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Ultradispersed Supported Silver Catalysts: Effect of Preparation and Reduction Procedures on Dispersion and Unusual Oxygen Adsorption Properties at High O_2 Pressures

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The effect of metal precursor and reduction procedure on dispersion of silver catalysts has been explored. Nearly identical dispersions were obtained using $AgNO_3$, AgO_2CCH_3, AgO_2CCF_3, and $AgO_3C_3H_5$ as precursor salts supported on TiO_2 at ~2% wt loading, implying little effect of the counterion within this series. Of the three reduction procedures: H_2 alone (573 K), formaldehyde treatment (300 K) + H_2, and hydrazine treatment (300 K) + H_2, the former consistently gave higher dispersions of Ag on SiO_2 and η-Al_2O_3 when $AgNO_3$ was used, whereas essentially identical dispersions were achieved on TiO_2 with the three reduction procedures. A 0.71 wt% and a 0.37 wt% Ag/TiO_2 catalyst had initial dispersions of 0.65 and 0.72, respectively, which are the most highly dispersed Ag catalysts yet reported. These high dispersions also imply that bulk Ag_2O formation is not likely with these small crystallites since a limiting oxygen-to-silver ratio of 0.50 is mandated by the latter. These ultrahighly dispersed samples also showed enhanced but reversible O_2 uptakes at high O_2 pressures (450–900 Torr, 1 Torr = 133 Pa). A limiting value near one oxygen atom adsorbed per silver atom present was obtained which approaches the stoichiometry of Ag_2O_2. © 1985 Academic Press, Inc.

INTRODUCTION

Silver metal is presumably difficult to prepare in high dispersion on typical catalytic supports, yet the preparation of highly dispersed silver catalysts would be desirable for several reasons. These include studies of particle size effects in catalytic reactions such as ethylene oxidation (*1–3*) as well as studies of the sintering properties of supported silver (*4*). For the latter, highly dispersed silver would be the necessary beginning to observe particle growth under various atmosphere and temperature conditions (*4*). Furthermore, ultrasmall silver crystallites with a high ratio of surface to bulk atoms would be expected to minimize problems associated with bulk oxidation and subsurface oxygen formation and thereby give more interpretable results during O_2 chemisorption analysis (*5*).

An ultrahighly dispersed supported silver catalyst could also be used to address a question which has arisen concerning the validity of the oxygen chemisorption technique to measure silver surface area (*5*). This technique assumes that at less than 200 Torr O_2 pressure, surface saturation occurs to yield a surface with approximately one oxygen atom chemisorbed for each silver surface atom, i.e., a 1 : 1 stoichiometry (*5, 6*). However, a referee of a previous paper in this series (*5*) had suggested that this assumption may not be correct as bulk Ag_2O could form which would give an oxygen-to-total silver stoichiometry of 0.5 : 1. A distinguishing test for these situations would be to prepare an ultradispersed catalyst which gives a dispersion greater than 0.50 using the 1 : 1 surface stoichiometry, which implies a dispersion greater than unity using the 0.5 : 1 stoichiometry. Since the latter is impossible, it could not be correct.

Herein we report the preparation of highly dispersed silver crystallites sup-

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ported on η-Al_2O_3, SiO_2, and TiO_2 and the effect of silver precursor salts and reduction procedures on silver crystallite size. Also described are the preparation of silver catalysts with dispersions of 0.65 ± 0.02 and 0.72 ± 0.03, the highest dispersions for silver yet reported in the literature, which provides strong evidence against the formation of bulk Ag_2O and supports the assumption of an O/Ag_s chemisorption stoichiometry near unity. These samples also showed unusual enhanced, but reversible, capacity for O_2 adsorption at high O_2 pressures (400–900 Torr) reaching a limiting value near one oxygen atom adsorbed per total silver atom present, surface and bulk.

TABLE 1

Hydrogen Reduction and Pretreatment

1. Evacuate sample overnight at 300 K
2. Heat the catalyst sample to 573 K under atmospheric hydrogen flowing at 20 cm^3/min at a rate of ~10 K/min
3. Maintain 573 K and hydrogen flow of 20 cm^3/min for 2.5 h
4. Evacuate the system and reduce the temperature to 443 K
5. Flow O_2 through the system at 15 cm^3/min for 10 min at 443 K
6. Evacuate the system for 10 min
7. Flow H_2 through the system at 20 cm^3/min for 15 min at 443 K
8. Evacuate the system for 15 min or until the pressure is below 2×10^{-4} Torr

EXPERIMENTAL

The catalysts used in this study consisted of approximately 2 wt% silver dispersed on η-Al_2O_3 (200 m^2g^{-1}, Exxon Research and Engineering Co.), SiO_2 (160 m^2g^{-1}, Cabot Corp., Cab-O-Sil M-5), and TiO_2 (50 m^2g^{-1}, Degussa P-25). Specific metal loadings were determined by plasma emission spectroscopy at the Dow Chemical Company, Midland, Mich. Silver catalyst precursors consisted of silver nitrate (Aldrich, Gold Label) for η-Al_2O_3, SiO_2, and TiO_2, silver acetate, silver trifluoroacetate, and silver lactate (all from PFALTZ & BAUER) for TiO_2. Catalysts were prepared by impregnation of aqueous salt solutions via incipient wetness techniques (*7*) utilizing doubly distilled water and an N_2 atmosphere. For silver lactate and silver acetate multiple impregnations were required to obtain the 2 wt% silver loading. Silver trifluoroacetate was deposited using trifluoroacetic acid to aid solubility. The supported samples were dried at 368 K *in vacuo* for 2–3 h and were stored in a desiccator prior to use. These samples were reduced either directly by the hydrogen reduction procedure outlined in Table 1 or by use of a chemical reducing agent at 300 K—either hydrazine monohydrate or a 37% aqueous formaldehyde solution—followed by the hydrogen reduction procedure in Table 1. These latter reductions were conducted under an N_2 atmosphere using standard Schlenk techniques (*8*), by adding dropwise, via syringe, the volume of each reducing agent required to fill the pore volume of the support. An excess of reducing agent was present in all cases. Catalysts were left overnight in the presence of the reducing agent and then dried at 323 K *in vacuo* for several hours.

Oxygen chemisorption and hydrogen titration (*5, 9*) measurements were determined following hydrogen reduction over a pressure range of 30–200 Torr at 443 K. Any reversible O_2 adsorption was determined by evacuating the sample for 20 min at 443 K after the O_2 chemisorption and then repeating the O_2 chemisorption. Hydrogen titration measurements were then made after another 20-min evacuation. Correction for physical adsorption on the catalyst was made by extrapolating the linear portion of the isotherms to zero pressure.

Adsorption studies were conducted in a grease-free vacuum system constructed of Pyrex and capable of achieving an ultimate vacuum of 3×10^{-6} Torr. Pressure readings in the adsorption manifold during isotherm measurements were made using an MKS 310CHS high-accuracy capacitance manometer with an MKS 270A Series electronics display unit. Temperatures greater than 473 K during pretreatment were controlled by a Versa-Therm temperature controller and a heating mantle while those below 473 K were controlled by a TECAM fluidized sand bath SBS-2. The temperature in the adsorption cell was monitored by a Doric 410A digital indicator.

Hydrogen and helium were admitted to the system through Whitey regulating valves; flow rates were measured and controlled by FC260 Tylan mass flow controllers. Oxygen was admitted through a Nupro high-vacuum bellows valve, and measurement and control were provided by a Matheson 610 rotometer and needle valve. Prior to use, all gases (hydrogen, MG Scientific UHP, 99.999%; helium, Linde Specialty Gases, UHP, 99.999%; and oxygen, Airco, Ultra Pure, 99.995%) were passed through 5A molecular sieve columns (Supelco, Inc.). Hydrogen was also passed through an Oxytrap (Alltech Assoc.).

Catalyst samples were also examined by X-ray diffraction (XRD) using a Rigaku 4036A1 diffractometer with a Cu$K\alpha$ source. Powder samples tightly packed in an aluminum holder were scanned between 2θ values of 20–80° at a rate of 4° min^{-1}. The four major silver peaks (2θ = 38.15° (100%), 44.13° (40%), 77.55° (26%), and 64.49° (25%)) were clearly visible on SiO_2-supported catalysts since SiO_2 has no interfering peaks. TiO_2 and η-Al_2O_3 supports, however, do have peaks which interfere with the 38.15° and 44.13° silver peaks. Where possible, silver crystallite sizes were calculated using the Scherrer equation, $d = 0.9\lambda/B\cos\theta$, with Warren's correction, $B = (B_m{}^2 - B_i{}^2)^{1/2}$, where B_m is the peak width at one-half maximum intensity, B_i is the instrumental broadening correction, λ = 1.542 Å for the Cu$K\alpha$ source, and 0.9 is Scherrer's constant.

RESULTS

Effect of Impregnation Salt on Silver Crystallite Size

In order to determine the effect of the silver salt used in catalyst preparation on the size of resulting Ag crystallites, approximately 2 wt% silver in the form of silver nitrate ($AgNO_3$), silver acetate ($AgO_2C_2H_3$), silver trifluoroacetate ($AgO_2C_2F_3$), and silver lactate ($AgO_3C_3H_5$) were supported on TiO_2. These were then reduced directly with hydrogen and characterized by oxygen chemisorption, hydrogen titration (*5, 9*), and X-ray diffraction. The chemisorption results are summarized in Table 2. All the dispersions for the ~2 wt% samples fall in the range 0.41–0.46 and are relatively independent of the precursor salt used. No peaks were observed by XRD, consistent with the presence of small crystallites.

Effect of Reduction Conditions on Silver Crystallite Size

Earlier work from these laboratories has shown that the hydrogen reduction pretreatment given in Table 1 is sufficient to reduce all the silver present to metal and also removes carbonaceous impurities (*9*). We wished to explore alternate reduction procedures, particularly treatment with chemical reducing agents such as formaldehyde (*11*) and hydrazine (*12*). Thus, catalysts were prepared from silver nitrate on η-Al_2O_3, SiO_2, and TiO_2 supports at a loading of approximately 2 wt% silver. Samples of each catalyst were reduced with an aqueous solution of formaldehyde or hydrazine, followed by hydrogen reduction and the pretreatment of Table 1, and also reduced by hydrogen and given the pretreatment alone for comparison. A series of color changes occur during these reductions, and these are summarized in Table 3.

The Ag/η-Al_2O_3 sample was easily reduced by formaldehyde as evidenced by an immediate change in the color of the supported catalyst from white to dark gray when the first few drops were added. Hydrazine also reduced this catalyst to give a light-brown-colored material. In contrast, addition of formaldehyde to the Ag/SiO_2 catalyst did not give an initial color change, but after sitting overnight in the presence of the reducing agent the catalyst had changed to a brown-colored material. Once dry, this

TABLE 2

Gas Adsorption on Supported Silver Salts

Catalyst	%Ag	Gas uptake[a,b]			% Disp.[e]		Particle size[f], Å	
		O_2[c]	H_2[d]	H_2/O_2	O_2	H_2	O_2	H_2
$AgNO_3/TiO_2$	1.99	37.8	75.8	2.00	41.0	42.3	33	32
$AgO_2C_2H_3/TiO_2$	1.94	38.4	77.8	2.03	42.4	44.5	32	30
$AgO_2C_2F_3/TiO_2$	1.64	34.2	67.2	1.97	44.3	45.7	30	29
$AgO_3C_3H_5/TiO_2$	2.40	50.7	99.5	1.96	45.5	45.7	30	29
$AgO_3C_3H_5/TiO_2$	0.71	21.5	41.7	1.94	65.9	63.2	20	21
$AgO_3C_3H_5/TiO_2$	0.37	12.4	24.7	1.99	72.3	72.0	19	19

[a] Values reported are the average of three isotherms with a variation of less than 2%.

[b] Micromoles per gram of catalyst.

[c] Corrected for reversible O_2 adsorption.

[d] Corrected for H_2 adsorption on the support.

[e] Assuming $O(a)/Ag_s = 1$.

[f] Value given is d_s where $d_s = 6S(M_w)/DN_a(\rho)$ and S is the surface area of Ag based on a plane distribution of 25%(100), 5%(100), and 70%(111) as determined in Ref. (*10*), M_w is the molecular weight, D is the calculated dispersion, N_a is Avogadro's number, and ρ is the density of silver.

catalyst's final color was a grayish pink. Hydrazine reduction of silver on SiO_2 was rapid, giving an immediate color change from white to black, with the dried sample olive in color. Silver on TiO_2 underwent slow color changes from white to light brown to blue–gray using formaldehyde as a reducing agent. A similar color change occured with hydrazine to give a final purple–gray catalyst. The hydrogen reduction and pretreatment alone gave light-gray samples for silver on η-Al_2O_3 and TiO_2, while silver on SiO_2 gave a dark brown color.

The catalysts treated with the chemical reducing agents underwent additional color changes during the hydrogen pretreatment. Samples with colors varying from red–brown to dark gray resulted. These reduced catalysts were characterized by oxygen chemisorption, hydrogen titration, and XRD with the results presented in Table 4. An

TABLE 3

Color Changes during Reduction of Supported Ag Catalysts

Support	Color				
	Initial	Formaldehyde reduction	Hydrazine reduction	H_2 reduction after chemical treatment	After chemisorption
Al_2O_3	White	Dark gray	Light brown	Red–brown to brown–gray	Light gray
SiO_2	White	Brown to gray–pink when dry	Black to olive when dry		Dark brown
TiO_2	White	Light brown to blue–gray	Light brown to purple–gray	Dark purple	Light gray

TABLE 4

Effect of Reduction Procedure on Silver Particle Size

Catalyst	%Ag	Pretreatment	Gas uptake[a]			% Dispersion		Particle size, Å		XRD
			O_2[b]	H_2[c]	H_2/O_2	O_2	H_2	O_2	H_2	
$AgNO_3/\eta\text{-}Al_2O_3$	1.73	H_2 only[d]	34.0	70.0	2.06	42.4	43.6	32	31	[e]
		37% CH_2O, H_2	10.3	18.2	1.77	12.5	11.3	107	119	[f]
		N_2H_4 H_2O, H_2	10.5	18.2	1.70	13.1	11.3	102	119	[f]
$AgNO_3/SiO_2$	1.84	H_2 only[d]	6.8	16.2	2.4	8.0	9.5	168	141	90 Å
		37% CH_2O, H_2	0.6	1.1	1.83	0.7	0.6	1920	2240	250 Å
		N_2H_4 H_2O, H_2	—	—	—	—	—	—	—	180 Å
$AgNO_3/TiO_2$	2.14	H_2 only[d]	39.7	82.5	2.08	40.0	41.6	34	32	[e]
		37% CH_2O, H_2	41.0	81.0	1.98	41.3	40.8	33	33	[e]
		N_2H_4, H_2O, H_2	43.7	82.0	1.88	44.0	41.3	31	33	[e]

[a] Micromoles per gram of catalyst.

[b] Corrected for reversible O_2 adsorption.

[c] Not corrected for H_2 adsorption on the support.

[d] Refers to hydrogen reduction and pretreatment outlined in Table 1.

[e] No silver peaks visible.

[f] Silver peaks are visible but with interference from the support.

anomaly in these data is the very low dispersion calculated from the chemisorption data for the Ag/SiO_2 catalyst reduced by CH_2O (~2 cm^3 of a 37% aqueous solution/g). This is presumably due to residual organic impurities blocking the Ag surface for O_2 uptake since the sample was reduced with a large excess of CH_2O and dried at 45°C. The particle size calculated from XRD measurements may be more accurate in this case, and it qualitatively agrees with transmission electron micrographs which showed the presence of particles in the range 200–600 Å, with an average particle size near 500 Å, as shown in Fig. 1.

Ultra Highly Dispersed Silver on TiO_2

To study the possibility of bulk Ag_2O formation with these catalysts, an ultrahighly dispersed silver sample was required. Of the 2 wt% silver catalysts on TiO_2, silver lactate gave the best dispersion. To increase the dispersion, the silver loading was reduced and 0.71 and 0.37% Ag/TiO_2 catalysts were prepared from aqueous silver lactate solutions. These catalysts were characterized by oxygen chemisorption and hydrogen titration, and the 0.71% catalyst was also characterized by XRD, which did not detect Ag crystallites implying their diameter to be less than ~40 Å. The chemisorption and titration results gave an average initial dispersion of 0.65 ± 0.02 for the 0.71% catalyst, assuming an oxygen atom-to-silver surface atom ratio of 1 : 1. This sample adsorbed 21.5 μmol of O_2 per gram of catalyst, whereas a maximum uptake of 16.3 μmol/g is predicted for bulk Ag_2O formation. Thus, the formation of the latter alone cannot account for the enhanced O_2 uptake for this sample. Likewise, the 0.37% catalyst had a dispersion of 0.72 ± 0.03 and a total oxygen uptake far in excess of that required only for bulk Ag_2O formation.

Oxygen Adsorption as a Function of Pressure

In other work in these laboratories it was observed that further O_2 uptake in excess of that measured at pressures below 200 Torr occurred on well-dispersed Ag on TiO_2 upon increasing the O_2 pressure above 400–

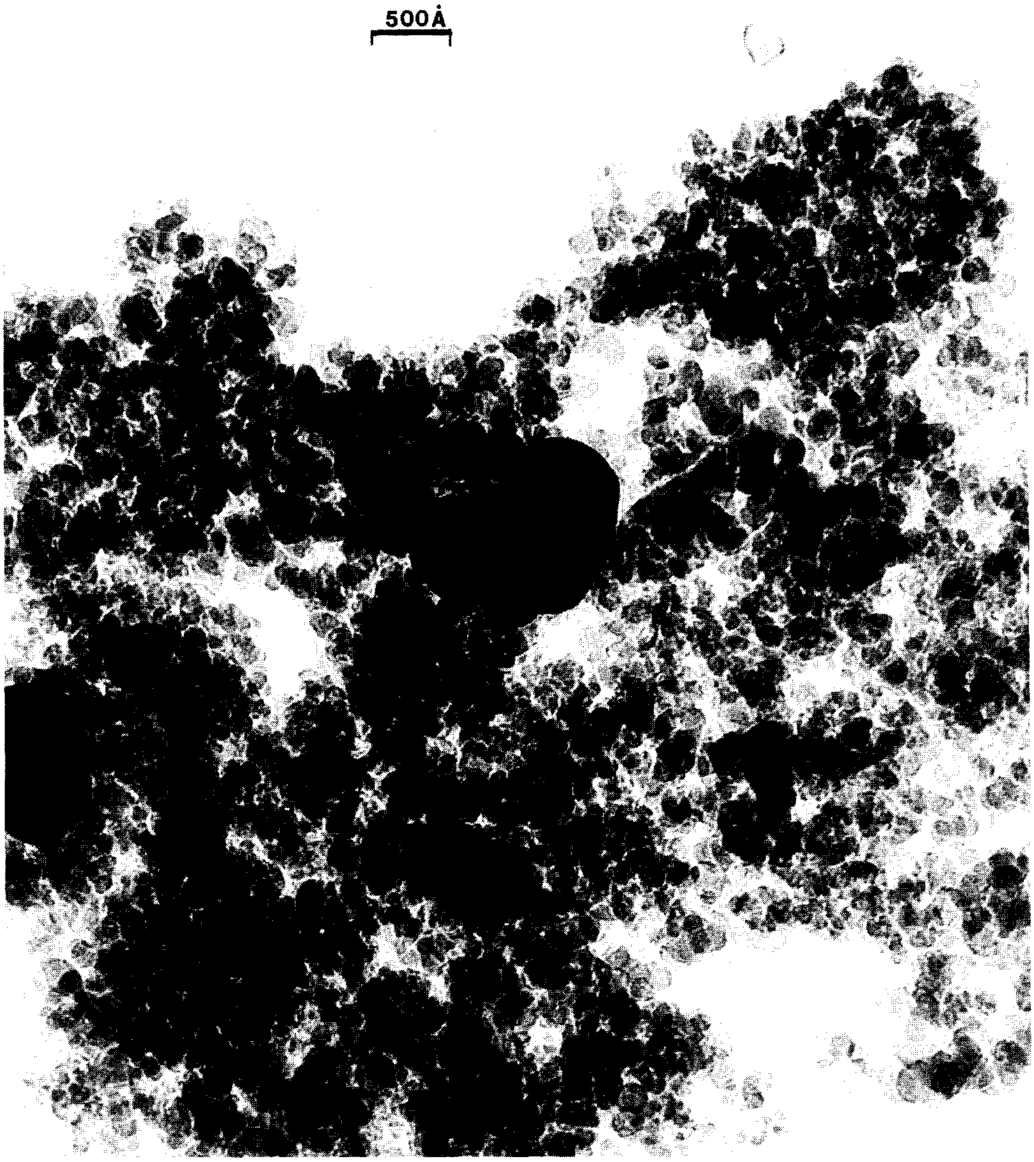


FIG. 1. TEM photograph of 1.84% Ag/SiO_2 following reduction with CH_2O, the pretreatment of Table 1, and the chemisorption measurements.

500 Torr (*4*). To put this phenomenon on a quantitative basis, we subjected the 0.37 and 0.71% Ag catalysts to O_2 pressures up to 830 Torr, allowing pressure equilibration to occur for each data point and the results for 0.37% Ag/TiO_2 are shown in Fig. 2. The small linear increase in O_2 uptake over the pressure range 60–400 Torr is due to physical adsorption on the TiO_2 support, as shown by the lowest isotherm in Fig. 2, which was measured after a 20-min evacuation following the initial O_2 isotherm. However, upon increasing the pressure above 400 Torr, a further increase in oxygen uptake occurred that cannot be attributed to physical adsorption on the support. After an equilibration period of 11 h at 830 Torr, the total uptake of 20 ± 1 μmol O_2/g, after

correction for physical adsorption on the support, corresponds to ~1.2 oxygen atoms adsorbed for every silver atom present, surface and bulk. The above-mentioned effect was reproducible since the increased O_2 uptake at elevated pressures occurred on the same sample for two successive reduction (Table 1) and adsorption cycles, as shown in Fig. 2. The only difference in the results obtained was a somewhat decreased O_2 uptake in the low-pressure regime (30–150 Torr) giving a value of 12 μmol/g in the second cycle, and the final uptake after high-pressure treatment increased to a value of 18 ± 1 μmol/g, after correction for O_2 physical adsorption on the support. The latter corresponds to 1.1 oxygen atoms present per Ag atom present, surface and bulk. Similar behavior was observed for the 0.71% Ag/TiO_2 sample although in some cases even larger amounts of oxygen were observed at high pressure after 20 h.

To determine if the additional O_2 taken up at high pressures could be pumped off following the high-pressure exposure, the sample from the first experiment mentioned above was given the standard 20-min evacuation after the O_2 isotherm was determined, and a repeat O_2 isotherm was measured (Fig. 2). No irreversible O_2 uptake occurred indicating that no chemisorbed oxygen was removed by the evacuation. However, other data taken during similar isotherm measurements on both samples showed that at lower O_2 pressures gas actually desorbed from the surface and was only readsorbed with time at the higher pressures. These data indicate that the "additional" adsorbed oxygen is only slowly desorbed from the catalyst sample during evacuation at 443 K and that the initial 20-min evacuation was not sufficient to remove all the oxygen adsorbed during the high-pressure exposure.

Following exposure to the high-pressure O_2 treatments and the 20-min evacuation–reversible O_2 isotherm described above, the catalyst was given the standard H_2 titration procedure. As the data in Fig. 2 show, the amount of hydrogen rapidly adsorbed is close to twice the O_2 taken up in the initial low-pressure regime, based on the average of the two runs. However, the "additional" oxygen is not readily removed by the titration procedure although the one data point illustrated in the figure for the H_2 adsorbed after extended exposure to H_2 indicates that this "additional" oxygen can be quantitatively, but slowly, removed by reaction

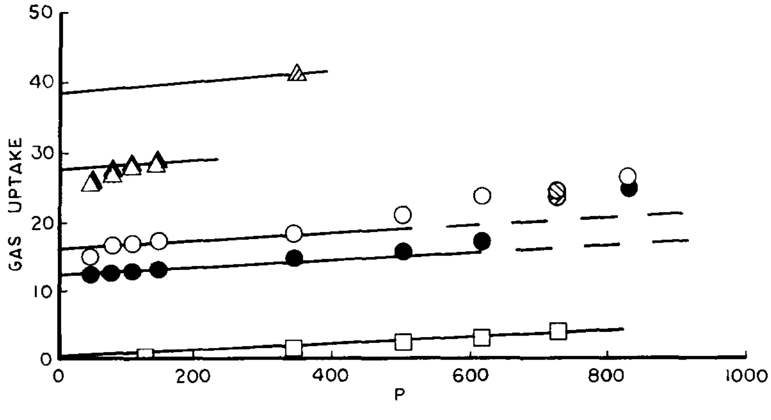


FIG. 2. Oxygen adsorption at 443 K on 0.37% Ag/TiO_2 with gas uptake (μmol/g) of catalyst versus pressure (Torr). ○, $(O_2)_{tot}$ cycle 1; ●, $(O_2)_{tot}$ cycle 2; □, $(O_2)_{tot}$ after 20-min evacuation at 443 K following cycle 1; △, $(H_2)_{tot}$ cycle 1; ▲, $(H_2)_{tot}$ cycle 2. Crosshatched data points are after extended exposure to H_2 (20.5 h) and O_2 (11 h each cycle) whereas all other points were recorded after 1–2 h exposures.

with H_2. The slopes of the H_2 isotherms are those measured previously for H_2 adsorption on pure TiO_2 (*5*).

DISCUSSION

The objectives of this research were to prepare supported silver crystallites with as high a dispersion as possible and to determine the effect of precursor silver salt and reduction procedures on particle size. Previous work had shown that of three supports, η-Al_2O_3, SiO_2, and TiO_2, the latter gave the most highly dispersed samples for a given wt% loading (*7*). This support was thus chosen as the most likely to yield ultradispersed silver. We had anticipated that the precursor silver salt used in catalyst preparation would affect the dispersion of the resultant catalysts, but as the data in Table 2 show, this is clearly not the case, at least with the salts used in this study. Each precursor gave essentially the same dispersion, 0.44 ± 0.03. However, silver lactate appears to be slightly superior, since its dispersion is the highest achieved even though it had the highest silver loading among the samples. However, this could be a consequence of the multiple impregnations required to achieve the desired silver loading.

The results described herein also show that of the three reduction procedures studied, direct high-temperature hydrogen reduction produced much smaller crystallites on Al_2O_3 and SiO_2 than did reducing agents such as formaldehyde and hydrazine. However, the titania-supported samples gave similar sized crystallites regardless of reduction procedure. It could be argued that the formaldehyde and hydrazine did not reduce the TiO_2-supported $AgNO_3$ and that reduction was achieved only during H_2 treatment, hence the similar particle sizes. However, this seems unlikely given the ease of reduction of Ag^+ and the color changes observed during the formaldehyde and hydrazine treatments which were characteristic of reduction on the other supports. In any case, it can be concluded that if small crystallites are desired on Al_2O_3 or SiO_2, then only a H_2 reduction should be used. However, if larger crystallites are desired *for the same weight percentage loading* then formaldehyde or hydrazine reductions should be employed.

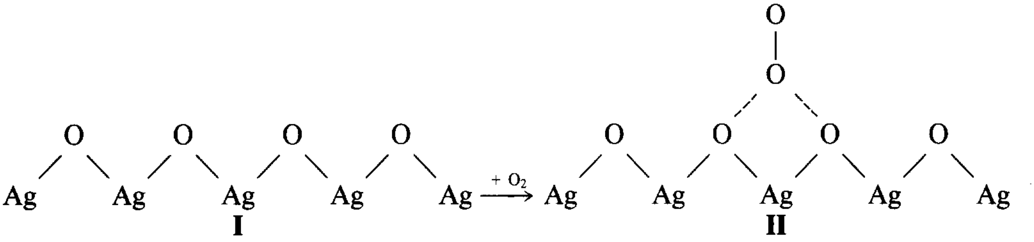
A significant result of this study is the preparation of the 0.71% and 0.37% Ag/TiO_2 catalysts which gave average initial dispersions of 0.65 ± 0.02 and 0.72 ± 0.03, respectively, based upon both O_2 adsorption and H_2 titration results. These are the most highly dispersed silver catalysts of which we are aware. These high dispersions, calculated on the basis of an assumed 1 : 1 O/Ag_s surface stoichiometry, rule out the possibility of bulk Ag_2O formation alone explaining these high O_2 uptakes because if that had occurred, more Ag would be required than present in the catalyst. Formation of bulk Ag_2O also seems unlikely based on phase diagrams for the Ag/O_2 system which show that this phase does not form at 443 K as long as the O_2 pressure is below 200 Torr (*13*).

A curious finding is the enhanced O_2 uptake at pressures above 400–500 Torr as shown in Fig. 2. At this time we do not attribute this additional oxygen uptake to the titania surface for the following reasons. First, control experiments with pure TiO_2 did not show this enhanced uptake at higher pressures. Second, the titania surface had already experienced an exposure to O_2 at 1 atm following reduction at 300 K (during the pretreatment) and at lower O_2 pressures during the low-pressure isotherm measurement. Any reoxidation of partially reduced surface sites would be expected to have been completed during these steps. Third, oxidation of reduced sites on the titania surface seems unlikely because all the oxygen taken up after the high-pressure exposure can be quantitatively removed by the H_2 titration reaction. Also, experiments with the 0.71% Ag/TiO_2 sample showed that about half the "additional" oxygen could be removed by evacuation at 443 K for 4 h; i.e., this oxygen could be slowly desorbed. Other work has shown that the

TiO_2 support in the absence of metals does not react with H_2 at these low temperatures (*14*), and it seems unlikely that silver, a metal which does not chemisorb H_2 to an appreciable extent, would facilitate this reaction. Indeed, Baker *et al.* (*15*) have recently shown that silver does not enhance the reduction of TiO_2, even at temperatures much higher than those employed here.

The above data imply that essentially all of the oxygen taken up under the high pressures must be associated with the ultrasmall silver crystallites, some possibly at the Ag–TiO_2 interface. Recall that the total oxygen taken up at 830 Torr corresponds to a bulk stoichiometry near that of silver peroxide, Ag_2O_2. Although bulk Ag_2O_2 is reported to decompose at temperatures above 373 K (*16*), small crystallites under 830 Torr O_2 may be more stable.

One possible interpretation of our data, based on UHV studies invokes the formation of atomically adsorbed oxygen (**I**) at low pressures with formation of a partial overlayer of adsorbed O_2 molecules (O_2-?) (**II**) on top of the initial Ag–O monolayer at high pressures,



[1]

Another possibility is that these very small Ag crystallites retain properties similar to bulk Ag metal and therefore go through a Ag metal-to-Ag oxide phase change as the O_2 pressure is increased from 300 to 800 Torr. Such a transition to Ag_2O at 170°C would be predicted from the Ag/O_2 phase diagram (*13*); however, a Ag_2O_2 phase does exist (*1*) which may be stable under these conditions and gives close correspondence to the 1 : 1 Ag : O stoichiometry observed at high pressures.

Neither of these suggestions appears to have been made in the literature, probably because the enhanced O_2 adsorption to approach the Ag_2O_2 stoichiometry has not been previously reported. Our present data are insufficient to comment on the merits of the above suggestions, but it should be noted that molecularly adsorbed O_2, perhaps bound as in **II**, has been suggested to be the active oxidizing agent in the ethylene-to-ethylene oxide reaction [1].

SUMMARY

We have shown that the effect of precursor salt used to prepare silver supported on TiO_2 is negligible. This being the case, silver nitrate is the salt of choice because of its superior solubility. The reduction precedures used have demonstrated a definite effect on the dispersion of silver when η-Al_2O_3 and SiO_2 are the supports. On these, lower dispersions were obtained with organic reductions as compared to the hydrogen reduction. Silver on TiO_2, however, showed similar dispersions regardless of the reduction method employed.

The 0.71% and 0.37% Ag/TiO_2 samples with initial dispersions of 0.65 and 0.72 rule out the formation of Ag_2O during the low-pressure oxygen chemisorption experiments since a greater amount of O_2 was taken up than would be possible for this stoichiometry. These samples also showed an enhanced uptake of oxygen at high O_2 pressures (400–900 Torr) giving a stoichiometry of near one oxygen atom for each silver atom in the catalyst. However, further studies are needed to provide an understanding of this phenomenon. A particularly important question concerns whether the enhanced oxygen uptake at high pressures is particle size dependent. The ultrasmall silver crystallites studied here are certainly unique, and they could facilitate the formation of unusual silver–oxygen species or phases that have not been previously observed, as well as altered catalytic properties. Studies to characterize these species and the catalytic behavior of these extremely small silver particles are continuing.

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