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# Electron Microscopy of $Pt/Al_2O_3$ Model Catalysts

## III. The Hydrogenolysis of Methylcyclopentane as a Function of Particle Size

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$Pt/Al_2O_3$ model catalysts were prepared by high vacuum evaporation of platinum onto alumina films produced either by reactive evaporation of Al in oxygen ("Type A") or by anodic oxidation of aluminum ("Type B"). The particle size of the catalysts was determined by electron microscopy and remained stable throughout the reactions. On these catalysts the hydrogenolysis of methylcyclopentane was studied at 510 and 560 K at 1 bar pressure of $H_2$. On catalysts of Type A the proportion of the three main products (2-methylpentane, 3-methylpentane and *n*-hexane) changed strongly with increasing particle size, whereas the changes were less pronounced on catalysts of Type B. The relatively higher *n*-hexane production on catalysts of Type B was reduced by the addition of $NH_3$ to the reactant gas and is presumably due to the acidic nature of the support. Several mechanisms possibly responsible for the particle size effect, namely, the coordination of the surface Pt atoms, spillover of hydrogen, phase boundary catalysis, and the influence of the particle shape, are discussed.

### 1. INTRODUCTION

The distribution of ring-opening products following the hydrogenolysis of methylcyclopentane (MCP) on platinum is known to be sensitive to the size of the metal particles (*1–4*). This size effect can be attributed to changes of the electronic levels of the metal associated with changes in the dispersion (*5*) or to the fact that distinct surface sites (low-coordinated or high-coordinated sites) (*6*) favor a distinct reaction pathway. On the other hand, the product distribution is also influenced by the type of the support (*7*), by the hydrogen partial pressure (*8*), and by the temperature (*2*). Experimental results of a particle size dependence originating from different laboratories are difficult to compare because the remaining parameters ($H_2$ partial pressure, temperature, and support) are generally not identical. Furthermore, additional effects may arise in connection with the preparation of the catalysts and may also interfere with the particle size effect. They may originate in various ways, e.g., from chlorine or acidic sites on the support (*2, 9*), from the thermal pretreatment (*10*), and from the experimental setup (differential flow reactor, static reactor, or pulse reactor). Finally, different methods of determining the metal particle size may yield different and sometimes incorrect results. For example, two catalysts of different size distributions, e.g., bimodal or Gaussian, respectively, would exhibit the same "mean particle size" if selective adsorption of X-ray line broadening is the method employed. However, the two samples would presumably behave very differently as catalysts.

For all these reasons it seems important to investigate a structure-sensitive reaction on well-defined model catalysts, e.g., on ultrathin platinum films prepared by evaporation onto supports suitable for electron microscopic determination of particle size, size distribution, and microstructure (*11*). In an investigation of this kind all the other parameters of the reaction should be held constant and additional effects should be eliminated as far as possible. Therefore, the hydrogenolysis of MCP was studied at con-

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stant reaction conditions with particle size and support being the only variables. The metal particle size was changed by varying the amount of evaporated platinum and by subsequent sintering procedures (*12*). Alumina is chosen as a support to facilitate comparison with commercial catalysts.

## 2. EXPERIMENTAL

### *2.1. Reagents*

The gases were supplied by Messer Griesheim. $H_2$ and Ar of 99.95 and 99.99% purity, respectively, were passed over a Deoxo-unit (Oxisorb) so that an oxygen content below 0.02 ppm was guaranteed. $O_2$ was used without further purification (99.95%). Methylcyclopentane (puriss, obtained from Fluka) contained only traces of *n*-hexane (0.05%, as determined by gas chromatography). This *n*-hexane content was negligible in comparison to the measured conversions.

### *2.2. Catalysts*

The $Al_2O_3$ support of "Type A" catalysts was prepared by reactive evaporation of Al metal in an oxygen atmosphere ($1.3 \times 10^{-2}$ Pa) onto glass slides. The support of Type B catalysts was prepared by anodic oxidation of Al foil (Goodfellow, 12 $\mu$m thick) in tartaric acid (*13*). The foil was washed thoroughly in distilled water and dried in air at 400 K before the deposition of the platinum. The support area used in the reaction was 80 $cm^2$ for either type of catalyst. Pt was evaporated onto these supports by electron bombardment heating at $10^{-4}$–$10^{-3}$ Pa, up to a mean film thickness ranging between 0.05 and 0.5 nm (mass thickness 0.1–1 $\mu g\ cm^{-2}$). The preparation of the catalyst is described in the preceding papers (*12, 14*). Stable particle distributions were obtained by iterative treatments in hydrogen and oxygen as reported there.

The size and shape of the particles were determined by electron microscopy. The specimens for electron microscopy were prepared in parallel to the supports for the catalysts (*14*). The supports for "Type A" specimens were produced by evaporating Al in $O_2$ reactively on NaCl, dissolving the NaCl, and mounting the film on gold EM grids. The support for specimens of Type B was an anodically oxidized $Al_2O_3$ film on gold EM grid, which had been dissolved from the Al in HCl or $HgCl_2$.

### *2.3. Apparatus*

The hydrogenolysis of MCP was investigated in a static reactor in order to achieve long contact times ($\geq$30 min). Before entering the MCP saturators and the reactor the reactant gas was passed through cold traps (ethanol, 170 K) in order to remove the condensable impurities. In order to avoid any contamination of the catalyst downstream of the cold traps only Teflon stopcocks (Rotaflo) were used instead of greased connections. Two MCP saturators were connected in series and the second was held at a lower temperature in order to control the partial pressure of MCP as carefully as possible. It ranged from 3 to 5 Pa.

The partial pressure of hydrogen was the ambient pressure (0.94 bar). The reactions were carried out at two temperatures, namely, 510 and 560 K. The reactor consisted of a vertical tube (20 mm i.d., 200 mm long). It was heated from the outside, while the temperature was measured inside by means of a Fe–constantan thermocouple. Since the reaction was carried out statically, temperature gradients along the catalyst could be neglected. The mass transport in the reactor was maintained by convection of the reactant gas and was estimated to be sufficiently large for this not to be the rate-controlling process. This can be expected because the catalysts were nonporous and the Pt crystallites were easily accessible from the gas phase. Multiple reactions could also be excluded from the fact that the obtained product distribution was neither a function of the time nor of the conversion (see Section 3.2). After the reaction the products were sampled in a cold trap (liquid nitrogen) for analysis by gas chromatography. The gas chromatographic separation was achieved by 10% squalane on Chromosorb W at 323 K. Detection was accomplished by means of a flame ionization detector.

## 3. RESULTS

### *3.1. Observation of the Particle Size Distribution*

In parallel to the preparation of the catalyst, specimens for electron microscopy had been prepared as described previously (*14*). The films of $Al_2O_3$ were always stripped from the supports (NaCl or Al foil) *before* Pt was deposited on them. They were mounted on gold EM grids and added to the catalysts so that the evaporation of Pt and the annealing in various ambients as well as the catalytic reactions were performed simultaneously on the catalyst and the EM grid. After every heat treatment and after a reaction one grid was removed from the reactor and inspected in the electron microscope. The specimens were characterized by their mean particle size, their particle size distribution, and, if appropriate, their crystallographic orientation. A detailed description is given in the preceding paper (*12*).

### *3.2. Hydrogenolysis of MCP*

Preliminary experiments were carried out in order to check the influence of the reaction time. They showed that the catalytic activity decreased during the reaction while the product distribution remained constant, as was also reported by Anderson and Shimoyama (*4*) for the hydrogenolysis of MCP on Pt/mica- and on Pt/NaCl-evaporated films. Because of the small amount of catalyst available (8–80 μg Pt) long contact times were necessary, in particular at 510 K, and therefore no initial catalytic activities could be determined. Because of the decreasing catalytic activity during the reaction, turnover numbers had no significance and a comparison between conversions obtained at different temperatures was also quite meaningless.

The total conversion in the experiments was between 1 and 15% at 510 K and above 30% at 560 K. The control reaction, using the supporting materials without Pt, showed no detectable conversion. Under the given experimental conditions 2-methylpentane (2-MP), 3-methylpentane (3-MP), and *n*-hexane (*n*-H) are the main reaction products. In principle the initial distribution of the three hexanes may be altered by their secondary reactions such as hydrocracking, formation of benzene, and isomerization. Under our experimental conditions, however, hydrocracking to alkanes with lower carbon content was negligible at 510 K and it was below 9% of the total conversion at 560 K. Benzene formation was not observed, neither at 510 K nor at 560 K, but at low conversions it could not be fully excluded that traces of benzene were unresolved in the gas chromatograph beside the large amount of MCP. The observed product distribution was neither a function of the time nor of the conversion. Therefore it seems very unlikely that isomerization of the hexanes (*3*, *15*) played an important role as a secondary reaction at the low conversions obtained at 510 K. At 560 K the conversions were above 30% and subsequent isomerization cannot be excluded. Therefore only the results obtained at 510 K are referred to when discussing the mechanism of the hydrogenolysis in Section 4.

The distribution of the three hexanes on the Pt/evaporated $Al_2O_3$/glass catalysts (Type A) in hydrogenolysis at 510 K is given in Table 1. Since the three products have all the same molecular mass, weight percentage and mole percentage are numerically equal. Table 1 reveals a particle size dependence typical for supported platinum catalysts (*1*). The content of 3-MP stays constant between 18 and 21% for all the particle sizes, while the proportion of 2-MP increases from 44% at a mean diameter of 1.55 nm to more than 70% at a mean diameter of 4.4 nm, and that of hexane decreases from about 40 to 9% in the same particle size range. The

TABLE 1

Product Distribution after Hydrogenolysis of MCP on Catalysts of Type A (Glass/Evaporated $Al_2O_3$/Pt) at 510 K as a Function of Dispersion

| Catalyst | | | | Pretreatment | Products | | | Ratio |
|---|---|---|---|---|---|---|---|---|
| No. | Mean thickness (nm) | Dispersion $\bar{d}_{eff}$ (nm) | D | | % n-H | % 3-MP | % 2-MP | $\frac{\text{2-MP}}{n\text{-H}}$ |
| 1 | 0.1 | 1.55 | 0.66 | $O_2$, 720 K | 39.5 | 16.3 | 44.2 | 1.12 |
| 1 | 0.1 | 1.9 | 0.54 | $O_2$, 720 K | 26.3 | 18.4 | 55.3 | 2.10 |
| 2 | 0.3 | 2.0 | 0.51 | $H_2$, 510 K | 19.2 | 19.9 | 60.9 | 3.17 |
| 2 | 0.3 | 2.25 | 0.45 | $O_2$, 720 K | 20.9 | 19.6 | 59.5 | 2.85 |
| 3 | 0.5 | 2.3 | 0.44 | $H_2$, 510 K | 16.6 | 23.1 | 60.3 | 3.64 |
| 3 | 0.5 | 2.75 | 0.37 | $H_2$, 510 K | 15.3 | 19.3 | 65.4 | 4.29 |
| 3 | 0.5 | 2.75 | 0.37 | $O_2$, 720 K | 17.9 | 18.0 | 64.1 | 3.57 |
| 2 | 0.3 | 2.8 | 0.36 | $O_2$, 720 K | 16.1 | 19.5 | 64.4 | 4.00 |
| 4 | 0.5 | 3.0 | 0.34 | $O_2$, 720 K | 13.2 | 20.8 | 66.0 | 5.00 |
| 3 | 0.5 | 3.5 | 0.29 | $O_2$, 720 K | 10.9 | 21.0 | 68.1 | 6.25 |
| 3 | 0.5 | 4.3 | 0.24 | $O_2$, 720 K | 8.9 | 18.7 | 72.4 | 8.13 |
| 4 | 0.5 | 4.4 | 0.23 | $O_2$, 720 K | 8.8 | 19.2 | 72.0 | 8.20 |

dependence of the n-hexane proportion on $\bar{d}_{eff}$ is shown in Fig. 1. The experiments performed on the same catalysts at 560 K yield a similar relation between the n-H proportion and $\bar{d}$, but the values were shifted to higher n-hexane contents as would be expected from the literature (e.g. Ref. (2)).

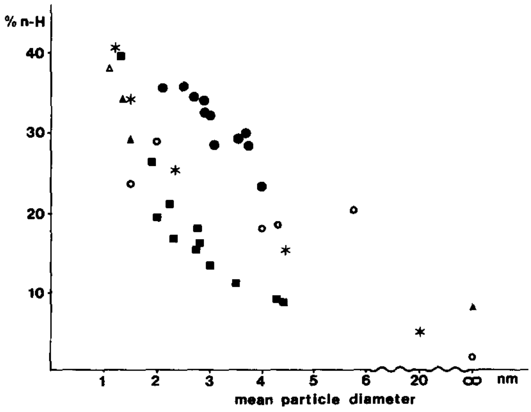

FIG. 1. Proportion of n-hexane in the products of hydrogenolysis as a function of mean particle diameter. ■, Catalysts of Type A; ●, catalysts of Type B; ▲, own measurements on Pt-supported catalysts and on Pt foil; *, Corolleur *et al.* (*1*); ○, Anderson and Shimoyama (*4*); △, Brandenberger *et al.* (*7*).

On the catalysts of Type B (Pt on anodically oxidized Al) the resulting product distributions (Table 2) were quite different from those obtained on catalysts A even when the pretreatment was identical and when the electron microscopy also revealed an identical microstructure of the platinum particles. The n-H content decreases with increasing particle diameter, but only from 36% at $\bar{d}$ = 2.1 nm to 23% at $\bar{d}$ = 4 nm. This is also shown in Fig. 1. In the same size range the content of 3-MP varies slightly between 18 and 15%.

## 4. DISCUSSION

### *4.1. Effect of the Particle Size*

The variation of product distribution with particle size is generally attributed to two different reaction pathways in the hydrogenolysis of MCP, called the selective and nonselective mechanisms, respectively (*3, 4, 15*). On highly dispersed catalysts the diadsorbed intermediate is assumed to be bound to low-coordinated atoms whereby statistical breaking of the cyclopentane ring occurs. On larger Pt crystallites high-coordinated sites on low-index planes are predominant. On those sites the tertiary car-

TABLE 2

Product Distribution after Hydrogenolysis of MCP on Catalysts of Type B (Al/Anodically Oxidized $Al_2O_3$/Pt) at 510 K as a Function of Dispersion

| Catalyst | | | | Pretreatment | Products | | | Ratio |
|---|---|---|---|---|---|---|---|---|
| No. | Mean thickness (nm) | Dispersion | | | % *n*-H | % 3-MP | % 2-MP | $\frac{2\text{-MP}}{n\text{-H}}$ |
| | | $\bar{d}_{eff}$ (nm) | $D$ | | | | | |
| 1 | 0.1 | 2.1 | 0.48 | $O_2$, 720 K | 35.5 | 18.2 | 46.3 | 1.31 |
| 2 | 0.3 | 2.5 | 0.41 | $H_2$, 510 K | 35.7 | 15.7 | 48.6 | 1.36 |
| 3 | 0.5 | 2.7 | 0.38 | $H_2$, 510 K | 34.4 | 15.0 | 50.6 | 1.47 |
| 3 | 0.5 | 2.9 | 0.35 | $H_2$, 510 K | 32.4 | 15.4 | 52.2 | 1.61 |
| 4 | 0.5 | 2.9 | 0.35 | $O_2$, 720 K | 34.0 | 15.8 | 50.2 | 1.48 |
| 5 | 0.5 | 3.0 | 0.34 | $H_2$, 510 K | 32.1 | 15.1 | 52.8 | 1.64 |
| 6 | 0.5 | 3.1 | 0.33 | $O_2$, 720 K | 28.6 | 16.0 | 55.4 | 1.94 |
| 7 | 0.5 | 3.55 | 0.29 | $H_2$, 510 K | 29.4 | 16.3 | 54.3 | 1.84 |
| 4 | 0.5 | 3.7 | 0.27 | $O_2$, 720 K | 29.8 | 16.5 | 53.7 | 1.80 |
| 5 | 0.5 | 3.75 | 0.27 | $H_2$, 510 K | 28.3 | 15.5 | 56.2 | 1.98 |
| 4 | 0.5 | 4.0 | 0.25 | $O_2$, 720 K | 23.3 | 17.8 | 58.9 | 2.53 |

bon atom of MCP may not be bound for geometrical reasons and presumably an $\alpha\alpha\beta\beta$ tetraadsorbed species results, followed by nonstatistical ring opening. Following this selective mechanism only 2-MP and 3-MP would be formed whereas the production of *n*-hexane would be inhibited. Other authors report that the observed distribution could not be expressed as a linear combination of two independent distributions originating from two different mechanisms, and other mechanisms have therefore been postulated (e.g. (*15*)).

The experimental results of different authors (*1*, *4*) and our observations seem to agree in the fact that the proportion of 3-MP is relatively constant at 20% independent of the particle size and the sum of the other two hexanes is about 80%. The proportion of *n*-hexane can therefore be regarded as a sensitive parameter for describing the particle size dependence. In Fig. 1 the *n*-H content at 510 K is plotted against the mean particle size of the catalysts of Types A and B, respectively. Results of previous work performed under comparable reaction conditions are also added to the plot and found to agree well with our results even in cases where the support and other parameters were not quite identical (*1*, *4*, *7*).

As already mentioned, the catalysts contain a spectrum of various particle sizes contributing to the overall catalytic activity. The proportion of particles of one distinct size range $i$ and their contributions $a_i$ to the total surface area of the catalyst can be determined from electron microscopy. In order to obtain the contributions of particles of different sizes to the overall specific activity it seems reasonable to divide them into different, but not too many, size ranges and to calculate the contributions of each particle range by applying an optimum fit to the experimental data. Hence the particles were tentatively divided into three classes (diameter $d_1 < 2$ nm, $2\text{nm} \leq d_2 \leq 3$ nm, and $d_3 > 3$ nm) that would lead to product distributions $(x_1:y_1:z_1)$, $(x_2:y_2:z_2)$, and $(x_3:y_3:z_3)$, respectively. The experimentally observed product proportion $(x:y:z)$ can be regarded as the sum of the contributions from each class of particles. It can be written as

$$x = \Sigma a_i x_i,$$

$$y = \Sigma a_i y_i,$$

$$z = \Sigma a_i z_i$$

under the assumption that the catalytic *activity* of every Pt site is the same regardless of the crystallite size. From the experimental data the parameters $x_i$, $y_i$, and $z_i$ were evaluated by the method of least-mean-square errors and the results of the calculation for the catalysts of Type A are given in Table 3. These values show even more clearly the sharp decrease of the *n*-hexane production with increasing particle size in the size region between 2 and 3 nm, which is in good agreement with the critical size obtained by Gault *et al.* (*3*). The *n*-H production is almost negligible on particles greater than 3 nm in diameter. The fact that the proportion of the number of edges and corner atoms to the total number of surface atoms on all kinds of metal clusters decreases also sharply in the same size range (*6*) seems to justify the assumption that these low-coordinated sites are responsible for the non-selective pathway of the reaction. In this connection the influence of the morphology of the small Pt crystallites is of interest. However, a distinct correlation between their crystallographic shape and catalytic activity (*16*) could not yet be established for this experimental system. It seems that even those crystallites which exhibit certain crystallographic faces or facets immediately after deposition are converted to rather rounded (spherical) particles by the subsequent process of sintering and annealing.

### 4.2. *Effect of the Suppport*

So far only the results obtained with the catalysts of Type A have been considered in the discussion. The differences between them and the results obtained with catalysts of Type B (Pt on anodically oxidized Al foil) can only be due to differences in the supporting film. The possibility of a parallel reaction on the support can be excluded since the support alone is inactive. From the hydrocracking patterns of catalysts A and B at 560 K no general trend could be deduced which could indicate a different behaviour of the two types of catalysts towards hydrocracking.

TABLE 3

Product Distributions for Different Particle Size Ranges Calculated by Fitting the Experimental Data

| Diameter range (nm) | Percentage *n*-H | Percentage 3-MP | Percentage 2-MP | $\frac{\text{2-MP}}{n\text{-H}}$ |
|---|---|---|---|---|
| <2 | 46.2 | 14.8 | 39.0 | 0.844 |
| 2–3 | 18.1 | 20.5 | 61.4 | 3.39 |
| >3 | 8.6 | 19.5 | 71.9 | 8.36 |

A support-sensitive behaviour in hydrogenolysis is also reported by Brandenberger *et al.* (*7*) at considerably higher temperature (760 K). These authors propose a dual-function mechanism to occur via an ionic intermediate formed on acidic sites of the support. This intermediate can be desorbed by abstraction of $H^+$ and the resulting alkene is hydrogenated in a second step at the platinum surface, as has also been demonstrated by Schlatter and Boudart (*17*) for the hydrogenolysis of methylcyclopropane.

In the present work the anodic oxidation of aluminum was performed in an acidic medium and the presence of acidic sites on the alumina support may provide a plausible explanation for the product distributions obtained. To confirm this possibility further, we placed a small amount of ammonium carbamate in the cold part of the reactor. The atmosphere during the hydrogenolysis hence contained a small partial pressure of $NH_3$ (0.06 bar).

In fact, the product distribution was altered strongly as indicated in Table 4. On a catalyst of Type B of 3.1-nm mean particle size the product distribution (*n*-H : 3-MP : 2-MP) was initially 23.3 : 17.8 : 58.9 at 510 K. In the $NH_3$ atmosphere it changed to 8.6 : 21 : 70.4 as would be expected for a catalyst of Type A of the same degree of dispersion. After the removal of the $NH_3$ atmosphere the proportion of *n*-hexane was again increased. After several annealing treatments in $H_2$ at 510 K and heating in Ar

TABLE 4

MCP Hydrogenolysis on a Catalyst of Type B ($\bar{d}_{eff}$ = 4 nm) at 510 K before and after $NH_3$ Gas Treatment

| | Products | | | Ratio |
|---|---|---|---|---|
| | % *n*-H | % 3-MP | % 2-MP | $\frac{2\text{-MP}}{n\text{-H}}$ |
| Before treatment | 23.3 | 17.8 | 58.9 | 2.53 |
| With $NH_3$ in reactant gas | 8.6 | 21.0 | 70.4 | 8.18 |
| After 30 min heating in $H_2$ at 510 K | 14.0 | 19.0 | 67.0 | 4.76 |
| After 17 h heating in $H_2$ at 510 K | 16.5 | 18.8 | 64.7 | 4.00 |
| After add. 14 h heating in $H_2$ at 510 K | 17.4 | 19.0 | 63.6 | 3.70 |
| After add. 14 h heating in Ar at 620 K | 23.1 | 17.6 | 59.2 | 2.56 |

at 620 K the previous product distribution was reestablished (Table 4). The total conversion on catalysts B (below 15%) was reduced by the $NH_3$ treatment and likewise reestablished after the removal of $NH_3$. The inhibition of acidic sites by $NH_3$ was hence reversible. A catalyst of Type A subjected to the same $NH_3$ treatment yielded exactly the same product distribution as before and the $NH_3$ treatment caused no reduction of the total conversion. This indicates that catalytic sites, which can be poisoned by $NH_3$, are not present on the surface of catalysts A (Table 5). The question arises whether the $NH_3$ treatment may only block some catalytic sites on the platinum and not specifically acidic sites on the support. However, if this were the case the overall activity and selectivity of catalyst A should also be changed. Therefore we conclude that the differences of the two catalysts are only due to the different supports. After the $NH_3$ treatment both catalysts behave identically and this is best explained by blocking of the "acidic" sites on the support of the catalysts B.

TABLE 5

MCP Hydrogenolysis on a Catalyst of Type A ($\bar{d}_{eff}$ = 1.9 nm) at 510 K before and after Treatment with $NH_3$ and HCl

| | Products | | | Ratio |
|---|---|---|---|---|
| | % *n*-H | % 3-MP | % 2-MP | $\frac{2\text{-MP}}{n\text{-H}}$ |
| Before treatment | 26.3 | 18.4 | 55.3 | 2.10 |
| With $NH_3$ in reactant gas | 26.3 | 18.4 | 55.3 | 2.10 |
| With HCl in reactant gas | 29.1 | 17.4 | 53.5 | 1.84 |

In a further experiment it was shown that the production of acidic sites by addition of HCl gas to a reaction on the nonacidic catalyst (Type A) is irreversible. A catalyst of Type A yielding an initial product distribution (*n*-H :3-MP : 2-MP) of 26 : 18 : 55 was employed in a hydrogenolysis reaction whereby the reactant gas contained a few percent of dry HCl gas. The *n*-hexane content of the products increased to 29% whereas the proportion of 3-MP and 2-MP decreased to 17 and 53.5%, respectively, as is shown in Table 5. However, this change was accompanied by a substantial increase in hydrocracking to smaller hydrocarbons. The cracking activity could not be reduced and the previous selectivity could not be reestablished.

These latter experiments show clearly that beyond the two mechanisms sensitive to the metal particle size, generally referred to as the nonselective and selective pathways, there is also a support-sensitive mechanism contributing to the product distributions obtained on catalysts with acidic sites. The mechanisms proposed for the bifunctional hydrogenolysis of methylcyclopropane at low temperature (*17*) or for the hydrogenolysis of MCP at 760 K (*7*) can be called upon to explain the observed results. MCP can react with acidic sites to form an ionic surface intermediate by a ring-opening process. The carbon atom adjacent to the methyl group has the highest electron density because of hyperconjugation, and will therefore be preferably attacked by the acid. Rupture of the adjacent C–C bond leads to a secondary carbonium ion while all the other alternative pathways would result in a less stable primary carbonium ion. Desorption of this intermediate can occur via $H^+$ abstraction leading either to *n*-hexene or, by assistance of atomic hydrogen, directly to *n*-hexane. However, the hexene formation is not thermodynamically favored at the temperature of reaction (510–560 K). The equilibrium constant for formation of the most stable hexene (t-hexene-2) from MCP at 510 K is $4.7 \times 10^{-4}$ (*18*). *n*-Hexene has therefore never been observed in control reactions on the $Al_2O_3$ support alone. Furthermore, with the exception of the strained cyclopropane ring (*17*) the skeletal reactions catalyzed by acidic sites are known to occur only at more elevated temperature to a measurable extent. Hence the question has to be answered whether a secondary carbonium ion can be formed from MCP at our temperature of reaction.

Skeletal conversions of olefins on alumina can proceed at about 620 K via carbonium ion formation, followed either by carbon bond shift or $\beta$-scission (*19*). On the other hand, a double-bond shift alone can occur at lower temperatures (e.g., 530 K (*20*) or 430 K (*21*)). Evidently the high temperature required for the skeletal conversion of olefins on alumina is necessary for the secondary processes but may not be necessary for the formation of the carbonium ion. The formation of carbonium ions in ring-opening processes of methylcyclopropane can proceed even at 273 K (*17*). For less strained rings no data are available but it seems reasonable to assume that at 510 K the formation of a secondary carbonium ion by ring opening of MCP is possible. The reaction of this intermediate to a hexene is not thermodynamically favored at this temperature but a reaction with hydrogen to *n*-hexane is possible. Since on the support alone no reaction is observed, spillover of atomic hydrogen from the platinum surface is apparently needed. Hydrogen gas is dissociatively adsorbed on platinum and hydrogen atoms migrate across the boundary of the Pt crystallites to the alumina, react with the carbonium ions, and form *n*-hexane which desorbs leaving again an acidic site on the alumina. The reverse process has been recently described by Fujimoto *et al.* (*22*) to account for the dehydrogenation of paraffins on carbon-supported catalysts. Spillover effects of that kind have been frequently described in the literature (*23, 24*) and have also been observed on $Pt/Al_2O_3$ by one of the present authors (*25*).

## 5. CONCLUSIONS

The experiments on the catalysts of Type A show clearly that a strong correlation exists between the selectivity in the hydrogenolysis of MCP and the platinum particle size. By relating the electron microscopic size distribution to the measured product distribution one finds that the size dependence of the selectivity is particularly strong for particle diameters below 3 nm.

On the Type B catalysts an excess production of *n*-hexane is observed, which is reduced by the presence of $NH_3$ in the reacting gas. The poisoning of the presumably acidic sites by $NH_3$ indicates a support effect in addition to the particle size effect. The excess production of *n*-hexane on Type B catalysts is assumed to proceed via carbonium ions which are hydrogenated by hydrogen spillover.

Generally two explanations for the particle size effect are given in the literature:

(i) The fact that the number of low-coordinated Pt sites (edge and corner atoms) decreases with increasing particle size, and

(ii) the changes in the shape of the particles with increasing particle size, i.e., that different faces of different catalytic activities are exposed as the diameter of the particles changes.

In either case the influence of the surface structure on the selectivity may be geometric or electronic in nature. However, the results presented in this paper indicate that, in addition, a phase-boundary-catalyzed reaction cannot be excluded which would also be particle size dependent. In this case the MCP molecules adsorbed on the support in the vicinity of a Pt crystallite, i.e., at the phase boundary, will be reduced by hydrogen dissociatively adsorbed on the platinum, yielding preferably *n*-hexane. Since the ratio of phase boundary to Pt surface area is higher on highly dispersed systems this reaction pathway will also lead to a particle size dependence of the final product distribution and the *n*-hexane production will be enhanced at low particle sizes.

An unambiguous experimental confirmation of a mechanism of the last kind seems rather difficult. However, it should at least be possible to prove or to exclude the existence of a particle shape effect by further experiments.

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