JOURNAL OF CATALYSIS 11, 35-45 (1968)

On the Selectivity of Platinum Catalysts

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Received January 23, 1968

Initial rates for the reaction of neopentane on supported platinum and platinum powder catalysts have been obtained at 300°C, 1 atm total pressure, and a hydrogen-to-neopentane ratio of 10. Silica gel, carbon, and η- and γ-alumina were used as supports. A hydrogen–oxygen titration technique was used to measure the number of exposed platinum atoms, and the platinum dispersion, defined as the percentage of the total platinum atoms which are the surface, was calculated. Values of the dispersion varied from 3×10^{-2} for the powder to greater than 70 for the supported catalysts.

Neopentane underwent two parallel reactions, isomerization to isopentane and hydrogenolysis to isobutane and methane. The selectivity for isomerization, defined as the ratio of the isomerization rate to the hydrogenolysis rate, varied by a factor of 100 for the catalysts studied. For the supported catalysts the selectivity increased with increasing catalyst pretreatment temperature, which varied from 425° to 900°C. This finding is explained, following Anderson and Avery, by triadsorption of neopentane at platinum atom triplets such as occur on (111) faces and at point defects, edges, and steps on the platinum surface.

INTRODUCTION

In any field of chemical reactivity the elaboration of theories with predictive value rests very largely on the accumulation of data leading to meaningful correlations between structure and reactivity. With solid catalysts two types of correlations are possible: either the structure of reactants is changed, or the structure of the catalyst is modified in a systematic way (*1*). Because of the difficulty in characterizing surface structures, the latter approach is fraught with difficulties that have not been resolved even in the case of pure metals. Indeed, although the use of evaporated films guarantees the chemical definition of the surface, it is fairly certain that the surface sites of a metallic evaporated film exhibit a wide spectrum of reactivity. Moreover, films have a number of undesirable characteristics. It is not easy to control their structure, and their susceptibility to sintering makes kinetic studies with them very difficult because a high-temperature standard activation and regeneration procedure is not practical in the majority of cases.

By contrast, supported metals provide long-lived, reproducible, stable, and frequently regenerable catalytic surfaces, and the techniques of their preparation have been developed to a fine art by industrial practice. On the other hand, if the activity of supported metals were sensitively dependent on the crystallite size, mode of preparation, and interaction with the support, their value in studies of catalyst reactivity would be sharply limited.

It is therefore most satisfying to find in the recent literature a substantial list of reactions involving oxidation, hydrogenation, dehydrogenation and hydrogenolysis, all catalyzed by supported or unsupported platinum. For each of these reactions it has been shown that the specific activity of the

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TABLE 1
List of Facile Reactions on Platinum Catalysts

Reaction	Platinum particle size d (in Å) or dispersion D, and support	Reference
Oxidation of sulfur dioxide Oxidation of hydrogen	$d > 40$ Silica gel and unsupported metal	Boreskov *et al.* (*2*, *3*)
H_2–D_2 exchange Hydrogenation of cyclohexene Dehydrogenation of cyclohexane Hydrogenation of hexene − 1 Dehydrogenation of isopropanol Hydrogenolysis of cyclopentane	$20 < D \sim 100\%$ silica gel	Poltorak *et al.* (*4*, *5*)
Hydrogenation of benzene	$40 < d < 440$ silica gel	Dorling and Moss (*6*)
Hydrogenation of cyclopropane	$10^{-3} < D < 75\%$ Alumina, silica gel, and unsupported metal	Boudart *et al.* (*7*)

metal, i.e., the activity referred to unit surface area of the metal, was very insensitive to particle size and nature of the supporting material (Table 1). As pointed out by Poltorak *et al.* (*5*), deviations from normal behavior characteristic of the bulk metal are expected especially for particles smaller than about 50 Å. The same views have also been expressed by Van Hardeveld and Van Montfoort (*8*), who have given strong evidence for the existence of special surface sites on metallic particles with a characteristic size between 15 and 70 Å. In view of this plausible suggestion, the most complete catalytic investigation on the question of lack of sensitivity of platinum is that of Boudart *et al.* (*7*). In our work it was shown that the specific activity for the hydrogenation of cyclopropane at 0°C on various platinum catalysts was independent of platinum content on two different forms of alumina, independent of the nature of the support, alumina or silica gel, and almost the same for highly dispersed samples in which nearly every platinum atom was a surface atom as for a platinum foil. This investigation clearly bridges the gap between very small particles and bulk metal and establishes the lack of effect of support on the catalytic activity of the metal.

While the list of reactions found in Table 1 is impressive enough, it is not to be expected that the phenomenon should always be found in catalysis even by platinum alone. Thus, in our previous paper (*7*), it was proposed, as a matter of convenience, to call a catalytic reaction *facile* if it conformed to the pattern depicted in Table 1; a facile reaction on a given metal would be one for which the specific activity of the catalyst is practically independent of its mode of preparation. In our paper it was anticipated, in accordance with a long history of catalytic experience, that for other reactions that might be called *demanding*, this great simplification valid for facile reactions would cease to operate because a demanding reaction would require some special surface configurations that are produced on a metal surface only as a result of a special mode of preparation.

The importance of such a classification for the prediction of catalytic activity is obvious: if a reaction is facile, in the sense defined above, then the catalyst may be characterized by a single parameter, e.g., the type of available orbitals at a metal surface. Otherwise, such a simple characterization will fail altogether. Before this classification may be considered seriously, it is of course necessary to discover examples of demanding reactions. The search for such reactions must be conducted on a metal which is known to possess a well-defined specific activity with respect to facile reactions. The only metal for which this property has been well established is platinum, and it was therefore concluded at the end of our previous investigation (*7*) that further work on platinum with more demanding reactions ought to be very revealing.

In this paper we present the results of such work. It was reasoned that for a demanding reaction a relatively complex molecule should be used, such as a hydrocarbon that is sterically interesting and reacts in a way more subtle than that involved in the facile hydrogenations, dehydrogenations, and hydrogenolyses listed in Table 1. The ideal candidate seemed to us to be neopentane, which, according to Anderson and Avery (*9*), reacts on platinum evaporated films in the presence of hydrogen around 300°C to give isopentane by isomerization and isobutane by hydrogenolysis. A particular appeal of this unusual reaction was that it was very unlikely that it could benefit from the acidity of some of the supports used in the preparation of the platinum catalysts.

The findings of Anderson and Avery have been confirmed and amplified in the present work. The selectivity of the reaction of neopentane to isopentane proved to be a very sensitive probe of special surface configurations as anticipated by Anderson and Avery and as hoped for in our search for a demanding reaction.

EXPERIMENTAL

Initial rates of the isomerization and hydrogenolysis of neopentane on platinum were obtained in a Pyrex recycle system operating batchwise under differential reactor conditions of about 0.02% conversion per pass. The total conversion was maintained below 1%; within this range the conversion to both isopentane and isobutane was generally found to vary linearly with time, and no other products were detected except methane from the hydrogenolysis reaction. A typical run is shown in Fig. 1. With the exception of a Wallace and Tiernan differential pressure gauge, which has been used here to monitor the reactor pressure, the apparatus was similar to that used by Chambers and Boudart (*10*) with a recirculation pump as described earlier (*11*). The reactor loop volume was 2.7 l. A small amount (0.1 to 1.0 g) of catalyst, equivalent to about 1 to 10 μmole of surface platinum atoms, was used in a run. The paramount advantage of this experimental arrangement is the absence of temperature and concentration gradients in the catalyst bed, as can be verified by separate calculations (*12*). All runs were performed at 307°C, a total pressure of 1 atm, and hydrogen-to-neopentane ratio of 10 to 1. These conditions will be referred to as the *standard conditions.*

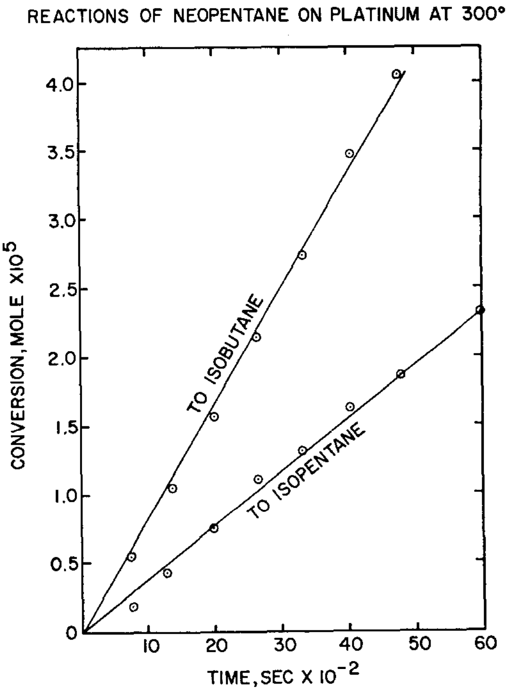

FIG. 1. Reactions of neopentane on platinum at 300°C.: A typical run under standard conditions on a Pt–γ-Al_2O_3 catalyst.

Analysis of the gas mixture was achieved by removing several aliquots during the course of the reaction. Each aliquot amounted to about 0.9% of the total gas initially present and was diverted to a Varian-Aerograph model A-90-P chromatograph equipped with a 10-ft dimethylsulfolane column operating at room temperature.

Phillips research grade neopentane was

TABLE 2

Specific Activities and Selectivities for the Reaction of Neopentane under Standard Conditions

Catalyst		% Dispersion D	Specific activities (10^3 molecules converted/surface Pt atom sec)		Isomerization selectivity $S = N_I/N_H$	Maximum temperature of pretreatment in reduced state, T_m (°C)
Wt% Pt	Support		Isomerization: N_I	Hydrogenolysis: N_H		
0.60	$Al_2O_3(\gamma)$[a]	73	2.6	4.7	0.55	425°
1.96	$Al_2O_3(\eta)$[a]	64	5.3	13	0.41	425°
0.60	$Al_2O_3(\gamma)$[b]	73	2.8	1.9	1.5	500°
1.96	$Al_2O_3(\eta)$[b]	64	3.4	2.3	1.5	500°
4.3	SiO_2[b]	17	3.8	13	0.29	500°
1.0	Spheron[c]	12	1.1	0.04	27	900°
1.96	$Al_2O_3(\eta)$[d]	7.6	11	4.5	2.4	650°
100.0	—[e]	0.028	0.73	0.08	9.1	500°

[a] Reduced at 425°C in hydrogen for 10 hr.

[b] Same, but at 500°C.

[c] Reduced at 500°C, evacuated at 900°C for 16 hr, stored in air before reduction as in *b*.

[d] Sintered in flowing hydrogen at 650°C before reduction as in *b*.

[e] Treated alternately and repeatedly in hydrogen and oxygen before reduction as in *b*.

stored in a liquid nitrogen bath after a purification of three or four pump–thaw–freeze cycles. The other hydrocarbon used, 2-methyl-1-butene, was supplied by Matheson, Coleman and Bell (practical grade, 95%) and was used without purification. Bottled hydrogen (99.95%) was diffused through a Milton Roy palladium thimble before being directed into the loop. The oxygen used for the pretreatment of the platinum powder had a purity of 99.6% and was used directly from the cylinder.

The catalysts used in this work are listed in Table 2. The preparation of the platinum samples supported on η-alumina and silica gel has been described earlier (*7*); they are experimental catalysts supplied by Esso Research and Engineering Company or prepared in our laboratory. The catalyst supported on γ-alumina was obtained from Cyanamid-Ketjen N.V.; it is a commercial catalyst, and its method of preparation is unknown. These catalysts were ground and sieved, and the 100/200 mesh fraction was used. The preparation of the catalyst supported on Spheron, a very pure carbon black supplied by the Godfrey Cabot Corporation, has been described elsewhere (*13*). A 100-mesh platinum powder was obtained from Engelhard Industries. A spectrographic analysis of the powder indicated that the impurities were as follows, in ppm: Au 150; Si 100; Fe and Pd less than 50; Cu, Ag and Ca 20; Mg less than 10.

Unless specified differently the pretreatment of the catalysts consisted of a 3–4 hr outgassing at 150°C followed by a 10-hr reduction in flowing hydrogen (70 ml/min) at 500°C. After the reduction period the samples were cooled to the reaction temperature in flowing hydrogen. While the catalyst was cooling from the reduction temperature the reactants were added and mixed in a section of the loop isolated from the catalyst chamber. When the catalyst had reached the reaction temperature the catalyst chamber was evacuated and the reactants admitted. If it was necessary to repeat the run the activity could be maintained if, after the completion of the first run, the catalyst was immediately purged with hydrogen without evacuating the sample. With this technique the activity would generally remain constant to within 10% over a period of several runs. In the experiments with the platinum-Spheron catalysts the sample was treated with flowing hydrogen (70 ml/min) at the reaction temperature for 1 to 2 hr after completion of the first run, evacuated and vented to the room for about 15 sec. After a second evacuation at the reaction temperature the sample was again reduced in flowing hydrogen at 307°C for 2 hr before beginning the subsequent run.

The activation of the platinum powder was performed, as in our previous investigation (*7*), by first cycling the sample three times in hydrogen and oxygen at 500°C, followed by the standard 10-hr hydrogen reduction, again at 500°C. The surface area of the platinum powder was determined by a BET adsorption of research grade krypton supplied by The Matheson Company.

For the supported platinum catalysts the metal dispersion was determined by the hydrogen–oxygen titration technique originally described by Benson and Boudart (*14*), in whose paper all experimental details can be found. All calculations were based on the dry weight of the catalysts.

RESULTS

For each of the supported catalysts the number of surface platinum atoms, as obtained from the hydrogen–oxygen titration, has been divided by the total number of platinum atoms to obtain the percentage platinum dispersion, D. The values of D for the various catalysts are given in Table 2. With a cross-sectional area of 19.5 Å^2 per krypton molecule (*7*), the surface area of the platinum powder was found to be 765 cm^2/g. The platinum dispersion for the powder was calculated from this surface area with a surface site density assumed to be equal to 1.12×10^{15} sites/cm^2.

The specific activities for both isomerization and hydrogenolysis of neopentane are presented in Table 2. The values correspond to molecules converted per surface platinum atom per second and are therefore a turnover number, N. Values of N were calculated from the slopes of the conversion–time straight lines. These were then divided by the corresponding value of the number of surface platinum atoms. The ratio of the isomerization activity, N_{I}, to the hydrogenolysis activity, N_{H}, is defined as the selectivity for isomerization, S, and values of the selectivity are also given in Table 2. The reproducibility of the kinetic data can be illustrated by values of N_{I} and N_{H} obtained in successive runs. For example, in three successive runs on a 0.6 wt % Pt on γ-Al_2O_3, values of N_{I} equal to 2.6, 2.4, and 2.7×10^{-3} sec^{-1} were obtained. Correspondingly, N_{H} was found to be equal to 5.0, 4.7, and 4.5×10^{-3} sec^{-1}. All values recorded in Table 2 are averages of at least two and sometimes many reproducible runs on a given sample under standard conditions.

The platinum-Spheron catalyst gave initially an isomerization activity of 1.3×10^{-5} sec^{-1} and an immeasurably small hydrogenolysis activity. After one 15-sec dose of air at 307°C, the isomerization activity increased to 7.6×10^{-4} sec^{-1} and after a total of four doses leveled off at the value given in Table 2. In subsequent air treatments the activity remained constant to within 10%. Exposing a platinum-alumina catalyst to air in a similar fashion was found to have no effect on either the isomerization or hydrogenolysis activities. It was noted that, during the activation of the Pt-Spheron catalyst as just described, the selectivity stayed almost constant while the activity went up by two orders of magnitude.

The initial run with the platinum powder gave evidence of surface contamination. During the first run, the isomerization activity increased from 4.5×10^{-6} sec^{-1} to 5.6×10^{-5} sec^{-1} over a period of 60 hr. Before the second run the catalyst was purged with hydrogen at 307°C for 14 hr. During the second run the activity increased from 4×10^{-4} to 5.3×10^{-4} sec^{-1}. After the third and fourth runs, the activity of the powder remained constant to within 10% of the value given in Table 2. It was again noted that during the activation of the powder, although the activity of the catalyst increased by more than two orders of magnitude, the selectivity stayed practically constant throughout.

In the absence of platinum, η-alumina was found to be inactive when exposed to neopentane for the same period and under the same conditions used for the platinum catalysts. The η-alumina was treated in flowing hydrogen for 10 hr at 425°C prior to exposure to 2-methyl-1-butene at 0.02 atm and 307°C. The product was *n*-butene, and no isobutene was formed.

Finally, it must be noted that isobutane's sole precursor is neopentane. No appreciable quantity of isobutane seems to be produced from isopentane under our reaction conditions. This fact is demonstrated very clearly by the kinetic curves shown in Fig. 1. They are typical of parallel processes.

DISCUSSION

First it must be stressed that the isomerization of neopentane takes place on the metal and not on the support. Separate experiments showed no isomerization under the standard conditions chosen for the present investigation when neopentane was passed over η-alumina. Dual-functional behavior of the catalysts supported on alumina is clearly not important in our work. It is impossible for neopentane to be dehydrogenated on the metal with subsequent reactions of the corresponding olefin on acidic sites of the support. Moreover, isobutane, the other major product of the reaction of neopentane, is not produced from isopentane by dehydrogenation on platinum followed by cracking of 2-methyl-1-butene on the alumina. The product of cracking of 2-methyl-1-butene on η-alumina is *n*-butene and not isobutene.

A very fortunate feature of the reaction that could not be predicted is that the selectivity, S, expressing the ratio of the rates of the two parallel reactions of neopentane on platinum, is an excellent index of surface behavior inasmuch as, on a given catalyst preparation, it stays almost constant even though the activity of the catalyst is changed over two orders of magnitude. This was particularly apparent in our work in the case of the platinum powder and of the platinum-Spheron preparations. In both cases, activation of the catalyst led to the removal of a surface contaminant, probably a carbonaceous residue, with resultant large increases in activity but without any appreciable changes in selectivity.

It was hoped that the reactions of neopentane on platinum would be "structure-sensitive." The results of Table 2 amply bear out that expectation. In particular, the contrast with our previous investigation of cyclopropane hydrogenation (*7*) is striking. In the previous work the turnover number of platinum surface atoms hardly changed with dispersion and catalyst preparation. In the present work the specific activity for the isomerization of neopentane was found to vary by a factor of 15, while the specific activity for the hydrogenolysis of neopentane changed over three-hundred-fold over the catalysts tested under standard conditions. The significant new result of this work is thus the large variation of selectivity for the various catalyst preparations. Because selectivity has been shown be to insensitive to surface contamination, the purpose of the discussion will be to explain the one-hundred-fold variation of selectivity shown in Table 2.

This discussion will be based on the considerations of Anderson and Avery (*9*), who studied the hydrogenolysis of ethane and the isomerization and hydrogenolysis of *n*-butane, isobutane, neopentane, and isopentane on platinum films at temperatures between 240° and 340°C and at a total pressure of about 50 torr. They first established that the reactions were intramolecular and involved a diadsorbed hydrocarbon intermediate. The comparable activity of neopentane with respect to the other hydrocarbons except ethane led Anderson and Avery to propose a 1,3-diadsorbed intermediate [Fig. 2(a)] at pairs of platinum sites (doublets), since neopentane cannot diadsorb at the metal surface in a 1,2-configuration.

In the case of isobutane, Anderson and Avery found that the selectivity for isomerization was enhanced by a factor of 3.5 on evaporated films of platinum exposing (111) faces predominantly. This enhancement of the selectivity was not observed for *n*-butane. Both facts were explained by the necessity for a triadsorbed intermediate [Fig. 2(b)] that can be formed by isobutane but not by *n*-butane. The arrangement of triple sites (triplets) found on (111) faces of platinum matches almost perfectly the postulated triadsorbed intermediate.

The increased selectivity for isomerization of isobutane, which can form these triadsorbed intermediates, can then be explained formally as follows. With a diadsorbed intermediate [Fig. 2(a)], a cyclic intermediate may form when a bond at position Z is formed. If the bond at Z is formed when the bond at X breaks, the molecule will be converted to the isomer. However, in the absence of a bond at Z, the molecule will undergo hydrogenolysis when the bond at X ruptures. Following a plausible argument similar to that first proposed by Anderson and Avery (*9*), the selectivity for isomerization can be related to the probability that, at any instant, the bond at Z is formed. The situation is quite different for a triadsorbed intermediate [Fig. 2(b)] since when bond X ruptures, there are two equivalent positions where bond Z may be formed. For isomerization when bond X breaks, only one of the two Z bonds must be made; on the other hand, for hydrogenolysis of the molecule, both Z bonds must not form when the bond at X ruptures.

Let us examine how the density of surface platinum triplets may be expected to vary with changes in catalyst pretreatment and degree of dispersion of the metal. Figure 3 presents examples of the manner in which neopentane may adsorb on a statistical platinum surface. The molecule has been represented simply by the 1.54-Å carbon–carbon bond distances appropriately oriented for the symmetrical neopentane molecule with the individual carbon and hydrogen atoms omitted. The neopentane molecule has been built to the same scale as the platinum surface. On the (100) face (left model) triadsorption is geometrically impossible because of the square-planar arrangement of the platinum atoms. In addition, triadsorption on the (110) face (right model) is impossible because the third platinum atom that could participate in triadsorption, as shown in the model, is inaccessible due to steric hindrance between the methyl group and the nearest neighbors in the (110) plane. Triadsorption is possible on the (111) plane and at point defects, edges, and steps on other crystallographic planes (middle models) where the platinum atoms have a triplet configuration similar to the (111) plane.

The temperature dependence of the surface structure of platinum has been investigated by Lyon and Somorjai (*15*) Variations in the low-energy electron diffraction patterns of the (100), (110), and (111) surfaces were observed between 300° and 1769°C. At temperatures near 600°C they found that the (110) surface was unstable with respect to faceting and surface reconstruction. As the temperature was raised to 1000°C, even the (100) plane

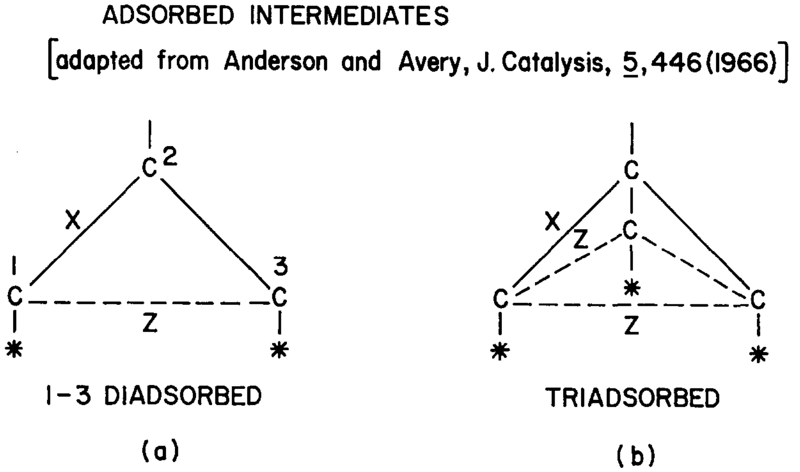

FIG. 2. Adsorbed intermediates, adapted from Anderson and Avery (*9*).

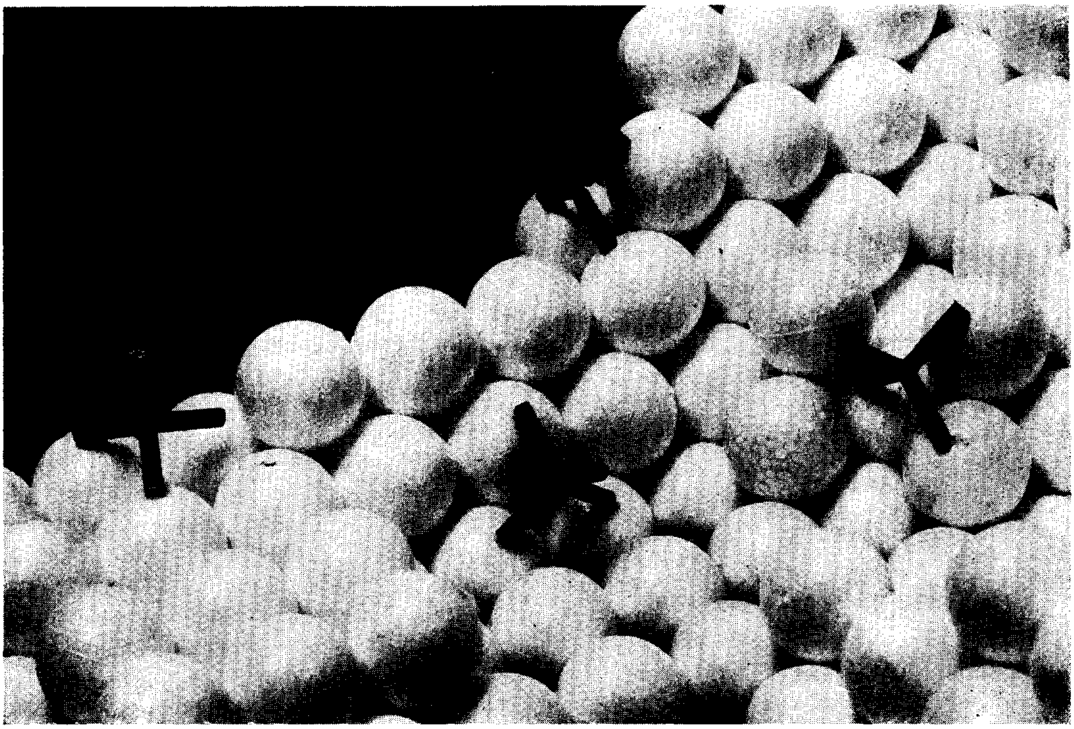

FIG. 3. Models of adsorbed intermediates.

faceted with the new surface containing steps and having Miller indices of (410). The (111) surface remained stable with respect to faceting all the way to the melting point. At 700°C, they observed the appearance of a ring pattern superimposed on the normal diffraction pattern of the (100) surface. When this surface was heated to 1000°C for 4 to 6 hr, the intensity of rings increased while the intensity of the normal diffraction spots decreased. The structural features of the surface giving diffraction spots decreased. The structural features of the surface giving rise to this ring pattern were irreversibly formed, remained as the sample was cooled, and could only be removed by ion bombardment. By analysis of this diffraction pattern Lyon and Somorjai concluded that the rings are a result of (111) domains, parallel to the substrate plane, randomly oriented and remaining stable up to the melting point. McLean and Mykura (*16*) have studied the temperature dependence of the surface energy for the (111) and (100) planes between 920° and 1500°C. In support of the work of Lyon and Somorjai, they find that within this temperature range the surface energy of the (111) face is less than that of the (100). Extrapolation of their data to lower temperatures suggests that the (111) face should always remain the most stable. Although the (111) surface is thermodynamically favored, its formation will be limited by the ability of the atoms in the crystal to rearrange to equilibrium, a process which will begin only when the sample has been heated to a sufficiently high temperature.

Smaller crystallites such as the ones found in highly dispersed platinum catalysts would be expected to begin this transition to their equilibrium shape at a lower temperature than the larger crystals used by Lyon and Somorjai, since the rearrangement of a smaller crystallite requires a correspondingly smaller number of elementary transport processes (*17*). Besides, for crystallites which are geometrically similar, the density of edges and

TABLE 3

SPECIAL EXPERIMENTS SHOWING THE INCREASE OF SELECTIVITY AS A RESULT OF FIRING AT HIGH TEMPERATURE, CATALYST: 1% Pt ON SPHERON

Treatment	% Dispersion	$N_I \times 10^3$ (sec^{-1})	$N_H \times 10^3$ (sec^{-1})	Selectivity S
Reduced in H_2 at 500°C	35	0.86	0.34	2.5
As above, followed by firing in vacuo at 900°C	35	0.26	0.02	13

thus of triplets is expected to decrease with increasing particle size, all other factors remaining equal.

If then the change in selectivity recorded in Table 2 is attributed to a change in the density of platinum triplets, it is expected that the selectivity for the isomerization of neopentane will depend on degree of dispersion of the metal and on catalyst pretreatment. These effects may overlap and be rather subtle to control. What appears to be most significant is that the highest values of selectivity were measured for the platinum powder and for the Spheron-supported sample that had been fired in vacuo at 900°C.

With respect to the powder, repeated activation of platinum in hydrogen and oxygen is known to roughen the metal surface (*18*) on an atomic scale. Hence, this sample probably contained a high surface concentration of triplets. Similarly, the Spheron-supported sample fired at the highest temperature (900°C) of all catalysts tested may be considered as having a very large amount of surface triplets. The fact that the Spheron-supported sample fired at 900°C exhibits the highest value of selectivity recorded in Table 2 is believed to be very strong support of the view that selectivity for isomerization of neopentane depends sensitively on the concentration of surface triplets.

A decisive argument in favor of this conclusion was provided by two crucial experiments recorded in Table 3. Two samples of impregnated Spheron-6 powder of the same batch from which the fired catalyst listed in Table 2 was prepared, were used as catalysts for these special runs. The first sample was treated in a normal way with a final reduction in hydrogen at 500°C. A second sample was treated in this way and then fired at 900°C in vacuo. The results shown in Table 3 show conclusively that exposure of the reduced platinum surface to high temperatures greatly increases the selectivity without changing the dispersion in any measurable way. The selectivity value $S = 13$ obtained after firing this sample is not as high as that measured on the other fired sample, listed in Table 2. But it must be noted that the dispersion of the fired sample of Table 2 had decreased appreciably, maybe because of a less perfect vacuum during the heat treatment. As a result of this sintering, additional equilibration of the surface probably took place with a further increase in selectivity to the largest value observed in this work. At any rate, the data of Table 3 show conclusively that two platinum catalysts with identical dispersion have different selectivities and that the higher selectivity is obtained after treatment at high temperature.

In agreement with the proposed explanation, the large gain in selectivity resulting from firing at high temperature is largely due to a reduction in the rate of hydrogenolysis, as shown by the data of Tables 2 and 3.

CONCLUSION

It has now been established by a variety of workers (*2–7*) that the specific activity of platinum depends very little on the mode of preparation of the catalyst for a large variety of reactions. These have been called facile reactions for that reason. In this work we have searched for and found a reaction that would not conform to this convenient rule of reactivity. It appears that the demanding reaction we studied, following the work of Anderson and Avery, can proceed through two different types of adsorbed intermediates. One of these, the triadsorbed intermediate, requires a particular geometric configuration that is not found everywhere on a statistical platinum surface. Because of this confining circumstance the specific activity for hydrogenolysis of neopentane was found to depend strongly on the catalyst pretreatment.

The concept of a demanding reaction has thus been demonstrated on a metal for which the lack of need of special structural features or special active centers had been illustrated for a large number of reactions. The reaction studied here necessitated in fact a geometrical configuration, representing an active center in the sense used by Taylor and Balandin, in particular.

It must be stressed that for systematic studies of catalyst reactivity it is essential to use a test reaction which is not demanding in the sense of the reaction of neopentane on platinum but one that is facile like the hydrogenation of cyclopropane on platinum. Otherwise, correlations of catalyst activity may well be obscured by the need for special kinds of active centers. Thus the advancement of our ability to predict catalytic activity and selectivity relies on judicious choice of facile reactions and a clear recognition of the absence of demanding structural features. With facile reactions, systematic studies of supported metals then appear very promising. On the other hand, with demanding reactions, we can send molecular probes that sense surface structures of catalytic interest.

The implicit formulation of these ideas is contained in the celebrated 1925 paper of Taylor (*19*) who wrote: *"There will be all extremes between the case in which all the atoms in the surface are active and that in which relatively few are so active."* Taylor also clearly stated in the same paper that *". . . the amount of surface which is catalytically active is determined by the reaction catalyzed."* More recently, Kemball and his school have contributed significantly to the refinement of these ideas and their experimental verification.

Thus Kemball studied the deuteration of ethylene on nickel in the form of films, wires, and bulk catalysts. He noted the similarity in the distribution of deuteroethanes in the reaction products and concluded that the reaction was comparatively insensitive to minor structural details of the nickel surface (*20*). This conclusion was confirmed by the subsequent work of Crawford, Roberts, and Kemball (*21*), who found that specific rates of ethylene hydrogenation on nickel films change only by a factor of 3 when, as a result of sintering, crystallite sizes change from 625 to 21,000 Å. The authors concluded that studies of sintering should be carried out with *"more structure-sensitive mechanisms."*

Such a study was subsequently reported by Crawford and Kemball (*22*), who found that sintering of nickel films had an effect on the catalytic exchange of alkylbenzenes with deuterium. As a result of this exploratory effort, the authors suggested that useful results could be obtained if such work were carried out on supported catalysts containing crystallites of different sizes.

This suggestion was taken up by Hightower and Kemball (*23*), who compared deuterium exchange and deuteration of *p*-xylene on various supported platinum catalysts. In our previous paper (*7*), we clearly recognized that this might be an illustration of a demanding reaction, although the details of interpretation were obscured by possible interference from water on the supports.

Very recently, the original ideas of Taylor were submitted to another quantitative verification by Kral (*24*), who measured the metal surface area of palladium catalysts supported on carbon, their hydrogenation specific activity for various reactions and their poisoning by thiophene. Kral succeeded in determining the fraction of metal surface active in each particular reaction: this he called the Taylor ratio. He found that this ratio changed from about 10^{-3} to unity, depending on the reaction.

Thus the results presented in this paper and our previous one (*7*) must be viewed as an attempt to verify and interpret ideas that have occupied a central position in catalysis since 1925. Of special importance is the use of supported catalysts, controlled dispersion, and specific activity in the operational distinction between facile and demanding reactions.

ACKNOWLEDGMENTS

We are much indebted to Dr. Anderson for letting us study his paper well ahead of publication, to Dr. Sinfelt and Dr. Robell for catalyst samples, and to Messrs. Vannice and Bergstrom for help in the last stages of experimental work. This work was supported by NSF GK 648 in our Catalysis Laboratory. Its continuity over the years has been made possible by a generous grant from the Petroleum Research Fund of the American Chemical Society.

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