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# NOTES

## On the Catalytic Properties and Structure of Small Platinum Particles Supported on Graphite

The crystallographic structure of small platinum particles was studied and correlated with their catalytic activity. The platinum particles are found to be fcc cubo-octahedra with either a (111) or a (110) face in contact with the basal graphite plane. Particles appear in well-defined azimuthal orientations on the surface which indicates the strong nature of their interaction with the substrate. The catalytic properties are studied using the conversion of neopentane as a test reaction. An interesting correlation between the number of $B_3$ sites on (111) faces of the cubooctahedral particles and the selectivity for neopentane conversion is reported. The findings are in agreement with an early model of isomerization proposed by M. Boudart, A. W. Aldag, L. D. Ptak, and J. E. Benson (*J. Catal.* 11, 35–45, 1968).

### 1. INTRODUCTION

It has been observed that the adsorptive and catalytic properties of some metals dispersed on a support depend on the particle size and in general on the mode of catalyst preparation (*1–4*). Reactions of this type are called demanding (*2*, *5*). Foger and Anderson (*6*) have shown that the isomerization selectivity ($S_i$) in the neopentane conversion by Pt catalysts is strongly influenced by the size of the metal particles. Furthermore, it seems that some surface configurations of the platinum atoms could favor isomerization over hydrogenolysis in this reaction. These platinum surface arrays could be formed during the particle growth process and are closely related to the shape and dimensions of the particles (*7*, *9*). It is clear that attention has to be paid to the morphology and structure of the particles participating in the reaction. In a previous work (*10*) we have reported that for the Pt/C catalyst the particles in the 20- to 250-Å size range have a regular cubo-octahedral shape. The particles are single crystalline with an fcc crystal structure. In the present work these studies are completed with X-ray and additional TEM data and correlated with kinetic measurements. Our aim was to find correlations between the shape and crystallography of the particles and their catalytic properties. The neopentane isomerization was used as a test reaction. It is known that catalytic activity for the skeletal isomerization of neopentane occurs only in the metal particles (*11*, *12*). Therefore this reaction provides a good model system for studying the influence of morphology and structure of the particles on the selectivity.

### 2. EXPERIMENTAL TECHNIQUES

(*a*) *Sample preparation.* The catalyst was prepared by deposition of chloroplatinic acid on the graphite from an organic solution of benzene and ethanol. The samples were reducėd in pure hydrogen at 850°C during 12 hr. A more complete discussion of the preparation method was given in a previous paper (*10*).

(*b*) *X-Ray diffraction.* The X-ray diffraction measurements were made using a standard Phillips diffractometer equipped with a monochromator. Profiles of the (111), (220), and (200) reflections of Pt were recorded and the peaks areas measured. The average crystallite diameter $D_v$, was calculated from the peak width using Scherrer's relation. Instrumental boradening correction was made using the Anantharaman and Christian (*13*) formula: $\beta = (B^2 - b^2)B$, where $B$ is the experimental width and $b$ is the instrumental factor taken

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equal to 0.15°. This expression is more realistic for large crystallite diameters as shown recently (*14*). The mean diameter was measured to be 153 Å for the (111) planes, 127 Å for the (200) planes, and 137 Å for the (220) planes. From those values an average of 139 Å was obtained.

(*c*) *Kinetic measurements.* The activity data of the neopentane conversion over a Pt/C catalyst were collected in a differential reactor flow system coupled with a Varian Aerograph-1200 chromatograph. The gas coming from the reactor was analyzed by flowing it through a column 6 m long, filled with chromosorb W (80 mesh) impregnated with dimethylsulfolane (20%). The chromatographic analyses were performed at reactor temperatures of 300 and 360°C, respectively, and at a total pressure of 1 atm. The reagent gas was a mixture of neopentane (Fluka, 99.9% purity) diluted in helium and hydrogen (air Liquide, 99.9%) with a hydrogen to neopentane ratio of 10. These reaction conditions are similar to those described by Boudart and Ptak (*15*). The reaction products were methane, ethane, propane, isobutane, and isopentane.

(*d*) *Electron microscopy.* The TEM techniques were described in detail in a previous work (*10*). To determine the size distributions we used experimental evidence that particles were cubo-octahedrons with either ⟨111⟩ or ⟨110⟩ directions perpendicular to the graphite basal surface. Those particles were called $H_1$ and $H_2$ types, respectively, in Ref. (*10*) and an example of them is shown in Fig. 1. The sides of the particles were measured, and from this the ratio of the equivalent sphere was calculated for both types of particles.

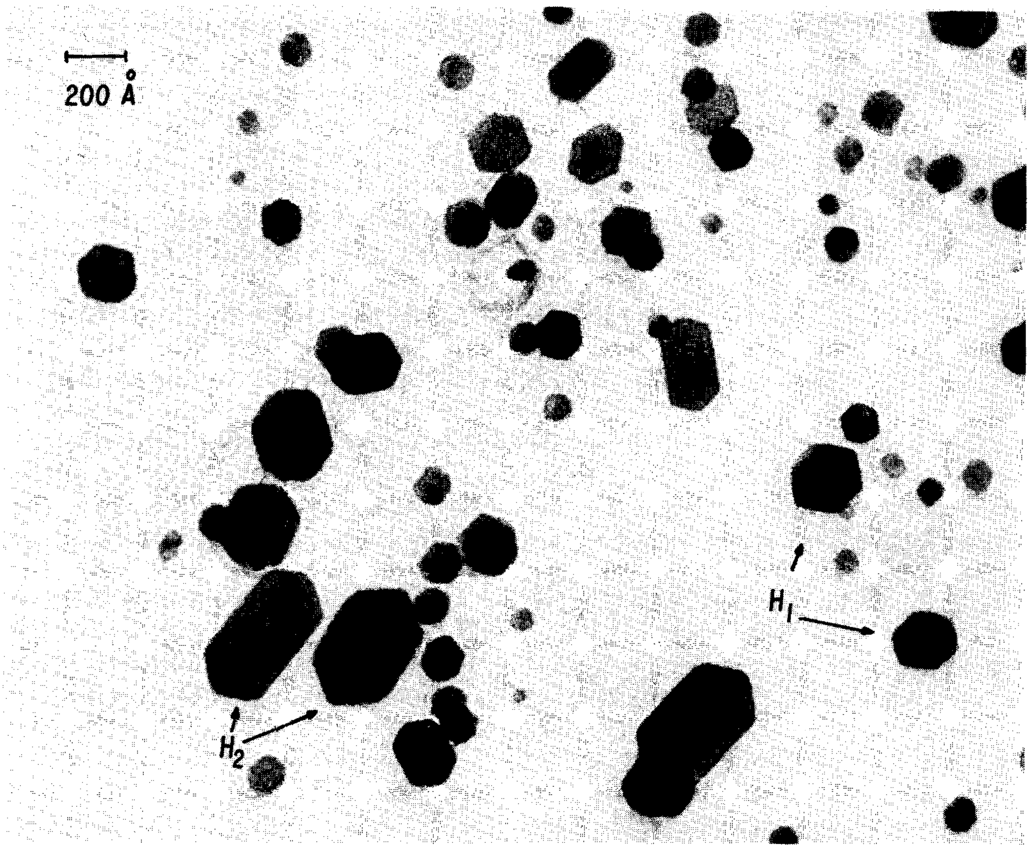

FIG. 1. Bright-field image of platinum particles showing the two characteristic hexagonal shapes $H_1$ and $H_2$. In this figure, 1 cm = 200 Å.

The data were taken from a sample containing about 1000 particles. The mean particle diameter was calculated as a weighted average of the equivalent sphere ratios for $H_1$ and $H_2$ particles. The final value was 137 Å which is in fair agreement with the value obtained by X-ray diffraction.

## 3. RESULTS AND DISCUSSION

The electron microscopy studies of particles $H_1$ and $H_2$ reported previously showed that both corresponded to a cubo-octahedron with a (111) face in contact with the basal graphite plane. The $H_1$ particle corresponded to a cubo-octahedron with a (111) face in contact with the basal graphite plane. $H_2$-Type particles tend to be larger than $H_1$-type particles. They appear, however, much less frequently. When graphite and platinum reflections are simultaneously included on the microscope objective aperture, Moiré patterns in the dark-field image are obtained. Figure 2 shows a typical $H_1$ particle with a Moiré pattern. The reflections used were (220) for Pt and (1120) for graphite. The Moiré patterns can be of the parallel type (fringes run perpendicular to both **g** and Δ**g** vectors), or of the rotation type (fringes run perpendicular to Δ**g** but not to **g**). The first interesting conclusion is that Pt particles are not strained to match the graphite surface; otherwise Moiré fringes would not be observed. Morever from the Moiré patterns it is possible to obtain the azimuthal orientation of the particles with respect to the graphite surface. The same information can be obtained from the relation between dark-field images and **g** vectors as discussed in Ref. (*10*). Using these two methods the orientations of the $H_1$ particles on the (0001) graphite plane were studied. The diffraction patterns have sixfold symmetry and the orientations can be well defined within two (1120)-type spots. The results are presented in Fig. 3. The angle of rotation indicates deviation with respect to the parallel epitaxial orientation. The most striking result is that the rotation angles correspond to well-defined values. Gómez and Dingley (*16*) have shown recently that these angles can be predicted using a coincidence lattice model for preferred orientations. It is clear that, when growing, the particles have the possibility to rotate to a position which corresponds to a minimum interfacial energy. The results in Fig. 3 indicate a strong interaction between the particles and the substrate. There is vast evidence in studies of epitaxy of evaporated metals on insulator substrates (*17*) which suggest that epitaxy is the result of the coalescence of critical nuclei. If the physical situation during the growth of evaporated particles is basically similar to the nucleation and growth of catalytic particles as suggested by Wymblatt (*18*), then one has to conclude that the results in Fig. 3 suggest a strong cluster mobility. Evidence showing cluster mobility is well documented in the litera-

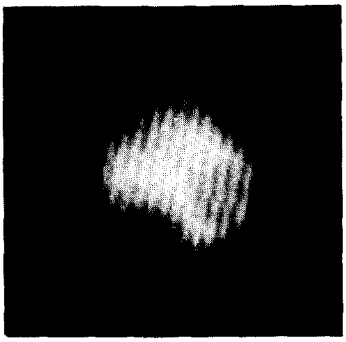

FIG. 2. A typical $H_1$ particle showing Moiré parallel fringes produced by (220) and (1120) reflections. In this figure, 1 cm = 80 Å.

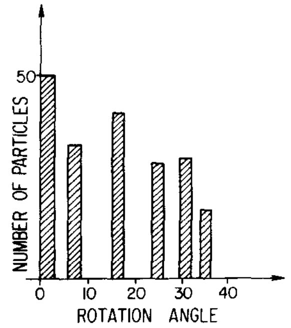

FIG. 3. Histogram showing the angular deviation of cubo-octahedral particles of type $H_1$ with respect to a parallel orientation in the basal plane of graphite.

ture (*19, 21*). Recent results of Heinemann *et al.* (*21*) showed that nucleation, growth, and cluster mobility can occur simultaneously. This means that the described effect can be important even for a highly dispersed catalyst. The results in Fig. 3 are also relevant for considerations on sintering-promoted deactivation of the catalyst. The work of Metois *et al.* (*22*) indicates that well-oriented clusters will have less mobility than the nonepitaxial ones. Thus well-oriented clusters will be more resistant to sintering. Although more experimental information is needed to test these ideas they appear to be very promising.

Table 1 shows the kinetic data which correspond to the two parallel reactions, hydrogenolysis and isomerization of neopentane at 300 and 360°C, respectively. The specific activities are expressed as the amount of product formed ($N°$ moles) per gram of metal. The selectivity of isomerization ($S_i$) was taken as the percentage of isopentane formed with respect to the total conversion. As is apparent from the table, isomerization is favored by the Pt/C catalyst at both tempertures, with selectivities equal to 87.2 and 82.8%, respectively. In addition the hydrogenolysis products such as $CH_4$ and iso-$C_4H_{10}$ are favored over intermediates such as $C_2H_6$ and $C_3H_8$. This means that the breaking of a single bond in the neopentane molecule is more likely. The quantity of isobutane which is produced decreases slightly with an increase in the temperature. It is possible that in the high temperatures some secondary reactions become important (like transformations into light hydrocarbons).

TABLE 1

Activity of Pt/C Catalyst in Neopentane Conversion at 300 and 360°C[a]

| Reaction pathway | Product | Conversion (%) | | Specific rate (× $10^8$ moles $sec^{-1}$ $g^{-1}$) | |
|---|---|---|---|---|---|
| | | 300°C | 360°C | 300°C | 360°C |
| Hydrogenolysis | $CH_4$ | 2.37 | 4.33 | 7.6 | 14.9 |
| | $C_2H_6$ | 1.5 | 2.5 | | |
| | $C_3H_8$ | 2.0 | 4.2 | | |
| | i-$C_4H_{10}$ | 6.87 | 6.1 | | |
| Isomerization | i-$C_5H_{12}$ | 87.2 | 82.8 | 51.8 | 72.1 |

[a] $H_2$/neopentane = 10; $P$ = 1 atm.

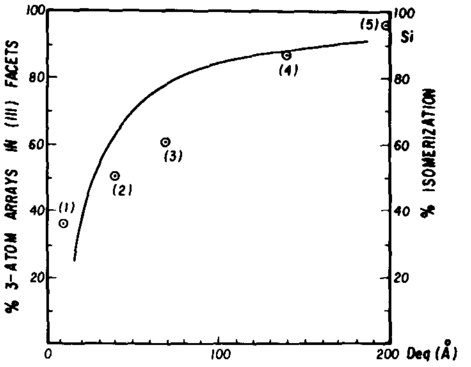

FIG. 4. Variation of the percentage of three-atom arrays on (111) facets for a perfect cubo-octahedral particle (solid line). Circled dots indicate experimental selectivity values. Points 1, 2, and 3 are from Ref. (*6*). Point 5 is from Ref. (*2*).

It has been suggested by Boudart *et al.* (*2*) that atom arrays of three sites ($B_3$-type sites) could favor the adsorption of the neopentane molecule. Such sites are present in (111) crystal planes. Foger and Anderson (*6*) have correlated the percentage of atoms in (111) planes with selectivity ($S_i$). These authors assumed cubo-octahedral and octahedral particle shapes, respectively.

In view of these ideas and the results of the present work a calculation was made of the number of $B_3$ sites (see Ref. (*3*) for notation) in a regular cubo-octahedron as a function of the average particle diameter. The results are shown in Fig. 4 along with some experimental selectivity values. In Fig. 4 we have not normalized the selectivity values as proposed by Anderson ($S_i$ = 90% for a ⟨111⟩ continuous film) because a value of $S_i$ = 90% has been reported for a Pt/$\alpha$-$Al_2O_3$ catalyst treated at high temperatures (*23, 24*). As is apparent from the figure the best agreement is found for larger sizes. It should be mentioned that the main disagreement is produced in data collected under different preparation conditions and with different types of supports. In fact there is no evidence that the particles in those catalysts were cubo-octahedra.

In addition we have also determined the surface area of the catalyst by hydrogen–oxygen titration. A specific surface area of 20 $m^2/g$ for a dispersion of 7.5% was obtained. If we calculate theoretically the ratio of the surface to volume atoms in a cubo-octahedral particle as a function of the size, we obtain for an average diameter of 140 Å a value equal to 9.8% which is close to the experimental value.

## 4. CONCLUSIONS

It was established that the particles in the Pt/C catalyst have a cubo-octahedral shape, which is bounded by (111) and (100) planes. Those catalysts promote the isomerization reaction for neopentane at both 300 and 360°C. It was also found that the break of a single bond is more likely, yielding predominantly methane and isobutane as main hydrogenolysis products. An encouraging correlation has been found between the high selectivity for neopentane conversion and the number of $B_3$ sites in the Pt particles calculated from the TEM data. Agreement was also obtained with the metal dispersion measurements.

It was clearly established that weak-beam dark-field electron microscopy can be an extremely powerful method in helping to understand kinetic data in catalysis.

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