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# Influence of Loading on Metal Surface Area for Ag/$\alpha$-$Al_2O_3$ Catalysts

ASTERIOS GAVRIILIDIS, BILAL SINNO, AND ARVIND VARMA[1]

*Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556*

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The silver surface area was determined quantitatively as a function of loading for Ag/$\alpha$-$Al_2O_3$ catalysts. This relationship was found to be nonlinear and was attributed to the fact that strong interactions between the metal precursor and the support do not exist. Selective chemisorption of oxygen using the dynamic pulse technique was employed to measure the silver surface area. Additional characterization of the catalysts was carried out using SEM and XRD analyses. The results have direct relevance for optimal catalyst distribution studies.

## INTRODUCTION

A wide class of catalytic materials are precious metals, so there is an economic incentive to utilize them efficaciously. This is one of the primary reasons for depositing catalysts in the form of small particles on high-surface-area porous supports. The increase of catalyst loading can have a pronounced effect on dispersion, depending on the preparation technique employed (*1*, *2*). Under reaction conditions, the performance of a catalyst pellet depends not only on the intrinsic reactivity of the active material, but also on difusion phenomena inside the porous support. The latter can result in significant concentration and temperature gradients within the pellet. When detrimental, these gradients are avoided by positioning the catalytic material on the surface of the pellet (*3*). However, when they are beneficial, one can take advantage of them by placing the catalyst at an appropriate location inside the pellet (*4*). Wu *et al.* (*5*) showed that for any catalyst performance index (i.e., conversion, selectivity or yield) and for the most general case of an arbitrary number of reactions, following arbitrary kinetics, occurring in a nonisothermal pellet, with finite external mass and heat transfer resistances, the optimal catalyst distribution is a Dirac-delta function. Physically, this means that the metal particles should be deposited radially in a zone of narrow width. The above result is valid when the catalyst dispersion does not depend on loading (i.e., the metal surface area varies linearly with loading) and there is no upper limit on the pellet loading. In practice, when the local loading becomes high, loss in dispersion occurs and it is desirable to broaden the catalytic zone. The optimal catalyst distribution can then be calculated numerically, if the dependence of metal surface area on loading is known (*6*). The present work is directed towards establishing this relationship for the Ag/$\alpha$-$Al_2O_3$ system.

Silver is unique in its ability to catalyze the ethylene epoxidation reaction, while $\alpha$-$Al_2O_3$ is the most commonly employed support (cf. *7*, *8*). Theoretical investigations of optimal catalyst distribution for ethylene epoxidation have shown that Dirac-type catalyst pellets have higher selectivity and yield than pellets in which the catalyst is distributed uniformly (*9*, *10*), and this has also been confirmed experimentally (*11*). For a complete analysis, it is necessary to take into account the dependence of silver surface area on loading. In this study, selec-

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[1] To whom correspondence should be addressed.

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tive oxygen chemisorption was employed to determine the silver surface area, and additional information was obtained using X-ray diffraction and scanning electron microscopy.

## EXPERIMENTAL

### *Catalyst Preparation*

The silver catalysts were prepared by impregnation of −325-mesh high-purity α-alumina powder, using a procedure similar to that of Klugherz and Harriott (*12*). Ten to 15 ml of lactic acid (85%, Fisher Scientific) was heated to 90°C. The appropriate amount of silver oxide (Fisher Scientific) and 0.4 ml hydrogen peroxide (15%, Aldrich) were then added to the continuously stirred solution. After the silver oxide dissolved completely, 5–10 g of Alcoa A-17 α-alumina powder (3 $m^2/g$) was added. The excess solution was evaporated, and the particles were dried at 220°C in air for 24 hr. In order to decompose the silver lactate, the catalyst was heated at 500°C under nitrogen for 5 hr. After cooling, it was subjected to two oxidation–reduction cycles at 350°C. Such treatment has previously been found to give reproducible oxygen adsorption behavior (*13*, *14*), and the catalyst thus obtained had stable long-term activity in ethylene epoxidation experiments (*11*). One cycle consisted of oxidizing the catalyst with a mixture of 20% oxygen in argon for 3 hr, flushing the system with nitrogen for 10 min, reducing it with a mixture of 20% hydrogen in argon for 3 hr, and flushing it again with nitrogen for 10 min. At the end of the second cycle, the catalyst was cooled to room temperature in nitrogen.

### *Atomic Absorption*

The loading of the catalysts was determined by atomic absorption spectroscopy. Silver was separated from the sample following a standard nitric acid leaching procedure (*15*). The solution which was used for atomic absorption measurements, contained about 5% nitric acid and 1–4 ppm Ag. This silver concentration range produced linear detector response in a Perkin–Elmer 2280 flame atomic absorption spectrophotometer. Calibration standards were prepared from a 1000 ppm silver reference solution (Fisher Scientific).

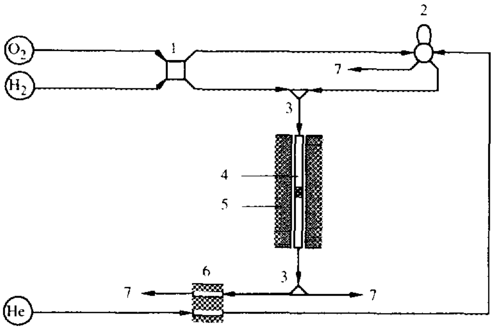

FIG. 1. Schematic diagram of the selective chemisorption setup: (1) four-way valve, (2) sampling valve, (3) three-way valve, (4) quartz tube, (5) furnace, (6) thermal conductivity detector, and (7) exhaust.

### *Chemisorption*

The silver surface area was determined by selective chemisorption of oxygen, in a pulse chemisorption apparatus according to the procedure described by Lemaitre *et al.* (*16*). A schematic of the apparatus is shown in Fig. 1. The carrier gas helium (Linde, UHP grade) was passed through copper turnings heated at 600°C in order to remove traces of oxygen (*17*). An indicating oxygen trap (Alltech) followed. The adsorbing gas was oxygen (Linde, Zero grade), or a mixture of 10% oxygen in helium (Linde, Primary grade), for catalysts with low silver loading. Both the carrier and the adsorbing gas, passed through glass tubes containing 5A molecular sieve (J & W Scientific) for removing traces of water and hydrocarbon impurities. In order to ensure that no particles escaped these traps, gas filters with openings of 7 μm were used. Needle micrometering valves permitted adjustment of the flowrates, which were typically 60 ml/min for the carrier and 3 ml/min for the adsorbing gas. The catalyst sample was placed in a quartz tube equipped with a thermowell and kept at the desired temperature by a split furnace (Lindberg). Pulses of oxygen were sent to the catalyst using a Valco sampling valve, having a 15-μl sampling loop. The average pressure in this loop was 3 psig. A Gow-Mac 10-077 thermal conductivity detector with WX filaments, along with a Gow-Mac 40-001 power supply, were used for the detection of unadsorbed oxygen pulses.

Prior to a chemisorption experiment the catalyst was treated with oxygen for 2 hr at 200°C, flushed with helium for 10 min, reduced with hydrogen for 2 hr at 200°C, and again flushed with helium for 10 min. The above treatment was utilized not only for removing organic contaminants before chemisorption, but also for minimizing complications due to adsorbed subsurface oxygen. This type of oxygen adsorbs ca. 150°C and does not desorb at temperatures lower than 450°C (*18, 19*), while hydrogen reduction at the temperature range used in the experiments removes only oxygen chemisorbed on the surface (*14, 20, 21*). After this pretreatment, the actual chemisorption experiment was performed. Reproducibility of the results was checked by performing at least three consecutive chemisorption experiments. The chemisorbed oxygen from the previous experiment was removed with hydrogen reduction for 15 min at 200°C, followed by helium flushing for 15 min. The experiments were performed at 200°C, because at this temperature oxygen monolayer coverage of silver occurs, and the stoichiometry of chemisorption corresponds nearly to one oxygen atom per surface silver atom (*22, 23*). A site density of $1.15 \times 10^{15}$ $Ag_s$ cm$^{-2}$ (*24*) was used to calculate the silver surface area.

### *X-ray Diffraction*

X-ray diffraction was also used to characterize the silver particle size. The catalytic powder diffraction patterns were obtained by a Diano/600660-G007 automated diffractometer with Cu*K*α radiation. The peak for Ag(220) at $2\theta = 64.5°$ was used for the line-

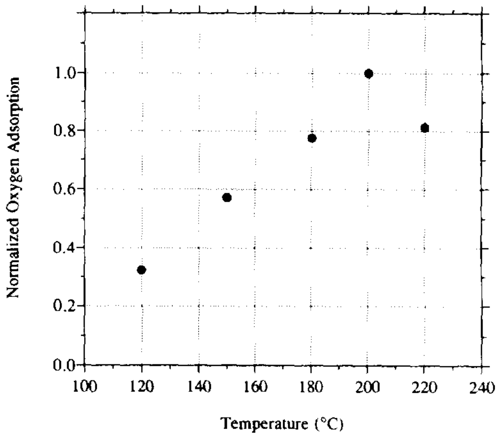

FIG. 2. Effect of temperature on oxygen adsorption. Catalyst loading: 14.3 wt% Ag.

broadening calculations because it did not interfere with the α-alumina peaks. Silver crystallite sizes were estimated using the Scherrer equation, $d = 0.9\ \lambda/B \cos\theta$, with Warren's correction, $B = (B_M^2 - B_I^2)^{0.5}$ where $\lambda = 1.542$ Å for the Cu*K*α source. $B_M$ is the peak width at one-half maximum intensity and $B_I$ is the instrumental broadening.

### *Scanning Electron Microscopy*

Scanning electron micrographs were taken using an ISI 60A scanning electron microscope, equipped with a Robinson detector. The signal obtained was differentiated, so that the contour and the shape of silver crystallites became clearer. This image processing technique also rendered the images two-dimensional.

## RESULTS AND DISCUSSION

A series of experiments were conducted, in order to investigate the effect of temperature on the amount of oxygen chemisorbed. The results are shown in Fig. 2, where the amount of oxygen adsorbed is normalized with respect to its maximum value. A maximum is observed at 200°C, in good agreement with previous investigations (*23, 25, 26*). The reproducibility of oxygen ad-

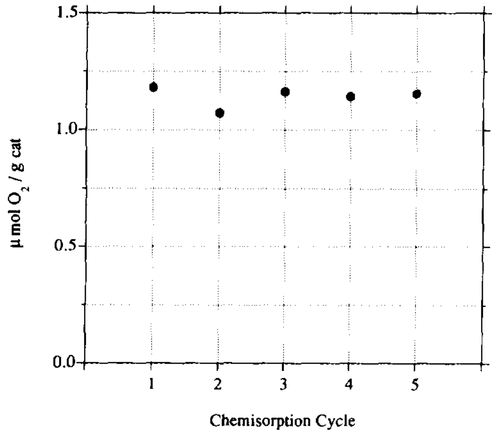

FIG. 3. Amount of oxygen adsorbed in successive chemisorption cycles. Catalyst loading: 24.7 wt% Ag.

sorption was good, as shown in Fig. 3 for five successive chemisorption cycles on the same catalyst. Reversible oxygen adsorption was also observed, in accordance with previous chemisorption studies (*14*, *26*). The technique utilized did not allow quantitative determination, but it may be noted that the amount of reversible adsorbed oxygen was small as compared to chemisorbed oxygen.

From X-ray diffraction line broadening, crystallite sizes were calculated to be between 30 and 135 nm, for the range of loadings investigated. The corresponding sizes obtained by chemisorption varied from 400 to 1350 nm, assuming that the particles were hemispherical. The difference in size obtained by the two techniques was larger at higher loadings. Similar behavior has also been observed previously in studies of Ag/$\alpha$-$Al_2O_3$ catalysts (cf. *21*) and arises mainly due to the low sensitivity of the line broadening technique to large crystallites. Scanning electron micrographs of selected catalysts are shown in Fig. 4. It is clear that for higher silver loadings a broader particle size distribution exists, which contributes to the above noted difference between the two techniques. Since X-ray diffraction is less sensitive to large silver particles, the results are indicative of the size of small silver particles and therefore provide a good estimate to the low end of particle size distribution, in agreement with SEM micrographs. On the other hand, the size of larger particles present in the micrographs appears to be in good agreement with the particle size predicted from chemisorption experiments.

The results of the oxygen chemisorption experiments are summarized in Fig. 5, for silver loading varying from 1 to 53 wt%. It may be seen that the surface area does not increase linearly with loading. For this reason, we need a parametric dependence of the silver surface area $S$ ($m^2$ Ag/g catalyst) on its weight fraction $C$ (g Ag/g catalyst), which is capable of representing the deviation from linearity. A reasonable choice is (*6*)

$$S = \frac{pC}{1 + bC}, \qquad (1)$$

where $p$ is the specific surface area of silver (i.e., silver surface area/silver weight) and $b$ is a constant (catalyst pellet weight/silver weight) which indicates the deviation from linear behavior. The experimental data are represented well by a value of $p = 0.66$ ($m^2$ Ag/g Ag) and $b = 1.06$ (g catalyst/g Ag), which correspond to the solid line shown in Fig. 5. From the above value of $p$, it is calculated that the average size of particles would be 860 nm if there were no loss in dispersion with increasing loading. In this case the behavior would be represented by a theoretical limit line for $b = 0$, which is also shown in the figure. This situation would be realized if newly added active metal leads to the formation of new particles, substantially of the same dimension as the previous ones (*2*). Since the experimentally obtained curve lies below this theoretical limit curve, it is concluded that by increasing loading the silver contributes to the growth of crystallites, as is also evident from the SEM micrographs.

It should be noted that $\alpha$-alumina is an inert support, and does not interact strongly with the impregnating solution (*27*, *28*). If

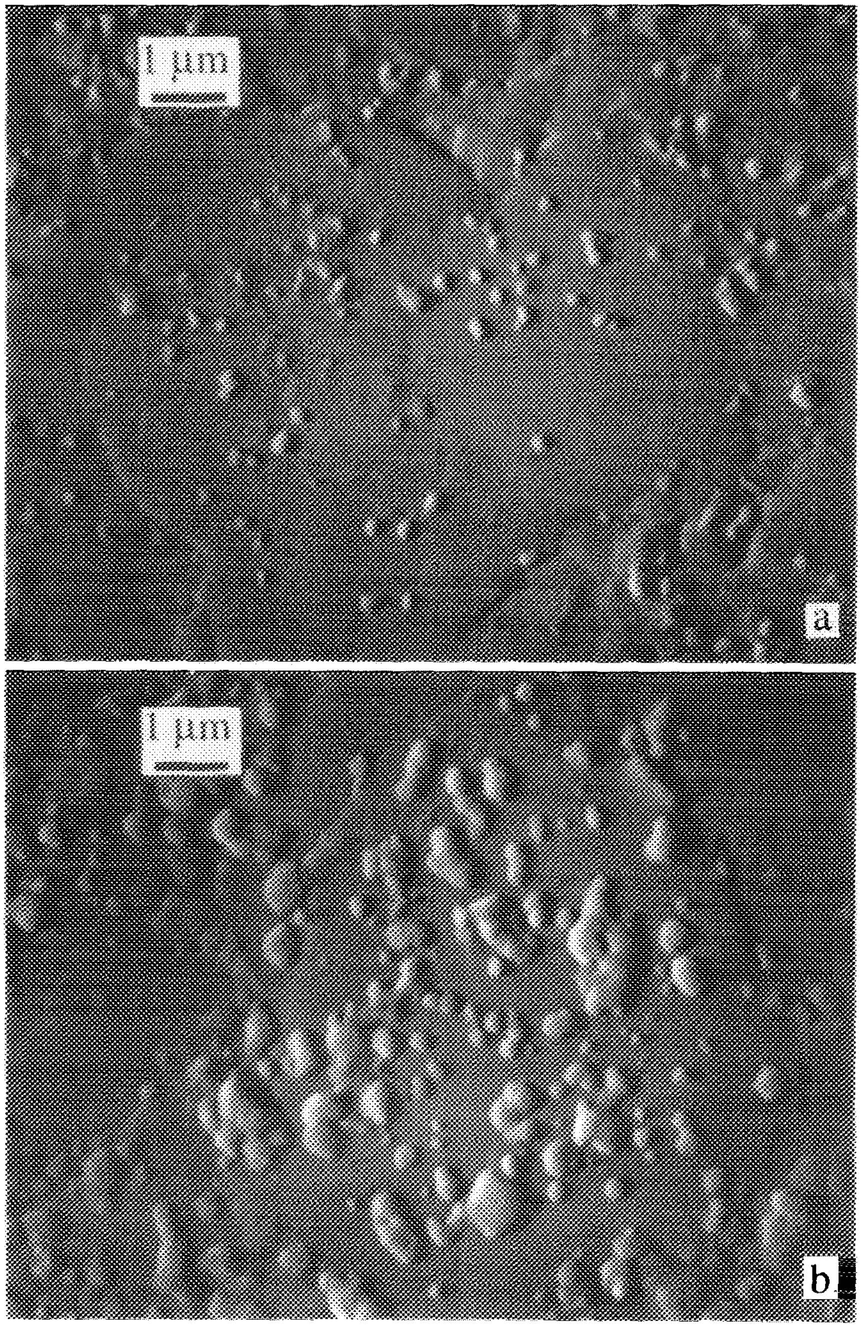

FIG. 4. Scanning electron micrographs (10,000×) of (a) 6.2 wt% Ag and (b) 33.8 wt% Ag catalysts.

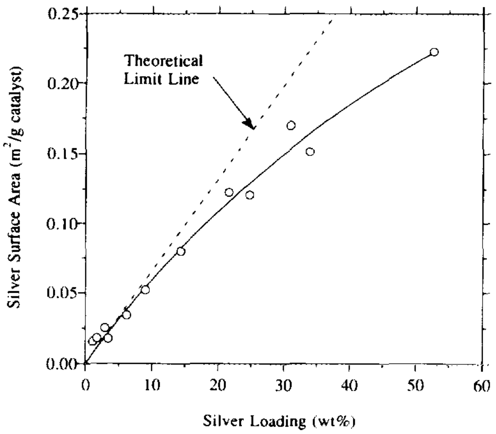

FIG. 5. Effect of loading on silver surface area.

during impregnation the metal precursor does not fix on the surface of the support, it deposits according to a process of crystallization and precipitation during the drying step. In such cases, the size of the crystallites is relatively large and depends on a number of factors such as support texture, precursor solubility and drying velocity (*29*). Seyedmonir *et al.* (*30*) found that the dispersion of an 18 wt% Ag/$\alpha$-$Al_2O_3$ catalyst was 0.0012, which compares very well with our results (see Fig. 6). The same investigators also prepared silver catalysts using supports that interacted strongly with the precursor solution, such as $SiO_2$ and $TiO_2$. In these cases catalysts with small crystallites (of the order of 4 nm) and high dispersions (up to 0.4) were obtained.

Cheng and Clearfield (*31*) studied the behavior of silver particles supported on zirconium phosphate. They increased the size of the crystallites in a manner similar to the present study, i.e., by increasing the catalyst loading. The crystallites formed were never larger than 100 nm, even at silver loadings as high as 53 wt%, while the particle sizes observed in the present study are an order of magnitude larger at similar loadings. The above behavior is consistent with the fact that zirconium phosphate has ion-exchange capabilities, therefore it interacts strongly with silver ions. Similarly for silica-supported platinum, when there is a strong interaction of the support with the precursor ions, as in the case of $Pt(NH_3)_4^{2+}$, a linear dependence of platinum surface area on loading is obtained. This dependence becomes nonlinear when relatively little interaction exists between platinum salt and silica, a situation encountered when platinum exists as the anion $PtCl_6^{2-}$ (*1, 2*).

An interesting feature of our system is illustrated in Fig. 6, where the catalyst dispersion as a function of loading is shown. The decrease of catalyst dispersion with increase of silver loading is more dramatic at low loadings (<5 wt%) when the crystallites are relatively small. At higher loadings, the rate of dispersion decrease is significantly lower. In this context, it is important to note that significant mobility of silver crystallites exists at the calcination temperatures used (350–500°C). Silver, which has a Tamman temperature of 480°C and a Huttig temperature of 320°C, should sinter above ca. 350°C (*32*). Indeed, Ruckenstein and Lee (*33*), studying the behavior of model Ag/$Al_2O_3$ catalysts under oxygen and hydrogen atmospheres in the temperature range 250–400°C, observed significant crystallite migration and coalescence. This, along with the fact that the rate of coalescence is proportional to the number of metal crystallites

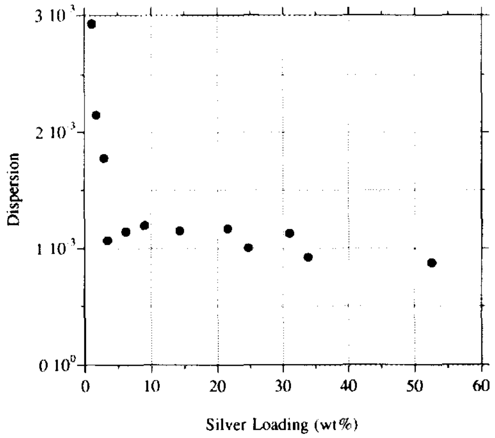

FIG. 6. Effect of loading on catalyst dispersion.

on the support (*34*), could explain the rapid loss of dispersion at low loadings. At high loadings, sintering of the larger silver crystallites would be hindered from mobility considerations. The smaller crystallites could still adhere to the larger ones, but the latter would not grow much in size. Certainly, more detailed studies of the preparation step, involving crystallite size measurements both prior to and after calcination are required in order to confirm these ideas.

## CONCLUDING REMARKS

The dependence of silver surface area on loading for Ag/$\alpha$-$Al_2O_3$ catalysts was established quantitatively. It was found to be nonlinear, which could be attributed to the fact that there were no strong interactions of the metal precursor with the support. The results obtained will be important for optimal catalyst distribution studies, for the ethylene epoxidation reaction where silver is a unique catalyst.

## ACKNOWLEDGMENTS

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