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Redispersion of Pt/Alumina via Film Formation

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Alternations in the size of the particles on alternate heating in H_2 and O_2 of model Pt/Al_2O_3 catalysts is reported. The catalysts have been investigated by electron microscopy and electron diffraction. The particles appear smaller on heating in oxygen and larger and extended on heating in hydrogen (on heating in hydrogen they regain more or less the size they had prior to the oxygen treatment). This behavior is apparently in contrast to the normally observed extension of particles on oxidation and contraction on reduction. The alternation in size is explained on the basis of the formation of a detectable film (in the form of a halo), or an undetectable film, around each particle due to the strong interactions between crystallites and support in an oxygen atmosphere, and its withdrawal to merge with the respective particle in a hydrogen atmosphere. The films remain in the immediate vicinity of and in contact with the parent particles and do not interconnect with one another to form a contiguous surface film. It is suggested that one of the possible mechanisms of redispersion (regeneration) of Pt/Al_2O_3 often observed in oxidizing atmospheres is by extension and film formation. © 1987 Academic Press, Inc.

INTRODUCTION

Pt/Al_2O_3 catalysts have been widely used in a number of industries. These supported catalysts, however, gradually lose their activity. This is attributed in part to the gradual decline in the exposed metal surface area due to sintering. Sintering of supported metal catalysts has been extensively investigated with both model and industrial catalysts (see (*1–3*) for reviews). The approach to the more significant problem of the regeneration of the sintered industrial catalyst has been more or less empirical. However, especially in the case of supported Pt catalysts, a number of investigations (*1–17*) regarding regeneration have been carried out and the mechanisms involved have been debated. Ruckenstein and Malhotra (*4*) suggested that the catalyst redispersion was a result of particle splitting due to a buildup of strain in the particles. Subsequently Stulga *et al.* (*9*) reported that (in the case of a similar system under similar conditions) they did not observe particle redispersion. Gollob and Dadyburjor (*10*), on the other hand, observed redispersion which they attributed to particle splitting. Ruckenstein and Pulvermacher (*11*) had suggested earlier that redispersion could occur by emission of particles, and Fiedorow and Wanke (*5*) attributed the observed increase in dispersion (measured by H_2 chemisorption) to a similar cause, namely emission of atoms or molecules. Dautzenberg and Wolters (*12*) suggested that an oxygen treatment could recover only the fraction of platinum complexed with alumina during prior high-temperature H_2 treatment and that it could not actually redisperse the sintered large platinum crystallites. Lieske *et al.* (*13*) also argued that oxygen by itself cannot lead to redispersion and that redispersion is possible only in the presence of chloride ions. Straguzzi *et al.* (*14*) and Bournonville and Martino (*15*) also suggested that chlorine plays a role in the redispersion of alumina-supported platinum catalysts. Ruckenstein and Chu (*16*) reported that in the case of Pt/Al_2O_3, following a few cycles of alternate heating in H_2 and O_2 at 750°C, sintering in H_2 and redispersion in O_2 were observed. They suggested that the redisper-

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sion in O_2 may be due to the coexistence of a two-dimensional phase of single atoms, or of a multilayer film, with the crystallites. The concept of the coexistence of single atoms and a particulate phase was used also by Yao *et al.* (*17*) to explain sintering or redispersion. Evidence for the redispersion of large crystallites via extension, film formation, and its breakup as well as by splitting of crystallites was reported recently in the case of Fe/Al_2O_3 (*18, 19*) and Ni/Al_2O_3 (*20*) model catalysts.

We report here results with model Pt/Al_2O_3 catalysts heated alternately in H_2 and O_2 at temperatures in the range 300–750°C, which show that there is an alternation in the size, namely an apparent decrease in the size of the particles on heating in O_2 and a recovery of more or less the original size on subsequent heating in H_2. This size alternation continued over a number of cycles and was observed at temperatures between 500 and 700°C. The results are discussed in terms of the redispersion of the crystallites via the formation of disconnected individual films around the particles, which is a result of the strong interactions between crystallites and support.

EXPERIMENTAL

The method of preparation of model Pt/Al_2O_3 catalysts and the treatment procedure are presented in detail in Refs. (*16, 21*) and they are therefore not elaborated here. The term hydrogen refers to the as-received ultra-high-purity hydrogen (≤ 1 ppm O_2 and ≤ 3 ppm moisture) from Linde Division, Union Carbide Corp., and "purified hydrogen" refers to the above hydrogen purified further by passing it through a Deoxo unit (Engelhard Industries), followed by a column of silica gel, a bed of 15 wt% MnO on silica, and finally, through a column of 13× and a column of 5-A molecular sieves immersed in liquid nitrogen.

RESULTS

The results presented here have been obtained with the same samples for which the sintering results were described in Ref. (*21*). The experiments have been carried out with a number of specimens. The results obtained with five of them are presented in some detail.

1. A 2-nm initial film thickness sample was heated at 500°C for 8 h in purified hydrogen; this generated small particles of about 1.6 nm average size. In order to more easily identify the processes that occur, the size of the particles was increased further by heating the sample in H_2 at 600°C for 4 h followed by heating at 700°C for 5 h, at 800°C for 2 h, and finally again at 600°C for 2 h. This heat treatment led to relatively large particles of about 7 nm average size. On subsequent heating of the sample in O_2 at 300°C, there was a decrease in the size of all the particles. Additional heating in O_2 at progressively higher temperatures in steps of 50°C up to 600°C (2-h duration at each temperature) did not result in significant changes in either the size distribution or the shape of the particles. However, when the sample was subsequently heated in H_2 at 500°C, all the particles, small and large, increased significantly in size. Few particles disappeared, indicating that neither ripening nor migration and coalescence involving the detectable particles were responsible for the growth. Further heating in O_2 at 500°C resulted again in a decrease in the size of all the particles. Subsequently, when the sample was heated in H_2 at 500°C, the particles again increased in size and regained more or less the size they had prior to the oxygen treatment. Alternate heating in H_2 and O_2 at 500°C was carried out over six cycles and the above alternation in size was observed in each cycle (Fig. 1). A decrease in size on heating in O_2 and an increase in size on heating in H_2 were also observed when the same specimen was subsequently heated at 700°C.

2. To verify whether the observed alternations in size were caused by the gradual and prolonged heat treatment in O_2 between 300 and 600°C prior to the cycling in H_2 and O_2 at 500°C, another sample with a

similar prehistory, but without the extended oxygen treatment between the initial size distribution and the cycling in H_2 and O_2 at 500°C, was investigated. During the first two cycles, the particles decreased in size only marginally on heating in O_2 and increased in size on heating in H_2. However, during the subsequent four cycles, the changes in size were more pronounced, even though the extent of size reduction was smaller than that for Sample 1. Perhaps the gradual heating in O_2 at progressively higher temperatures prior to the cycling in H_2 and O_2 enhanced the wetting of the substrate by the particles in the case of Sample 1. It is also to be noted that following the heating in O_2 at 500°C, the smallest of the detectable particles were still present on the substrate and did not appear to have disintegrated via molecular emission. In addition, following the heating in O_2, detectable films in the form of a halo around each particle could be seen (Fig. 2a). Subsequent to the above six cycles, the treatment in oxygen was carried out at higher temperatures. On heating in O_2 at 600°C few particles disappeared and the films around the particles could be seen even better than at 500°C (particles marked with large arrows in Fig. 2c). Even the smallest particles remained (particles marked with small arrows in Figs. 2a–2d) and regained more or less their previous sizes on subsequent heating in H_2 at 500°C. A large number of crystallites considerably extended to form thin, light patches on the substrate on subsequent heat treatment in O_2 at 700°C (Regions 1, 2, and 3 in Fig. 2e, for example). Some particles are no longer detectable. Not all the particles present before the last O_2 treatment were regained on subsequent heating in H_2 at 500°C. Smaller particles were generated in regions where the particles had extended considerably before (Regions 1–3 in Figs. 2e and 2f). Films around some particles could still be seen (particles marked with large arrows). A decrease in the number of detectable particles on the substrate surface during heating in O_2 may suggest the possibility of material loss via evaporation. Evaporation of Pt as PtO_2 in oxygen atmospheres at temperatures greater than 700°C has been suggested before (*22–24*). However, in light of the observations indicating the presence of detectable films around the particles on heating in O_2 and the generation of smaller particles in some regions where the particles had considerably extended before, it is more likely that a part of the material (Pt or PtO_x) diffused into or spread over the surface of the substrate. These probably happen due to the strong interactions between particles and substrate. Further, particles 0.8 nm in size or even smaller remained without disappearing through the various cycles of alternate heating in H_2 and O_2 at 500°C and also following the high-temperature (up to 700°C) O_2 treatments (particles marked with small arrows in Figs. 2a–2f), suggesting that molecular emission and/or evaporation played a minor role, if any.

3. A third sample of 2 nm initial film thickness and from the same batch as the preceding sample was heated in a slightly different sequence. Particles were generated as before by heating the Pt/alumina sample in purified H_2 at 500°C for 12 h and subsequently at 600°C for 5 h. Before the alternate heating in H_2 and O_2, Sample 1 described above was heated in O_2 between 300 and 600°C in steps of 50°C, without hydrogen treatments in between. If the particles were already oxidized at the lower temperature of 300°C, subsequent heat treatment of the oxidized sample in O_2 at higher temperatures would cause little change as observed up to 600°C with Sample 1. In order to verify whether there is a threshold temperature beyond which film formation is detected following heating in O_2, it is appropriate to start with a reduced sample prior to the oxidation step at each temperature. Therefore, the present sample was also heated in O_2 in the range 300–600°C in steps of 50°C, but unlike in Sample 1, in between each oxidation step, this sample was heated in H_2 at 500°C in

order to reduce the oxide to metal prior to the next oxidation. As reported earlier (*21*), except for some marginal sintering, mostly by the coalescence of neighboring particles, there was very little change in the size or shape of the particles up to the 500°C O_2 treatment. No detectable decrease in the particle size or the formation of films around the particles could be detected following the 300 to 450°C O_2 treatments. Particles as small as 0.8 nm in size or even smaller remained essentially unaffected following the above treatments in H_2 and O_2 as observed also with Sample 2 on cycling at 500°C. This indicates that even though an oxide might have formed at or below 500°C, no significant molecular emission was involved. (It is to be noted that oxidizing atmospheres are more likely to induce molecular/atomic emission.) At 500°C, changes regarding particle size and film formation begin to be noticed. As for Sample 2, the decrease in the size of the particles following heating in O_2 at 500°C was marginal during the first two cycles of heating but more pronounced during the subsequent cycles; the extent of size reduction was again smaller than that for Sample 1.

The behavior of this sample on subsequent heating in O_2 at higher temperatures was slightly different. On heating in O_2 at 600°C a number of particles disappeared, as observed before (Fig. 3). Some large particles have decreased in size considerably or disappeared, while nearby smaller particles have only decreased marginally in size (Regions 1–5 in Fig. 3). Subsequent heating in O_2 at 700°C resulted in an almost complete disappearance of the existing particles on the substrate. Instead, a number of very large, thin, irregular hexagonal patches could be observed. These patches can be a result of either a redistribution of the parti-

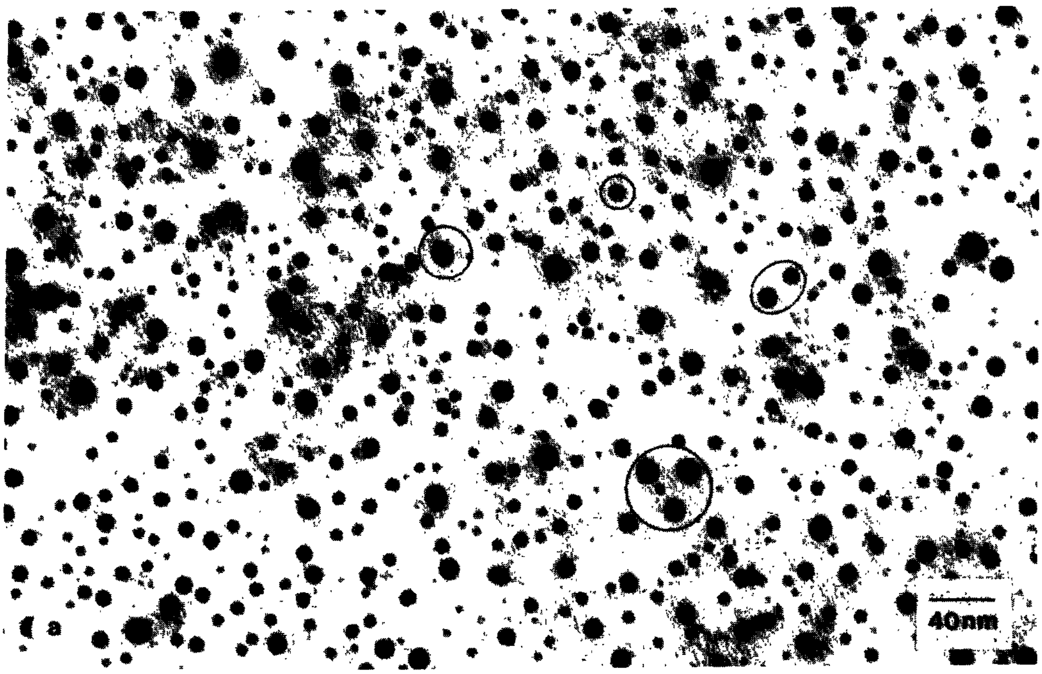
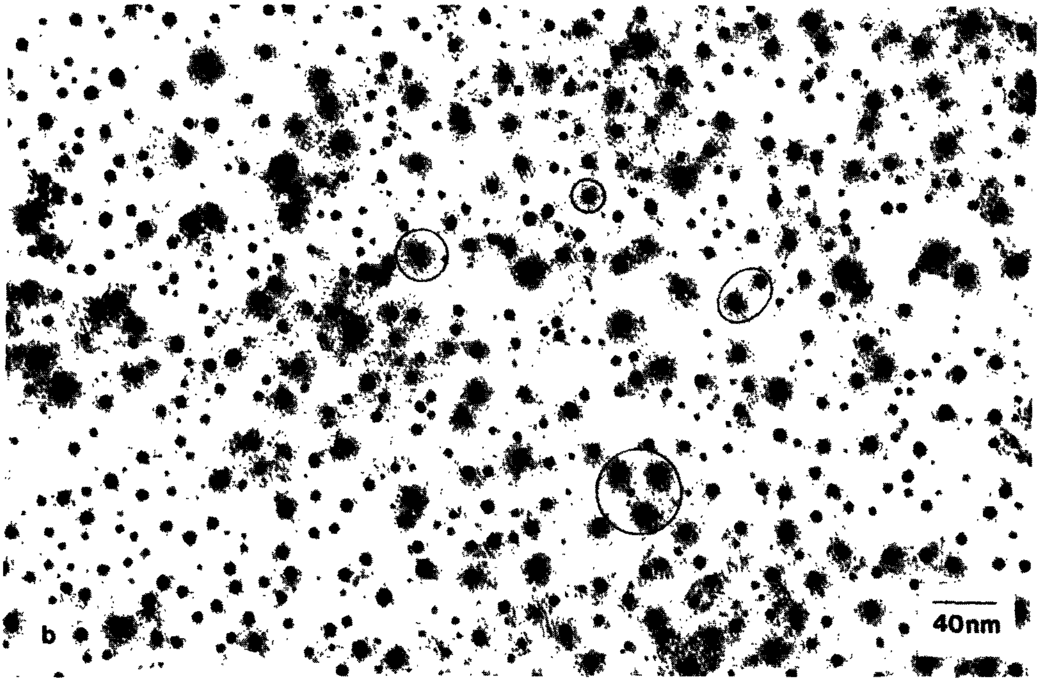


FIG. 1. Changes in particle size of a 2 nm initial film thickness Pt/Al_2O_3 sample on alternate heating in H_2 and O_2 at 500°C. The sample has had a long heating history prior to Fig. 1a (see text). (a) H_2, 500°C, 2 h; (b) O_2, 500°c, 2 h (or 16 h); (c) H_2, 500°C, 4 h.



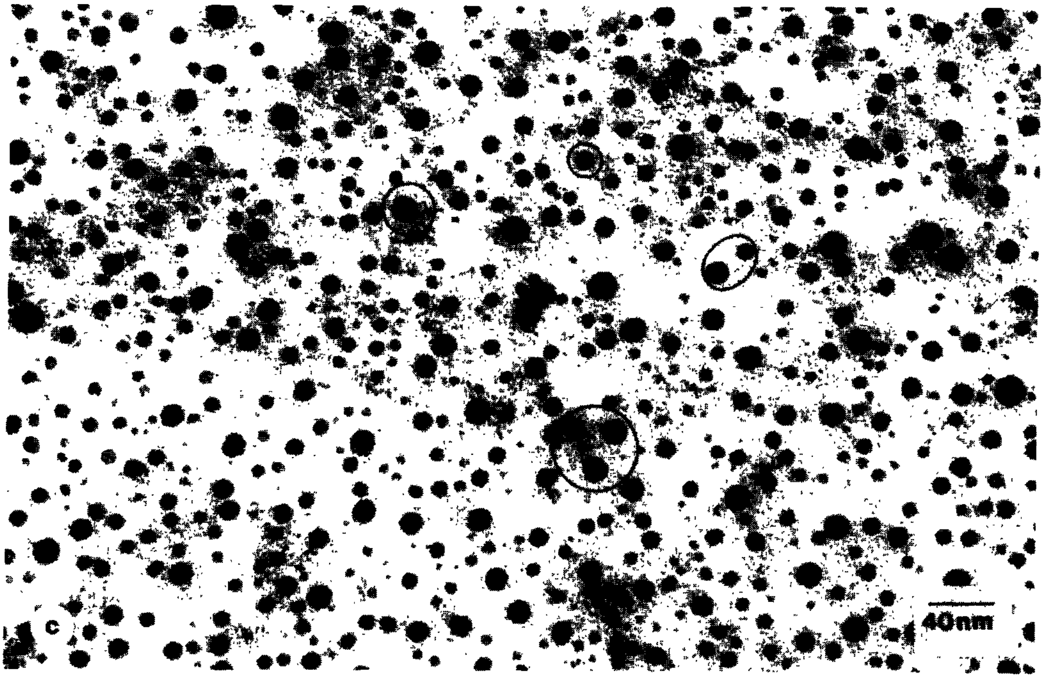


FIG. 1—*Continued.*

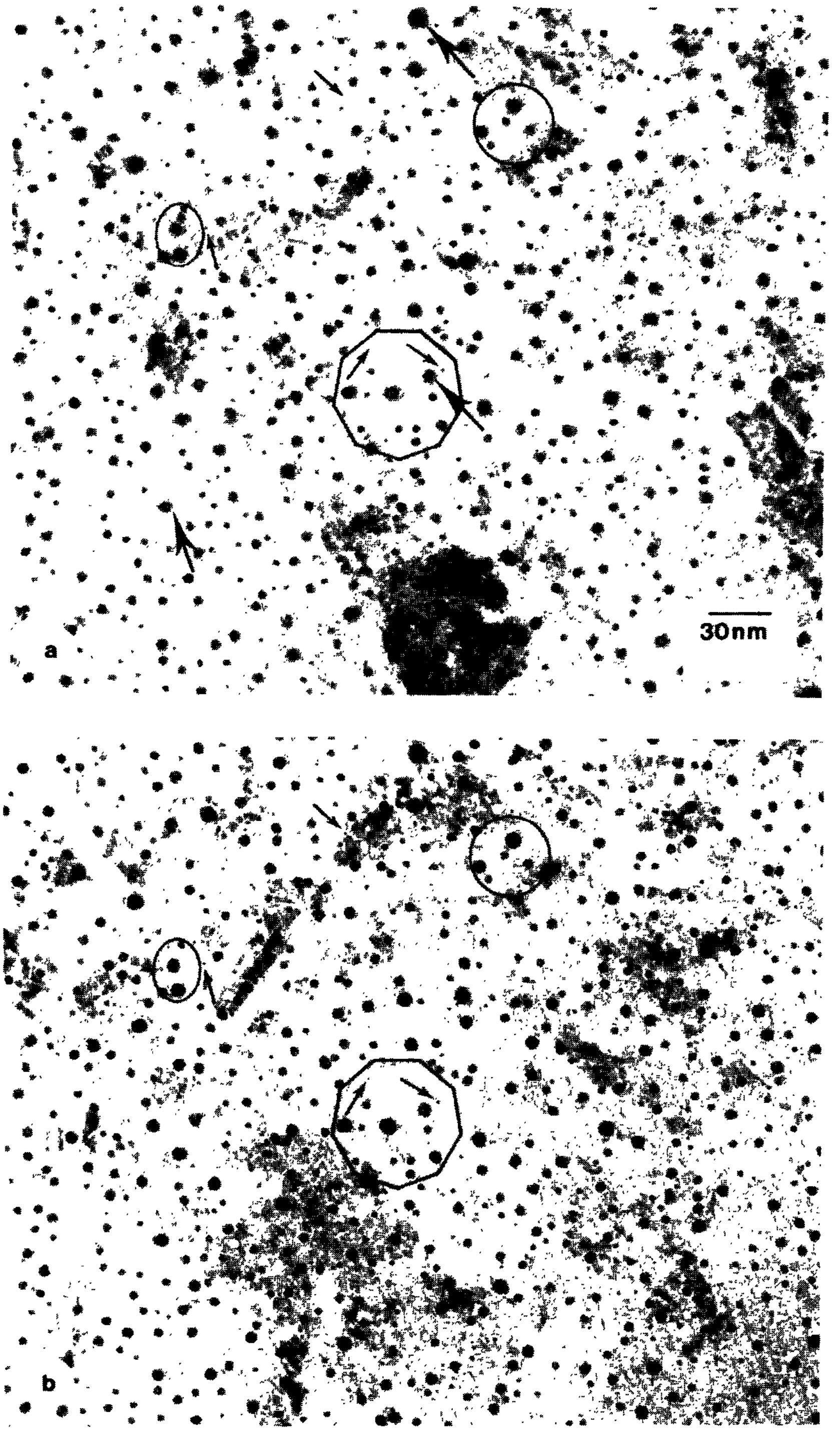


FIG. 2. Changes on heating a 2 nm initial film thickness Pt/Al_2O_3 sample alternately in H_2 and O_2. Micrographs for only a few cycles of alternate heating are shown. Prior to the following, the sample had undergone a few cycles of alternate heating in H_2 and O_2 (see text). (a) O_2, 500°C, 5 h; (b) H_2, 500°C, 2 h; (c) O_2, 600°C, 5 h; (d) H_2, 500°C, 2 h; (e) O_2, 700°C, 5 h; (f) H_2, 500°C, 2 h.

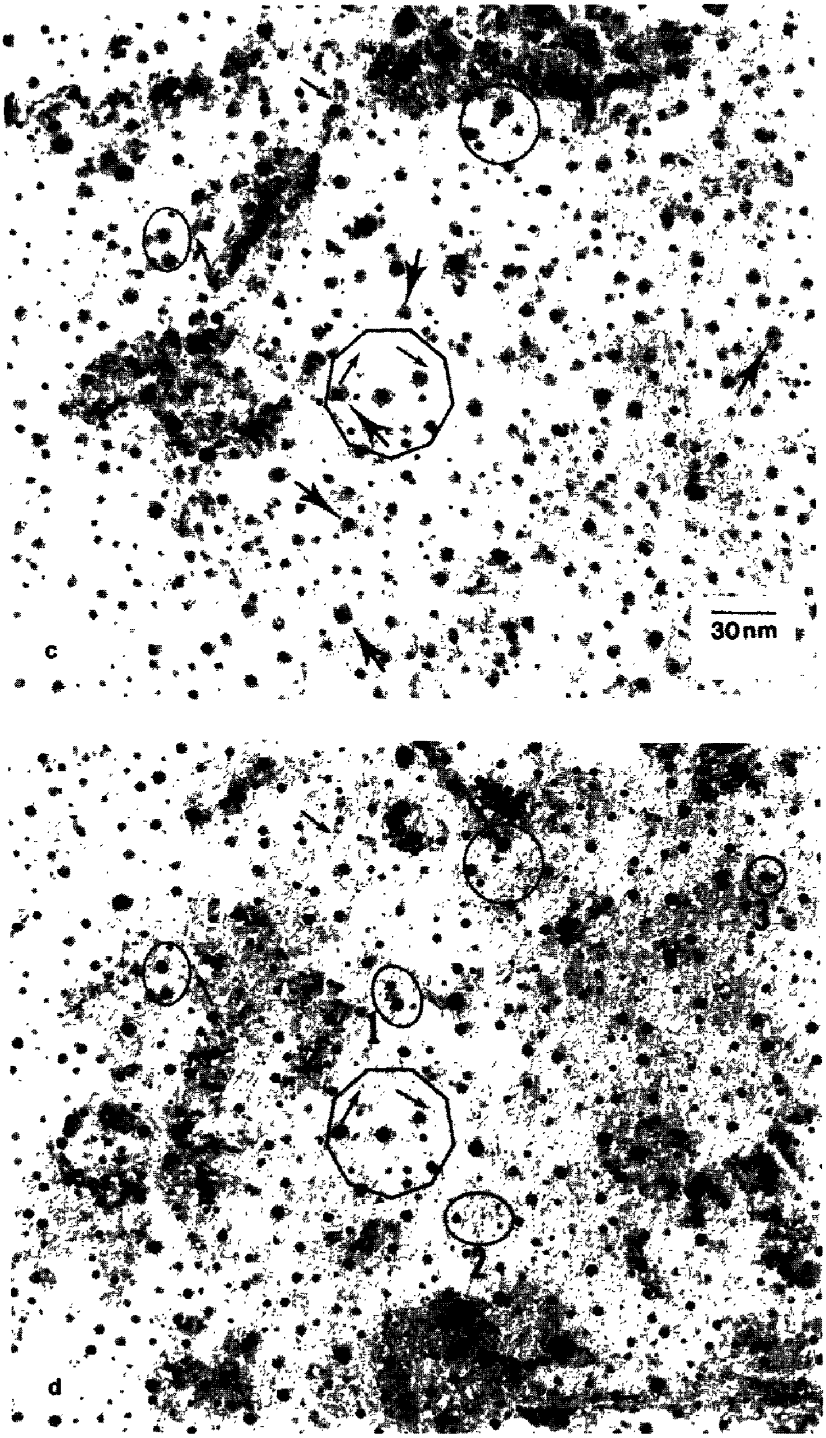


FIG. 2—*Continued.*

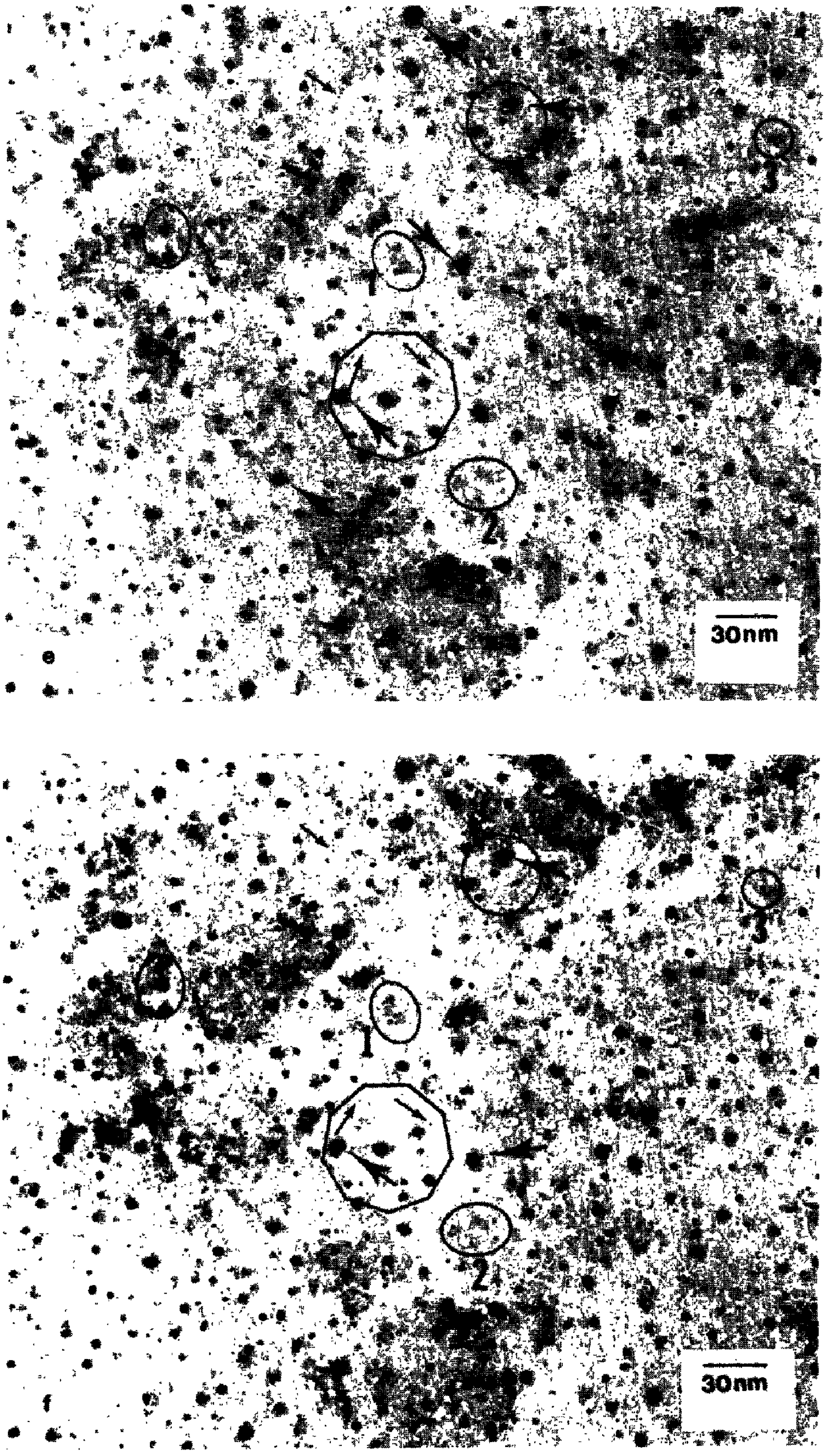


FIG. 2—*Continued.*

cles (due to the strong interactions between particles and substrate) or contamination. These patches remain, however, and even increase in size, on heating in O_2 at 800°C. One would expect that they would disappear on heating in O_2 if they were hydrocarbon or carbon impurities. The patches have sharp edges and are facetted in irregular, hexagonal shapes as seen in Figs. 3d and 3e. (Fig. 3e shows a larger area of the sample.) Some patches overlap (particles marked (a) and (b)). The patches remain essentially unchanged on subsequent heating in H_2 at 500 or 700°C. From the micrographs, it appears that the patches represent large extended particles, which are formed as a result of the strong interactions between particles and support (which in turn are enhanced by the high-temperature, 700 or 800°C, oxygen treatment). The interactions are probably so strong that little change in their morphology occurs on subsequent heat treatment in H_2 or O_2. It is to be noted that a thin, hexagonal, pill box morphology of Pt particles observed on heating in H_2 at $\geq$500°C was previously attributed to the so-called "SMSI," which was reported to be restricted to particles on reducible oxide supports, such as TiO_2 (*28*).

4. In order to verify whether the observed alternation in size was also exhibited by samples with smaller average sizes (since the average particle size in industrial Pt/Al_2O_3 catalysts is usually small), another sample with a smaller loading (0.75 nm initial film thickness) was heated in H_2 and O_2 at 500°C. Since this specimen was not heated in H_2 or O_2 at >500°C at any time during either the pretreatment or the cycling in H_2 and O_2, the particles were small. Any marginal decrease in size of such small particles on heating in O_2 will not be easily detectable unless the particles spread completely. Consequently, very little change, other than that due to sintering, was observed. After heating the sample for a total of 80 h, which incidentally generated sufficiently large particles, clearly detectable alternations in size were subsequently observed on cyclic heating in H_2 and O_2 at 500°C. These results indicate that the films around the particles, or an apparent decrease in the particle size as a result of the film formation, become detectable only when the particles are sufficiently large. The inability to detect such changes by electron microscopy does not imply, however, that they do not occur for small particles as well.

5. Whether the alternation in size on cyclic heating in H_2 and O_2 and the formation of films around particles in O_2 were restricted to temperatures below the decomposition temperature of PtO_2, namely $\simeq$580°C, or it is possible also at higher temperatures was verified by heating another sample at 750°C. The formation of films around the particles following heating in O_2 was in fact more obviously exhibited by a sample (of 1.5 nm initial film thickness) heated at 750°C. After Pt deposition, the sample was heated in as-received ultra-high-purity H_2 at 750°C for 15 h. This generated very large particles in the range 5–15 nm (Fig. 4). When this specimen was subsequently heated in O_2 at 750°C, a large number of small and large particles disappeared without any kind of preference or pattern (Figs. 4a and 4b). All the remaining particles, including the small ones decreased in size. It could be surmised that because of the higher temperature, emission of atoms/molecules to the substrate or material loss via evaporation was involved. However, on subsequent heating in H_2 at 750°C for 5 h, the remaining particles considerably increased in size while some grew even larger than their size prior to the O_2 treatment. There was very little decrease in the number of detectable particles. The increase in average particle size on switching to H_2 from O_2 was greater than could possibly be explained by the very small decrease in the number of detectable particles (Figs. 4b and 4c). This indicates that the decrease in size during prior heating in O_2 could not have been solely due to the loss of material by evaporation. Two of the

possibilities are (i) the material was present on the substrate surface as single atoms/molecules following the O_2 treatment, which were subsequently captured by the particles on H_2 treatment, and (ii) following the O_2 treatment the material was present as individual unconnected films around each particle which subsequently contracted and merged with the respective particle on heating in H_2, to result in the observed increase in size.

A subsequent prolonged heat treatment of this sample for 12 h in H_2 at 750°C led to the appearance of films around the particles (Fig. 4d). This behavior is reminiscent of a similar observation in the case of Fe/Al_2O_3 on prolonged heat treatment in as-received H_2 (*18*). There it was suggested that the extension of the particles was a result of the oxidation of iron by the residual O_2 and H_2O present in the H_2 and the subsequent strong interaction between the iron oxide

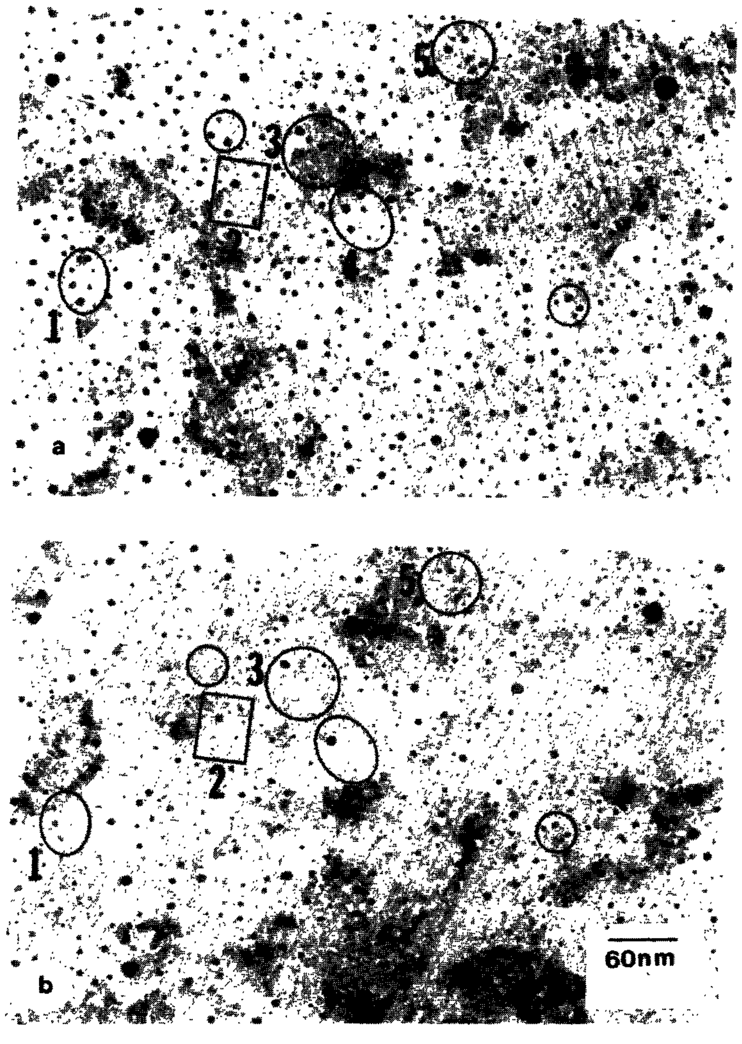


FIG. 3. Micrographs showing changes in a 2 nm initial film thickness Pt/Al_2O_3 sample subsequent to a few cycles of alternate heating in H_2 and O_2 (see text). (a) H_2, 500°C, 2 h; (b) O_2, 600°C, 5 h; (c) (O_2, 700°C, 5 h) + H_2, 500°C, 2 h; (d) O_2, 800°C, 3 h; (e) same as (d), a larger area shown at a lower magnification.

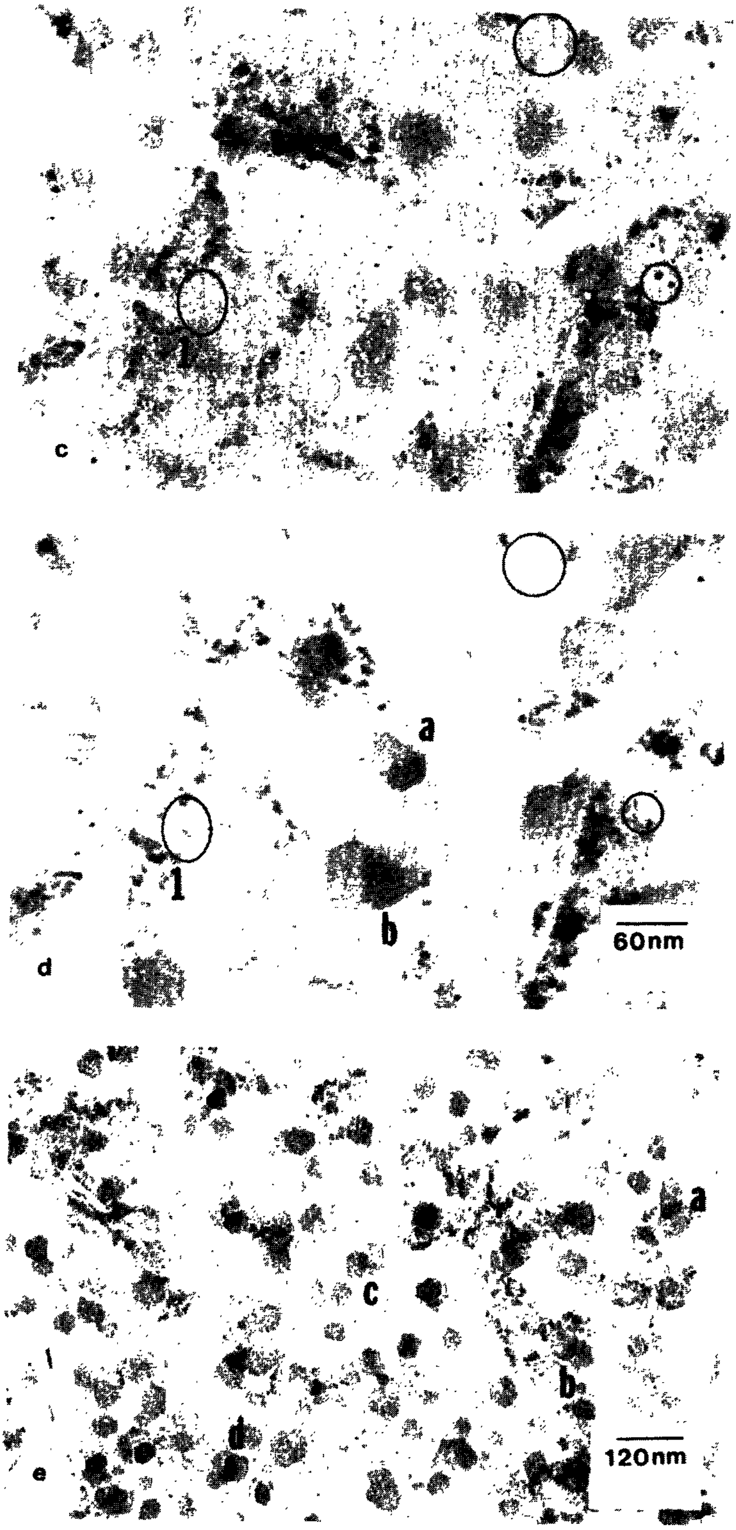


FIG. 3—*Continued.*

and the alumina. In the present case even though a stoichiometric platinum oxide (PtO_2) is not stable at 750°C, transient phases of platinum oxide might have formed which might have reacted with alumina. Even otherwise, because of the high temperature, an interaction compound between Pt and Al_2O_3 might have formed leading to the extension of the particles. In this regard, it is noted in the next section that the presence of an interaction compound is suggested in the electron diffraction patterns in both H_2 and O_2. Subsequently, an apparent decrease in size of the solid core and the appearance of films around the particles on heating in O_2 and an apparent increase in size on heating in H_2 were observed following three more cycles of alternate heating of this sample in H_2 and O_2 at 750°C (Fig. 5).

It follows from the above experimental results that an apparent decrease in size on heating in O_2 and a recovery in size on heating in H_2 is exhibited by model Pt/Al_2O_3 catalysts over a range of temperatures (500–750°C used in the present experiments) and initial metal loadings (0.75–2 nm initial film thickness) even though there are some differences perhaps due to the differences in the history of the samples.

DISCUSSION

A few mechanisms have been suggested in the literature for the redispersion of sintered supported metal catalysts in an oxidizing atmosphere. The sintered crystallites can emit atoms or molecules to the substrate which can then coexist with the crystallites as a two-dimensional dispersed phase, thereby increasing the dispersion

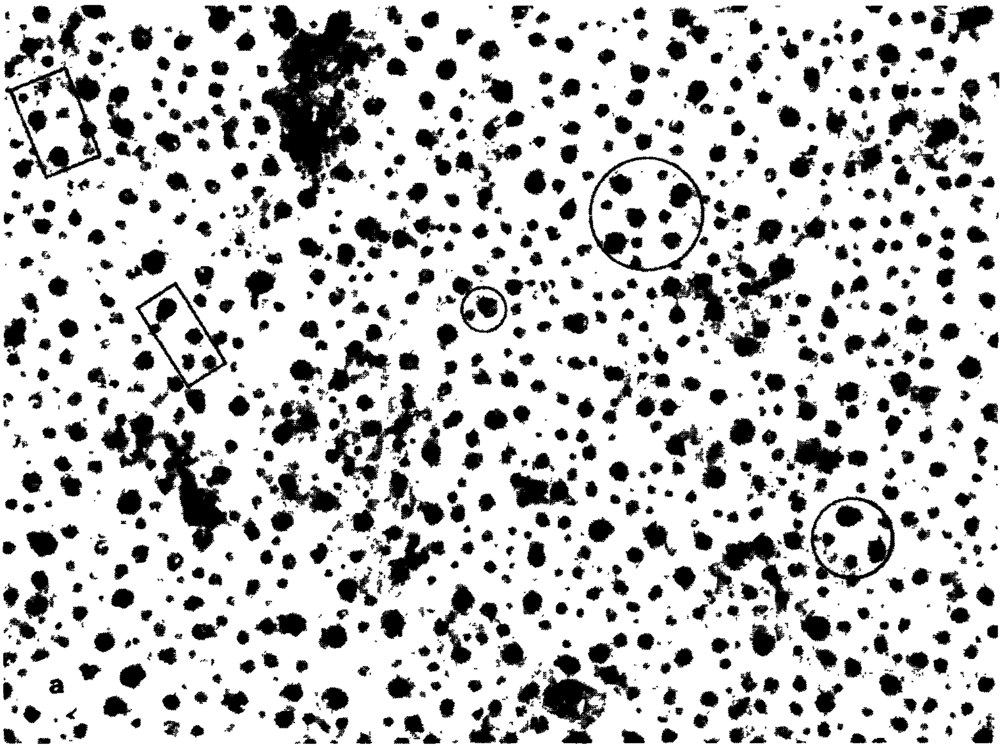


FIG. 4. Electron micrographs showing sequence of changes in a 1.5 nm initial film thickness Pt/Al_2O_3 specimen heated at 750°C. (a) Initial (H_2, 750°C, 15 h); (b) O_2, 750°C, 5 h; (c) H_2, 750°C, 5 h; (d) H_2, 750°C, + 12 h (17 h); (e) H_2, 750°C, + 6 h (23 h).

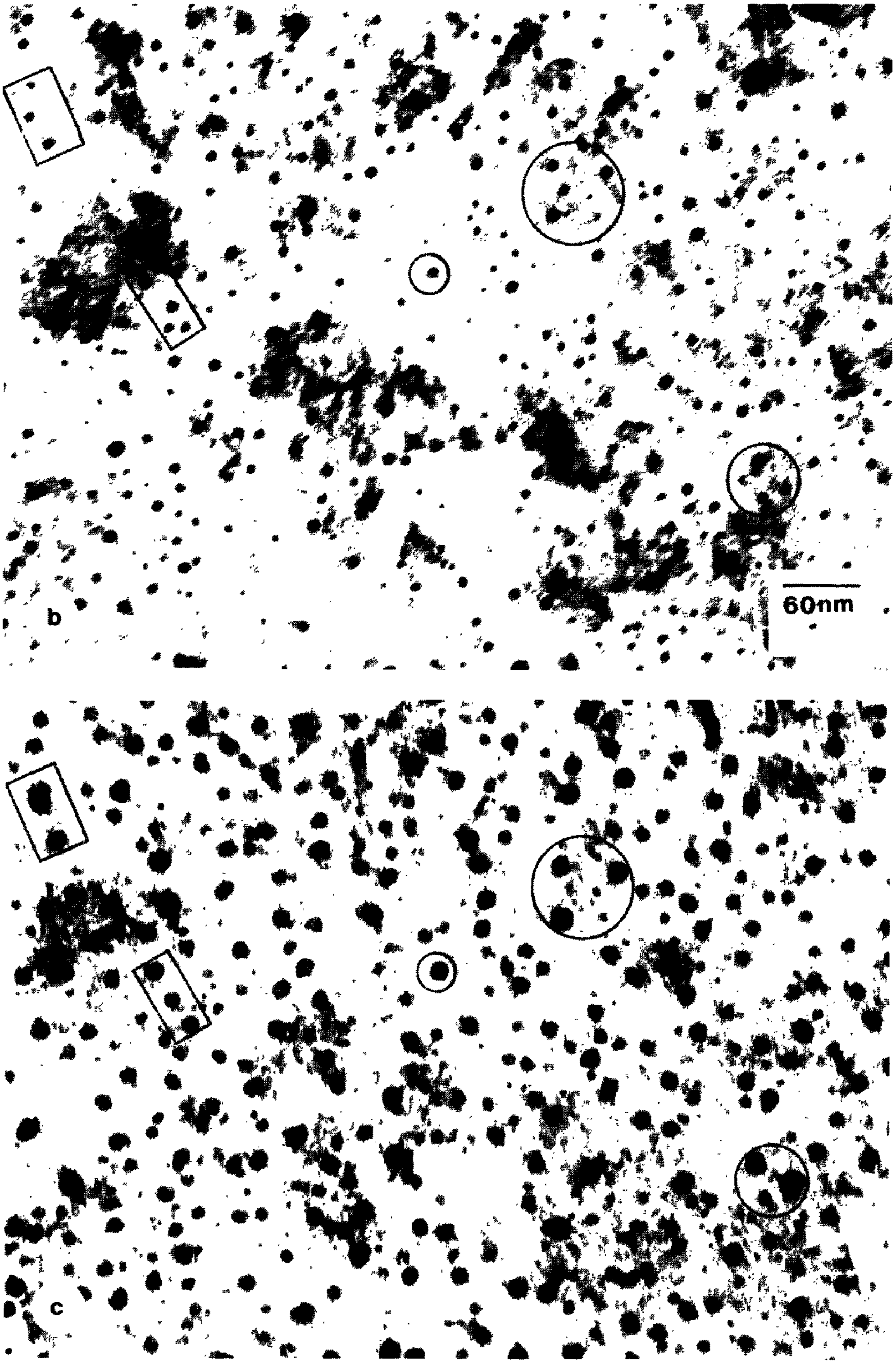


FIG. 4—*Continued.*

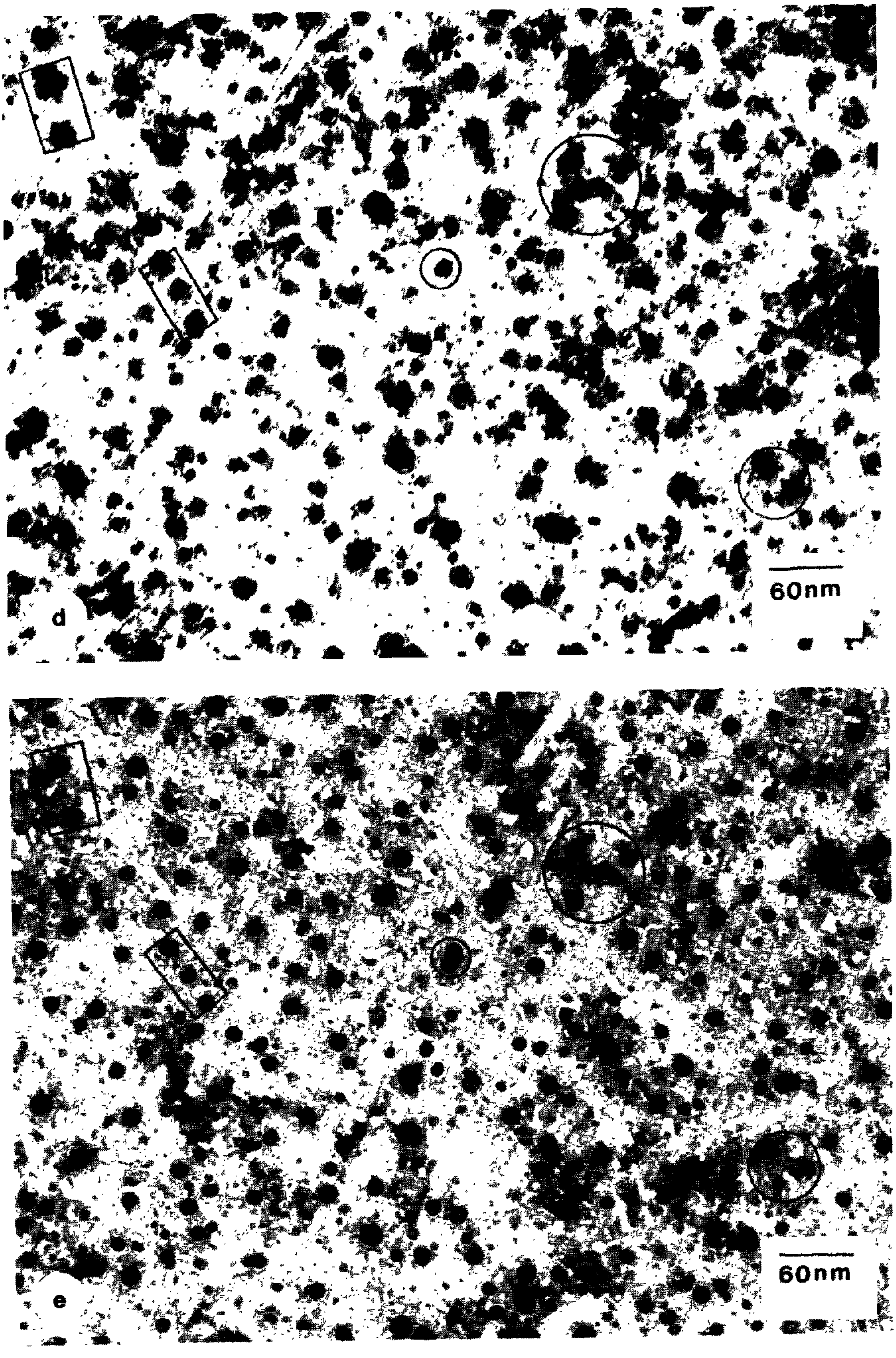


FIG. 4—*Continued.*

(*5*, *16*, *17*). Such a molecular emission mechanism is expected to be favored at high temperatures and in an oxidizing atmosphere rather than in a reducing one, since in oxidizing atmospheres the possibility of a decrease in the free energy of the system via the strong interactions between the platinum oxide molecules and the alumina substrate creates a driving force for the emission of molecules from the particles to the substrate. On subsequent heating in H_2, the dispersed oxide molecules and the small crystallites are reduced (to metal), the interactions with the support become weaker, and subsequently two possibilities can arise. (i) Either new small particles are formed (not necessarily in the same locations where the particles might have disintegrated by emission of atoms or molecules to the substrate), and/or (ii) the atoms (reduced molecules) are captured by the existing three-dimensional crystallites. Since new particles have not been generated in our experiments either following heating in O_2 or on subsequent heating in H_2, one could suppose that on heating in O_2, dispersed single molecules were present on the substrate and that they were captured by the existing crystallites on subsequent heating in H_2. However, the extent of capture of atoms by various crystallites will be different because of the differences in their radii of curvature. Since their rate of emission is smaller, the large crystallites are expected to have a greater growth than the smaller ones (*1*, *3*). Consequently, a size distribution different from the one before is expected. However, as noted under Results, especially at 500°C, all the detectable particles increase in size and attain more or less the size they had prior to the O_2 treatment. Therefore, it appears that a mechanism based on emission and capture of single atoms from a two-dimensional phase of single atoms located on the substrate surface is unlikely to be responsible for the observed behavior.

Another possible, and in the present case more likely, mechanism for redispersion in an oxygen atmosphere is by the spreading of a film in the form of a halo around each particle. As discussed in detail in (*18*, *25*), the surface free energy (γ_{cg}) of a metal is larger than the surface free energy of the corresponding oxide. Also, since, in general, a metal oxide (platinum oxide in the present case) interacts more strongly with the substrate (which is another oxide) than a metal does, the interfacial free energy γ_{cs} between the crystallite and substrate is also smaller in an oxidizing than in a reducing atmosphere. Since γ_{cg} and γ_{cs} are both smaller in an oxygen atmosphere, the contact angle θ is also smaller as can be seen from Young's equation shown below and the particle would be more extended in an O_2 atmosphere than in a H_2 atmosphere:

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{cs}}{\gamma_{cg}}.$$

The interfacial free energy γ_{cs} is related to the net interaction energy U_{cs} between crystallite and substrate via the expression

$$\gamma_{cs} = \gamma_{cg} + \gamma_{sg} - (U_{int} - U_{str}) = \gamma_{cg} + \gamma_{sg} - U_{cs},$$

where U_{int} is the interaction energy per unit contact area between substrate and supported material and U_{str} is the strain energy per unit contact area due to the mismatch of their lattices. The net interaction energy is larger when the support and the supported material are similar in structure (two oxides, for instance, rather than an oxide and a metal), or when there are covalent interactions between the two. In the present case, if the interactions between the platinum oxide and the alumina are strong enough, the small particles (which will be more completely oxidized than the larger ones) could spread out completely (because of the large driving force for spreading when U_{cs} is very large or γ_{cs} is very small) while the larger particles would only extend. Therefore, the small particles would no longer be detected in the micrographs following heating in O_2, while the larger particles would appear smaller if the films extending from the leading edge of the particles are so thin as not to be detectable by electron microscopy. If the above interactions are not very strong (i.e., if the driving force for spreading is not very large), or if the kinetics of wetting is slow, even the smallest particles would only extend and could therefore still be detected in the micrographs (of couse, with a smaller apparent size and an undetectable film around). In some cases, for example when the particle size is large, the extended film around the particles may be thick enough to be detected in the micrographs (particles marked with large arrows in Figs. 2 and 5). In these cases, the particles do not spread completely, but only acquire detectable or undetectable films around them. These films would contract and merge with the respective crystallites on subsequent heating in H_2 and , depending upon the reconstruction that occurs, the particles can regain the sizes they had prior to the oxygen treatment. This scenario appears to explain the observed results better than the two-dimensional phase of single atoms or molecules that covers the entire substrate can.

It is to be noted that at 500°C, the films around the particles are not likely to be interconnected to form a contiguous patch as observed in the case of Fe/Al_2O_3 at high temperatures (*19*). If the films were to be interconnected, the particles would be pulled closer together and sinter when the interconnecting film contracts on subsequent heating in H_2. Since little sintering is observed, it appears that the film constitutes an atmosphere around the particle (in

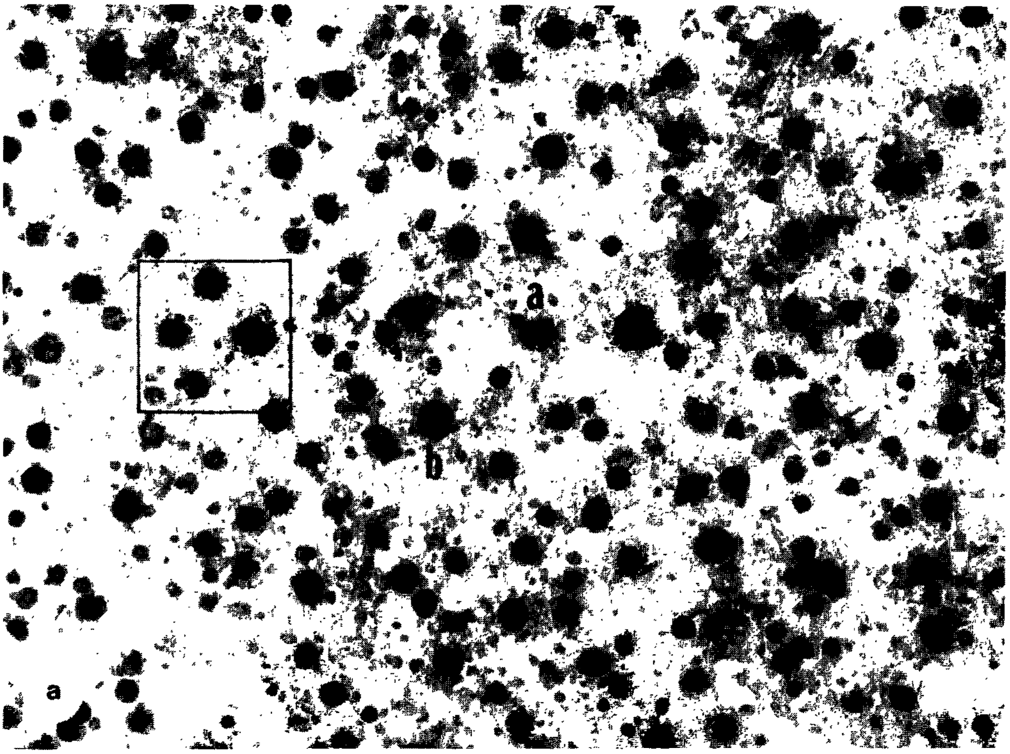


FIG. 5. Same sample as that of Fig. 4. Micrographs shown are from a different region, at a different magnification, and for treatments subsequent to those in Fig. 4e. (a) H_2, 750°C, 32 h; (b) O_2, 750°C, 12 h; (c) H_2, 750°C, 12 h.

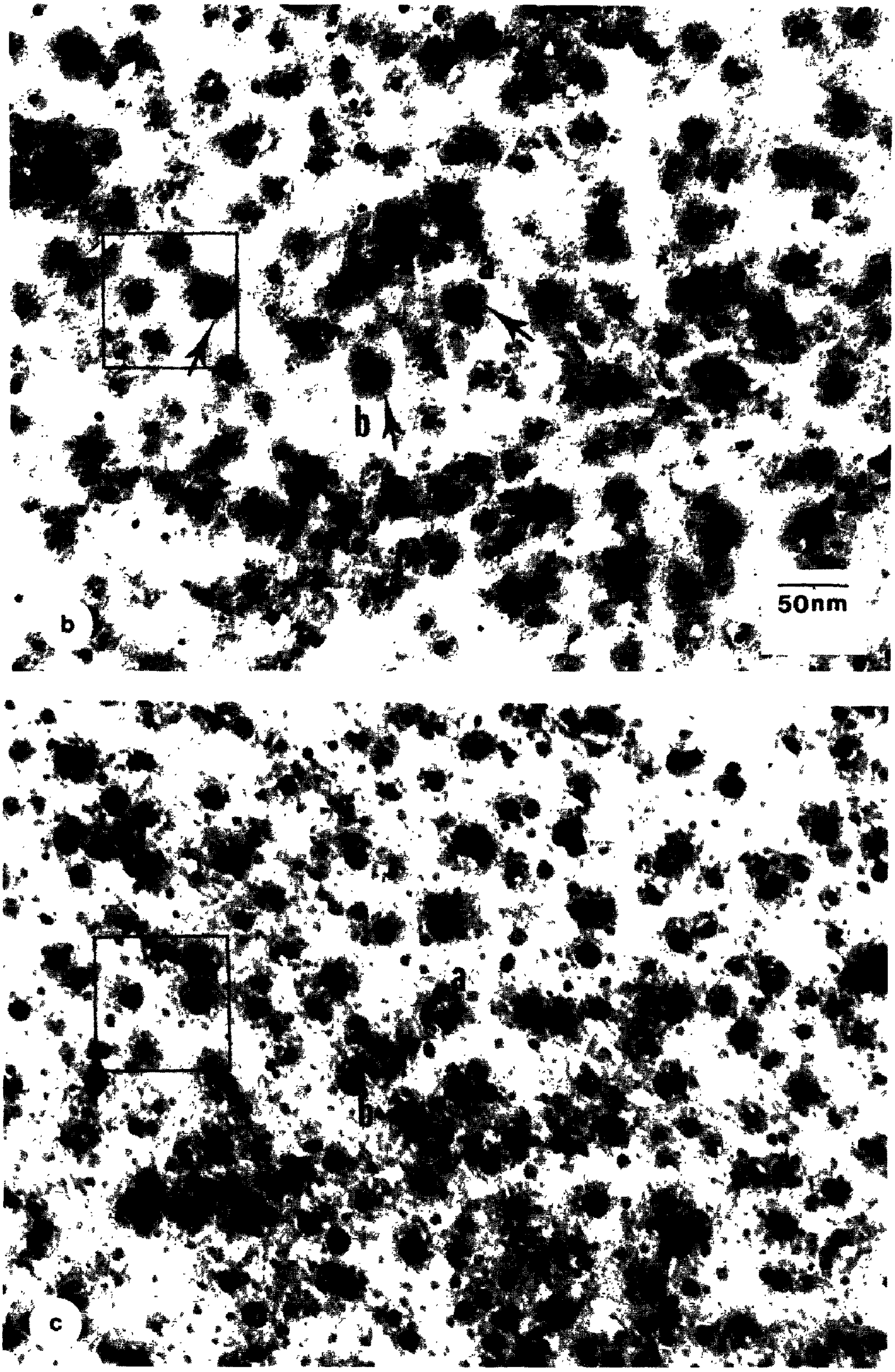


FIG. 5—*Continued.*

the form of a halo), extended only in its immediate vicinity, so that on subsequent heating in H_2 it contracts and merges entirely with the parent particle. However, it is likely that there exists a critical metal loading beyond which the films would extend farther away from the particles, interconnect with those from nearby particles, and form a contiguous film covering the substrate surface. Similarly, when two or more particles are close to one another, the films around them may overlap and become interconnected.

Another alternative could also be envisioned. In a H_2 atmosphere, the Pt crystallites can catalyze the partial reduction of alumina. Similar suggestions have already been made (*26*). The partially reduced substrate is relatively more reactive. Also, because of its nonstoichiometric nature, the surface free energy γ_{sg} of the partially reduced substrate is larger than that of Al_2O_3. In addition, as suggested for Pt/TiO_2 (*27, 29*), the reduced substrate species may migrate onto the crystallites and because of their interaction with the crystallites they may decrease γ_{cg}. Similarly, because of its reactive nature, the net interaction energy U_{cs} between the substrate and the crystallite at the base of the crystallites is increased and therefore γ_{cs} may be decreased. As a result of the increase in γ_{sg} and decreases in γ_{cg} and γ_{cs}, the contact angle will decrease and the crystallite would extend on the substrate in a reducing atmosphere, as in the case of Pt/TiO_2 (*28*). That is, in the present case, the larger size of the crystallite, observed following heating in H_2, is because of its extended form. On subsequent heating in O_2, the partially reduced substrate can be reoxidized to Al_2O_3 and γ_{sg} will therefore decrease. If the interactions between platinum oxide and Al_2O_3 are weaker than those between Pt and the reduced alumina, γ_{cs} may increase compared to its value in the reducing atmosphere. Also, because now the interactions between the particles and the partially reduced substrate species migrated onto them are absent, γ_{cg} may also increase although it may be smaller compared to the initial γ_{cg} of the metal. As a result of the increases in γ_{cg} and γ_{cs} and the decrease in γ_{sg}, the contact angle will increase and the particles would appear contracted and smaller. That is, the smaller size of the particles, observed following heating in O_2, is a result of their contraction to a larger wetting angle. However, this mechanism is not likely to be responsible for the observed behavior especially since in a few micrographs a kind of film is detected around the particles following heating in O_2. It is more likely that stronger interactions and extension occur in an oxygen atmosphere rather than in a reducing one.

Apart from the indirect evidence, via film formation, for strong interactions between the crystallites and support, there is also some direct evidence for such interactions from electron diffraction results, even though the compounds formed could not be identified with certainty. Electron diffraction patterns were recorded for all the samples following each heat treatment. Following heating in oxygen, especially above 500°C, additional rings, a few of which corresponded to Pt_3O_4 and Al_2Pt, appeared in the diffraction patterns. The rings corresponding to the compound between Pt and Al did not disappear on subsequent heating in H_2, only their *d* values changed marginally. This indicates that once an interaction compound is formed it is not easily decomposed. This compound formation may involve the diffusion of Pt species into the bulk of the alumina substrate and it may be difficult to be reversed. However, at the interface between the particle and the substrate, the compound may be relatively easily reduced (even if only partly) and lead to the observed contraction of the particles. It is to be noted that especially on heating in O_2 at temperatures greater than 600°C a large number of particles disappeared, suggesting possible loss of material by evaporation. In this regard, Chen and Schmidt (*24*) have reported that there is considerable loss of Pt as PtO_2 when Pt/SiO_2 is heated in air or O_2 at ≥700°C. However Leitz *et al.* (*30*) have noted that only in the case of chlorine-containing samples and at ≥800°C was some loss of Pt observed. It was pointed out in the previous section that only a small fraction, if any at all, of the material must have been lost via evaporation, since substantial recovery of the material in the form of crystallites occurred on subsequent heating in H_2 (Figs. 4a–4c). As suggested before, the apparent "loss" of material might have been due to considerable extension of the particles (formation of thin undetectable films on the substrate) as well as to the diffusion of material into the substrate to form an interaction compound with alumina.

Even though the identity of the compounds formed could not be ascertained, the appearance of additional rings in the electron diffraction pattern (some of which correspond to some known Pt–Al compounds) nonetheless suggests compound formation between PtO_x and Al_2O_3 to yield $Pt_pAl_qO_r$, where r can also be zero. In this regard it is to be noted that den Otter and Dautzenberg (*31*) proposed the formation of Pt_3Al to explain the suppression of room temperature H_2 adsorption activity following high-temperature (≥500°C) reduction. Lagarde *et al.* (*32*) suggested that a Pt–O bonding between crystallites and Al_2O_3 is more likely than a Pt–Al bonding. But they were inclined to the view that chlorine atoms are also present in the complex. As pointed out in the Introduction, Leiske *et al.* (*13*) argued that oxidative redispersion is possible only in the presence of chlorine or chloride ions, and that oxygen alone does not lead to redispersion. Even though the presence of chlorine or chloride ions in our samples is very unlikely, it cannot be ruled out completely. It is worth noting that in the procedure followed to obtain electron transparent alumina films, subsequent to the anodic oxidation of an aluminum foil, the alumina films are stripped of their aluminum backing by dissolving the latter in mercuric chloride solution. Even though the alumina films are washed repeatedly in distilled water, there may be strongly bound chloride ions left behind and, therefore, we cannot rule out its absence or confirm its presence. A number of other authors have postulated complex formation between crystallites and support in Pt/Al_2O_3 samples (*6, 32–36*) and the exact nature and mechanism of formation of the complex have been debated. The present results have shown, both via electron diffraction and via film formation, that there are strong interactions between the crystallites and support in Pt/Al_2O_3 model catalysts and that the oxidative redispersion (regeneration), routinely achieved in industries by oxidative treatments between 500 and 600°C, occurs more via spreading and film formation than by emission of molecules to a two-dimensional phase of single atoms or molecules. It can be further noted that while Pt/Al_2O_3 is differentiated as being a "non-SMSI" system, the results indicate that there are strong interactions in this system as well, similar to those exhibited by the SMSI systems.

CONCLUSION

Pt/Al_2O_3 model catalysts are observed to undergo alternate changes in particle size when heated alternately in H_2 and O_2 in the range 500–700°C. When a sample heated previously in H_2 at $T \geq 500°C$ is heated in O_2 at $500 \leq T \leq 700°C$, there is an apparent decrease in the particle size. On subsequent heating in H_2, approximately the previous sizes of the particles are recovered. Even the smallest of the particles exhibit this behavior and (particles down to about 0.8 nm are observed to) remain on the substrate through the various cycles of heating, suggesting that the molecular emission–capture mechanism is unlikely to be the cause of the alternations in size. In some cases, especially at 600 or 700°C, on heating in O_2, a kind of film, in the form of a halo, is observed around each particle and some particles extend out considerably into detectable or undetectable patches. In light of these observations, the alternation in size at 500°C is explained on the basis of the formation in O_2 of a thin, undetectable film around each particle which results in the appearance of a smaller size of the particles since only the solid core is detected. It is surmised that the film is in the immediate vicinity of and in contact with the parent particle and that the films around the particles do not interconnect to form a contiguous patch. On subsequent heating in H_2, the films contract and merge with the respective parent particle. Depending upon the reconstruction that follows, the particles can recover approximately their previous sizes. Such extension in O_2 and contraction in H_2 are enhanced by prolonged pretreatment in O_2 and/or by a few initial cycles in H_2 and O_2 which perhaps improve the wetting characteristics. It is suggested that extension and film formation are possible and likely mechanisms for the routinely observed oxidative redispersion of supported platinum catalysts.

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