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Dispersion Changes of Platinum Supported on Silica Glass during Thermal Treatment in Oxygen and Hydrogen Atmospheres

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Dispersion and chemical composition changes of thin platinum films supported on fused silica, caused by thermal treatment at temperatures of 773 and 823 K in hydrogen and oxygen atmospheres at pressures of 10^{-1} to 10^{-3} Pa, have been investigated by electron microscopy and electron diffraction. Heating the Pt/SiO_2 system in hydrogen leads to an increase of the metal–support interaction, resulting in the flattening of the metal particles, formation of platinum–silicon intermetallic compounds, and generation of strain. During a subsequent heating in oxygen, redispersion of the platinum by splitting of the particles has been observed. Redispersion by spreading of platinum oxide over the support has been found after long (10 h) heating of the Pt/SiO_2 system at 823 K in oxygen at a pressure of $\sim 10^{-2}$ Pa. The mechanisms of platinum redispersion presented above are documented by electron micrographs.

INTRODUCTION

Investigations aimed at the understanding of the mechanisms of deactivation of supported metal catalysts (e.g., sintering, interaction with the support) are of both academic and practical interest. In such investigations, model systems composed of vacuum-evaporated metal deposited on a thin layer of nonmetallic support, making possible electron microscopic observation, are often used (*1–19*). Experiments of this kind have established the phenomenon of redispersion of platinum (*7, 9, 14*), iridium (*4*), rhodium (*5*), palladium (*11, 12*), and nickel (*19*), as well as the phenomenon of strong metal–support interaction (SMSI) (*8, 15–17, 20, 21*).

In the course of studying changes in thin films of platinum on quartz glass substrates under high vacuum, in oxygen (*20*) and in hydrogen (*21*), we established a strong influence of these gases, even at low pressures, on the processes taking place during thermal treatment. In the present paper we describe another series of experiments in which we have heated platinum "island" films in alternating oxidizing and reducing atmospheres at low pressures (10^{-1}–10^{-3} Pa). We believe that the results of such experiments can assist the understanding of the deactivation and regeneration processes occurring in platinum catalysts used in practice.

EXPERIMENTAL

The experimental method and apparatus used were described in detail in a previous paper (*20*). In brief, the course of experiments was the following. Thin platinum films were obtained by evaporation and condensation in a glass vacuum cell with a base pressure of 10^{-7} Pa. The films had a nominal thickness of about 3 nm and an initial electrical resistance of about 2.5×10^3 Ω and were evaporated onto a quartz plate provided with gold electrodes (made by evaporation before assembling the cell), making it possible to measure the electric resistance, and simultaneously onto five pairs of electron microscope (EM) grids, covered with thin quartz membranes. The quartz membranes were prepared by taking thin-walled spheres blown from quartz tubing and etching them in HF solution until the thickness was reduced to below 50 nm and in some small areas even below 20 nm. The quartz plate with the electrodes and the

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electron microscope grids were placed on a quartz support, sealed through a quartz–glass intermediate seal to the outer glass envelope of the cell. This support could be heated from outside by a resistance heater, so that temperatures up to 900 K could be reached on the film. The electron microscope grids were mounted in special holders which allowed them to be moved magnetically out of the heated zone and to be stored at room temperature inside the vacuum cell until the end of the experiment.

Thermal treatment of the films was carried out under high vacuum or in a flow of oxygen or hydrogen in the pressure range of 10^{-1}–10^{-3} Pa. Spectroscopically pure gases were used throughout without further purification. To change the surrounding gas, the apparatus was pumped down to the limiting vacuum, and the new gas then was flowed through at room temperature. After each stage of the thermal treatment one holder with a pair of electron microscope grids was moved out of the heated support; this enabled us to observe subsequent changes in the Pt/SiO_2 system after each stage in the later EM examination.

We used a Tesla BS 613 transmission electron microscope, with a resolving power of about 0.5 nm and with a diffraction lens. Each sample of a grid pair obtained after a given stage of the experiment presented very similar changes in the film; the most typical of them are reproduced in Figs. 1, 4, 6, and 8.

Although a disadvantage of the above procedure is that it allowed us to compare changes in the film morphology only on different samples (albeit obtained under the same conditions), the advantage is the avoidance of exposure of the electron microscope grids to the ambient air between separate stages of the treatment, which would not be the case in an experiment carried out with a single grid. The observation of the *same* region of a *single* sample during the whole experiment can only be done, however, in a true *in situ* experiment, i.e., in the EM apparatus itself.

RESULTS

Experiment 1

After evaporation and condensation of films with an initial resistance of $\sim 2.5 \times 10^3$ Ω and several hours of "aging" at room temperature, the films were heated to 823 K at the rate of 10 K $\min^{-1}$ and then maintained for 10 h at this temperature in a vacuum of 10^{-5} Pa (stage a). After cooling to room temperature, hydrogen at a pressure of 1×10^{-2} Pa was admitted and allowed to flow at this pressure at the rate of 1000 liters h^{-1}. A thermal treatment in hydrogen was performed at 773 K (stage b) and 823 K (stage c), lasting 10 h at each temperature. The apparatus was then carefully pumped down, oxygen at 7×10^{-3} Pa (flow rate ~ 1500 liters h^{-1}) was admitted, and the films were heated at 773 K (stage d) and 823 K (stage e) for 10 h at each temperature. After each heating stage one pair of grids was moved off the heated support and stored in the apparatus at room temperature. A series of electron micrographs and the size histograms obtained from them are presented in Figs. 1 and 2, respectively. Table 1 shows a set of data describing the investigation as a whole.

Heating the film *in vacuo* at 823 K (stage a) leads to the growth of crystallites with a mean size of 30 nm. The mean size was calculated using the formula

$$\overline{D} = \frac{\sum_i n_i \overline{D}_i^2}{\sum_i n_i \overline{D}_i},$$

where n_i is the number of crystallites with diameter between D_i and $D_i + \Delta D_i$, while $\overline{D}_i = D_i + (\Delta D_i/2)$. Particle diameters were determined by visual counting in the given size intervals on EM micrographs. No less than 700, and in some cases even over 2000 particles, have been counted and classified to obtain each histogram. Further heating in hydrogen at 773 K (stage b) does not change the mean diameter and the surface density of particles (Table 1). When the

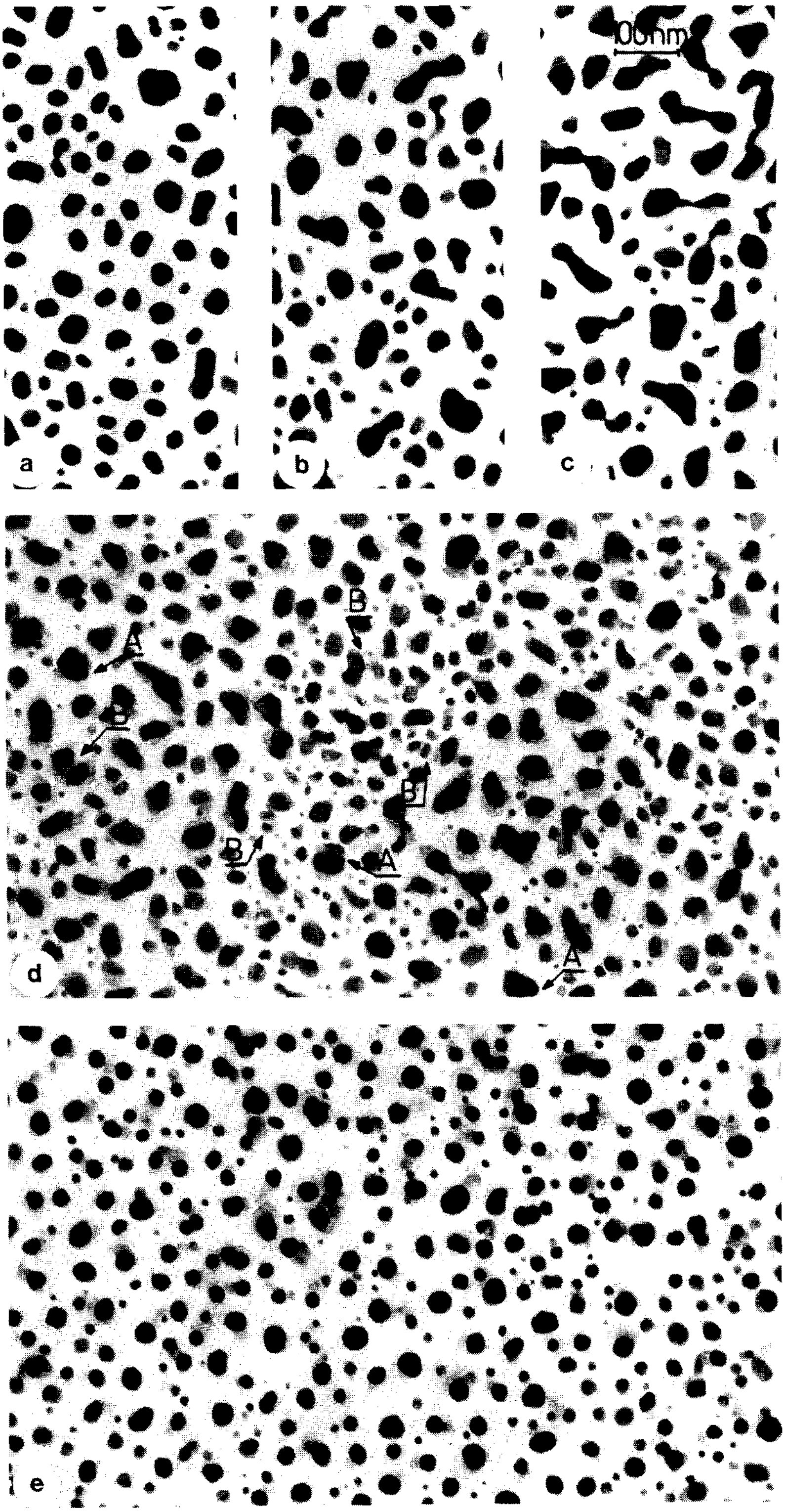

FIG. 1. Electron micrographs of the Pt/SiO$_2$ film in Experiment 1 (magnification, $10^5\times$). (a) After heating under vacuum at 823 K; (b) after subsequent heating at 773 K in 1×10^{-2} Pa hydrogen; (c) after further heating at 823 K in 1×10^{-2} Pa hydrogen; (d) after further heating at 773 K in 7×10^{-3} Pa oxygen; (e) after further heating at 823 K in 7×10^{-3} Pa oxygen.

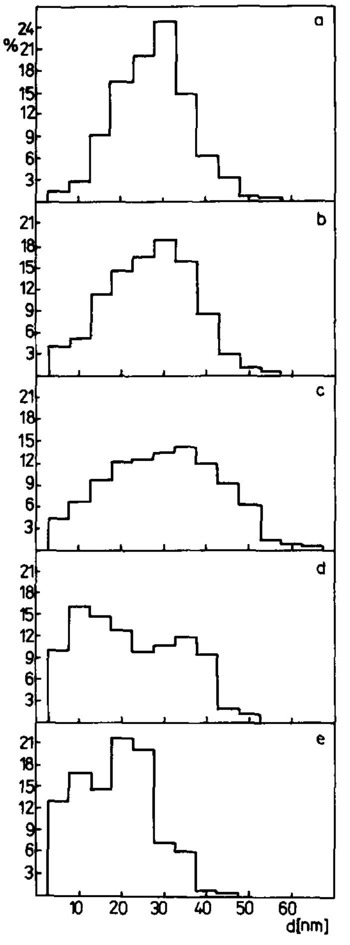

FIG. 2. Particle size histograms for the Pt/SiO_2 film (Experiment 1) after subsequent stages of treatment, as in Fig. 1.

TABLE 1

Dispersion of Platinum in Experiment 1 after Subsequent Stages of Heat Treatment in Various Atmospheres

Stage	Mean particle size (nm)	Standard deviation (nm)	Particle surface density (cm^{-2})	Degree of coverage (%)	Nominal film thickness[a] (nm)
a	30	9	3.75×10^{10}	23	2.6
b	30.5	11	3.80×10^{10}	24	2.8
c	35	14	3.20×10^{10}	25	3.2
d	28.5	13.5	5.40×10^{10}	27	2.9
e	22	10	4.50×10^{10}	15	1.3

[a] Calculated assuming a hemispherical shape of particles.

temperature was raised to 823 K (stage c), the mean diameter of the crystallites increased to 35 nm, their surface density decreased (Table 1), and some broadening of the particle size distribution occurred (Fig. 1c). It should be noted that after heating in hydrogen the degree of coverage of the support area with crystallites increased (the "effective film thickness" also increased, see Table 1).

Heating in oxygen at 773 K (stage d) results in distinct changes in the film morphology (Fig. 1d). The size histogram becomes bimodal (Fig. 2d): a considerable number of particles with sizes in the range 10 to 20 nm appear (Fig. 1d). The mean size consequently decreases to 28.5 nm, and the surface density of the particles and the coverage degree increase (Table 1). These changes indicate the "redispersion" of platinum. Figure 1d shows the splitting of crystallites (marked as A) and the ensembles of the particles which were probably formed by division of larger ones (marked as B), which seems to indicate that redispersion of the platinum takes place by cracking of the particles. Moreover, in the electron micrographs there are regions with a weaker contrast visible in the vicinity of most particles. Electron diffractograms taken from these samples contained a series of "additional" rings (Fig. 3), which can be assigned to platinum oxide (PtO_2) (*22*), so one can suppose that the "halos" around the particles visible in the micrographs are due to platinum oxides. Similar platinum oxide was obtained by Chu and Ruckenstein (*23*) during heating of thin platinum films supported on amorphous carbon in oxygen atmosphere under low pressure.

Figure 1e shows the film after heating at 823 K in oxygen. The platinum particles now have circular (or nearly so) contours and there are also regions of weaker contrast (platinum oxide) in their neighborhood. The mean particle size (22 nm), surface density of particles, degree of coverage, and nominal thickness of the platinum films are decreased (Table 1). These

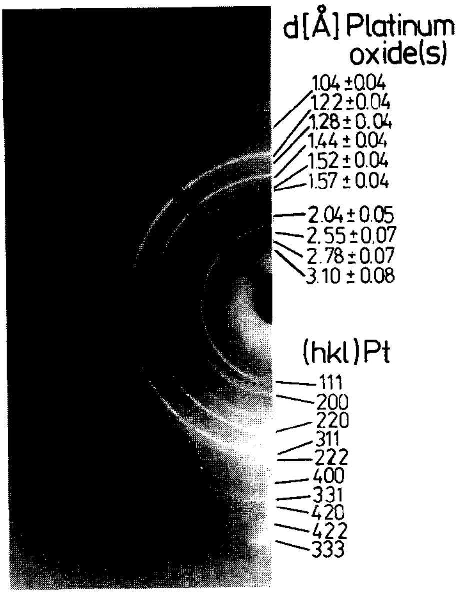

FIG. 3. Electron diffractogram obtained for the sample heated in oxygen at 773 K (stage d of Experiment 1).

changes suggest the removal of platinum after the treatment in the oxidizing atmosphere. In electron diffractograms the same additional rings as are obtained after heating in oxygen at 773 K were found.

Experiment 2

The first stage of the thermal treatment of the film used was the same as in Experiment 1 (stage a). Other stages were as follows:

(i) heating at 823 K in hydrogen, 7×10^{-2} Pa, flow rate 1000 liters h^{-1} (stage b),

(ii) oxidation at 773 K in oxygen, 3×10^{-2} Pa, flow rate 1000 liters h^{-1} (stage c)

(iii) additional oxidation at 823 K at the same oxygen pressure but flow rate increased to 1500 liters h^{-1} (stages d and e).

The heating time was 10 h at each temperature, but during the heating at 823 K in oxygen one of the samples was removed from the heater after 2 h (stage d) while the last sample was heated for a further 8 h (stage e).

The electron micrographs illustrating the evolution of the platinum dispersion are shown in Fig. 4 and the corresponding histograms in Fig. 5. Characteristic parameters of the film after stages a–e are summarized in Table 2.

The film after heating *in vacuo* at 823 K is shown in Fig. 4a. It is composed of crystallites with a mean size of 35 nm, which is larger than that in the former experiment, while the surface density of particles is lower (see Tables 1 and 2). Additional heating at 823 K in hydrogen results in some increase of the particle size to 37.5 nm and a decrease of the surface density (Table 2).

The oxidation at 773 K leads to distinct changes in the particle size distribution (Fig. 5c): the number of particles in the size range 20 to 30 nm increases, and the mean size decreases to 35 nm. These changes, however, are not as large as those in Experiment 1 after similar heat treatment. Two hours of heating in oxygen at 823 K (stage d) causes an increase in the surface density of particles and a decrease of their mean size (Table 2), a broadening of the particle size distribution, and the appearance of a considerable number of particles of size less than 10 nm (Figs. 4d and 5d). Most of the crystallites now have the rounded shape (no sharp edges and corners). Still greater change occurs after 10 h of oxidation at 823 K (Figs. 4e and 5e): a great number of particles with sizes 3 to 8 nm appear, with a surface density over 10 times greater than

TABLE 2

Dispersion of Platinum in Experiment 2 after Heat Treatment under Vacuum, Hydrogen and Oxygen

Stage	Mean particle size (nm)	Standard deviation (nm)	Particle surface density (cm^{-2})	Degree of coverage (%)	Nominal film thickness[a] (nm)
a	35	13.5	2.54×10^{10}	21	2.8
b	37.5	12.5	2.10×10^{10}	21	2.9
c	35	11.5	2.10×10^{10}	18	2.6
d	31	16.5	3.55×10^{10}	19	2.3
e	10	7	5.80×10^{11}	25	1.7
	23[a]	8[a]	4.92×10^{10}[a]	19[a]	1.5[a]

[a] Calculated without the particles smaller than 10 nm.

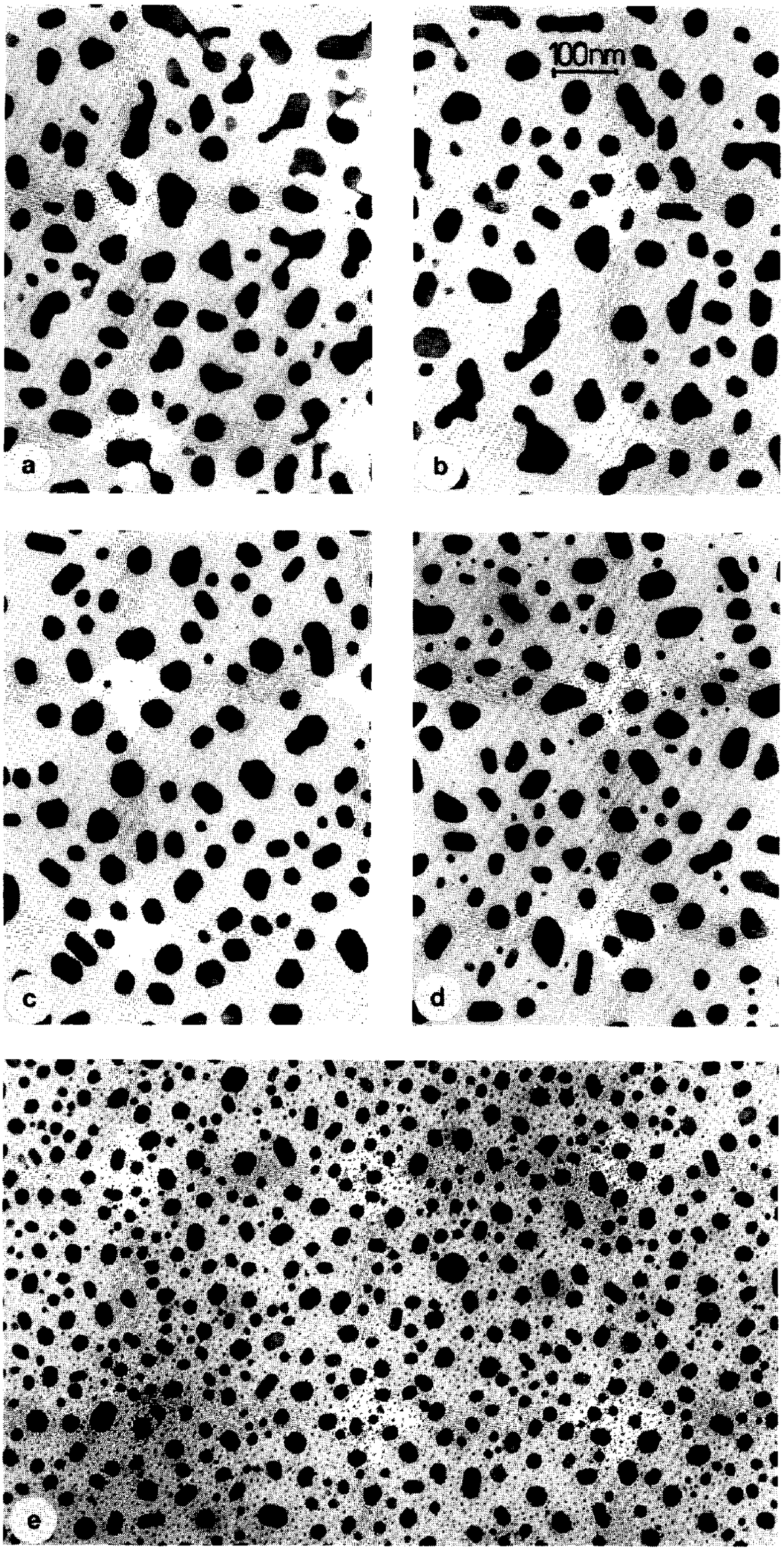

FIG. 4. Electron micrographs of the Pt/SiO$_2$ film in Experiment 2 (magnification, $10^5\times$). (a) After heating at 823 K under vacuum; (b) after additional heating at 823 K in 7×10^{-2} Pa hydrogen; (c) after further heating at 773 K in 3×10^{-2} Pa oxygen; (d) after further heating at 823 K in 3×10^{-2} Pa oxygen; (2 h), (e) after further heating at 823 K in 3×10^{-2} Pa oxygen (2 + 8 h).

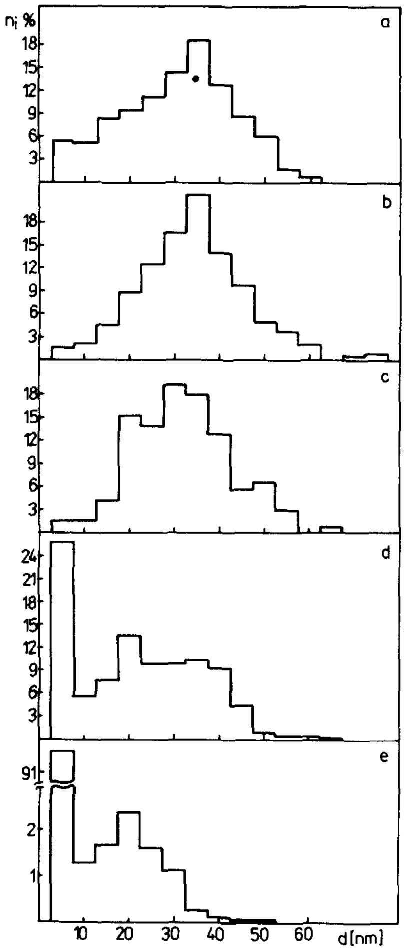

FIG. 5. Histograms of particle sizes at the stages a–e of Fig. 4.

that of large crystallites (Table 2). These small particles are situated not only on the quartz substrate but also on the larger platinum particles (Fig. 4e). The mean particle diameter in the film now becomes 10 nm (the mean size of larger crystallites, 23 nm), the effective thickness decreases to 1.7 nm, and the coverage degree of the substrate increases to 25% (Table 2). In the electron diffractograms of samples oxidized at 823 K new rings similar to those observed in Experiment 1 appeared, but with lesser intensity. Diffractograms of all other samples contained only rings characteristic of metallic platinum.

Experiment 3

In this experiment a thinner platinum film was obtained (nominal thickness, 1.5 nm). After several hours of aging at room temperature, hydrogen at the pressure of 3×10^{-2} Pa was introduced into the cell; the film was then heated to 823 K and heated at this temperature for 10 h (stage a). Additional stages of thermal treatment were the following:

(i) oxidation in oxygen at 7×10^{-3} Pa; flow rate, 1500 liters h^{-1}; 773 K (stage b);

(ii) as above, at 823 K (stage c);

(iii) reduction in hydrogen at 3×10^{-2} Pa; 823 K (stage d);

(iv) reoxidation at 823 K in oxygen at 3×10^{-2} Pa; flow rate, 1500 liters h^{-1} (stage e).

The heating time was 10 h at each stage (b–e).

Electron micrographs of the samples in this experiment are shown in Fig. 6, and the corresponding size histograms in Fig. 7.

The heating of the film in hydrogen at 823 K resulted in the formation of droplike platinum islands (Fig. 6a) with a broad size distribution (Fig. 7a). Oxidation at 773 K caused a decrease of the mean particle diameter, narrowing of the size distribution (Fig. 7b), and an increase in the particle surface density. Further heating at 823 K in oxygen (stage c) led to increased redispersion, as indicated by the increase of surface density and the decrease in the mean particle size (Figs. 6c and 7c).

Figure 6c contains some interesting details. First, there is an ensemble of particles, marked as A, whose mutual arrangement suggests their formation as a result of the division (splitting) of a larger particle. Additionally, in the vicinity of larger particles, ensembles of very small particles are visible, which were not observed in the earlier stages of the same film. Heating of the film in hydrogen at 823 K changed the film morphology dramatically: the surface density of particles decreased, and the mean size increased (Fig. 6d).

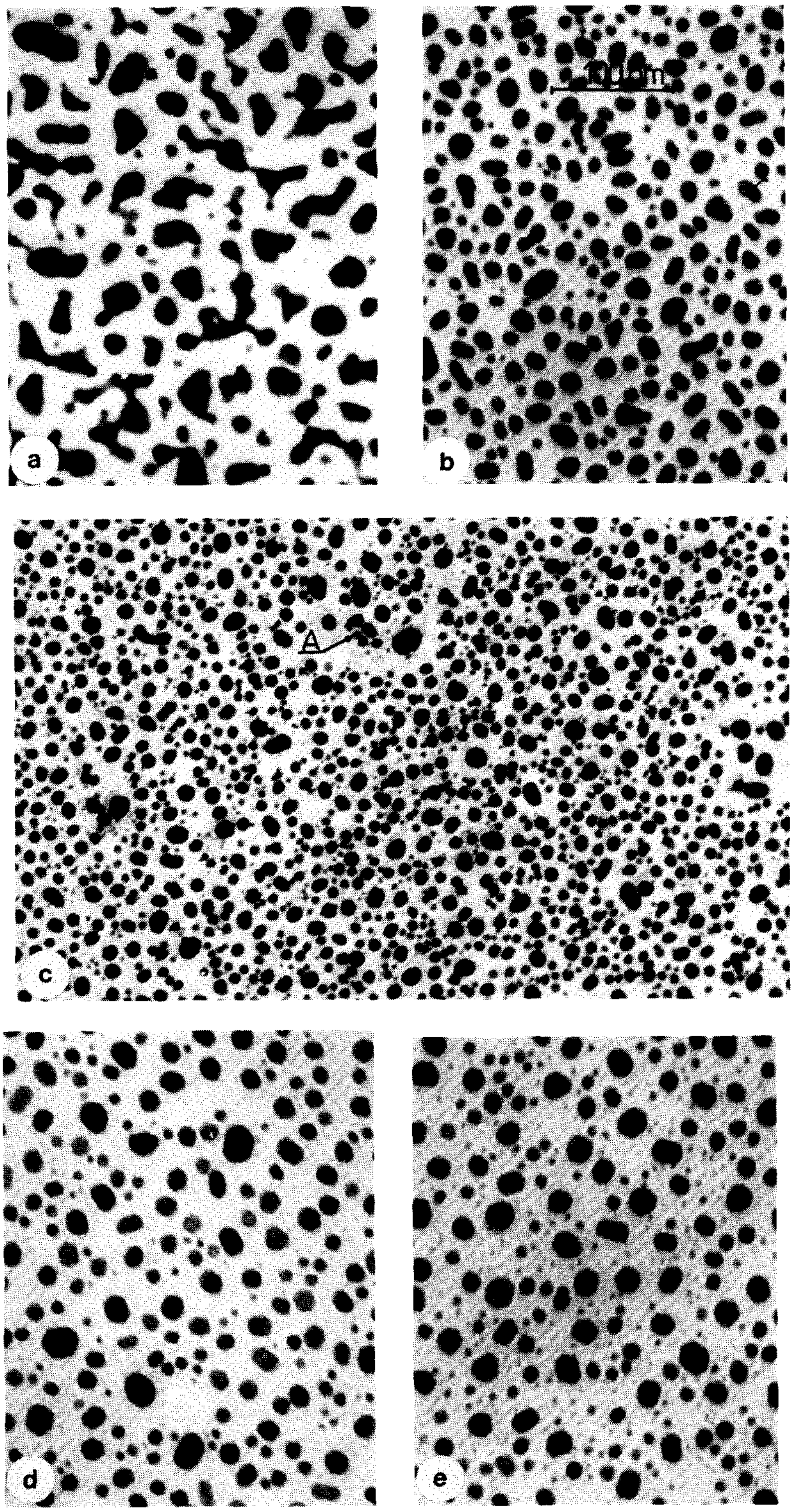

FIG. 6. Electron micrographs of the Pt/SiO$_2$ films in Experiment 3 (magnification, $2 \times 10^5\times$). (a) After heating at 823 K in 3×10^{-2} Pa hydrogen; (b) after further heating 773 K in 7×10^{-3} Pa oxygen; (c) after further heating 823 K in 7×10^{-3} Pa oxygen; (d) after further heating 823 K in 3×10^{-2} Pa hydrogen; (e) after further heating 823 K in 3×10^{-2} Pa oxygen.

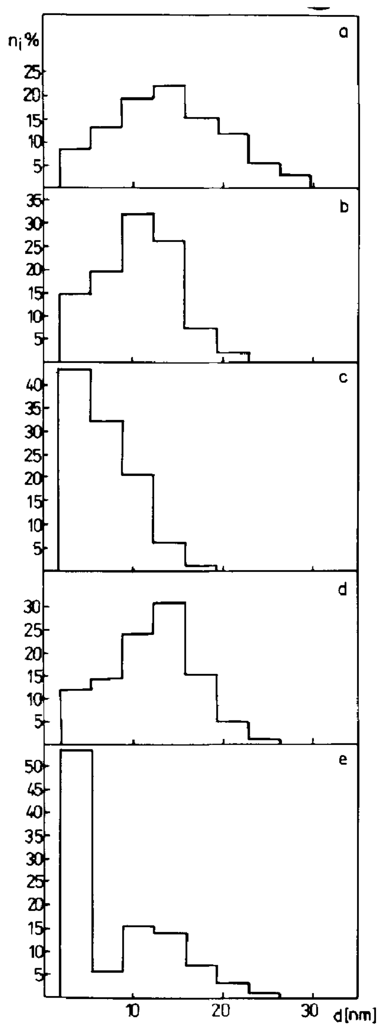

FIG. 7. Particle size histograms at the stages a–e of Fig. 6.

Reoxidation at the same temperature in 3×10^{-2} Pa oxygen again resulted in redispersion: a new class of small particles appeared (similar in shape and size to those obtained in Experiment 2) at the expense of the decrease in size of larger crystallites.

No additional rings were found on diffractograms obtained after subsequent stages of treatment.

Experiment 4

The film used in this experiment was again of the same thickness as those used in Experiments 1 and 2 (initial resistance ~$2.5 \times 10^3\ \Omega$). Its thermal treatment consisted of heating in 2×10^{-1} Pa hydrogen at 673, 723, and 773 K, for 5 h at each temperature, and finally at 823 K for 10 h (stage a). The next stages of the treatment were as follows:

(i) oxidation at 773 K in oxygen at 7×10^{-3} Pa; flow rate, 1000 liters h^{-1} (stage b);

(ii) as above, at 823 K (stage c);

(iii) reduction at 823 K under a pressure of 2×10^{-1} Pa in hydrogen (stage d);

(iv) reoxidation at 823 K in oxygen at 7×10^{-2} Pa; flow rate, 2000 liters h^{-1} (stage e).

Heating time was 10 h at each stage.

After heating in a reducing atmosphere, a film of complicated structure was obtained, as presented in Fig. 8a. Only further heating in oxygen at 773 K caused the growth of large metal islands with low surface density (Fig. 8b, Table 3), and the degree of coverage by metal of the substrate was low. The next stage (oxidation at 823 K) resulted in a decrease of the mean particle size and an increase of the surface density (Table 3). Reduction of this film at 823 K in 2×10^{-1} Pa hydrogen led to an increase in island size and a decrease in their density, which is characteristic for a sintering process, but similar to Experiment 1, the degree of coverage of the substrate also increased (Table 3). The following oxidation at 823 K with 7×10^{-2} Pa oxygen gave rise to a strong redispersion: the surface density of particles increased significantly and the mean particle size decreased (Table 3, Fig. 8e).

TABLE 3

Dispersion of Platinum in Experiment 4 after Heat Treatment in Hydrogen and Oxygen

Stage	Mean particle size (nm)	Standard deviation (nm)	Particle surface density (cm^{-2})	Degree of coverage (%)	Nominal film thickness (nm)
a	—	—	—	—	—
b	40	20.5	1.87×10^{10}	17.5	2.5
c	31	11	2.84×10^{10}	19	2.2
d	35.5	11.5	2.55×10^{10}	23	2.8
e	18.5	8.5	1.00×10^{11}	21	1.5

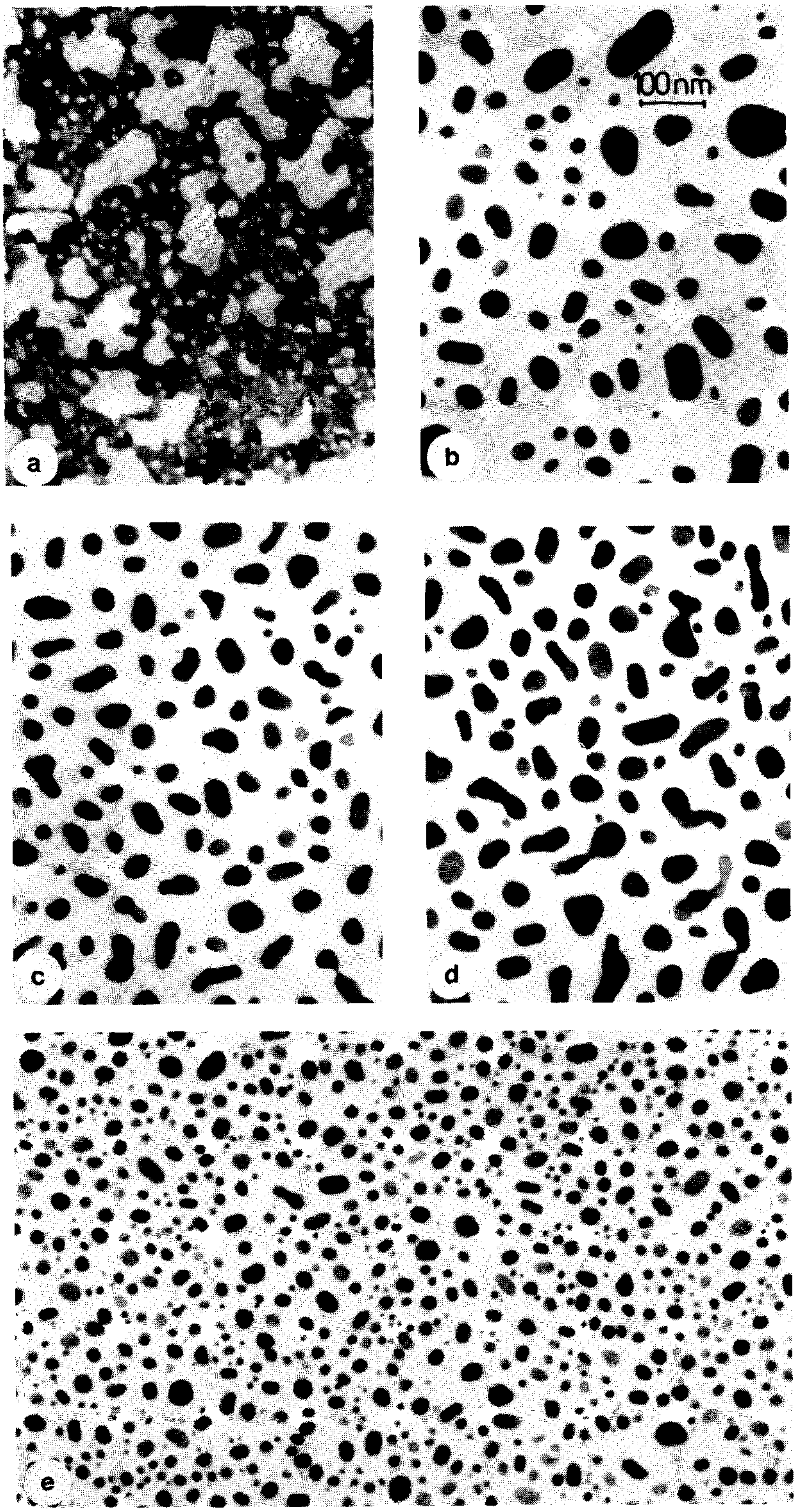

FIG. 8. Electron micrographs of the Pt/SiO$_2$ film in Experiment 4 (magnification, $10^5\times$). (a) After heating at 673, 723, 773, and 823 K (5 h at each temperature) in 2×10^{-1} Pa hydrogen; (b) after further heating at 773 K in 7×10^{-3} Pa oxygen; (c) after further heating at 823 K in 7×10^{-3} Pa oxygen; (d) after further heating at 823 K in 2×10^{-1} Pa hydrogen; (e) after further heating at 823 K in 7×10^{-2} Pa oxygen.

Electron diffraction analysis of films after the first reduction stage showed the presence of diffraction rings characteristic of platinum silicides (*21*) (Fig. 9), while those after stage e indicated the presence of platinum oxide.

DISCUSSION

Redispersion of Platinum

Redispersion of platinum has been observed both in industrial (*25–27*) and model catalysts (*7, 9, 14*). The supposition has been made that the redispersion occurs as the result of a twofold mechanism:

(a) oxidation of platinum particles and "spreading" of the platinum oxide onto the support (*9, 25*); and

(b) splitting of platinum crystallites due to strains generated in particles during their oxidation (*7, 9, 14*).

The redispersion of platinum observed in our experiments can be described, at least qualitatively, by these mechanisms. In Experiment 1, the redispersion at 773 K seems to consist of the splitting of the crystallites (details A, B, Fig. 1d). This splitting can take place as a result of internal strains, the latter being related to defects in the structure of crystallites and other stresses generated during their oxidation (*14*). When a strong interaction between the metal particle and the support (substrate) occurs, one should take into account the considerable strains which arise due to the difference in the thermal expansion coefficients of the metal and substrate (e.g., this coefficient for platinum is 16 times greater than that for quartz (*28*)). Because in previous experiments we did indeed find a strong metal–support interaction (SMSI) in the Pt/SiO_2 system during heating in a reducing atmosphere (flattening of platinum particles and formation of Pt silicides), and because there is evidence for this interaction also in the experiments described above, we believe that this mode of generation of strains occurs in our work. One can expect that after changing the atmosphere to an oxidizing one and slightly raising the temperature the splitting and separation of smaller crystallites thus generated will occur. One can expect also that splitting will occur mainly in places such as grain boundaries, twinning planes, since the strength of crystallites is lowered and the oxidation rate is enhanced in such regions.

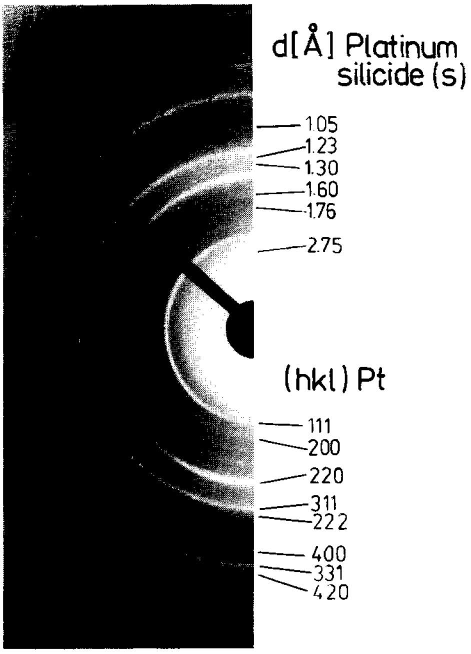

FIG. 9. Electron diffractogram obtained for a sample heated in hydrogen at 823 K (stage a of Experiment 4). The platinum silicide rings correspond to the compounds Pt_3Si and Pt_2Si (*24*).

In Fig. 10 we present a scheme for this mechanism, where the strain is related to the strong interaction of the metal with the substrate. We have assumed that a metal particle after heating in vacuum has initially a hemispherical shape (contact angle ≈90°) (Fig. 10a). During the heat treatment in the reducing atmosphere the adhesion of the metal to the substrate increases, the contact angle decreases, and the particle becomes flatter (i.e., its shape is a smaller section of the sphere) (Fig. 10b). During cooling to room temperature stretching strains arise in the particle, owing to the difference in the thermal expansion coeffi-

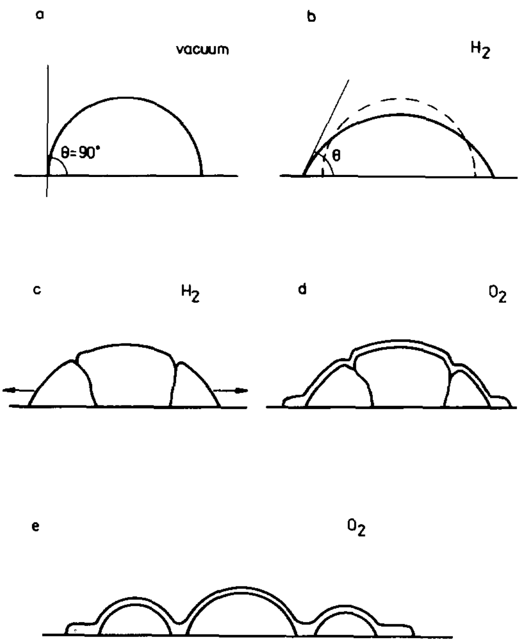

FIG. 10. Modeling of the redispersion by the splitting of crystallites as the result of strain, generated by strong metal–support interaction. (a) A Pt particle obtained after heating under vacuum, contact angle $\theta \simeq 90°$; (b) changes during heating in a reducing atmosphere (increase in the metal–support interaction, $\theta < 90°$); (c) after cooling to room temperature stretching strains appear, due to the difference in the coefficients of thermal expansion; (d) oxidation of platinum during heating in oxygen; (e) splitting of the Pt crystallites.

cients of Pt and SiO_2 (Fig. 10c). On subsequent heating in an oxidizing atmosphere, the oxidizing of platinum and the separation of the oxidized parts occur (Figs. 10d and 10e). The splitting of crystallites should be the dominant process in the first stage of the heating in oxygen, as stated by Gollob and Dadyburjor (*14*). Further redispersion by the oxide transport is a much slower process. This is illustrated by the redispersion observed in Experiment 2. The first stage of the heating in oxygen at 773 K (stage c) gave only moderate changes in platinum dispersion, while further heating at 823 K resulted in the formation of a great number of smaller particles (Fig. 4e), which are most probably platinum oxide. The nucleation and growth of small platinum oxide particles could take place during oxidation and formation of increasing quantities of platinum oxides in the form of "two-dimensional liquid," as postulated by Yao *et al.* for platinum supported on Al_2O_3 (*29, 30*). It is also possible that the nucleation and growth of PtO_2 particles to the size observed in the electron micrographs occurred only during a slow cooling of the system to room temperature. The formation of platinum oxide in the form of such small particles has been observed by us also in Experiment 3, after repeated oxidizing treatment (stage e) (see Fig. 6e and also the histograms in Figs. 5e and 7e, containing a large number of particles in the size range 3 to 8 nm).

In the first oxidation cycles in Experiment 3, especially in stage c, we found ample evidence for both mechanisms to be operative. Detail A in Fig. 6c is an ensemble of crystallites formed by the splitting of the crystallite into several parts, and the groups of very small particles seen in the vicinity of larger ones indicate migration of platinum oxide onto the substrate. The redispersion of the film in stage e of Experiment 4 can be interpreted in a similar way, i.e., with the participation of both mechanisms.

The Metal–Substrate Interaction

Evidence for the strong interaction of platinum with fused quartz in a reducing atmosphere at elevated temperature, leading to the formation of platinum silicides, has been presented in our previous publications (*20, 21*). In the experiments described in the present paper, platinum silicides have been observed only in Experiment 4, in the film which was heated in hydrogen and also at lower temperatures (similar to former experiments (*20, 21*)) before the final heating at 823 K. No platinum silicide was found in island films obtained during previous heating under high vacuum (Experiments 1 and 2). This indicates that some Pt silicide can be formed during the hydrogen treatment at lower temperatures, when the metal–substrate contact area is larger and the platinum crystallites are smaller, and/or that the platinum silicide formed under these conditions was amorphous and could not be detected by electron diffraction.

It should be noted also that, although no formation of platinum silicide was found during the hydrogen treatment of island films, the observed increase of the degree of coverage of the substrate (Experiment 1, stages b and c; Experiment 4, stage d) and the increase in the effective thickness (Experiment 1, stages b and c) indicate flattening of particles, due to the increase of metal–support interaction. The observation that no well-formed polyhedral crystals of platinum were found when the film was heated after evaporation in hydrogen (Experiments 1 and 2), but instead there were rather droplike crystals (Experiment 3), or still more complex structures (Experiment 4, Fig. 8a), can be explained also by a strong interaction. Such a strong interaction decreases the diffusivity of the metal on the substrate and, if the range of this interaction is comparable to the thickness of the film, also self-diffusion of platinum. Since silicon has been found also on the surface of platinum films evaporated onto silica glass (*31*), the self-diffusion of platinum can be restricted also by surface platinum silicides formed during hydrogen treatment at higher temperatures. Only the decomposition of platinum silicides by heating in an oxidizing atmosphere and/or by the removal of SMSI makes it possible for platinum to fully restore diffusion and the growth of larger particles (Experiment 4, Fig. 8b).

The presence of silicon on the surface of thin platinum films evaporated onto SiO_2, reported by van Langeveld *et al.* (*31*), complicates further the description of the redispersion of platinum, since one has to account for the presence of SiO_2 "molecules" or small SiO_2 clusters on the platinum surface in the oxidizing atmosphere which arise as a result of the decomposition of the surface Pt silicide.

Changes of the Effective Thickness of Thin Platinum Films

The values of the effective film thickness, shown in Tables 1–3, were estimated under the assumption of a hemispherical shape for the platinum particles. There are considerable differences between the films heated under vacuum or in hydrogen and those heated in oxygen. In estimating of the thicknesses of the films which had undergone heating under vacuum, or in hydrogen, values rather too large might have been obtained, since the particles were flattened and their shape should more correctly be approximated by a section of a sphere smaller than a hemisphere (SMSI effect). The values for the films heated in oxygen might be closer to the real ones. The possibility that values too small for nominal thickness are obtained in oxygen (which could take place when the contact angle was larger than 90°) can be excluded, on the grounds that the heating in the oxidizing atmosphere increases the adhesion of the metal or SiO_2 as a result of chemical bond formation between metal and oxygen atoms in the substrate (*32*), thus leading to the wetting of the substrate by the metal.

Thus we find that both in hydrogen and in oxygen we have to do with particles with contact angles below 90°, and not knowing their shape exactly we have to accept the approximation of a hemisphere and the "nominal thickness" calculated on this basis. It may be expected that *large* differences in the values of nominal thickness correspond at least qualitatively to reality.

The heating of films at temperatures of 773 K and higher under low pressures of oxygen leads to significant metal deficit, caused by oxidation. The volatile oxide formed in this process partly evaporates and is partly spread by diffusion on the quartz substrate, as shown by the presence of PtO_2 diffraction rings in the corresponding redispersed samples.

CONCLUSIONS

1. Heating platinum island films supported on silica glass at temperatures of 673–823 K in hydrogen results in an increase of metal–support interaction, which leads to flattening of the platinum crystallites, formation of platinum silicide, and generation of stretching strains in the platinum particles.

2. A change of the atmosphere to oxygen causes oxidation of the platinum during subsequent heating and leads to redispersion by splitting of the platinum particles.

3. During heating of the Pt/SiO_2 system at 823 K in oxygen at a pressure of $\sim 10^{-2}$ Pa, additional appreciable oxidation of the metal occurs and there is further redispersion of the platinum by transport in the form of oxide.

4. From the above observations it follows that platinum on silica can be obtained in a high degree of dispersion (particles with size below 10 nm) in island films (or catalysts) from preparations containing originally larger Pt particles by treatment with oxygen at 823 K and a subsequent reduction at much lower temperature. In such a way not only does the dispersion become enhanced, but strong metal–support interaction can also be reduced.

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