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The Hydrogenolysis of Methylcyclopentane on Platinum Model Catalysts: Particle Size Effect Due to a Reaction Occurring at the Phase Boundary Metal–Support

R. KRAMER AND H. ZUEGG

Institut für Physikalische Chemie, Universität Innsbruck, Innrain 52 a, A-6020 Innsbruck, Austria

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The hydrogenolysis of methylcyclopentane at 520 K on platinum model catalysts was studied and the mechanism of this reaction investigated. Catalysts of low metal dispersion (<0.15) were prepared by high-vacuum evaporation of platinum onto thin films of amorphous alumina. After annealing at 770 K in air and hydrogen treatment at 520 K the mean size of the Pt particles was about 10 nm as determined by electron microscopy. On these catalysts the reaction products are mainly 2-methylpentane and 3-methylpentane and only 9–14% *n*-hexane is formed, as is to be expected for large Pt particles. On top of these catalysts a thin layer of Al_2O_3 (0.3 nm mean thickness) was then deposited in order to reduce the surface area of platinum in relation to the phase boundary platinum/alumina. Thereafter a decrease of the catalytic activity, as well as a shift in the product distribution, was observed. The *n*-hexane content was significantly enhanced (up to 22%) and the ratio of the three products was comparable to that usually obtained with Pt catalysts of higher dispersion. This result supports a reaction model which consists of two parallel reactions (i) occurring on the platinum surface and producing mainly 2-methylpentane and 3-methylpentane and (ii) occurring on the phase boundary platinum/support and producing additional *n*-hexane.

1. INTRODUCTION

In recent years numerous studies have been concerned with the selectivity of the platinum metals in catalytic hydrocarbon skeletal reactions (*1–9*). These studies have shown that the selectivity of platinum catalysts for the hydrogenolysis of methylcyclopentane (MCP) depends on the structure of the catalyst (*1–4*), on the reaction temperature (*1*), as well as on the hydrogen pressure (*5, 6*). However, the dependence of the selectivity on the reaction temperature can be experimentally verified only to a limited extent over a narrow temperature range, since at low temperatures the reaction does not proceed, while at high temperatures coking of the catalysts inhibits the reaction. Similarly, the variation of the hydrogen pressure has very little effect on the selectivity. Although at low hydrogen pressures the selectivity of the hydrogenolysis is changed, it is of minor practical importance, since under these conditions increased coking of the catalyst is observed. At high hydrogen pressures the changes in the product distribution are very small (*6*). Thus the main influence on the product distribution of the MCP hydrogenolysis comes from the structure of the catalysts, i.e., from the size of the Pt particles, as well as from the nature of the support.

The most important parameter determining the selectivity of the reaction is the size of the platinum particles. On small Pt particles the MCP hydrogenolysis occurs nonselectively leading to about 40% *n*-hexane (*n*H), 40% 2-methylpentane (2-MP), and 20% 3-methylpentane (3-MP), which corresponds to statistical ring opening. On the contrary, on very large Pt particles the branched hexanes 2-MP and 3-MP are formed almost selectively. In a recent review, the influence of the particle size on the selectivity of the MCP hydrogenolysis has been discussed (*8*).

The main objective of the present paper is to investigate the possible mechanisms

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responsible for this particle size effect. Previously, this effect has been attributed to the geometry of the platinum particles (changes in the surface site distribution or in the lattice structure with decreasing size of the metal particle) or to the electronic structure of the catalysts (changes of the electronic structure when particle size is decreased).

In an earlier paper (*9*) we have proposed a different explanation of the particle size effect by assuming two parallel reactions leading to different product distributions. Considering the concept of adlineation proposed by Schwab and Pietsch (*10*) about 50 years ago, it is assumed that one reaction takes place at the phase boundary platinum/support and favors statistical, nonselective ring opening of MCP. This reaction competes with the second reaction catalyzed by the platinum surface producing selectively 2-MP and 3-MP. Therefore, it can be expected that the first reaction becomes more important at small particle sizes, since the phase boundary is increased with respect to the platinum surface and hence the overall product distribution is shifted to the nonselective pathway.

In order to investigate further the feasibility of this model, we have now studied the selectivity of the hydrogenolysis of MCP over Pt catalysts by systematically varying the ratio of Pt surface area to Pt–support phase boundary without changing the basic Pt particle size.

This was accomplished by first preparing catalysts as in our previous work (*7*) by evaporation of Pt onto alumina supports. After measurement of the product distributions, the catalysts were modified by additional evaporation of a very thin film of alumina, thereby partially covering the metal particles. Thus the proportion of Pt/alumina phase boundary to Pt–metal area was increased, without changing the size of the metal particles. With these samples the selectivity in the hydrogenolysis of MCP was again determined. From a comparison of the product distributions obtained with the bare and the partially covered Pt particles conclusions can be drawn as to the applicability of the concept of adlineation.

2. EXPERIMENTAL

2.1. Preparation of the Catalysts

The alumina supports were prepared by two different methods as described previously (*7*). (i) Type A alumina films of about 10 nm thickness were deposited onto thin Al foils (Goodfellow, 12.5 μm thick) by reactive evaporation of Al in an oxygen atmosphere (1.3×10^{-2} Pa). (ii) A second type of alumina support (Type B) was produced by anodic oxidation of the Al foils in tartaric acid. The foils were washed thoroughly in distilled water. The supports of either type were then heated in air at 770 K to ensure that the films were thoroughly oxidized. Platinum was then evaporated on these supports at 10^{-4} to 10^{-3} Pa with a mean thickness ranging from 1.3 to 2 nm. The film thickness was controlled by a quartz crystal oscillator. Both Pt and Al were deposited by electron beam evaporation.

After the Pt film deposition each catalyst was heated in air to 770 K in order to obtain a stable size distribution of large platinum particles. Subsequently, the catalytic behavior of these catalysts was determined. To remove carbonaceous residues the catalysts were again heated in air at 770 K before they were covered with a thin Al_2O_3 film (0.3–0.5 nm mean thickness). In order to facilitate complete oxidation of the new Al_2O_3 film the catalysts were once more heated in air at 770 K prior to the repeated measurement of the catalytic behavior.

2.2. Characterization of the Catalysts by Transmission Electron Microscopy (TEM)

For the TEM characterization specimens of Type A catalysts were prepared but the Al foil was replaced by 300-mesh gold grids precoated with carbon films. The specimens of the Type B support were prepared by separating the Al_2O_3 films from the Al

foil in diluted HCl. The films were then mounted on gold grids. The EM grids were treated in the same way as the catalysts (see above). For the transfer to the electron microscope (Siemens Elmiscope 1a) they had to be exposed to air.

2.3. *Apparatus for the Catalytic Measurement*

The hydrogenolysis of MCP was investigated in a recirculating reactor providing the long contact times necessary due to the low catalyst area (170 cm^2). The gases H_2 and He (99.99% purity, supplied by Messer Griesheim) were passed over a Deoxo-unit (Oxisorb) while O_2 (99.95%) was used as supplied. Before entering the recirculating system the gases were purified from a possible contamination with grease or humidity by a cold trap. The recirculating system (300 cm^3 total volume) was made of Pyrex glass, the connections were polytetrafluoroethylene (PTFE)-sealed screw-cap joints (Young scientific glassware), and the valves were also PTFE-sealed O-ring taps (Young). The recirculation pump was constructed similarly to that described by Sime *et al.* (*11*) with the exception that the rotor was made of PTFE in order to reduce the weight and hence the mechanical friction. MCP was introduced by vapor diffusion as the gases were recirculated bypassing the MCP container. After sufficient mixing the mixture was supplied to the reactor. The withdrawal of 1 cm^3 of the reaction gases for analysis in the gas chromatograph was accomplished by a system of four PTFE-sealed valves. The temperature was measured inside with a NiCr/Ni thermocouple encapsulated into Pyrex glass to avoid any additional catalytic activity. Therefore the gases were inhibited from any contact with grease or with metals except that of the catalysts.

3. RESULTS

3.1. *Characterization of the Catalysts*

The high mean thickness (1.3–2.0 nm, mass thickness 3–5 $\mu g/cm^2$) was chosen to obtain large platinum particles after treatment in air at 770 K and in hydrogen at 520 K (*12*). A micrograph of the Pt/Type A–Al_2O_3 specimen (1.37 nm Pt deposited) pretreated in this way is shown in Fig. 1. The particles are rounded or elliptically shaped. The mean diameter is 6.8 nm. For elliptic particles the effective diameter was calculated from the square root of the largest times the smallest diameter. In order to obtain a parameter for the deviation from spherical shape we calculated the mean ratio of the largest to the smallest diameter. The obtained value of 1.27 shows that the particles are rather rounded and confirms the assumption that they can be described as calottes of spheres. With the knowledge of the particle density (7×10^{11} cm^{-2}) and of the mass thickness (2.9 μg cm^{-2}) the height of the platinum particles is estimated to be 5.4 nm, i.e., 80% of the diameter of the spheres. From this geometry the area of the platinum exposed to the reaction mixture is calculated to be 84% of the geometric support area.

The shape of the platinum particles supported by the Type B alumina was examined in the same way and resulted in somewhat different values. The larger mean thickness of platinum deposited (2.0 nm) resulted in a larger mean particle size of 12.7 nm. The particle density was lower (2×10^{11} cm^{-2}) than that for the Type A catalyst. The particles were slightly more spherical, the degree of deviation from the round shape was 1.14, and the height of the particles was only about 67% of the diameter. The geometry of the particles can therefore be described by calottes of spheres which are larger than half-spheres, assuming that after a treatment in air at 800 K the most stable shape with a nearly spherical surface is established. The estimated shape of the Pt particles is shown schematically in Fig. 2a.

The treatment with H_2 and O_2 at 670 K during the measurement of the catalytic properties did not change the particle density and the size distribution. The thin lay-

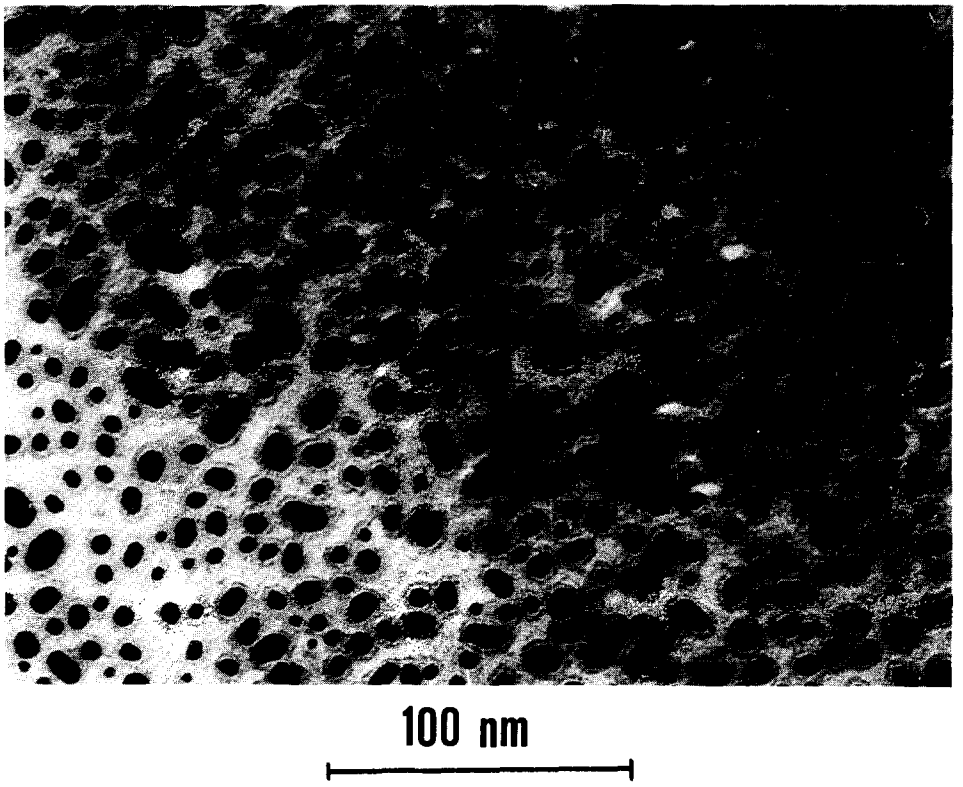

FIG. 1. Micrograph of 1.37 nm Pt on Type A alumina, after annealing in air at 800 K and in hydrogen at 670 K. Magnification, 400,000 : 1.

ers of Al_2O_3 (0.3–0.5 nm mean thickness) deposited on these particles by high-vacuum evaporation were intended to inhibit the catalytic activity of the upper side of the platinum particles as is shown in Fig. 2b. The lower side of the particles is shadowed from the evaporating beam because of the overhanging of the particles and should therefore retain its catalytic activity. To prove whether the covering layer of Al_2O_3 on the platinum particles is continuous and has survived the heating cycle after deposition we applied a decoration technique (*13*). A very thin layer of platinum (mean thickness 0.3 nm) was deposited on specimens both without any additional alumina layer and with the cover layer. This additional platinum layer was allowed to grow to TEM-visible crystallites by treating it in hydrogen at 520 K. The scheme of a covered and decorated Pt particle is shown in Fig. 2c. The corresponding micrograph of a Type B catalyst (2.0 nm) covered by the alumina layer shows the small Pt particles originating from this second Pt deposition both between and on top of the large Pt particles of the original catalyst (Fig. 3a). The blank experiment done without the alumina cover layer (Fig. 3b) shows the small

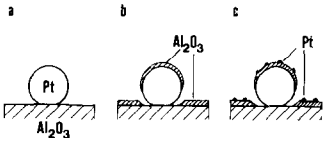

FIG. 2. Schematic of a catalyst particle: (a) uncovered, (b) covered by a thin film of alumina, (c) covered by a discontinuous thin film of platinum for EM inspection.

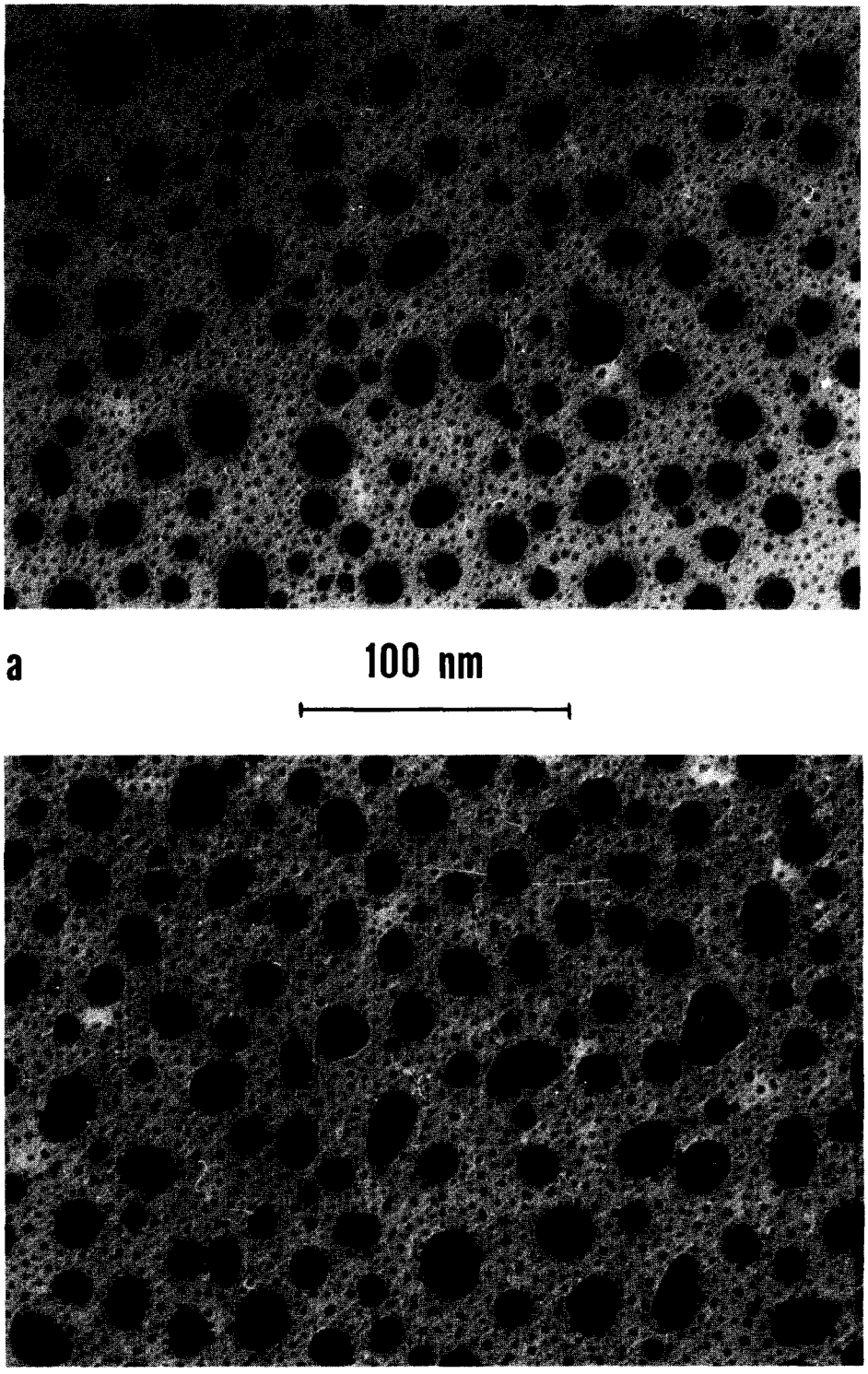

FIG. 3. (a) Micrograph of 2.0 nm Pt on Type B alumina, after annealing in air at 800 K and in hydrogen at 670 K, covered by 0.3 nm of Al_2O_3, annealed in air at 800 K, covered by 0.3 nm Pt, and heated in hydrogen at 520 K. (b) Same as (a), but without the 0.3 nm Al_2O_3 film deposited.

Pt particles from the second deposition only between the large catalyst particles. Thus the platinum atoms impinging onto the large platinum particles are incorporated into the bulk lattice, unless this process is inhibited by the isolating cover layer. Therefore, small crystallites are formed only on top of the covered particles.

While describing this experiment it is important to point out that the alumina not only covers specific sites (edges, corner atoms, or B5-sites) of the platinum but it forms a continuous layer. Otherwise the platinum deposited for the purpose of decoration had not necessarily formed new clusters but had grown at the bare platinum surface which had remained uncovered between the alumina islands. Depending on the evaporation conditions the coverage of the catalyst particles is more or less complete. For example, it was found that an oxygen partial pressure of about 10^{-3} Pa during the evaporation of Al is not sufficient to form a continuous Al_2O_3 layer. Therefore, the evaporation was done at an oxygen pressure of about 10^{-2} Pa, and a stable cover layer of Al_2O_3 was then formed on top of the platinum particles.

3.2. *Hydrogenolysis of MCP*

Most of the experiments were made after the standard pretreatment: Heating in oxygen at 670 K for 2 h followed by sweeping in helium, cooling to 520 K, and reduction in hydrogen at this temperature. In a few cases the temperature of reduction was 670 K. The reaction temperature was kept constant at 520 K for all reactions, the hydrogen pressure was about 940 mbar, and the partial pressure of MCP was about 5 mbar.

The conversion and the product distribution were measured for contact times ranging from 5 to 60 min. The proportion of the three main products 2-methylpentane (2-MP), 3-methylpentane (3-MP), and *n*-hexane (*n*H) was found to be constant during the reaction time indicating that possible isomerization and the formation of smaller hydrocarbons due to hydrocracking was negligible. However, the catalytic activity decreased considerably during the reaction. Because of the small catalyst area applied the contact time for measuring the products was at least 5 min. Hence the given turnover numbers are only mean values of the activity during the first 5 min and are given only for the purpose of comparing relative activities of the catalysts (Table 1).

(*a*) *Effect of the alumina cover layer on the catalytic behavior.* The product distributions for the bare catalysts after standard pretreatment are to be expected because of the large size of the Pt particles. The *n*-hexane proportion of the products obtained after the standard pretreatment varied between 8 and 14% depending on the size of the platinum particles. Despite the low dispersion of the catalysts (0.08–0.14) the particle size dependence of the MCP hydrogenolysis is clearly shown, i.e., the proportion of *n*-hexane is smaller if the particles are larger.

A significantly different product distribution has been obtained with the covered catalysts. The portion of *n*-hexane was considerably enhanced at the expense of the branched hexanes and varies now between 18 and 23%. However, the activity of the catalysts has been reduced by about 70%. As the surface of the Pt particles is covered with alumina to almost the same degree, the loss of activity is explained purely by the geometry.

(*b*) *Effect of the pretreatment on the catalytic behavior.* The hydrogen pretreatment of the catalyst at 670 K caused a distinct loss of activity. As an example this is demonstrated for one catalyst in Table 1. In parallel to the loss of activity a shift of the product distribution to a lower *n*-hexane content was obtained. However, the former activity and product distribution of the bare catalysts could be restored by the standard pretreatment, which involved heating in oxygen at 670 K.

For the covered catalysts the loss of activity and the parallel shift of selectivity were more pronounced than those for the

TABLE 1

Hydrogenolysis of Methylcyclopentane on Bare and Covered Platinum Model Catalysts

Catalyst (mean thickness)	Mean particle size (nm)	State and pretreatment[a]	TON[b] (10^{-3} sec^{-1})	Product distribution		
				2-MP	3-MP	*n*H
Type A (1.37 nm)	6.8	Bare a	16	62	24	14
		Covered a	4	54	23	23
Type B (2.0 nm)	12.7	Bare a	9	64	25	11
		Covered a	3	56	24	20
Type B (1.5 nm)	10.0	Bare a	20	60	27	13
		b	8	66	26	8
		Covered a	5	57	25	18
		b	0.1	66	31	3
		+add. a	11	57	27	16
		+add. c	15	57	28	15
		+add. c	18	58	29	13

[a] Pretreatment conditions: a: standard pretreatment; b: reduced at 670 K; c: hydrogen treatment at 670 K followed by a standard pretreatment.

[b] Turnover number related to the number of exposed Pt atoms of the bare catalyst.

bare catalysts. However, due to the low conversion the product distribution could not be measured with sufficient accuracy in this case and values for the product distribution given in Table 1 are only rough estimates.

In contrast to the bare catalysts the initial behavior of the covered catalysts could not be reestablished by the standard pretreatment. After a cycle of high-temperature reduction followed by the standard pretreatment the catalytic activity was higher than before. On the other hand, the *n*-hexane proportion, which changed from 18 to about 3% after the high-temperature hydrogen treatment, was again enhanced to a somewhat lower value (16%) by the standard pretreatment. Each additional cycle of high-temperature hydrogen treatment followed by the standard pretreatment caused a further increase of the activity and a reduction of the *n*-hexane portion, i.e., the behavior of the catalyst approached stepwise that of the bare catalyst. We take this to indicate that the Pt particles are uncovered by the treatment in hydrogen at 670 K, although they withstand the treatment in oxygen or helium at the same temperature or the treatment in air at 770 K. However, when the "uncovered" catalyst was again covered by a thin layer of alumina, the activity was decreased and the *n*-hexane proportion enhanced again as is found for "freshly covered" catalysts.

4. DISCUSSION

4.1. Particle Size Effect of the MCP Hydrogenolysis

The sensitivity of the product distribution of the MCP hydrogenolysis to the particle size of platinum is well known and generally attributed to two different reaction pathways called the selective and the nonselective mechanisms. On large platinum particles (low dispersion) the hydrogenolysis yields mainly 2-MP and 3-MP corresponding to the selective mechanism, whereas on highly dispersed platinum ring opening occurs nearly statistically, yielding a product distribution 2-MP : 3-MP : *n*H of about 40 : 20 : 40.

The most conclusive explanations for this particle size effect have been reviewed recently by Gault (*8*). The selective ring opening is assumed to take place on the

highly coordinated surface atoms of the large particles via an $\alpha\alpha\beta\beta$-tetraadsorbed species that allows only the formation of 2-MP and 3-MP (*1*). In particular it is assumed that four adjacent edge atoms, existing only on particles larger than 2.5 nm, are necessary for this reaction mechanism (*14*).

On highly dispersed platinum low-coordinated surface atoms predominate (*15*). At these sites the intermediate C_5-ring is assumed to be bound to one single surface atom forming an $\alpha\beta$-π-adsorbed or an $\alpha\alpha\beta$-triadsorbed species, respectively. Hence the tertiary carbon atom is not excluded from the reaction intermediate and statistical ring opening may occur.

Other explanations for the nonselective mechanism are based on the properties of very small metal particles:

(i) The lattice type of very small particles can be different from that of the bulk, i.e., the hcp lattice becomes more stable when the particle size is smaller than 1.5 nm (*16*).

(ii) The lattice constant of small Pt particles is contracted due to the surface stress and the different geometry causes a different catalytic behavior (*17*).

(iii) The crystallographic orientation of the exposed faces may change when the particle size is changed (*18*).

However, recent experiments performed on model catalysts exposing different crystal faces of platinum (111) and (100) showed no face sensitivity of the MCP hydrogenolysis, at least for the two faces investigated (*19*).

Changes in the electronic structure of metal clusters smaller than 1.5 nm (*20*) have also been claimed to be responsible for catalytic particle size effects. However, the results of this work show that also for large particles the "size effect" exists. Since in the model catalysts investigated no platinum particles smaller than 2.5 nm could be found by electron microscopic inspection, we assume that influences from very small particles, namely, smaller than 2.5 nm, cannot completely explain the "particle size" effect.

The influence of bifunctional effects arising from presumably acidic support sites has also been proposed to be the reason for the particle size sensitivity of the MCP hydrogenolysis (*21*). Recent experiments in this laboratory (*7*) have shown that effects of an acidic support can be superimposed on the particle size effect even at 510 K but cannot alone explain the dependence of the product distributions on the particle size.

4.2. Effect of the Metal–Support Phase Boundary on the Selectivity of the Reaction

In an earlier paper (*9*) we proposed an additional mechanism for the particle size effect considering the concept of adlineation that has been already discussed by Schwab and Pietsch (*10*) and by Boudart *et al.* (*22*). This model assumes that the selective hydrogenolysis occurs at the bare platinum surface, while for the nonselective ring opening adjacent sites of the metal and of the support situated nearby at the phase boundary are responsible. Therefore the contribution of the nonselective reaction should be proportional to the length of the phase boundary that is in turn proportional to the diameter of the metal particle. On the other hand, the contribution of the selective reaction should be proportional to the bare surface of the platinum which depends on the square of the diameter. Hence the ratio of the contributions of selective to nonselective mechanism should also be proportional to the diameter, a result virtually confirmed by the experiments (*9*).

In this work we tried to separate the effect of the particle size from the influence of the phase boundary. The particle size was held constant and the contribution of the bare platinum surface was reduced by further evaporation of an alumina layer. However, due to the geometry of the platinum particles, the platinum was only partially covered by the alumina layer. Particularly, the region at the phase boundary platinum–support was not affected by the coverage, since this region was shadowed from the evaporating beam. The results show that the contribution of the nonselective mecha-

nism is indeed enhanced on the covered catalysts, i.e., the *n*-hexane portion of the product distribution is distinctly increased if compared to the noncovered catalysts. As the particle size is not changed by the coverage, the proportion of sites situated on faces, edges, or corners should remain constant. As the number of atoms per platinum particle is not changed, the electronic properties of the particle as such should also be unchanged. However, the enhanced contact with Al_2O_3 could cause minor effects on the electronic structure of the platinum, which are indeed observed after hydrogen pretreatment at high temperatures as discussed later. Thus, we assume that the shift of the selectivity in the direction of the nonselective reaction is caused by the enhancement of the length of the phase boundary in relation to the bare platinum surface as a consequence of the partial coverage of the platinum particles. Following this model, only the branched hexanes 2-MP and 3-MP are formed at the bare platinum surface possibly via the $\alpha\alpha\beta\beta$-tetraadsorbed species proposed earlier (*1*). On the other hand, the reaction intermediate for the nonselective MCP hydrogenolysis occurring at the metal–support phase boundary may be bound with one carbon atom to a support site by more ionic interaction, whereas the adjacent carbon atom is bound to a platinum site (presumably diadsorbed). The ionic interaction to the support site does not exclude the tertiary carbon atom of the MCP ring and the formation of *n*-hexane is no longer inhibited. On the contrary, the bond of the tertiary carbon atom of the MCP ring to the support site should be favorably formed, since this carbon atom is the easiest to be ionized and should therefore preferably be attacked by the more ionic site of the support.

4.3. Effect of the High-Temperature Hydrogen Pretreatment

The pretreatment of the catalyst in hydrogen at 670 K causes a loss of the catalytic activity. The deactivation of platinum catalysts for skeletal reactions by a hydrogen pretreatment at high temperatures has been observed by several authors (*23–26*). While on one side the formation of a Pt–Al alloy is claimed to be responsible for this deactivation (*23*), other authors assume an interaction of the support with the metal (SMSI) causes the deactivation (*24*). The results obtained with the model catalysts show that, simultaneously with the deactivation, the product distribution of the MCP hydrogenolysis is shifted to the selective mechanism, i.e., that the proportion of *n*-hexane is decreased.

Considering the dependence of the selectivity on the pretreatment conditions due to presumably electronic interactions with the support, one would suppose that the particle size effect is caused by such metal–support interactions which may also exist after the hydrogen treatment at reaction temperature. Such effects from the support like SMSI or alloying should particularly influence the small Pt particles. The results of this work indicate that the support interaction causes a shift to the selective pathway, i.e., less *n*-hexane formation, at least after hydrogen pretreatment at 670 K. In contrast the MCP hydrogenolysis proceeds on small platinum particles via the nonselective pathway, i.e., in the opposite way than would be derived from support interaction. Hence we assume that interactions of this type cannot explain the particle size effect. However, the hydrogen pretreatment at the high temperature can decrease the activity and change the product distribution due probably to electronic interactions from the support. Considering the model proposed by us, the influence of such interactions should certainly affect more strongly the metal sites adjacent to the support than the sites far away from the phase boundary. Thus the hydrogen treatment at 670 K particularly deactivates the platinum sites at the phase boundary. Therefore the nonselective reaction pathway occurring at these sites is more suppressed than the selective pathway, a result which is indeed obtained in our experiments.

The covered catalysts are affected by the hydrogen treatment at 670 K in a more pronounced way. The loss of catalytic activity, as well as the shift in the product distribution, is clearly shown by the results, although the product distribution could only be estimated due to the low turnover number of the reaction. We assume that this strong deactivation of the covered catalysts is again caused by influences of the support on the metal. The thin layer of alumina grown on top of the platinum particles may react with hydrogen more easily than the bulk Al_2O_3 to cause the SMSI or the incorporation of aluminum atoms in the platinum particle. Furthermore, the partial denudation of the platinum particles during the treatment with hydrogen at 670 K indicates a higher mobility of the alumina when treated in hydrogen instead of helium or oxygen. This higher mobility in hydrogen again shows that hydrogen can cause a chemical change in the Pt/Al_2O_3 system at the high temperature applied. The species formed by the reaction with hydrogen may account for both the higher mobility of the alumina and for the loss of catalytic activity of the Pt/Al_2O_3 catalyst.

5. CONCLUSION

The experiments reported in this paper show clearly that the metal–support phase boundary contributes to the nonselective pathway of the MCP hydrogenolysis. The given model can explain some features of the particle size effect of the MCP hydrogenolysis. Nevertheless the question remains, whether the proposed model is able to explain all results obtained with the hydrogenolysis of any substituted cyclopentane or with the isomerization of the hexanes via the C-5 cycle intermediate.

Further experiments are thus needed to clarify whether other supports (SiO_2, carbon, or TiO_2) are able to contribute to the phase boundary-catalyzed reaction. Recent experiments on a similar platinum/silica model catalyst done in our laboratory (*27*) will further prove the applicability of the proposed model of adlineation. Additional experiments on catalysts with selectively poisoned supports can possibly help to find the support sites necessary for the phase boundary-catalyzed reaction.

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