JOURNAL OF CATALYSIS **68**, 388–396 (1981)

Electron Microscopy of Pt/Al_2O_3 Model Catalysts

II. Sintering in Atmospheres of H_2, O_2, and Ar

H. GLASSL, R. KRAMER, AND K. HAYEK

Institut für Physikalische Chemie, Universität Innsbruck,
A-6020 Innsbruck, Austria

Received March 10, 1980; revised September 17, 1980

Thin films of amorphous alumina were prepared by anodic oxidation of Al foil or by reactive evaporation of Al in oxygen. Onto these supports ultrathin films of Pt (0.05–0.5 nm thick) were deposited under high vacuum. The resulting catalysts were characterized in the electron microscope and their particle density, their particle size distribution, and their dispersion were studied after various annealing treatments in Ar, H_2, and O_2 at 510 and 720 K. It was shown that a treatment in hydrogen has the strongest effect on sintering and that stable particles can be produced by iterative treatments in H_2 and O_2 at 510 and 720 K, respectively. These stabilized platinum films are well suited as model catalysts for the study of particle size effects.

1. INTRODUCTION

Supported metal catalysts may undergo changes of surface area, particle size distribution, and microstructure when heated at elevated temperature. This process, generally referred to as sintering or aging, has been described extensively in the literature and several theoretical models have been discussed (cf. reviews in Refs. (*1–3*)). In Pt/Al_2O_3 catalysts a coarsening of the Pt particles is generally observed of varying degree depending on pretreatment, environment, and time (e.g., Refs. (*2–5*)) and only under special treatments may a redispersion be expected (*6, 7*).

Changes of the dispersion during use not only limit the industrial applicability of a catalyst but may also prevent an unambiguous determination of particle size effects in catalysis. In an effort to investigate the dependence of the selectivity of Pt/Al_2O_3 model catalysts on the size and microstructure of the metal particles (*8*) we evaporated Pt under high vacuum onto different Al_2O_3 substrates (supports) and tried to stabilize the Pt clusters by various thermal treatments. The aim of the treatments was to obtain a number of catalysts with as many different size distributions as possible, in particular of small mean size. In this paper we show how such Pt films behave under the influence of different environments at relatively low temperatures and how particle size distributions could be produced that are stable under the conditions of a subsequent reaction at or below 570 K in H_2. The sintering temperatures are below those discussed generally in the literature. The extent of sintering is therefore relatively small and care had to be taken to avoid erroneous results due to artefacts that may occur during the preparation of the specimens for transmission electron microscopy (*9*).

2. EXPERIMENTAL

2.1. Preparation of Al_2O_3 Substrates (Supports)

Two types of substrate were used:

(i) Alumina films produced by anodic oxidation of Al foil as described previously (*6, 9*). The oxidized Al foil was washed and dried at 380 K or heated below the transformation temperature to γ-Al_2O_3 (~870 K). The resulting film of nonporous amorphous ("a") Al_2O_3 (thickness $\geq$ 15 nm) was sepa-

0021-9517/81/040388-09$02.00/0

rated from the Al foil in diluted HCl or $HgCl_2$, washed, mounted on gold EM grids, and dried.

(ii) Al_2O_3 films obtained by reactive evaporation of Al metal onto NaCl substrates in an oxygen atmosphere. An Al rod (2 mm ϕ) was placed as an anode in an electron bombardment gun (*10*) and evaporation was performed at 2 kV, at a partial pressure of $1.3 \cdot 10^{-2}$ Pa of oxygen, at a rate of 0.01 nm s^{-1}, the distance between source and substrate being 0.3 m. The transparent films (thickness 10–20 nm) were floated in water, mounted on gold grids, and heated in oxygen at 720 K for several hours. After this treatment they showed only diffraction features attributable to amorphous alumina.

The microstructure of a film obtained by vacuum evaporation and that of a film obtained by anodic oxidation are compared in Figs. 1a and b.

Despite the differences in grain size and surface roughness, the results of sintering of Pt were, in general, identical on both surfaces. Only in those cases where the

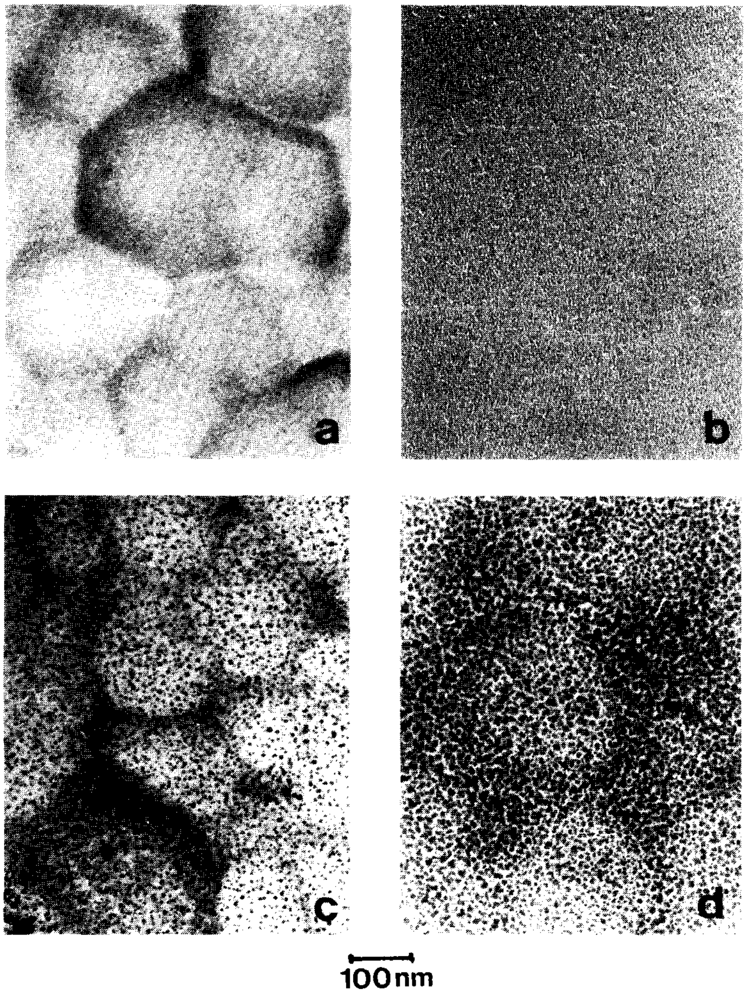

FIG. 1. Support film a-Al_2O_3, 20 nm thick, (a) prepared by anodic oxidation of Al foil, (b) prepared by reactive evaporation of Al in O_2, (c) segregation of Al metal on the substrate after heating in H_2 at 720 K for 5 h, (d) formation of Pt–Al alloy on the substrate. Magnification 80.000 : 1.

Al_2O_3 foil contained metallic aluminum, either because of incomplete oxidation or incomplete dissolution of the Al foil, could sintering in nonoxidizing ambients above 470 K bring about segregation of aluminum (Fig. 1c).

Films of γ-Al_2O_3 were also produced by heating films of type (i) or (ii) above 870 K in air. With respect to sintering of Pt they were found to behave similarly to the amorphous films. Since the electron microscopy of γ-Al_2O_3 substrates is impeded by their nonuniform thickness and by diffraction effects, most of the investigations were restricted to amorphous alumina and hence we shall not differentiate further between the substrates.

2.2. *Deposition of Platinum and Description of the "Untreated" Pt Films*

Platinum was evaporated onto the alumina substrates at room temperature, at rates between 10^{-3} and 10^{-1} nm s^{-1} up to a mean thickness between 0.05 and 0.5 nm so that different initial particle densities and size distributions were obtained. As mentioned in Ref. (*9*) the as-deposited unprotected specimens changed slightly on exposure to the air. The air-exposed specimens were taken as a reference ("untreated films"). Their particle density lies between 6 and $12 \cdot 10^{12}$ cm^{-2}. Electron micrographs of three "untreated catalysts," referred to as Nos. 2, 5, and 7 in Table 1, are shown in Figs. 3a, 4a, and 5a, respectively. The particle size distribution of catalyst 5 (0.3-nm mean thickness) is shown in Fig. 2a. It should be stated at this point that the electron microscopic determination of particle diameters below about 1.0 nm is already uncertain and that the assumption of a spherical shape is too simplifying (*11*, *12*). Also the other methods of determining particle sizes such as X-ray line broadening and selective chemisorption (unknown surface stoichiometry) yield inaccurate or doubtful results for particle diameters below 1 nm. However, when the mass thickness of our samples was calculated from their size distribution, the agreement with the mean thickness indicated by the quartz microbalance was surprisingly good if the particles were assumed to be truncated spheres with a contact angle about 120°. From the measured size distributions the mean particle diameter $\bar{d}$ and the dispersion D were calculated and inserted in Table 1. For nonspherical ("elliptical," etc.) particles an effective diameter $\bar{d}_{eff}$ (*1*) was used.

2.3. *Heat Treatments*

The time of the treatments was generally chosen to be long enough to impede changes of the catalyst during the subsequent catalytic reaction (hydrogenolysis of methylcyclopentane in 1 bar H_2 at temperatures below 570 K) but the influence of the time was not investigated explicitly.

The treatments were performed in a flow reactor at 510 and 720 K in atmospheres of 1 bar H_2, Ar, and O_2 for periods up to 24 h. A few samples were heated *in vacuo*, in oxygen or in air at 870 K. Higher temperatures were not applied because of the possible transformation of the support to γ-Al_2O_3 (*13*).

2.4. *Electron Microscopy*

After the treatment an EM grid was removed from the reactor and examined in the electron microscope (Siemens Elmiskop 1a or JEOL 100). The particle density and the particle size distribution were determined from the micrographs at high magnification.

3. RESULTS

3.1. *General Remarks*

As mentioned above a segregation of particles was observed when supporting foils of anodically oxidized Al were heated in nonoxidizing ambients, particularly H_2, above 470 K (Fig. 1c). These particles were probably Al metal which had remained dispersed in the Al_2O_3 substrate during the preparation. With platinum deposited onto supports such as these a heat treatment in

TABLE 1

Particle Density N, Mean Particle Diameter $\bar{d}_{\text{eff}}$, and Dispersion D of Different Catalysts after Sintering in Various Atmospheres

Catalyst		Treatment (ambient, time)	After treatment				Remarks
No.	Mean thickness (nm)		$N \cdot 10^{-12}$ (cm^{-2})	$\bar{d}_{\text{eff}}$ (nm)	D	$\frac{N}{N_0}$	
1	0.06	Untreated	6.3	Undet.	$\sim$1.0	1	
		2 h H_2, 720 K + 14 h O_2, 720 K	1.7	1.7	0.60	0.27	f
2	0.1	Untreated	8.5	1.25	$\sim$1.0	1	Fig. 3a
		1 h H_2, 510 K	3.5	1.75	0.58	0.41	Fig. 3b
		18 h O_2, 720 K	2.4	1.9	0.54	0.28	Fig. 3c
3	0.1	Untreated	8.5	1.25	$\sim$1.0	1	
		2 h H_2, 510 K + 15 h O_2, 720 K	2.2	2.1	0.48	0.26	f
4	0.2	Untreated	10.5	1.35	$\sim$1.0	1	
		2 h H_2, 720 K + 12 h O_2, 720 K	3.6	1.9	0.54	0.34	f
5	0.3	Untreated	9.2	1.8	0.60	1	Figs. 4a, 2a
		1 h H_2, 510 K	3.8	2.45	0.42	0.41	Figs. 4b, 2b
		15 h O_2, 720 K	2.6	2.8	0.36	0.28	Figs. 4c, 2c
		1 h H_2, 510 K + 13 h Ar, 720 K + 10 h O_2, 720 K	2.0	3.3	0.31	0.22	Fig. 2d, f
6	0.5	Untreated	9.0	2.1	0.48	1	
		2 h H_2, 510 K	4.0	2.8	0.36	0.45	
7	0.5	Untreated	8.8	2.15	0.47	1	Fig. 5a
		3 h Ar, 510 K	8.8	2.15	0.47	1	Fig. 5b
		13 h H_2, 510 K	3.9	2.8	0.36	0.45	Fig. 5c
		Add. 5 h Ar, 720 K	2.5	3.4	0.30	0.28	
		Add. 3 h H_2, 720 K	2.1	3.7	0.27	0.24	
		Add. 13 h O_2, 720 K	1.9	3.9	0.26	0.21	f
		Add. 24 h air, 870 K	1.4	4.4	0.23	0.16	f
		2 h H_2, 720 K	2.2	3.65	0.28	0.25	Fig. 5d
8	0.5	Untreated	8.6	2.2	0.46	1	
		5 h H_2, 510 K + 11 h O_2, 720 K	2.8	3.2	0.32	0.32	
		Add. 3 h H_2, 720 K + 11 h O_2, 720 K	2.3	3.5	0.29	0.27	f
9	0.5	Untreated	10.6	2.0	0.51	1	
		13 h O_2, 720 K	3.6	3.1	0.33	0.34	
10	0.5	Untreated	6.5	2.4	0.42	1	
		15 h O_2, 720 K	3.7	3.0	0.34	0.57	Fig. 5e
		Add. 3 h H_2, 720 K + 12 h O_2, 720 K + 3 h H_2, 720 K + 3 h O_2, 720 K	1.4	4.4	0.23	0.21	Fig. 5f, f
11	0.5	Untreated	6.9	2.35	0.43	1	
		2 h Ar, 720 K	2.7	3.25	0.31	0.39	
		14 h Ar, 720 K	2.2	3.6	0.28	0.32	
		Add. 1 h H_2, 510 K + 5 h O_2, 720 K	1.7	4.1	0.25	0.24	

Note. The subscript "0" refers to the initial "untreated" state. The letter "f" denotes a "final" state with a stable particle size distribution.

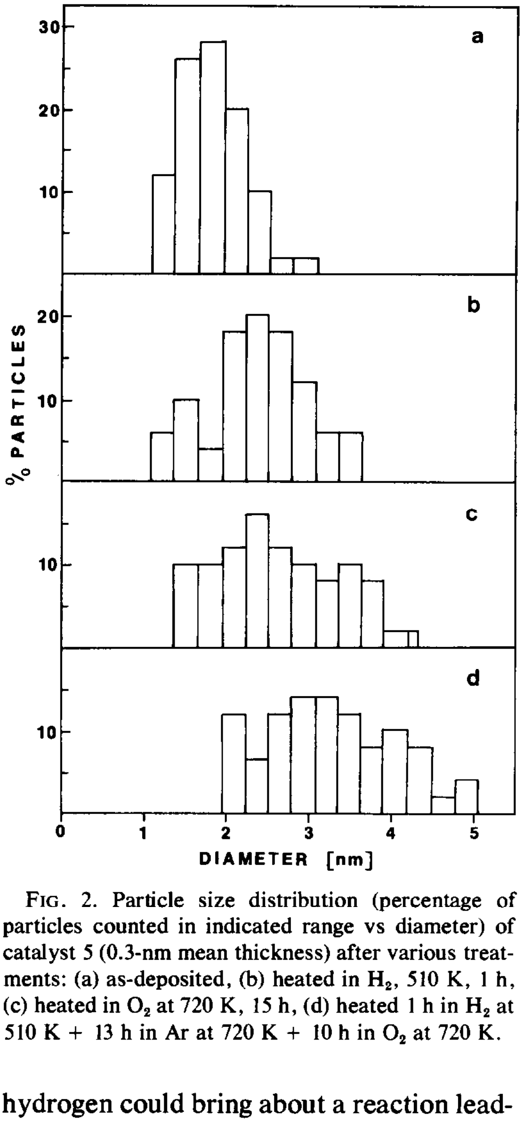

FIG. 2. Particle size distribution (percentage of particles counted in indicated range vs diameter) of catalyst 5 (0.3-nm mean thickness) after various treatments: (a) as-deposited, (b) heated in H_2, 510 K, 1 h, (c) heated in O_2 at 720 K, 15 h, (d) heated 1 h in H_2 at 510 K + 13 h in Ar at 720 K + 10 h in O_2 at 720 K.

hydrogen could bring about a reaction leading to a "mixed layer" like that shown in Fig. 1d. Electron diffraction indicates that here a Pt–Al alloy has been formed. Similar interactions between metal and support have been reported by den Otter and Dautzenberg (*15*). Such artefacts did not appear when the support was heated in O_2 at 720 K *prior* to the deposition of Pt and the results described in the following were all obtained with Al_2O_3 supports heated in oxygen.

The changes of particle size and particle density with various heat and ambient treatments are given in Table 1 for a number of catalysts. In addition, the change of the size distribution of one typical catalyst is shown in the histogram of Fig. 2 and the changes of the microstructure due to various treatments are illustrated in the micrographs of Figs. 3–5. The "untreated catalysts" differ in their mean thickness (0.05–0.5 nm), in their mean particle size (1.2 nm $\leq \bar{d} \leq$ 2.4 nm) and, to a minor extent, in their particle density ($6.3 \cdot 10^{12}$ cm^{-2} $\leq N_0 \leq 10.6 \cdot 10^{12}$ cm^{-2}, cf. Figs. 2a, 3a, 4a, 5a). Specimens labelled with the remark "f" in Table 1 do not change further under the conditions of a chemical reaction (hydrogenolysis of methylcyclopentane at 1 bar H_2 and 560 K) and are therefore well suited for investigations of catalytic activity and selectivity.

3.2. *Effect of Hydrogen*

A treatment in 1 bar hydrogen at and below 510 K leads already to appreciable changes. After a 1-h treatment at 510 K (catalysts 2 and 5 in Table 1) the particle density is reduced to 40–45% of its initial value (Figs. 3b, 4b) and the size distribution is broadened (Fig. 2b). Prolonged annealing at the same temperature, e.g., for 6 h (catalyst 6) or 13 h (catalyst 7) does not lead to further changes of the dispersion. At low mean thickness (<0.3 nm) the particle shape is rather spherical, whereas thicker films (≥0.3 nm) are composed of "coalescing" particles of irregular shape (Figs. 4b, 5c) after the hydrogen treatment at 510 K.

After heating the "untreated samples" in H_2 at higher temperature, e.g., for 2 h at 720 K, an irregular shape was still observed (catalyst 7, Fig. 5d), but the particle density was further reduced to ~25% of its initial value.

3.3. *Effect of Oxygen and Argon*

In contrast to the results obtained with hydrogen, heating in O_2 below 510 K produces only small changes of the film structure. Heating in Ar below 510 K leaves the film structure unchanged (Fig. 5b, catalyst 7 in Table 1).

Heating in oxygen at 720 K (catalysts 2,

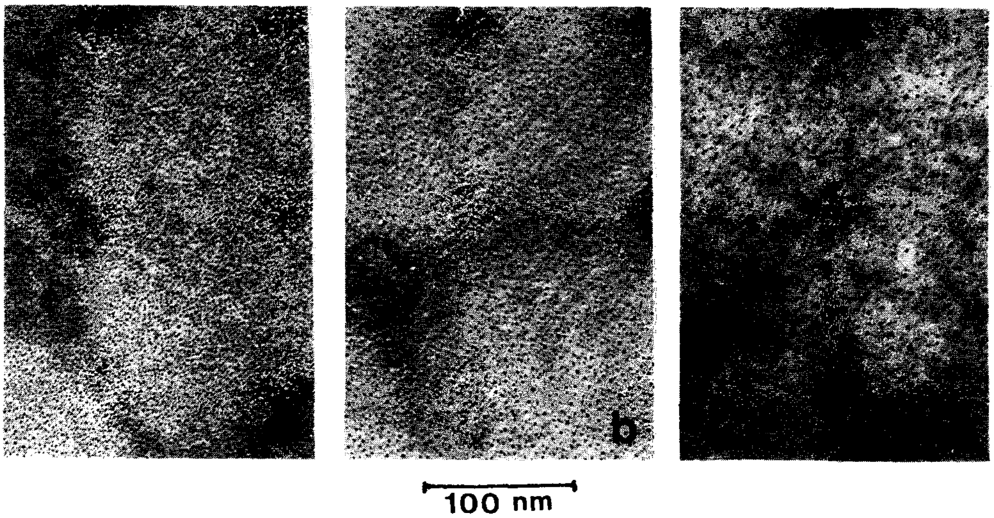

FIG. 3. Structural changes of catalyst 2 (0.1-nm mean thickness) after several treatments. Magnification 200.000: 1. (a) Untreated; (b) heated in H_2 at 510 K, 1 h; (c) heated in O_2 at 720 K, 18 h.

5, 9, and 10 in Table 1) leads to a substantial decrease of the number of particles. The resulting density depends mainly on the amount of Pt on the surface, i.e., on the mean thickness, and not so much on the initial particle density. It is about $2.4 \cdot 10^{12}$ cm^{-2} at 0.1-nm mean thickness and $3.6 \cdot 10^{12}$ cm^{-2} at 0.5-nm mean thickness. After an O_2 treatment at 720 K the size distribution is broadened (Fig. 2c, catalyst 5) and the micrographs reveal particles of almost equiaxed shape (Figs. 3c, 4c, 5e). At 720 K the influence of the different ambients on sintering was found to increase in the following order: oxygen, (vacuum), argon, and hydrogen.

Strong sintering in oxygen was always observed when O_2 was admitted to a Pt surface onto which hydrogen was already preadsorbed, or vice versa, when H_2 was

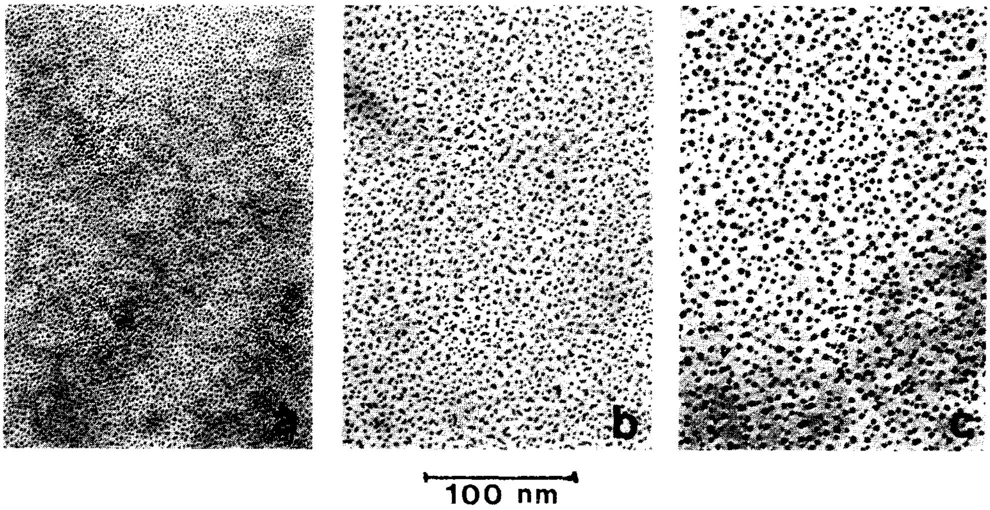

FIG. 4. Structural changes of catalyst 5 (0.3-nm mean thickness), after various treatments. Magnification 200.000: 1. (a) Untreated; (b) heated in H_2, 510 K, 1 h; (c) heated in O_2, 720 K, 15 h.

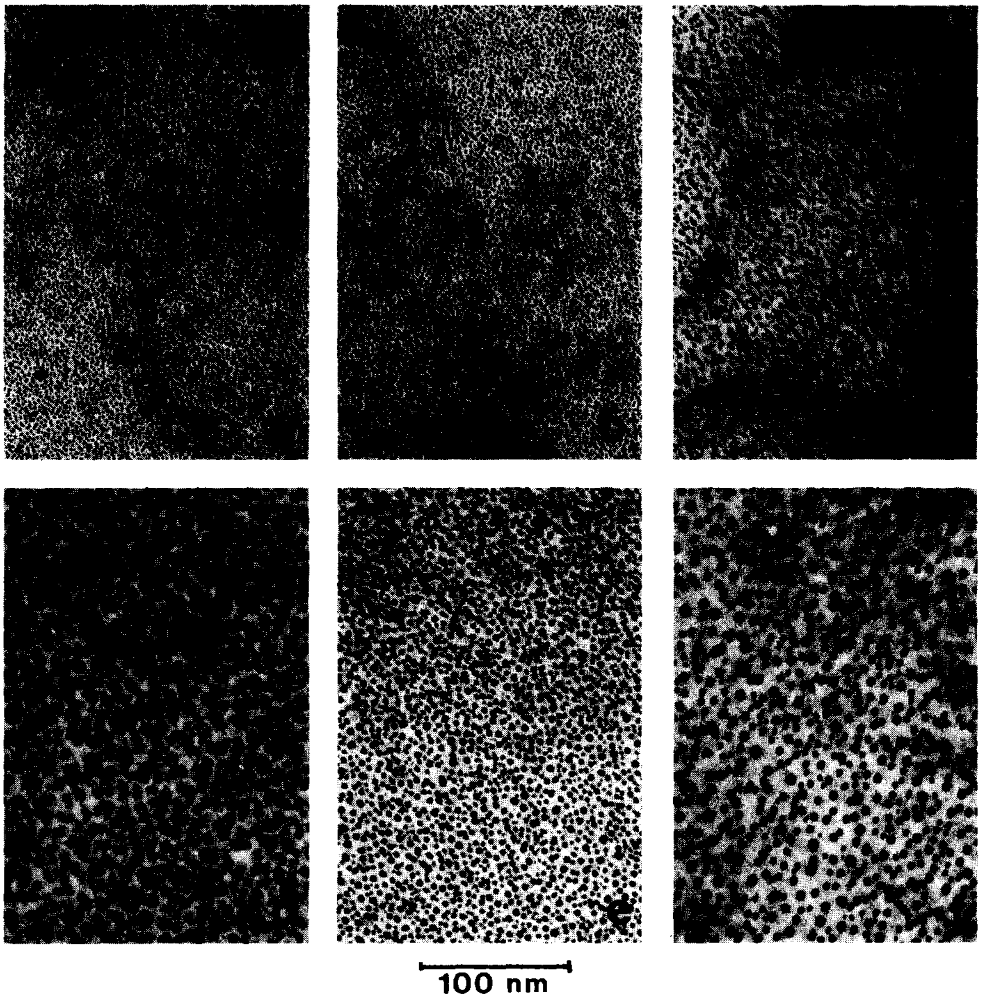

FIG. 5. Structural changes of catalysts 7 and 10 (0.5-nm mean thickness) after various treatments. Magnification 200.000 : 1. (a) Catalyst 7, untreated; (b) heated in argon at 510 K, 3 h; (c) heated in H_2 at 510 K, 13 h; (d) heated in H_2 at 720 K, 2 h; (e) catalyst 10 heated in O_2 at 720 K, 15 h; (f) as (e) heated in H_2 at 720 K, 3 h + O_2, 720 K, 12 h + H_2, 720 K, 3 h + O_2, 720 K, 3 h.

admitted to preadsorbed oxygen on Pt. Since this kind of treatment is necessary in catalytic investigations in order to activate the catalyst, several specimens (catalysts 1, 3–5, 7, 8, 10, 11) were subjected to such combined procedures with the aim of obtaining "stable" catalysts. As is seen from Table 1 and Figs. 2d and 5f, the particle size distribution was then shifted to higher values and the particle density was further reduced while rather spherical clusters were formed. In Figs. 5a–f the changes of the microstructure after each step of a combined treatment are demonstrated on catalysts 7 and 10.

4. DISCUSSION

4.1. Particle Density and Size

From the values in Table 1 it is apparent that the vacuum evaporation of platinum, followed by annealing of island stage films, yields only a rather limited range of stable particle densities and dispersions available for catalytic investigations.

The "final" particle density lies between

1.4 and 3.6 · 10^{12} cm^{-2}, the mean particle diameter between 1.7 and 4.4 nm and the dispersion between about 0.2 and 0.5 (spherical particles assumed). Although a variation of the evaporation rate by a factor of 100 has a distinct (but limited) influence on the primary particle density, the differences between films of equal mean thickness but differing density are practically obliterated by the subsequent annealing process.

Lowering the Pt mean thickness below 0.05 nm leads to highly dispersed films which are hardly characterizable by EM and the catalytic reactions yield very low and hardly measurable conversions because of the small amount of Pt. On the other hand, a mass thickness above 1 nm results in particles of 5 nm and more in diameter whose catalytic properties are almost those of the bulk.

Moreover, the size histograms of O_2-treated and "final" specimens reveal a relatively broad size distribution (cf. Figs. 2c, d). However, as will be discussed in Part III (*8*), the final catalysts obtained in this manner differed appreciably in their catalytic properties.

4.2. *Shape of the Particles*

The geometrical shape of the Pt particles was not determined in detail and their height was therefore only estimated, e.g., from the size distribution. However, it was apparent that H_2-treated particles were in general more irregularly shaped than the samples heated in Ar and O_2 and than the "final" catalysts. The latter were composed of rather spherical or hemispherical clusters. Particles bounded by crystallographic facets were observed after high-temperature treatments (870 K) but only seldom after prolonged treatments (at 720 K) in "final" catalysts. One explanation for the different shape after a H_2 treatment is that the reducing atmosphere favours the diffusion of particles as a whole, whereas the oxidizing atmosphere promotes rather the self-diffusion of Pt and therefore the contraction of the particles. One other reason for the rounded shape after a combined treatment may, of course, be the locally evolved heat of reaction if the surface of a particle with adsorbed H_2 is exposed to oxygen.

4.3. *Rate and Mechanism of the Process*

From the two mechanisms that may be responsible for sintering the interparticle transport or Ostwald ripening can certainly be excluded because of the low temperatures applied. The size distributions are broadened (*16*) and the size histograms are in good agreement with a log-normal distribution (*17*). This indicates that the sintering process is governed by particle migration and liquid-like coalescence (*2*, *18*). For such processes high-power rate laws are generally established and observed experimentally. This means that, after an initial period of a very fast reaction, the particles soon obtain an almost-constant distribution. Such a behaviour was generally observed in the present experiments, although the influence of the time was not determined in detail. For example, the effect of a 15-h treatment in H_2 at 510 K (or in O_2 at 720 K) is almost identical to that of a 2-h treatment. Additional sintering is then induced only by changing the ambient or the temperature. The strong sintering obtained by the alternating oxygen–hydrogen treatment could be due to the heat of reaction evolved but also the "cleaning" of the surface and the water formed during the reaction can contribute to this effect.

4.4. *Comparison with Previous Results*

Of the numerous publications dealing with the sintering of Pt on Al_2O_3 only few apply to evaporated model catalysts (*13*, *19*, *20*) and very few data are available for temperatures below 770 K. Most of the supported catalysts were produced by impregnation and reduction at already elevated temperature. Furthermore, measurements of the dispersion are frequently derived from H_2 chemisorption data *only* and cannot be considered reliable for predicting changes of the particle size distribution.

Of the few data available for $T < 770$ K most indicate that sintering is more pronounced in hydrogen than in oxygen (*13, 21, 22, 23, 27*). At higher temperature a stronger effect of an oxidizing atmosphere was also reported (*4, 24*). On the other hand, a redispersion of Pt particles in oxygen as found by several authors (*6, 7, 19, 22, 25*) was neither observed nor expected under our experimental conditions. It is generally assumed that a redispersion would imply the formation of platinum oxide which is followed by either reduction or decomposition. However, this occurs only at more elevated temperature (*14, 21, 26*).

Finally, it should be noted that recent LEED observations on stepped Pt surfaces have shown that hydrogen induces step coalescence and terrace broadening above 470 K, the same temperature range as reported here (*28*).

ACKNOWLEDGMENTS

We thank Professor H. L. Gruber for helpful discussions. This work was supported in part by the Fonds der wissenschaftlichen Forschung of Austria (Projects 1678 and 2997).

REFERENCES

1. Anderson, J. R., "The Structure of Metallic Catalysts." Academic Press, New York/London, 1975.
2. Wanke, S. E., and Flynn, P. C., *Catal. Rev. Sci. Eng.* **12,** 93 (1975).
3. Wynblatt, P., and Gjostein, N. A., *in* "Progress in Solid State Chemistry (J. McCaldin and G. A. Somorjai, Eds.), Vol. 9, p. 21. Pergamon, Oxford, 1975.
4. Dautzenberg, F. M., and Wolters, H. B. M., *J. Catal.* **51,** 26 (1978).
5. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **56,** 390 (1979).
6. Ruckenstein, E., and Malhotra, M. L., *J. Catal.* **41** 303 (1976).
7. Flynn, P. C., and Wanke, S. E., *J. Catal.* **37,** 432 (1975).
8. Glassl, H., Hayek, K., and Kramer, R., *J. Catal.* **68,** 397 (1981).
9. Glassl, H., Kramer, R., and Hayek, K., *J. Catal.* **63,** 167 (1980).
10. Zingsheim, H. P., Abermann, R., and Bachmann, L., *J. Phys. E* **3,** 39 (1970).
11. Gillet, M., and Renou, A., *Surface Sci.* **90,** 91 (1979).
12. Yacamán, M. J., and Dominguez, J. M., *Surface Sci.* **87,** L263 (1979).
13. Chu, Y. F., and Ruckenstein, E., *J. Catal.* **55,** 281 (1978).
14. Chu, Y. F., and Ruckenstein, E., *Surface Sci.* **6,** 517 (1977).
15. den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* **53,** 116 (1978).
16. Baker, R. T. K., Thomas, C., and Thomas, R. B., *J. Catal.* **38,** 510 (1975).
17. Granqvist, C. G., and Buhrman, R. A., *J. Catal.* **42,** 477 (1976).
18. Ruckenstein, E., and Chu, Y. F., *J. Catal.* **29,** 224 (1973).
19. Ruckenstein, E., and Chu, Y. F., *J. Catal.* **59,** 109 (1979).
20. Wynblatt, P., and Gjostein, N. A., *Scr. Met.* **7,** 969 (1973).
21. Fiedorow, R. M., and Wanke, S. E., *J. Catal.* **43,** 34 (1976).
22. Fiedorow, R. M., Chahar, B. S., and Wanke, S. E., *J. Catal.* **51,** 193 (1978).
23. Hassan, S. A., Khalil, F. H., and El-Gamal, F. G., *J. Catal.* **44,** 5 (1976).
24. Somorjai, G. A., *Progr. Analyt. Chem.* **1,** 101 (1968).
25. Yao, H. C., and Plummer, H. K., Jr., *J. Catal.* **59,** 365 (1979).
26. Johnson, H. F. L., and Keith, C. D., *J. Phys. Chem.* **67,** 200 (1963).
27. Baird, T., Paál, Z., and Thomson, S. J., *J. Chem. Soc. Faraday Trans. I* **69,** 50, 1237 (1973).
28. Maire, G., Bernhardt, P., Legaré, P., and Lindauer, G., *in* "Proceedings, 3rd Int. Conf. Solid Surfaces" (R. Dobrozemsky *et al.*, Eds.), p. 861. Vienna, 1977.