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Spreading and Surface Tension Gradient Driven Phenomena during Heating of Alumina-Supported Palladium Crystallites in Oxygen

INTRODUCTION

In the present note, observations concerning the behavior of alumina-supported Pd crystallites heated at various temperatures in 1 atm oxygen are reported. At temperatures below the decomposition temperature of bulk PdO in 1 atm oxygen (870°C), pits developed into the crystallites from the free surface. During further heating, the pits coalesced to form large cavities. In addition, spreading to a lower wetting angle of the oxidized crystallites on the alumina surface was observed. At 920°C no pits or cavities formed and the crystallites sintered into faceted crystallites. Spreading is due to the changes in the surface and interfacial tensions produced by the oxidation of Pd. Pit formation is explained tentatively as resulting from interfacial tension gradients occurring during oxidation. While the role of interfacial phenomena in supported catalysis has been emphasized earlier (*1–4*), the present observations provide some direct evidence; only a few typical micrographs are included here.

EXPERIMENTAL RESULTS

Samples consisting of Pd crystallites with sizes in the range of 30–350Å supported on thin γ-alumina films were heated in 1 atm O_2 at 350, 500, 750, and 920°C for various time durations. After repeated heat treatment at the same temperature, the same areas of the samples have been examined by a JEOL 100U transmission electron microscope to follow the changes in shape, size, and location of each crystallite.

During the early stages of heating in O_2 at 350°C, Pd crystallites became porous. Figure 1b shows the porous structure of some large crystallites, after being heated at 350°C for 2 hr, while Fig. 1a shows the same crystallites before heating. Pits have developed into the crystallites from the free surface. As the heating proceeded, large cavities formed through the coalescence of the pits, and the crystallites acquired a torus shape with a boundary in the central part of the crystallites while their size and leading edge remained largely unchanged (Fig. 1c). No significant changes were detected after further heating for 20 hr. Along with the formation of pits and cavities, the smaller crystallites heated at 350°C and the crystallites of various sizes heated at 500 and 750°C spread on the surface of the substrate and became irregular in shape. Figure 2a shows a region of an unoxidized specimen, while Figs. 2b and c show the same region after being heated at 750°C for 20 min and 24 hr, respectively. Even more extensive spreading was detected for small crystallites at 350°C and for all the crystallites at 500°C.

DISCUSSION

The formation of pits and cavities and the spreading of the oxidized crystallites on the alumina surface are related to the oxidation of palladium to palladium oxide because these two phenomena have not been observed during heating in hydrogen (*5*) and during heating in 1 atm oxygen at 920°C (temperature at which the PdO is unstable). The pits probably start from some particular active sites on the heter-

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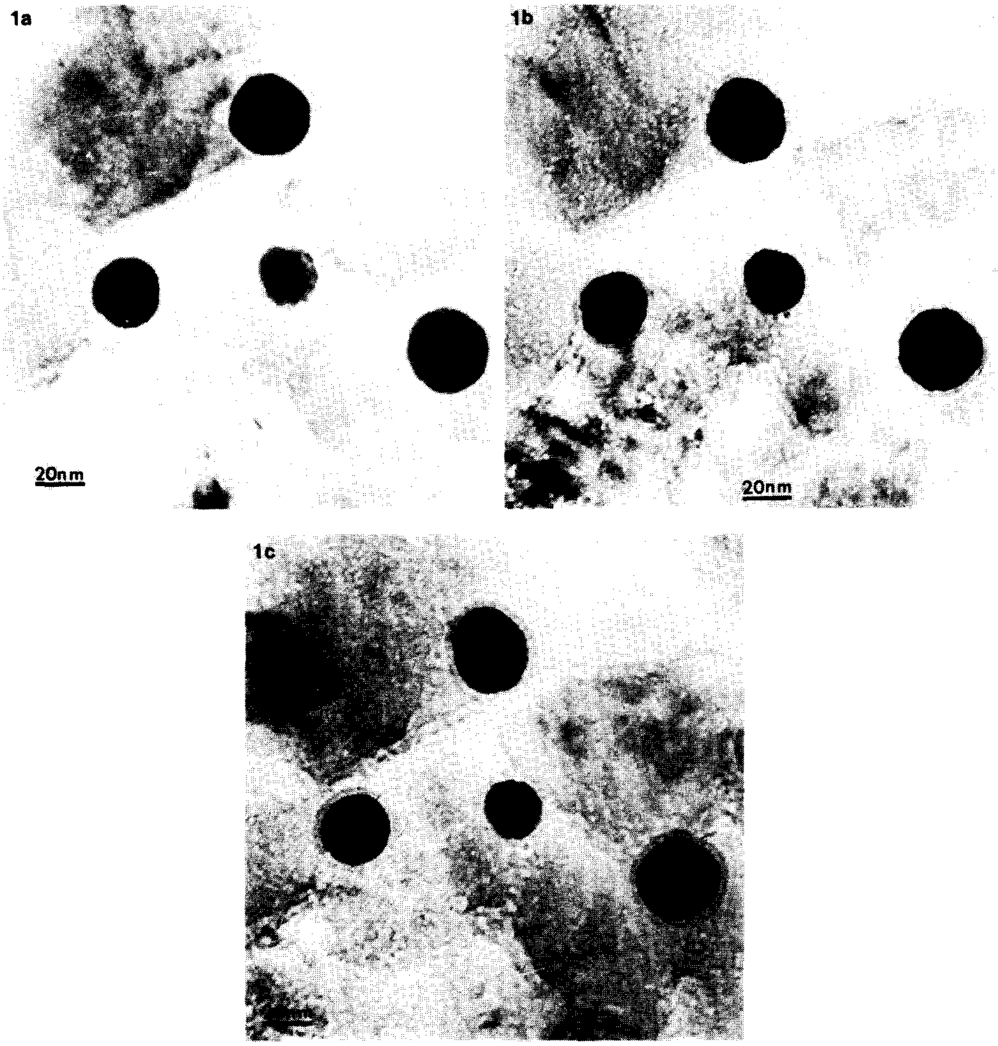

FIG. 1. Transmission electron micrographs showing the same region of a Pd/Al_2O_3 specimen: (a) unoxidized specimen; after being heated in 1 atm O_2 at 350°C for (b) 2 hr, (c) 4 hr, respectively.

ogeneous crystallite surface. The palladium oxide molecules could migrate out of their original locations to cover the unoxidized palladium because the oxide has a lower surface tension than the pure metal. This motion, driven by the surface tension gradient towards larger surface tensions, has been already observed for liquid–fluid interfaces, where it is known under the name of the Marangoni effect (*6*). The migration of palladium oxide would expose fresh reactive palladium layers to oxygen and oxidation proceeds, leading to the formation of pits. The formation of cavities might occur via the coalescence of pits.

The extension by spreading of the crystallites occurs because the surface tension of the oxidized palladium and the interfacial tension between the oxidized crystallites and substrate are smaller than those for palladium. The experimental results show that the extent of spreading of the crystallites on the alumina surface is dependent on the temperature and crystallite size. At 350°C, the torus shape of the large crystallites was stable after prolonged heat-

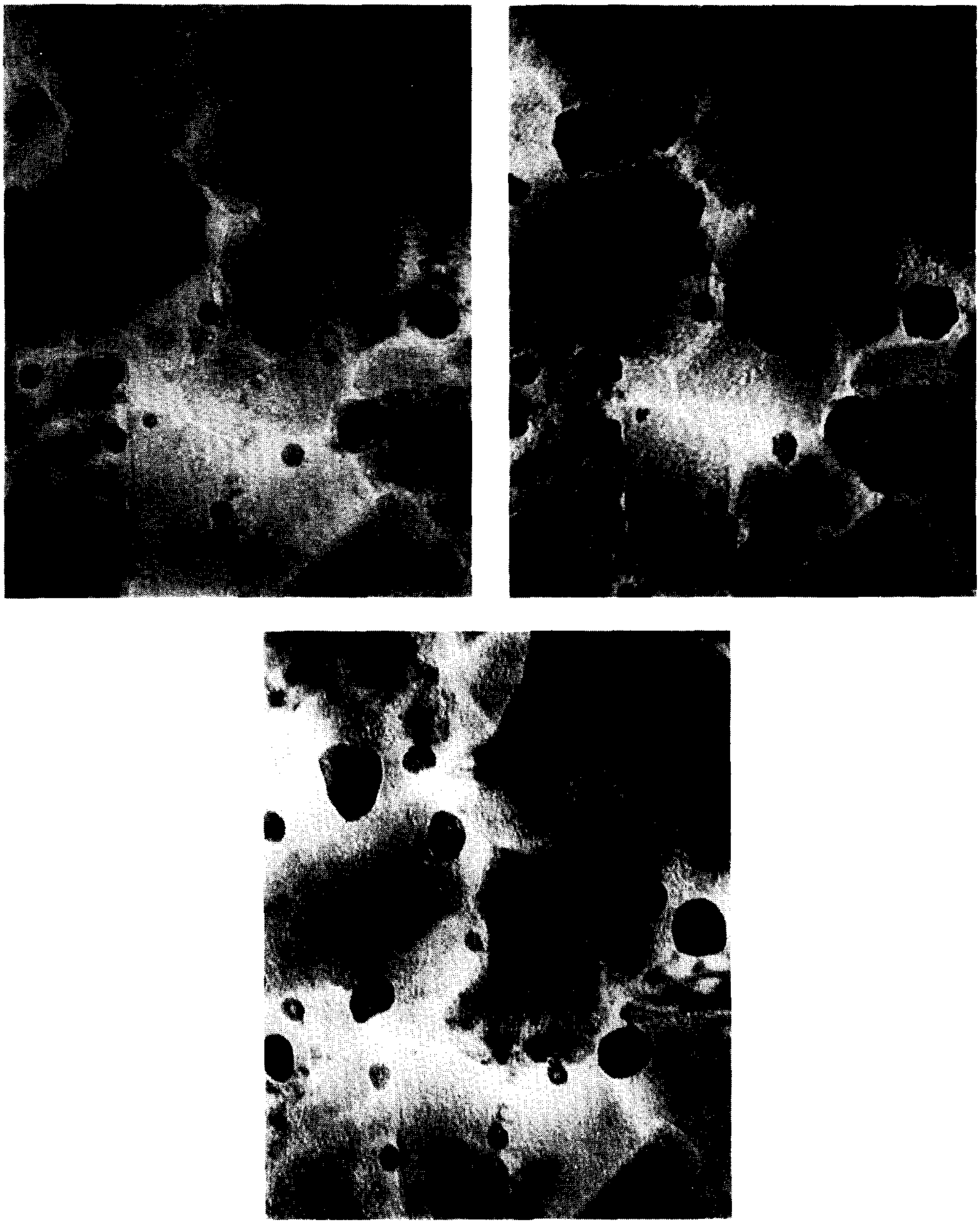

FIG. 2. Transmission electron micrographs showing the same region of a Pd/Al_2O_3 specimen: (a) unoxidized specimen; after being heated in 1 atm O_2 at 750°C for (b) 20 min, (c) 24 hr, respectively.

ing probably because the crystallites were not completely oxidized. The smaller crystallites at 350°C and all the crystallites at 500°C showed extensive spreading probably because the complete oxidation reduces the interfacial tension between crystallite and substrate and thus decreases the wetting angle. The milder extent of spreading of the crystallites at 750°C than at 500°C could be because: (1) the palladium oxide is less stable at 750°C than at 500°C, so that the crystallites could not be as easily oxidized as those at 500°C, after the same period of heat treatment and/or (2) the wetting angle of palladium oxide is larger at 750° than at 500°C. The irregular shapes of the crystallites are probably caused by nonuniform oxidation and the associated nonuniform spreading. Some pits appear to be generated during the nonuniform spreading (see, in particular, the large crystallite in the upper left corner of Figs. 2a and b).

During heating in 1 atm O_2 at 920°C no pits and cavities formed and no spreading occurred; instead the crystallites sintered to faceted crystallites. It is interesting to note that PdO is no longer stable at 920°C.

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