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Characterization of Supported Silver Catalysts

III. Effects of Support, Pretreatment, and Gaseous Environment on the Dispersion of Ag

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Small Ag crystallites at low loadings on certain supports appear to be quite resistant to sintering under a variety of gas environments. The metal fraction exposed (dispersion) of such crystallites on η-Al_2O_3, SiO_2, and TiO_2 was monitored using oxygen chemisorption and H_2 titration methods before and after exposure to He, H_2, and O_2 (3 and 10%) at 673 K as a function of time, and effects of various pretreatments on adsorption behavior were examined. Selected samples were also characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Exposures to O_2 up to 16 hr at 673 K caused only small decreases (20–30%) in the dispersion of η-Al_2O_3-supported silver, virtually no change for the TiO_2-supported silver, while a substantial increase in Ag surface area occurred for SiO_2-supported Ag. The Ag surface area of the 1.89% Ag/η-Al_2O_3 catalyst treated in H_2 for 16 hr at 673 K showed no change when monitored by the H_2 titration method, whereas heating in He under the same experimental conditions decreased the silver dispersion by approximately 15%. The 1.81% Ag/TiO_2 showed virtually no change in Ag metal surface area after similar treatments in either H_2 or He. Although heating in H_2 did not cause any change in dispersion, some reduction of the TiO_2 support occurred. Because of irreversible adsorption of oxygen by the reduced TiO_2 support and complications attributed to "subsurface" or "bulk" oxygen formation in some sintered samples, the H_2 titration of the chemisorbed surface oxygen provides a more accurate method than the O_2 chemisorption method alone for monitoring the dispersion of these catalysts.

INTRODUCTION

The standard industrial process to produce ethylene oxide involves the partial oxidation of ethylene over supported silver catalysts. However, one of the problems associated with these silver catalysts is deactivation brought about by loss of metal surface area due to sintering under reaction conditions. The exothermic nature of this reaction causes a significant increase in the local temperature of the catalyst which, along with the existing gaseous components, especially O_2, can cause drastic changes in the state of the catalyst and help to agglomerate metal crystallites. Therefore, maximizing and stabilizing the degree of dispersion (fraction exposed) of a supported Ag catalyst is both of scientific interest and technological importance. Although several processes, among them treatment with oxygen (and chlorine), have been found to redisperse some metals such as Pt on a support (*1*, *2*), a similar redispersion technique does not exist for supported Ag catalysts. Therefore, preparation of supported catalysts with stable metal surface area and prolonged service life along with satisfactory activity and selectivity is of greater importance with silver.

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Oxygen chemisorption has been the usual technique to measure silver surface area because other gases such as CO and H_2 do not adsorb on reduced Ag surfaces to a significant degree so as to provide monolayer coverage. However, one of the common problems with the adsorption of oxygen on silver is the formation of "bulk" or "subsurface" oxygen, especially with larger Ag crystallites, which complicates the measurement of the true metal surface area, and a more reliable and rapid monitoring technique would be desirable. Recently we have shown that H_2 titration of chemisorbed oxygen on supported Ag crystallites is an alternative technique, and it appears to be a preferred method for measuring the Ag surface area in these catalysts (*3–5*). This paper describes the application of this technique, along with O_2 chemisorption, transmission electron microscopy (TEM), and X-ray diffraction (XRD) to determine changes in Ag surface areas versus time of well-dispersed catalysts heated at 673 K under controlled He, H_2, and O_2 atmospheres.

EXPERIMENTAL

Materials. The catalysts used—1.33% Ag/SiO_2, 1.89% Ag/η-Al_2O_3, and 1.81% Ag/TiO_2 (silver metal loadings in wt%)—were prepared by impregnation of the supports with an aqueous solution of $AgNO_3$ (Aldrich Co.) using an incipient wetness technique (*6*). The η-Al_2O_3 support was obtained from Exxon Research and Engineering Company and had been prepared by the calcination in air of Davison β-alumina trihydrate for 4 hr at 863 K, and the final powder product had a reported BET surface area of 245 m^2g^{-1} (*7, 8*). With the exception of this η-Al_2O_3, the SiO_2 (Davison, grade 57, 220 m^2g^{-1}, mesh $\leq$ 40), and TiO_2 (P-25 from Degussa Co., 50 m^2g^{-1}) were pretreated in a flow of dry O_2 at 723 K for 2 hr to remove any organic contamination prior to impregnation. Silver loadings were determined by plasma emission spectroscopy or neutron activation analysis at the Dow Chemical Company.

Before their use, hydrogen (Airco or MG Scientific, 99.999%) was passed through a tube containing 5A molecular sieve (Supelco, Inc.), helium (Airco or MG Scientific, 99.9999%) was passed through an Oxytrap (Alltech Assoc.), and oxygen (Airco, 99.997% and MG Scientific, 99.999%) was passed through a drying tube (Supelco, Inc.).

Apparatus. The adsorption and sintering studies were conducted in a grease-free, high-vacuum system constructed of stainless-steel and Pyrex which provided an ultimate vacuum below 10^{-8} Torr (1 Torr = 133 Pa) near the pump and 10^{-7} Torr in the manifold farthest from the pump. Pressure readings in the adsorption manifold during isotherm measurements were made using a Texas Instruments Model 145 pressure gage. Gas flow rates during pretreatment and sintering were controlled by micrometering valves (Hoke, Inc.) and flow rates were measured by Teledyne-Hastings Raydist mass flow meters. A Tylan Model FC-260 mass flow controller was also used for oxygen in some experiments. Heating rates and temperature control were obtained using a Theal Engineering temperature programmer/controller and furnace. The temperature of the catalyst cell was also monitored by a Doric 412A digital indicator. The catalyst cells could be isolated from the atmosphere by Ace Glass stopcocks with FETFE O-rings at each end, and they were attached to the adsorption system by spherical joints using Buna N O-rings. During sintering experiments five of these catalyst cells were attached to the system by a glass union with five radially oriented joints, an arrangement which allowed all five sample cells to be placed in one furnace, to be held at the same temperature and to have approximately equal gas flow rates through each cell. The procedure and apparatus for TEM and XRD measurements have been described previously (*4, 5*).

Procedure. The pretreatment procedures used in this study have been described in

TABLE 1

Pretreatment Procedures for Ag Catalysts[a]

Pretreatment A

1. Reduce at 443 K in flowing hydrogen for 2.5 hr
2. Evacuate, then flow oxygen through system for 10 min at 443 K
3. Evacuate, then flow hydrogen through system for 15 min at 443 K
4. Measure isotherms at 443 K

Pretreatment B

1. Reduce at 573 K in flowing hydrogen for 3 hr
2. Evacuate for 1 hr at 573 K, then cool under vacuum to 443 K
3. Measure isotherms at 443 K

Pretreatment C

1. Reduce at 573 K in flowing hydrogen for 2.5 hr
2. Evacuate, cool, then flow oxygen through the system for 10 min at 443 K
3. Evacuate, then flow hydrogen through the system for 15 min at 443 K
4. Measure isotherms at 443 K

[a] 1 atm of pure gas used at a flow rate of 20 cm^3 min^{-1}.

detail previously (*3–5*) and are summarized in Table 1. All adsorption isotherms were measured at 443 K over a typical range of 30 to 200 Torr. Any reversible O_2 adsorption was determined by evacuating the sample for 20 min at 443 K after the O_2 isotherm, then repeating the O_2 adsorption experiment. Irreversibly adsorbed oxygen was obtained from the difference of these two isotherms. Hydrogen titration measurements were made after an identical evacuation step. Corrections for physical adsorption on the catalyst were easily made by extrapolating the linear isotherms to zero pressure, as is routinely done. Uptake values were also determined by curve fitting (linear regression) of the data points and correlation factors were routinely above 0.99. The agreement between the two methods was excellent in most cases.

All sintering runs were conducted at 673 K, and the variables examined were type of gas environment (He, H_2, or O_2), sintering time (1–16 hr) and oxygen partial pressure (2–3 and 10% in He). For each sintering environment, five separate, fresh catalyst samples weighing between 0.15 and 0.5 g were simultaneously placed in the furnace with a gas flow of approximately 50 cm^3/min (STP) passing through each cell at atmospheric pressure. The only exceptions to this were the 0.1 atm oxygen (10% O_2 in He) sintering experiments where the gas flow rate through each cell was approximately 20 cm^3/min for η-Al_2O_3- and 35 cm^3/min for TiO_2-supported catalysts. Prior to sintering studies, samples were given one of the pretreatments listed in Table 1. After the pretreatment, the system was flushed with helium flowing at 50 cm^3/min per cell for 15 min, then the samples were heated to the sintering temperature of 673 K at a rate of 10 K/min in flowing He. Then, either helium was continued for the set of runs conducted under helium or a switch to an identical flow rate of hydrogen was made for the runs conducted under hydrogen (in some H_2 sintering experiments H_2 was introduced after the last step of the pretreatment, evacuation, without He flush) or the appropriate flow rate of oxygen was introduced to provide partial pressures of 0.02, 0.03, or 0.1 atm of O_2 in He.

The catalyst samples were removed at 1-, 2-, 4-, 8-, and 16-hr intervals, with these samples being designated as t_1, t_2, t_4, t_8, and t_{16}, respectively (the initially reduced, nonsintered samples are designated as t_0). After the appropriate exposure time for each sample, the stopcocks at the inlet and outlet of the adsorption cell were closed which isolated the sample from exposure to the atmosphere when removed. After careful removal of each sample from the system, the connection joint was quickly capped and the gas flow rate in the system was then reduced to maintain a constant flow rate of 50 cm^3/min through each sample cell. After removal, the isolated sample cells were stored in a glove bag under dry N_2 until further analysis. Sintered samples were analyzed by O_2 chemisorption and/or H_2 titration methods without being exposed to air, with the exception of the 1.89% Ag/η-Al_2O_3

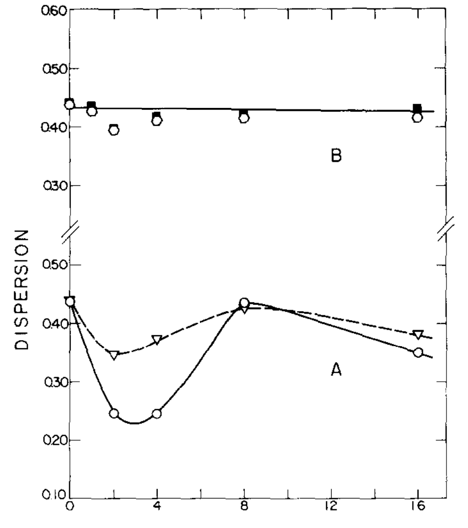

FIG. 1. Dispersion (O/Ag or H_2/Ag) versus time for 1.81% Ag/TiO_2 in He at 673 K. Sintered samples were (A) given evacuation only, ○—based on O_2 uptake; ▽—based on H_2 titration. (B) Given pretreatment C; ○—based on O_2 uptake; ■—based on H_2 titration.

catalysts which were very briefly (few seconds) exposed to the atmosphere during connection of the sample cells to the adsorption system. Blank sintering runs with TiO_2 and Al_2O_3 supports alone were also carried out under conditions similar to those used for the catalyst samples.

RESULTS

Heating under He. The influence of heat treatment in an "inert" gas atmosphere on the dispersion of supported silver catalysts was examined first in order to establish a base-case comparison to reactive gases such as O_2 and H_2. Figure 1 shows the variations in apparent Ag dispersion of the 1.81% Ag/TiO_2 catalyst after treatment in He at 673 K as a function of time. Dispersions were calculated by dividing the number of irreversibly chemisorbed O atoms by the total number of Ag atoms, i.e., assuming an adsorption stoichiometry of $O_a/Ag_s = 1$ in agreement with previous work (*9, 10*), or assuming an $(H_2)_{titr}/Ag_s$ ratio of 1 based on the stoichiometry of the H_2 titration reaction: $Ag_s - O_a + H_2(g) \rightarrow Ag_s + H_2O_{(ads)}$ (*3–5*). The uptake values and dispersions for the t_0 (nonsintered) samples in all cases were calculated based on the average value of several chemisorption measurements. Gas uptake values on the TiO_2 support alone after similar blank sintering experiments in He were very near zero. Adsorption measurements on each sample (except t_1) of the 1.81% Ag/TiO_2 catalyst heated in He at 673 K were made after two different pretreatments. First, the sintered samples (without exposure to atmosphere) were evacuated at 443 K for 30 min and then characterized by O_2 chemisorption and H_2 titration measurements. These same samples were then given pretreatment C and identical chemisorption experiments were conducted. Both the slopes and the intercepts of the adsorption isotherms for sintered samples were very similar to those of nonsintered samples (*3–5*).

The O_2 uptake values determined after evacuation decreased significantly only after 2 and 4 hr of sintering, as indicated by the t_2 and t_4 samples, whereas the H_2 titration values showed a much smaller decrease. As a consequence, the apparent dispersion values based on these uptakes show a minimum after 2–4 hr of sintering time, as shown in Fig. 1A. Although all adsorbed oxygen was irreversibly held on the other sintered samples, with these two catalysts small amounts (1–3 μmole/g cat) of reversibly held oxygen occurred. More importantly, a stoichiometry very near 2.0 existed between $(H_2)_{titr}$ and $(O_2)_{irrev}$ values for all samples except t_2 and t_4, which had larger values near 3.0. However, after these samples were given pretreatment C they all had O_2 uptake values which were very similar to that of the nonsintered sample (t_0) and all showed an $(H_2)_{titr}/(O_2)_{irrev}$ titration stoichiometry very near 2.0 as indicated by the excellent agreement in Fig. 1B. Although dispersion appears to vary noticeably and a 15–20% decrease in Ag dispersion is indicated in Fig. 1A after 16 hr of sintering, the results in Fig. 1B indicate virtually no

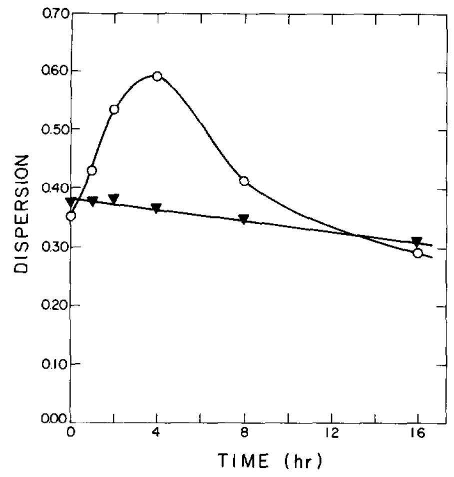

FIG. 2. Dispersion versus time for 1.89% Ag/η-Al_2O_3 in He at 673 K. O—based on O_2 uptake; ▼—based on H_2 titration. All heated samples (except t_1 for which pretreatment A was used) were given pretreatment C.

change within experimental error in the Ag dispersion. XRD patterns of 1.81% Ag/TiO_2 before and after the 16-hr heating in He were almost identical to those of the pure TiO_2, and no Ag peaks could be clearly identified.

Some intriguing behavior was observed for the 1.89% Ag/η-Al_2O_3 catalyst treated in He at 673 K. All sintered samples in this case were given pretreatment C before the chemisorption measurements. A significant increase in total oxygen uptake occurred for samples t_1–t_8 with a maximum uptake occurring after 4 hr of sintering (t_4) as shown in Fig. 2. Although $(O_2)_{rev}$ values were not determined for these sintered samples, they are expected to be near zero (*4*). Titration measurements were very well behaved, however, and clearly indicated that not all the adsorbed oxygen was reactive to hydrogen. The enhanced O_2 uptake, which inferred an apparent increase in dispersion, was not observed after the 16-hr treatment, and at this point a decrease of about 15% in Ag dispersion occurred. It is important to emphasize that for all sintered samples, dispersion values calculated based on the H_2 titration values showed more predictable behavior, i.e., a small monotonous decrease as shown in Fig. 2. Because no $(H_2)_{ads}$ values were determined, $(H_2)_{tot}$ values were used without correction; however, these residual surface coverages of hydrogen are very low and introduce little error (*3–5*). Adsorption isotherms obtained for sintered samples were linear with somewhat steeper slopes compared to nonsintered (t_0) samples of 1.89% Ag/η-Al_2O_3 (*3, 4*). Irreversible gas uptakes on the η-Al_2O_3 support alone were zero after similar sintering experiments. Except for the initial and final samples (t_0 and t_{16}), which had a titration stoichiometry very near 2.0, all other sintered 1.89% Ag/η-Al_2O_3 catalysts showed values smaller than 2.0 (~1.5).

The particle size distribution for the t_{16} sample of 1.89% Ag/Al_2O_3 sample calculated from TEM micrographs is shown in Fig. 3A, and it is in good agreement with the average particle size calculated from the chemisorption data. The particle size distribution did not change significantly from one sample (t_0) to another (t_{16}). Although no distinct XRD peaks were observed for the nonsintered (t_0) 1.89% Ag/η-Al_2O_3 sample, all sintered samples showed occasional weak peaks or shoulders due to the Ag phase which overlapped severely with peaks due to the η-Al_2O_3 support, and this difficulty prevented the determination of an unambiguous average particle size.

Heating under H_2. Similar sintering experiments were conducted in H_2 using fresh samples of the 1.81% Ag/TiO_2 catalyst. Again, chemisorption measurements were made after only evacuation at 443 K and then repeated after pretreatment C. Figure 4A shows changes in the apparent dispersion of Ag under H_2 as a function of time. The amounts of irreversibly chemisorbed oxygen increased significantly on all heated samples, and indicated an apparent 40% increase in Ag dispersion; however, all the $(H_2)_{titr}$ values for the sintered samples were similar and almost the same as that of the nonsintered (t_0) sample, and dispersions based on this adsorption technique were essentially constant with time, as shown in

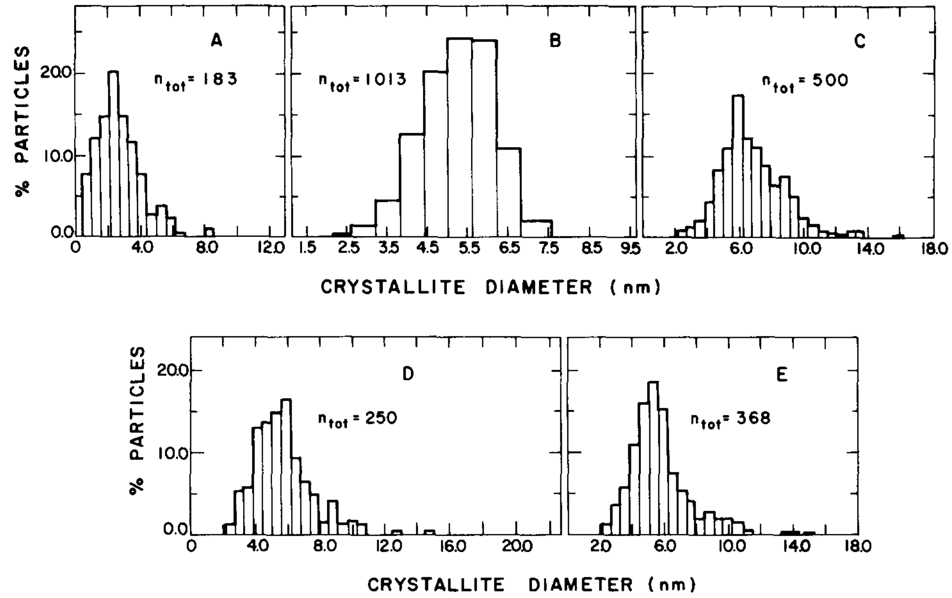

FIG. 3. TEM crystallite size distributions of 1.89% Ag/η-Al_2O_3 samples after heating at 673 K: (A) in He for 16 hr; (B) in H_2 for 4 hr; (C) in H_2 for 16 hr; (D) in 0.02 atm O_2 for 8 hr; (E) in 0.1 atm O_2 for 4 hr; n_{tot} represents total number of particles counted in each micrograph.

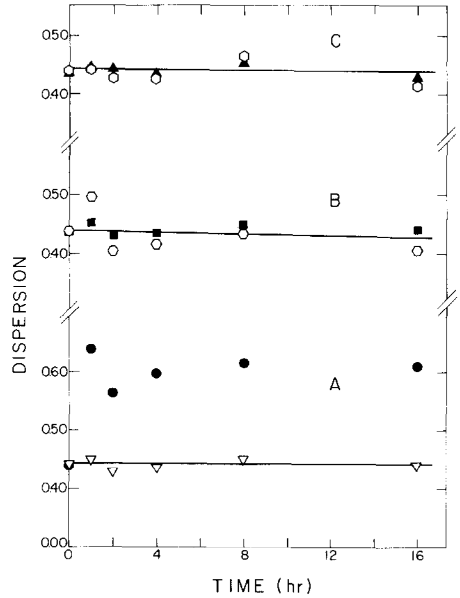

FIG. 4. Dispersion (O/Ag or H_2/Ag) versus time for 1.81% Ag/TiO_2 in H_2 at 673 K: Heated samples were: (A) given evacuation only; ●—based on O_2 uptake; ▽—based on H_2 titration; (B) same as (A) but corrected for O_2 adsorption on the reduced support (see Table 2); ○—based on O_2 uptake; ■—based on H_2 titration; (C) given pretreatment C; ○—based on O_2 uptake; ▲—based on H_2 titration.

Fig. 4A. No reversible oxygen adsorption occurred on these sintered samples, and a titration stoichiometry substantially lower than 2.0 (~1.5) was obtained on these sintered samples after using no pretreatment (only evacuation).

Similar sintering experiments with the TiO_2 alone revealed that some reduction of TiO_2 surfaces occurred in H_2 at 673 K, causing significant amounts of irreversible O_2 uptake at 443 K, as shown in Table 2, which also lists a representative set of uptake results. This chemisorbed oxygen on the reduced titania surface did not react with H_2 at 443 K. After correcting total oxygen uptakes for that on the TiO_2 surface, the adsorption values on the silver were similar and slightly lower than that on sample t_0 except for sample t_1, which had a somewhat higher O_2 uptake even after this correction, and the stoichiometries between $(H_2)_{titr}$ and corrected O_2 uptakes were now near 2.0. The dispersions based on these corrected O_2 uptakes and those from $(H_2)_{titr}$ values were then in close agreement, as shown in Fig. 4B. When these

TABLE 2

Adsorption at 443 K on 1.81% Ag/TiO_2 and TiO_2 after Heating in H_2[a]

Sample	Gas uptake (μmole/g cat)					Particle size from $(H_2)_{titr}$ (nm)
	$(O_2)_{irrev}$ (Total)	$(O_2)_{TiO_2}$[b]	$(O_2)_{irrev\,(Ag)}$[c]	$(H_2)_{titr}$	$\frac{(H_2)_{titr}}{(O_2)_{irrev\,(Ag)}}$	
t_0	36.0	0	36.0	72.2	2.01	3.1
t_1	52.7	11.8	40.9	73.9	1.81	3.0
t_2	46.3	13.0	33.3	70.2	2.11	3.1
t_4	49.2	15.0	34.2	71.5	2.09	3.1
t_8	50.7	15.2	35.5	74.3	2.09	3.0
t_{16}	50.3	17.0	33.3	72.2	2.17	3.1

[a] No pretreatment given after sintering, only evacuation at 443 K for 30 min.

[b] $(O_2)_{TiO_2}$: Irreversibly adsorbed oxygen on TiO_2 support after heating in H_2 for different times.

[c] $(O_2)_{irrev\,(Ag)} = (O_2)_{irrev\,(Total)} - (O_2)_{TiO_2}$.

sintered samples were subjected to pretreatment C prior to the chemisorption measurements, this enhanced O_2 uptake did not occur, and again no significant change in Ag dispersion was indicated during the time period studied, as shown in Fig. 4C. The $(H_2)_{titr}/(O_2)_{irrev}$ ratios were also very near 2.0 for all samples.

After similar sintering experiments in H_2 with the 1.89% Ag/η-Al_2O_3 catalyst, all sintered samples were given pretreatment C prior to chemisorption measurements. Enhanced oxygen uptakes occurred, which caused an apparent maximum to appear after 4 hr in the dispersion curve shown in Fig. 5. After heating 16 hr, an overall apparent increase of approximately 35% in oxygen adsorption capacity occurred. As with the unpretreated, evacuated-only 1.81% Ag/TiO_2 catalyst, dispersions calculated based on H_2 titration did not parallel this increase in O_2 uptake and essentially no change in Ag dispersion was indicated by this technique. Reversible oxygen adsorption on the H_2-sintered samples was zero or near zero in all cases. Blank experiments showed that both O_2 and H_2 uptakes were zero for pure η-Al_2O_3 after heating in H_2 at 673 K. Comparison of the adsorption isotherms of nonsintered (t_0) and sintered samples showed that they were essentially linear in all cases, but a change in the slope sometimes occurred.

Figures 6 represents a typical TEM electron micrograph of the 1.89% Ag/η-Al_2O_3 catalyst after sintering in H_2, and calculated particle size distributions are shown in Figs. 3B and C. As listed in Table 4, particle sizes determined from TEM and chemisorption experiments were in good agreement, and essentially no significant change

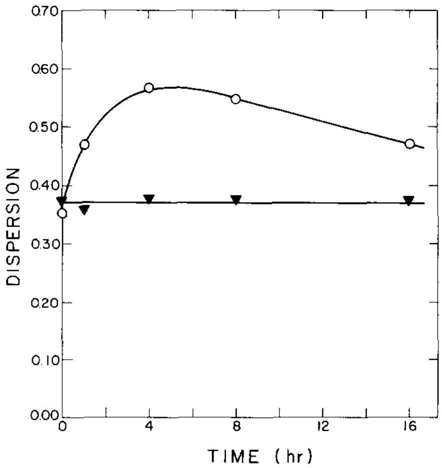

FIG. 5. Dispersion (O/Ag or H_2/Ag) versus heating time in H_2 at 673 K for 1.89% Ag/η-Al_2O_3. ○—based on O_2 uptake; ▼—based on H_2 titration. All samples were given pretreatment C.

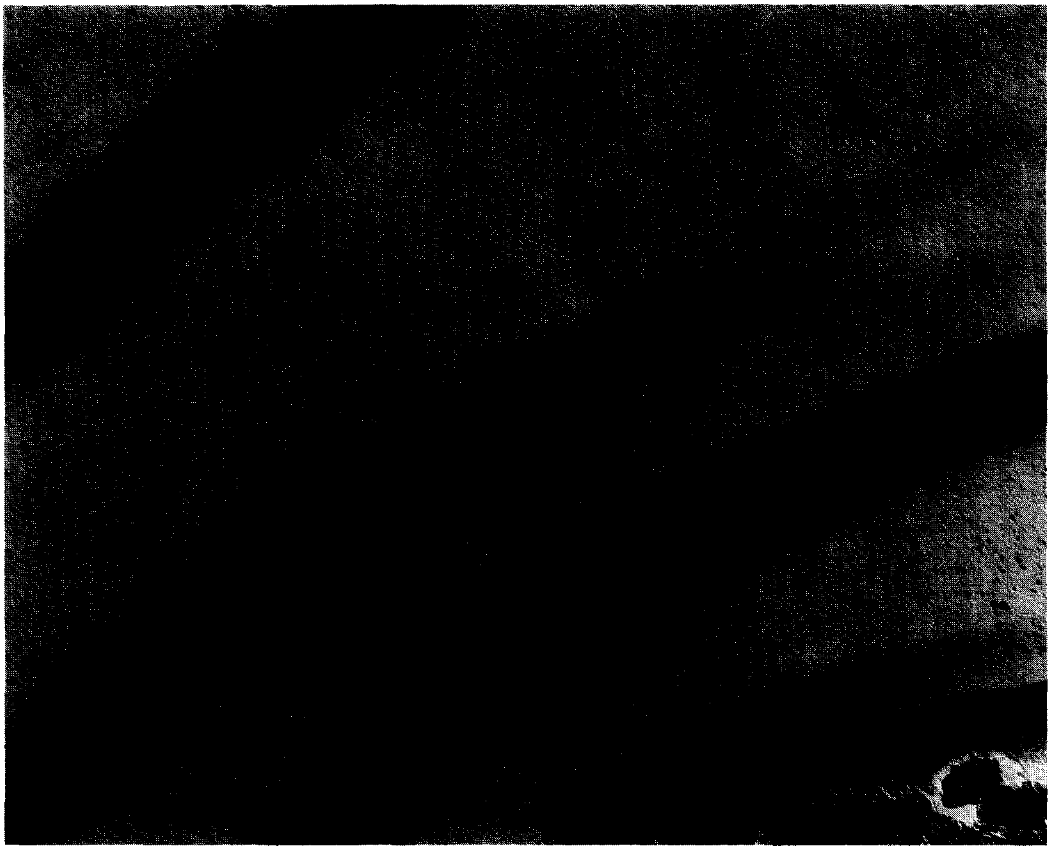

FIG. 6. Electron micrograph of 1.89% Ag/η-Al_2O_3 heated in H_2 at 673 K for 16 hr. Magnification, 170,000×; 1.7 mm = 100 Å. Ag particles marked by arrows were analyzed by energy dispersive X-ray spectroscopy.

in particle size was observed even after 16 hr of sintering time. No Ag XRD peaks could be sufficiently distinguished from those of the η-Al_2O_3 support to allow meaningful Ag crystallite sizes to be calculated for the 1.89 Ag/η-Al_2O_3 samples.

Heating under O_2. To examine the effect of the partial pressure of O_2 on sintering behavior at 673 K, experiments in O_2 were conducted at two different partial pressures of oxygen. In all cases, reversible oxygen uptakes at 443 K on sintered samples were either zero or very small. Blank experiments with all three support materials showed that no O_2 or H_2 uptake occurred after sintering in O_2. Figure 7A shows dispersion values plotted versus heat treatment time in 3% O_2 for the sintered 1.81% Ag/TiO_2 samples determined directly by H_2 titration after evacuation only (no pretreatment). No change is apparent in Ag metal dispersion. After this titration, samples were given pretreatment C followed by O_2 chemisorption and H_2 titration, and again calculated dispersions from either technique showed no significant change as indicated by Fig. 7B. Also, the titration stoichiometry was very near 2.0 in all cases.

Sintering of 1.89% Ag/η-Al_2O_3 in 2 and 10% O_2 in He resulted in a loss of adsorption capacity for both oxygen and hydrogen of titration, with the exception of sample t_1 sintered under 2% O_2. Figure 8 shows changes in apparent dispersion versus time when heated under oxygen. As with the He and H_2 sintering runs, the results based on

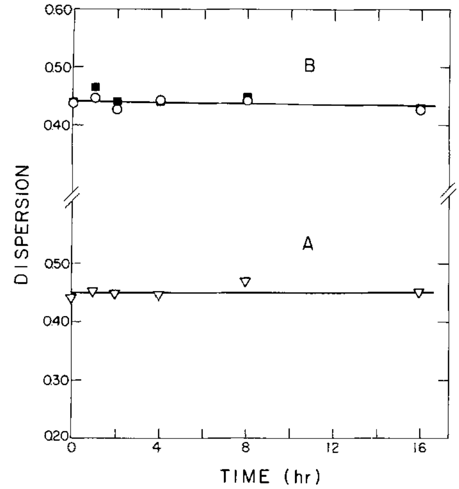

FIG. 7. Dispersion versus time for 1.81% Ag/TiO_2 in 0.03 atm O_2 at 673 K. Heated samples were: (A) given evacuation only, ▽—based on H_2 titration; (B) given pretreatment C; ○—based on O_2 uptake, ■—based on H_2 titration.

the H_2 titration values showed a more consistent and expected behavior whereas the dispersions calculated based on the O_2 uptakes were much more scattered. After 16 hr of sintering under O_2, a 20–30% decrease in overall dispersion was observed and the partial pressure of O_2 appeared to have no significant effect within the range examined. The titration ratios of the O_2-sintered 1.89% Ag/η-Al_2O_3 samples varied between 1.5 and 2.0 under 2% O_2, but were slightly higher than 2.0 in the 10% O_2 experiments except for t_2, which showed a ratio of 2.8. Adsorption isotherms of sintered samples were again quite linear although the slopes of the H_2 titration isotherms were noticeably higher for the 1.89% Ag/η-Al_2O_3 catalysts sintered in O_2.

A typical TEM micrograph of a 1.89% Ag/η-Al_2O_3 sample sintered in O_2 is shown in Fig. 9, and particle size distributions are shown in Figs. 3D and E. As in previous cases, no significant changes in particle size were detected although the morphology of the samples seems to be distinctly different. Almost all the 1.89% Ag/η-Al_2O_3 samples sintered in O_2 showed weak Ag XRD peaks which severely overlapped with those of the η-Al_2O_3 support and again prohibited a determination of particle size.

In contrast to the other two catalysts, the SiO_2-supported silver catalyst showed a significant increase in both O_2 and H_2 uptakes after heating in 10% O_2 at 673 K, as shown also in Table 3. Prior to the runs at 673 K, the samples were given pretreatment C. More experiments with this catalyst are planned to investigate this phenomenon.

DISCUSSION

Although the sintering behavior of certain supported metals has been studied (*1*), the sintering of supported silver catalysts has received little attention. This situation exists despite the awareness that silver catalysts deactivate because of loss of metal surface area. Therefore, finding reliable and accurate methods to measure Ag dispersion is essential. In addition, the nature of the chosen technique can noticeably affect the interpretation of the experimental results and understanding of the sintering phenomenon, as will be discussed later.

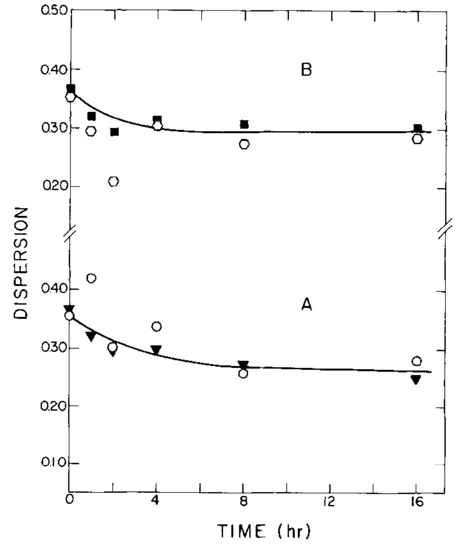

FIG. 8. Dispersion versus time for 1.89% Ag/η-Al_2O_3 after sintering at 673 K: (A) 0.02 atm O_2, ○—based on O_2 uptake; ▼—based on H_2 titration; (B) in 0.1 atm O_2, ○—based on O_2 uptake; ■—based on H_2 titration.

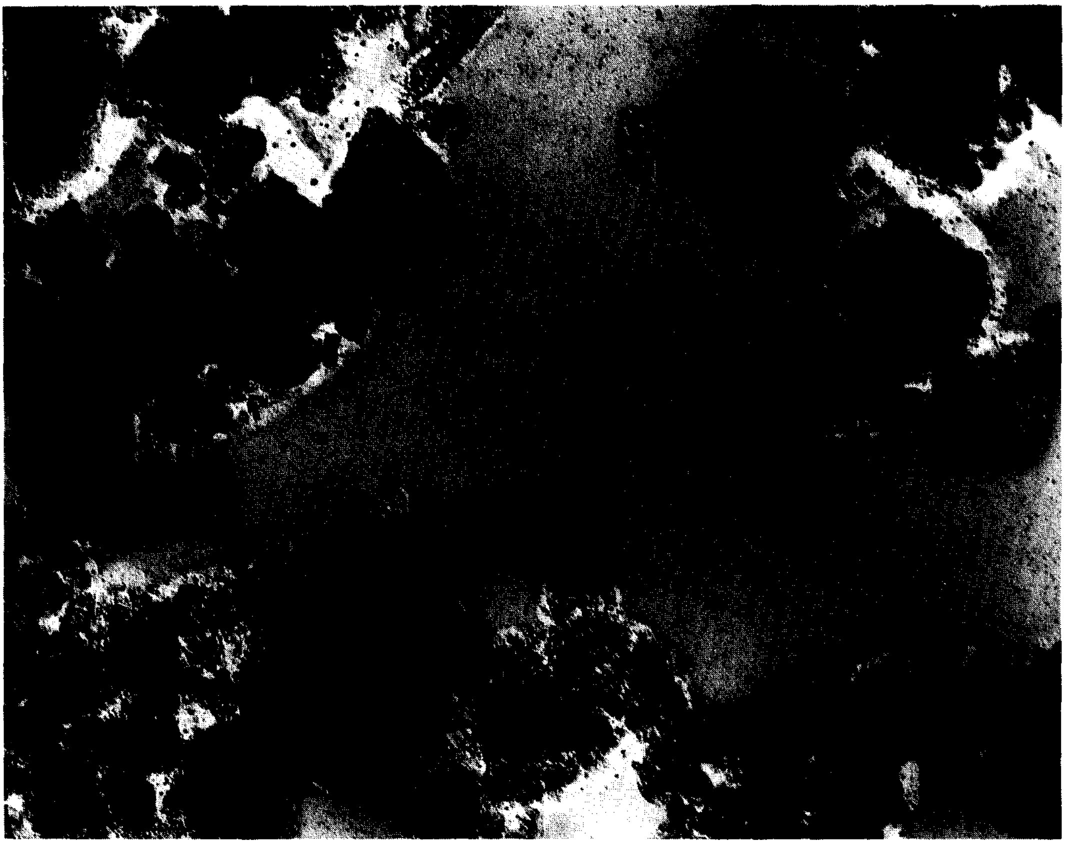

FIG. 9. Electron micrograph of 1.89% Ag/η-Al_2O_3 after sintering in 0.02 atm O_2 at 673 K for 8 hr. Magnification, 170,000×; 1.7 mm = 100 Å. Ag particles marked by arrows were analyzed by energy dispersive X-ray spectroscopy.

TABLE 3

Adsorption at 443 K on 1.33% Ag/SiO_2 after Heating in 0.1 atm O_2[a]

Sample	Pretreatment	Gas uptake (μmole/g cat)							Particle size (nm)	
		$(O_2)_{tot}$	$(O_2)_{rev}$	$(O_2)_{irrev}$[c]	$(H_2)_{tot}$	$(H_2)_{ads}$	$(H_2)_{titr}$[d]	$\frac{(H_2)_{titr}}{(O_2)_{irrev}}$	$(O_2)_{irrev}$	$(H_2)_{titr}$
t_0	—	7.5	0.3	7.2	15.2	0.4	14.8	2.06	11.4	11.0
t_1	[b]	—	—	—	34.5	—	34.5	—	—	4.8
	C	9.1	0.5	8.6	21.2	2.0	19.2	2.23	9.6	8.4
t_{16}	[b]	—	—	—	31.9	4.9	27.0	—	—	6.1
	C	11.7	0.4	11.3	28.1	2.1	26.0	2.30	7.1	6.4

[a] 0.1 atm O_2 + 0.9 atm He.

[b] No pretreatment—evacuation only at 443 K.

[c] $(O_2)_{irrev} = (O_2)_{tot} - (O_2)_{rev}$.

[d] $(H_2)_{titr} = (H_2)_{tot} - (H_2)_{ads}$.

The results presented in Fig. 1 indicate that heating under He at 1 atm and 673 K had essentially no effect on the surface area of well-dispersed silver on TiO_2, and the very close correspondence of dispersion values calculated based on either H_2 titration values or O_2 uptakes, after correction for adsorption on the support, provides further confirmation that the adsorption was well behaved. This result is in agreement with previous studies on large unsupported Ag particles and thin silver films which showed that minimal sintering occurs under He or Ar (*11–13*). However, from comparison of Figs. 1A and B the role of the pretreatment prior to chemisorption measurements in "stabilizing" the Ag surface as well as altering the O_2 and H_2 uptakes is evident. When only evacuation was used (Fig. 1A), significant reduction in gas uptakes, particularly O_2, resulted in a rather peculiar trend in dispersion.

Although no definitive explanation can be given at this time, several possibilities can be considered. First, the possibility that the observed minimum in O_2 uptake after 2–4 hr of sintering is indeed due to a true decrease in dispersion is not supported by the smaller variation in H_2 titration uptakes and the titration ratios above 2.0, which indicates some oxygen was on the surface prior to O_2 adsorption measurements. In addition, both O_2 and H_2 uptakes after the pretreatment showed little change, as shown in Fig. 1B. Second, it can be proposed that as a result of treatment in He at 673 K structural changes in the Ag crystallites occurred which altered the amounts of oxygen uptake. After similar experiments with the TiO_2 support, XRD results showed basically no change in the TiO_2 phases present, and in addition, the TiO_2 peaks in sintered samples verified this. Although surface reconstruction of Ag films under certain experimental conditions has been reported (*14, 15*), because of higher H_2 uptakes than O_2 ($(H_2)_{titr}/(O_2)_{irrev} > 2.0$), it is necessary to postulate that this reconstruction, if it occurred, had either altered the reactivity of adsorbed oxygen with H_2 or the amount of hydrogen adsorbed on the reduced Ag surface, both of which seem unlikely. For example, the amount of H_2 adsorbed on all these samples after reduction and evacuation varied only between 2.0 and 4.3 μmole H_2/g. A third explanation seems most likely; namely, as a result of this He treatment some oxygen migrated from the TiO_2 support surface to the Ag surface, thereby providing an internal source of oxygen and causing lower O_2 and higher H_2 uptakes than predicted.

It is difficult to establish with certainty the distribution of oxygen vacancies between the surface and the bulk of the TiO_2 support; however, this possibility seems plausible because TiO_2 can be partially reduced in either vacuum or inert gases at these temperatures to nonstoichiometric oxides (*16*). Our experiments with pure TiO_2 show that after heating in H_2 at high temperatures considerable amounts of O_2 can be chemisorbed (Table 2), i.e., after these reductions the oxygen surface vacancies can be removed by exposure to O_2 at 443 K (an irreversible O_2 uptake which does not react with H_2). If the number of such surface vacancies are not markedly altered by the presence of the silver, the total O_2 uptakes can be corrected for irreversible adsorption on the support. This third explanation is favored since it is expected that as the surface oxygen layer of the TiO_2 support is depleted, surface oxygen vacancies, at least in part, can be filled by lattice oxygen diffusing from the bulk to the surface. This would provide a reservoir of *in situ* oxygen during the heat treatment.

The results are more straightforward for the heat treatments of 1.81% Ag/TiO_2 catalysts in H_2. As shown in Fig. 4, essentially no change in Ag dispersion occurred as a result of treatment in H_2, even after 16 hr, as monitored by H_2 titration values. The apparent inconsistency if no pretreatment is used is clearly a result of irreversible O_2 adsorption on the reduced TiO_2 support and, after correction for this additional uptake, results based on the H_2 and O_2 uptakes agree well with each other (see Fig. 4B). Similar O_2 uptakes on TiO_2 reduced at high temperatures have been reported by others (*17, 18*). The fact that the oxygen adsorbed on the TiO_2 is unreactive toward H_2 emphasizes one of the advantages of the H_2 titration technique over oxygen chemisorption methods. This absence of sintering under H_2 is in agreement with previous studies with Ag powders and films which showed heating the catalyst under a reducing atmosphere (such as H_2 or C_2H_4) had little influence on surface area (*12, 13, 19–21*).

Similarly, little or no sintering of the small Al_2O_3-supported Ag crystallites occurred in He and H_2, when monitored by H_2 titration, as shown in Figs. 2 and 5. However, all samples except one showed higher O_2 uptakes than the initial t_0 sample, and a maximum in O_2 uptake under either gas occurred after 4 hr. Again, the results based on H_2 titration show a smooth consistent trend which argues against these increases in O_2 uptakes being truly due to redispersion of the silver. We are not aware of any reports of Ag redispersion and know of no volatile, gas phase Ag species; therefore, we do not believe that redispersion has occurred. All these samples showed titration stoichiometries less than 2.0, indicating that all of the adsorbed oxygen was not reacting with H_2. This behavior is unlike all nonsintered (*4, 5*) and most sintered samples, in which this stoichiometry was typically very near 2.0 after pretreatment C. This is strong evidence against the idea that all chemisorbed oxygen on these sintered samples is on the Ag surface. Alternatively, we propose that the amounts of oxygen which did not react with H_2 had diffused into the crystallites to become "subsurface" or "bulk" oxygen, and this form of absorbed oxygen was not reactive toward H_2 at 443 K within the time used for the titration measurement. We have followed oxygen uptakes on these samples with time and have found that a change in slope occurs at approximately monolayer coverage (*22*). Our interpretation is that the rapid uptake corresponds to adsorption while the slower uptake may represent diffusion of oxygen from the Ag surface into the crystallites.

Evidence for subsurface oxygen in silver has been reported previously (*23–28*) and this phenomenon seems to be more pronounced with larger Ag crystallites. Based on TEM and chemisorption data, no significant change in particle size occurred after sintering; however, a change in Ag morphology as a result of surface reconstruction, which could enhance "subsurface" or "bulk" oxygen formation, is a possibility. As mentioned earlier, evidence for such reconstruction has been reported (*14, 15*).

An alternative explanation for these higher oxygen uptakes can be suggested; namely, changes occur in the adsorption stoichiometry of oxygen on silver as a result of restructuring or surface faceting. For example, if an increase in molecular versus atomic adsorbed oxygen occurred, an additional amount of oxygen uptake would occur. However, it is then necessary to postulate that this molecular species was irreversibly adsorbed at 443 K and also that it was unreactive toward hydrogen because the expected increase in hydrogen titration did not occur. This explanation is not completely satisfying since existing data in the literature indicate that the formation of molecularly adsorbed oxygen is favored at low adsorption temperatures, and even then the amount of this form of adsorbed oxygen on Ag is extremely small and the species is rather weakly bound to the surface (*29–31*). From the stoichiometries obtained, one must postulate that approximately one-third of the total oxygen uptake occurred as molecular species on the Ag/η-Al_2O_3 catalysts after treatment in He or H_2, which is more than an order of magnitude higher than any values reported in the literature (*29–31*). Furthermore, previous experiments with N_2O adsorption showed that little or no molecular adsorption was found

TABLE 4

Comparison of Average Ag Crystallite Sizes Determined from Adsorption Methods and TEM

Catalyst	Sample	Pre-treatment	Sintering gas	Gas uptake			Cryst. size (nm)		
				$(O_2)_{irr}$	$(H_2)_{titr}$	H_2/O_2	$(O_2)_{irr}$	$(H_2)_{titr}$	TEM
1.81% Ag/TiO_2	t_0	C	none	36.0	72.2	2.01	3.1	3.1	3.0–7.0
1.81% Ag/TiO_2	t_{16}	C	He	34.6	71.6	2.07	3.2	3.1	—
1.89% $Ag/\eta\text{-}Al_2O_3$	t_0	A	none	30.2	62.5	2.07	3.8	3.7	3.5–8.0
1.89% $Ag/\eta\text{-}Al_2O_3$	t_{16}	C	He	25.0	53.5	2.14	4.6	4.5	0.6–6.0
1.89% $Ag/\eta\text{-}Al_2O_3$	t_4	C	H_2	48.7	65.0	1.33	2.4	3.5	3.0–6.5
1.89% $Ag/\eta\text{-}Al_2O_3$	t_{16}	C	H_2	40.5	64.0	1.58	2.8	3.6	3.0–9.0
1.89% $Ag/\eta\text{-}Al_2O_3$	t_4	C	0.1 atm O_2	26.5	53.7	2.02	4.3	4.3	3.0–10.0
1.89% $Ag/\eta\text{-}Al_2O_3$	t_8	C	0.02 atm O_2	22.1	46.8	2.12	5.2	4.9	2.5–8.8

on these surfaces (*4, 5*), evidence which again favors subsurface oxygen as an explanation.

The results of the experiments with 1.33% Ag/SiO_2 heated under O_2 were somewhat surprising. A significant increase in adsorption capacity occurred as a result of this treatment, as listed in Table 3, and both O_2 and H_2 titration uptakes indicated an apparent increase in Ag surface area. This phenomenon is being investigated further to determine if enhanced cleaning of the Ag surface (and the support via removal of any adsorbed contaminants) or surface restructuring is responsible. Although limited redispersion as a result of O_2 treatment is known to occur for some noble metals such as Pt (*1, 2*), this phenomenon has not been reported for Ag and is not expected because no volatile Ag oxides are known. The explanation of this behavior remains to be established.

Selected catalyst samples were also characterized by TEM, and some particle size distributions are shown in Fig. 3. The ranges in crystallite size are in good agreement with average sizes calculated from O_2 adsorption and from H_2 titration, as shown in Table 4. This table also lists uptake values on these samples and demonstrates that the $(H_2)_{titr}/(O_2)_{irrev}$ ratios are usually near 2. The lower values after the treatment in H_2 have been previously discussed.

The 1.81% Ag/TiO_2 catalyst was very stable under O_2 at 673 K and essentially no change in dispersion was observed by either O_2 uptake or H_2 titration. This unexpected resistance to sintering is unlike the behavior of the 1.89% $Ag/\eta\text{-}Al_2O_3$ catalyst and the behavior reported for unsupported Ag metal and films (*11, 12, 19, 21, 32, 33*). As expected, the sintering behavior of $Ag/\eta\text{-}Al_2O_3$ in the presence of oxygen was quite different from that seen in either hydrogen or helium. Results based on O_2 and H_2 uptakes were in good agreement, and dispersion losses were similar under 15 and 75 Torr O_2, indicating little effect of O_2 partial pressure in this range, as shown in Fig. 8. Once again results based on the H_2 titration technique showed more reliability than those based on O_2 chemisorption. This decrease in dispersion is also in agreement with previous reports in which it has been clearly demonstrated that the presence of oxygen facilitates the sintering of unsupported silver powders and films (*11, 12, 19, 21, 32, 33*). Presland and co-workers studied hillock formation on thin silver films evaporated on nonporous silica (*19, 21, 32, 33*), and they found that oxygen facilitated the growth of large silver islands. Similar results were observed by Riassian *et al.* for Ag films on a variety of nonporous glassy materials (*12, 20*).

Two different mechanisms have been proposed to describe the sintering of metals on a substrate surface—one presumes that sintering occurs by the migration, collision, and coalescence of metal crystallites on the support surface, and the other envisages sintering occurring by the dissociation of molecular or atomic species from the crystallite surface followed by migration and capture of these species by other crystallites or by trapping sites on the support surface (*1*). The good agreement between experiment and predictions based on theories of surface diffusion has lead to the conclusion that silver sintering occurs via metal migration involving surface diffusion (*12, 33*). The role of oxygen appears to be that of reducing the surface tension of solid silver thereby facilitating the motion of surface atoms, and several studies have shown that only very low oxygen partial pressures are required to produce significant reductions in surface tensions (*33–35*). Such a model predicts that the nature of the support surface should have a significant effect on the rate of sintering and, indeed, such an influence has been observed (*12, 20*). Although there is not enough experimental data in this study to reach a conclusion regarding the sintering mechanism of supported silver catalysts, the support surface and the gaseous environment are confirmed as important variables, and one principal role of the support appears to be the physical separation of these small Ag crystallites within its pore structure. At these low loadings, the probability of particle coalescence is markedly decreased by the barriers to diffusion provided by the pores, particularly if crystallite migration must occur.

SUMMARY

We have found that small silver crystallites on TiO_2, Al_2O_3, and SiO_2 were very stable at 673 K under He and H_2, and little or no change in dispersion was observed after 16 hr of sintering. The effect of sintering in O_2 at 673 K was quite different for these three catalysts. Essentially no change in metal dispersion occurred for TiO_2-supported Ag, and this catalyst was the most stable and well behaved of all three catalysts. A decrease in dispersion of 20–30% was observed for η-Al_2O_3-supported silver after sintering in 15 and 75 Torr O_2, and the partial pressure of O_2 in this range had little effect. Heat treatment of a 1.33% Ag/SiO_2 catalyst in O_2 caused an increase of 60–80% in adsorption capacity, and this behavior is now being investigated further to determine if surface cleaning or reconstruction is primarily responsible. At low loadings and with small Ag crystallites, these supports with reasonably high surface areas provide effective barriers to surface diffusion and coalescence of silver, which presumably occurs via crystallite migration. Finally, H_2 titration of chemisorbed oxygen on Ag surfaces has again been demonstrated to be a preferred method to measure silver surface area.

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