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The Role of Pd-Alumina Catalyst in the Dehydrogenation of Cyclohexane

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To study the dehydrogenation of cyclohexane to benzene in the presence of Pd-alumina at 175–210°C, it was tentatively assumed that the reaction proceeds via a mechanism whose slow step is a monomolecular decomposition of reactant on the catalyst surface. An apparent value of the site density was then calculated, using transition state theory and the observed, zero order reaction rate and activation energy (15.5 kcal mole^{-1}). The value obtained, $\sim 10^9$ sites cm^{-2}, seems to be unrealistically low in view of other results on similar systems. Even though the tentative model is probably incorrect, the calculation does aid in elucidation of the reaction. Thus, it is shown that the reaction is much more complicated than suggested by the model and the results are consistent with evidence that cyclohexene is a necessary intermediate.

INTRODUCTION

Of the many reactions catalyzed by Group VIII metals, the dehydrogenation of cyclohexane to benzene is among the easier to study. We reported earlier on Pt-alumina catalysis of this reaction (*1*) and the present report describes our study of this reaction using Pd-alumina. In both studies the purpose was to elucidate the reaction.

The method used in the Pt-alumina study utilized the tentative assumption that there is a slow step in the reaction, a surface step involving one molecule of cyclohexane. Then, if the active surface is fully covered, i.e., if the reaction is zero order in partial pressure of cyclohexane, we have from transition state theory (*2*),

$$\text{rate} = c(kT/h)\exp(\Delta S_a/R)\exp(-\Delta E_a/RT), \qquad (1)$$

where c is the number of sites per unit area, the site density, k and h are the Boltzmann and Planck constants, respectively, T is the temperature, R is the gas constant, and ΔS_a and ΔE_a are the entropy and heat of activation, respectively. For a monomolecular surface step, where the reactant and the activated complex are both absorbed, ΔS_a should be small enough to permit neglecting it. (In the product desorption step as with the step just described, both reactant and activated complex are adsorbed and Eq. (1) applies. Therefore Eq. (1) with $\Delta S \approx 0$, applies here also and the model does not distinguish between these two steps.) If the zero order rate is determined at various temperatures, ΔE_a can be determined from an Arrhenius plot and c can be obtained using Eq. (1). Such a value of the site density should agree with the value obtained by Boudart (*3*), who showed that the whole platinum surface is active in this reaction. That is, if the tentative assumption is correct, we should obtain a value of $\sim 10^{14}$ sites cm^{-2} for c. We actually obtained 10^9 sites cm^{-2}, and concluded that the reaction is more complex than assumed in the simple model corresponding to the tentative assumption. Specifically, it seems likely that cyclohexene and/or cyclohexadiene is a necessary intermediate. Equation (1) would then not be usable. The same procedure, with the same tentative assumption, is used in the present work with Pd-alumina.

There is some reason for making use of this somewhat unusual procedure to determine whether or not the reaction follows a simple path. We have shown, using transition state theory as well as other, independent methods, that it is probable that values of site densities on the surfaces of many catalysts are very low, perhaps 10^{11} sites cm^{-2} (i.e., 0.01% coverage) or less (*4*, *5*). This conclusion, if correct, can aid in the solution of some problems. For example, the unexplained gap between the supposedly low turnover numbers of inorganic catalysts and the high ones for enzymes may be removed, and the "impossibly" high entropies of activation which have been calculated for some reactions may be artifacts. Of special interest in the present work are those attempts to obtain values of site densities which indicate precisely what was indicated in the Pt-alumina case, viz, the incorrectness of the assumption underlying the attempt. Attempts to obtain values of site densities can be revealing even when those attempts fail.

The Pd-alumina study was carried out between 175 and 225°C even though the back reaction, hydrogenation of benzene, is much favored at these relatively low temperatures. The low temperature range was chosen so that the reaction would be zero order in cyclohexane partial pressure at atmospheric pressure, a condition necessary for the determination of c from Eq. (1).

When Pd catalysts are used in the presence of H_2, it is often necessary to decide whether H_2 dissolves in Pd enough to alter the system in some indeterminate manner. The problem is apparently minimized in the present study, where, except for one set of experiments, H_2 is present only as a reaction product. It has been shown (*6*) that H_2 does not dissolve in the Pd of Pd-alumina if the substance is less than 1% Pd, as ours was. In addition, the amount of H_2 produced in the experiments upon which we base our side density calculation was always very small.

EXPERIMENTAL METHODS

The Pd-alumina catalyst was prepared by impregnating Houdry 100S alumina pellets (pore volume, 0.45 ml g^{-1}; surface area, 75–85 m^2 g^{-1} (BET); all manufacturer's data) with $PdCl_2$ solution. The catalyst was dried for 27 hr at 125°C in air. The product was then ground to $-100 + 200$ mesh and reduced at 500°C in H_2 for 2 hr. Following reduction the catalyst was cooled in N_2 and stored for later use. By spectrophotometric analysis of the $PdCl_2$ solution before impregnation and of the equilibrium solution after impregnation, the catalyst was found to contain 0.81 wt% Pd. An EDTA titration of the equilibrium solution to determine the total of the Pd and the Al species present indicated, by comparison with the spectrophotometric results, that $PdCl_2$ impregnation did not release a measurable amount of Al from the surface.

Phillips Research Grade Cyclohexane was used throughout.

The two catalytic reactors used have been described (*1*). The absolute values of the activities obtained from runs in the two reactors for a given set of conditions were not quite the same. Therefore in the study of a given variable, such as the partial pressure of cyclohexane, only one reactor was used. The total pressure was always atmospheric pressure, i.e., 725–10 Torr (1 Torr = 133.3 N m^{-2}).

In a catalytic run, a weighed amount (usually 10 mg) of the previously reduced catalyst was introduced on a glass tray into the reactor at approximately the desired temperature with N_2 (purified over Cu) passing through the reactor. After N_2 flush of at least 10 min, the cyclohexane flow (always 1.81×10^{-3} ml liquid sec^{-1}) was begun, using a syringe driven by a Sage pump. Samples of the product were taken by either a gas sampling valve or, as a liquid, from a water condenser, 10–15 min after cyclohexane entered the preheater and at intervals of approximately 10 min thereafter. All analyses of product mixtures were made by gas chromatography, using a column of 10% Ethofat on 60–80 chrome T. All conversions were low, usually $<0.5\%$.

When the cyclohexane vapor was diluted with hydrogen, the hydrogen was purified by passing through a Deoxo unit followed by a drying tube. The partial pressures of cyclohexane and hydrogen were calculated

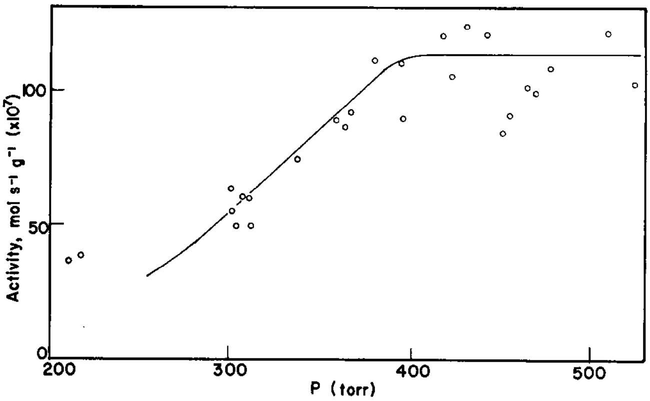

FIG. 1. Catalyst activity at 225°C as a function of partial pressure of cyclohexane, with hydrogen as diluent.

from the values of the two flow rates and the barometric pressure.

RESULTS

The catalyst activity decreased by about 20%/hr when H_2 was not present. However, the first activity measured, at 10–15 min, was usually rather low. Presumably the cyclohexane had not sufficiently displaced the nitrogen which was in the reactor before the beginning of the run. Therefore, the activities which are used are interpolated values, at 25 min in the studies of the effects of catalyst mass and cyclohexane partial pressure and 30 min in the study of the temperature effect.

In the temperature range of our experiments, 175 to 225°C, the back reaction, hydrogenation of benzene, predominates. To insure that our results pertained to the forward reaction, activity as a function of catalyst weight was extrapolated to zero weight, holding the cyclohexane flow rate constant. [This procedure and other procedures referred to in this section are similar to those we used in investigating Pt-alumina catalyzed dehydrogenation of cyclohexane (1).] In a series of 12 runs at 225°C, with a cyclohexane partial pressure of 0.4 atm where the diluent was H_2 and with the catalyst weight varying from 6 to 106 mg, it was shown that the 10 mg value differed from the extrapolated value by 2.5% at most. In all subsequent work activities were obtained using 10 mg of catalyst.

Catalyst aging was evidently due to poison accumulation on the catalyst. Since poison may have accumulated in other parts of the reactor, it was cleaned daily by use of flowing oxygen at 450°C for 16 hr.

In Fig. 1 catalyst activity at 225°C is shown as a function of the partial pressure of cyclohexane, with H_2 as diluent. The points above 400 Torr are apparently randomly scattered around a horizontal straight line. (At lower partial pressures of cyclohexane the activity is lower either because the reaction is no longer zero order, or the back reaction becomes important.) Therefore, it is highly probable that the reaction is zero order at atmospheric pressure at 225°C, and even more probable that it is zero order between 175 and 210°C, the region in which the temperature coefficient data were obtained. The temperature data are shown in an Arrhenius plot in Fig. 2.

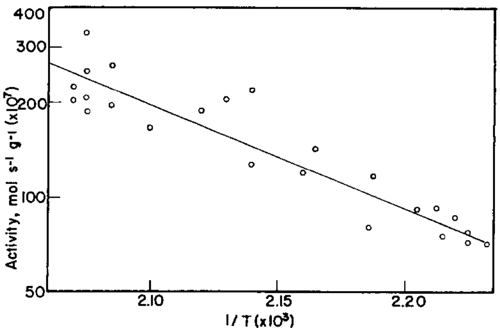

FIG. 2. Arrhenius plot of catalyst activity between 175 and 210°C.

The plot is linear with a correlation coefficient of −0.93. From the slope of the line the heat of activation is calculated to be 15.5 kcal/mole.

Gas chromatographic analysis of the product mixture indicated a trace amount of a substance which was apparently cyclohexene. This result may be in agreement with the results of Minachev and Garanin (*7*), who found 3–8% cyclohexene at conversions >80% in cyclohexane dehydrogenation using Pd-fluorinated alumina.

DISCUSSION

Since *c* in Eq. (1) is to be calculated for the number of sites per unit area of metal, the Pd area in our catalyst is needed. This value was not obtained directly, but it can be assumed that it is within an order of magnitude of 1 m^2/g of Pd-alumina. We showed (*1*) that a similar assumption can be made for Pt-alumina at this metal concentration, and Aben, Plateeuw, and Stouthamer (*8*) showed by H_2 chemisorption that a given amount of supported metal corresponds roughly similar dispersions in Pd-alumina and Pt-alumina catalysts. The approximate area assumption we make serves our purpose and the considerable discussion in the literature concerning the best method to obtain accurate Pd areas is not relevant. If it can be assumed that $\Delta S_a \approx 0$, Eq. (1) gives for *c*, with a rate of 1.75×10^{-5} mole benzene produced/sec/g of Pd-alumina at 200°C and $\Delta E_a = 15.5$ kcal mole^{-1}, a value of 10^8–10^{10} sites cm^{-2} Pd.

Before the consequences of our calculation are discussed, two comments must be made. First, since H_2 was not added in the temperature coefficient experiments, there can be appreciable deactivation of the fresh surface after cyclohexane contacts it but before our first activity measurements are made. We observed deactivation, as reported above, as have others in somewhat similar systems (*9*, *10*). Yet in view of the rate of deactivation that we observed, ~20% per hour, it seems unlikely that the activity decreased several orders of magnitude during the first minutes. In any case, our conclusions concerning the catalyst surface and the reaction which it catalyzes pertain to the active surface which exists between 175 and 210°C after 30 min of contact with cyclohexane without added H_2.

Second, the question of hydrogen "spillover" could arise in determining what area of catalyst should be used in order to apply Eq. (1). Several workers have discussed for the reverse reaction, the hydrogenation of benzene, the possibility that active sites are created by the migration of hydrogen from Pd to the alumina surface (*11*). If this effect is real and active sites in the dehydrogenation reaction are created in our system by the H_2 which is produced, the effective catalyst area is increased. Then the value of *c* which is calculated using Eq. (1) is even smaller than that obtained above and the only effect is to widen the gap between the calculated value and the value corresponding to a filled surface, 10^{14}–10^{15} sites/cm^2. Thus, the gap is in any case large, and the spillover question does not affect any argument which depends on the size of the gap.

Aben, Plateeuw, and Stouthamer (*8*) found for both Pt and Pd catalysts that a reaction model for the hydrogenation of benzene based on a high site density (one in which it is assumed that all surface atoms take part) is consistent with their experimental results. If their conclusion is correct, then it seems that the site density of our Pd-alumina catalyst is actually high in the dehydrogenation reaction. Then our reaction system is more complicated than assumed in the simple, tentative model. One might expect that the complication is that there is at least one intermediate, including cyclohexene, and we did find cyclohexene. Ryashentseva, Minachev, and Avaev (*10*) also postulated an intermediate in the dehydrogenation of cyclohexane over Pd-alumina. Pd-alumina is known to catalyse the dehydrogenation of cyclohexene (*12*) and the disproportionation of cyclohexene to benzene and cyclohexane could be closely related to, if not the same reaction as, the dehydrogenation of cyclohexene. If cyclohexane dehydrogenation proceeds *via* cyclohexene disproportionation, the conclusion that the site density is actually high may be accounted for by the following considerations: (1) The disproportionation reaction has been shown to be a bimolecular surface reaction (*12*). (2) Such reactions almost always require a high site density (*5*).

Thus, the work of others and our low calculated value of the site density probably indicate that the reaction is not as simple as the model for which Eq. (1) was written. Very likely the actual site density is high, corresponding to a fully covered surface. If a substance such as cyclohexene is a necessary intermediate, the reaction would almost certainly be too complex to warrant the use of Eq. (1). The results for this system parallel those we obtained for the dehydrogenation of cyclohexane catalyzed by Pt-alumina.

If our principal conclusion is not correct and the site density is indeed very low, such a low value could be accounted for in at least two ways. First, as discussed earlier, the catalyst to which the conclusions apply is partially aged and there is the (rather unlikely) possibility that the hypothetical initial activity would be several orders of magnitude higher. Also, it is always possible that the site density in our fresh catalyst was actually very low. A few surface Pd atoms could be different from, i.e., much more active than, the others. Then any cyclohexene which is formed is not necessarily an intermediate.

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