{-1}. In Reactor A the product stream passed directly into a 4-ml loop attached to a gas sampling valve on a gas chromatograph whose column contained 10% ethofat on 30–60 Chrome T. In Reactor B the product stream was condensed (using a water condenser) before analysis by the same gas chromatograph. The condensation method was shown to be valid by a blank run, one in which the composition of a cyclohexane–benzene mixture proved to be the same before and after condensation. With Reactor B it was possible to add nitrogen to the cyclohexane after the cyclohexane was brought to the temperature of the reaction. The two gases were well mixed before passing over the catalyst. By varying the nitrogen flow rate the partial pressure of the cyclohexane, P_{CH}, was varied according to

$$P_{\mathrm{CH}} = \left(\frac{F_{\mathrm{CH}}}{F_{\mathrm{CH}} + F_{\mathrm{N}}}\right) P_T,$$

where F_{CH} and F_{N} are the gas flow rates of cyclohexane and nitrogen at the reaction temperature and P_T is the barometric pressure. Flow rates were measured at room temperature and corrected to F_{CH} and F_{N} by means of the ideal equation of state. (Calculation showed that the ideal equation of state is equivalent to the van der Waals equation in this range of temperature and pressure.) The catalytic activities reported are given in terms of moles of benzene produced per second per gram of catalyst.

To measure catalytic activities, 40 mg of the catalyst (except where another weight is indicated) was spread in a thin layer on a glass tray which was then put into the reactor next to a thermowell. Since our conversion level was always low, we were not able to observe the temperature drop commonly observed when cyclohexane first contacts the catalyst at a much higher temperature (*9*). The reactor chamber was flushed for 20 min with nitrogen under reaction conditions; cyclohexane flow was begun; and samples from the product stream were taken 10, 20, and 30 min after the first cyclohexane appeared at the product end of the reactor. The conversion to benzene was never higher than 0.5%, except for experiments in which we deliberately attempted to attain equilibrium. Activities reported (except where noted) are the averages of the three determinations.

Benzene was always the only hydrocarbon product, although our gas chromatograph can detect cyclohexene under the conditions of analysis. Cyclohexene has been found in the product of cyclohexane dehydrogenation over Pt–alumina only at conversions somewhat higher and space velocities much higher than those attained in our experiments (*10*).

RESULTS AND DISCUSSION

Impregnation

In Fig. 1 are shown the amount of Pt reacted with the surface, y_R, and the amount of Al^{3+} released, y_{Al}, both as a function of C_f, the concentration of H_2PtCl_6 solution in contact with alumina at the time indicated. (In both Fig. 1 and the discussion which follows, it is assumed that the species of aluminum in solution is not necessarily Al^{3+}, although for convenience that symbol is used.) Between 5 and 20 days the amount of Pt reacted did not change, but the amount of Al^{3+} released increased considerably.

The amount of Pt species which reacts with the surface is shown more extensively in Fig. 2. It is obvious from Figs. 1 and 2 that there is a very large scatter in the

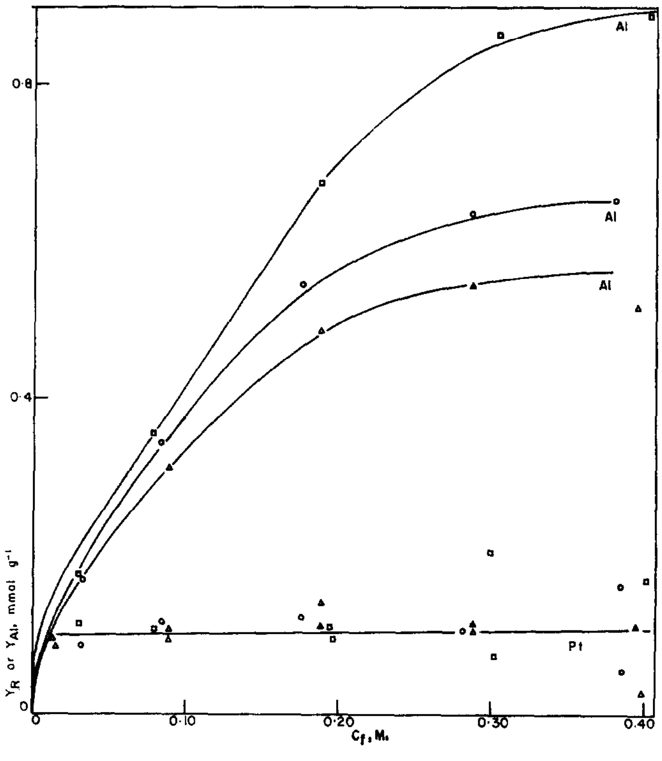

FIG. 1. Platinum reacted and aluminum released from alumina in H_2PtCl_6–Al_2O_3 reaction. △, contact time of 5 days; ○, 10 days; □, 20 days. (Twenty-two points, all lying close to the indicated curve, below $C_f = 5 \times 10^{-3} M$, are not shown.)

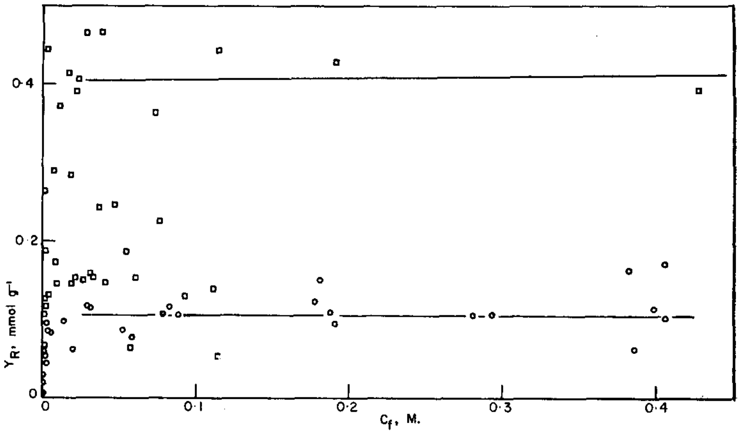

FIG. 2. Platinum released from 100S (○) and 200S (□) alumina in H_2PtCl_6-Al_2O_3 reaction.

reaction "isotherms," particularly with the higher area, more porous 200S alumina. Even so, several conclusions can be made.

(1) The scatter suggests the reaction is irreversible. That is, since the movement of Pt species within an alumina particle is slow (*6*, *7*), the reaction is probably sufficiently complex to warrant considering it irreversible for all practical purposes. In such a case, reproducing the amount of reaction for a given value of C_f would be difficult. Slow, irreversible reactions between alumina and aqueous solutions of transition metal compounds and of LiCl have been reported earlier (*3*, *11*, and references given therein). We have shown earlier that the presence of a time-invariant shoulder on a reaction isotherm indicates that the reaction is reversible (*11*), and we have used this criterion to aid in understanding complicated systems (*12*, *13*). We assume, given our scatter, that we have no evidence of a shoulder. Although a reversible reaction with a large equilibrium constant would prevent one from observing a shoulder, it is highly likely that our reaction is irreversible.

(2) The maximum amount of Pt species which reacts with alumina (Fig. 2) is probably proportional to the surface area of the alumina. We can conclude this even though at low C_f values the 200S data are rather unreliable for the reasons already cited. In our experiments, there was no evidence that the aluminas differed in any way other than area and pore volume.

(3) Since H_2PtCl_6 is a strong acid, stronger, in fact, than H_2SO_4 (*14*), it was of interest to find out if Al^{3+} was released merely because of the presence of the hydrogen ion. This question can be answered by studying the reaction of an acid which corresponds to salts which do not react extensively with the surface. We have shown that NaCl, KCl, and $CaCl_2$ react only slightly with alumina, and even then without release of Al^{3+} (*11*). Therefore, the reaction of HCl with alumina was examined. Ten ml of HCl was mixed with 2 g of 100S Al_2O_3; the initial HCl concentrations (*M*) and amounts of Al^{3+} (in mmole g^{-1}) released are, respectively: 0.1, 0.195; 0.1, 0.185; 1.0, 0.965; 1.0, 0.995 (cf. Fig. 1). Since HCl releases a large amount of Al^{3+}, it is suggested that H_2PtCl_6 releases Al^{3+} because of its acidity. Others have made conclusions about certain aspects of the reaction of H_2PtCl_6 with the surface of alumina. Krause's mechanism (*15*) allows at the most for one Al^{3+} to appear in solution for each platinum atom deposited, and Vergnaud *et al.* (*16*) showed for a 30-min contact of 200 ml of 0.012 *M* H_2PtCl_6 solution with 5 g of alumina powder that the Al^{3+} concentration in solution was 50 mg/liter, and still rising. Our minimum contact time was 5 days, and it is seen (Fig. 1) that the amount of Al^{3+} released is much higher than

that given by either Vergnaud *et al.* or Krause. (Vergnaud *et al.* showed that HCl (pH = 2.5) released in the same time about one-third as much Al^{3+} as in the H_2PtCl_6 experiment described.) A reaction which can account for the large amount of Al^{3+} removed compared to the amount of Pt species which reacted in our experiments is the following:

$$n\mathrm{Al(OH)_3(s)} + 3n\mathrm{H^+(aq)} + \mathrm{PtCl_6^{2-}(aq)} \rightarrow \text{“}\mathrm{PtCl_4}\text{”}\mathrm{(s)} + n\mathrm{Al^{3+}(aq)} + 2\mathrm{Cl^-(aq)} + 3n\mathrm{H_2O}, \quad \mathrm{(I)}$$

where $Al(OH)_3(s)$ denotes the hydrated surface of alumina, and “$PtCl_4$” (s) represents a surface species of tetravalent platinum in which chloride is adsorbed to preserve charge neutrality. (“Soluble platinum,” Pt(IV) complexed with the alumina surface, is known to exist before the catalyst has been reduced (*17*, *18*).) In (I) the amount of Al^{3+}–H^+ exchange is not controlled by the amount of $PtCl_6^{2-}$ which reacts. According to this model, a large amount of aluminum can react (and some of this aluminum would subsequently hydrolyze), with a marked increase in the pH of the solution, as a relatively small amount of Pt deposits. The ratio of reacted aluminum to reacted platinum is as high as nine in Fig. 1. We were not able to show conclusively that (I) is the correct model. Thus, in an attempt to determine the concentration of H^+ in a solution which had contacted alumina by means of a pH titration, using the special method for solutions containing $PtCl_6^{2-}$ we developed earlier (*14*), we could trust neither the pH measurement nor a pH titration because Al^{3+} interfered. The pH of a solution which had contacted alumina which was 0.187 *M* with respect to Pt (presumably as $PtCl_6^{2-}$) and 9.74×10^{-2} *M* with respect to Al^{3+} was 1.16 (measured by a glass electrode); in a pH titration (with NaOH) a break between pH 2 and 3 was observed. Since no such break was observed with H_2PtCl_6 solution free of Al^{3+}, we have neither proved nor disproved that the pH increase predicted by the suggested reaction actually occurred.

The platinum on the calcined catalyst consists not only of the Pt species which reacts with the surface, as given in Figs. 1 and 2, but also that which is dissolved in the pore-volume liquid just before the liquid is removed. The amount of solute in the impregnating liquid which is dissolved is large compared to the amount which reacts in systems containing alumina and aqueous solutions of rare-gas-type ions (*3*, *11*). With H_2PtCl_6 solutions, however, a large amount reacts in the time allowed and the amount which remains dissolved is relatively small. The difference between the total amount of Pt in the pores of 1 g of solid, y_T, and y_R (the ordinate of Figs. 1 and 2) is the amount dissolved, y_D. The relation between these different kinds of Pt is discussed later in connection with the catalytic activity of supported Pt.

Dehydrogenation of Cyclohexane

In the 130–150°C range, hydrogenation of benzene is greatly favored over the dehydrogenation of cyclohexane. Using standard thermochemical data along with the heat capacities of reactant and products, we calculate for dehydrogenation at 130 and 150°C values for $\log K_p$ (where K_p is the equilibrium constant using pressure units) of -7.64 and -6.20, respectively. An equation for K_p determined experimentally, reported by Patrikeev and Shakhova (*19*), indicates these values are -8.00 and -6.60. Therefore, at 150°C the equilibrium conversion is between 0.98% (for $\log K_p = -6.60$) and 1.24% (for $\log K_p = -6.20$). Two of the tests which convinced us our system functioned satisfactorily (carried out in Reactor B) are related to these equilibrium calculations. (1) In a system in which the conversion was 0.5% in our normal experiment, the conversion was below the observable level ($\sim$0.01%) when the partial pressure of hydrogen was as low as 0.2 atm. Calculation shows this result is consistent with the value of the equilibrium constant which we calculated. (2) In an attempt to approach equilibrium at 150°C by using larger and larger weights of a high-Pt catalyst (y_T = 0.414 mmole g^{-1}), we were able to obtain conversions of 0.87 to 0.98%, i.e., 89–100% (or 70–79%, depending upon the value of

K_p used) of the theoretical value. This is about what one would expect when it is attempted to approach equilibrium from one side in a flow system.

Most of the data we report is for activity determined at the 0.1 to .5% conversion level. Even at this level the activity of the catalyst increased with space velocity. This increase was observed when we measured activities as the liquid flow rate was held constant and the amount of catalyst used was decreased. We believe this increase occurred principally because of the effect of the back reaction (which Kraft and Spindler (*18*) found very important at much higher conversions at 350°C). It is also possible that product molecules occupied a significant fraction of the reaction sites with higher conversion and lower activity; this is another effect important even at higher temperatures (*20–22*). Interparticle diffusion might be important at the larger catalyst weights (*20*); intraparticle diffusion is not, however, a problem with $-100 + 200$ mesh Pt–alumina particles in this reaction at least as high as 430°C (*20*).

We assumed that these effects can be eliminated if the activity for an infinite space velocity is obtained. Such "corrected" activities were obtained (Fig. 3) by plotting measured activity against catalyst weight and extrapolating to zero weight. In the temperature study described below, it was necessary to estimate the error in the corrected activities and, therefore, the extrapolation shows the upper and lower limits of the extrapolated value. Although corrected activities are higher than uncorrected activities (i.e., those obtained using a catalyst weight of 40 mg), the data presented below show that neither the relation between the activities of different catalysts nor the temperature dependence of the activity of a given catalyst changes significantly when the correction is made.

The activities measured in Reactor A were somewhat lower than those measured in Reactor B. In both reactors there was a tendency for the activity to increase at first and then to decrease as the catalyst aged beyond 20 min. Typical results are given in Table 1, where the activity at various times

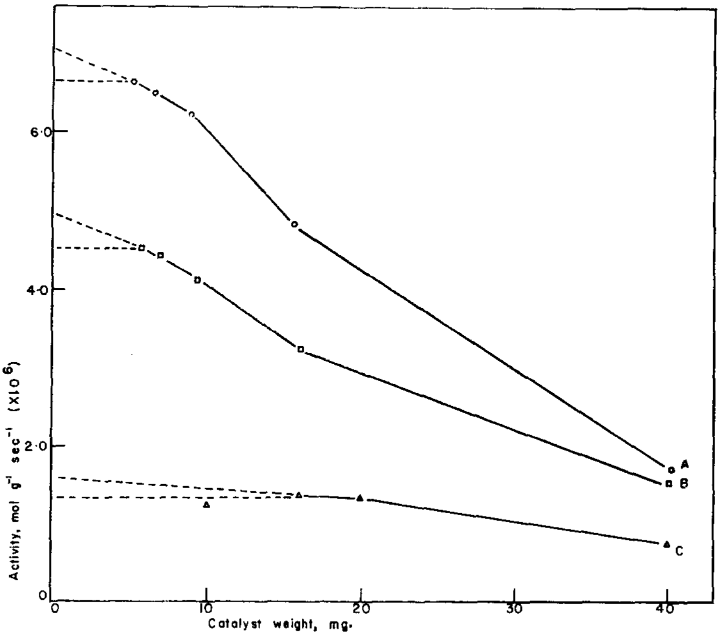

FIG. 3. Activity vs weight of catalyst used. Dashed-line extrapolation illustrates method of obtaining upper and lower limits of corrected value. (See text.) Catalyst, H_2PtCl_6 contact time in days, and y_T in mmole g^{-1}: A, 5, 0.15; B, 20, 0.086; C, 20, 0.054.

TABLE 1

COMPARISON OF REACTORS AND PRETREATMENTS[a]

Reactor	Pretreatment	Activity (mmole g^{-1} sec^{-1})($\times 10^6$)		
		10 min	2 min	30 min
A	H_2[b]	3.59	4.50	3.32
A	N_2[c]	3.63	4.90	3.98
B	H_2[b]	5.38	4.70	3.90
B	N_2[c]	5.27	5.42	4.65

[a] Catalyst used: 20 days H_2PtCl_6–100S Al_2O_3 contact time, with $y_T = 0.285$ mmole g^{-1}. For the runs 10-mg catalyst was used and P_{CH} was 1 atm.

[b] One hr flowing H_2 in reactor at 500°C, with cooling to 150°C, the reaction temperature, in flowing N_2.

[c] The normal treatment, as described in the Experimental Methods section.

after cyclohexane contacted the catalyst is given. We take these observations to mean that (1) the catalyst deactivates rapidly, at least partially because of poisons formed in side reactions catalyzed by acid sites associated with alumina or chlorine on alumina, and that (2) a small difference in reactor geometry can bring about a large difference (a) in the contact of product poisons with the active sites and (b) in the time which should be considered as the beginning of a run, i.e., the time at which $t = 0$, when the nitrogen atmosphere over the catalyst is effectively replaced by cyclohexane. Ritchie and Nixon (*23*) observed almost no aging of Pt–alumina in 90 min even though no hydrogen was added to the system, but presumably these results can be explained by the very high conversion (>95%) and high pressure (10 atm) of their experiments. Rohrer and Sinfelt (*24*) showed for the dehydrogenation of methylcyclohexane to toluene that the presence of added hydrogen markedly improved catalyst activity, with less aging, at the 20% conversion level. They suggested that hydrogen removes surface residues which act as poisons. It is probable that our results pertain to partially deactivated surfaces. (Since the question of partial deactivation could be thought to confuse the issue with respect to our results, we show later for the most sensitive case, i.e., where we measure the temperature coefficient of activity of a catalyst, that the differences between the two reactors are not important, cf. Table 2.)

TABLE 2

HEATS OF ACTIVATION AND APPARENT SITE DENSITIES[a]

Catalyst			Apparent site density Sites (cm^{-2})[c]		
y_T (mmole g^{-1})	Contact time (days)	E_a[b] (kcal $mole^{-1}$)	Ave	Max	Min
0.054	20	15.8[d]	1.6×10^9	6.1×10^9	4.0×10^8
0.054[e]	20[e]	15.9[f]	1.6×10^9	2.3×10^9	5.7×10^8
0.10	5	17.4[f]	1.4×10^{10}	5.8×10^{10}	3.5×10^9
0.14	20	16.4[d]	7.9×10^9	8.0×10^{10}	5.4×10^8
0.21	20	13.0[f]	7.4×10^7	2.6×10^8	2.1×10^7
0.23	10	19.6[d]	5.7×10^{11}	2.0×10^{12}	6.7×10^{10}

[a] Tabulated data are calculated using activities determined in Reactor A. With Reactor B, using corrected activities determined for the last catalyst in the table, E_a (in kcal $mole^{-1}$) and the apparent site density (in sites cm^{-2}) for the 10-, 20-, and 30-min samples are respectively, 16.4, 1.8×10^{10}; 19.1, 4.2×10^{11}; 18.9, 3.1×10^{11}.

[b] Derived from the average slope.

[c] Determined using the average, maximum, and minimum slopes.

[d] Heats and site densities are calculated using corrected activities.

[e] Same catalyst as previous catalyst.

[f] Heats and site densities are calculated using uncorrected activities; maximum and minimum site densities are calculated using the maximum and minimum slopes which can be constructed, using the experimental scatter, for curves like curves C and D of Fig. 9.

The question of the relation between the calcining procedure used in catalyst preparation and the state of Pt in the reacting system has often been a subject of interest. Since our catalysts were ordinarily stored in contact with air after reduction and subsequently heated only in nitrogen before a run was begun, we determined the effect of a second reduction, with the catalyst in the reactor at 500°C in hydrogen for 1 hr just prior to a 150°C run. The results are given in Table 1. We conclude for our normal run that the catalytic Pt was in approximately the same state it would have been had there been reduction just before the run was started. If our finished catalysts contain any "soluble" Pt, Pt supposed to be inactive in dehydrogenation (*17*), the amount of such Pt does not decrease significantly with a second reduction.

The Order of the Reaction

The activities of three catalysts as a function of the partial pressure of cyclohexane, with nitrogen as the diluent, measured in Reactor B, are given in Fig. 4. We conclude that there is at most a very small pressure effect at 150°C (and consequently, at lower temperatures as well) in the vicinity of $P_{CH} = 1$ atm. Thus, the reaction is zero order or very close to zero order. In what follows, we assume that under the conditions of our reaction that the reaction is essentially zero order and that the active part of the Pt surface is fully covered. Since coverage decreases with increasing temperature, it is expected for some sufficiently higher temperature that the order would be found to be greater than zero. Accordingly Li P'ang *et al.* (*25*) found the reaction at low benzene partial pressure to be first order at 300°C and Martyshkina *et al.* (*26*) found the reaction to be first order at 310–340°C when Pt is supported on silica gel. With methylcyclohexane, which might be expected to adsorb more strongly, Sinfelt *et al.* (*27*) found the dehydrogenation reaction to be zero order in reactant partial pressure even at 315–372°C.

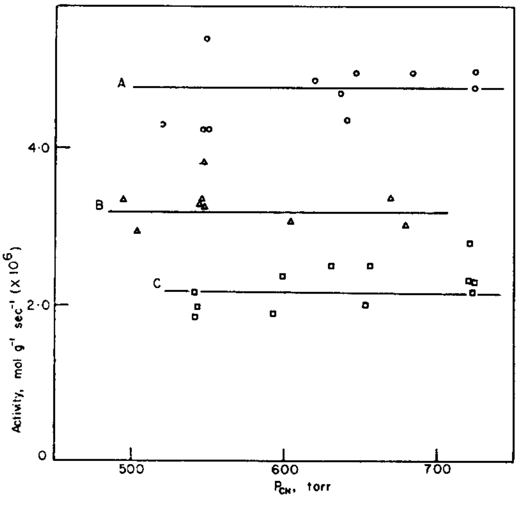

FIG. 4. Activity vs P_{CH}. Catalyst, H_2PtCl_6 contact time in days, and y_T in mmole g^{-1}: A, 20, 0.29; B, 5, 0.23; C, 20, 0.054. 10 mg samples of catalyst used.

Since the cyclohexane reaction is zero order, the rate of reaction is not determined by the rate of adsorption of cyclohexane gas on active sites. Thus, the effects described in the next and the last section are related

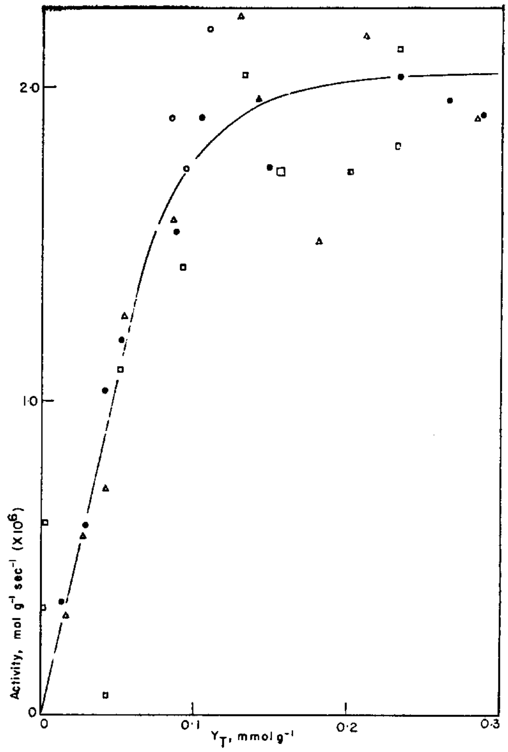

FIG. 5. Uncorrected activity vs y_T. ●, 5 days contact time; □, 10 days; △, 20 days; ○, 23 days.

to either a surface process or a desorption process; and for reasons outlined in the last section we conclude that a surface process is the slow step.

Activity and Catalyst Preparation

Uncorrected activities of a series of catalysts are given in Figs. 5, 6, and 7 as a function of y_T, y_R, and y_D, respectively. Corrected activities as a function of y_T are given in Fig. 8 for representative catalysts of this group. Plots of corrected activities as a function of y_R and y_D, i.e., plots analogous to Figs. 6 and 7, are not given because these plots differ from Figs. 6 and 7 in about the same way Fig. 8 differs from Fig. 5.

Five facts shown in Figs. 5, 6, 7, and 8 are of special interest. (1) The correlation between uncorrected activity and y_T (Fig. 5) is poor above $y_T \sim 0.1$ mmole g^{-1}. (2) In this y_T range, the correlation between corrected activity and y_T is even worse (Fig. 8). (3) Both corrected and uncorrected activities are approximately proportional to y_T below $y_T = 0.1$ mmole g^{-1} and, to the extent that there is correlation above $y_T = 0.1$ mmole g^{-1}, the activity is constant in this range. (4) The sum of the reacted (Fig. 6) and the unreacted (Fig. 7) Pt is the total Pt (Fig. 5), and a comparison of these three figures suggests strongly that the unreacted Pt contributes little to the activity. (5) The time of H_2PtCl_6 contact had apparently no effect on the activity. It was noted above that the amount of Pt deposited did not vary with time, but that the amount of Al^{3+} released to the solution exhibited a strong time dependence.

We suggest that these results are to be expected. First, the activity in Fig. 5 might be expected to approach a constant value for two reasons. At higher activities the effect of the back reaction (and possibly, product poisoning and interparticle diffusion) is greater, and a leveling off occurs. Second, there is sufficient evidence (*5, 18, 28*) to prove that the activity of Pt–alumina catalysts is proportional to the Pt area, not

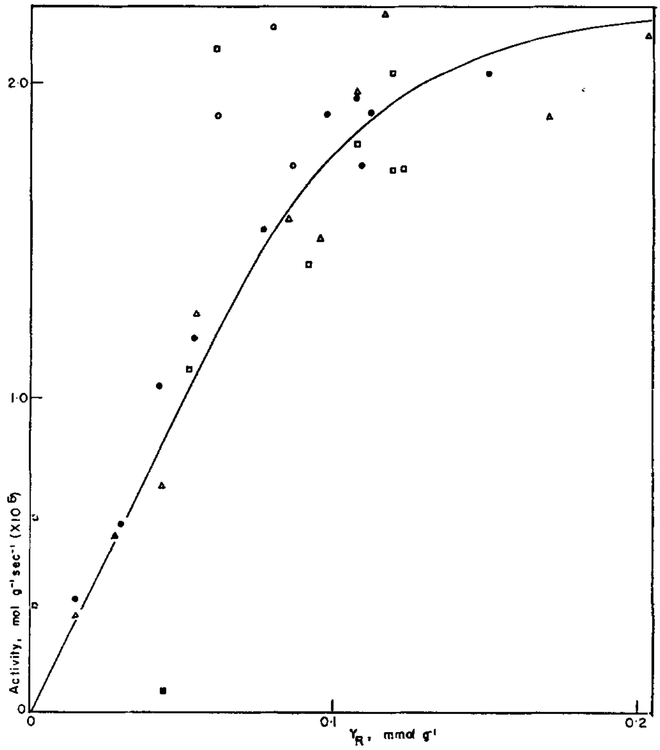

FIG. 6. Uncorrected activity vs y_R. Same contact times as in Fig. 5.

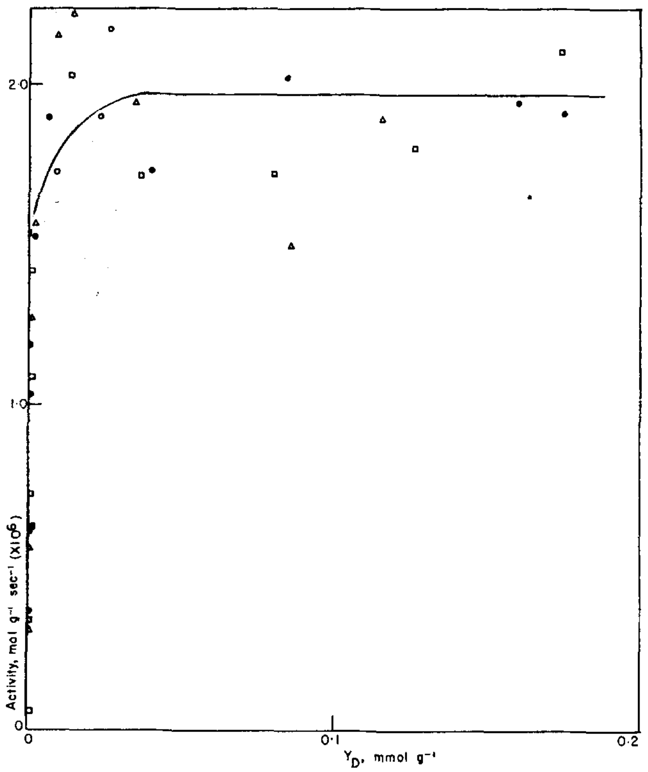

FIG. 7. Uncorrected activity vs y_D. Same contact times as in Fig. 5.

Pt weight, although the latter is used in Figs. 5, 6, 7, and 8. (We were unable to measure the Pt areas of our samples.) Since Pt area increases slowly with y_T at high y_T values, a corresponding slow increase in activity in that y_T range is expected. In the calcining process unreacted Pt should sinter much more easily than the Pt which was originally attached to the surface. The scatter in the "flat" part of Fig. 5 thus reflects the difficulty of producing identical Pt areas for the same amount of Pt in the (probably) irreversible, heterogeneous H_2PtCl_6–alumina reaction. The first reason given for the leveling out in Fig. 5, the effect of the back reaction, does not hold for the corrected activities. The other reason, the area effect, still holds, and we can conclude that the scatter in Fig. 8 is a better measure of the difficulty of reproducing areas for a given Pt weight than is the scatter in Fig. 5. In other words, the dif-

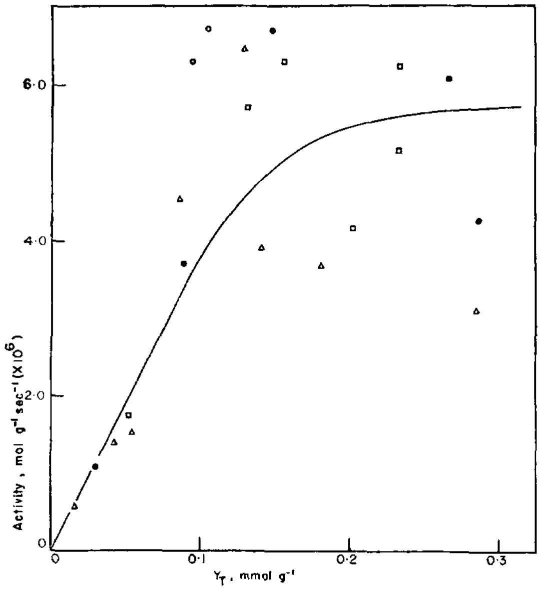

FIG. 8. Corrected activity vs y_T. Same contact times as in Fig. 5.

ference between Figs. 5 and 8 arises because the back reaction reduces the measured activity of the most active catalysts the most, and differences between the most active catalysts tend to disappear.

The shapes of the curves and the scatter in Figs. 5, 6, 7, and 8 are thus consistent with the idea that activity for the dehydrogenation of cyclohexane is proportional only to the area of the platinum in the reduced catalyst, and is related to the method used to prepare the catalyst only to the extent that the method determines the area. The lack of an effect of the H_2PtCl_6–alumina contact time also fits into this picture. With increasing contact time the amount of Pt species which deposits does not change while the amount of Al^{3+} released increases. Very likely the release of Al^{3+} affects the alumina but not the area of Pt, and consequently the activity is not related to contact time. Another indication that the nature of the alumina is not important in this reaction is the conclusion of Swift *et al.* (*29*), who showed that Pt behaved the same in η–alumina and γ–alumina. Doping the catalyst might, however, alter it enough to affect its tendency to catalyze the dehydrogenation of cyclohexane (*30*).

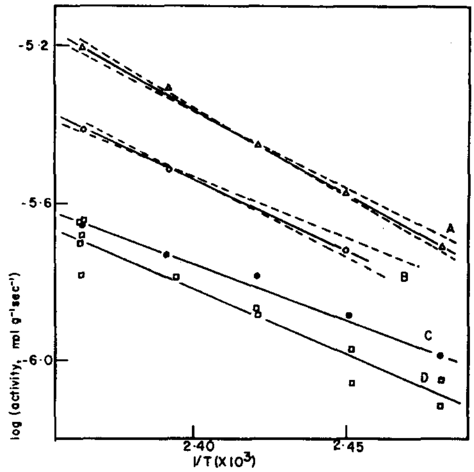

FIG. 9. Arrhenius plots for four catalysts. Catalyst, H_2PtCl_6 contact time in days, and y_T in mmole g^{-1}: A, 10, 0.23; B, 20, 0.14; C, 20, 0.21; D, 5, 0.10. For catalysts A and B, corrected activities are given and the maximum and minimum slopes shown (dashed lines) are obtained according to the method described in the text. Uncorrected activities are given for catalysts C and D.

The Temperature Coefficient of the Surface Reaction

Representative Arrhenius plots of the rates, both corrected and uncorrected, are given in Fig. 9. The uncertainty in how to extrapolate to obtain the corrected activity (the uncertainty is illustrated in Fig. 3) gives rise to an uncertainty in the ordinates of Fig. 9 for the catalysts whose corrected activities are reported. Therefore, there is an uncertainty in the slopes of the Arrhenius plots, and the dashed lines associated with the plots show the limits of this uncertainty. The heats of activation derived from the Arrhenius slopes of all our temperature studies are given in Table 2. Using either corrected or uncorrected activities, maximum, minimum, and average slopes can be obtained and calculations based on these three slopes (see below) were made. The data in Table 2 indicate that the heat of activation is between 13 and 23 kcal mole^{-1}. Since the reaction is zero order, this value is a "true" heat of activation, i.e., a heat of activation which does not include the adsorption step. This value is in fair agreement with those reported by others. Around 300°C Li P'ang *et al.* (*25*) had to distinguish between the true activation energy and the observed, the apparent, value; a true value of 16.5 kcal mole^{-1} was reported. (The apparent value was somewhat higher because benzene adsorption was a complication.) Popescu and Nicolescu (*21*) reported an apparent value of 11.4 kcal mole^{-1} between 460 and 500°C. At a temperature as high as 460°C, where the surface is less than fully covered, the absolute value of the Arrhenius slope and, therefore, the apparent activation energy, are expected to be smaller than the slope and true activation energy we obtained.

Kraft and Spindler (*18*) reported a low-version, no back-reaction rate of 1.6×10^{16} molecules of cyclohexane reacted at 350°C per second per square centimeter of Pt supported on alumina. Although the reaction is more than zero order at 350°C, this value can be compared with ours if the surface is at least largely covered at 350°C. Assuming the heat of activation to be 16.3 kcal mole^{-1} (the average value determined on Reactor A, Table 2), the 150°C rate corresponding to the above rate is 1.0×10^{14} molecules sec^{-1} cm^{-2}. We assume the Pt area of our most active catalysts to be the order of 1 m^2/g of Pt–alumina. The corrected activity on the level part of the curve in Fig. 8 is then 3.4×10^{14} molecules sec^{-1} cm^{-2}, in reasonable agreement (in view of the assumptions made) with the 150°C value we calculate for Kraft and Spindler.

Since the dehydrogenation reaction is zero order, the reaction can be further analyzed with the use of the equation for the rate derived from transition state theory (*31*).

$$\text{Rate} = c_a \frac{kT}{h} e^{\Delta S_a/R} e^{-E_a/RT} \qquad (1)$$

where c_a is the number of active sites per unit area, k and h are the Boltzmann and Planck constants, respectively, T is the temperature, R is the gas constant, and ΔS_a and E_a are the entropy and heat of activation, respectively. (The transmission coefficient is usually assumed to be approximately unity. Since both the reactant and the activated complex are assumed to be adsorbed, their partition coefficients cancel and are not included in the equation.) We have discussed the use of this equation earlier (*4*). We assume that the area of Pt in our catalysts is ~ 1 $\text{m}^2/\text{g-cat}$, since this is the order of the area found for similarly treated catalysts by Maat and Moscou (*32*) and Kraft and Spindler (*18*). Tentatively assuming $\Delta S_a = 0$, an assumption often made with unimolecular surface reactions because the molecule loses a large part of its entropy when it is adsorbed, we calculate the apparent site densities listed in Columns 4–6 of Table 2.

If every surface Pt were part of an active site, there would be the order of 10^{14} sites cm^{-2} (*33*). The most probable value of the apparent site density, taken from Table 2, is $\sim 10^9$ sites cm^{-2}. Although we concluded earlier (*4*) that the site densities of many catalysts are indeed quite small—perhaps 10^{11} cm^{-2} or less in 20–40% of a group of representative catalysts—there are good reasons to believe that the site density of Pt supported on alumina is not small in the dehydrogenation of cyclohexane. Boudart has argued convincingly that this reaction over supported Pt is a *facile* reaction, i.e., one in which the entire metal surface is expected to be active. (For a survey of the problem, see Ref. (*5*).) Aben *et al.* (*33*), using transition state theory, have shown that assuming a site density of 10^{14} cm^{-2} is quite consistent with a reasonable model which they propose for the hydrogenation of benzene. We suggest, then, that the values for the site density given in Table 2 are too small. If Eq. (1) holds and if c_a is $\sim 10^{14}$ cm^{-2} instead of $\sim 10^9$ cm^{-2}, then the difficulty would disappear were ΔS_a to be -23 e.u.

But in both surface and desorption reactions the reactant and the activated complex are adsorbed, and it is doubtful that the entropy loss upon activation can be as large as 23 e.u. Thus, it is quite likely that the situation is more complicated than we have assumed above, and that Eq. (1) is not adequate for an analysis of the system being studied. It, therefore, seems that the slow step cannot be desorption of benzene, a step which would be relatively uncomplicated and which would presumably take place on all the reaction sites. Although the situation is not likely to be different at the conditions Kraft and Spindler used (350°C, high conversion, and a 3:1 H_2:cyclohexane ratio), they did assume that at their conditions the desorption of benzene is the slow step (*18*). Also Sinfelt *et al.* (*27*) concluded that the slow step in the dehydrogenation of methylcyclohexane between 315 and 372°C over Pt–alumina is the desorption of toluene. In this connection, it is of interest to note that Aben *et al.* (*33*) seem to prove that the slow step in the reverse reaction, the hydrogenation of benzene, is a surface step. Similarly, Katsuzawa *et al.* (*34*) find their results for the reverse reaction to be consistent with the Rideal–Eley mechanism.

We suggest, therefore, that the slow step or steps in the dehydrogenation of cyclohexane over Pt–alumina are associated with one or more reactions in which both reactant and product are adsorbed. Since the reaction is apparently more complex than the simple surface reaction for which Eq. (1) was written, it is quite possible that the complexity is the formation of one or more intermediates. Using a very high space velocity and working at high conversions, Haensel *et al.* (*10*) did detect cyclohexene in the product when cyclohexane was dehydrogenated over Pt–alumina. Smith and Prater (*35*) argued that the data of Haensel *et al.* did not prove impossible a cyclic mechanism, i.e., one in which benzene is formed *directly* from *either* cyclohexane or cyclohexene. The same conclusion can be made concerning the results of Block (*36*), who showed for the dehydrogenation of cyclohexane occuring at a Pt tip in a mass spectrometer that cyclohexene, cyclohexadiene and benzene are all products.

Our data indicate that there is an intermediate, and that the cyclic mechanism does not hold. The intermediate may be cyclohexene; cyclohexadiene is not ruled out. Obviously, the argument depends partially on what one means to exclude when it is stated that benzene is not formed "directly" from cyclohexane, in the sense that the term was used above in connection with the cyclic mechanism discussed by Smith and Prater.

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REFERENCES

1. Maatman, R. W., Leenstra, D. L., Leenstra, A., Blankespoor, R. L., and Rubingh, D. N., *J. Catal.* **7,** 1 (1967).

2. Maatman, R. W., Blankespoor, R. L., Ligtenberg, K., and Verhage, H., *J. Catal.* **12,** 398 (1968).

3. Maatman, R. W., and Vande Griend, L. J., *J. Catal.* **20,** 238 (1971).

4. Maatman, R. W., *J. Catal.* **19,** 64 (1970).

5. Boudart, M., *Advan. Catal. Relat. Subj.* **20,** 153 (1969).

6. Maatman, R. W., *Ind. Eng. Chem.* **51,** 913 (1959).

7. Maatman, R. W., and Prater, C. D., *Ind. Eng. Chem.* **49,** 253 (1957).

8. Ayres, G. H., and Meyer, A. S., Jr., *Anal. Chem.* **23,** 299 (1951).

9. Potapova, A. A., *Zh. Obsch. Khim.* **29,** 421 (1959).

10. Haensel, V., Donaldson, G. R., and Riedl, F. J., *Proc. Int. Congr. Catal., 3rd, 1964* **1,** 294 (1965).

11. Williams, K. C., Daniel, J. L., Thomson, W. J., Kaplan, R. I., and Maatman, R. W., *J. Phys. Chem.* **69,** 250 (1965).

12. Maatman, R. W., Geertsema, A., Verhage, H., Baas, G., and Du Mez, M., *J. Phys. Chem.* **72,** 97 (1968).

13. Maatman, R. W., and Kramer, A., *J. Phys. Chem.* **72,** 104 (1968).

14. Maatman, R. W., and Addink, C. J., *J. Catal.* **15,** 210 (1969).

15. Krause, A., *Nature (London)* **183,** 1615 (1959).

16. Vergnaud, J. M., Rey-Coquais, B., Buathier, B., and Neybon, R., *Bull. Soc. Chim. Fr.,* 3881 (1968).

17. Bursian, N. R., Kogan, S. B., and Davydova, Z. A., *Kinet. Katal.* **8,** 1283 (1967).

18. Kraft, M., and Spindler, H., *Proc. Int. Congr. Catal., 4th, Moscow, 1968* **3,** 1252 (1969).

19. Patrikeev, V. V., and Shakhova, S. K., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1365 (1963).

20. Lago, R. M., Prater, C. D., and Weisz, P. B., *Amer. Chem. Soc., Div. Petrol. Chem., Prepr., Gen. Pap.* **1,** 87 (1956).

21. Popescu, A., and Nicolescu, I. V., *Analele Univ. "C. I. Parhon," Ser. Stiint. Nat.* **10,** No. 30, 119 (1961).

22. Mencier, B., Figueras, F., De Mourges, L., and Trambouze, Y., *C. R. Acad. Sci., Paris, Ser. C* **266,** 596 (1968).

23. Ritchie, A. W., and Nixon, A. C., *Ind. Eng. Chem., Process Des. Develop.* **7,** 209 (1968).

24. Rohrer, J. C., and Sinfelt, J. H., *J. Phys. Chem.* **66,** 1193 (1962).

25. Li P'ang, et al., *Acta Foculio-Chim. Sinica* **6,** 175 (1965); (*Chem. Abstr.* **65,** 18379d (1966)).

26. Martyshkina, L. E., Strel'nikova, Z. V., and Lebedev, V. P., *Vestn. Mosk. Univ. Khim.* **21,** 21 (1966).

27. Sinfelt, J. H., Hurwitz, H., and Shulman, R. A., *J. Phys. Chem.* **64,** 1559 (1960).

28. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11,** 35 (1968).

29. Swift, H. E., Lutinski, F. E., and Tobin, H. H., *J. Catal.* **5**, 285 (1966).

30. Pfeil, W., *Z. Phys. Chem. (Leipzig)* **243**, 52 (1970).

31. Glasstone, S., Laidler, K., and Eyring, H., "The Theory of Rate Processes," p. 376. McGraw-Hill, New York, 1941.

32. Maat, H. J., Moscou, L., *Proc. Int. Congr. Catal., 3rd, 1964* **2**, 1277 (1965).

33. Aben, P. C., Plateeuw, J. C., and Stouthamer, B., *Proc. Int. Congr. Catal., 4th, Moscow, 1968* **2**, 543 (1969).

34. Katsuzawa, H., Kobayashi, J., and Higuchi, I., *Kogyo Kagaku Zasshi* **72**, 823 (1969).

35. Smith, R. L., and Prater, C. D., *Chem. Eng. Progr.* **63**, 105 (1967).

36. Block, J., *Proc. Int. Congr. Catal., 4th, Moscow 1968* **4**, 1601 (1969).