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Characterization of Supported Silver Catalysts

I. Adsorption of O_2, H_2, N_2O, and the H_2-Titration of Adsorbed Oxygen on Well-Dispersed Ag on TiO_2

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Very small (3-nm) silver crystallites on TiO_2 were prepared and characterized by XRD, TEM, chemisorption of O_2, H_2, and N_2O, and the H_2-titration of adsorbed oxygen. Similar monolayer coverages were obtained on these clean reduced Ag crystallites using O_2 and N_2O as oxygen precursors, with the latter producing only slightly lower coverages. In all cases, H_2 was found to react stoichiometrically with the adsorbed oxygen layer at 170°C, and this could be described by the reaction, where Ag_s is a surface atom:

$$Ag_s\text{–}O_a + H_{2(g)} \rightarrow Ag_s + H_2O_{(ads)}$$

because monolayer coverages of hydrogen were very low. This stoichiometric reaction between hydrogen and surface oxygen provides the following advantages for characterizing silver catalysts: (1) rapid equilibration, (2) increased sensitivity, (3) no oxygen contamination effects, and (4) distinguishes any irreversible oxygen uptake on support from that on silver.

INTRODUCTION

Silver is a unique catalyst because of its ability to provide high selectivity in the partial oxidation of olefins, such as in the production of ethylene oxide from ethylene. Adsorption on silver surfaces is of particular interest for several reasons. First, oxygen is one of the few gases that chemisorb on reduced silver to the extent that monolayer coverages can be attained. Second, various types of adsorbed oxygen species have been proposed with certain oxygen species being associated with the formation of the desired product, such as C_2H_4O, whereas other species are held responsible for complete oxidation to CO_2. Finally, of principal interest to us was the fact that, although chemisorption is a standard characterization technique for determining surface area and dispersion (fraction exposed) for many metals, a standard procedure does not yet exist for silver because of the complications associated with oxygen chemisorption, such as bulk oxidation and possible variations in the adsorption stoichiometry on the surface. In fact, an ASTM committee is presently studying adsorption procedures in an effort to find an accurate chemisorption technique (*1*). Such a method is particularly needed in this case because sintering under reaction conditions is a principal reason for deactivation in commercial processes, and a rapid, accurate monitoring technique is required.

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This current study was begun to examine the sintering of silver catalysts and these results will be reported in later papers; however, in the course of preparing well-dispersed silver catalysts on TiO_2, η-Al_2O_3 and SiO_2, we found that certain pretreatments minimized problems during oxygen adsorption and that hydrogen reacted stoichiometrically with chemisorbed oxygen. This offered the possibility that a H_2-titration technique, similar to those used for Pt and Pd, could be applicable to silver (*2*). Therefore, an extensive study was made of this reaction along with the chemisorption of O_2, H_2, and N_2O on well-dispersed Ag catalysts. Studying adsorption behavior on these small Ag crystallites minimized or eliminated complications due to subsurface oxygen and bulk oxidation. The effect of different pretreatment procedures was also examined. Of special interest was the comparison of oxygen monolayer coverages achieved by N_2O adsorption with those obtained from molecular oxygen because an earlier study had reported significant differences, which were attributed to different ratios of atomic versus molecular oxygen on the surface (*3*). The results for the Ag/TiO_2 catalysts are reported in this paper, while the behavior of small silver crystallites on Al_2O_3 and SiO_2 and the influence of crystallite size will be discussed elsewhere (*4*).

EXPERIMENTAL

The adsorption 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. 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 system by spherical joints using Buna N O-rings. The system was also equipped with a UTI Model 100C quadrupole mass spectrometer and an atmospheric pressure reducing module, which allowed *in situ* analysis of the gas phase. Additional details are given elsewhere (*4*).

Before their use, hydrogen (MG Scientific, 99.999%) was passed through a tube containing 5A molecular sieve (Supelco, Inc.), helium (MG Scientific, 99.9999%) was passed through an Oxytrap (Alltech Assoc.), and oxygen (MG Scientific, 99.999%) was passed through a drying tube (Supelco, Inc.). Nitrous oxide (AIRCO, 99.995%) was used without further purification. The composition (purity) of each gas used was determined by mass spectrometry prior to its use and, in particular, no O_2 could be detected in N_2O by this technique.

The catalysts used, 1.81 and 1.83 wt% Ag/TiO_2, were prepared by impregnation of TiO_2 (P-25 from Degussa Co., 50 m^2 g^{-1}), which had been pretreated in flowing dry O_2 at 450° for 2 h to remove any organic contamination prior to impregnation, with an aqueous solution of $AgNO_3$ (Aldrich Co.) using an incipient wetness technique (*5*). A third catalyst, 1.86 wt% Ag/TiO_2, was also prepared by the same technique except that the TiO_2 support was used as received without any pretreatment in oxygen. Silver loadings were determined by plasma emission spectroscopy at the Dow Chemical Company. X-Ray diffraction (XRD) measurements were performed using a Rigaku 4036 Al diffractometer with a Cu$K\alpha$ source. Powder samples tightly packed in an aluminum holder were scanned between 2θ values of 20–90° at a rate of 4° min^{-1}. TEM studies were conducted at the Dow Chemical Company with a Philips EM 300 electron microscope or JEOL 100-B electron microscope. The latter was fitted with a Kevex Si(Li) energy dispersive X-ray spectrometer and Tracor Northern NS-880 analysis system.

Prior to all adsorption studies, catalyst samples were pretreated by one of the procedures listed in Table 1. Pretreatment *A*

TABLE 1[a]

Pretreatment Procedures for Ag Catalysts

(a) Pretreatment *A*

1. Evacuate catalyst briefly at R.T.
2. Heat catalyst sample to 170°C at a rate of 10°C/min in atmospheric hydrogen flowing at 20 cc/min.
3. Hold at 170°C in flowing hydrogen (20 cc/min) for 2.5 h.
4. Evacuate the system for 5 min (to less than 10^{-3} Torr) at 170°C.
5. Flow oxygen through system (1 atm) at 20 cc/min for 10 min at 170°C.
6. Evacuate system for 10 min at 170°C, recording vacuum attained after 10 min.
7. Flow hydrogen at 20 cc/min (1 atm) through system for 15 min at 170°C.
8. Evacuate system for 15 min at 170°C, again recording vacuum attained after 15 min.
9. Run isotherms at 170°C evacuating 20–30 min between each isotherm.

(b) Pretreatment *B*

1. Evacuate catalyst briefly at R.T.
2. Heat catalyst sample to 300°C at a rate of 10°C/min in hydrogen (1 atm) flowing at 20 cc/min.
3. Hold at 300°C in flowing hydrogen (20 cc/min) for 3 h.
4. Evacuate for 1 h at 300°C, record pressure after 1 h.
5. Cool to 170°C while still evacuating system (approx 10 min).
6. Stabilize temperature at 170°C, recording vacuum attained.
7. Run isotherms at 170 C evacuating 20–30 min between each isotherm.

(c) Pretreatment *C*

1. Evacuate catalyst briefly at R.T.
2. Heat catalyst sample to 300°C at a rate of 10°C/min in hydrogen (1 atm) flowing at 20 cc/min.
3. Hold at 300°C in flowing hydrogen (20 cc/min) for 2.5 h.
4. Evacuate catalyst while cooling to 170°C (total of 30–45 min) record pressure.
5. Flow oxygen through the system (1 atm) at 20 cc/min for 10 min at 170°C.
6. Evacuate the sample for 10 min at 170°C, record pressure.
7. Flow hydrogen (1 atm) at 20 cc/min through the system for 15 min at 170°C.
8. Evacuate the catalyst for 15 min, record pressure.
9. Run isotherms at 170°C evacuating 20–30 min between each isotherm.

[a] Evacuation times might slightly vary depending on the final desired base pressure.

represents a series of steps suggested as optimum by previous studies (*3*, *6–10*) and is very similar to that employed by the ASTM Task Group studying silver catalysts (*1*, *11*). Pretreatment *B* employed a higher reduction temperature and eliminated the O_2–H_2 cycle at 170°C. These changes were made to facilitate desorption of any organic species, to enhance cleaning and reduction of the Ag surface, and to examine the influence of the O_2–H_2 cycle on stabilization of gas uptakes. All isotherms were measured at 170°C, as suggested by previous work (*3*, *8*), over a typical range 30–200 Torr. Any reversible O_2 adsorption was determined by evacuating the sample for 20 min at 170°C after the O_2 isotherm, then repeating the O_2 adsorption experiment. Hydrogen titration measurements were made after an identical evacuation step. Corrections for physical adsorption on the catalyst surface and support were made by extrapolating the linear portion of the isotherms to zero pressure, as is routinely done. Uptake values were also determined by curve fitting (linear regression) of the data points and the agreement between the two methods was excellent.

The amounts of oxygen adsorbed during N_2O decomposition–adsorption experiments, according to

$$Ag_s + N_2O_{(g)} \rightarrow Ag_s\text{–}O_a + N_{2(g)}, \quad (1)$$

where Ag_s represents a surface Ag atom, were quantitatively determined by mass spectrometry via *in situ* monitoring of the gas phase composition (N_2-evolution) before and after contact of N_2O with the catalyst. Corrections were made for the background gases and this interference was minimized by baking the adsorption system prior to the N_2O experiments. Corrections were also made for the physical adsorption of N_2O on the TiO_2 support itself.

RESULTS

Oxygen Chemisorption

The results of O_2 and H_2 adsorption and

TABLE 2

Summary of Gas Adsorption at 170°C on TiO_2-Supported Ag

Catalyst	Run	Pre-treatment	Gas Uptake (μmole/g cat)[a]							$\frac{(H_2)_{titr}}{(O_2)_{irrev}}$	Dispersion		Particle size (nm)			
			$(O_2)_{tot}$	$(O_2)_{rev}$	$(O_2)_{irrev}$	$(H_2)_{tot}$	$(H_2)_{ads}$	$(H_2)_{titr}$	$(O_2)^*$		$(O_2)_{irrev}$	$(H_2)_{titr}$	Chemisorption		XRD	TEM
													$(O_2)_{irrev}$	$(H_2)_{titr}$		
1.86% Ag/TiO_2	1	*A*	42.0	2.0	40.0	77.0	2.0	75.0	—	1.88	0.47	0.44	2.9	3.0	NV[b]	3.0–7.0[c]
	2	*A*	36.0	—	36.0	74.0	2.0	72.0	—	2.00	0.43	0.43	3.1	3.1	—	—
	3	*B*	46.0	0.5	36.0	77.5	7.0	70.5	—	1.96	0.43	0.42	3.1	3.2	—	—
TiO_2	4	*B*	9.5	—	—	—	0	—	—	—	—	—	—	—	—	—
	5	*A*	0	—	—	—	0	—	—	—	—	—	—	—	—	—
1.83% Ag/TiO_2	6	*C*	35.9	0	35.9	73.0	4.1	68.9	—	1.92	0.43	0.41	3.1	3.3	NV[b]	—
	7	*C*	34.4	0.11	34.3	73.1	4.1	69.0	35.2	2.01	0.41	0.41	3.3	3.3	—	—
	8	*C*	—	—	—	—	4.1	—	—	—	—	—	—	—	—	—
TiO_2	9	*C*	0	—	—	—	0	—	—	—	—	—	—	—	—	—
1.81% Ag/TiO_2	10	*C*	36.2	0	36.2	75.8	3.1	72.7	—	2.01	0.43	0.44	3.1	3.0	—	—
	11	*C*	36.1	0	36.1	76.5	4.4	72.1	—	2.00	0.43	0.43	3.1	3.1	—	—

[a] $(O_2)_{tot}$: total amounts of oxygen adsorbed on a reduced catalyst.
$(O_2)_{rev}$: amounts of oxygen which could be evacuated at the adsorption temperature (reversibly held).
$(O_2)_{irrev} = [(O_2)_{tot} - (O_2)_{rev} - (O_2)_{support}]$: amounts of oxygen irreversibly held.
$(O_2)^*$: total amounts of oxygen adsorbed on catalyst after H_2-titration and further evacuation.
$(H_2)_{tot}$: total amounts of hydrogen uptake on an oxygen covered surface (evacuated).
$(H_2)_{ads}$: amounts of H_2 adsorbed on reduce silver surface.
$(H_2)_{titr} = [(H_2)_{tot} - (H_2)_{ads}]$: amounts of hydrogen reacted with $(O_2)_{irrev}$.

[b] NV = not visible.

[c] Calculated based on limited number of particles after 48 hr in flowing mixture of 90% He, 5% ethylene and 5% O_2 at 250°C.

the H_2-titration reaction on three different Ag/TiO_2 catalysts are listed in Table 2, and a series of typical isotherms is shown in Fig. 1. Similar isotherms were obtained using pretreatments *A* and *B* as reported previously (*2*). Adsorption isotherms on the TiO_2 support material are shown in Fig. 2. Dispersions were calculated by dividing the number of irreversibly chemisorbed O atoms by the total number of Ag atoms as reported previously (*2*); i.e., an adsorption stoichiometry of $O_{(ad)}/Ag_s = 1$ was assumed. Dispersions were also calculated based only on the stoichiometry of the H_2-titration reaction (Eq. (3)). With the exception of O_2 adsorption on TiO_2 after pretreatment *B*, all blank uptakes on the support were zero as shown in Fig. 2. Fresh catalysts in all cases showed a slightly higher total O_2 uptake, but subsequent values were quite similar providing that the same pretreatment was employed. Pretreatment *C* provided the most reproducible adsorption results, but the values of $(H_2)_{tot}$ varied little with pretreatment or cycling as the catalyst was aged by repeated pretreatment and chemisorption runs.

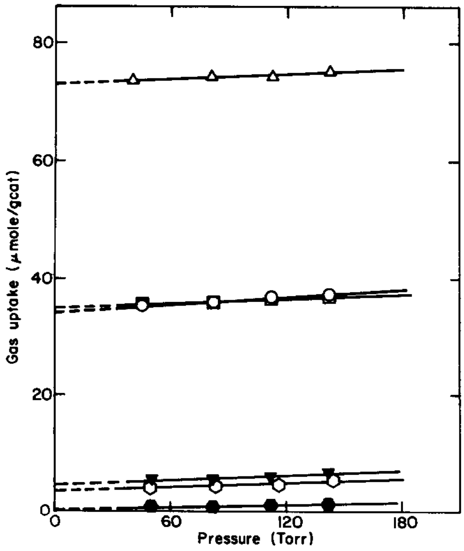


FIG. 1. Gas adsorption on 1.83% Ag/TiO_2 at 170°C given pretreatment *C*. ○, $(O_2)_{tot}$; ●, $(O_2)_{rev}$; △, $(H_2)_{tot}$; □, $(O_2)^*$; ▼, $(H_2)_{ads}$; ○, reversible $(H_2)_{ads}$.

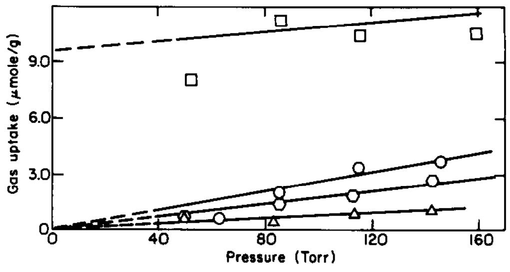


FIG. 2. Gas adsorption on TiO_2 support material at 170°C. O_2 isotherm after pretreatment: ○, A; □, B; ○, C; △, H_2 isotherm after pretreatment *C*.

Some important results should be emphasized here: 1) Essentially all the adsorbed oxygen was irreversibly held as evacuation at 170°C for 20–30 min removed only extremely small amounts (if any) of this chemisorbed layer. 2) A very reproducible stoichiometry near 2.0 existed between the hydrogen of titration and the irreversibly adsorbed oxygen, and this value was not noticeably dependent on pretreatment. 3) Only small amounts of hydrogen were adsorbed (approx 10% of the O monolayer) on clean reduced Ag surfaces after pretreatments *A* and *C*, and most of this hydrogen could be removed by evacuation at 170°C; e.g., 3 μmole H_2/g cat in run 7 with 1.83% Ag/TiO_2 were desorbed. Comparable amounts of H_2 (~3 μmole/g cat) could be adsorbed on the catalyst surface at 170°C after H_2-titration and further evacuation.

It should also be pointed out that oxygen adsorption prior to titration, $[(O_2)_{tot}]$, and immediately following titration, $[(O_2)^*]$, was very similar indicating that all the adsorbed oxygen was removed by hydrogen and that the same amount of O_2 could be readsorbed on the catalyst surface following H_2-titration and evacuation. This confirms the complete reactivity of the adsorbed oxygen on these small crystallites toward H_2. Gas uptakes on these samples were also followed as a function of time and typical results are shown in Fig. 3. The minimization of drifting in O_2 uptakes on these small Ag crystallites is clear, as over 90% of the O_2 adsorption occurred within 5 min;

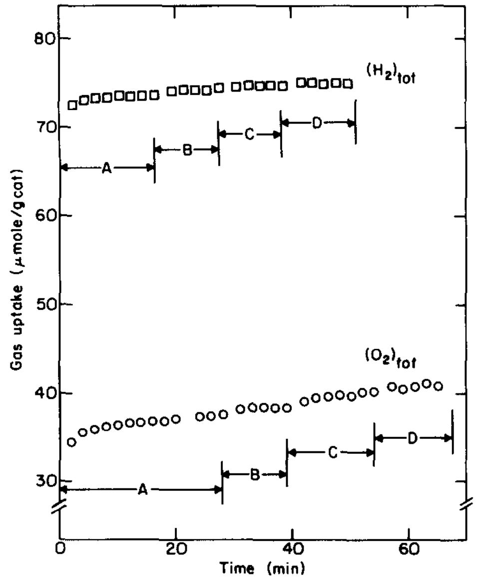


FIG. 3. Gas uptake with time on 1.83% Ag/TiO_2 at 170°C, given pretreatment *C*. Equilibrium pressures of A, 45 Torr; B, 82 Torr; C, 112 Torr; D, 142 Torr.

however, slow continual uptakes were observed over longer periods of time, indicative of a recognized problem with Ag. In contrast, the reaction of H_2 with oxygen-covered surfaces occurred very rapidly, and H_2 uptakes on Ag were always completed in less than 5 min. This provides a clear advantage for the H_2-titration technique.

N_2O Decomposition-Adsorption

Oxygen adsorption via decomposition of N_2O on clean reduced Ag surfaces was also studied at similar conditions, and the identical catalyst samples used in O_2-chemisorption studies were used in N_2O experiments. Table 3 summarizes the results of N_2O experiments on TiO_2-supported Ag catalysts. *No oxygen in the gas phase was detected by mass spectrometry* after periods of 20 h contact time at 170°C although evolution of O_2 at higher temperatures has been reported (*3*) for other supported silver catalysts after extended periods of contact time up to 20 h. The appearance of gas phase O_2 in these previous studies was attributed to the quasi-homogeneous decomposition of N_2O according to the reaction

$$2N_2O_{(g)} \leftrightarrows 2N_{2(g)} + O_{2(g)}. \qquad (2)$$

However, it should be pointed out that if reaction (2) does occur, the small amounts of O_2 evolved are expected to adsorb on the Ag surface, particularly in the early stages of the N_2O experiments where much of the Ag surface is not covered by oxygen. This may account for the observation of O_2 in the gas phase after 20 h (*3*) when the surface is almost fully saturated and no further O_2 adsorption can occur readily. Due to the identical stoichiometry of Eqs. (1) and (2), the overall calculations of the amounts of O_2 adsorbed in the study were not affected because no O_2 was detected. However, corrections for Eq. (2) must be made should residual oxygen be observed. In order to check the gas phase contribution from reaction (2) in our system, identical experiments using an empty cell were carried out. Under our experimental conditions, no O_2 was detected in the gas phase by mass spectrometry after 19 h at 170°C and, therefore, the contribution of O_2 from Eq. (2) to the adsorption process on Ag was ruled out in our experiments. Also, we determined that N_2O decomposition did not occur on oxygen-covered Ag surfaces.

It was found that if catalyst samples were evacuated at 170°C after N_2O experiments and were then exposed to O_2, again measuring two O_2-isotherms as in the oxygen chemisorption experiments, only very small additional amounts of O_2 could be irreversibly adsorbed as shown by the $(O_2)_{II}$ values in Table 3. Blank adsorption experiments on the pure TiO_2 support material (given pretreatment *C*) indicated no N_2O decomposition and no irreversible adsorption, but some physical adsorption of N_2O on TiO_2 occurred, as shown in Fig. 4.

A comparison of Tables 2 and 3 indicates that the following conclusions can be reached. First, similar oxygen coverages and, by inference, similar dispersions and particle sizes, could be obtained using O_2 or N_2O as the oxygen precursors with the lat-

TABLE 3

Summary of N_2O Decomposition–Adsorption on 1.83% Ag/TiO_2 at 170°C

Run	Pre-treat-ment	Contact time (h)	P_{N_2O} (Torr)	Gas Uptake (μmole/g cat)[a]								$\frac{(H_2)_{titr}}{(O_2)_{irrev}}$	Dispersion		Particle size (nm) (chemisorption)	
				$(O_2)_I$	$(O_2)_{II}$	$(O_2)_{rev}$	$(O_2)_{irrev}$	$(H_2)_{tot}$	$(H_2)_{ads}$	$(H_2)_{titr}$	$(O_2)^*$		$(O_2)_{irrev}$	$(H_2)_{titr}$	$(O_2)_{irrev}$	$(H_2)_{titr}$
1	C	17½	149	—	2.3	0	—	72.2	4.1	68.1	—	—	—	0.41	—	3.3
2	C	21	153	31.4	0.53	0	31.9	72.4	4.1	68.3	—	2.14	0.38	0.41	3.5	3.3
3	C	20	252	33.9	0.19	0.24	33.9	72.1	4.1	68.0	34.9	2.01	0.41	0.41	3.3	3.3
4	C	20	252	39.1	1.1	0.23	40.0	72.7	4.1	68.6	—	1.72	0.48	0.41	2.8	3.3
5	C	3	252	28.2	3.6	0.10	31.7	73.0	4.1	68.9	—	2.17	0.38	0.41	3.5	3.3
6[b]	C	19	249	0	0	0	0	0	0	0	—	—	—	—	—	—

[a] See footnotes in Table 2 except: $(O_2)_I$: total amount of oxygen adsorbed calculated from mass spectrometry via N_2O decomposition. $(O_2)_{II}$: total amount of oxygen adsorbed via O_2 after N_2O experiments and further evacuation. $(O_2)_{irrev} = (O_2)_I + (O_2)_{II} - (O_2)_{rev}$.

[b] On pure TiO_2.

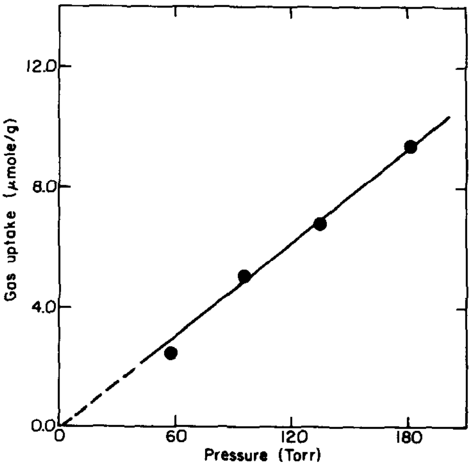


FIG. 4. N_2O adsorption isotherm at 170°C on TiO_2 support material given pretreatment *C*.

ter molecule produced only very slightly lower coverages than molecular O_2 under the experimental conditions used in this study. Second, stoichiometries very near 2.0 existed between $(H_2)_{titr}$ and chemisorbed oxygen from either O_2 or N_2O, $[(O_2)_{irrev}]$, but due to the larger error in determining $(O_2)_I$ values from mass spectrometry, compared to those from O_2 isotherms, this ratio varies over a wider range. However, the average value of 2.0 in Table 3 is in excellent agreement with values in Table 2. Isotherms for H_2 and O_2 uptakes following N_2O adsorption were very linear, as shown in Fig. 5, and essentially identical to those in Fig. 1. The extent of oxygen surface coverage after 20 h exposure to N_2O, as indicated by the $(O_2)_{II}$ values, did not vary significantly as the *initial* N_2O pressure was varied between 150 and 250 Torr. However, the contact time of N_2O with the catalyst was found to be an important factor and longer contact times produced higher coverages, although small amounts of O_2 could still be irreversibly adsorbed on the catalyst surface after 20 h.

TEM and XRD Measurements

Some small (3- to 10-nm) Ag crystallites could be identified in the TEM micrographs; however, the number which could

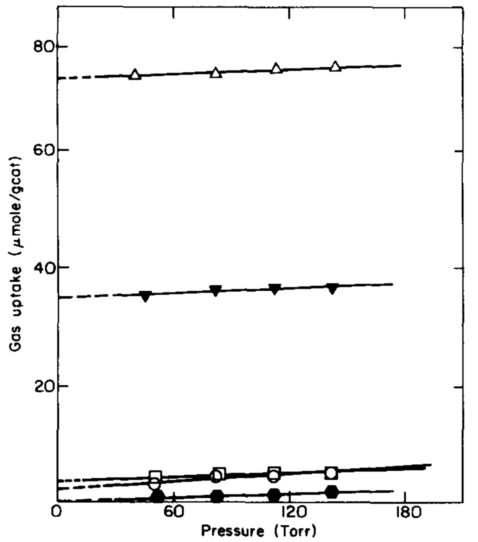


FIG. 5. Gas adsorption at 170°C on 1.83% Ag/TiO_2 after 17½ hr N_2O adsorption followed by evacuation. O, $(O_2)_{II}$; ●, $(O_2)_{rev}$; △, $(H_2)_{tot}$; □, $(H_2)_{ads}$; ▼, $(O_2)^*$.

easily be distinguished from the small titania crystallites was very small. This is a common problem with TiO_2-supported metals and prohibited the determination of a meaningful particle-size distribution. XRD measurements showed that the pure TiO_2 support was approx 78% anatase and the 1.81% Ag/TiO_2 catalyst support contained 70% anatase. No silver peaks were distinguishable; however, an unambiguous identification of the Ag peaks in the catalyst was difficult due to the overlap of the major Ag peaks with those of the support.

DISCUSSION

Oxygen adsorption on silver surfaces is a complex phenomenon and questions pertaining to the nature of the adsorbed oxygen species are still not fully answered. Many published results remain contradictory (*7, 12, 13,* and references therein), and a survey of the literature indicates that much of the variation in results reported in the various investigations may be a consequence of experimental parameters which have an especially marked effect on oxygen chemisorption on silver surfaces. These factors include 1) catalyst preparation (Ag precursors), 2) sample pretreatment, 3) O_2 pressure and adsorption temperature (i.e., bulk oxidation), 4) surface restructuring, 5) impurities, and 6) support effects. Important questions still exist regarding the adsorbed state of oxygen on silver surfaces, such as: 1) To what extent does atomic and molecular adsorption occur? 2) What is the extent of subsurface oxygen (including bulk oxidation) formation? 3) What are the charged states of the surface oxygen species? 4) Under what conditions, if any, can well-defined surface adsorption stoichiometries be obtained? These questions have been addressed previously and the current status has been summarized in recent review articles (*7, 12, 13*).

The intent in this investigation was to prepare and study *well-dispersed* silver catalysts, which would maximize the formation of only surface oxygen species, i.e., by minimizing bulk oxidation and subsurface oxygen, and to define a set of experimental conditions which would give calculated average crystallite sizes consistent with XRD and TEM results. Because of the low reactivity of reduced silver surfaces toward most gases, utilization of a chemisorption method for characterization of this metal has been rather difficult. Among simple diatomic gases, oxygen is the only one which chemisorbs on reduced Ag surfaces to provide monolayer coverages (*14*); however, many uncertainties exist with this technique due to the formation of subsurface (bulk) oxygen (*15–19*). Therefore, alternative methods of characterization would be highly desirable.

The most significant result of this study is that oxygen chemisorbed on small silver crystallites with high Ag_s/Ag_b ratios, where Ag_b is a bulk silver atom, will react completely with hydrogen at 170°C according to the equation

$$Ag_s\text{–}O_a + H_{2(g)} \rightarrow Ag_s + H_2O_{(ads)}. \quad (3)$$

The water formed should adsorb readily on the support. This equation infers that no hydrogen adsorbs on the silver surface whereas small fractional coverages do occur, as shown in Table 2. Correction for this adsorbed hydrogen can be made, if desired, as has been done in this study; however, the error introduced by ignoring this amount is small (<10%), and rapid, accurate surface area measurements can be obtained by utilizing reaction (3) as written. These results clearly show that the hydrogen titration of chemisorbed oxygen on silver appears to be an alternative adsorption technique for dispersion measurements of this metal, and is similar in concept to methods developed for Pt (*20*) and Pd (*21*). In fact, it may well be a preferred method for the following reasons: 1) The sensitivity is doubled. 2) Surface contamination problems due to oxygen are minimized or eliminated. 3) The H_2 reaction with surface oxygen is rapid, whereas slow, continual oxygen uptakes frequently occur on silver surfaces, especially those of large crystallites. 4) Oxygen adsorbed on the support can be distinguished from the reactive oxygen on the silver. In addition, a fifth advantage may exist in that the rapid uptakes during H_2 titration on *large* Ag crystallites appear to represent reaction only with surface oxygen while slower, continuous H_2 adsorption processes may represent reaction with subsurface (bulk) oxygen diffusing to the surface (*22*). This allows the possibility of distinguishing surface oxygen species from subsurface oxygen (*2*), and this will be discussed in greater detail in another paper (*22*).

The results in Tables 2 and 3 show that all the oxygen chemisorbed, whether from O_2 or from N_2O, can be reproducibly titrated by hydrogen. On these small 3- to 4-nm crystallites, complete removal of bulk (subsurface) oxygen is facilitated, should it exist, because of the short diffusion distances to the surface, and the pretreatment utilized had no significant effect on O_2 uptakes or titration values on these TiO_2-supported Ag catalysts although correction for oxygen adsorption on the TiO_2 support was required after pretreatment *B*, which did not expose the titania to oxygen prior to the isotherm measurements. However, pretreatment *C*, which combines the higher reduction temperature of pretreatment *B* with the O_2/H_2 cycle at 170°C in pretreatment *A*, is preferred for the following reasons: It eliminates the O_2 blank on TiO_2, it facilitates complete Ag reduction, and it enhances desorption of water and organic species, should they exist, from the support. In regard to the first point, run 4 in Table 2 shows that only the oxygen associated with the silver surface is reactive during H_2 titration, and it supports one of the previously mentioned advantages of this technique. Although the last consideration was not important with these catalysts, which were prepared from $AgNO_3$ and reduced in H_2, it was found to be much more important with samples prepared from silver organic compounds and reduced by organics such as formaldehyde (*23*). The time/temperature combination used in pretreatment *A* was not sufficient to completely remove adsorbed organic compounds from the catalyst prior to adsorption runs, and desorbing species complicated measurements (*2*). The insensitivity of the titration reaction to pretreatment is evident. Finally, if the additional oxygen adsorption on silver following the N_2O experiments is molecular in nature, it comprises only a small fraction of the surface species and also has similar reactivity to hydrogen as the $(H_2)_{titr}$ values in Table 3 are almost identical to those of runs 6 and 7 in Table 2 for the 1.83% Ag/TiO_2 catalyst given pretreatment *C*.

Although several workers have investigated the interaction of N_2O with various silver surfaces (*3, 24–26*), only the study of Scholten *et al.* (*3*) has dealt with a thorough examination of N_2O adsorption on silver under a variety of experimental conditions. They found that uptakes of molecular O_2 gave coverages about 25% higher than those obtained from N_2O experiments. Our results show that very similar surface coverages are obtained using either O_2 or N_2O

as the oxygen precursor as shown by the extremely small amounts of oxygen adsorbed after N_2O interaction, the $(O_2)_{II}$ values in Table 3, and the similarity of the $(H_2)_{titr}$ values in Table 3 and those of runs 6 and 7 in Table 2. This may well be a consequence of Ag crystallite size as the average sizes in their study were 1–2 orders of magnitude larger. Scholten *et al.* found that surface oxygen coverage using N_2O increased with contact time and temperature and maximum coverage was obtained at 170°C. Although this trend was similar for both supported crystallites (~30 nm) and silver powders (~1600 nm), they noted that the smaller crystallites were more reactive for interaction with N_2O than the larger unsupported Ag crystallites under the same experiment conditions. These results, combined with those presented here, suggest a crystallite size effect may exist for the interaction of N_2O with reduced Ag surfaces. It should also be noted that catalysts studied by Scholten *et al.* had been prepared using organic compounds, and the possibility of carbon contamination exits, as mentioned in their paper.

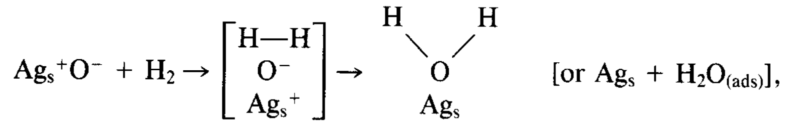
The increased surface coverage using O_2 was attributed to the formation of molecular oxygen species on silver surfaces (*3*). Assuming N_2O produces only atomic oxygen species on Ag surfaces (disregarding any recombination of the atomic species), whereas O_2 uptakes could result in both atomic and molecular species, from our results it can be concluded that the formation of adsorbed molecular oxygen species on these small TiO_2-supported Ag crystallites is extremely small, if not completely absent. The apparent absence of molecular oxygen on these small Ag crystallites is currently being examined by EPR spectroscopy and kinetic studies because the presence of molecular oxygen has been proposed as a necessary surface species for ethylene oxide formation (*27*), although this has been disputed by others (*19b, 29, 30*).

Although this stoichiometric reactivity of chemisorbed oxygen with hydrogen has not been reported in the surface science literature, it has been reported recently by Boreskov and co-workers for silver powder in an paper which appeared after this study was initiated (*28*).

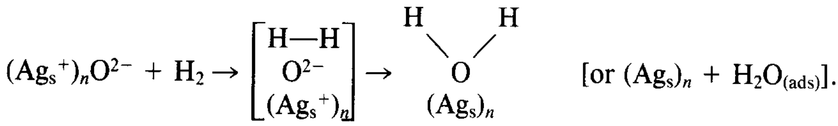
Further studies are needed to clarify and understand the elementary steps involved in the mechanism of H_2O formation summarized by Eq. (3). Oxygen adsorbed on noble metal surfaces such as Pt and Pd can also be titrated with H_2 (*20, 21*); however, these noble metals are known to readily dissociate hydrogen molecules, whereas dissociation of H_2 is not expected on Ag (*14*). The high reactivity of this adsorbed oxygen toward H_2 (almost complete reaction occurs in less than 1 min) is perhaps surprising and furthermore, because of the oxygen-saturated surface, any dissociation of H_2 must involve adsorbed oxygen species. However, ethylene also adsorbs on oxygen-covered silver surfaces although it does not chemisorb on reduced surfaces (*31*), thereby indicating the enhanced chemisorption capacity of silver surfaces after exposure to oxygen. The types of surface oxygen species present are of considerable interest.

The ability of oxygen to chemisorb on silver has generally been attributed to the oxidizing (pseudoradical) character of oxygen (*3*). One implication of this is that O_2 chemisorption on Ag can be regarded as a "redox reaction" and, therefore, electron transfer to some degree from silver to oxygen is expected due to the higher electronegativity of the oxygen, with silver at the surface being oxidized during chemisorption. As a result, some of the negatively charged oxygen species produced, such as O^- and O_2^-, would be paramagnetic and indeed the existence of latter has been proposed based on EPR spectroscopy (*25, 32–35*). Other negatively charged species, such as O_2^{2-} or O^{2-}, are diamagnetic and no EPR signal would be detected. In the case of titania-supported Ag, it is believed that O_2^- is stabilized on the TiO_2 support rather than on silver crystallites (*36*). This possibility exists for other supported silver catalysts as well, especially when the metal (Ag) loading of the catalyst is very small. Although silver metal can act as an electron donor for the formation of O_2^-, these O_2^- species may possibly migrate onto the support. The mobility of the adsorbed layer has also been studied using different techniques such as LEED and EPR, and from the latter method a correlation time of 10^{-6} s^{-1} at 0°C has been reported for O_2^-/Ag systems (*37*).

Similarities may exist between the reactivity of negatively charged oxygen species on oxide surfaces and adsorbed oxygen species on silver surfaces. For example, it has been shown that O^- ions produced by irradiation on MgO (*38*) and supported oxide catalysts such as V_2O_5–SiO_2 and MoO_3–SiO_2 (*39*) are active centers for dissociation of H_2 and hydrocarbons. Although the exact mechanism of catalytic oxidation of hydrogen on silver is not known and various mechanisms have been postulated (*40–42*), the relevance of this process to the H_2-titration reaction studied in this work is of interest. The kinetics of interaction of H_2 with adsorbed oxygen on small supported silver crystallites, such as those studied in this work, may indeed be different from kinetics on larger Ag crystallites because of the different surface/volume ratios and the possible slow diffusion of bulk oxygen to the surface (*2*). Although we cannot distinguish between reactions of various oxygen species, such as those illustrated in Eqs. (4) and (5), it is important to point out the rapid reaction of *all* adsorbed oxygen with hydrogen on these small crystallites. The similarity of coverage obtained from O_2 and N_2O adsorption would infer atomic species on the surface, and if more than one species exist either both are very reactive or they interconvert readily.



$$\mathrm{Ag_s^+O^-} + \mathrm{H_2} \rightarrow \left[\begin{array}{c} \mathrm{H{-}H} \\ \mathrm{O^-} \\ \mathrm{Ag_s^+} \end{array}\right] \rightarrow \begin{array}{c} \mathrm{H}\quad\ \mathrm{H} \\ \backslash\ / \\ \mathrm{O} \\ \mathrm{Ag_s} \end{array} \quad [\text{or } \mathrm{Ag_s} + \mathrm{H_2O_{(ads)}}], \qquad (4)$$



$$(\mathrm{Ag_s^+})_n\mathrm{O^{2-}} + \mathrm{H_2} \rightarrow \left[\begin{array}{c} \mathrm{H{-}H} \\ \mathrm{O^{2-}} \\ (\mathrm{Ag_s^+})_n \end{array}\right] \rightarrow \begin{array}{c} \mathrm{H}\quad\ \mathrm{H} \\ \backslash\ / \\ \mathrm{O} \\ (\mathrm{Ag_s})_n \end{array} \quad [\text{or } (\mathrm{Ag_s})_n + \mathrm{H_2O_{(ads)}}]. \qquad (5)$$

Finally, on this subject, fundamental studies of the H_2-titration reaction on oxygen-covered single crystal Ag surfaces might shed some light on mechanistic aspects of this reaction.

A metal-support interaction has been proposed for some metals supported on TiO_2 which resulted in suppressed H_2 and CO chemisorption (*43*); however, oxygen chemisorption does not appear to be affected as dramatically (*44, 45*). Silver alone on TiO_2 does not appear to exhibit unusual behavior as Baker and co-workers (*46*) have recently reported that after treatment in H_2 at 550°C, a temperature sufficiently high to induce morphological changes in other systems (*43*), silver metal particles on titania were rather large, relatively dense, and globular in outline, indicative of quite normal behavior. Only after subsequent introduction of Pt into these Ag/TiO_2 systems, followed by a further reduction cycle, were significant changes observed in the morphology of Ag. The formation of thin, pillbox structures, almost indistinguishable from Pt, was attributed to the formation of Ti_4O_7 produced by the Pt-catalyzed reduction of TiO_2 by hydrogen. Although Elipe and co-workers (*36*) have shown using EPR spectroscopy that treatment of Ag/TiO_2 catalysts in H_2 at temperatures of 200°C or lower caused the formation of Ti^{3+} ions, indicating reduction of the TiO_2 support, it should be pointed out that EPR spectroscopy has a high sensitivity and only an exceedingly small extent of reduction would provide detectable Ti^{3+} cations. In agreement with Baker *et al.*, electron micrographs of our Ag/TiO_2 catalyst showed rather spherical particles and the particle size estimated from these TEM data was reasonable compared to that calculated from oxygen chemisorption and H_2-titration data. The possibility that some atomic hydrogen species, occurring as a result of H_2 dissociation on oxygen-covered Ag surfaces, may diffuse onto the TiO_2 surface and cause significant reduction of the support during the H_2-titration reaction can be discounted because of the stoichiometric agreement and the absence of slow, continued H_2 uptakes.

The absence of bulk Ag_2O formation has been assumed in the interpretation of these results because the phase diagrams for bulk Ag/O_2 systems shows only metallic silver exists in the temperature-pressure region employed here (*47*). Although thermodynamic properties for very small crystallites may be different from bulk properties and some ambiguity exists regarding the presence of Ag_2O, we presently do not believe it exists at our adsorption conditions for the following reasons. First, Baetzold has found a cluster-size effect on Cl adsorption on silver up to 30–40 atoms/cluster, but UPS spectra showed bulk-like behavior for larger clusters (*48*). A 3- to 4-nm crystallite on TiO_2 contains hundreds of Ag atoms, and bulk-like behavior would therefore be predicted. Second, we have measured O_2 uptakes on 1.83% Ag/TiO_2 from 4 to 600 Torr and found that they were constant at 35.5 ± 0.5 μmole O_2/g to 340 Torr, which gives an $O_{(a)}/Ag$ ratio of 0.41. However, additional uptakes occurred at the higher pressures, under which Ag_2O formation is expected, and at 600 Torr an $O_{(a)}/Ag$ ratio of 0.49 was achieved. Had Ag_2O been formed at the lower pressures, this additional uptake would not have occurred. Third, $O_{(a)}/Ag$ ratios greater than 0.5 have been obtained on more recently prepared samples. Fourth, the very rapid H_2 uptakes favor a surface reaction. Fifth, bulk Ag_2O formation does not occur for 10-nm Ag crystallites on SiO_2 (*4*). Sixth, no evidence has been found to indicate interactions between Ag and TiO_2 to form Ag_2TiO_3, e.g., (*46*). Despite these arguments, we are aware that Ag_2O formation cannot be unequivocably discounted in these systems, and we plan future solid-state NMR studies of Ag and ^{17}O adsorbed on Ag to clarify this situation.

SUMMARY

Very small silver crystallites dispersed on titania can reproducibly be prepared by an incipient wetness technique using aqueous solutions of $AgNO_3$. On these 3-nm crystallites, which have over 40% of their atoms present at the surface, very similar oxygen monolayer coverages are achieved using either O_2 or N_2O as the adsorbate. Although hydrogen does not adsorb appreciably on these Ag surfaces (10% monolayer coverage or less), it reacts rapidly and stoichiometrically with irreversibly adsorbed oxygen in all cases to form H_2O, which is adsorbed on the support. This titration reaction provides advantages over oxygen chemisorption methods for determining silver surface areas because it is rapid, more sensitive, and minimizes or eliminates problems from oxygen contamination and subsurface (bulk) oxygen formation. In addition, we believe that the H_2-titration reaction can be used to distinguish surface oxygen from bulk oxygen in larger silver crystallites, with the rapid, initial uptakes detecting adsorbed oxygen and slower continual H_2 uptakes reflecting reaction with bulk oxygen diffusing to the surface. Studies are in progress to verify this hypothesis.

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