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Influence of Metal Crystallite Size and Morphology on Selectivity and Activity of Ethylene Oxidation Catalyzed by Supported Silver

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The kinetic effects of total surface area, average silver crystallite size, and silver crystallite morphology of supported silver catalysts were investigated under ethylene oxidation conditions. Catalysts were prepared by impregnation of α-alumina with silver nitrate solution followed by drying, reduction, and calcination. They were characterized as to total surface area (0.02–3.03 m^2/g) by the BET method, average silver crystallite size (300–7400 Å) by selective oxygen chemisorption and X-ray diffraction line broadening, and silver crystallite morphology by scanning electron microscopy. The specific activity and selectivity of the catalysts were found to be strong functions of the total surface area. The specific rates to ethylene oxide and to carbon dioxide and water formation exhibited strong structure sensivity with minimum rates at silver crystallite sizes in the range of 500–700 Å. The changes in specific activity and selectivity appeared to be related to changes in the morphology as well as the size of the silver crystallites.

INTRODUCTION

Silver is unique among metals in its ability to promote the epoxidation of ethylene to ethylene oxide in preference to the complete oxidation to carbon dioxide and water. Much empirical effort and a smaller amount of scientific work have brought the technology of this catalyst to such a stage of development that appreciable amounts of ethylene oxide can be obtained with selectivities as high as 75%.

In addition to its industrial importance, this catalytic system involves many phenomena of fundamental interest and challenging scientific questions. Of fundamental interest is the uniqueness of silver to promote selectively the epoxidation reaction. Attempts to define the particular characteristic of silver which enhances this selectivity in contrast to the other substances which have been investigated remain in the realm of hypothesis and speculation. Another aspect of considerable catalytic importance is the adsorption characteristics of the reactants on the catalyst surface. The nature of the adsorbed oxygen species which participates in the reactions seems to direct the route of the reaction, and, thus, the selectivity of the catalyst. Another long-standing question has been whether ethylene participates in the reactions directly from the gas phase or from a weakly adsorbed phase.

Studies concerned with the effects of structural and geometric factors on the performance of supported silver catalysts include investigation of the effects of the carrier (*1, 2*), of silver-crystallite orientation (*3–5*), of alloying (*5–7*), and of additives (*8–11*) on the specific activity and selectivity of silver catalysts under ethylene oxidation conditions. The results of these and other studies are summarized and discussed in a number of reviews (*12–14*).

The influence of surface structure on the catalytic activity and selectivity of supported silver catalysts has been reported by Presland *et al.* (*15*) and by Wu and Harriott

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(*16*). The latter authors, using catalysts with average silver crystallites between 20 and 500 Å, observed that both specific rates (epoxidation and complete oxidation) decrease with increasing crystallite size while the selectivity increases.

The present study was undertaken to investigate the effects of certain structural factors on the specific catalytic activity and selectivity of supported silver catalysts under ethylene-oxidation conditions. The effects of total surface area of the catalysts, silver crystallite size, and silver crystallite morphology were experimentally obtained and related to theories concerning the fundamentals of this catalytic system.

EXPERIMENTAL METHODS AND TECHNIQUES

Catalysts used in this study were prepared by impregnation of α-alumina supports in an excess silver nitrate solution. During impregnation the solution with suspended alumina was vigorously stirred, and the temperature was controlled at 80°C. After removal of the impregnating solution by decantation, the catalysts were dried slowly at 50°C, washed with deionized water, dried again, and then reduced in flowing hydrogen at 200°C for approximately 3 days.

Portions from each batch of catalysts thus prepared were sintered at various temperatures (400–850°C) and for various periods of time to obtain series of catalysts having the same total surface area and silver content, but differing in the metallic silver surface area and in the average size of the silver crystallites. The supports employed were of high-purity α-alumina of low surface area. They were either commercially obtained (Norton, SA-5202-Series 100; Carborundum, SAH7-99-Series 200; Coastal, MAG-99-Series 300; Alcoa, T-61-Series 400), or prepared in the laboratory (Series 500) from high-purity hydrated alumina obtained from Alcoa (C-331). Hydrated alumina is transformed to the α-alumina form when sintered over 1150°C (*17*).

Total surface areas were measured by argon adsorption at liquid nitrogen temperature, and free-metallic-silver surface area by selective chemisorption of oxygen. The chemisorption experiments were conducted in a constant volume ultra-high-vacuum apparatus at 200°C and at oxygen pressures between 0.1 and 10 mm Hg. Under these conditions oxygen monolayer coverage of the silver surface occurs, and the stoichiometry of the chemisorption corresponds to nearly one oxygen atom per silver surface atom (*18–20*). In order to obtain a reproducibly clean silver surface before characterization by chemisorption, the samples were subjected to the following treatment: degasing for 3 hr; treating with oxygen at 4 to 5 mm Hg for 5 hr; degasing for 1 to 2 hr; hydrogen reduction until no further uptake of hydrogen was observed upon introducing a new portion of gas; degasing for 10 hr. During this treatment the sample was maintained at 200°C.

The average size of the silver crystallites was obtained from the chemisorption data, assuming spherical particles, and by X-ray diffraction line broadening. An X-ray-source Geiger counter Siemens diffractometer employing copper k_α radiation at 40 kV and 18 mA was used. A nickel filter was employed to filter out k_β radiation. The goniometer was operated with a scanning speed of $\frac{1}{8}$ degree per minute. A proportional type detector was used at 1722 V with a count rate of 500. High-precision divergence and receiving slits were used. The true X-ray diffraction pattern was obtained using Warren's correction for instrumental broadening (*21*). A sample from each series of catalysts was sintered at a high temperature to obtain silver crystallites larger than 1000 Å, and these samples were used as a standard for each series of catalysts.

The properties of the catalysts used in this study are summarized in Table 1.

Specific reaction rates were obtained us-

TABLE 1

Catalysts Prepared and Their Properties

Catalyst number	Sintering		Silver (wt%)	Sg (m^2/g cat.)	Sm (m^2 Ag/g cat.)	*dc* Å	*dx* Å
	Temp. (°C)	Time (hr)					
100	—	—	13.92	0.63	0.62	1280	—
101	400	16	13.92	0.63	0.56	1410	—
102	500	24	13.92	0.63	0.48	1660	—
200	—	—	5.60	0.97	0.59	546	512
201	400	18	5.60	0.97	0.46	695	682
202	500	25	5.60	0.97	0.41	780	734
203	600	12	5.60	0.97	0.32	1000	—
204	700	27	5.60	0.97	0.26	1216	—
300	—	—	1.01	0.20	0.16	358	336
301	400	17	1.01	0.20	0.14	425	442
302	480	25	1.01	0.20	0.12	469	472
303	600	9	1.01	0.20	0.11	530	517
304	750	70	1.01	0.20	0.09	588	612
500	—	—	6.43	3.03	1.20	305	281
501	410	6.5	6.43	3.03	0.85	431	428
502	510	15	6.43	3.03	0.49	754	706
503	700	15	6.43	3.03	0.34	1083	—
504	850	24	6.43	3.03	0.30	1231	—

ing a bench-scale apparatus which included a tubular, plug-flow, differential reactor, immersed in a constant-temperature bath. The catalyst bed was diluted with two parts of inert alumina to one part of the catalyst particles in order to obtain a nearly isothermal temperature profile along the length of the reactor.

Catalyst particle sizes and feed-gas flow rates were such that external and internal diffusion effects would not be expected. Maximum particle size and minimum flow rate were determined experimentally. In addition, calculations from an empirical correlation (*22*) showed that residence-time–distribution effects had been eliminated.

The reaction rates were obtained from the analysis of the product mixture by treating the reactor as differential. This assumption was justified by the low conversions that were measured. Gas chromatographic analysis of the product mixture was done using a thermal conductivity detector operated isothermally at 130°C. A Porapak-Q column was employed, and helium was used as the carrier gas.

The experiments were conducted at temperatures between 180 and 240°C, at an elevated pressure (approximately 15 atm) in order to approximate conditions of industrial practice. Three different feed compositions were employed: Composition A consisting of 3% ethylene and 15% oxygen; Composition B consisting of 6% ethylene and 6% oxygen; and Composition C consisting of 6% ethylene and 10% oxygen. Nitrogen was used as the diluent.

Catalyst deactivation was studied in preliminary experiments up to 30 hr in duration. Measurements made within such time periods indicated no observable deactivation. The maximum variation in such measurements was ±4%. Similar reproducibility was obtained for rate measurements made to ascertain that internal and external diffusional artifacts were absent. Each data point plotted in this paper is the average of at least three assays made after the flow-reactor system had reached steady state,

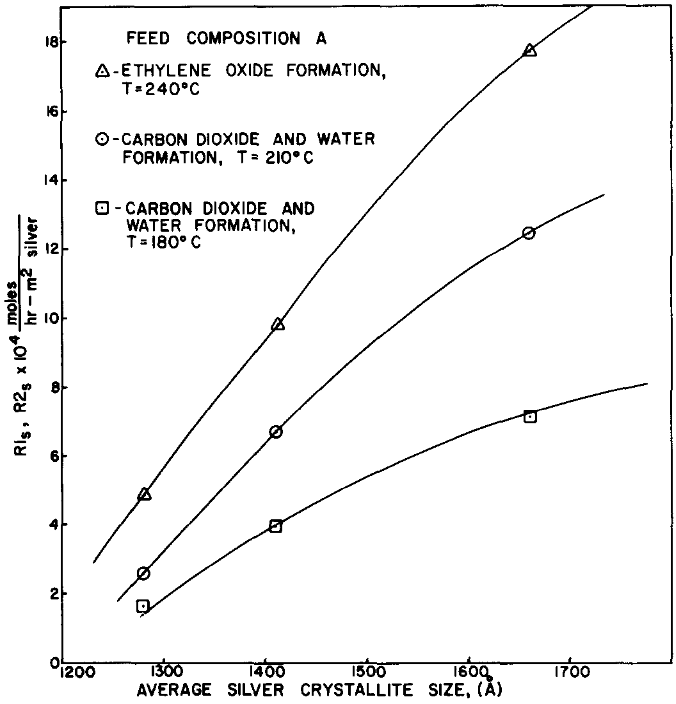

FIG. 1. Effects of silver crystallite size on the specific activity; catalyst #100 series.

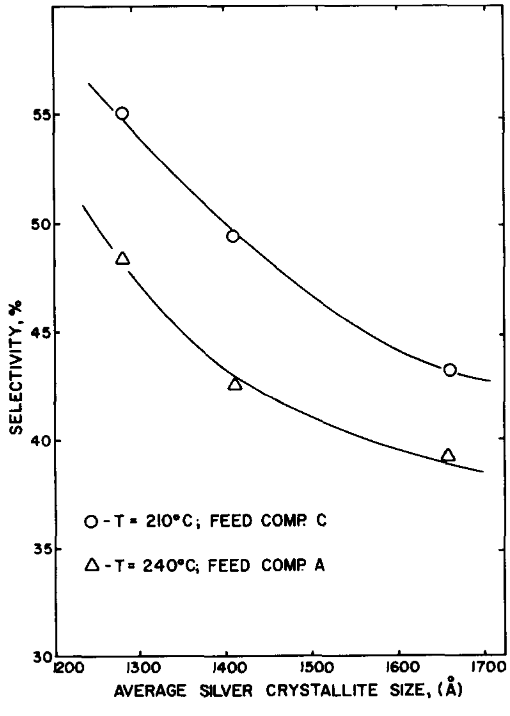

FIG. 2. Effects of silver crystallite size on selectivity; catalyst #100 series.

and at intervals of about 30 min. Maximum variation in such measurements was less than ±3%. The dissertation (*29*) upon which this paper is based, contains further details.

The reproducibility for different samples of the same catalyst was not checked experimentally but if one assumes measurement errors of 5% in surface area, 1% in flow rate, 1% in pressure and temperature control to ±0.5°C then one computes a corresponding error in the final computed rates of about ±6%.

RESULTS

The performance of the various catalysts depends not only on the specific reaction rates of epoxidation but also on the total oxidation rate. These specific rates, or turnover numbers (expressed per square meter of silver surface), can be strongly affected by sintering of the metal crystallites which can change the extent of the metal surface exposed.

The dependence of activity and selectivity on mean silver crytallite size is shown in Fig. 1 where $R1_S$ is specific rate of epoxidation and $R2_S$ is specific rate of complete oxidation. Figure 1 shows that both specific rates increase with increasing average silver crystallite size for the 100 series of catalysts. The results shown in Fig. 1 should not be extrapolated to smaller crystallite sizes for which no data are available for this series of catalyst [Series 100, $S_g \approx 0.6$]. Based on analogy with results for other series of catalysts, there is some reason to believe that the activity trends shown in Fig. 1 might be expected to show minima (and not simply zero activity) at a particle size of about 1000 Å. Further discussion of this point is given later in this section. The specific rate of the complete combustion reaction increases with crystallite size more rapidly than that of epoxidation; this decrease in epoxidation selectivity with increasing silver crystallite size is shown in Fig. 2 for the 100 catalyst series. Figure 2 also shows that selectivity toward ethylene oxide formation is higher for the lower temperature, a trend which was observed for all temperatures and catalysts tested. This behavior indicates that the activation energy of the epoxidation reaction is lower than that of the complete oxidation reaction as has been reported previously (*14*).

A peculiar dependence of the specific rates upon the average size of the silver crystallites is shown in Fig. 3 for the 200 series of catalysts. Both specific rates initially decrease with increasing silver crystallite size, go through a minimum at an average crystallite size of approximately 700 Å, and then increase again at larger crystallite sizes. The corresponding selectivity of this series of catalysts increases with increasing silver crystallite size, as shown in Fig. 4.

The catalysts of the 300 series were sintered under an atmosphere of nitrogen in order to retard rapid growth of the silver crystallites. Figure 5 shows that with this series both specific rates decrease with increasing silver crystallite size over a size range of about 350–600 Å. The selectivity of this series of catalysts was found to increase with increasing silver crystallite size.

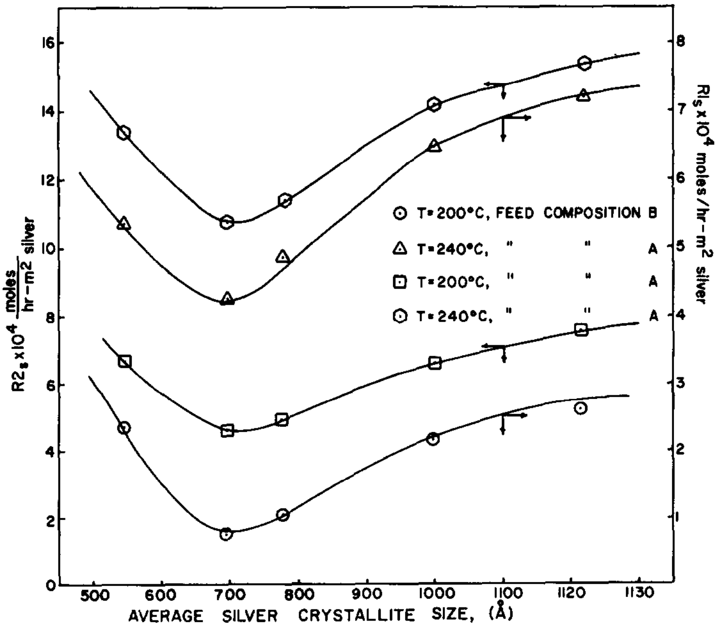

FIG. 3. Effects of silver crystallite size on the specific activity; catalyst #200 series.

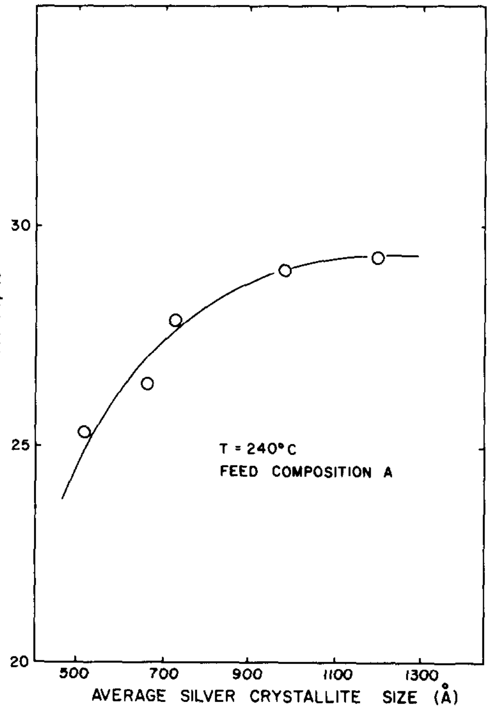

FIG. 4. Effects of silver crystallite size on selectivity; catalyst #200 series.

Results of the 500 series (shown in Fig. 6) indicate the same type of dependence of specific rates upon silver crystallite size as was observed with the 200 series. Both specific rates for the 500 series exhibit minima at an average silver crystallite size of approximately 500 Å.

Activity minima with respect to crystallite size are evident in Figs. 3 and 6 for the 200 series and 500 series. This suggests that such minima might also be observable for the 100 series (Fig. 1), if the corresponding data were available. The results of Figs. 3 and 6 suggest that the location of the minima may be correlated with S_g^{-1}, approximately (minima at 700 Å for $S_g \approx 1$ and at 500 Å for $S_g \approx 3$ m^2/g). Assuming that the 100 series of Fig. 1 also conforms to this trend would suggest corresponding minima at about 1000 Å for the results shown in Fig. 1.

The influence of total surface area on activity (shown in Figs. 8 and 9) indicates different behavior when the silver crystallites are small (~400 Å) in contrast to the larger sizes (600, 1000, and 1250 Å). The epoxidation turnover number (Fig. 7) for the small 400 Å crystallites may be somewhat more sensitive to the total surface area of the support but the trends appear similar. Figure 8, however, shows quite the opposite trend of turnover number for total

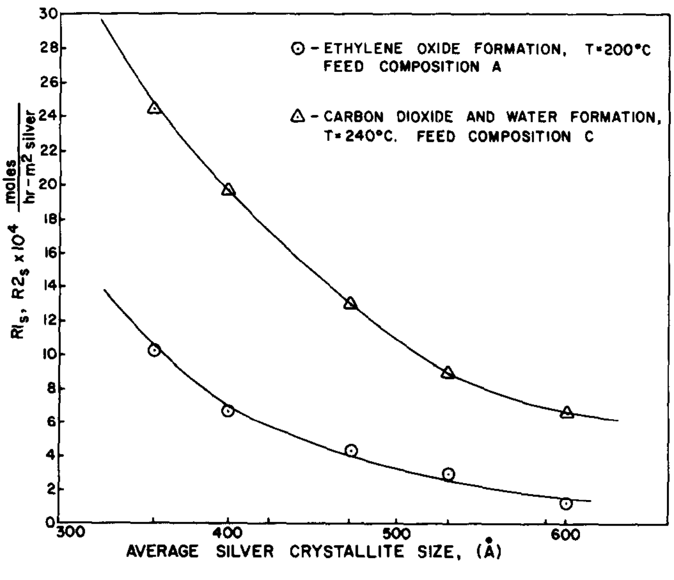

FIG. 5. Effects of silver crystallite size on the specific activity; catalyst #300 series.

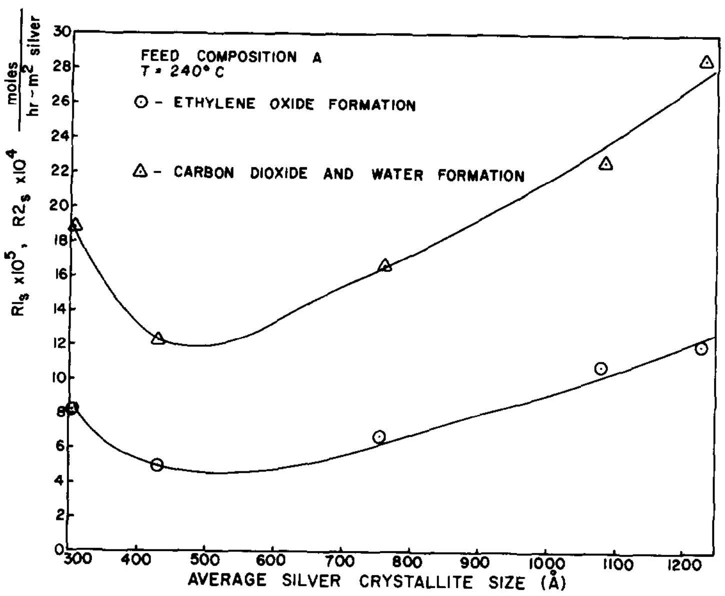

FIG. 6 Effects of silver crystallite size on the specific rate; catalyst #500 series.

combustion which seems to decrease with support area when the metal crystallites are small (400 Å) but to increase with support surface area when the metal crystallites are larger (600, 1000, and 1250 Å). Nevertheless, in spite of these contrasts, Fig. 9 shows that epoxidation selectivity follows a similar pattern of decrease with increasing support area for either 400 or 600 Å mean metal crystallite size; similar trends would be evident if the selectivities for 1000 and

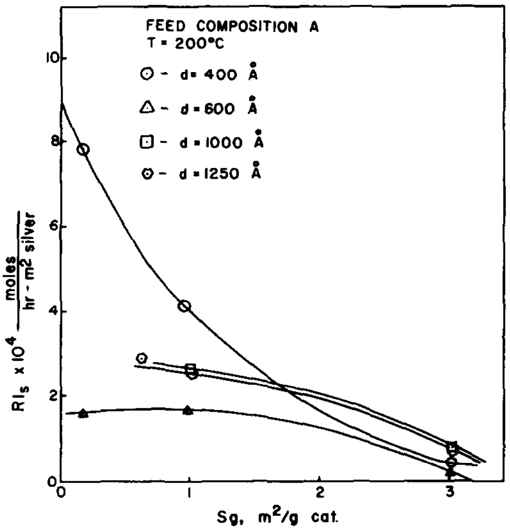

FIG. 7. Effects of total surface area on the specific rate to ethylene oxide.

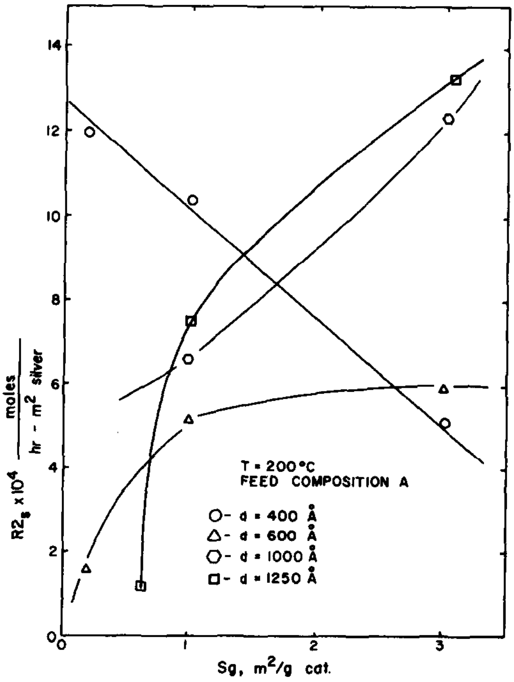

FIG. 8. Effects of total surface area on the specific rate to carbon dioxide and water.

1250 Å were also plotted in Fig. 9. The behavior pattern of Fig. 9 agrees with results reported previously (*13*). By way of caution it should be pointed out here that the 400 Å data on Figs. 7, 8, and 9 have been obtained by extrapolating results for the series 200 catalyst. Also the data for 1250 Å on Figs. 7 and 8 have been obtained by interpolation between two crystallite sizes and a temperature correction using the Arrhenius relationship.

DISCUSSION AND CONCLUSIONS

The particle size of supported metal crystals, also known as the degree of dispersion of the metal on the nonmetallic support, has been observed to play a significant role in certain heterogeneous catalytic reactions. Such reactions are called "structure sensitive" or "demanding" (*23, 24*) as opposed to "structure insensitive" or "facile" reactions for which the turnover number is not a function of the dispersion of the metal.

It would be expected that the oxidation of ethylene over silver catalysts is a structure sensitive reaction. The uniqueness of silver as a catalyst for ethylene epoxidation reaction as well as the sensitivity of this catalyst to pretreatment conditions (*14*) suggest that this reaction is "demanding." Indeed, structure sensitivity has been shown to be the case by Wu and Harriott (*16*) who measured specific activities for a series of catalysts having average silver crystallite sizes in the range of 20 to 500 Å. They observed that with increasing silver crystallite size, both specific rates decrease while the selectivity increases.

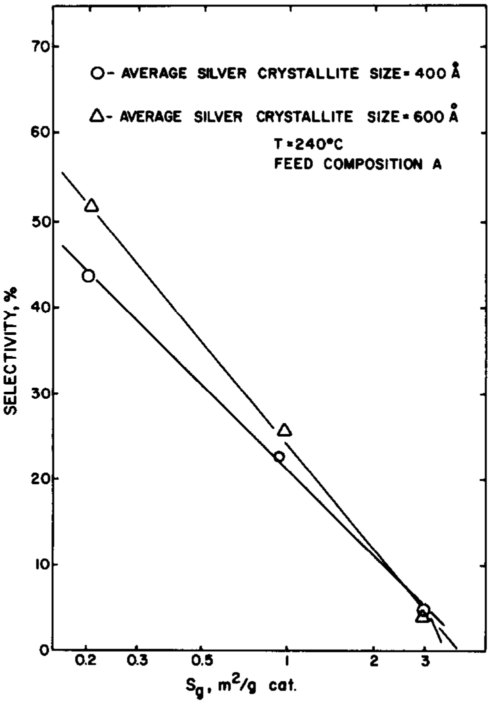

FIG. 9. Effects of total surface area on selectivity.

Beyond supporting the former conclusion that the oxidation of ethylene over supported silver is a structure sensitive reaction, the present results also show that the mode of this dependence changes when the average silver crystallites become larger than 500–700 Å.

To attempt an explanation for these crystallite size effects, we consider the processes which take place during the sintering of supported metal catalysts. When sintering reduces the surface area and increases the metal crystallites:

(1) The relative number of surface-to-bulk atoms and of surface-to-edge atoms decreases.

(2) Different crystallographic planes are exposed changing the coordination number of surface atoms.

(3) Imperfections can arise in the form of steps or kinks; defects can also be removed or destroyed by annealing.

(4) Changes in morphology of the metal particles can occur.

Crystallite size effects can be significant in small crystallites in which the surface atoms constitute a significant fraction of the total number of atoms in the crystal. Furthermore, edge and corner atoms constitute a significant fraction of the total number of surface atoms in small crystals (*18*). It is expected that edge and corner atoms exert different catalytic activities because they have a different coordination number than other surface atoms. Binding energies between surface atoms and between bulk atoms are different; for small crystallites such difference can be expected to depend on the size of the crystallites. These differences can influence the bonding energy with an adsorbed molecule and, therefore, affect the specific catalytic activity.

It is generally believed that if catalytic activity depends on crystallite size, then this dependency should be observable for crystals in the size range of 10 to 50 Å (*23, 25*). For crystals larger than this size the effects of edge and corner atoms would be overwhelmed by surface atoms in other positions. The same conclusion is supported by Fig. 10 in which the metal dispersion is plotted versus crystallite size. The calculation of dispersion was done for the face-centered-cubic crystalline structure of silver with a lattice parameter of 4.08 Å. It is apparent from Fig. 10 that the dispersion does not change appreciably for crystallite sizes greater than 100 Å.

We hypothesize that the changes in activity and selectivity with variations in crystallite size, as observed in this study, cannot be attributed only to variations in the degree of dispersion or to variations in the relative number of surface-to-bulk atoms and of surface-to-edge atoms. One would not expect such variations to be appreciable because the silver crystallites of the catalysts tested were all larger than approximately 300 Å.

Only ambiguous evidence seems to be available regarding the reactivity of the various crystallographic planes of silver in the oxidation of ethylene. The first to propose that crystallographic orientation affects the activity and selectivity of silver catalysts for the oxidation of ethylene were Orzechowski and MacCormak (*26*). Kummer (*3*) did not observe any effects of crystallographic orientation on the rates of either partial or complete oxidation of ethylene over single crystals of silver. It was later shown (*4*), however, that oriented silver crystals lose their orientation and rapidly recrystallize to a random orientation under reaction conditions.

We suggest, therefore, that it is not known whether different crystallographic planes of silver exhibit different catalytic activity toward the partial or the complete oxidation of ethylene. Reorganization of the metal which occurs during sintering might cause differences in the distribution of crystallographic planes, differences which might bring about variations in the activity and selectivity of silver catalysts. Because the equilibrium distribution of crystallographic planes of the catalysts was

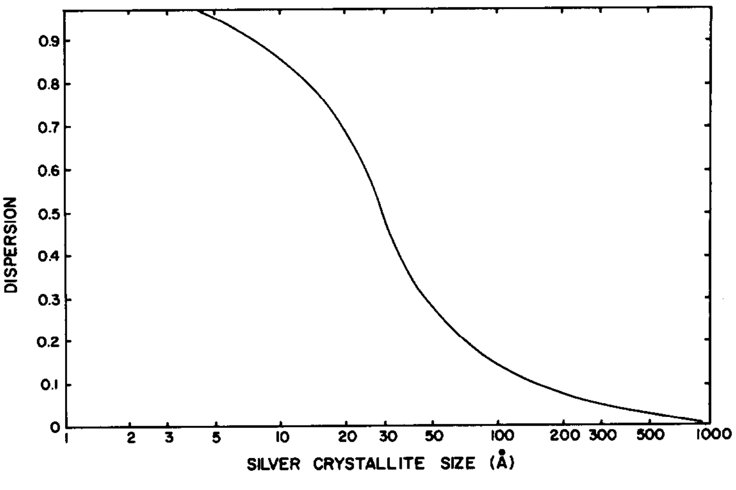

FIG. 10. Dispersion as a function of silver crystallite size.

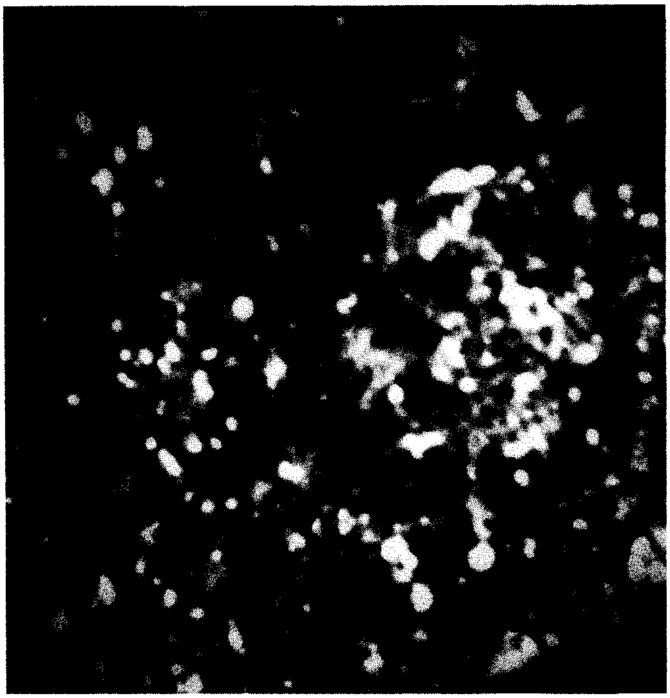

FIG. 11. SEM photograph of catalyst #500. ×4000.

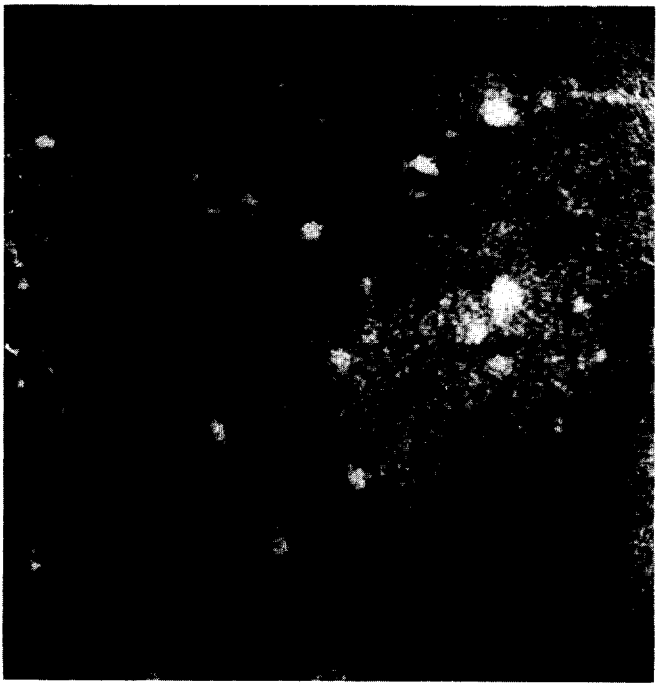

FIG. 12. SEM photograph of catalyst #501. ×4000.

not determined, this study can neither support nor exclude the possibility of crystallographic-orientation effects.

Sintering of supported silver catalysts could also introduce imperfections in the form of steps or kinks; the probability of finding a defect in the crystal increases with the size of the crystal (*27*). Woodward and co-workers (*5*), however, studied the effects of dislocations on the activity of silver catalysts for the oxidation of ethylene and concluded that dislocations do not act as active sites for the oxidation of ethylene. If their evidence is accepted, then the changes in activity and selectivity observed in this work with different sizes of silver crystallites cannot be attributed to changes in the dislocation density of the silver crystallites.

The question of morphology, or shape, of the metal particles and its effect on the activity and selectivity of supported metal catalysts has not received much attention. Astier *et al.* (*28*), however, did observe differences in catalytic activity between spherical and polyhedral particles of titanium dioxide (anatase) for the oxidation of carbon monoxide. Scanning electron photomicrographs of some of the catalysts used in the present study reveal the shapes and sizes of the silver crystallites very clearly as shown in Figs. 11–15. All of the pictures presented here are for the 500 series of catalysts.

Figure 11 shows catalyst number 500 as prepared (not sintered). The silver crystallites (the lighter spots) are small and spherical, as might be expected. Figure 12, a photomicrograph of catalyst number 501, which was sintered at 410°C for 6.5 hr, shows that the silver crystallites have grown larger, but have retained their sphericity. Figure 13 shows catalyst number 502, sintered at 510°C for 15 hr. As a result of this treatment, the silver crystallites have grown quite large and have began to lose their sphericity, although the spherical shape of the smaller particles is still discernable.

For catalyst number 503, which was sin-

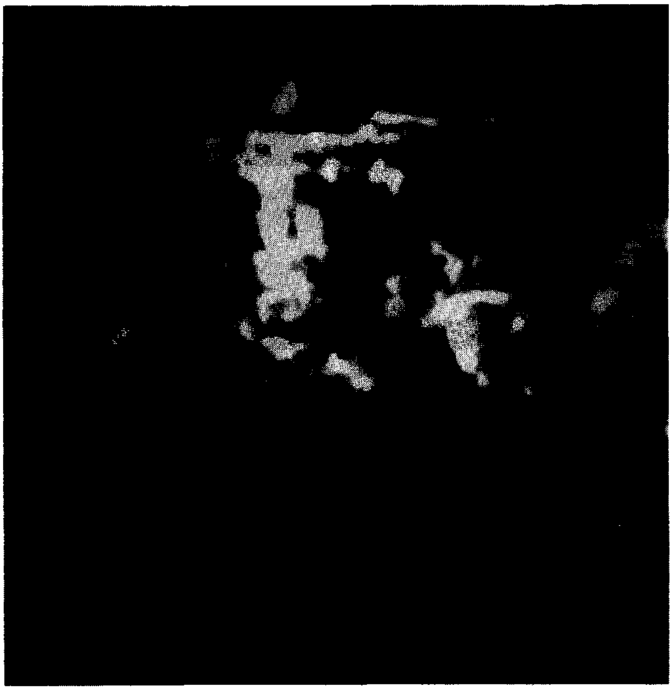

FIG. 13. SEM photograph of catalyst #502. ×4000.

FIG. 14. SEM photograph of catalyst #503. ×7200.

tered at 700°C for 15 hr, Fig. 14 clearly shows that some silver particles have grown to very large dimensions and have lost their sphericity. A dendritic type of formation seems to be present. For the most extensively sintered catalyst, number 504 (850°C for 24 hr), Fig. 15 shows the silver crystallites have not only lost their sphericity, but also have grown into particles of a decidedly dendritic morphology. These observations are summarized in Table 2.

The changes in morphology caused by sintering the catalysts may be associated with corresponding changes in the specific activity of the catalysts. A definite pattern in the relationship between the specific activity of the catalysts and the shape of the silver crystallites can be discerned. Comparing Figs. 6 and Figs. 11–15, reveals two trends:

(1) Specific activity decreases with increasing crystallite size so long as the silver crystallites are spherical in shape. This trend was also observed by Wu and Harriott (*16*).

(2) Specific activity tends to increase with crystallite size when the crystallites begin to lose their sphericity and develop dendritic formations.

It cannot be decided from the results of this study whether the increase in specific catalytic activity with crystallite size is due exclusively to changes in morphology of the silver crystallites, or whether changes in the distribution of crystallographic planes affects the specific activity of the catalysts. Nevertheless, morphology and crystallographic plane distribution are closely related, and such a distinction might neither be important nor real.

It should be recognized that the present study explores crystallite sizes larger than any previously reported to our knowledge, and gives evidence of trends different than previously reported for smaller sizes. That trends dependent on silver particle size seem to defy prediction may mean that as

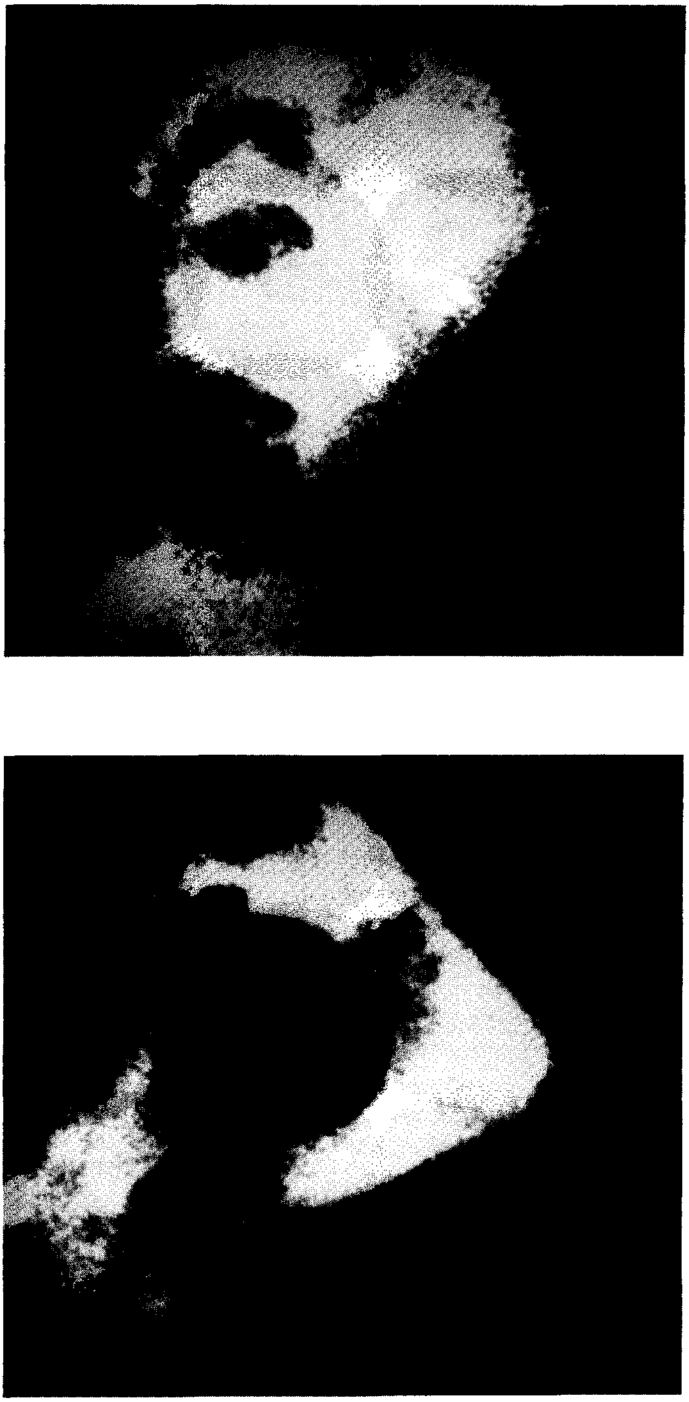

FIG. 15. SEM photographs of catalyst #504. ×16,000.

TABLE 2

Efects of Sintering on Size and Morphology of Silver Crystallites and Subsequent Effects on the Specific Reaction Rates

Catalyst number	Sintering Temp. (°C) Time (hr)	Silver crystallites	Tendency of specific rates
500	—	Small and spherical	
			Decrease
501	410/65.	Larger but spherical	
			Minimum
502	510/15	Mixture of small spherical and larger nonspherical	
			Increase
503	700/15	Very large nonspherical dendritic formation	
			Increase
504	850/24	Very large amorphous	

the particle size changes, other effects dependent on preparation, on metal–support interaction, or catalyst pretreatment may intrude. As will be reported in another paper (*30*) strong metal–support interactions occur in these catalysts; the extent and nature of such interactions may also change as metal particle size changes.

Another recent study (*31*) of ethylene epoxidation over silver supported on silica also investigated the influence of metal particle size over the range of 55–400 Å. In this work a maximum in epoxidation rates was observed at a particle size of about 175 Å and selectivity increased monotonically with particle size over the range studied. Although they indicate rather different trends in a lower particle size range, these results are not inconsistent with our own in the very few instances where the particle size ranges overlap; the fact that the support was different in each case, however, suggests no further comparison should be sought. Recent surface science studies (*32–34*) have shown that different crystal faces of silver exhibit different affinities for oxygen adsorption; this behavior combined with metal–support interaction effects and the other phenomena already mentioned may underlie the rather variable nature of reactivity dependence on silver particle size.

Our conclusions drawn from this study are summarized as follows:

(1) The partial and the complete oxidation of ethylene over supported silver catalysts are structure sensitive reactions. Specific catalytic activity as well as selectivity are strong functions of the size of the silver crystallites.

(2) Differences in the specific activity and selectivity of the catalysts seem to be associated with differences in morphology obtained by sintering.

(3) Different types of active centers exist on the surface of silver. The relative number and type of these centers changes with silver crystallite size and morphology to produce differences in the specific activity and selectivity of the catalysts.

(4) More than one surface atom is required in the rate-determining process of the reactions. If only one surface atom was required, then the specific activity of the catalyst would not be expected to change with the atomic structure of the surface. Changes in specific activity and selectivity with surface structure suggest participation of several adjacent surface atoms.

(5) The crystallite-size distribution could well be an important catalytic parameter. Metal crystallite sizes obtained by the usual experimental or calculational methods are merely average sizes; in all probability these averages do not adequately represent the real structure of the surface of the catalyst.

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