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Reactions of 2,2-Dimethylbutane on Iridium: The Role of Surface Carbonaceous Layers and Metal Particle Size

M. W. VOGELZANG[1] AND V. PONEC[2]

Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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The reactions of isomerization and hydrogenolysis of 2,2-dimethylbutane (neohexane) have been studied using Ir/SiO_2 catalysts with "small" Ir particles (~1.5 nm diameter) and "large" particles (~500 nm diameter), respectively. The selectivity of the Ir catalyst was found to be not very sensitive to the variation in particle size. The structure sensitivity detected is most probably due to a difference in the structure of the inactive layer (self-poisoning) on the Ir surface. © 1988 Academic Press, Inc.

Ever since the appearance of Taylor's classic paper (*1*) and many others demonstrating the failure of the Langmuir adsorption model for many systems (*1, 2*) there has been discussion on the importance of the heterogeneity of surfaces. The question is whether the catalytic properties are essentially a matter of the chemical composition of the catalyst and vary only marginally with the varying physical structure of the catalysts. In the case of metals as catalysts, one needs to ask whether the catalyst properties are determined mainly by the position of the element in the periodic system or whether the structure of the catalyst is of a comparable or even higher importance. By "structure" here is meant the difference in the geometrical arrangement of atoms on different crystallographic planes, with consequent differing adsorption and catalytic properties due to the defects as steps or kinks. Such factors determine the distances, binding strength, and coordination of the chemisorption complexes.

The questions posed above have some fundamental aspects: for instance, are we allowed to speak about a specific catalytic activity of a material (*3*) (expressed as the turn over number (T.O.N.) or the specific rate per square meter or per site), or should we always speak of the activity of certain active centers or of ensembles of active sites (*1, 2, 4*)? Furthermore, there are important practical aspects of the same questions: when designing a new catalyst with a higher activity and selectivity, should our attention be mostly concentrated on the chemical composition of the catalyst or should we always attempt to create and stabilize a certain structure?

Only since the introduction of UHV technique has work on single-crystal planes been made possible. Before that time the only possibility of checking ideas on the role of different sites (structures) was to vary (by different preparation methods) the particle size and to correlate the catalytic data obtained with the expected variations in the abundance of sites of different geometry and coordination (*5–8*). Early research on the problem was confined to relatively simple reactions such as SO_2 or H_2 oxidation (3), benzene hydrogenation (*8*), and similar ones, and no variations within the limits of error (one order of magnitude in rates per site or square meter) were found. Later, also more complicated reactions, such as, for example, the skeletal rearrangements of hydrocarbons, were studied

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[1] Shell Co., Pernis, The Netherlands.

[2] To whom all correspondence should be addressed.

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and sometimes a pronounced sensitivity to particle size was observed. Important progress was achieved when research on single-crystal planes and on "stepped" surfaces supplied reliable data on the behavior of well-defined defects and of atoms with unusual coordination (for a review, see Ref. (*9*)). These data allow also a more detailed interpretation of the results. However, for well-defined metal surfaces as well as for metal powders, the general picture is very much the same; some reactions are more sensitive than others.

Boudart (*10*) pointed out that any study of the problem mentioned above must start from a reliable determination of the number of metal atoms exposed to the reaction mixture (the "dispersion") (*11, 12*) and postulated further that all reactions can be subdivided into two groups, namely,

(I) structure sensitive reactions
(II) structure insensitive reactions.

The experience of the last decade teaches us that it is better to speak separately about groups of reactions which are

(1) particle size sensitive and
(2) particle size insensitive,

reserving the term of structure sensitivity for the influence of the geometrical structure of different crystallographic planes.

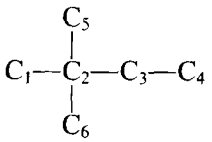
Some reactions sensitive to particle size variations appeared to be also sensitive to variations in the size of the ensembles of the active metal atoms in alloys with an inactive (much less active) metal (*13, 14*). Boudart (*10*) suggested that the size of the ensembles required by the reactions might be the common reason for the "structure," "size," and "alloying" sensitivity. However, the situation is more complicated (see below). Boudart's classification proved to be a very fruitful and stimulating idea, but, as might be expected, modifications of the basic idea soon appeared. It was pointed out (*15*) that the particle size can influence the properties of a catalyst directly or indirectly, in the first case by changing the population of sites of different coordination and in the second by influencing the side reactions or self-poisoning of the catalyst. Furthermore, ideas in the original papers on the so-called strong metal support interaction (SMSI) represent not only a revival of the old concepts of support effects once postulated by Schwab, Boudart, and others, but they also represent a warning that diminution of the particle size may have more complicated consequences than just variations in the population of various sites (*16*).

With regard to the possible parallelism between alloying and diminution of particle size effects reference should be made to an important paper by Coenen *et al.* (*18*). These authors showed that although alloying has a dramatic effect (*19*) in suppressing hydrogenolysis of cyclopropane (and promoting hydrogenation), diminution of particle size has a small effect, and the smaller particles show a higher selectivity in hydrogenolysis.

These examples suffice to demonstrate that much must still be done before the relation between the catalytic activity and the structure of the active sites is well understood.

Earlier papers from the authors' laboratory reported particle size effects in the reactions of hexane (*20*) and neohexane (*21*) on Pt. In the present paper the study is extended to iridium. Iridium has been chosen because of its importance in various catalytic processes (reforming, hydrazine decomposition, hydrogen/oxygen reaction) and its resemblance to Pt in many respects. Another reason was the considerable controversy (*22–26*) over Ir with regard to the particle size effects. Some authors found none (*23*), while others observed effects (*24, 26*). This might be related to the fact that some authors (*22, 25*) reported isomerization with Ir, while others did not, at least with some hydrocarbons (*23*).

Regarding the choice of 2,2-dimethylbutane (neohexane) for this study, we note that this molecule allows us to check the preference of various metals for either isomerization or hydrogenolysis and furthermore to study the selectivity with which various chemisorbed complexes are formed on the surface under a continuous reaction involving skeletal rearrangements. For example, when neopentane and methane are the only, or strongly prevailing, products, it is evident that the most populated reactive chemisorption complex (intermediate) is that which is attached to the surface by two carbon atoms in the C_3 and C_4 position:



$$C_1-\overset{\overset{C_5}{|}}{\underset{\underset{C_6}{|}}{C_2}}-C_3-C_4$$

This complex is further referred to below as a $2C\alpha\beta$ complex. At low temperatures and during one sojourn of the molecule on the surface only one rearrangement (one bond broken or shifted) takes place. In that case the products observed in the gas phase immediately identify the chemisorption complex from which they are formed. At higher temperatures, rearrangements may occur as multiple, consecutive reactions with the same molecule. When more than one rearrangement takes place during one sojourn of the molecules on the surface the exact identification of complexes and determination of their contribution to the total reaction become more difficult. However, as will be shown below, even under such conditions useful information can be gained from the study of neohexane reactions, although sometimes only in a form of a qualitative description of the processes.

Some examples of the identification of reaction intermediates and individual reaction steps are shown in Table 1.

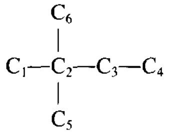
EXPERIMENTAL

Apparatus

All experiments were performed in a tubular, continuous flow, fixed bed reactor, working under differential conditions. The ratio H_2/neohexane was 18 (partial pressure of neohexane was about 40 Torr). At a flow rate of 12.5 cm^3/min primary products were observed when the overall conversion

TABLE 1

Relation of Primary Products to Structure of Complexes



$$C_1-\overset{\overset{C_6}{|}}{\underset{\underset{C_5}{|}}{C_2}}-C_3-C_4$$

Attached as	Products of single-step conversions	
	Isomerization	Hydrogenolysis
$\alpha\gamma'$, C_3–C_5	2,3-Dimethylbutane, 2-methylpentane	Methane, 2-methylbutane, ethane, 2-methylpropane
$\alpha\gamma$, C_1–C_5, C_1–C_6	3-Methylpentane	Methane, 2-methylbutane
$\alpha\beta$, C_3–C_4		Methane, neopentane
Examples of products of some multiple reactions in the adsorbed state		
$\alpha\beta$, $\alpha\gamma'$, $\alpha\gamma'$ repeated		Methane only
$\alpha\gamma'$, $\alpha\gamma$ repeated		Methane > ethane ≫ other products
$\alpha\gamma'$ followed by $\alpha\beta$ (into 2,2-dimethylbutane at the first step)		Much propane without ethane and methane
Tripod-like complex or $\alpha\gamma$, $\alpha\gamma'$ repeated		2-Methylpropane, ethane or propane, ethane, methane

stayed lower than about 4%; most of the measurements were thus performed under these conditions. The products were analyzed by GLC, as in previous papers (*20, 21*). Particle size has been checked by electron microscopy. To make the analysis feasible a small reactor with a Pt catalyst kept at about 350 K (no influence on the products of skeletal reactions) was placed behind the reactor to hydrogenate olefins.

Several parameters have been evaluated in order to characterize the selectivity of the catalyst studied. Introduction of several global parameters was necessary in particular because at higher temperatures several reaction steps (skeletal rearrangements) took place upon one sojourn on the surface. A characteristic product distribution at very low conversions, independent of the apparent contact time, was considered as indication that rearrangements follow each other consecutively in one adsorption stay on the surface (see below).

Selectivity for nondestructive reactions (S_{ndr}), which comprise mainly isomerizations, concerns all conversions to all C_6 products:

$$S_{\mathrm{ndr}}\% = 100\,\frac{[\mathrm{2MP}] + [\mathrm{2{,}3DiMeBu}] + [\mathrm{3MP}] + [n\text{-Hex}] + [\mathrm{MCP} + \text{cy-Hex}]}{[\text{all products}]}$$

$$S(\text{hydrogenolysis})\% = 100 - S_{\mathrm{ndr}}.$$

There are products observed at high temperatures which most probably are formed by two consecutive reactions, namely an isomerization combined with a hydrogenolytic step or two combined hydrogenolytic steps. These were characterized by a parameter S_{multi} defined as

$$S_{\mathrm{multi}} = \frac{[\text{propane}] + [n\text{-But}] + [n\text{-Pent}]}{[\text{all products}]}.$$

Hydrogenolysis can be characterized by its extent [S(hydrogenolysis)] and by the way in which hydrogenolysis occurred. It can easily be shown that when a fission parameter M_f is defined as

$$M_f = \sum_{i=2} \frac{C_i(6 - i)}{[\mathrm{CH_4}]^*}$$

(*, experimentally observed; the sum above is CH_4 calculated as a product of strictly consecutive terminal fissions of bonds, in a one-by-one manner). The extreme values characterize the following cases: $M_f = 1$, terminal fission, one-by-one splitting-off of C_1 units; $M_f \gg 1$, internal fission, bonds in and near the middle of the molecule are preferentially split; $M_f \ll 1$, multiple fission, neohexane species are broken down to C_1 during one sojourn on the surface. Parameter M_f appeared to be a good and sufficient parameter to characterize splitting of *n*-hexane (*20, 21*), pentane, etc. However, with neohexane one observes in some cases a particularly high extent of fission of neohexane into isobutane and ethane, naturally without any methane formed. These molecules, among others, are then responsible for the high values of M_f. In order to follow also smaller effects on M_f which might have been masked if M_f is evaluated as described above, another parameter was evaluated,

$$M_f^{\neq} = \frac{[4(\text{ethane} - \text{isoBut})] + [3\mathrm{C_3}] + [\text{neoPent}] + [\text{isoPent}]}{[\mathrm{CH_4}]^*},$$

in which only ethane, in excess of that formed by $C_6 \rightarrow C_4 + C_2$, is considered.

Catalyst Preparation

Iridium catalysts were prepared in two extreme forms, which are designated below as small-particle and large-particle Ir catalysts, respectively. Small-particle Ir catalyst was prepared by making a suspension of $(NH_4)_2\ IrCl_6$ (Drijfhout, Amsterdam) in H_2O/NH_3 with SiO_2 and allowing it to dry. Loading (calculated) was 1 wt% Ir metal. This catalyst was very active and in order to be able to measure at low conversions at temperatures up to 650 K, the dry product had to be diluted strongly (up to 1 : 50) with inert SiO_2, mechanically admixed. Large-particle Ir catalyst was prepared by mixing mechanically crystals of $(NH_4)_2IrCl_6$ with SiO_2; loading (calculated) was again 1 wt% metal/SiO_2. Electron microscope photographs revealed that the first catalyst contained particles mainly of about 1.5 nm diameter, and the second catalyst of about 500 nm diameter. The "large-particle" Ir catalyst contained also a rather small fraction of small particles ($d \approx 3$ nm) which evidently originate from the part of $(NH_4)_2IrCl_6$ which reacted with the SiO_2 surface upon mechanical mixing.

It should be noted that not all Ir adsorbed complexes are reducible by H_2 at $T = 720$ K (*28*). When the color is violet, the catalyst converts easily into a black (bimetallic) product, whereas when it is green the color does not change by reduction. Extensive stirring at exactly 363 K is obligatory to form the violet complexes. A standard *in situ* reduction consisted of H_2 treatment at 673 K overnight.

Catalyst Poisoning Procedure

One of the reasons why the controversy with regard to isomerization and the particle size effects with Ir exists (*21–26*) could be a different state of the "carbon" layers in experiments performed by different authors. Therefore, both the "small"- and "large"-particle Ir catalysts were tested after they had deliberately been "poisoned," or better formulated, after they had been subjected to a procedure which was meant to deposit "carbon" on the surface. This procedure, which has certainly caused deposition of carbon in the case of Pt catalysts (*20*), was as follows. Virgin catalyst, after a reduction by H_2 at 723 K overnight, was treated by H_2/neohexane mixture at 723 K, for 30 min. Then the catalysts were flushed at 723 K with N_2 (oxygen free) until no desorbing molecules could be detected (24 h flushing with N_2 was necessary) and after that the reactor was cooled to about 600 K and the catalyst was flushed with H_2. Under these circumstances mostly methane was observed in the gas flow coming from the reactor. Having slowly raised the temperature to 723 K, the catalyst was reduced during the night in order to be able to perform catalyzed neohexane reactions the next day.

RESULTS

At low temperatures, say $T < 500$ K, the main products observed are neopentane and methane. This means that 2C-$\alpha\beta$ complexes are being formed, and the strongly prevailing reaction is hydrogenolysis. This is the same result as that obtained in pulse experiments (*29*) with H_2 as a carrier gas, i.e., under conditions such that the surface contains the minimum possible amount of deposited carbon and firmly bound carbonaceous residues (throughout this paper we will refer to "carbon"). Under the conditions (T, p) applied, only small-particle Ir showed some activity.

A typical result is presented in Fig. 1 showing the product distribution as a function of the temperature (T, K). Ir (1%)/SiO_2 was diluted in this experiment in a 1 : 7 ratio with inert SiO_2. As can be seen from Fig. 1, at low temperatures isomerization is not observed and the contribution of the 3C-$\alpha\gamma'$ and 3C-$\alpha\gamma$ complexes to the overall reaction leading to hydrogenolysis is also rather

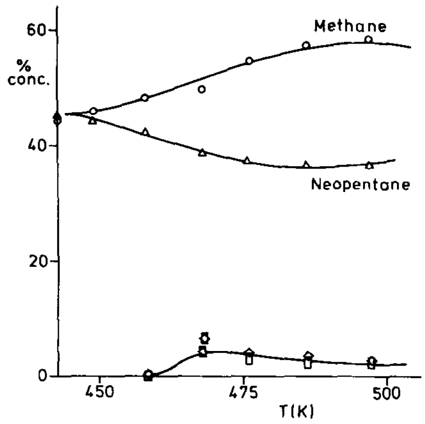


FIG. 1. Product distribution as a function of temperature, in the low-temperature region. (○) Methane, (△) neopentane, (□) isobutane, (◇) ethane. The small-particle Ir catalyst, diluted 1 : 7 by SiO_2.

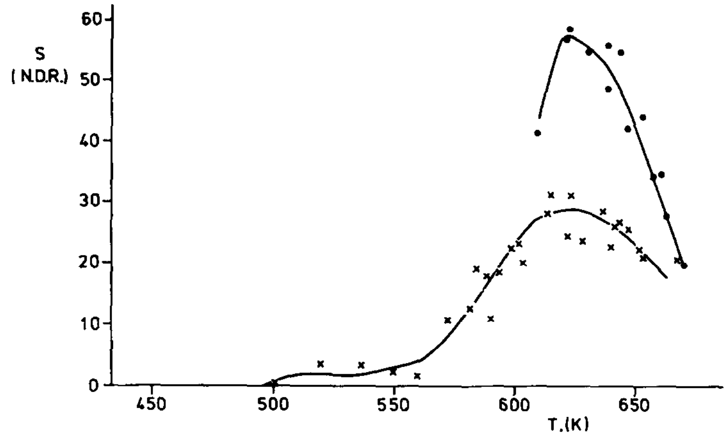


FIG. 2. Selectivity S_{ndr} in the nondestructive reactions (see under Experimental for definitions) as a function of temperature. (●) Large-particle Ir catalyst, an experiment with the virgin surface. (×) Small-particle Ir catalyst, various runs, with or without poisoning performed according to the procedure described under Experimental, before the catalytic experiment. (After a high-temperature reaction or treatment, the large-particle Ir reveals a similar S_{ndr} vs T behavior.)

small. However, when small amounts of small-particle (strongly 1 : 50 diluted) or large-particle catalysts are investigated at $T > 500$ K, isomerization and conversion into other C_6 products, including even some benzene (under standard analytical conditions, it appears as cyclohexane among the products), occur. These products are all summed up in "nondestructive reaction products" S_{ndr}. Selectivity toward these reactions, S_{ndr}, is plotted in Fig. 2 as a function of temperature. The upper curve is for a virgin surface of large-particle Ir catalyst (catalytic reactions followed starting from low temperatures); the lower curve is for small-particle Ir catalysts, with or without applying the procedure described as "poisoning" under Experimental. When the large-particle Ir catalyst is self-poisoned by neohexane reactions at $T > 650$ K, it then behaves identically to the small-particle Ir catalyst (the presence of carbonaceous layers manifests itself by lower rates).

The drop in the selectivity S_{ndr} above 630 K is due to secondary cracking reactions of the original isomerization products. The lower curve of Fig. 3 shows the increasing contribution of these reactions to the overall reaction, in terms of the selectivity S_{multi}. In calculating S_{multi} selectivity, all products are considered which may be suspected to appear or which can only appear, when a given hydrogenolysis is preceded by isomerization or by another hydrogenolytic step. The global parameter S_{ndr} indicates the important changes which occur when the temperature is increased. Qualitatively, there is no difference between the "small"- and "large"-particle Ir catalysts. However, a difference in the numerical values of S_{ndr} is obvious from Fig. 2. More details of the differences can be derived from the product distributions, such as those shown in Fig. 4. Note in this figure the following shifts in the product distributions. With both "small"- and "large"-particle Ir, the relative contribution of methane to the product distribution decreases, with increasing temperature. On the other hand, the relative contribution of isobutane and also of other products, which must have arisen from isomerization products, increases with increasing temperatures. This all indicates that with increasing temperature the role of 3C-$\alpha\gamma'$ and 3C-$\alpha\gamma$ complexes increases. An interesting shift in selectivities with particle

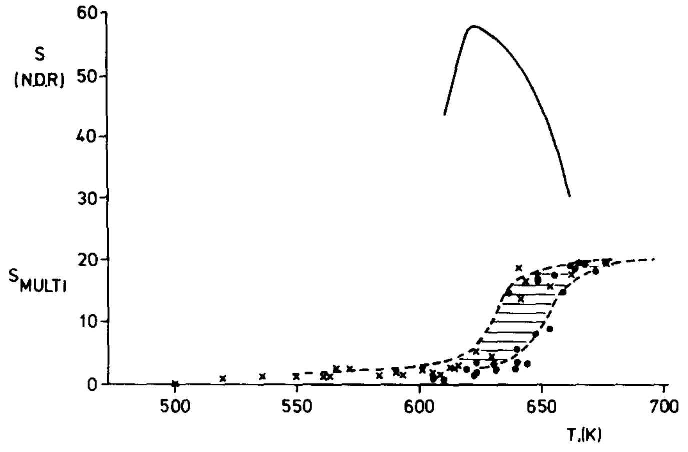


FIG. 3. Above: S_{ndr} for the large-particle Ir catalyst. Below: S_{multi}; both S's as a function of temperature. Symbols as in Fig. 2; see under Experimental for definitions.

size can be noted for the 639 K contributions: the 3C-$\alpha\gamma$ (γ') hydrogenolysis ($i-C_4$, $i-C_5$) prevailing on small-particle Ir is replaced on large-particle Ir by 3C-$\alpha\gamma$ (γ') isomerization (2MP, 3MP) and by dehydrocyclization of the products of isomerization (MCP, cy-Hex).

Figure 4 supplies even more information on the mechanism. For example, at higher temperatures butane increases markedly as primary gas product and this molecule can only be produced by multiple reactions, e.g., repeated hydrogenolysis in the adsorbed state. Similarly, hexane or benzene requires most probably combined isomerization and aromatization steps. Most of these reactions require a repeated function of 3C complexes or a tripod-like (4C) complex formation, which are obviously easier at higher temperatures.

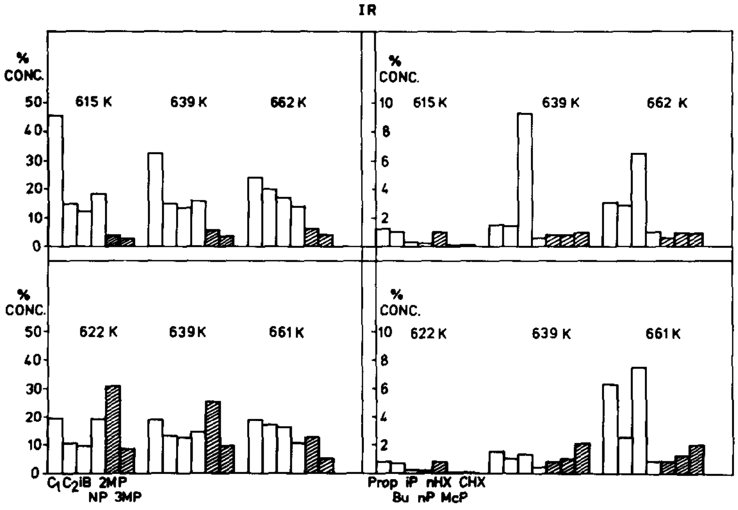


FIG. 4. Product distributions for (above) small-particle Ir catalyst and (below) large-particle Ir catalyst, at the three temperatures indicated. For all three temperatures the sequence of products is the same. The main products are indicated at the bottom left side.

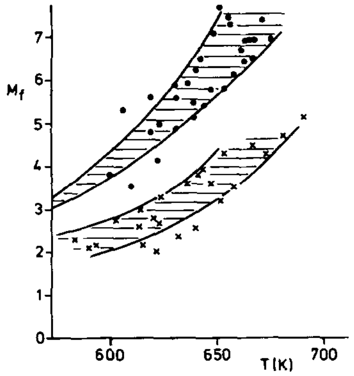


FIG. 5. Fission parameters M_f of Ir catalysts as a function of temperature. Symbols as in Fig. 2 (see under Experimental for definitions).

Hydrogenolytic splitting can be characterized by the parameter M_f. As already mentioned, the higher the value of this parameter, the higher is the contribution of types of fission other than the successive terminal splitting of C_1 groups. Figure 5 demonstrates that the parameter M_f increases considerably with T, reflecting among others the increasing contribution of the 3C complexes at higher temperatures. When the production of isobutane and ethane (3C-$\alpha\gamma'$ complex fission) is excluded from the considerations the increase in the modified fission parameter $M_f^{\neq}$ with T is much less pronounced, although it can still be observed (Fig. 6) at $T > 630$ K.

DISCUSSION

We start the discussion by recalling our earlier results obtained with hexane over a series of Pt/SiO_2 catalysts with varying particle size (2–7 nm) (*20*). According to those results, catalysts with the indicated range of sizes behave very similarly at low temperatures (the T.O.N.s vary by less than a factor of 3). However, when these catalysts are treated by the reaction mixture at 723 K for 30 min and in this way deliberately poisoned, their behavior at low temperatures shows subsequently more differences than before the "poisoning." The poisoning as applied in Ref. (*20*) had a larger effect the larger the particles were. The data are rationalized by the model once suggested by Blakely and Somorjai (*9*a), a model which seems to be gaining more support by various recent publications (*9*b–d). According to this model, the flat surfaces (e.g., (111), (100) planes of Pt) are very easily covered by "carbon" and become inactive. On the other hand the stepped surfaces have edges, corners, etc., which are more difficult to cover and they keep their activity better than planes. It is important to recall in relation to the data on Ir that the above authors (*9*) found that the activity of carbon covered (flat) surfaces can sometimes be restored simply by a heat treatment. Heating causes a recrystallization of the carbonaceous layers, which leads to the (re)appearance of larger ensembles of active Pt sites. We believe that this model (*9*) is also the key to understanding the data presented here and in the earlier paper (*20*).

Before we proceed further in our discussion a few points concerning the state of the "working" surface must be mentioned. As shown above, our procedure of a deliberate deposition of a carbonaceous layer did not markedly change the selectivity of the small-particle Ir catalyst in the high-temperature (600–650 K) range reactions. The question arises whether the method of "poisoning" really deposited any (or sufficient) "carbon" on the Ir surface. Therefore, the presence of "carbon" has been proven in the following way. The small-par-

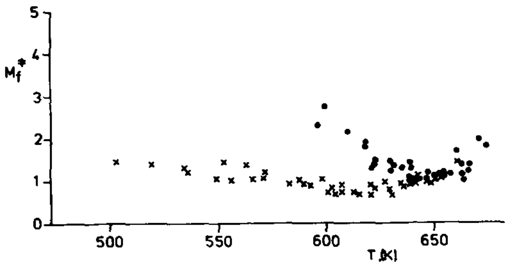


FIG. 6. A modified parameter $M_f^{\neq}$ as a function of temperature. Symbols as in Fig. 2 (see under Experimental for definitions).

ticle 1% wt Ir catalyst has been first tested (dilution 1 : 7) in the low-temperature region where the rate changes reversibly with temperatures. An Arrhenius plot of these data has then been extrapolated to 600–650 K and the extrapolated rate values were compared with those measured directly in the mentioned temperature region (dilution used in high T region was 1 : 50). It appeared that the extrapolated rates were 0.5–10 × 10^3 times higher for the same amount of Ir than the measured ones. This means that the small-particle Ir catalyst is covered by a carbonaceous layer to a very high extent.

Figure 2 indicates (note the heights of the maxima in the S_{ndr}) that the carbon layer formed on the virgin surface by the reaction at low temperatures leaves those ensembles operating which favor isomerization and high-temperature dehydrocyclization but are less suited for hydrogenolysis (see also Fig. 4 and the product distribution therein). Due to the constant presence of H_2 in the adsorbed layer and low temperature this is likely to be a carbon layer with rather randomly distributed carbon atoms. Heating of this layer, or the treatment of deliberate poisoning (described above), causes the maximum S_{ndr} to be lower with large-particle Ir. The large-particle Ir, when deliberately "poisoned," behaves like small-particle Ir and the deliberate poisoning is of virtually zero influence with the small-particle Ir catalyst. It may be expected that heating or the deliberate poisoning produces a rather stable recrystallized layer (as envisaged in Ref. (*9*)), which, however, still contains some ensembles which are active even for hydrogenolysis. The picture of recrystallization of the carbonaceous layer at higher temperatures is further supported by the fact that the activity of the deliberately poisoned large-particle Ir is even slightly higher than that of catalysts without such pretreatment. For example, it is observed that when a virgin surface (without pretreatment) is exposed to the reaction mixture at successively increasing temperatures up to 673 K, a slightly lower activity is found that when measurements of the same catalyst are made at decreasing temperature starting from the highest one. This result supports the idea of the "carbon"-layer recrystallization. As mentioned above, after such recrystallization the selectivity of a large-particle Ir catalyst is rather similar to that of a small-particle Ir catalyst, apart from some details.

Although they are not very pronounced, let us summarize now the particle size effects observed. When the surface of Ir large-particle catalyst is modified by the self-poisoning at low temperatures only, i.e., by a random deposition of "C" by the reaction itself, two main effects are observed:

(i) the role of the 2C-$\alpha\beta$ fission is relatively diminished;

(ii) the 3C-$\alpha\gamma$ species become more populated and they are converted rather into isomerization products than into hydrogenolytic products.

This is the same shift in selectivities as that which we have already observed earlier with neohexane or hexane and Ni and Ni–Cu alloys (*21, 27*). We observed in Ref. (*21*) with Ni–Cu that alloying causes the same effects as "C" deposited on the surface. Therefore, we suggest the following. Randomly deposited carbon increases the intrinsic tendency of a metal (Ir or Pt) to form 3C-$\alpha\gamma$ complexes. When the carbon layer is heat-treated (and by that, presumably, recrystallized) larger Ir ensembles reappear and a part of the above-mentioned effect becomes lost. Small particles of Ir are more difficult to cover by "C" and therefore they do not reach the maximum level of S_{ndr} of the large particles, although they are covered by "carbon," as the rate measurements indicate.

We found in this work, and it is also a common experience, that it is more difficult to poison Ir than Pt. It can be expected that this reflects the state of the surfaces of these two metals under steady-state reactions: Pt is blocked "better" than Ir. Iridium releases the products of the 2C-$\alpha\beta$ splitting of neohexane from the surface at such a rate that the 3C-$\alpha\gamma$ modes of reaction do not have a chance to manifest themselves, unless the surface is poisoned and the temperature is sufficiently increased. With hexane the blocking by the surface complexes and their products is relatively more effective than with neohexane.

We turn now to the problem of isomerization with iridium. Wreesman (*28*) has already confirmed with hexane reactions that Ir can cause isomerization. This paper confirms, with neohexane, the isomerization activity of Ir. This finding is thus in full agreement with the results obtained in Refs. (*21, 22, 24–26*). The condition to observe isomerization is that the temperature be high enough, although it need not be always as high as that with neohexane (see Ref. (*22*) for isomerization of 2-methyl- and 3-methylpentanes). The amount of Ir and the rate of the feed must be kept at such a level that not all molecules in the feed are consumed by a repeated hydrogenolysis. Poisoning blocks the hydrogenolysis and poisoning by the feed itself is easier with a large-particle Ir catalyst and with a higher total pressure and higher hydrocarbon partial pressure. Low pressures probably favor the C–C fission (which is usually preceded by deep dehydrogenation), since with Ir films or massive Ir catalysts no isomerization was observed at low pressures (*23, 29*).

The last point is the problem of different particle size sensitivity of Pt and Ir.

Chemisorption of hydrocarbons has been followed on various crystallographic planes of Ir on Pt, on both macroscopic and microscopic (FEM) (*30*) planes. The latter investigations showed quite clearly that there is no principal difference in the behavior of Ir and Pt in the respect that the rough (open) planes react much faster with the hydrocarbons than the flat planes. Nevertheless, for some reactions Ir showed much less crystal plane specificity and particle size sensitivity than Pt (*9, 21–26*). We suggest that this difference is related to the different state of "C" on both metals. We suggest further that the differences between the results of various authors with various reactions are also caused by a different structure of the "carbon" layer, the formation of which is itself "particle size" and "hydrogen pressure" sensitive. This layer is also responsible for the rather limited particle size sensitivity of the selectivity of Ir catalysts in the reactions followed.

CONCLUSIONS

The structure sensitivity of reactions on Ir is less pronounced than that of Pt. This is rationalized in this paper by relating the structure sensitivity (and the differences in it) to the properties of the "carbon" layers. As a consequence, in this model the activity and the selectivity of a metal are determined not only by the properties of individual metal atoms, i.e., by its position in the periodic table, but also by the extent and character of a side reaction, which in the present case is "carbon" deposition.

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