JOURNAL OF CATALYSIS 109, 100–119 (1988)

The Behavior of Model Ag/Al_2O_3 Catalysts in Various Chemical Environments

E. RUCKENSTEIN AND SUNG H. LEE

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

Received June 8, 1987; revised August 18, 1987

The sintering behavior of silver crystallites supported on nonporous alumina substrates has been investigated by means of transmission electron microscopy. When the specimens were heated in O_2 at temperatures in the range 250–400°C, the following phenomena were observed: crystallite migration and coalescence, disappearance of small and large particles, decrease in size of small crystallites, and appearance of a large number of small crystallites of circular or wormlike shape. A few possible explanations are suggested for the appearance of a large number of small particles. The behavior of silver particles heated in H_2 at temperatures in the range 300–400°C was qualitatively similar to that observed in O_2. Sintering was, however, less severe, and the number of small particles that appeared was smaller. When heated in C_2H_4, the particles changed their shape from circular to ellipsoidal and, with few exceptions, remained almost unchanged in their locations, most probably as a result of carbon deposition on the surface and around the particles. When heated in a mixture of C_2H_4 and O_2, the particles exhibited milder sintering than in O_2, but acquired more irregular shapes, as during their heating in C_2H_4.

INTRODUCTION

Silver is a well-known catalyst for the partial oxidation of ethylene to ethylene oxide. The catalytic oxidation of ethylene over silver has been reviewed by several authors (*1–5*). Most of the studies have been carried out to investigate the mechanism and mode of adsorption of oxygen on the surface of the catalyst, since this affects the selectivity and activity of the catalyst. The loss of active metal surface area caused by sintering has been investigated much less. The sintering behavior of supported metal particles is affected by many factors, such as the support material, reaction atmosphere, metal–support interaction, etc. In general, when alumina or silica are the supports, heating in H_2 causes sintering, while heating in an oxidizing atmosphere, such as O_2 or steam, can bring about redispersion (*6–8*). The behavior of supported silver has been reported by a number of authors. Presland *et al.* (*9, 10*) investigated the effect of oxygen and hydrogen on a silver film supported on an amorphous silica substrate. When heated in a hydrogen atmosphere which was either dry or saturated with water vapor, the silver films remained unchanged. In contrast, in an oxidizing atmosphere, hillocks were observed to form as the first stage; on further heating silver islands were generated. Seyedmonir *et al.* (*11*) investigated the dispersion of silver crystallites heated in He, H_2, and O_2. Very little or no change in dispersion was observed for silver crystallites supported on TiO_2, η-Al_2O_3, or SiO_2, on heating in H_2 or He at 400°C. The dispersion of silver crystallites supported on η-Al_2O_3 decreased, however, by 20–30% after heat treatment in O_2 at 400°C for 15 h. For Ag/TiO_2, no change in metal dispersion was observed in O_2. Recently, Plummer *et al.* (*12*) reported that silver particles supported on alumina coalesced and formed large particles when heated in air at 200–300°C. Employing *in situ* transmission electron microscopy, Heinemann and Poppa (*13*) observed crystallite migration

0021-9517/88 $3.00

followed by coalescence as well as ripening for silver particles supported on graphite, in the temperature range of 25–450°C and for a gas pressure of 10^{-9} Torr. Evidence for crystallite migration and coalescence for Ag/graphite, during heat treatment in hydrogen at temperatures between 320 and 515°C, was also presented by Baker and Skiba (*14*). There is, however, very little information about the behavior of silver crystallites supported on alumina, even though this is the most widely used catalyst for the partial oxidation of ethylene.

The aim of this paper is to investigate, in some detail, the behavior of alumina-supported Ag crystallites. For this purpose, model alumina-supported silver catalysts were employed. The specimens were heated in various gaseous atmospheres, O_2, H_2, C_2H_4, and a mixture of C_2H_4 and O_2, at temperatures in the range encountered in industrial processes. The behavior of the silver crystallites supported on alumina has been examined by following the changes in the same regions of the specimen after each heat treatment.

EXPERIMENTAL

Preparation of the Sample

Electron-transparent, nonporous, amorphous alumina films of approximately 300 Å thickness were prepared by anodization of chemically polished, thin, high-purity aluminum foils (99.999%, Alfa Products Inc.). The oxide film was stripped off by dissolving the unoxidized aluminum in a mercuric chloride solution (*15*). The oxide films were then washed in distilled water, picked up on gold electron microscope grids, and allowed to dry. They were subsequently heated in air at 800°C for 72 h to transform the amorphous alumina films into polycrystalline γ-alumina. High-purity silver wire (99.9%, Alfa Products) was vacuum-evaporated onto alumina films supported on gold electron microscope grids, under a pressure of less than 10^{-7} Torr, in an Edwards 306 vacuum evaporator.

The Heat Treatment

The specimens were heated in a quartz tube located in a furnace. After the specimen was introduced into the quartz tube, the tube was flushed with helium for at least 30 min. The specimen was then heated in a helium atmosphere. As soon as the desired temperature was reached, helium was replaced by the desired gas. After being heated at the desired temperature for the predetermined duration of time, the tube was cooled to room temperature in a helium atmosphere. The specimens were heated in the following gas streams: O_2, H_2, C_2H_4, and a mixture of C_2H_4 and O_2. The volume ratio in the mixture was 1 : 2. Most of the heat treatments were carried out at 250 or 300°C, temperatures in the range employed in industry. Some specimens, however, were heated at 400°C in O_2 or H_2. The flow rate of the gases was maintained at about 150 cm^3/min. The gases used in the experiments were purchased from Linde Division, Union Carbide Corporation. Hydrogen and helium were 99.999%, and oxygen was 99.99% pure. The purity of ethylene was 99.5%. Hydrogen was further purified by being passed through a Deoxo (Engelhard Industries) unit and a molecular sieve bed immersed in liquid nitrogen. Helium was also purified by being passed through a molecular sieve bed immersed in liquid nitrogen. After each heat treatment, the specimen was examined in a JEOL 100U transmission electron microscope.

RESULTS

The Behavior of the Silver Crystallites on Alternate Heating in H_2 and O_2

Figure 1 is a micrograph of a specimen after deposition of a silver film of 10 Å thickness. Detectable small crystallites with a large number density were formed soon after deposition even at room temperature. Similar micrographs were also obtained for loadings of specimens with 7.5 and 5 Å.

When the specimen of Fig. 1 was heated

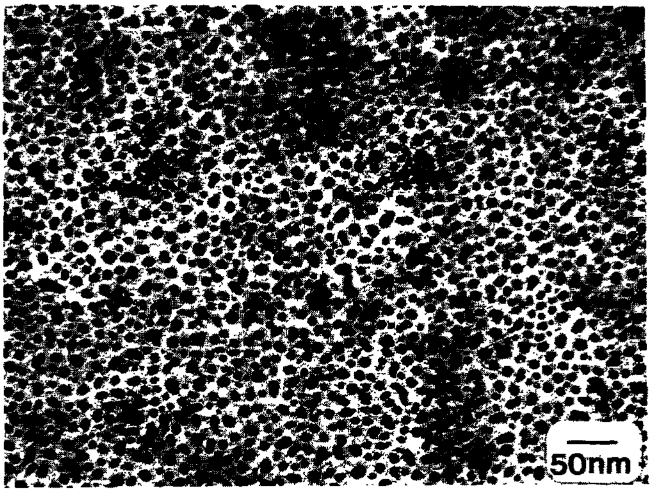

FIG. 1. Ag/Al_2O_3 specimen after deposition of a 10 Å-Ag film on Al_2O_3.

in H_2 at 300°C for 1 h, large crystallites formed (Fig. 2a). The electron diffraction pattern indicated that the crystallites were present as Ag. After an additional 1 h of heating in H_2 at 300°C, many small particles disappeared (A in Figs. 2a, 2b). Some particles (B) migrated over the substrate. In other regions (C), several neighboring particles disappeared and new larger particles appeared in locations where no particles were observed before, most likely as a result of migration and coalescence. One may also note that some elongated particles changed their shape to almost a circular one (D in Figs. 2a, 2b). The elongated particles (D) of Fig. 2a were a result of collision and incomplete coalescence of two particles. Upon further heating of the specimen in H_2 at 300°C for 1 h more, events similar to the preceding ones occurred again (Fig. 2c). Some small particles (A) disappeared, while other particles (B) migrated over the substrate. In several regions, considerable sintering occurred, resulting in a redistribution of the crystallites (C in Figs. 2b, 2c). In addition, a few particles decreased in size (E in Figs. 2b, 2c).

The specimen was then heated in oxygen. Heating for 0.5 h at 300°C brought about severe sintering (Fig. 2d), much more severe than in H_2. Neighboring particles coalesced to form larger particles (F in Figs. 2c, 2d), and many small crystallites, 100–150 Å in size, disappeared because of either migration and coalescence or direct ripening. In addition, a large number of extremely small crystallites, 50 Å or less in size, appeared all over the substrate. Only Ag was detected in the electron diffraction pattern. After heating in O_2 at 300°C for 0.5 h more, most of the large crystallites remained unaffected, a few crystallites disappeared (G in Figs. 2d, 2e), but the number of small crystallites increased. These small crystallites were either circular or wormlike. The electron diffraction pattern indicated that the particles remained as Ag throughout the heating in O_2.

FIG. 2. Changes on heating the specimen of Fig. 1 alternately in O_2 and H_2. The micrographs are from a different region than that of Fig. 1. (a) H_2, 300°C, 1 h; (b) H_2, 300°C, 1 h; (c) H_2, 300°C, 1 h; (d) O_2, 300°C, 0.5 h; (e) O_2, 300°C, 0.5 h; (f) H_2, 300°C, 0.5 h; (g) H_2, 1.5 h (1 h at 300°C and 0.5 h at 400°C); (h) H_2, 400°C, 0.5 h; (i) O_2, 400°C, 0.5 h; (j) O_2, 400°C, 0.5 h; (k) H_2, 300°C, 1 h; (l) H_2, 300°C, 1 h.

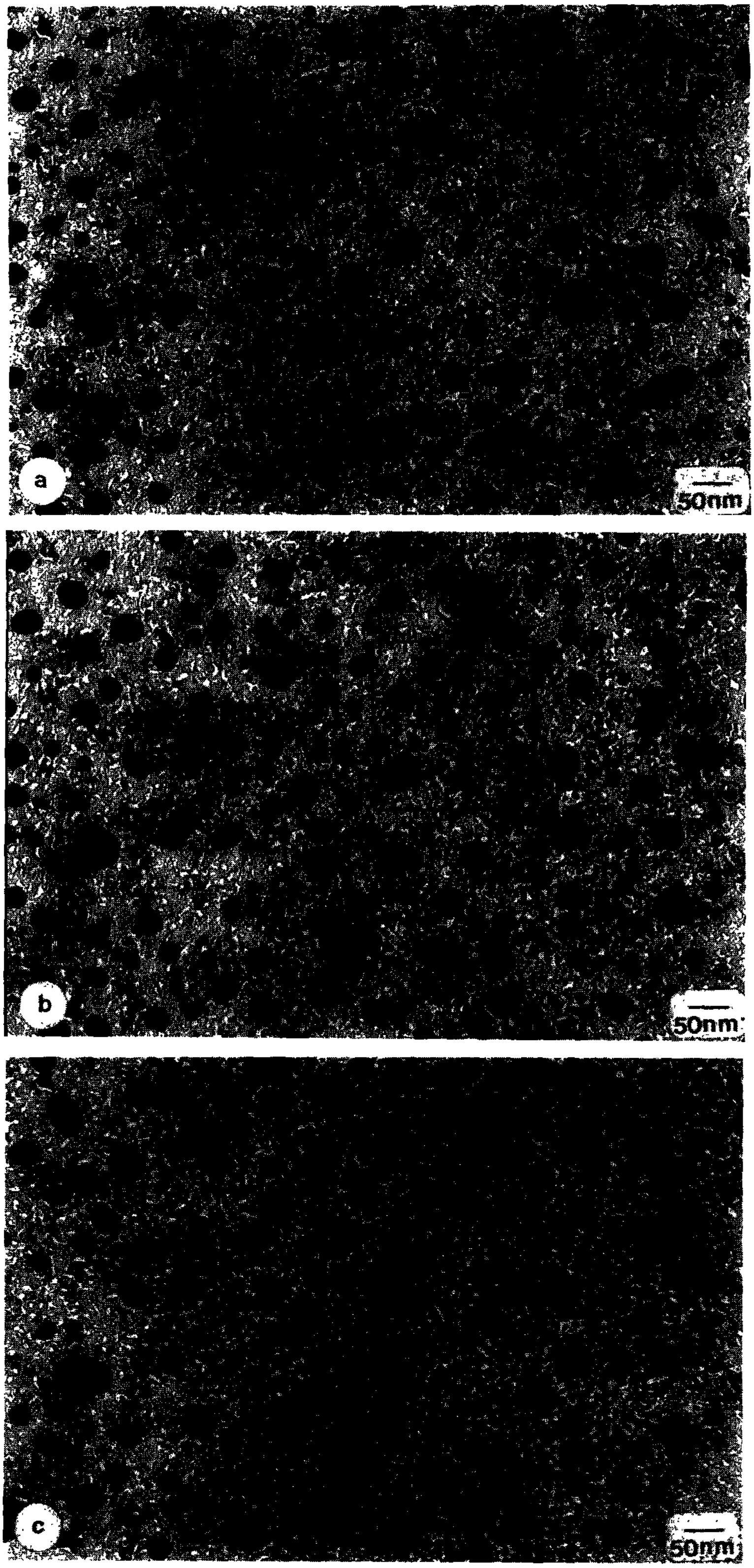

FIG. 2

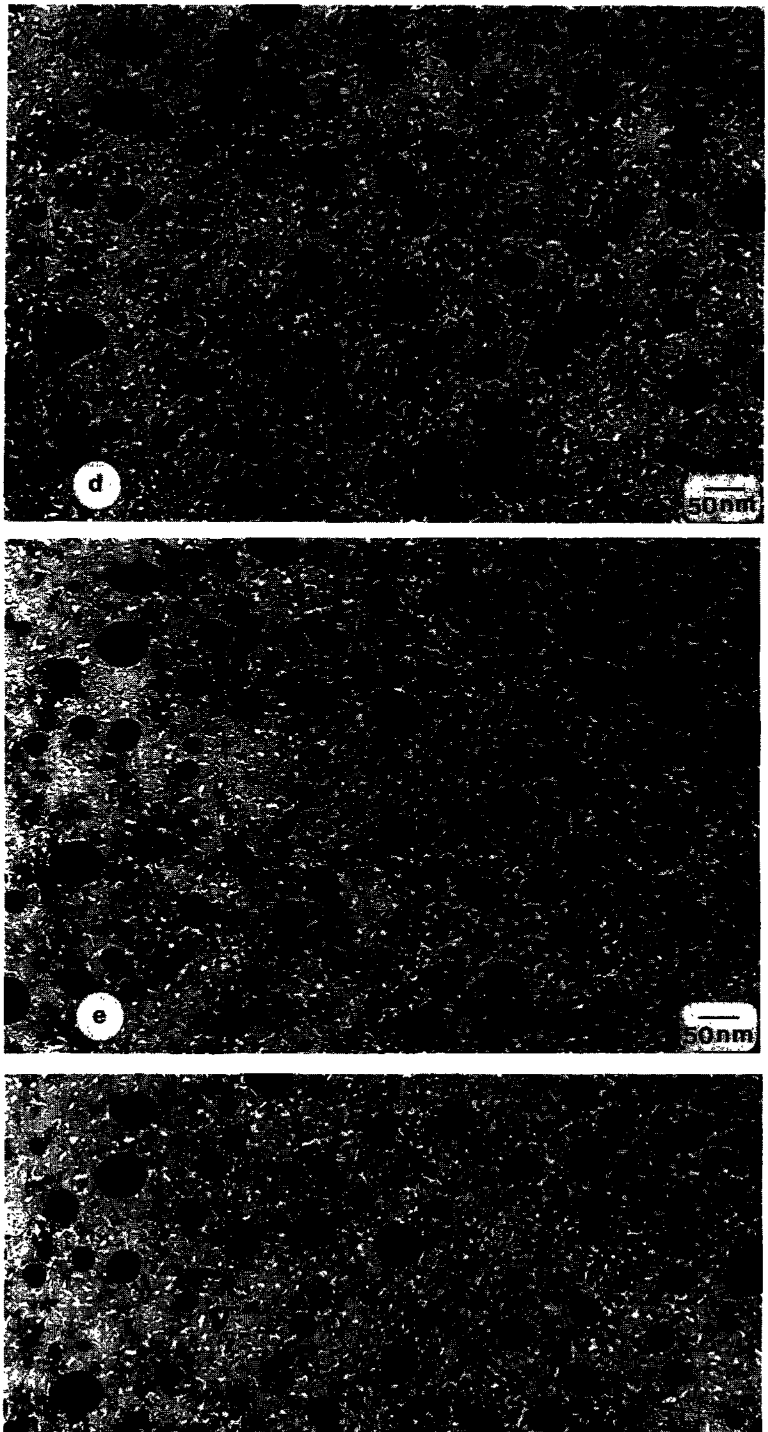

FIG. 2—*Continued.*

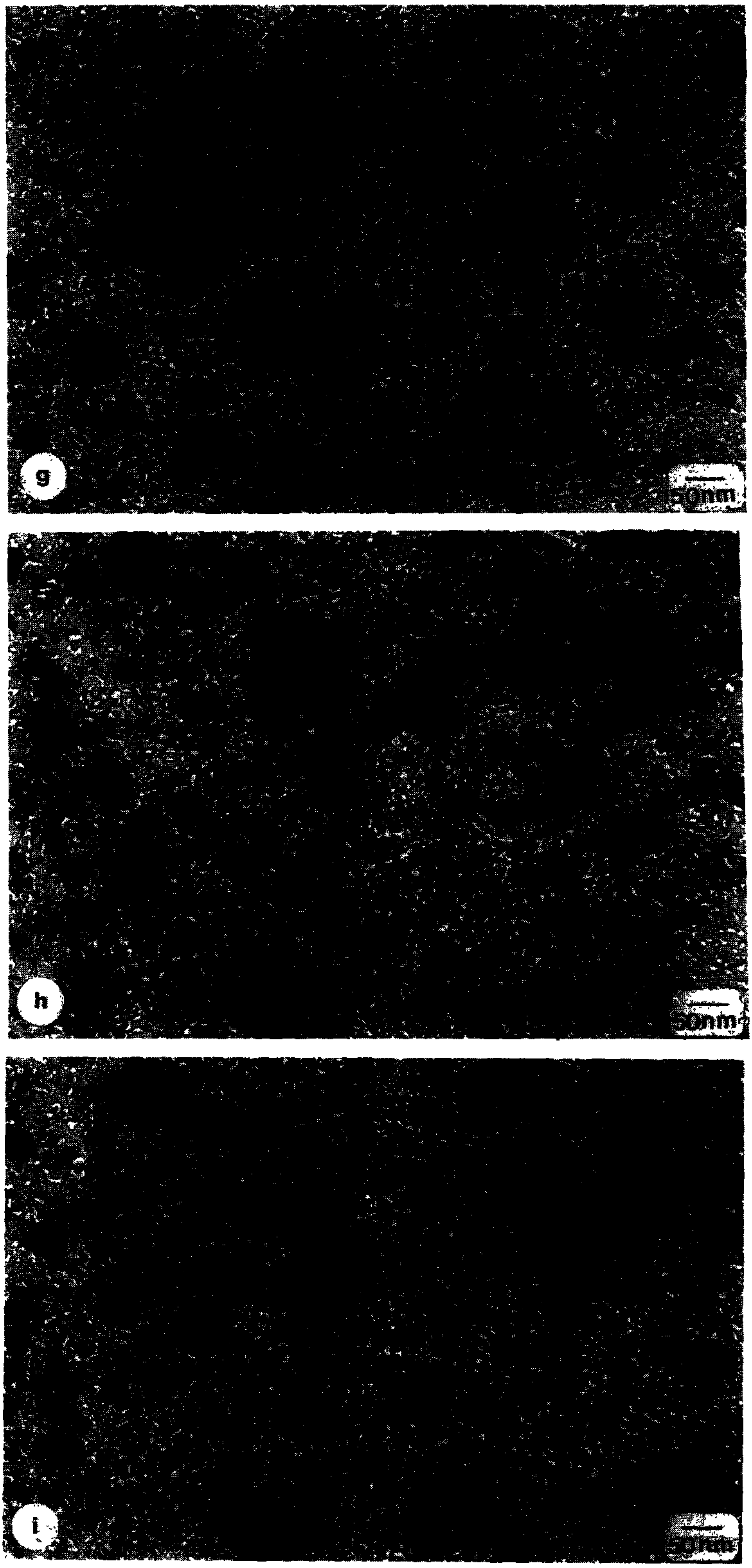

FIG. 2—*Continued.*

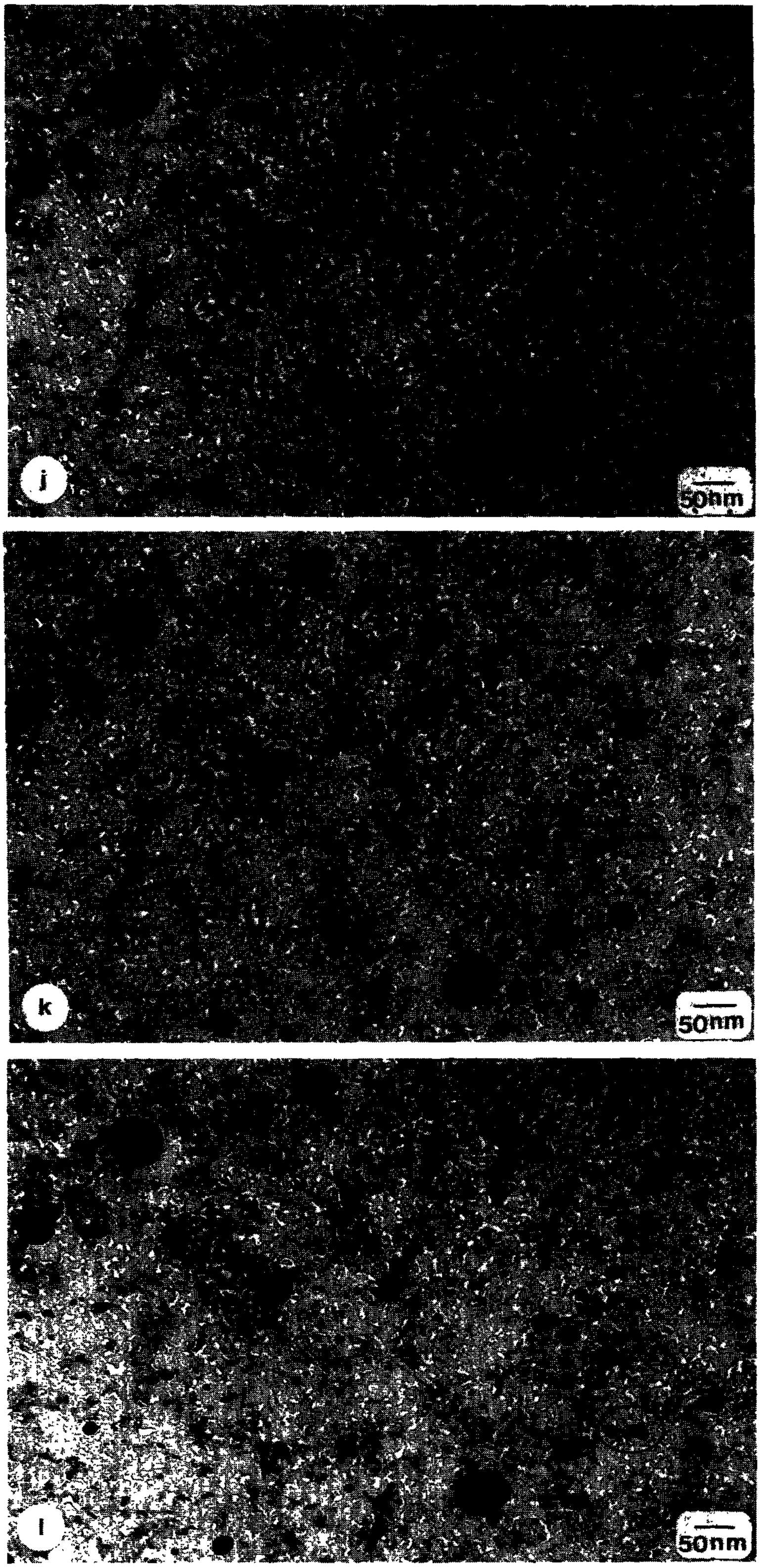

FIG. 2—*Continued.*

The specimen was subsequently heated in H_2. After heating for 0.5 h in H_2 at 300°C (Fig. 2f), the small, wormlike crystallites remained unchanged, while most of the small, circular, crystallites disappeared (H in Figs. 2e, 2f). The large particles remained unaffected. Heating in H_2 for 1 h more at 300°C resulted in little change.

The specimen was subsequently heated at 400°C. Heating in H_2 at 400°C for 0.5 h resulted in considerable sintering with a redistribution of the crystallites (Fig. 2g). In spite of the severe sintering of the circular particles, the small, wormlike crystallites remained unchanged throughout heating (Ic in Figs. 2f, 2g). On further heating in H_2 at 400°C for 0.5 h more, sintering continued to occur, resulting in a further redistribution of the crystallites (Fig. 2h). The existing wormlike particles remained unaffected, while their number increased, and new, small, circular particles appeared (I in Figs. 2g, 2h). One may also note that some cystallites became faceted (J in Fig. 2h).

Subsequently, the specimen was heated in O_2 at 400°C for 0.5 h (Fig. 2i). Some particles disappeared, probably as a result of migration and coalescence with other particles. The faceted particles became circular, and new, small crystallites appeared. On further heating in O_2 at 400°C for 0.5 h more (Fig. 2j), many large particles disappeared, while new, small crystallites appeared. It is possible that a fraction of the particles which disappeared was permanently lost to the gas stream, while the rest remained on the substrate as small crystallites.

The specimen was again heated in H_2 at 300°C for 1 h. As shown in the micrograph (N in Fig. 2k), the circular, small crystallites increased in size, while much smaller crystallites disappeared. However, the wormlike crystallites and most of the large particles remained unaffected. On further heating in H_2 at 300°C for 1 h more (Fig. 2l), some of the small crystallites of circular shape migrated over the substrate (P in Figs. 2k, 2l).

The Behavior of the Silver Particles Following Oxidation of Ethylene

To investigate the behavior of silver particles in the actual process of ethylene oxidation, specimens of 7 Å loading were heated in O_2, C_2H_4, and a mixture of O_2 and C_2H_4, respectively. Since ethylene oxidation is usually carried out in the range 200–300°C, the specimens were heated at 250°C.

Heating in O_2 at 250°C. Figure 3a represents the initial state after heating in H_2 at 300°C for 4 h. The specimen was subsequently heated in O_2 at 250°C. During 20 min heating in O_2, considerable sintering occurred, resulting in a redistribution of the particles (Fig. 3b). However, as observed earlier at 300 and 400°C, small crystallites also formed. Some of them had a wormlike shape and were present in the white regions of the substrate. Considerable sintering continued to occur on further heating in O_2 for 20 min more (Fig. 3c). Many small crystallites (R) disappeared, while new, small crystallites (S) appeared in regions where no crystallites were observed before. During heating for an additional 20 min in O_2 (Fig. 3d), many of the large particles (T) remained unaffected. However, some large particles (U) disappeared, probably because they migrated over the substrate and coalesced with other particles, while new crystallites of large size (V) appeared in regions where no crystallites were observed before (most likely via the coalescence of two or more migrating crystallites). Crystallites, marked W, migrated over the substrate. After further heating for an additional 0.5 h in O_2, the events observed were similar to those that occurred during the preceding heating in O_2 (Fig. 3e). In addition, a number of small crystallites appeared (X in Figs. 3d, 3e). Even though the large particles were relatively stable, a large number of silver atoms, undetectable in the electron microscope, were probably present on the substrate. Subsequently, small detectable crystallites probably

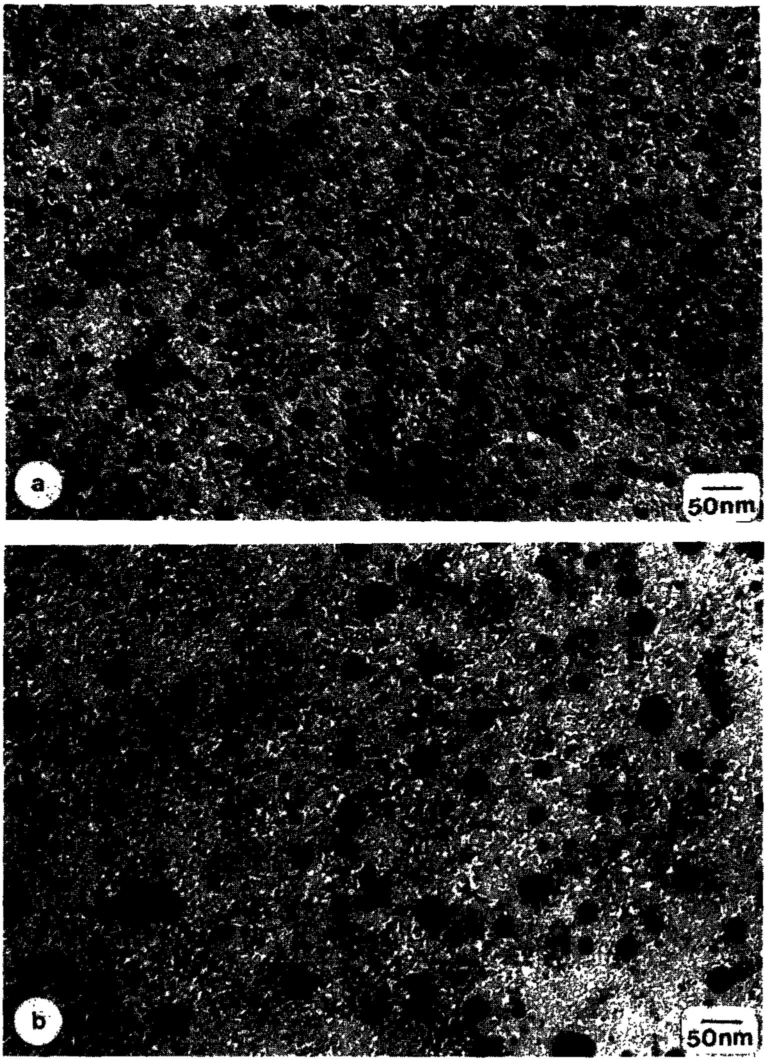

FIG. 3. Sequence of changes in an Ag/Al_2O_3 specimen with 7 Å initial film thickness heated in O_2 at 250°C. (a) H_2, 300°C, 4 h; (b) O_2, 20 min; (c) O_2, 20 min; (d) O_2, 20 min; (e) O_2, 30 min; (f) O_2, 30 min; (g) O_2, 1 h; (h) O_2, 1 h.

formed via migration and coalescence of undetectable clusters. On heating for an additional 0.5 h in O_2 at 250°C (Fig. 3f), many small crystallites, 50 Å or less in size, disappeared while new crystallites approximately 150 Å in size appeared. In addition, large neighboring crystallites merged in some regions (Y1, Y2, and Y3). In region Y1, a large amount of the material of one particle is transferred to the other one. However, in regions Y2 and Y3, the two neighboring particles are connected through a bridge. The behavior of the smaller crystallites was similar to that in the preceding heating. After heating in O_2 for 1 h more (Fig. 3g), small particles of 50 Å or less appeared again. In region Y1, the transfer of material from one particle to the neighboring one through the bridge connecting them was nearly completed. For the particles in region Y2, which were connected through a bridge, there was no sig-

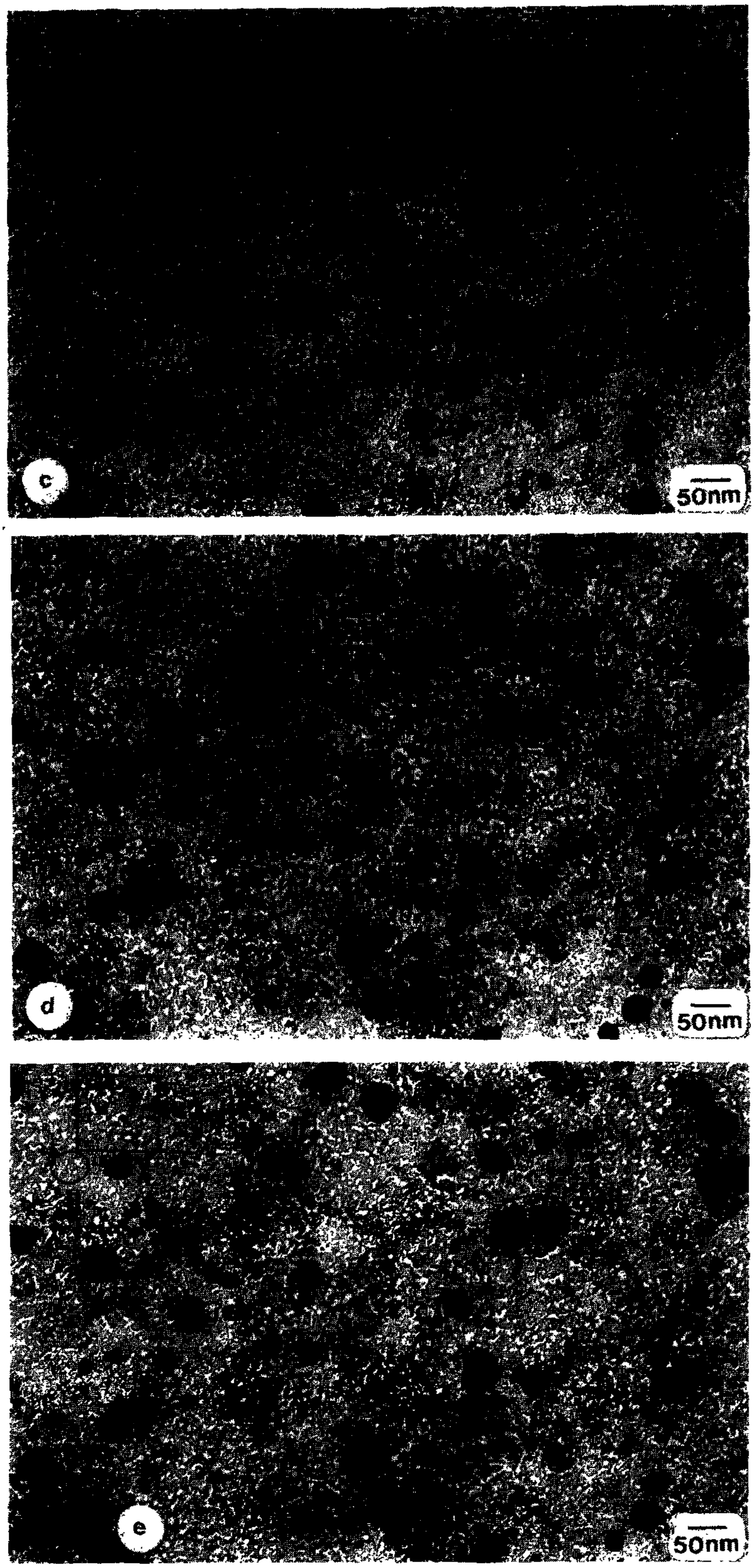

FIG. 3—*Continued.*

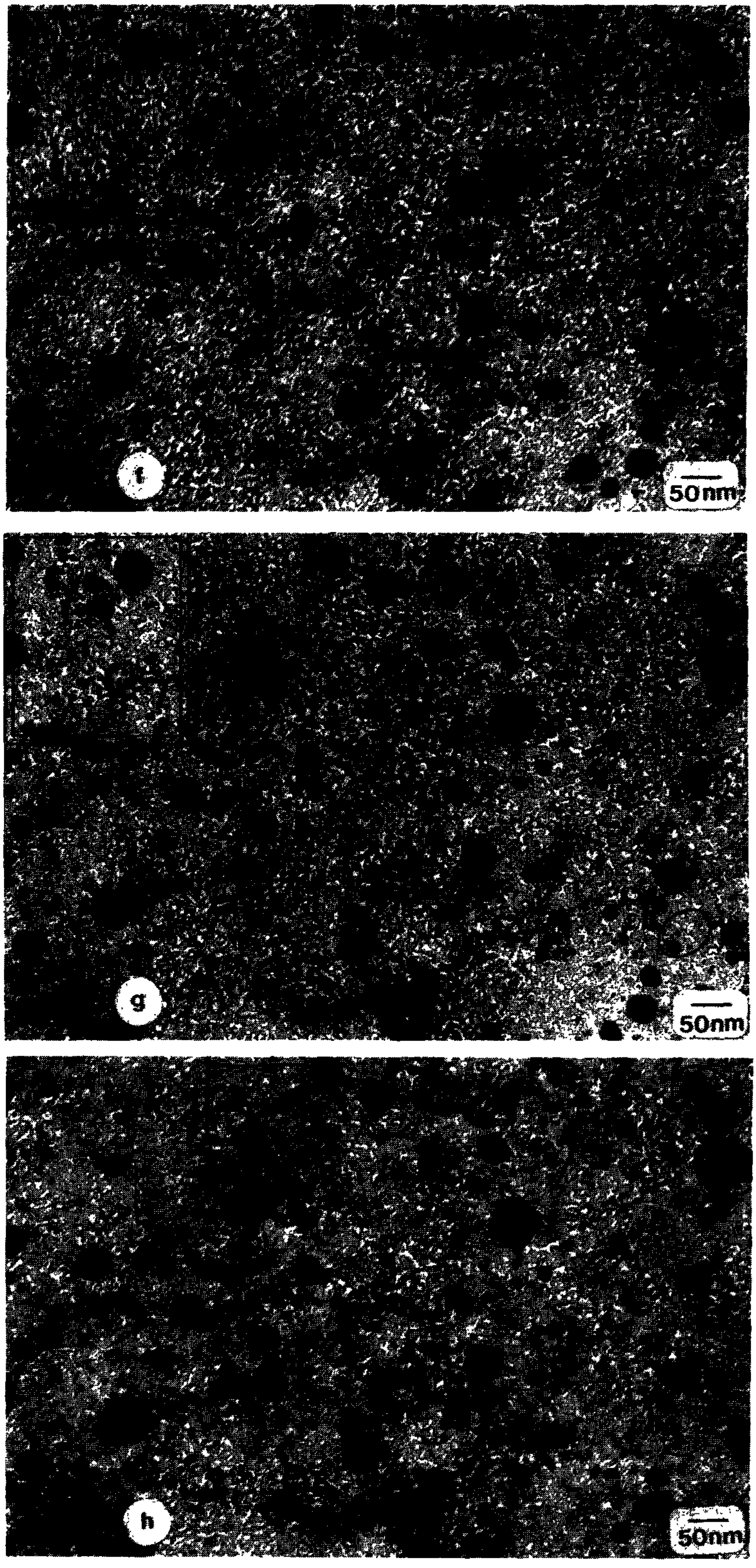

FIG. 3—*Continued.*

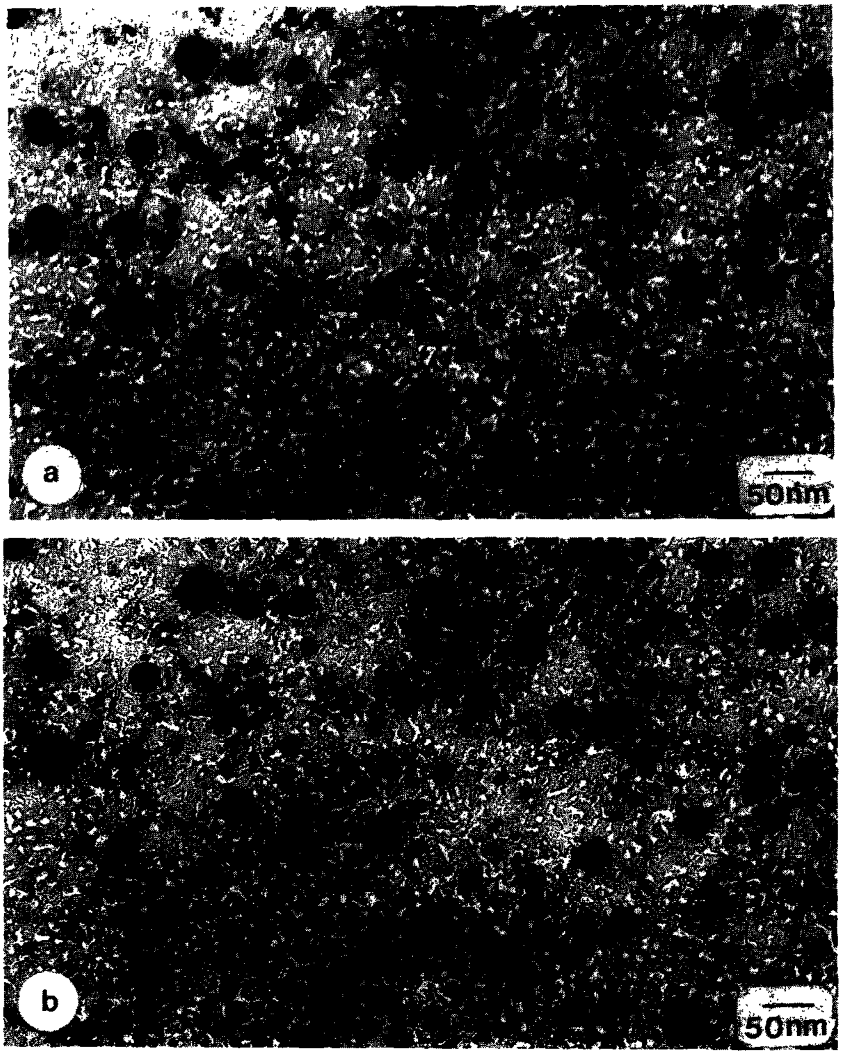

FIG. 4. Sequence of changes in an Ag/Al_2O_3 specimen with 7 Å initial film thickness heated in C_2H_4 at 250°C. (a) H_2, 300°C, 4 h; (b) C_2H_4, 20 min; (c) C_2H_4, 80 min; (d) C_2H_4, 110 min; (e) O_2, 250°C, 30 min.

nificant change (Fig. 3g). On subsequent heating for 1 h more in O_2, a large amount of material was, however, transferred into the other particle through the bridge (Fig. 3h). For the particles in region Y3, the bridge between the two particles increased in width on further heating (Figs. 3g, 3h). A similar behavior was observed before for Pt and Fe (*16–18*).

After a total of 4 h of heating in O_2 (Fig. 3h), the small crystallites increased in size, while 150–200 Å particles decreased or disappeared (a in Figs. 3g, 3h). In region b, a particle decreased in size, while several smaller crystallites appeared in the vicinity of the decreasing particle, probably as a result of the coalescence of the atoms and/or clusters which were lost by the decreasing particles.

Heating in C_2H_4 at 250°C. Figure 4a is a micrograph of a specimen heated in H_2 at 300°C for 4 h. Large crystallites of about 400 Å formed. In addition, very small crystallites of about 30 Å as well as wormlike

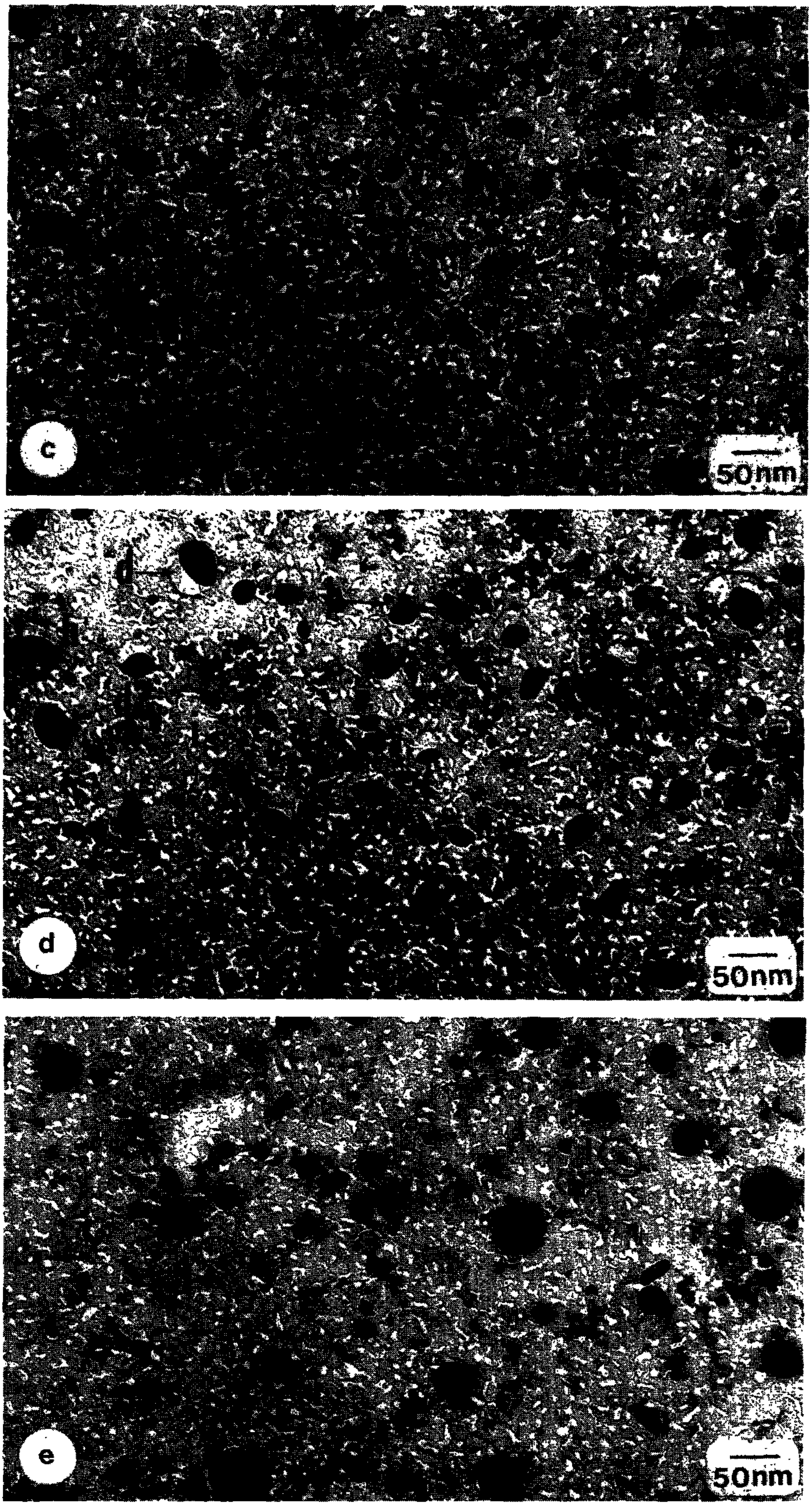

FIG. 4—*Continued.*

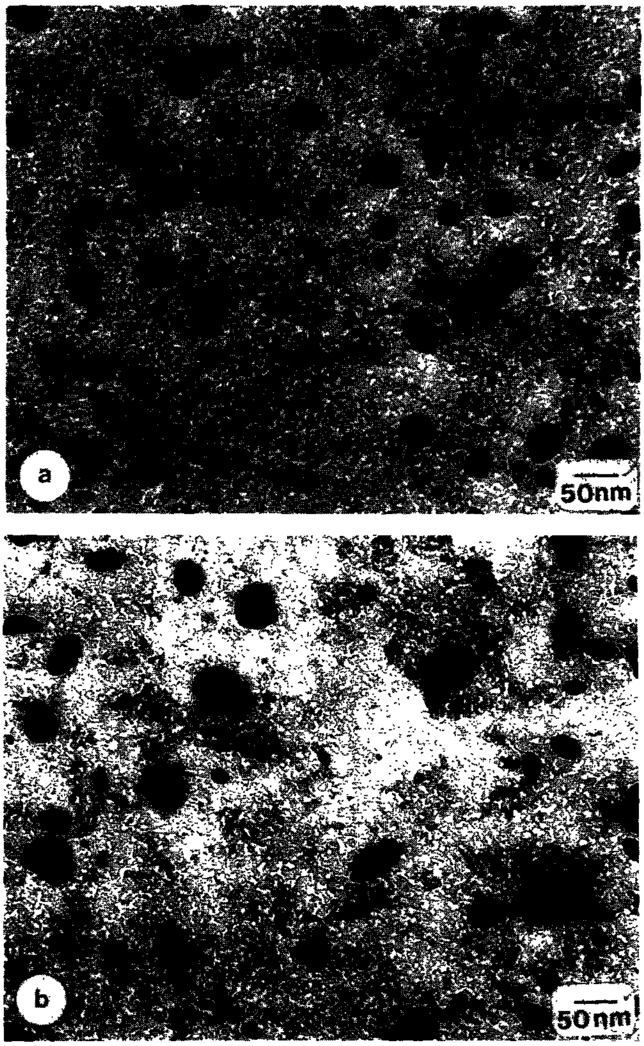

FIG. 5. Sequence of changes in an Ag/Al$_2$O$_3$ specimen with 7 Å initial film thickness heated in a mixture of C_2H_4 and O_2 at 250°C. (a) H_2, 300°C, 4 h; (b) C_2H_4 and O_2, 20 min; (c) C_2H_4 and O_2, 20 min; (d) C_2H_4 and O_2, 50 min; (e) C_2H_4 and O_2, 1 h.

crystallites appeared. The specimen was subsequently heated in C_2H_4 at 250°C. Heating for 20 min in C_2H_4 did not cause any significant change (Fig. 4b). Even the small particles remained unaffected. After 20 min more of heating in C_2H_4, the crystallites remained again unchanged. Upon heating for a total of 1 h 40 min in C_2H_4 (Fig. 4c), most of the crystallites changed their shape from circular to ellipsoidal without changing their locations. Some crystallites (d in Fig. 4c) had a straight edge over half of their periphery. In region e, two neighboring crystallites migrated over the substrate and formed a doublet. After heating for up to 3.5 h in C_2H_4, the crystallites in contact merged completely to form single particles (e in Fig. 4d). Two neighboring particles migrated and subsequently contacted each other (f in Figs. 4c, 4d), while nearby particles coalesced to form single particles (g in Figs. 4c, d). Most of the crystallites, however, remained almost unchanged. Their shape remained ellipsoi-

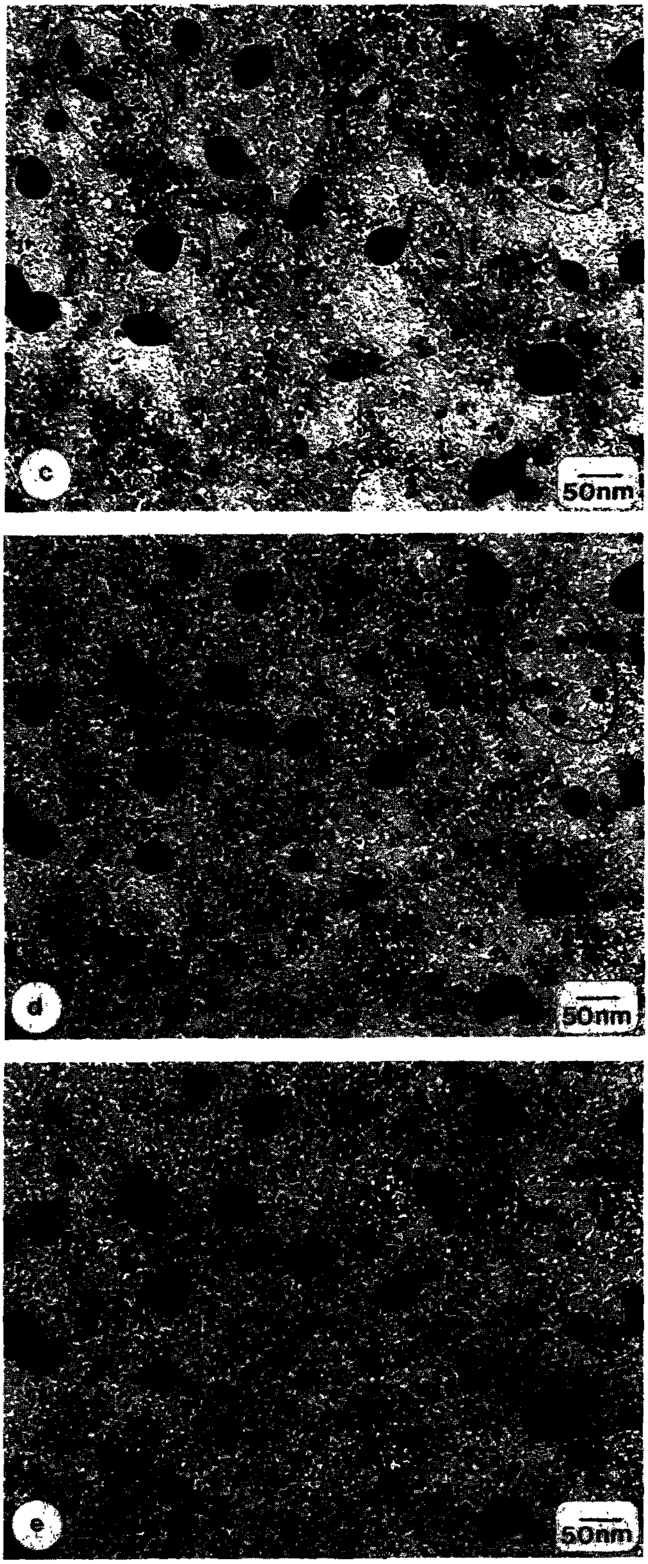

FIG. 5—*Continued.*

dal but became somewhat more elongated. In addition, some particles rotated (h in Figs. 4c, 4d), and the particles which had a straight edge over a part of their peripheries acquired ellipsoidal shapes (d in Fig. 4d). The small crystallites did not sinter and remained in their original locations without any change (indicating that they were very stable during heating in C_2H_4), and no new small crystallites were generated. In contrast, during heating in O_2 or H_2, the very small crystallites underwent various changes such as disappearance and coalescence, and new crystallites appeared as well. The specimen of Fig. 4d was heated further in O_2 at 250°C for 0.5 h. As shown in the micrograph (Fig. 4e), considerable sintering occurred. Most of the particles acquired circular shapes, and some small crystallites, of 80 Å or less in diameter, appeared in regions where no crystallites were observed before (i in Figs. 4d, 4e).

Heating in C_2H_4 + O_2 at 250°C. Figure 5a shows the initial state of the specimen after heating in H_2 at 300°C for 4 h. Subsequently, the specimen was heated in C_2H_4 + O_2 at 250°C. During heating in C_2H_4 + O_2 for 20 min, considerable sintering occurred and the crystallites acquired irregular shapes (Fig. 5b). Sintering was most probably caused by O_2, and the change in the crystallites' shape was brought about by C_2H_4. Very small crystallites also appeared. After further heating for 20 min more in C_2H_4 + O_2 (Fig. 5c), the behavior was very similar to that during the preceding heating. Upon heating for up to 1.5 h in C_2H_4 + O_2 (Fig. 5d), most of the large crystallites remained without changing their locations. Some particles about 200 Å in size migrated over the substrate (j in Figs. 5c, 5d), and in region k two neighboring particles coalesced and migrated over the substrate. In region m, new crystallites appeared without any evidence of migration. Also, the number of small crystallites decreased. During additional heating for a total of 2.5 h in C_2H_4 + O_2 (Fig. 5e), most of the large particles remained in their locations and events similar to those which occurred in regions j and m during the previous heat treatment continued to occur (j, m in Figs. 5d, 5e).

DISCUSSION

Several mechanisms have been proposed for the sintering of supported metal catalysts. One of them, known as the crystallite migration model, considers sintering to occur by migration of metal crystallites over the surface of the support and their subsequent coalescence following collision (*19, 20*). In a second mechanism, the crystallites smaller than a critical size lose atoms or molecules to a two-dimensional phase of single atoms on the substrate, while those of a larger size gain atoms from the two-dimensional phase (*21–23*). This process, called Ostwald ripening, involves a two-dimensional surface phase of migrating atoms which is supersaturated with respect to the large crystallites and undersaturated with respect to the small ones. However, the process of emission of atoms by a small particle and their capture by a larger neighboring particle can also occur directly, without the involvement of a pool of single atoms covering a large surface area. In contrast to Ostwald ripening, which is global, the latter involves only a few neighboring particles and is called direct ripening (*24*).

As mentioned earlier, evidence for crystallite migration and coalescence as well as for ripening in graphite-supported silver catalysts has been reported by a few authors (*13, 14*). In Ref. (*24*) it was shown that the ripening identified in Ref. (*13*) was direct ripening. Let us now examine a number of events reported in this paper in some detail.

Sintering Behavior

While, as expected, very small particles have migrated (p in Fig. 21), it is worth noting that even large crystallites 200–400 Å in diameter migrated over the substrate

(B in Figs. 2a–2c; W in Figs. 3c, 3d; and j in Figs. 5c–5e). Some particles migrated and subsequently coalesced (e in Figs. 4b–4d). The "localized" disappearance of some small crystallites indicates that direct ripening could play a role in sintering (A in Figs. 2a–2c; N in Figs. 2j, 2k; and R in Figs. 3b, 3c). The migration of the smaller crystallites and their subsequent coalescence with larger ones, however, cannot be ruled out as a possible mechanism for the disappearance of the small crystallites. The decrease in size of a small crystallite near a larger crystallite provides clear evidence for direct ripening (E in Figs. 2b, 2c). In some regions (b in Figs. 3g, 3h), small particles appeared in the vicinity of large particles which decreased in size, suggesting the possibility that the small particles resulted from the atoms or clusters emitted by the larger particles. Note also that new small crystallites appeared not only in regions close to large particles but also all over the substrate (c in Figs. 3g, 3h). This may mean that the very small particles which were lost by the large particles to the substrate migrated long distances before colliding with other particles (undetectable by electron microscopy) to generate the "new" detectable particles.

An observation which deserves to be noted was the appearance of small crystallites. The micrographs showed that during heating in O_2 at 300°C for 0.5 h following heating in H_2 at the same temperature, a large number of small crystallites appeared, even though other particles sintered to form larger particles (Figs. 2c, 2d). After an initial severe sintering of the crystallites, most of the large particles were unaffected by further heating in O_2 (G1 in Figs. 2d, 2e). Similar behavior was also observed on another specimen heated in O_2 at 250°C (Figs. 3g, 3h). Figs. 2g and 2h show that heating in H_2 at 400°C resulted both in the appearance of very small crystallites (region I) and in the sintering of large particles to generate even larger particles.

The appearance of small crystallites was observed in O_2, H_2, and a mixture of C_2H_4 and O_2. Their number was the largest in O_2, intermediate in H_2, and the smallest in the mixture of C_2H_4 and O_2. Indeed, upon heating in C_2H_4 alone, small crystallites did not appear on the substrate. Harriott (*25*) reported that when the catalyst was exposed to the ethylene oxidation reaction, a large amount of silver was present as small particles which could not be detected by X-ray diffraction. The small crystallites of the present investigation are either circular or wormlike. While the circular crystallites sintered easily, the wormlike particles remained unchanged (H in Figs. 2e, 2f; L in Figs. 2g–2j). It should be noted that the wormlike particles are located in the white regions of the micrographs and have the shape of the white regions (K in Figs. 2g, 2i). The white regions of the substrate may be depressions of some kind in the substrate. When the migrating atoms or clusters of atoms fell into these depressions, they could not escape from them easily. More atoms or clusters of atoms were captured until the depressions were filled with atoms. As a result, the captured particles acquired the shape of the white regions and remained unchanged upon further heating.

Regarding the appearance of small particles, let us now examine a few possible explanations. The presence of silver atoms or clusters of atoms on the substrate may be a consequence of the diffusion of oxygen into the silver particles. The dissolved oxygen could oxidize silver. However, when the temperature is higher than the decomposition temperature of the oxides, only transient, unstable oxide phases can form. From the unstable oxides, some oxygen can penetrate further into the subsurface of the particles, generating internal microstresses. The internal microstresses can be released by partial disintegration, leading to an increase of atoms or clusters of atoms over the substrate. Indeed, silver oxides are not stable at the temperatures employed in the present experiment, 250–400°C. Ag_2O and Ag_2O_2 are reported to decompose at 230 and 100°C, respectively (*26*). Evidence for the existence of the subsurface oxygen in silver has been reported (*27–29*). Backx *et al.* (*27*) investigated oxygen adsorption on the (111) surface of Ag and reported that below −100°C, oxygen adsorbs on the (111) surface as molecules; above −100°C, the oxygen molecules dissociate and only atomic oxygen could be detected. In addition, at temperatures above 150°C, the absorbed atomic oxygen diffuses into the subsurface region. From the change in the work function and from field emission pattern, Czanderna *et al.* (*28*) found that oxygen starts to diffuse into the bulk of silver at temperatures between 100 and 200°C. In addition, at the temperatures employed in the present experiments, 250–300°C, which are close to the Tammann temperature ($\sim 0.5\ T_{\text{melting}}$ in K) for silver, 345°C, the lattice atoms have higher mobility and can detach from the particle more easily. The migration, collision, and coalescence of the species resulting from disintegration may be responsible for the appearance of the small crystallites.

The appearance of the extremely small crystallites during heating in H_2 might be a result of the coalescence of undetectable migrating atoms or clusters of atoms which were generated during previous heating in O_2. In addition, oxygen, which was adsorbed on the surface and subsurface of silver when the specimen was exposed to air, might have contributed to the presence of silver atoms or clusters of silver atoms on the substrate.

In a previous paper from this laboratory (*7*) concerning the behavior of Fe/Al_2O_3 in O_2 at high temperatures, evidence for the coexistence of a thin film with crystallites was presented. During subsequent heating in H_2, the thin film was reduced to the metal and became unstable, and a large number of small crystallites were generated via the rupture of the film. A detailed explanation of this behavior was given in Ref. (*7*) and was based on the observation that the interactions of the metal with the substrate are weaker than those of the oxide with the substrate. As a result, the metal atoms prefer the more favorable interactions within the particle to those within the film. The appearance of a large number of small particles in the present experiments may perhaps be explained along similar lines. Transient, unstable, silver oxides form, and undetectable thin films of silver oxide detach from the silver particles. Because the silver oxides are unstable at the temperatures employed, the resulting silver films rupture to form a large number of small crystallites. The appearance of small crystallites during heating in H_2 may be due to the rupture of the undetectable patches which were formed during heating in O_2.

More likely, the large number of detectable small particles may be a result of the migration and coalescence of undetectable particles present on the substrate from the beginning. The number of detectable particles is larger in oxygen than in hydrogen because sintering is more severe in the former case. A final explanation involves the following considerations: At the temperatures employed, the number of atoms of the two-dimensional phase in equilibrium with the crystallites is relatively large and dependent on the gaseous environment of the experiment. On cooling the sample in He to room temperature for TEM observations, the two-dimensional phase becomes supersaturated and may condense, particularly on the large crystallites. Some atoms may condense on undetectable crystallites to form detectable ones, or even may nucleate new crystallites. However, since the diffusion coefficient at room temperature is small, it hinders the capture of atoms by the large particles as well as the formation of nuclei and their growth.

Comparison of Sintering in Various Atmospheres

The experimental results show that sintering of Ag particles supported on alumina occurs both in O_2 and H_2, being more severe in O_2. Similar observations have been also made by previous investigators, for both discrete particles and continuous films (*9–11, 30*).

When the specimen was heated in C_2H_4, the silver particles were very resistant to sintering. The particles changed their shape from circular to ellipsoidal and very few coalesced to form large particles; most of the particles, including the small ones, remained in their locations. Presland *et al.* (*30*) also reported that silver particles sintered slowly during heating in ethylene. The absence of migration and the shape change of the silver particles during heating in C_2H_4 are a result of deposition of carbon species on the surface and around the particles. Recently, the shape change of Fe, Co, and Ni particles supported on alumina and heated in atmospheres containing CH_4 and/or CO (*31*) was examined. The authors suggested that the shape change of the particles was due to the deposition of coke on the surface of the particles and its penetration inside. It was also reported (*12*) that when carbon was deposited on the specimen consisting of silver particles supported on alumina, the silver particles, because of their encapsulation, did not migrate over the substrate. McBreen and Moskowits (*32*), employing surface-enhanced Raman scattering, detected the presence of amorphous carbon when supported silver catalysts were heated in C_2H_4 or in a C_2H_4 and O_2 mixture up to 172°C. It is likely that in the present experiments also, amorphous carbon was deposited on the silver surface and caused the shape change as well as the encapsulation of the silver particles.

The behavior of silver particles during heating in a mixture of oxygen and ethylene at 250°C was a combination of the behaviors in O_2 and in C_2H_4. Sintering in the mixture of oxygen and ethylene was less severe than in oxygen but more severe than in ethylene, and the silver particles acquired irregular shapes.

Comparing the results of heating in various atmospheres, one may conclude that sintering of the silver particles supported on Al_2O_3 decreases in the order $O_2 > H_2 > C_2H_4$. The degree of sintering in the mixture of C_2H_4 and O_2 is between that in O_2 and C_2H_4.

CONCLUSION

The present results provide evidence for various phenomena that occur during the heat treatment of Ag/Al_2O_3 model catalysts. On heating in O_2 at 250 and 300°C, various events, such as migration of crystallites, followed by coalescence, disappearance of small and large particles, decrease in the size of the small particles, coalescence of nearby particles, connection of two neighboring particles by a bridge and material transfer through the bridge were observed to occur. In addition, a large number of small crystallites of two different shapes, circular and wormlike, appeared. The circular small particles were observed to grow, coalesce, or disappear, while the wormlike particles were located in valleys of the substrate and remained unchanged on further heating. A few possible explanations have been provided for the presence of a large number of small particles on the substrate.

The events observed during heating in H_2 were similar to those observed in O_2, but sintering was less severe. The presence of a large number of small particles is probably a result of the previous heating in O_2. During heating in C_2H_4 at 250°C, most of the silver crystallites, both small and large, remained in their locations and only changed their shape from circular to ellipsoidal. Carbon deposition on the surface of the particles seems to be responsible for both the immobility and shape change of the silver particles. In the mixture of C_2H_4 and O_2, sintering of the silver crystallites was less severe than in O_2 and the particles acquired irregular shapes because of the presence of C_2H_4.

REFERENCES

1. Margolis, L. Ya., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 14, p. 429. Academic Press, New York, 1963.

2. Voge, H. H., and Adams, C. R., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 151. Academic Press, New York, 1967.
3. Dadyburjor, D. B., Jewur, S. S., and Ruckenstein, E., *in* "Catalysis Review" (H. Heinemann and J. J. Carberry, Eds.), Vol. 19, p. 293. Dekker, New York, 1979.
4. Carra, S., and Forzatti, P., *in* "Catalysis Review" (H. Heinemann and J. J. Carberry, Eds.), Vol. 15, p. 1. Dekker, New York, 1977.
5. Hucknall, D. J., "Selective Oxidation of Hydrocarbons," Chap. 2. Academic Press, New York, 1974.
6. Ruckenstein, E., and Lee, S. H., *J. Catal.* **86,** 457 (1984).
7. Ruckenstein, E., and Sushumna, I., *J. Catal.* **97,** 1 (1986).
8. Ruckenstein, E., and Hu, X. D., *J. Catal.* **100,** 1 (1986).
9. Presland, A. E. B., Price, G. L., and Trimm, D. L., *Surf. Sci.* **29,** 424 (1972).
10. Presland, A. E. B., Price, G. L., and Trimm, D. L., *Surf. Sci.* **29,** 435 (1972).
11. Seyedmonir, S. R., Strohmayer, D. E., Guskey, G. J., Geoffroy, G. L., and Vannice, M. A., *J. Catal.* **93,** 288 (1985).
12. Plummer, H. K., Jr., Watkins, W. L. H., and Gandhi, H. S., *Appl. Catal.* **29,** 261 (1987).
13. Heinemann, K., and Poppa, H., *Thin Solid Films* **33,** 237 (1976).
14. Baker, R. T. K., and Skiba, P., Jr., *Carbon* **15,** 233 (1977).
15. Chu, Y. F., and Ruckenstein, E., *J. Catal.* **41,** 385 (1976).
16. Sushumna, I., and Ruckenstein, E., *J. Catal.* **94,** 239 (1985).
17. Sushumna, I., and Ruckenstein, E., *J. Catal.*, in press.
18. Arai, M., Ishikawa, T., Nakayama, T., and Nishiyama, Y., *J. Colloid Interface Sci.* **97,** 254 (1984).
19. Ruckenstein, E., and Pulvermacher, B., *AIChE J.* **19,** 356 (1973).
20. Ruckenstein, E., and Pulvermacher, B., *J. Catal.* **29,** 224 (1973).
21. Chakraverty, B. K., *J. Phys. Chem. Solids* **28,** 2401 (1967).
22. Wynblatt, P., and Gjostein, N. A., *Prog. Solid State Chem.* **9,** 21 (1975).
23. Ruckenstein, E., and Dadyburjor, D. B., *J. Catal.* **33,** 233 (1977).
24. Ruckenstein, E., and Dadyburjor, D. B., *Thin Solid Films* **55,** 89 (1978).
25. Harriott, P., *J. Catal.* **21,** 56 (1971).
26. "Handbook of Chemistry and Physics," 62nd ed. CRC Press, Boca Raton, Florida, 1981–1982.
27. Backx, C., De Groot, C. P. M., and Biloen, P., *Surf. Sci.* **104,** 300 (1981).
28. Czanderna, A. W., Frank, O., and Schmidt, W. A., *Surf. Sci.* **38,** 129 (1973).
29. Kagawa, S., Iwamoto, M., and Morita, S., *J. Chem. Soc. Faraday Trans. 1* **78,** 143 (1982).
30. Presland, A. E. B., Price, G. L., and Trimm, D. L., *J. Catal.* **26,** 313 (1972).
31. Lee, S. H., and Ruckenstein, E., *J. Catal.* **107,** 23 (1987).
32. McBreen, P. H. and Moskovits, M., *J. Catal.* **103,** 188 (1987).