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Electron Microscopy of Pt/Al_2O_3 Model Catalysts: Artifacts in Sample Preparation

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It is shown that the structure of an evaporated model catalyst (Pt on amorphous or γ-alumina on Al foil) is altered by preparation for electron microscopy. These changes are often larger than the sintering effects during a catalytic reaction.

1. INTRODUCTION

It is well known that supported metal catalysts lose their activity during the catalytic process or during prolonged annealing at elevated temperature. This deactivation may be caused by contamination effects, but frequently sintering and coalescence of the dispersed particles are considered responsible (*1*). In recent years the microstructure and the occurrence of structural changes of supported Pt catalysts have been studied by many methods (*2*). In particular, high-resolution electron microscopy has been widely utilized to determine the dispersion and size distribution of Pt particles. For electron microscopic studies of sintering and size effects in catalysts-evaporated Pt films are very suitable as model catalysts (*3, 4*). Aluminum oxide which serves as support in industrial catalysts is often used as a supporting film ("substrate") for evaporated platinum.

Thin alumina films suitable for transmission electron microscopy have been prepared in various ways; for example, by electron beam evaporation (*5*) and by anodic oxidation of aluminum foils (*3*). If either of these two methods is applied the alumina film has to be separated from the substrate (glass or Al foil) by chemical stripping. This preparation for electron microscopy is known to involve artifacts which change the catalyst structure. They may interfere with the actual changes due to the originally studied effect and may be considerably larger than those changes.

As an example we wish to demonstrate how the structure of an evaporated model catalyst (Pt on alumina) is altered during preparation for electron microscopy and we shall compare the magnitude of these changes with those caused by thermal sintering, e.g., under conditions of a catalytic reaction.

2. EXPERIMENTAL

2.1. *Preparation of Alumina Substrates*

The alumina substrates were prepared by anodization of 0.15-μm-thick sheets of ultrapure Al following the procedure of Ruckenstein and Malhotra (*3*). Nonporous films of amorphous oxide between 10 and 30 nm thick were obtained in a 3% solution of tartaric acid adjusted to pH 5.5 with NH_4OH. In order to prevent the oxidation of both sides of the Al foil one side was covered with varnish (Formvar) before the anodization and the varnish was removed afterward by dissolving in $CHCl_3$. One part of the oxidized Al foil was heated in a furnace in air at 923 K for 20 hr yielding crystalline γ-alumina of, however, nonuniform thickness. The rest of the foil was washed and dried at 400 K, part of it also heated at 700 K, whereby the amorphous modification ("a-alumina") is retained. Both γ- and a-alumina carrier films were stripped by dissolving the Al in HCl or in $HgCl_2$ solution. When amalgamation

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started, the specimens were transferred into distilled water and the amalgamation continued until the Al was dissolved. The carrier films were washed and dried and mounted onto EM grids of copper or gold.

2.2. *Deposition of Pt*

Pt films of medium thickness between 0.1 and 1.5 nm were deposited simultaneously onto the specimens on EM grids and onto the Al foil covered with γ- and a-alumina, respectively. The ultrapure platinum was evaporated by electron bombardment heating (*6*) at a pressure of 10^{-9} bar at a constant rate of 0.1 nm min^{-1}. The thickness was monitored by a quartz crystal microbalance. The substrates were kept at room temperature.

2.3. *Preparation for Electron Microscopy*

Onto one part of the specimens a protective coating of SiO (5–10 nm) or carbon (~3 nm) was evaporated at 10^{-8} bar before the stripping. This coating was also applied to one part of the Pt films deposited previously onto the alumina on grids.

The specimens were separated from the Al foil by dissolving in various agents: (a) $HgCl_2$, as above; (b) acidic media (HCl 2–10%, HF); (c) alkaline media (NaOH 1–4%). After washing the specimens were mounted onto EM grids, dried, and examined in the electron microscope (Siemens Elmiskop 1a).

2.4. *Heat Treatments*

Some of the deposits were annealed inside the vacuum unit, some were heated in air, O_2, or N_2, at different temperatures up to 873 K before and after the stripping.

3. RESULTS

Using the resulting electron micrographs the following comparisons have been made:

(3.1) "Initial" deposits on alumina on grids, protected and unprotected with SiO or C, versus those attacked by different agents (mainly H_2O) for short times.

(3.2) "Initial" microstructure of as-deposited Pt on alumina on grids versus microstructure of the Pt deposits after being stripped from the Al substrate.

(3.3) As (3.2), but specimens protected with SiO or C before stripping.

(3.4) Effect of heat treatments on the structure of the various specimens.

3.1. *Fresh Evaporated Films, Effectiveness of Protective Coatings*

Platinum evaporated onto alumina under the above conditions generally exhibits a microstructure of fine dispersed grains of nonspherical appearance. In the following a 1-nm-thick film is taken as an example and the results are presented in Table 1 and in the corresponding Figs. 1a to 2d. At this mean thickness of 1 nm the coalescence stage is not yet reached (Figs. 1a, 1b, 2a). The density of particles of approx $1.4 \cdot 10^{13}$ cm^{-2} is close to the maximum obtainable value ("maximum density" in nucleation theory). This initial value is the same on a- and γ-alumina substrates if the SiO-protected films are taken as a reference.

Films exposed to the atmosphere show a slight reduction of the density, as measured on the unprotected films ($1.3 \cdot 10^{13}$ cm^{-2}). Such a reduction is in agreement with observations on Au and Ag films in the literature (e.g., (*7*)). Heating the EM grids *in vacuo* (10^{-9} bar) to 873 K leads to a reduction of the crystallite density by 21–27% and to a "contraction" of the particles. Neither the substrate (a- or γ-alumina) nor the coating seems to influence this initial sintering process (Fig. 1c).

Dipping the "fresh" specimens in cold H_2O for 10 sec leads to a pronounced reduction of the particle number (35–39%) on the unprotected films and on the SiO-protected film on a-alumina (29%) (Fig. 1d). The Pt deposit which is sandwiched between γ-alumina and SiO was attacked only in small areas, resulting in a reduction by 29%, whereas the rest remained unchanged. When the specimens dipped in water were subsequently heated in vacuum

TABLE 1

Changes of a 1-nm Pt/Alumina Catalyst on Cu Grid After Various Treatments

Support and treatment	Density ($\cdot 10^{-12}$ cm^{-2}) and shape of Pt particles		Relative change of density (%)		Figure	
	Unprotected	SiO protected	Unprotected	SiO protected	Unprotected	SiO protected
1. Amorphous Al_2O_3 on Cu grid 1-nm Pt freshly evaporated	13 as deposited	14	0	0	1a	1b
2. As 1, grid heated to 873 K *in vacuo*	10 slightly contracted	11	−23	−21	1c	
3. As 1, grid dipped into cold H_2O for 10 sec	8 slightly contracted	10	−39	−29	1d	
4. As 3, grid heated to 873 K *in vacuo*	8 as in Fig. 1d	undetermined strong coalescence	−39			1e
5. Grid dipped into dilute HCl[a]	2.7 coalesced	2.3	−73	−77		
6. γ-Al_2O_3 on Cu grid 1-nm Pt freshly evaporated	13 as deposited	14	0	0		2a
7. As 6, grid heated to 873 K *in vacuo*	9.5 as in Fig. 1c	10.5	−27	−25		
8. As 6, grid dipped into cold H_2O for 10 sec	8.5 contracted	14.10	−35	0, −29	2b	
9. As 8, grid heated to 873 K *in vacuo*	4 isolated rounded	10 little change	−69	−29	2c	2d

[a] Amorphous Al_2O_3 Au grid. Original Pt deposit 1.5-nm mean thickness, density $10 \cdot 10^{12}$ particles cm^{-2}.

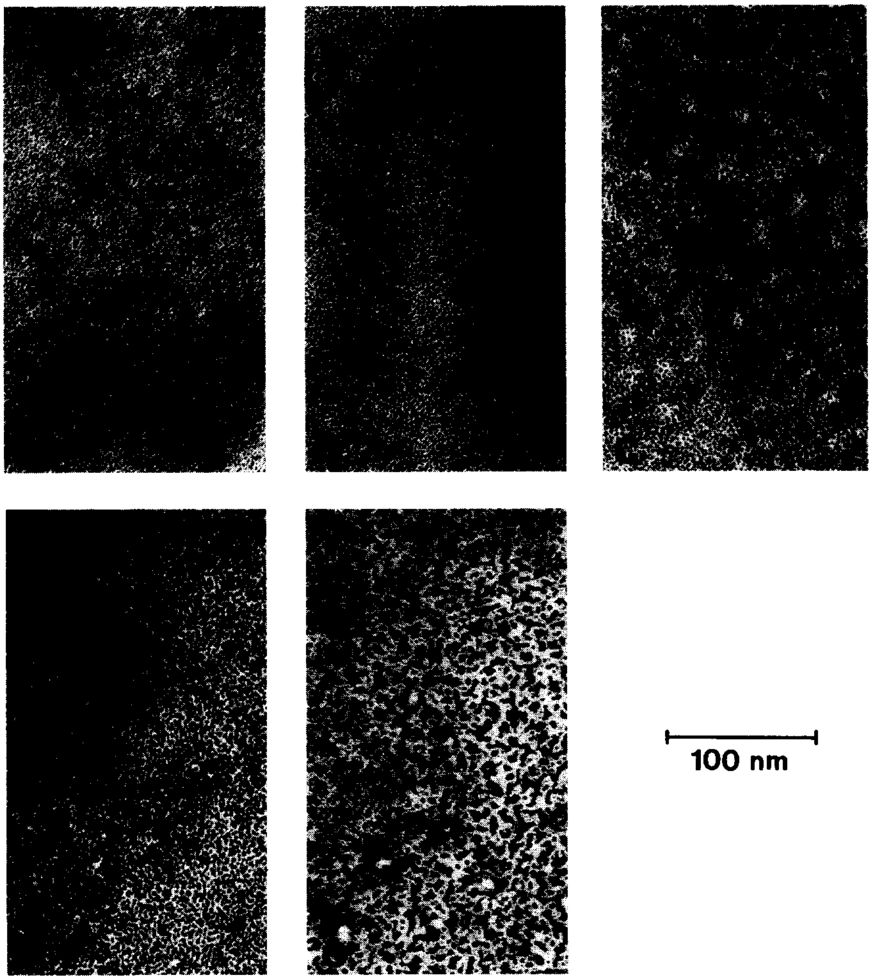

FIG. 1. 1-nm Pt film evaporated onto "a-alumina" on Cu grid. (a) As deposited, unprotected; (b) as deposited, protected with 10-nm SiO; (c) unprotected, heated *in vacuo* to 873 K; (d) unprotected, dipped in cold H_2O for 10 sec; (e) protected, dipped in H_2O and heated to 873 K. Magnification 200,000 : 1.

at 873 K the γ-Al_2O_3/Pt/SiO sandwich and the uncovered a-alumina/Pt suffered only insignificant changes whereas the structure of the other two, particularly that of the a-Al_2O_3/Pt/SiO, was strongly altered (Figs. 1e, 2c). A probable explanation for this behavior is that in the two latter specimens adsorbed or absorbed water was retained during the heating process which is known to have a strong effect on sintering.

Dipping the gold EM grids into dilute acid (HCl) has a very strong effect on all the specimens. It leads to coagulation, to loss of particles, and hence to a reduction of the overall number of particles by a factor of 5. For other Pt film thicknesses below the coalescence stage the results differ only in the absolute particle densities. Above the coalescence stage strong coagulation is always observed.

3.2. *Structural Changes of Pt/Al_2O_3 Catalysts*

From the previous discussion it is not surprising that Pt/Al_2O_3 model catalysts may lose their original appearance when they are stripped from the underlying Al foil.

TABLE 2

Effect of Stripping in Different Solvents on the Microstructure of Pt/Al_2O_3 Catalysts

Support and treatment	Density of Pt particles ($\cdot 10^{-12}$ cm^{-2})			Relative change of density (%)			Figure		
	Unprotected	Protected with 10-nm SiO	Protected with 3-nm C	Unprotected	Protected with 10-nm SiO	Protected with 3-nm C	Unprotected	Protected with 10-nm SiO	Protected with 3-nm C
1. Amorphous Al_2O_3 on Cu grid 1-nm Pt freshly evaporated	13	14	14	0	0	0	1a, 3a	1b	4a
2. Amorphous Al_2O_3 on Al foil with 1-nm Pt. Al dissolved in 2% HCl		5	7.5		−64	−46			4b
3. As 2, Al dissolved in 4% HCl	2.5		6.3	−81		−55	3b		4c
4. As 2, Al dissolved in $HgCl_2/H_2O$	3.5	7.5	5	−73	−46	−64	3c	3d	
5. As 2, Al dissolved in 5% HF	FSD[a]		6.1			−56			
6. As 2, Al dissolved in 0.8% HF	FSD		5.7			−59			
7. As 2, Al dissolved in 0.05% NaOH	FSD		4.7			−66			
8. As 2, Al dissolved in 1% NaOH	FSD		2.6			−81			4d

[a] Film structure destroyed.

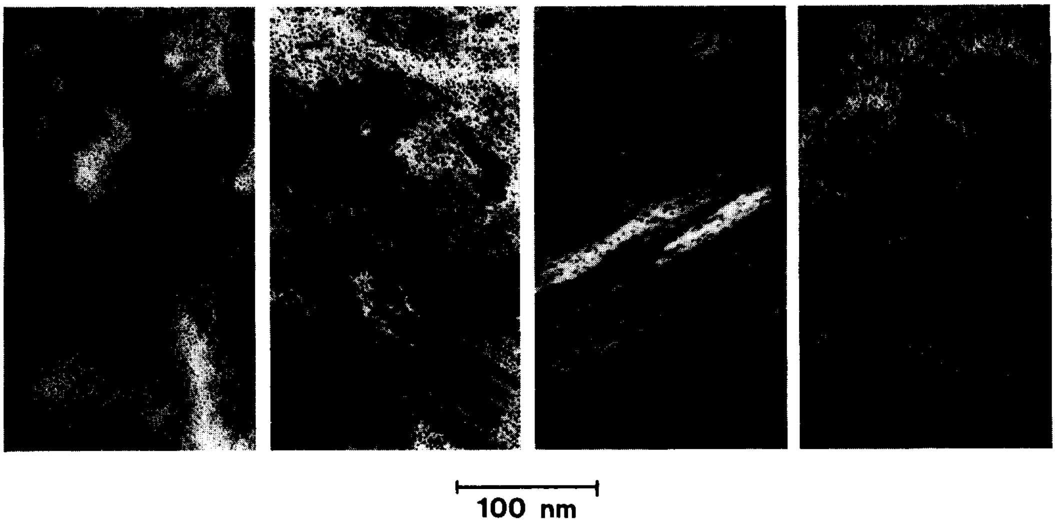

FIG. 2. 1-nm Pt film on γ-alumina on Cu grid. (a) As deposited, protected with 10-nm SiO; (b) unprotected, dipped in H_2O; (c) unprotected, dipped in H_2O and heated to 873 K; (d) protected, dipped in H_2O and heated to 873 K. Magnification 185,000 : 1.

In Table 2 the results are again represented by those for a 1-nm-thick Pt film showing an initial density of $1.4 \cdot 10^{13}$ or $1.3 \cdot 10^{13}$ particles/cm^2 (first column, unprotected film).

It must be assumed that the microstructure of the film evaporated onto the alumina substrate (a or γ) *on the EM grid* represents also the true morphology of the initial deposit on the Al_2O_3/Al substrate. This assumption cannot be proved directly. However, it appears that neither the chemical nature nor the surface (roughness, etc.) of the alumina substrate is appreciably changed by the attack of the solvent during the stripping and hence the nucleation and growth processes of Pt on the stripped and the unstripped surface are expected to be

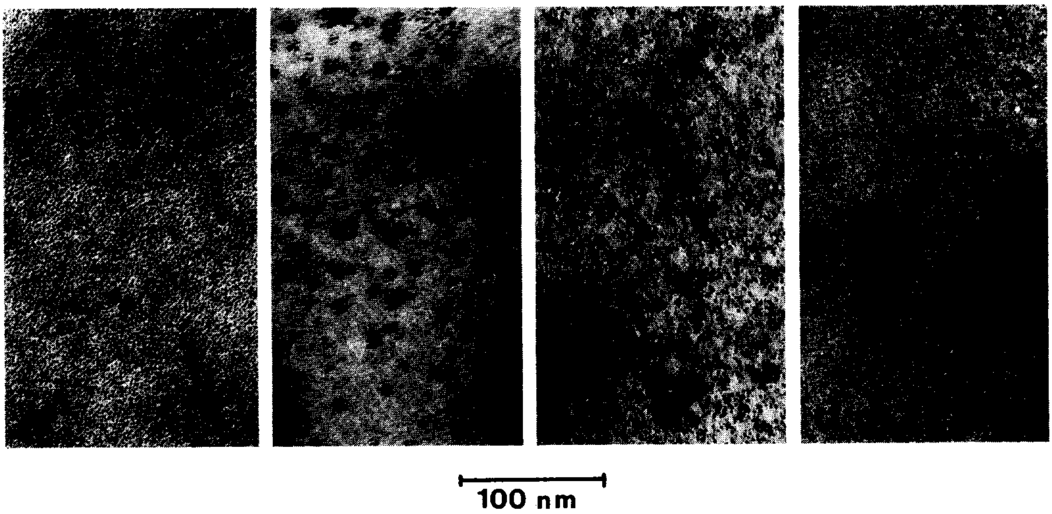

FIG. 3. 1-nm Pt on "a-alumina." (a) As deposited, unprotected; (b) dissolved from Al in 4% HCl, unprotected; (c) dissolved from Al in $HgCl_2/H_2O$, unprotected; (d) dissolved from Al in $HgCl_2/H_2O$, protected with SiO. Magnification 190,000 : 1.

identical. The fresh evaporated film (Figs. 1a, 1b, 3a, 4a) is therefore compared with specimens from which the underlying Al was dissolved in various media. Evidently all of these solvents cause strong artifacts which can only be partly avoided by protective coatings. Lower acid concentrations of the solvent do not improve the results because of the longer reaction times involved.

3.3. Prevention of Artifacts by Protective Coatings

Table 2 also contains a summary on particle densities and particle shapes of a 1.0-nm-thick Pt film sandwiched between a 20-nm-thick a-Al_2O_3 and a protective coating of 10-nm SiO and 3-nm carbon, respectively. As can be seen from the corresponding figures the structural changes are less pronounced, but nevertheless the observed particle density is always reduced by more than 50%. The attack of the solvent leads apparently to an initial coalescence of neighboring particles without appreciable contraction of the resulting aggregates (Figs. 4b and c). Second, agglomeration of these aggregates is observed whereby empty regions and more densely packed clusters of aggregates are formed (Figs. 3b–3d, 4d).

3.4. Heat Treatments

As already mentioned (cf. Table 1 and corresponding figures), heat treatments *in vacuo* or in various atmospheres lead to changes of the catalyst structure which are quite well known and discussed, e.g., by Chu and Ruckenstein (*4*).

In Fig. 5 the structure of a 0.5-nm deposit on a-Al_2O_3 on a gold grid is shown before and after heating at 720 K in pure oxygen in a flow reactor. This treatment leads to a sintering and the particle density is reduced by a factor of 3. The same reduction would be obtained by stripping the initial deposit in 2% HCl. Heating the catalyst to reaction temperature (in general 473–673 K) involves, of course, even smaller changes than those of Fig. 5. One question which remains open is whether Pt films on Al_2O_3/Al which have been stabilized by annealing under reaction conditions are also affected by subsequent stripping. Our observations show that these specimens are sometimes less altered, but frequently the changes are more severe even if the film was protected by a SiO coating.

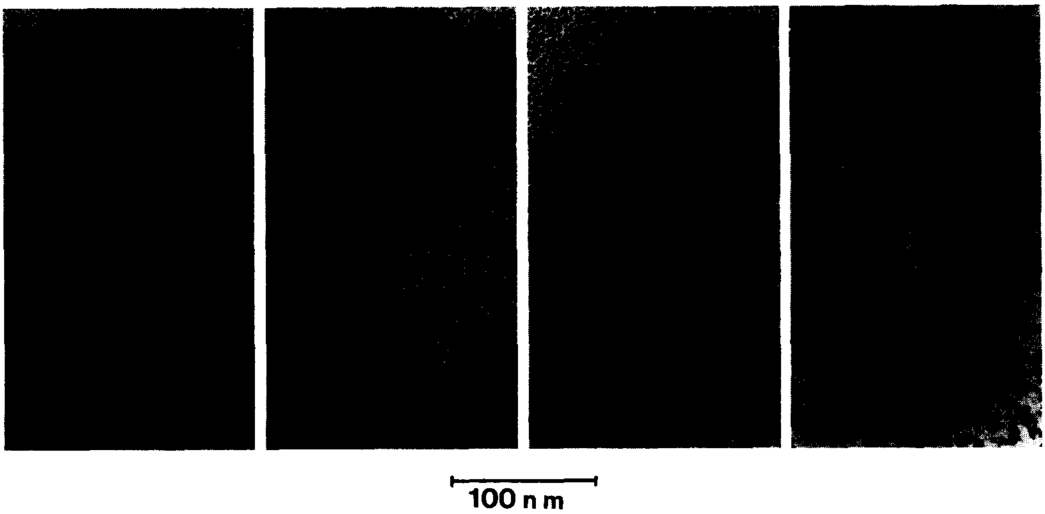

FIG. 4. 1-nm Pt on "a-alumina." (a) As deposited, protected with 3-nm C; (b) protected with C and dissolved from Al in 2% HCl; (c) as (b), dissolved in 4% HCl; (d) as (b), dissolved in 1% NaOH. Magnification 190,000 : 1.

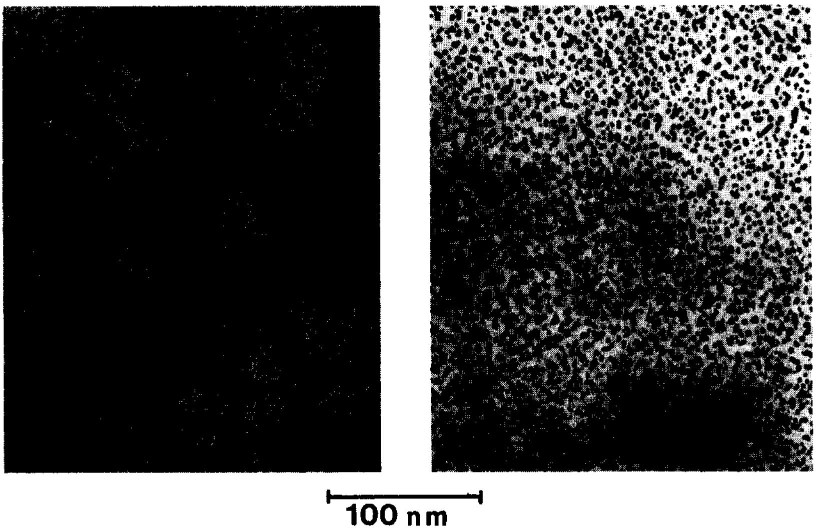

FIG. 5. 0.5-nm Pt on "a-alumina" on Au grid. (a) As deposited, particle density $1.1 \cdot 10^{13}$ cm^{-2}; (b) after heating in oxygen at 720 K, particle density $3.2 \cdot 10^{12}$ cm^{-2}. Magnification 200,000 : 1.

4. CONCLUSIONS

From earlier investigations on silver and gold (*7*, *8*) it is known that water vapor or water can affect the microstructure of as-deposited films in the island or coalescence stage in a similar way as a thermal treatment.

While between H_2O and silver a chemical reaction almost certainly takes place at least at the interface, the sintering of gold as well as of Pt is probably due to the lowering of the activation energy for diffusion by the adsorption or absorption of water on the substrate surface. A protective coating is only effective against exposure to atmosphere but not against the attack of solvents. On the other hand, increasing the thickness of either the alumina substrate or of the SiO or carbon covering layer, which might reduce the possibility of artifacts, leads also to loss of resolution and transparency in the electron microscope. It is hence concluded that the study of sintering and size effects must be restricted to as-deposited films which have not been transferred to the electron microscope by chemical stripping.

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