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Continuous Observation of the Particle Size Behavior of Platinum on Alumina

Since the advent of catalytic converters for automobile emission control considerable effort has been devoted to the behavior of platinum/alumina catalysts in the presence of various gaseous environments. It is surprising, therefore, to find that only a few studies have been reported on the use of electron microscopy for examining the behavior of such catalysts (*1–4*). In the present investigation we have used the technique of controlled atmosphere electron microscopy (*5*) to follow the behavior of platinum particles, derived from three different sources, supported on a γ-alumina film when heated to 920°C in oxygen or nitrogen.

Transmission specimens of alumina were prepared according to an electrolytic method described by Varon *et al.* (*6*), and characterized by electron diffraction as γ-alumina. Platinum was introduced on the alumina in three forms: (a) as the pure metal by vacuum evaporation of platinum from a wire mounted on a tungsten filament, (b) from an atomized spray of a 0.5% solution of chloroplatinic acid, and (c) from an atomized spray of a 0.5% solution of tetrammine platinous hydroxide. An attempt was made to keep the platinum concentration on alumina the same in all experiments at approximately a monolayer coverage. The gases used in this work, oxygen and nitrogen (both >99.9% purity), were used without further purification.

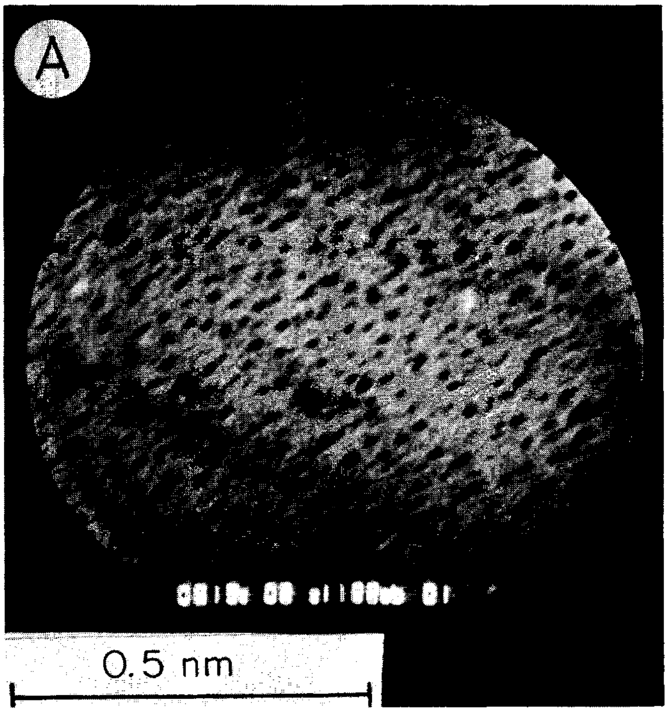

FIG. 1A–C. Sequence of transmission electron micrographs showing the changes in appearance of a platinum metal/alumina specimen on heating in 2 Torr oxygen at 813 to 877°C.

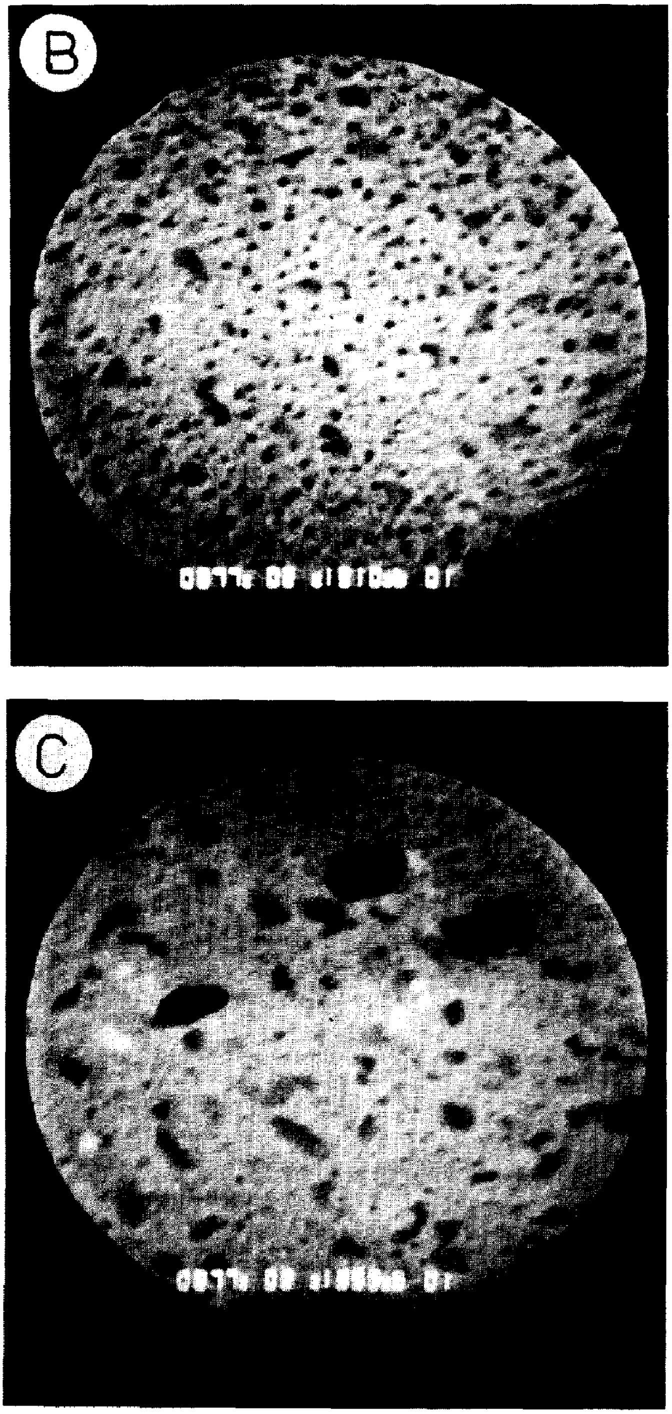

FIGURE 1B and C.

When platinum metal/alumina specimens were heated in 2 Torr oxygen the evaporated metal film nucleated at 500°C to form small particles, 3 nm diam. As the temperature was gradually raised to 800°C the average particle size increased to 14 nm. Above this temperature several dramatic changes in the appearance of specimens was observed; particles decreased in both number and size, there was a tendency for particles to reconstruct to form diffuse islands on the surface, and at 877°C material appeared to collect quite suddenly in the form of well-defined dense shapes and then rapidly disappeared. It is probable that this material had diffused into the alumina rather than that it had evaporated from the surface. Figure 1A to C are photographs taken from the video record illustrating this sequence of events. The decrease in number and size of particles is apparent from Fig. 1A and B and in Fig. 1B the grey patches are islands, which predominate in Fig. 1C along with the denser material. Experiments were usually terminated at 920°C as the γ-alumina had been previously found to undergo the phase change at 1000°C.

The behavior of specimens of tetrammine-platinous hydroxide/alumina in 2 Torr oxygen was almost identical to that of the metal, differing only in the relative sizes of particles found at various temperatures, which was almost certainly a result of the difficulty in obtaining reproducible loading of platinum species on the alumina.

Platinum particle growth from specimens of chloroplatinic acid/alumina heated in 2 Torr oxygen was quite different from the other two systems. Here, particles of 2.5 nm diam were only just discernible at 650°C and showed very little change in size on heating to 800°C. Above this temperature all particles decreased in size, many being below the 2.5 nm resolving power of the technique and at temperatures of about 900°C whiskers (600 nm in length and 30 nm width) were observed. Similar behavior to that described above could be induced with platinum metal/alumina specimens. In this case specimens were heated to 500°C in 2 Torr oxygen, removed from the microscope and exposed to hydrogen chloride at room temperature, and then reheated in 2 Torr oxygen to 900°C. It was interesting to find that island formation did not occur readily in these experiments.

In a final series of experiments platinum metal/alumina specimens were heated in 2 Torr nitrogen. In this system particle growth appeared to be significantly faster than in oxygen and no decrease in particle size was observed at temperatures >800°C. It was significant that in all experiments reported here the platinum particles once formed remained irregularly shaped and immobile on the surface throughout the entire heating cycle, indicating that particle growth probably occurred via the movement of particles <2.5 nm in size.

Quantitative analysis of average particle size variations with temperature for the five systems examined are shown graphically in Fig. 2. These measurements were made from the projected image of a 16 mm cine film and in each case are taken when particles had been at a given temperature for a period of 5 min. In these determinations no account of islands or whisker growth was made, the values being based entirely on isolated particles.

From examination of Fig. 2 it is evident that the overall shapes of the particle growth curves in oxygen are similar and quite different to that obtained in nitrogen. It is possible that the decrease in particle sizes observed at temperatures >800°C is influenced by the tendency of platinum to form a volatile oxide at elevated temperatures (*7*). This reaction would not occur in nitrogen and therefore one would not expect to find a comparable decrease in particle size. Similarly shaped curves were found for the growth of particles from the

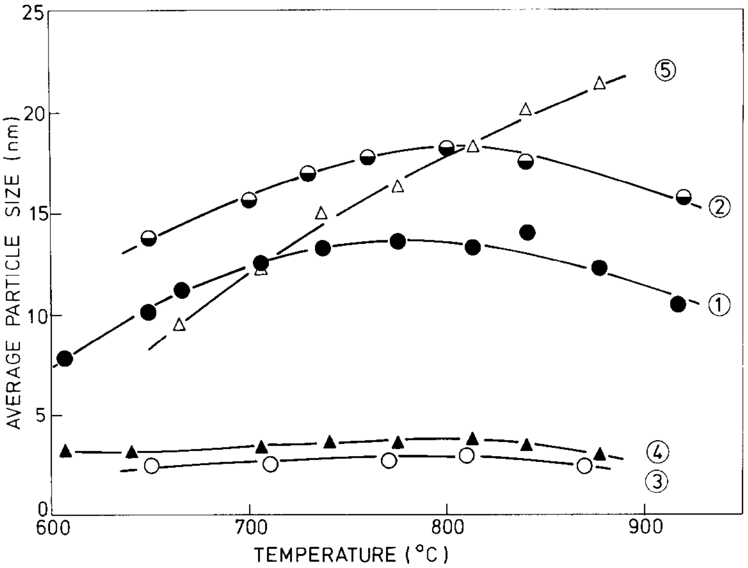

FIG. 2. Variation of platinum particle size on alumina with temperature: (1) platinum metal/alumina in 2 Torr O_2; (2) tetrammine-platinous hydroxide/alumina in 2 Torr O_2; (3) chloroplatinic acid/alumina in 2 Torr O_2; (4) platinum metal/alumina after treatment with HCl in 2 Torr O_2; (5) platinum metal/alumina in 2 Torr N_2.

other sources of platinum in nitrogen, but are omitted from Fig. 2 for the sake of clarity.

Perhaps the most striking feature in this study is the difference in magnitude of particle sizes induced by exposure of platinum metal/alumina specimens to hydrogen chloride compared with direct reaction in oxygen (curves 4 and 1). The similarity between curves 3 and 4 clearly indicates that the presence of chloride ions has a dramatic effect on the behavior of this system, tending to inhibit the growth of platinum particles on alumina. From this work it is not possible to present any definite explanation for this observed phenomenon. It is interesting to compare the curves presented in Fig. 2 with that obtained by Dorling and Moss (*8*) from the interaction of chloroplatinic acid/silica with oxygen. Their particle size–temperature dependence curve was similar in both magnitude and size to curves 1 and 2 (this work), which suggests that chloride ions may not exert the same influence on platinum particles supported on silica as we have found on alumina.

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