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Spheroidization of Silver Ethylene Oxidation Catalyst Particles as Induced by γ-Irradiation

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Following γ-irradiation and then exposure of a supported silver catalyst to ethylene and O_2 at 280°C, scanning electron microscopy (SEM) reveals spheroidization of the silver particles, a phenomenon not observed in the absence of preirradiation. Electron Spectroscopy Chemical Analyses (ESCA) studies and etching of the samples suggest the presence of a distinct, included phase of Ca oxide within the Ag. Irradiation apparently causes multiple ionization with ejection of ionized Ca to the Ag particle surface, spheroidization being one consequence.

INTRODUCTION

In the course of our studies of the influence of γ-irradiation upon catalytic selectivity (rate of desired species generation relative to that of an undesired byproduct), the supported silver catalyst particles were subjected to scanning electron microscopy (SEM). Under conditions described below, γ-ray induced spheroidization of these particles was revealed. To the best of our knowledge, such a phenomenon has not been heretofore reported.

BACKGROUND AND RESULTS

The catalytic system studied was oxidation of ethylene to ethylene oxide and byproduct CO_2. While the details of activity and selectivity alterations induced by preirradiation with γ-rays are set forth elsewhere (*1*), a brief summary of the experimental program as it bears upon the phenomenon reported herein is in order:

Stage A. A commercial supported silver catalyst (Engelhard) containing, among other impurities, Ca, was tested for activity–selectivity characterization in the oxidation of ethylene at 1 atm and 280°C. This catalyst was also subjected to Electron Spectroscopy Chemical Analyses (ESCA) and SEM.

Stage B. Sample used in stage A was irradiated in air in a Co-60 source (10^{-18} eV/min gm) for 10 hr, then exposed to ethylene oxidation, ESCA, and SEM.

Stage C. Sample used in stage B was reduced in H_2 for 3 hr at 300°C, reoxidized, and employed as a catalyst as in A; then subjected to ESCA.

Stage D. Sample used in stage C was reirradiated in air as in B, exposed to reaction and then ESCA. The following facts became manifest in the above program:

ESCA (1, 2)

While surface Ca was not detected by ESCA for the catalyst at stage A, following irradiation (stage B) definite ESCA evidence for surface Ca appeared (1, 2). Reduction (stage C) caused the disappearance of Ca. Reirradiation caused the reappearance of surface Ca (stage D).

SEM

The unirradiated sample, both before and after catalysis, revealed no morphological change in the Ag particles (Fig. 1a).

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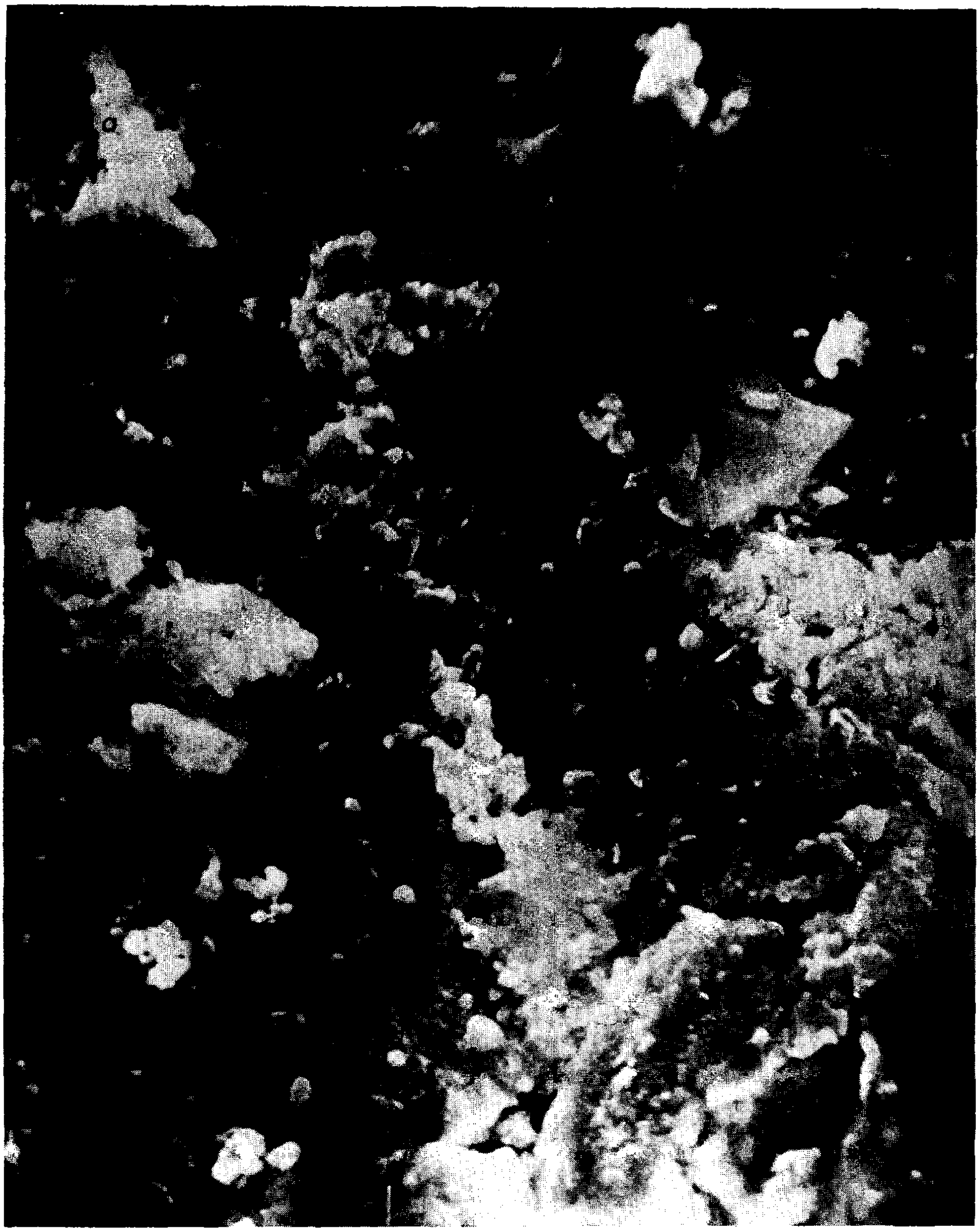

FIG. 1. Scanning electron microscope photographs of the surface of supported Ag catalyst: (a) nonirradiated and heated at 300°C for about 300 hr (×4,792.5); (b) γ-irradiated, then heated at 300°C for about 100 hr (×4,828); (c) γ-irradiated, then heated at 300°C for 250 hr (×3,834).

After irradiation but prior to catalysis, no morphological change was evident. Following catalysis for 50–100 hr the irradiated sample revealed partial spheroidization (Fig. 1b). After 300 hr of catalysis, spheroidization appears complete (Fig. 1c). A catalyst prepared with a lower level of Ca impurity, spheroidized less drastically

FIG. 1 (*continued*).

following irradiation and 100 hr of catalysis (Fig. 2).

Etching

To ascertain the distribution of Ca within the Ag, etching with HNO_3 was undertaken on Sample A. Ca appeared after about ten atomic layers of silver were removed, and did not appear after removal of ten more layers.

Four inferences are permitted: (1) γ-irradiation followed by catalytic action

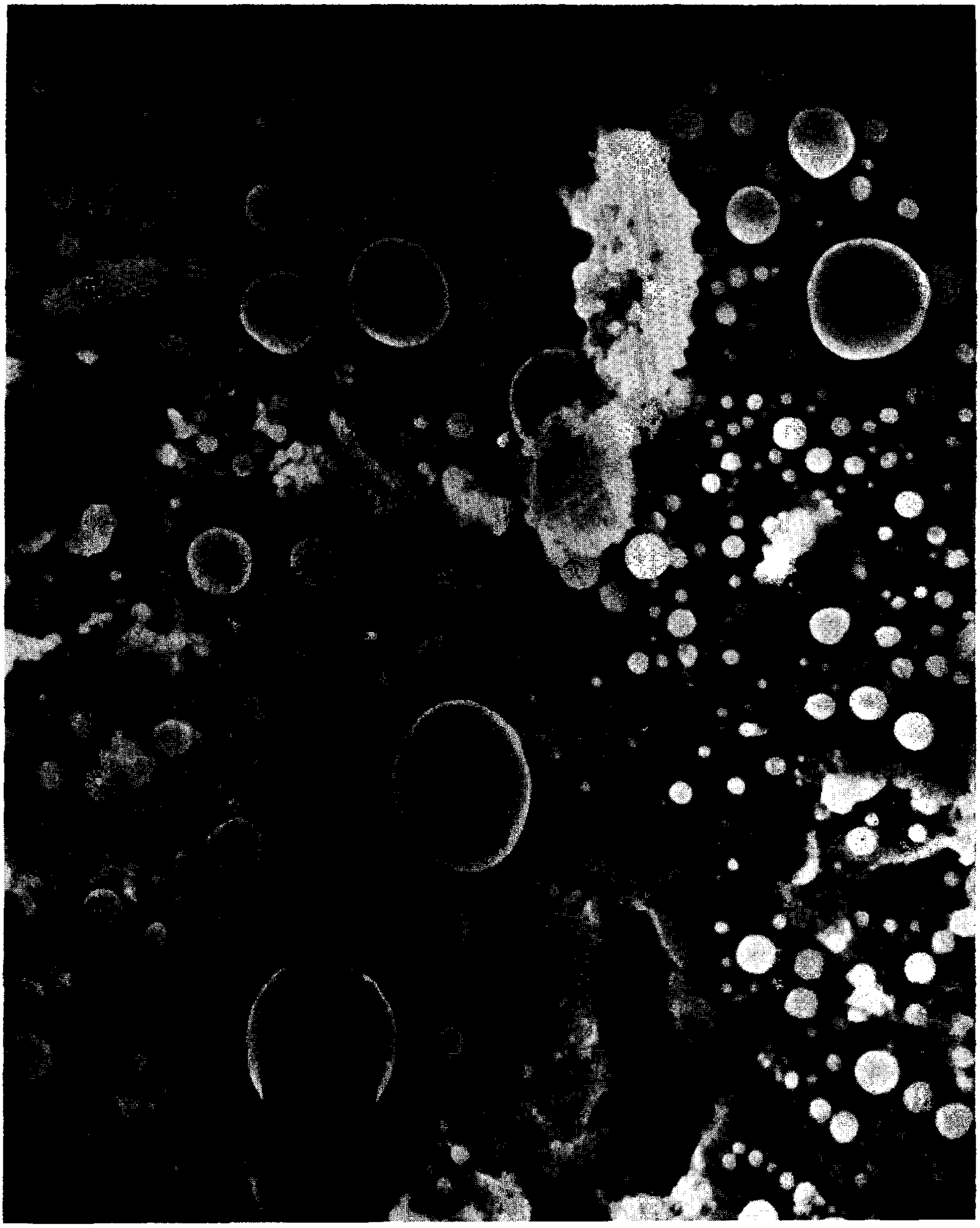

FIG. 1 (*continued*).

prompts spheroidization of the catalytic metal particles. (2) Calcium appears on or adjacent to the silver surface following irradiation and returns into the bulk upon reduction in H_2. (3) Calcium in the normal, unirradiated catalyst is inhomogeneously dispersed, suggesting that Ca as an oxide or hydroxide is included within Ag as a separate, distinct phase. The oxide particle diameter seems to be about 10–30 Å. (4) Contrasting Figs. 1b and 2, it appears that the lower level of Ca impurity prompts a

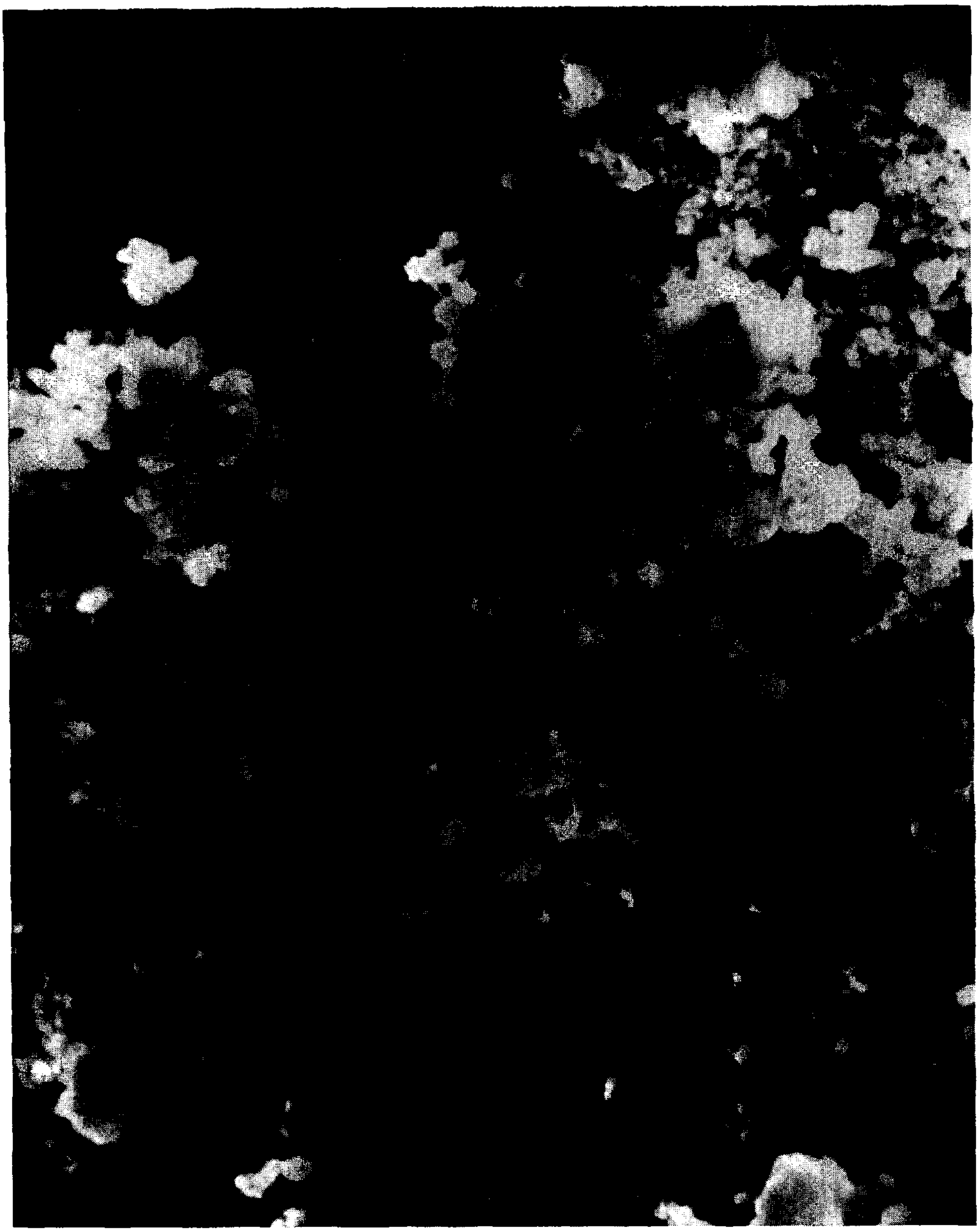

FIG. 2. Scanning electron microscope photograph of the surface of supported Ag catalyst containing a small amount of Ca, γ-irradiated and then heated at 300°C for 100 hr (×4,402).

slower rate of spheroidization. The possible role, then, of irradiation-induced Ca migration to the Ag surface in sponsoring spheroidization deserves comment.

DISCUSSION

Considering the small atomic displacement cross-section of Compton electrons produced by γ-irradiation, the noted effect of γ-rays on Ca migration appears puzzling. One would not expect more than one or two collisions in a silver particle of about 1000 Å diameter, while the observed effects would require the transfer of thousands of Ca atoms from the interior to the surface of the Ag particle.

However as noted above, the etching–ESCA studies suggest that Ca, being in excess of its solubility limit, is not dissolved in Ag but is present as oxide or hydroxide inclusions or layers within the Ag particle. Two possible mechanisms of Ca atom transport can be suggested:

(1) CaO is reduced by γ-rays and Ca atoms diffuse through a thin layer about 10-atoms thick to the surface. This is only possible if the grain boundaries are present because at room temperature the volume diffusion coefficient is too small to account for transfer of Ca even through a layer as thin as ten atomic diameters. However, the existence of the grain boundaries in the particles as small as ours may be put in doubt.

(2) A multiple ionization mechanism similar in spirit to that put forth by Varley (*3*, *4*) may be responsible for the phenomenon observed. For the chief effect of γ absorption is ionization of atoms within the irradiated target. In metals this ionization does not produce a lasting effect by reason of high electronic conductivity; consequently, ionized atoms cannot maintain a positive charge for a period greater than about 10^{-13} sec, a time required for ejection via repulsive Coulomb forces. But, in an insulator oxide cluster of quite low conductivity, the impinging photons can produce multiply ionized cations and anions of sufficient lifetime to allow their ejection.

The oxide particles within our Ag particles probably do not contain more than about 10^3–10^4 atoms, hence the electrons arising from ionization are transferred to the surrounding metal phase to form eventually a negatively charged oxide–metal interface. Ca and O are ejected via Coulomb repulsion, that energy even for modest ionization greatly exceeding 25 eV, the *threshold* energy for Frenkel pair formation. The ejected ions will, of course, acquire electrons in their course through the metal. They can nevertheless penetrate some 10–50 atomic layers of silver and so come to rest upon the Ag particle surface where they are fixed via chemisorption of oxygen. It should be noted that the repulsive ejection mechanism requires clusters of the oxide, so that several neighboring ions have to be further ionized simultaneously, possibly by the same photon.

Whatever may be the precise mechanism of Ca migration to the Ag surface, its surface presence as a result of irradiation and heating (we do not necessarily suppose that a reacting atmosphere is necessary) is a fact. The observed spheroidization may then be attributed to surface Ca which causes higher rates of surface diffusion of Ag and thus spheroidization at a rate far greater than that which could be actuated by self-diffusion.

A comment should be made about disappearance of Ca from the catalyst surface after heating in hydrogen at 280–300°C. The authors do not wish to suggest that calcium oxide or hydroxide was actually reduced to metal. It seems that the oxide was converted into hydride and as such diffused into silver. The oxygen present in metal is sufficient to recreate calcium oxide particles of essentially the same size as those existing there before irradiation–reduction treatment. Thus the phenomenon of reappearance of Ca on Ag particle surface upon reirradiation appears reversible.

CONCLUSIONS

γ-irradiation followed by heating is accompanied by spheriodization of the supported silver catalyst particles, an event paralleled by γ-ray induced appearance of Ca upon the Ag surface, as judged by ESCA. Evidence (etching–ESCA) suggests an original Ca oxide or hydroxide phase dispersed within the Ag phase. It would seem that ionization of the included oxide phase causes energetic ejection of the Ca into Ag and thence to its surface. This γ-induced surface chemistry change accounts for the observed spheroidization of the silver particles.

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