JOURNAL OF CATALYSIS 26, 313-317 (1972)

Particle Size Effects During the Sintering of Silver Oxidation Catalysts

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Received August 9, 1971

The activity of evaporated silver films used as model supported silver catalysts has been examined as a function of catalyst life during the oxidation of ethylene and of hydrogen. Electron optical examination of the surface shows that significant sintering of the metal occurs when the catalyst is exposed to oxygen at the temperatures of the reaction, and changes in catalytic activity are shown to be related to the reorganization of the metal. Particularly large changes in activity were noted as small particles of silver (<500 Å diameter) were removed by aggregation.

INTRODUCTION

Although supported metal catalysts are known to sinter under reaction conditions, comparatively few investigations of the process have been reported in the literature. In recent years, attention has been largely focused on supported platinum, in connection with its use as a reforming catalyst. Empirical equations have been shown to describe the process under particular experimental conditions (*1*), while Furuoya and Shirashaki (*2*) Echigoya, Furuoya and Morikawa (*3*) have shown by more careful investigation that sintering of platinum appears to involve at least two processes. One of these, the annealing of defects in the metal, occurred when the catalyst was heated, while the other, particle growth by surface migration, was catalyzed by the presence of oxygen.

Sintering may lead to decreases in activity beyond those expected from the observed decrease in metal surface area. Considerable evidence is available that the activity of many reactions depends on the degree of dispersion and the crystallinity of the catalyst (*4*, *5*) and there are some recent reports that particle size effects may be important in oxidation reactions (*6*). In this case any surface reorganization or metal agglomeration may have a significant effect on the activity of the reaction.

The present studies were initiated in order to study sintering effects during the oxidation of ethylene to ethylene oxide and of hydrogen to water over supported silver catalysts. Examination of the reorganization of the metal in the presence of individual reactants and products has shown that reorganization occurs only in the presence of oxygen (*7*), and it has been possible to quantify these effects in terms of a surface diffusion mechanism. The studies reported in the present paper are concerned with changes in activity that occur during the reaction.

EXPERIMENTAL METHODS

Evaporated 99.99% silver films deposited at 1.5×10^{-5} Torr on to clean 19 mm Pyrex circular discs were used throughout. The silver was deposited on the disc either through a copper gauze, 0.21 cm mesh of 0.04 cm diameter wire (shadowed catalyst), or through an aluminium plate drilled

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with 15 mm diameter holes (continuous catalyst). The area covered by silver was approximately 65 and 60%, respectively. The thickness of the deposit was measured by multiple beam interferometry from stepped samples prepared beside the specimen (ca. 1100 Å). The film was continuous within the squares of the shadowed catalyst.

The films were transferred through the air to a small Pyrex reactor closed by a conical greaseless glass seal in which catalytic oxidations were completed. The catalyst was separated one disc from another by short sections of 0.02 cm diameter silver wire and, for the oxidation of hydrogen, only one disc in five was coated with catalyst. A total of 62 discs could be fitted into the reactor. During a reaction, the temperature of the catalyst was maintained at 228°C to within ±0.05°C in a stirred air oven controlled by an A.E.I. RS4XVI temperature controller.

The catalytic activity for the oxidation of ethylene was measured using a 2:1 oxygen:ethylene flow. The flow rate of 45 ml min^{-1} corresponded to a residence time of 5 sec in the reactor, which was maintained at 228°C. The hydrogen:oxygen feed (2:1 vol ratio) was used at a total flow rate of 67.5 ml min^{-1}, corresponding to a residence time of 7.5 sec.

Mixtures of the fuel and oxygen in the chosen proportions were allowed to flow through the reactor for ca. 30 min: this did not affect the texture of the film nor the subsequent sintering in any way. The reaction was then started by lowering the reactor into the furnace while still maintaining the flow of gas. The products of reaction were analyzed by gas chromatography using a katharometer detector. Air, carbon dioxide, ethylene, water and ethylene oxide were separated on a Porapak Q column (4′:120°C), an alternative column of molecular sieve (8′:20°C) being used to separate the air peak where necessary.

The texture of the catalyst was examined at various stages of reaction using reflection scanning electron microscopy (s.e.m.) and transmission electron microscopy (t.e.m.); for this, the samples were coated with ca. 200 Å amorphous carbon by vacuum evaporation, and the metal was stripped from the pyrex disc. Washing and conventional copper grid mounting was then used to prepare the samples for examination. The interfacial area between the silver and the disc could be measured from transmission micrographs, using a "Quantimet" image-analyzing computer to give the percentage disc coverage.

The adsorption surface areas were measured using krypton at 78°K in an apparatus similar to that described by Aylmore and Jepson (*8*).

Results and Discussion

Surface areas and interfacial areas were measured for the continuous catalyst at the start of an experiment, and after various annealing times. Surface areas, obtained from 155 Pyrex circles, are summarized in Table 1, which shows that the films are essentially nonporous; the area available for gas adsorption is very close to the geometric area of the initial film.

The increase in area on annealing the films results from the development of hillocks on the top of the silver (7) and from the breakup of the film into islands. The increase in surface area is not large compared with the activity changes which occur at the same time (see below).

The activity of the catalyst for the oxidation of ethylene and of hydrogen was measured both with the continuous and the shadowed catalysts. The choice of reaction

TABLE 1

Surface and Interfacial Areas of the Catalysts[a]

Annealing time oxygen: 266°C (min)	Surface area (cm^2)[b] Continuous catalyst	Surface area (cm^2)[b] Shadowed catalyst	Interfacial area continuous catalyst %
0	805	776	56
6	1020	—	53
60	1090	1050	19

[a] Geometric area = 878 cm^2. Area covered by one krypton molecule taken as 19.5 Å^2.

[b] Accuracy ± 5%.

conditions, flow rates, etc., was governed by the results of Twigg (9) for ethylene, while a stoichiometric mixture with oxygen was used for hydrogen. For the oxidation of ethylene, the activity of the continuous catalyst was found to be substantially constant over a 5 hr period; if the film was annealed for several hours in oxygen at 410°C in order to produce an island structure (7) the activity was again constant, although at a lower level (Fig. 1). The final metal-support area of this sintered catalyst was found to be ca. 31% of the original.

Similar experiments carried out over a shadowed catalyst showed much greater effects. The initial activity was much higher than the continuous film, and the activity dropped off markedly with time (Fig. 1). In addition, the spectrum of products changed with usage, the amounts of ethylene oxide and of carbon dioxide passing through a distinctive maximum (Fig. 2). This pattern of activity was found not to be affected by pre-annealing in ethylene or in hydrogen at 228°C, nor by cooling from this temperature in oxygen. However, if the catalyst was pre-annealed in oxygen for a given time at the same pressure and temperature as the reaction, the catalytic activity varied as if that amount of reaction had occurred. The changes in activity observed were much higher than would be expected in terms of surface area changes of the metal.

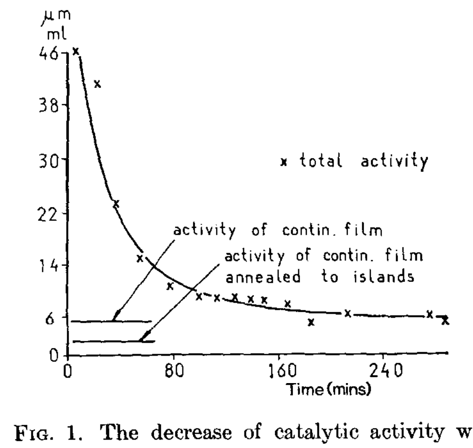

FIG. 1. The decrease of catalytic activity with time for the oxidation of ethylene: ethylene:oxygen, 2:1; (ordinate) conversion of ethylene; (abscissa) time; $T = 228°C$; residence time, 5 sec. Crosses correspond to the activity of the shadowed catalyst. Total activity = total products (µm ml^{-1}).

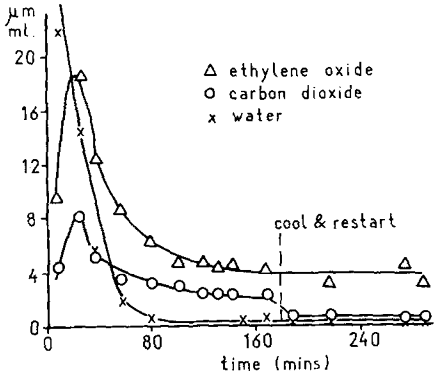

FIG. 2. The products of ethylene oxidation versus time: ethylene:oxygen, 2:1; (ordinate) products; (abscissa) time; $T = 228°C$; residence time, 5 sec.

The experiments were repeated for the oxidation of hydrogen. The results obtained, summarized in Fig. 3, show the activity–time pattern to be very similar to that obtained for ethylene. Again, the effect of pre-annealing in oxygen was found to duplicate the activity decrease due to reaction.

The morphology of the catalysts was then examined as a function of reaction time using both t.e.m. and s.e.m. Even at

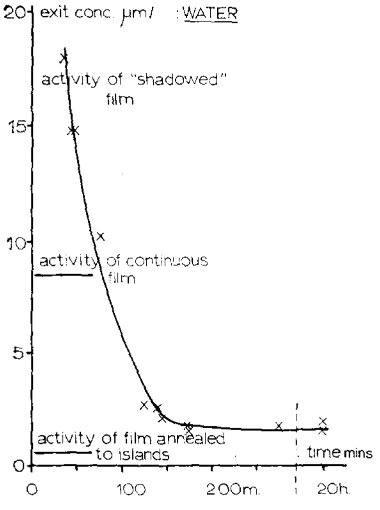

FIG. 3. The decrease of catalytic activity with time for the oxidation of hydrogen: hydrogen:oxygen, 2:1; $T = 228°C$; residence time, 7.5 sec.

low magnifications, it was possible to see that appreciable amounts of silver had migrated into the "shadow" area of the fresh grid-prepared catalyst. T.e.m. showed, in fact, that particles of 2000–100 Å diameter were present in the shadow, and s.e.m. examination showed a general distribution of material in the shadow, decreasing towards the channel center.

Annealing in hydrogen or ethylene had little effect on this structure, although the crystal size in the large squares of silver did tend to increase slowly. Heating in oxygen, or using the solid as a catalyst, had a marked effect on these smaller particles while leaving the larger squares very little changed. A typical result, obtained after 30 min heating in oxygen at 228°C, is shown in Fig. 5. S.e.m. and t.e.m. showed a complete loss from the channel center of islands having a diameter of less than 500 Å, apparently by aggregation into larger particles. Heating for longer times led gradually to the agglomeration of all the smaller particles into large islands, together with the break up of the larger squares, until the final sintered catalyst form was reached.

Large changes in activity seemed to be related with this disappearance of small particles. Figure 2, for example, shows that the amount of ethylene oxide passes through a pronounced and reproducible maximum when the catalyst had partially agglomerated (Fig. 5). Further, no appreciable changes in activity were observed once the smaller islands had agglomerated (ca. 80 min at the conditions associated with Fig. 2), and the activity changes with the continuous catalyst, where there was a very much smaller proportion of islands that could sinter, were very small.

There is little doubt that island aggregation during the initial stages of the reaction results from the presence of oxygen. The mobility of silver under these conditions has been reported elsewhere (7) and

FIG. 4. Silver as deposited in the shadow: no treatment; magnification ×22,000.

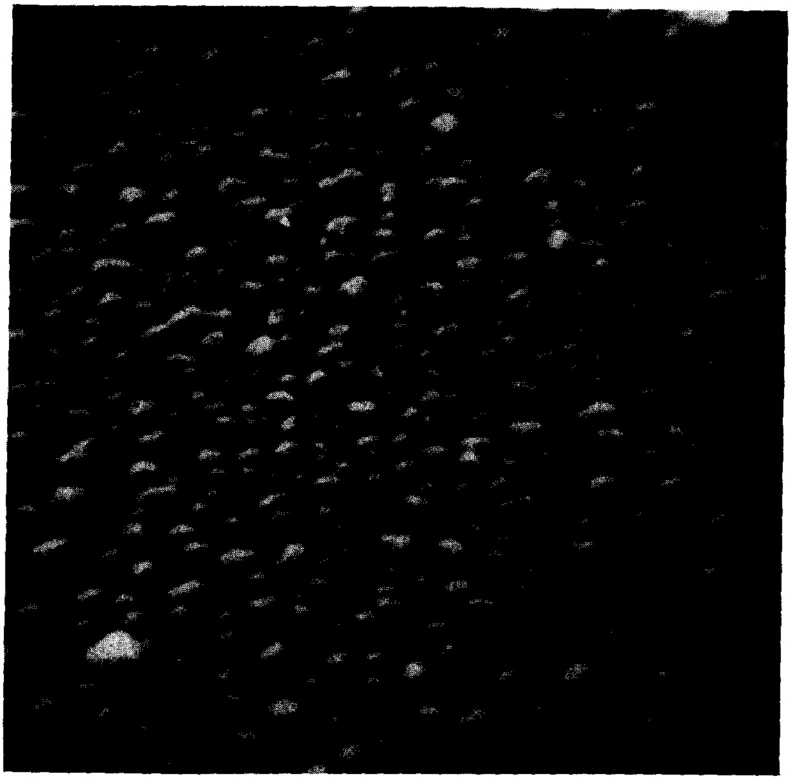

FIG. 5. Silver in the shadow after heating to 228°C for 30 min in oxygen; magnification ×22,000.

calculation of surface reorganization on this basis is in agreement with the results observed. The loss of activity with increasing particle size is in agreement with results reported by Harriott (*6*) although the selectivity of the reaction does not appear to change markedly (Fig. 2). It is not certain whether the maximum and the subsequent loss of activity results from rearrangement of facets which are highly active, from the aggregation of small particles, or whether a support-metal interaction, which would be favored by small particles of metal, is responsible for the high initial activity.

ACKNOWLEDGMENTS

The authors express their thanks to I.C.I. (Petrochemical and Polymer Laboratories) for financial support and to Dr. J. Dewing for valuable discussions. One of them (G.L.P.) is grateful for secondment from I.C.I. for the period of these studies.

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