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NOTE

Growth Characteristics of Supported Palladium Particles in Gaseous Environments

Supported metal particles are being used extensively as catalysts in many industrial processes. Since the performance of the catalyst is dependent on the surface area of the particles it is important to follow changes in both size and shape of particles during reaction. Controlled atmosphere electron microscopy (CAEM) (*1*) offers a distinct advantage over the more conventional techniques (*2*) in that changes in particle morphology can be observed while the reaction is in progress. At present the resolving power of the technique is limited to 2.5 nm. We have used CAEM to study the effect of various gases including argon, oxygen, hydrogen, ethylene and acetylene (all research grade) on the nucleation and growth of evaporated palladium particles on graphite supports over the temperature range of ambient to 1000°C.

Transmission specimens of single crystal graphite were prepared by a standard procedure (*3*). Palladium was introduced on the graphite as a thin film approximately one atom thick, by evaporation of spectrographically pure palladium wire at 10^{-6} Torr from a tungsten filament. Particle size determinations were performed from single frame projection of 16 mm cine film of growth sequences, each determination being made of particles which had been at a given temperature for a period of 5 min.

The temperature at which the supported palladium nucleated to form particles (about 10 nm diameter) was dependent upon the nature of the gaseous environment. At 5 Torr pressure, for acetylene this was 230°C; oxygen, 260°C; ethylene, 400°C; argon, 535°C and for 1 Torr hydrogen it was 230°C. The subsequent changes in average particle size with increasing temperature is presented in Fig. 1. The reaction of palladium particles with hydrogen was so rapid that it was difficult to obtain comparable data for this system. With the exception of the latter system there was no detectable difference in shapes of particles in the various environments. Particle growth was somewhat hindered at the higher temperatures in acetylene (>650°C) and ethylene (>830°C) due to the formation of filamentous carbon on many of the particles.

Of the systems shown in Fig. 1, general particle mobility was only observed in the presence of oxygen and temperatures of about 850°C were required to induce such movement. The sharp increase in particle size over the higher temperature region in oxygen is a result of agglomeration of large particles (>50 nm diam). From Fig. 1, it is apparent that while the sizes of all particles increased with temperature their growth rates were extremely sensitive to the nature of the surrounding gas. In systems where particle mobility was not observed it is probable that particle growth took place by transport of molecular metal species from one crystallite to another either by migration across the support surface or via the gas phase. It is expected that the ease of escape of molecular species from a crystallite and their speed of migration would be affected by the nature of the gaseous environment (*4*). A further contributory factor would be dif-

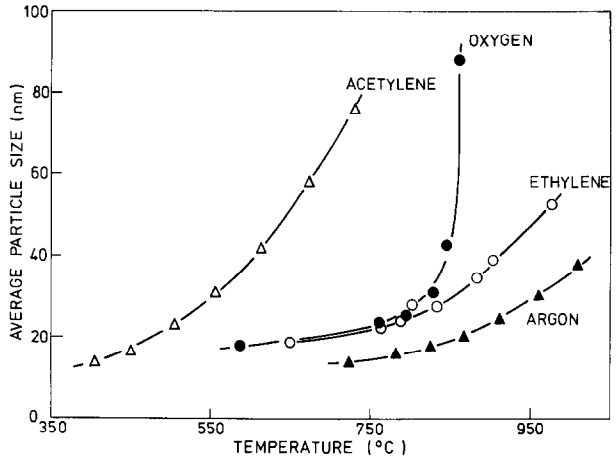

FIG. 1. Palladium particle size dependence on temperature in the presence of various gases.

ferences in exothermic decomposition reactions occurring on particle surfaces which would cause the particle temperature to exceed that of the support.

The change in appearance of supported palladium particles when exposed to 1 Torr hydrogen at 435°C is shown in a sequence (Fig. 2A to D) taken from the TV monitor over a 3.7 min period. In the early stages of the reaction the palladium particles (2.5 nm diam) tended to form into chains, Fig. 2A. As the temperature was raised to 435°C the chains restructured to form discrete mobile particles, 20 nm diam, Fig. 2B. These particles underwent a rapid expansion to form angular shaped electron transparent platelets, about 150 nm width, Fig. 2C. On continued reaction the platelets increased in size and thickness, Fig. 2D. Channels were seen to develop on the thinner regions and disappeared almost as rapidly as they formed. This intermittent process occurred all over the specimen even on areas which had not previously been exposed to the electron beam, and was probably caused by diffusion of hydrogen through the metal. If hydrogen flow was switched off at this stage and the specimen was evacuated while the temperature was maintained at 400°C then the platelets shrank in size and became thinner. Reintroduction of hydrogen again resulted in the effects described above. Similar behavior was observed with palladium supported on either carbon or silica indicating that the reaction was independent of the support. Electron diffraction examination performed while the reaction of an unsupported palladium film with 1 Torr hydrogen was in progress showed that structural changes occurred at 435°C; the original ring pattern of palladium changed to a very complicated spot pattern, but it was not possible to identify a hydride phase. Duggan *et al.* (*5*) used electron microscopy to examine the effects of electrolytically produced hydrogen on palladium foils, and also found that transmission specimens of palladium became opaque as hydrogenation proceeded. It is difficult to rationalize our observations with reported data for the behavior of the bulk palladium–hydrogen system (*6,7*), and a clear understanding must await the results of further studies.

In a final series of experiments palladium/graphite specimens were heated in a 2 Torr mixture of 1:1 ethylene and hydrogen. In this case, palladium particles did not show any of the characteristics observed with pure hydrogen. In contrast, when the temperature reached 650°C carbon filaments grew on most of the particles.

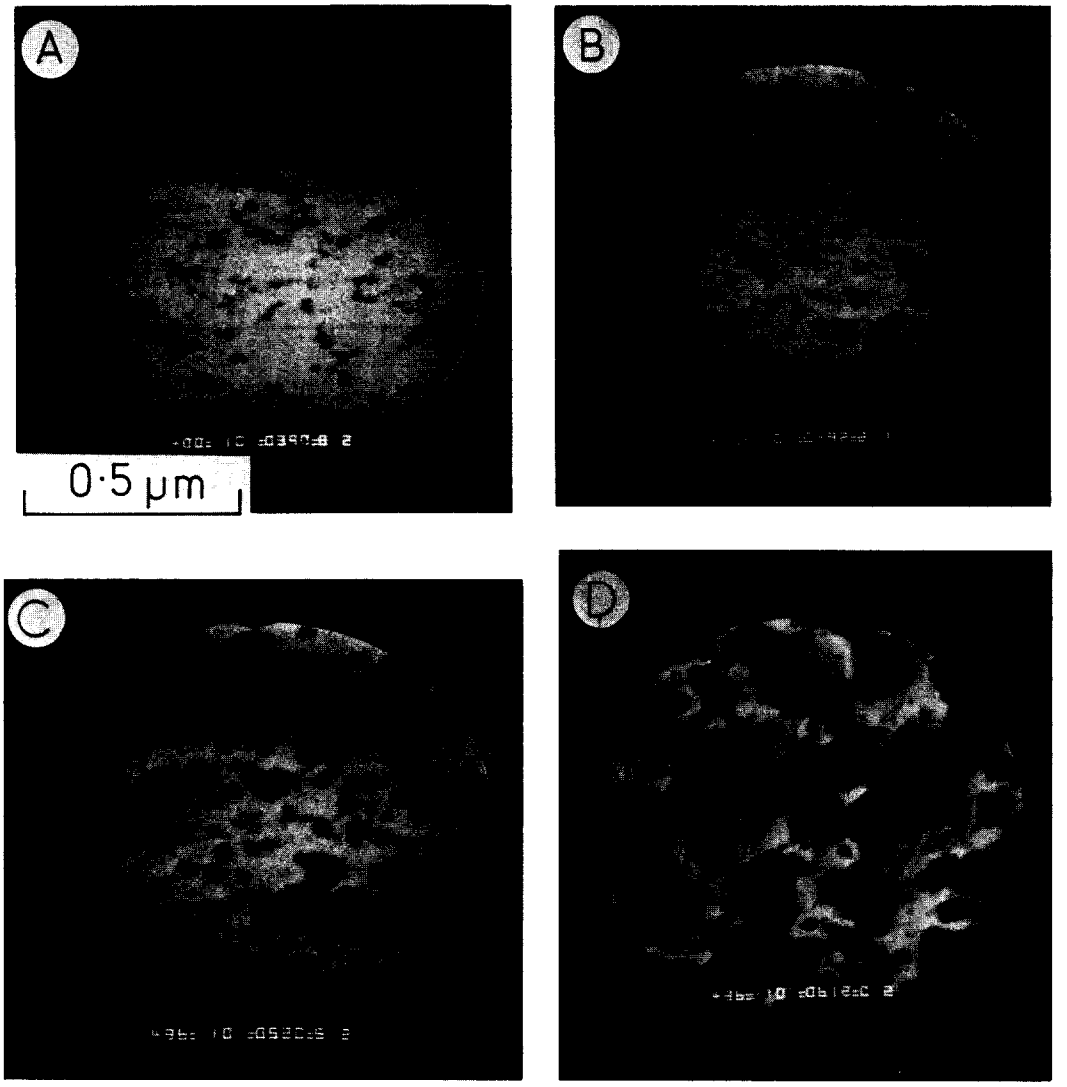

FIG. 2A–D. Sequence showing the effect of 1 Torr hydrogen on palladium particles supported on graphite at 435°C.

It is clear from this preliminary study that CAEM is an ideal tool for monitoring the growth characteristics of supported metal particles and as a consequence their catalytic efficiency in various gaseous environments. It is doubtful whether this kind of information could be obtained from conventional electron microscopy as specimens would have to be removed from the reaction environment for examination. Such a procedure involves cooling of the specimen, which can induce phase changes and transient reactions. Moreover, removal of the reactant gas from the specimen could also alter the nature of the active surface due to desorption effects and adsorption of poisons.

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