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On the Specific Activity of Platinum Catalysts

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The specific activity for hydrogenation of cyclopropane at 0°C on platinum catalysts was found to be independent of platinum content on two different forms of alumina, independent of the nature of the support with alumina or silica gel, and almost the same for highly dispersed samples in which nearly every platinum atom is a surface atom as for a platinum foil. The difference between the highly dispersed samples and the others (sintered, less dispersed, foil) was a modest twofold change in specific activity, while the platinum specific surface area varied by more than four orders of magnitude. In contradistinction, a very marked susceptibility to oxygen poisoning was found for the well-dispersed catalysts that was not observed for the other samples.

INTRODUCTION

As atoms are put together to form metallic embryos, nuclei, and crystallites, how does the catalytic activity of the particles vary with their size? Is a minimum lattice exhibiting bulk properties required for normal catalytic behavior? Does an optimum dimension exist beyond which catalytic activity of a crystallite will decline?

These are fundamental questions which have been asked many times over the past 40 years because they are intimately linked with theories of catalytic action, in particular with the existence and nature of active centers. However, quite apart from the difficulty of preparing stable catalytic particles of known size, starting with the smallest ones, an answer to the question of specific catalytic activity had to await the development of methods of measurement of surface area. Indeed, the catalytic activity, for a valid comparison, must be referred to the number of exposed surface atoms of a specified kind. Thus a convenient way to express catalytic activity is by means of a turnover number equal to the number of reactant molecules converted per minute per catalytic site for given reaction conditions.

The first systematic investigations of the problem of specific catalytic activity were those of Boreskov and co-workers who were able to perfect a technique of measurement of the surface area of platinum catalysts by means of the selective chemisorption of hydrogen (*1*). With this necessary background, they succeeded in showing that the specific activity of platinum in the oxidation of sulfur dioxide (*2*) and of hydrogen (*3*) varied by less than an order of magnitude for platinum samples differing in their platinum specific surface area by four orders of magnitude, e.g., platinum supported on silica gel, platinum sponge, wire, and gauze. In the case of hydrogen–deuterium exchange at low temperature (*4*), an apparent exception to this lack of substantial variability of the specific activity of platinum was found for samples supported on silica gel. The enhanced activity in this case was attributed to the interference of the support, a complication which may be hard to avoid for certain reactions, as illustrated again by the recent work of

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Sinfelt (*5*) on the hydrogenolysis of ethane over supported platinum.

In view of the far-reaching significance of the findings of Boreskov *et al.*, it was decided to extend their work by taking advantage of the extreme state of dispersion of platinum on η-alumina, a system which was not investigated by the Soviet workers. Yet, from a large variety of studies involving selective chemisorption of hydrogen (*6, 7, 8*), carbon monoxide (*9*), and benzene (*10*), as well as the methods of electron microscopy (*11*), light scattering (*12*), and X-ray diffraction line-broadening (*13*), there is general agreement on the fact that almost every platinum atom in a fresh sample is a surface atom and that if crystallites of platinum are present on the alumina surface after reduction of the catalyst, their size is certainly less than 35 Å (*13*) and probably less than 15 Å (*16*).

The platinum-alumina system appears to be well-suited to a study of the specific activity of platinum since the very small aggregates dispersed on a fresh catalyst can be made to grow by heat treatment at increasingly higher temperatures until their size can be measured by X-ray diffraction line-broadening (*6, 14, 15, 16*). Furthermore, in the region where the platinum particles are too small to be detected by physical methods, a measure of the platinum surface area may now be obtained readily by a titration method consisting of selective hydrogen adsorption on a surface platinum oxide (*17*).

As a matter of convenience, the hydrogenation of cyclopropane was then selected as the test reaction since, according to the literature (*18, 19, 20*), kinetic data could be readily gathered at a temperature low enough for parasitic contributions from the support to be negligible. The present study thus concerns itself with the low-temperature (0°C) hydrogenation of cyclopropane to propane, catalyzed by a platinum foil and by various platinum catalysts on three different supports differing vastly in the average particle size of the metal. Additional observations on the poisoning effect of oxygen complement this study of the specific activity of platinum.

EXPERIMENTAL

The catalysts used in this investigation are listed in Table 1. The samples supported on η alumina were supplied by Esso Research and Engineering Company. The η alumina was prepared from β-alumina trihydrate (Davison Chemical Company) by calcining in air for 4 hr at 593°C. The η-alumina powder was then impregnated with aqueous chloroplatinic acid solutions and calcined again in air at 593°C for 4 hr. These catalysts were obtained in the form of pellets. They were crushed lightly and sieved. For all runs with supported catalysts, the 48/100-mesh portions were used.

The samples supported on γ alumina were obtained from Cyanamid-Ketjen N.V. They are commercial reforming catalysts and the method of their preparation is unknown. They were supplied in the form of extrudate particles, which were crushed and sieved like the other samples.

The samples supported on silica gel were

TABLE 1
ACTIVITY AND PLATINUM SURFACE AREA OF CATALYSTS FOR THE 0°C HYDROGENATION OF CYCLOPROPANE

Wt % Pt on catalyst	Specific surface area of platinum, expressed in μmole H_2/g sample	Activity in μmole cyclopropane per minute per g sample	Percentage dispersion $D(\%)$
0.3% on η alumina	10.2	82.4	44
0.3% on γ alumina	13.5	100.	59
0.6% on γ alumina	33.5	186.	73
1.96% on η alumina	97.0	637.	64
Same as above, sintered	11.5	44.0	7.6
4.3% on silicagel	57.3	160.	17.
100% (foil)	0.55	1.4	0.0039

prepared in our own laboratory following the method of Ciapetta and Hunter (*21*) using silica gel from Davison Chemical Company and chloroplatinic acid from Baker and Adamson.

Sintering of the sample of 2 wt % platinum on η alumina was carried out in flowing hydrogen at 650°C in a quartz tube.

The platinum foil used was 12.7 μ in thickness. It was pretreated by being washed in benzene, etched in aqua regia, and washed in distilled water. After being placed in the reactor, the foil was alternately exposed to static oxygen and pure hydrogen at 500°C before being reduced in a manner similar to the supported catalysts. The geometrical surface area of the foil sample (2.04 g) was 140 cm^2.

The hydrogen used in this work was of electrolytic grade (Liquid Carbonic Corporation) purified by distillation in the Low Temperature Laboratory of the University of California or purchased from the Matheson Company. All hydrogen was further purified by diffusion through a palladium membrane purifier manufactured by the Milton Roy Company. Cyclopropane (99.5% minimum purity) obtained from the Matheson Company was purified further by passage over magnesium perchlorate, followed by two bulb-to-bulb distillations at low temperature in which the first and last thirds of each distillation were discarded. The oxygen used in the poisoning studies was research grade (99.9% minimum purity). It was used as obtained from the Matheson Company without further treatment.

Rates of cyclopropane hydrogenation were measured in a glass recirculation system. The circulation loop was attached, through a trap cooled with liquid nitrogen, to a manifold pumped by a rotary mechanical pump and an oil-diffusion pump and, through a trap filled with porous gold powder, to a mercury manometer.

Weighed samples of the supported catalysts ranging from 15 to 500 mg were charged to the reactor consisting of a cylindrical chamber (approximately 1.5 cm long and 2 cm in diameter) with a coarse grade fritted disc at its bottom to support the catalyst particles. Standard activation treatment consisted of evacuation *in situ* for approximately 30 min at room temperature and for 2–3 hr at 150°C. The reactor chamber was then isolated from the recirculation loop and a hydrogen flow of 70–80 ml/min at ambient conditions was started through the sample as the furnace temperature was increased slowly to 500°C. Reduction in flowing hydrogen was continued for 12 hr, after which the catalyst cooled in hydrogen. During the reduction and cooling, a downstream oil bubbler prevented the back-diffusion of oxygen and a liquid nitrogen cold trap prevented contamination by the oil vapor.

Hydrogen remaining in the preheater and catalyst chamber was used as a reactant. It was expanded into the evacuated portion of the circulation loop not directly connected to the manometer. The section of tubing connected to the manometer served as part of a calibrated volume used for adjusting the amount of cyclopropane. These reactants were then circulated for premixing and for reaction by means of a magnetically driven, noncontaminating reciprocating pump developed for this and other studies and described elsewhere (*22*). This pump provided a circulation rate of 4–5 liter/min under reaction conditions in a system of 1.8-liter total volume.

Conditions of operation were chosen to ensure differential reactor operation with less than 0.5% conversion per pass. The catalyst particles were sufficiently small that effects due to heat and mass transfer limitations were negligible, according to the criteria of Weisz (*23*) and Anderson (*24*). Details of the pertinent calculations can be found in ref. (*25*).

For reaction temperature control, the reactor and preheater (a 160-cm coil of 8-mm OD Pyrex tubing) were immersed in a stirred thermostated water bath. In all runs reported here, the reactor temperature was 0°C.

All rates reported were measured with an initial cyclopropane partial pressure of 10 torr and an initial hydrogen:cyclopropane ratio in the range 4.6:1 to 4.8:1.

The mercury manometer was used only

briefly for the initial pressure measurement, the reaction being monitored by sampling the gas phase with an Aerograph XA-210 sampling valve, modified (*25*) for sampling under vacuum, followed by injection of the sample into an Aerograph A-90-P gas chromatograph using helium as a carrier gas. The components (hydrogen, propylene, propane, and cyclopropane) were separated at 40°C on a column of 20% dimethylsulfolane on 60/80-mesh firebrick. The output of a thermal conductivity detector was potentiometrically recorded, and the peak heights were shown to be a quantitative measure of hydrocarbon concentrations under reaction conditions (*25*).

Platinum surface areas for the supported catalysts were measured by means of the hydrogen titration technique developed by Benson and Boudart, with the apparatus described in their paper (*17*). The surface area is conveniently expressed in μmoles of hydrogen gas taken up per gram of sample.

The BET surface area of the platinum foil was measured in the same apparatus using krypton as the adsorbate at liquid nitrogen temperature. A surface area of 196 cm^2/g was calculated by assuming a cross section of 19.5 $Å^2$ per krypton molecule (*26*).

Those catalysts containing crystallites of a size amenable to the technique were subjected to X-ray line-broadening studies. The conditions used were essentially identical with those described by Adams *et al.* (*11*). A sample of the catalyst powder was pressed into a depression in a glass slide and placed in a General Electric XRD-5 diffractometer. Copper K_α radiation, filtered by nickel, was introduced through a 3° beam slit. A 0.1° receiving slit and a medium resolution Soller slit were used, and the counting rate was recorded as a function of scanning angle. Corrections to the observed linewidths for instrumental broadening were made using the curves of Klug and Alexander (*27*).

RESULTS

Preliminary determination of an absolute blank showed that the recirculation system itself exhibited no detectable activity. Runs made with 150–200 mg of the η-alumina support showed no propane formation below 50°C. Propylene formation over the η-alumina at 25°C was detectable only after 80 min of reactor operation. This was the highest temperature used for testing the activity of the supported platinum, and, since most runs were at 0°C, the blank corrections for the support were completely negligible. No blank was performed with the silica gel support, which is known to be much more inert than alumina in the reactions of hydrocarbons.

Preliminary experiments also indicated that the platinum-alumina catalysts would partially deactivate from run to run, losing approximately 15% of their initial activity. All runs with the supported catalysts reported were thus made with fresh charges. In spite of the difficulty in reproducing data from one catalyst charge to another, this procedure was considered satisfactory, if somewhat tedious.

The rate of hydrogenation of cyclopropane was found to be practically constant up to 50% conversion. Measurements of initial rates are therefore very easy to obtain by extrapolation of the curve of amount of propane versus time. Initial rates, expressed in μmoles of cyclopropane per minute per gram of catalyst, at 0°C, at the initial pressures mentioned earlier, are tabulated in Table 1 and plotted in Fig. 1. These initial rates under these specified standard conditions are referred to as the activity.

Under the best conditions, the activity from run to run with a new sample of the same catalyst was good. The arithmetic average activity for several runs is reported in Table 1 for each supported catalyst. Some more pronounced deviations from run to run may be attributed to the great sensitivity of the highly dispersed catalysts to poisoning.

The poisoning was studied in separate runs reported in Table 2. In one method of poisoning, a total of about 400 μmoles of oxygen was introduced into the circulating hydrogen-cyclopropane mixture during a rate measurement. This quantity, which is much larger than the amount required to

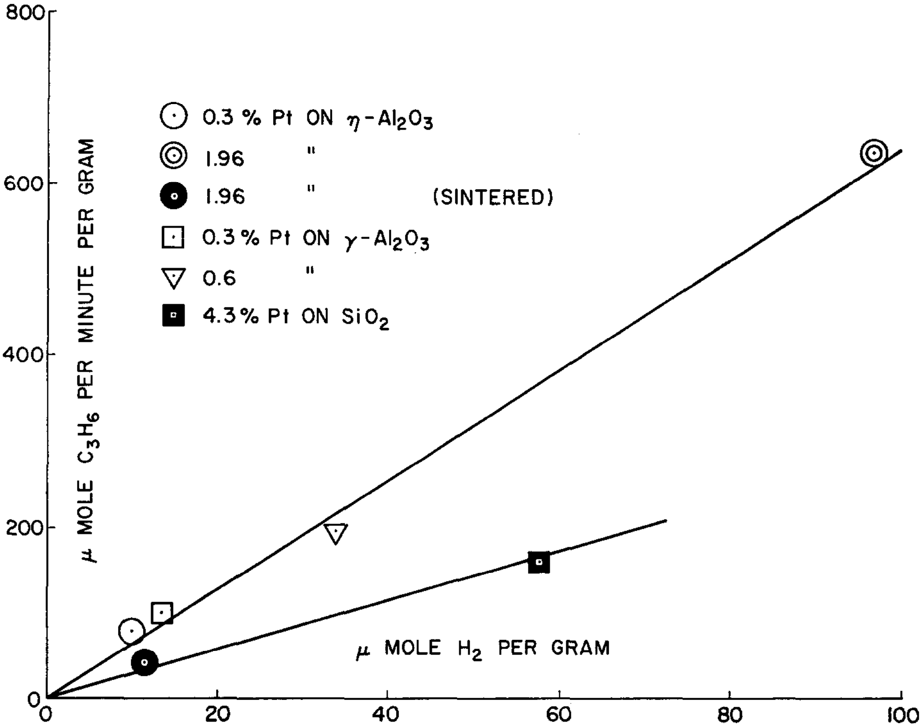

FIG. 1. Activity as a function of platinum surface area.

TABLE 2
SUSCEPTIBILITY OF PLATINUM CATALYSTS TO OXYGEN POISONING

Catalyst	Activity μmole cyclopropane per minute per gram sample	
	Before poisoning	After poisoning
0.3% on η-Al_2O_3	82.4	1.2
1.96% on η-Al_2O_3 sintered	44.	26.1
4.3% on SiO_2	160.	93.4
Platinum foil	1.4	0.75

cover the surface of the platinum with a monolayer, was usually introduced in two doses. First a smaller dose of 80 μmoles was introduced, followed later by a dose of 300 μmoles.

The second poisoning procedure, yielding the rates reported in Table 2, consisted of prepoisoning the catalyst by circulating an identical amount of hydrogen-oxygen mixture over the catalyst. The loop and catalyst were held at 0°C and outgassed to 10^{-5} torr before fresh hydrogen and cyclopropane were added for a normal run. The results of the two methods were in qualitative agreement. Pressure changes during the prepoisoning experiments suggested that water formation was quantitative and that the supported catalyst retained all of the water formed.

Also reported in Table 1 are the values of platinum surface areas and a measure of platinum dispersion, defined as the ratio of platinum surface atoms titrated by hydrogen to the total number of platinum atoms in the sample. This platinum dispersion can be expressed as a percentage, *D*. In the calculation of *D*, use was made of the previously established stoichiometry of the titration (*17*)

$$\text{Pt-O(surface)} + \tfrac{3}{2}H_2 \rightarrow \text{Pt-H(surface)} + H_2O$$

according to which each molecule of hydrogen taken up corresponds to ⅔ of a platinum surface site. To convert the krypton surface area of the platinum foil to a number of surface atoms, a site density of 1.1×10^{15} cm^{-2} was assumed (*6*).

DISCUSSION

As regards activity, there is a clear distinction between the platinum samples with a high dispersion and the others. The former comprise fresh catalysts supported on γ or η alumina. The latter include the sintered sample on η alumina, the silica-gel-supported catalyst, and the platinum foil.

As shown by the two straight lines passing through the origin of Fig. 1, the specific activity, i.e., the ratio of activity to platinum surface area, is approximately a constant in both categories. The slope of the line, multiplied by the factor ⅔, is actually a turnover number, N, a convenient measure of specific activity. It is equal to 4.3 per minute for the catalysts with high D, and is equal to 2.0 per minute for the other supported catalysts. The value of N for the platinum foil is almost the same, namely 1.7 per minute.

Thus, from the viewpoint of activity, there is a difference, by a factor of 2, between the two groups, but this is an insignificant variation relative to the large change in dispersion, D. The difference in the two groups in their susceptibility to poisoning is, however, very marked. For the fresh catalysts well dispersed on alumina, the activity after oxygen treatment was only about one-hundredth of its original value. By contrast, oxygen poisoning reduced by only about 50% the activity of the sintered platinum-alumina, the platinized silica gel, and the foil (Table 2).

Besides the difference in degree of dispersion as measured by D, another notable difference between the two groups is provided by the X-ray data. No X-ray pattern was obtained on the well-dispersed samples, while X-ray line-broadening suggested a mean platinum particle size of 135 ± 30 Å for the sintered sample of Pt/η alumina and 525 ± 50 Å in the case of Pt/SiO_2. Since the dispersion, D, is 7.6% and 17%, respectively, it appears that there must be a very wide distribution of particle size in both samples if the X-ray data and the values of D are to be reconciled. Yet, the turnover number was practically the same in the two cases, as well as for the foil.

It must be concluded that the observations of Boreskov *et al.* concerning the lack of sensitivity of the specific activity of platinum in the oxidation of sulfur oxide and hydrogen and (with one exception) in the hydrogen–deuterium exchange are confirmed and considerably strengthened by the present findings. Indeed, it is the first time that the specific activity of the highly dispersed platinum-alumina system has been included in a study of this kind. It is remarkable that the turnover numbers on samples where almost every atom is a surface atom differ only by a factor of 2 from the turnover numbers on catalysts where bulk metal is clearly present.

A sharp difference in activity can be perceived only on the catalysts poisoned with water. This must be connected with the dispersion and the nature of the support. As shown elsewhere (*17*, *28*), an oxygenated platinum surface can be cleaned by hydrogen at room temperature or below. The fact that this cleaning is quantitative, within experimental error, is the basis for the hydrogen titration technique for obtaining the platinum surface area. It follows that a platinum surface exposed to oxygen around room temperature will be cleaned by hydrogen also around room temperature. The cleaning may not be complete, as indicated by Tucker's recent work (*29*). Tucker, using the low-energy electron diffraction technique of studying gas adsorption on platinum surfaces, confirms that hydrogen immediately removes oxygen structures from a (111) Pt face; but he then observes that there remains on the surface a new scattering entity, the nature of which was not elucidated. It was suggested that water might be responsible for the unknown structure observed.

That the platinum surface of our catalysts is not completely clean after exposure to oxygen in the presence of hydrogen, at 0°C, is compatible with the observations on the reduction in activity by one-half for the second group of catalysts. But a reduction in activity of the highly dispersed catalysts by two orders of magnitude requires a more subtle explanation. Unless one can justify the coverage of 50% of the active platinum sites in one case, and 99% coverage of the platinum sites in another case, by the water formed, one must invoke some special active centers. Such a conclusion seems incompatible with the almost constant specific activity observed on the unpoisoned catalysts. Since the effect disappears with a moderate amount of sintering, as shown by the data in Table 2, it is believed that the water formed at 0°C stays on the support in the immediate vicinity of a platinum site and reduces the activity by some sort of interaction.

Efforts to extend the range of platinum/η-alumina activity measurements to lower concentrations of platinum were made in addition to the experiments discussed above. Catalysts containing 0.05 and 0.1 wt % platinum were unexpectedly low in activity. In view of the great sensitivity to poisoning of the fresh 0.3 wt % platinum-on-alumina catalyst and the reduced precision of the measurements on the low platinum samples, there must be some doubt as to whether this observation is conclusive. However, the satisfactory nature of the results obtained with the catalyst containing only three times as much platinum prevents us from discarding the possibility that at very low platinum concentrations, platinum-alumina interactions may again be reducing activity, even in the absence of oxygen (water) poisoning.

In conclusion, we have found a remarkable lack of sensitivity of the turnover number to crystal size, nature of support, or details of preparation. It is emphasized that this relative constancy of specific activity, observed by Boreskov's school and now by ourselves, is not expected generally. Indeed, our results on poisoning immediately reveal a striking difference between two classes of platinum catalysts. This constancy of activity would only be expected for what might be termed *facile reactions,* for which the majority of sites possesses ample activity under the conditions of operation. These facile reactions are those that fail to sense the nonuniformities of solid surfaces that become important under more probing or demanding circumstances, in particular, when stereospecificity is involved or when the reaction is difficult from the viewpoint of reactivity. An example of a difficult reaction (where nonuniformity of the surface has been generally invoked) is the synthesis of ammonia (*31*), where the lack of reactivity of molecular nitrogen provides a difficult step. A case where difficulty of reaction and possibly where stereospecificity may come into play is provided by the study of Hightower and Kemball of the reactions of *p*-xylene with deuterium (*32*). In that case an effect of the support on platinum activity was apparent.

In future work it may be important, then, to distinguish between *facile* and *demanding reactions* from the viewpoint just discussed and we propose that a facile reaction may be defined as one for which the specific activity of the catalyst is practically independent of its mode of preparation.

On this basis, it might be argued that the choice of the facile hydrogenation of cyclopropane was ill-advised since it was rather an undiscriminating probe of catalytic activity. In spite of this drawback, it appears that another consequence of our data is to support the view (*30, 33*) that platinum-on-alumina is essentially reduced to the metal in spite of the fact that metal crystallites have thus far eluded all physical attempts at identification, for *the specific activity of the* $Pt\text{-}Al_2O_3$ (γ *or* η) *systems was found to be almost the same as that of bulk platinum.* It appears, therefore, that the platinum-alumina system is indeed a very interesting one for the further testing of the fundamental questions raised in the introduction. Further work on this catalyst with more demanding reactions ought to be very revealing.*

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* As this paper is going to press, Professor Selwood kindly brings to our attention a study by T. A. Dorling and R. L. Moss which will appear in the February issue of *J. Catalysis* [**5**, 111 (1966)]. These authors report data on a series of $Pt\text{-}SiO_2$ samples used as catalysts for the gas-phase hydrogenation of benzene at 25°C. The dispersion of the metal was varied, as in our work, by sintering. For catalysts fired up to 500°C and differing in their percentage dispersion by almost two orders

of magnitude, they find, in striking agreement with our results that the turnover number changes only by a factor of approximately 2. Thus, the catalytic behavior of platinum discussed here, has been verified independently for another reaction, in agreement with our results and those of Boreskov *et al.* (*2, 3, 4*).

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