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Reaction of Nitrous Oxide and Oxygen with Silver Surfaces, and Application to the Determination of Free-Silver Surface Areas of Catalysts

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This paper deals with the adsorption and decomposition of nitrous oxide and the chemisorption of oxygen on silver powders and silver-on-carrier catalysts. Adsorption–decomposition was studied at temperatures between 25 and 250°C and 15 cm Hg nitrous oxide pressure; the chemisorption experiments were performed at 50–250°C and 10^{-3} to 200 mm Hg.

Methods are indicated for calculating the free-silver surface area. In cases where different techniques can be employed the results appeared to be in rather good agreement with X-ray line broadening and electron microscopy data.

Special attention is given to the influence of surface contaminations on the sorption behaviour of oxygen. The presence of carbonaceous contaminations may introduce subsurface oxidation.

At full coverage silver adsorbs about 25% more oxygen from O_2 than it does from N_2O.

INTRODUCTION

It is well-known that silver is an important catalyst for the epoxidation of ethylene. Promoters like hydroxides, oxides, or peroxides of alkaline earth metals (*1*) are often added to improve the activity, while increased selectivity is obtained by addition of moderators like chlorine (*2*, *3*), bromine, iodine, sulphur, selenium, phosphorus (*4*). Silver may also be applied for oxidizing methanol to formaldehyde (*5*).

The degree of silver dispersion in these catalysts can be studied by various methods, e.g., by electron microscopy or X-ray line broadening. However, to gain information on the *free* metallic part of the silver crystallites, it is necessary to develop a chemisorption method for covering that part of the surface area of the silver crystallites *not* occupied by interaction with the carrier material, promoters, moderators or catalyst poisons.

We decided to study whether this objective could be achieved by means of oxygen chemisorption, starting from oxygen or from nitrous oxide, as this would have the advantage of simultaneously providing some information on an adsorption step which may play an important role in the catalytic oxidation itself. Hydrogen and carbon monoxide cannot be used for determining the surface area, as they are hardly chemisorbed on silver (*6–8*).

In a former publication (*9*) we have shown that in the case of copper the reaction:

$$N_2O(g) \rightarrow O(ads) + N_2(g) \qquad (1)$$

can be used for determining the free-copper surface area. This adsorption–decomposition of nitrous oxide differs in some respect from surface oxidation with oxygen. With nitrous oxide the heat of reaction is 19.5 kcal/mole higher owing to the endothermic nature of the compound. Kinetically, however, the reactivity of nitrous oxide is much lower than that of oxygen. The most striking difference is seen in the behavior of the two gases with respect to a copper surface covered with a monolayer of oxygen. Whereas oxygen is highly reactive with such a surface, even to the extent that the whole bulk is rapidly oxidized, bulk oxidation of the copper with nitrous oxide proceeds well only above 100°C, because it needs an activation energy of about 20 kcal/mole. This points to a difference in oxidation mechanism, which could be related to a difference in electronic structure between the two molecules (*9*). The linear nitrous oxide molecule being stabilized by resonance, has the lower activity, whereas oxygen is the more reactive molecule owing to its pseudoradical character.

During bulk oxidation with oxygen, which proceeds rapidly with low activation energies, copper ions diffuse through the oxide layers and oxygen atoms form at the surface by taking up two electrons (*10*). The mechanism of *bulk oxidation via nitrous oxide*, however, is unknown; it might be initiated by a rate-determining precursor reaction in which nitrous oxide decomposes into nitrogen and oxygen on the oxygen monolayer covering the copper surface. This precursor reaction would be an activated reaction ($E \sim 20$ kcal/mole), achieving a measurable rate only at temperatures above 100°C.

It seemed worthwhile to investigate to what extent the above principles may be useful to us in determining the area of the free-silver surface. Silver oxide (Ag_2O) having a low stability, we thought it unlikely to be confronted with the complicating phenomenon of bulk oxidation as occurs on copper surfaces.

Oxygen adsorption can also be applied for measuring free-silver surface areas. Smeltzer *et al.* (*12*) measuring oxygen adsorption isobars at oxygen pressures of 200, 400 and 700 mm Hg, found the optimum temperature to lie at about 200°C; above this temperature the rate of desorption exceeds the rate of adsorption. Their results indicate that at about 200°C the equilibrium value (which is nearly independent of the oxygen pressure, in the range from 200 to 700 mm Hg) corresponds to adsorption of about one oxygen atom per silver atom in the surface layer.

From the oxygen adsorption isobar measured at 10 mm Hg oxygen pressure, Czanderna (*13*) derived an optimum temperature of about 180°C. At the low pressure used by this author, the oxygen uptake is always somewhat less than one oxygen atom per silver surface atom. Kholyavenko *et al.* (*14*) determined the oxygen adsorption isotherm at 200°C; at an oxygen pressure of 2–3 mm Hg, they found a saturation value corresponding to one monolayer. Sandler and Hickam (*15*), however, showed that thoroughly cleaned silver samples may take up much more oxygen than corresponds to one monolayer at about the same pressure and within the same temperature range as used by Czanderna. Even after ½–16 hr of pumping at 500°C oxygen was left occluded in the sample, the maximum being equivalent to 2.5 monolayers.

In view of this controversy, we decided to reinvestigate the adsorption of oxygen on silver samples from various sources, giving special attention to the relation between the presence of surface impurities and the occurrence of bulk oxidation after adsorption.

EXPERIMENTAL

Apparatus and Procedure

The apparatus schematically illustrated in Fig. 1 has been designed for degassing the samples at a pressure of 10^{-6} mm Hg. The sample is contained in vessel A, which can be kept at a constant temperature in the range between −196 and 550°C. The nitrous oxide can be circulated over the sample by means of an all-glass electromagnetically actuated piston pump F. After defined time intervals a negligibly small gas sample can be withdrawn from the circulating gas via stopcock D to be analyzed by means of a thermal conductivity gauge C. This method of analysis is described by Farkas (*16*). At the end of the decomposition run, a sample is taken in vessel R, and analyzed mass spectrometrically. The dead volume of the appa-

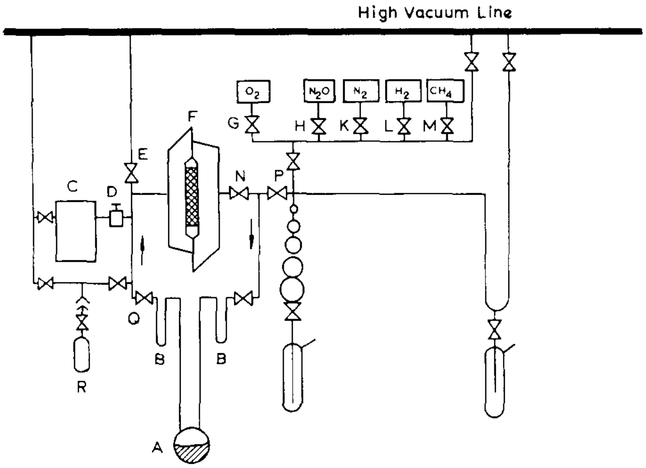

FIG. 1. Diagram of the apparatus.

ratus can be reduced by closing stopcocks N and Q; this facilitates determination of the total surface areas by the BET method with nitrogen or methane being used as adsorbate. Poisoning of the sample with water and mercury is prevented by two traps B cooled with liquid nitrogen. The cross-sectional area of the nitrogen molecule is taken to be 16.2 Å^2, that of the methane molecule 16.0 Å^2. Several gases can be introduced into the apparatus via stopcocks G, H, K, L and M, and the system can be evacuated through stopcock E.

Materials

Gases. Hydrogen for reducing the silver samples was tank hydrogen purified by means of a Johnson-Matthey type A 1 Pd-Ag alloy diffusion unit. Nitrous oxide was dried over molecular sieve type 3A. Analysis: 99.8 vol% N_2O and 0.2 vol% N_2. Nitrogen containing 0.3% H_2 and about 10 ppm O_2 was freed of oxygen over a Johnson-Matthey "deoxo catalyst" type D (0.5 wt% Pd on γ-Al_2O_3), dried over molecular sieve type 5A and further purified by liquefaction and distillation. Methane (Air Liquide grade N 45; purity, 99.995 vol%) was dried over molecular sieve type 3A for use in the BET measurements.

During the first experiments we used oxygen prepared by thermal decomposition of reagent grade potassium permanganate, and in the subsequent experiments we used oxygen (Air Liquide grade A 40, purity 99.99 vol% O_2), dried over molecular sieve 4A.

Silver catalysts (see Table 1). Samples 1 and 2 were prepared from reagent grade silver nitrate (*17*). To a well-stirred solution of $AgNO_3$ a potassium hydroxide solution is added. After precipitation of the silver oxide a 30-wt% solution of formaldehyde is introduced into the agitated suspension, whereupon the mixture is heated to 100°C. The silver powder is separated by filtration, suspended in a 2% nitric acid solution, again separated by filtration, and rinsed with distilled water.

Samples 3 and 4 were made from a reagent grade $AgNO_3$ solution by reduction with hydrazine hydrate (*17*). After precipitation, the silver powder is first rinsed with a 2% nitric acid solution and then with distilled water.

Samples 5 and 6 were activated Raney silver species, stored in methanol (Degussa). Before use the methanol is removed by evaporation in vacuo.

Samples 7, 9 and 11 were prepared by a controlled precipitation technique (*18*). A suspension of the carrier material in a solution of the silver complex of "Komplexon III" (disodium salt of EDTA) is vigorously stirred, a small amount barium Komplexon III is added, after which the two complexes are decomposed by oxida-

TABLE 1
SURVEY OF SAMPLES

Sample no.	Sample	Carrier	Temperature of reduction (°C)	Evacuation		Total surface area (BET) (m²/g)	Ba promoter content (wt%)	Carbon content (wt%)	$\bar{d}_{v.s.}$ mean crystallite size of Ag, from BET surface area (μ)	$\bar{d}_w$, mean crystallite size, from X-ray line broadening (Å)
				Temperature (°C)	Time (hr)					
1	silver powder from $AgNO_3$ (reagent grade) precipitation with KOH, and wet reduction with formaldehyde at 100°C	—	170	170	24	0.35	—	<0.01	1.6	—
2	as 1	—	250	250	24	0.35	—	<0.01	1.6	—
3	silver powder from $AgNO_3$ (reagent grade) wet reduction with a hydrazine hydrate solution at 0°C	—	200	200	24	0.17	—	<0.001	3.4	—
4	as 3	—	250	250	24	0.11	—	<0.001	5.0	—
5	Raney Silver from Degussa	—	170	170	24	0.98	—	—	0.6	—
6	as 5	—	250	250	24	1.15	—	—	0.5	—
7	10.6 wt% silver	γ-Al_2O_3 Type P110, from Degussa	150	150	20	113	0.1	0.11	—	650
8	10.5 wt% silver	γ-Al_2O_3 Type P110, from Degussa	200	200	16	107	0.7	1.2	—	300
9	9.3 wt% silver	α-Al_2O_3 Type A3, from Alcoa	200	200	16	16.2	0.1	0.02	—	250
			250	250	16	16.0	0.1	0.02	—	—
10	10.1 wt% silver	α-Al_2O_3 Type A3, from Alcoa	200	200	16	16.4	1.0	0.2	—	175
			250	250	16	16.5	1.0	0.2	—	—
11	11.9 wt% silver	SiO_2 aerosil 200 V, from Degussa	150	150	16	100	0.1	0.7	—	300
			170	170	20	100	0.1	0.7	—	

tion with hydrogen peroxide in an alkaline solution at 100°C. Silver and $Ba(OH)_2$ are, thus, deposited on the carrier.

Samples 8 and 10 were prepared by controlled reduction with a glucose solution (*19*); the silver is precipitated on carrier particles suspended in a solution of the ammonia complex of the silver; during the precipitation a small amount of $Ba(NO_3)_2$ solution is added.

Before each nitrous oxide adsorption–decomposition or oxygen adsorption run, the sample is reduced in pure hydrogen for 24 hr and degassed (degassing time and temperature are indicated in Table 1).

Results and Discussion

Oxygen Adsorption via Decomposition of Nitrous Oxide

The study was started with silver powder sample no. 1, after this had been reduced and evacuated as indicated in Table 1. Figure 2 gives the number of oxygen atoms adsorbed per m² of silver surface area as a function of the time of reaction with the circulating nitrous oxide. The runs were conducted at temperatures of 25–250°C. The initial pressure of the nitrous oxide was 15 cm Hg; in the course of the reaction, with the total pressure remaining constant, the partial pressure of the nitrous oxide decreased by at most 5% in the experiment at 25°C, and by at most 15% in the experiment at 170°C. Analysis showed (see Fig. 2) that up to 170°C in all experiments the gas phase was enriched with nitrogen only, that the degree of enrichment gradually increased with the time of reaction and, further, that no other gases were evolved. Between the various measurements the samples were rereduced and evacuated under the conditions indicated in Table 1. Changes in the BET surface areas due to the repeated surface oxidation with nitrous oxide and subsequent reduction could not be established.

Comparing the various experiments plotted in Fig. 2, we see that the reaction with the silver surface proceeds rapidly at first, to slow down until, after a contact time of over 100 hr, the coverage with

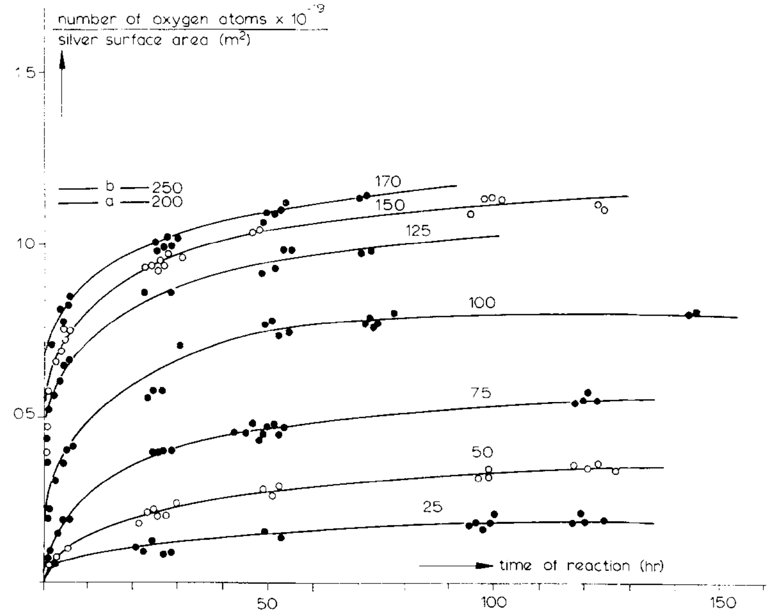

FIG. 2. Oxygen chemisorption via nitrous oxide adsorption–decomposition on silver powder (sample no. 1) at various temperatures versus time of reaction. Initial pressure of nitrous oxide: 15 cm Hg. The numbers in the figure refer to the reaction temperature in °C. The meaning of levels a and b is explained in the text.

oxygen reaches a nearly constant level. It is seen that the degree of oxygen adsorption increases with the reaction temperature. This means that the degree of adsorption is kinetically determined by an activation energy which increases with coverage. Calculation of the activation energies from Arrhenius plots gives the values mentioned in Table 2. These values are not very accurate owing to the scattering of the points, but the conclusion that the activation energy increases with oxygen coverage seems to be justified.

In the experiment at 170°C, the reaction becomes extremely slow after a contact time of 75 hr. The number of oxygen atoms then adsorbed is about 1.2×10^{19} per m^2 of silver surface area. From Sundquist's work (*20*) it appears that the equilibrium surface plane distribution corresponds to about 25% of (100) planes, 5% of (110) and 70% of (111) planes, from which a number of 1.31×10^{19} silver atoms per m^2 can be calculated. Hence, the oxygen coverage reached in the experiment at 170°C is about 0.9.

At reaction temperatures above 170°C an essential change takes place in the reaction pattern. We refer here to the fact that at 200°C, after a reaction time of 24 hr oxygen is found in the gas phase (mass spectrometrically), the gas composition being N_2O 82%, N_2 13% and O_2 4.7%. The figures at 250°C and 4 hr of reaction are 80% N_2O, 15% N_2 and 5.2% O_2. Correcting the total amount of nitrogen evolved for the amount produced by the quasi-homogeneous decomposition of nitrous oxide: $2\ N_2O \rightleftarrows 2\ N_2 + O_2$, we arrive at the oxygen coverages indicated by the levels a and b in Fig. 2.

TABLE 2

ENERGY OF ACTIVATION OF NITROUS OXIDE DECOMPOSITION AS A FUNCTION OF THE DEGREE OF OXYGEN COVERAGE OF THE SILVER SURFACE

θ[a]	E (kcal/mole O_2)
0.15	7.0 ± 1.0
0.20	11.5 ± 1.0
0.25	18.5 ± 4.0
0.30	22.0 ± 7.0

[a] The coverage θ is put equal to one if the number of adsorbed oxygen atoms equals the estimated number of silver atoms in the surface.

It may be concluded from this that at temperatures higher than 170°C nitrous oxide starts being decomposed by a reaction proceeding parallel to the adsorption–decomposition process, probably under the catalytic influence of the surface oxide. This is substantiated by the observation that the coverages reached at these higher temperatures do not exceed the value found at 170°C and that, unlike copper, no bulk oxidation takes place. The nonoccurrence of bulk oxidation agrees with what is known about the equilibrium: $2\ AgO(ads) \rightleftarrows 2\ Ag + O_2(g)$ described by Czanderna (*13*) who indeed found that at 200°C the rate of desorption of the surface oxygen starts to exceed the rate of adsorption. Fig. 3 refers to an analogous set of experiments with a silver–α-alumina catalyst (sample no. 9, Table 1) at 50, 100, 150 and 170°C. The mean silver crystallite size found from X-ray line broadening was approximately 250 Å.

Comparison with Fig. 2 shows that, for this system of small crystallites, the levels of maximum adsorption as a function of temperature follow about the same trend as those for the silver powder with its mean crystallite diameter of about 16,000 Å, i.e., the higher the reaction temperature the more oxygen is adsorbed and the maximum level is reached at 170°C. Similarly as in the runs with silver powder at 200°C, oxygen evolved by decomposition of nitrous oxide was found in the gas phase; after correction for this effect, the amount of oxygen adsorbed appeared to correspond to level a in Fig. 3.

In Fig. 4 the maximum coverages measured on both the silver powder and silver-on-carrier catalysts after reaction times of 50 and 100 hr, respectively, are plotted versus the reaction temperatures. The points in Fig. 4 have been so plotted that the coverages on both samples at 170°C correspond to $\theta = 1$. Comparison of the coverage curves in Fig. 4 reveals that the

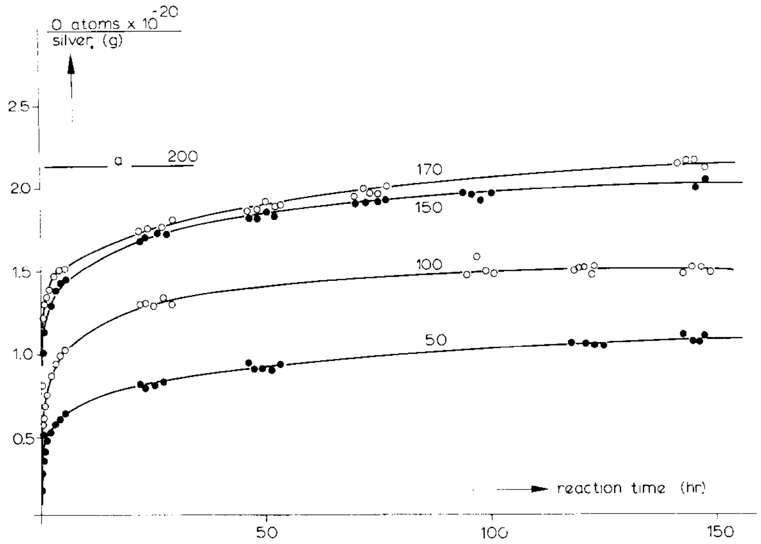

FIG. 3. Oxygen chemisorption via nitrous oxide adsorption–decomposition on a silver-on-α-alumina catalyst (sample no. 9) at various temperatures as a function of the time of reaction. Initial nitrous oxide pressure 15 cm Hg. The numbers in the figure refer to the reaction temperature in °C.

small silver crystallites on the α-alumina carrier are more reactive than the silver crystallites in the silver powder, as with the silver on carrier sample higher coverages are arrived at, at the same temperature and after the same reaction time. Another interpretation is that the higher reactivity towards oxygen adsorption is due to the presence of barium oxide (0.1%) in the metal-on-carrier sample. However, this difference in reactivity does not exist in the range of coverages between 0.7 and 1.0.

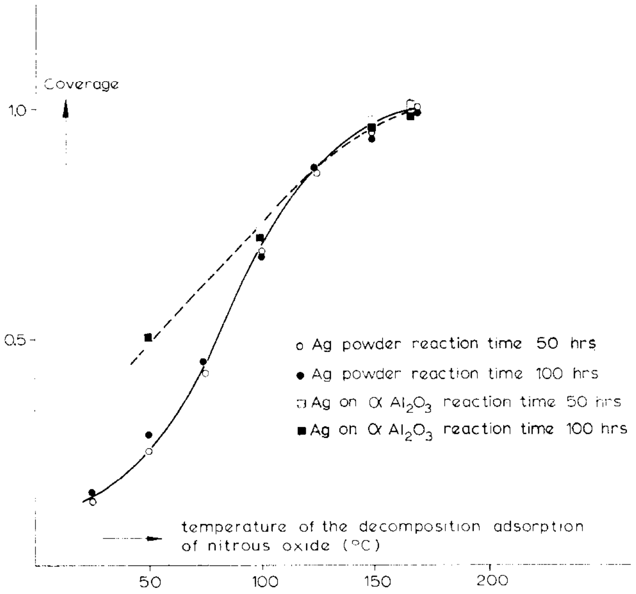

FIG. 4. Oxygen adsorption via nitrous oxide adsorption–decomposition on silver powder (circles) and on silver-on-carrier (squares) as a function of reaction temperature. Samples no. 1 and 9.

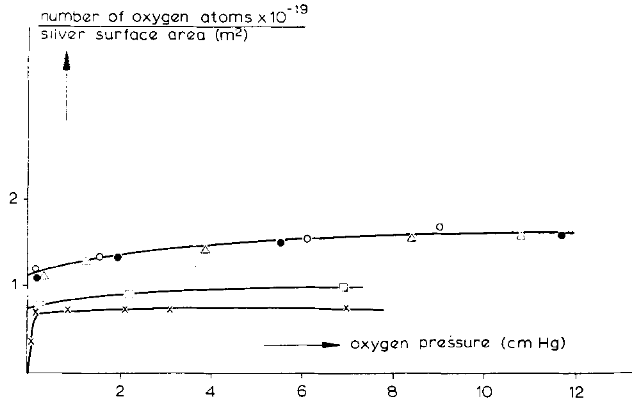

FIG. 5. Oxygen chemisorption isotherms on silver powder (samples nos. 3 and 4). ×, 50°C; △, 100°C; ●, 150°C; ○, 170°C; □, 200°C.

Furthermore, it is seen from Fig. 4 that prolongation of the reaction from 50 to 100 hr has hardly any influence on the final coverage.

Oxygen Adsorption

Figure 5 gives the oxygen adsorption isotherms for sample no. 3 (Table 1). Between the various runs no changes were detected in the BET surface area. During the very first contact of the sample with oxygen at 100°C, 0.03 cm^3 (STP) of carbon dioxide per gram of silver was evolved. In subsequent runs no further evolution of carbon dioxide was observed. The coincidence of the isotherms at 100, 150 and 170°C agrees with Kholyavenko's results (*14*). The maximum adsorption in this temperature range corresponds to an oxygen-to-silver ratio in the surface of about unity. The 200°C isotherm has its maximum level at approximately 0.75 coverage; the lower position of this level agrees with Czanderna's results (*13*).

Our results with sample no. 1 (Table 1) are particularly interesting. The carbon content of the silver was analytically determined to be 0.01% which is a multiple of the figure for sample no. 3. Owing to this higher carbon content, there is an essential difference in chemisorption behavior between the two samples [as can be seen from a comparison between the respective 150°C isotherms in Figs. 5 and 6 (isotherm a)]. During the first contact with oxygen, the pressure decrease caused by oxygen adsorption is followed after a few minutes by a small pressure increase brought about by evolution of carbon dioxide. A monolayer coverage with oxygen is found at an oxygen pressure of 2 mm Hg. Then, unlike what was observed in sample 3, subsurface oxidation sets in; as can be seen from this part of the isotherm, the amount of oxygen adsorbed during this stage is nearly a linear function of the oxygen pressure. After 16 hours of pumping at 150°C, the subsurface adsorption part of the isotherm could be reproduced (curve b in Fig. 6). This indicates that the adsorption represented by the linear part of the curve is more reversible than that described by the monolayer part; the oxygen in the monolayer starts desorbing at 200°C.

The experiment just described demonstrates that the presence of a carbonaceous contamination probably initiates subsurface oxidation of the silver to a degree which at 18 cm Hg oxygen pressure is equivalent to the statistical thickness of approximately four monolayers. This is further substantiated by the fact that, after thorough oxidation of all carbon in the sample with air at 170°C and subsequent reduction and degassing in vacuo at 170°C, the chemisorption behavior of the nearly carbon-free sample (number 3) could be exactly reproduced (see Fig. 7). That carbonaceous contaminations have an effect on the sorption behavior of oxygen was

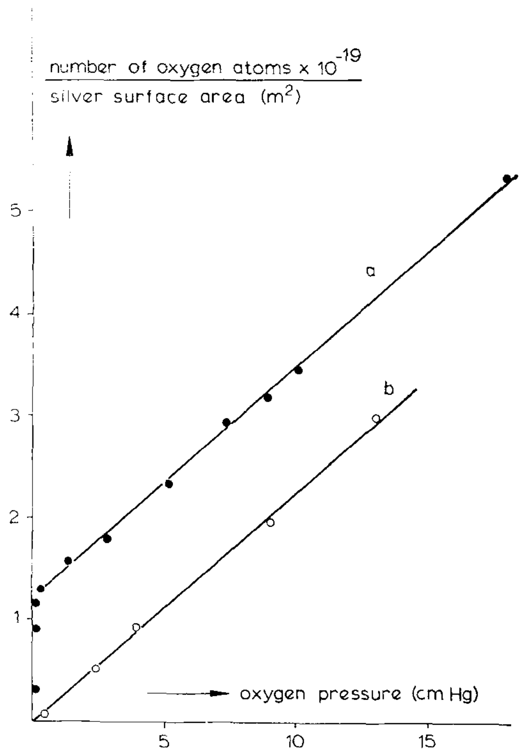

FIG. 6. Oxygen adsorption isotherms at 150°C on silver sample no. 1. ●, Irreversible plus reversible adsorption; ○, Reversible adsorption after degassing in vacuo at 150°C during 20 hr.

noted also in the runs with silver-on-carrier catalysts. For example, sample no. 9 (carbon content 0.02 wt%) exhibited monolayer adsorption at 170°C, but a sample containing 1.2% carbon (no. 8) sorbed an amount of oxygen corresponding to three statistical layers at 12.5 cm Hg and 170°C.

Adsorption–decomposition of nitrous oxide never gave rise to the evolution of carbon dioxide in experiments below 200°C. Obviously the nitrous oxide has a much lower reactivity towards the carbonaceous material than oxygen. Surface area determinations by means of nitrous oxide or oxygen adsorption (see hereafter) of carbon-containing samples, did not lead to different results. Hence, the carbonaceous material is not molecularly dispersed over the entire silver surface, but concentrated in some spots.

Application for Determining Free-Silver Surface Areas

In Fig. 8 the amount of nitrogen evolved per gram of silver during decomposition–adsorption of nitrous oxide at 150°C is plotted as a function of the BET surface area. The measurements were performed on four silver powders of high purity. It can be concluded from this figure that 0.4 cm^3 of evolved nitrogen corresponds to 1 sq.m of silver. This result can be used as a basis for determining the free-silver surface area of silver-on-carrier catalysts (cf. Table 3). The method requires a rather long reaction time (at least 50 hr). If necessary, time can be saved by applying a temperature of 200°C and correcting for the amount of

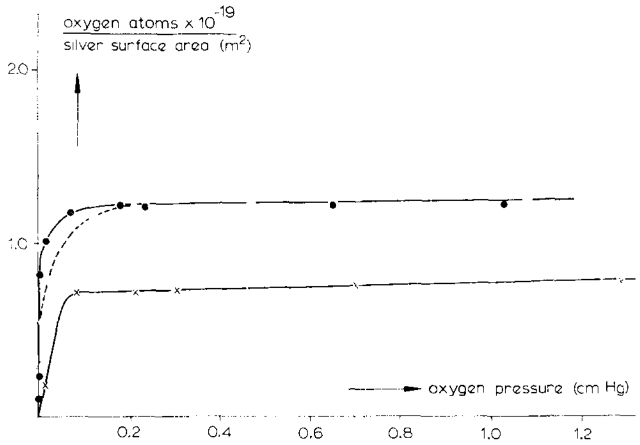

FIG. 7. Oxygen adsorption isotherms on silver sample no. 1, after oxidation in air at 170°C and subsequent reduction and degassing in vacuo at 170°C. ×, 50°C; △, 100°C; ●, 150°C.

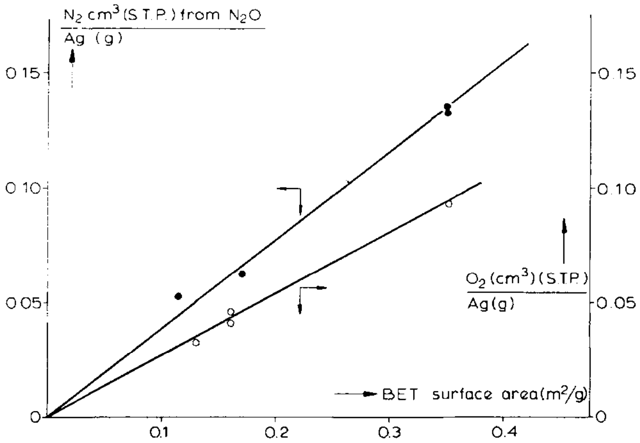

FIG. 8. Nitrogen evolution per gram of silver and oxygen chemisorption on four pure silver samples (nos. 1, 2, 3, 4) as a function of the BET surface area.

nitrogen evolved during the decomposition of nitrous oxide into oxygen and nitrogen (cf. levels a and b in Fig. 2). The results found at 200°C are also incorporated in Table 3.

Another method for determining the free-metal surface area is to measure the oxygen chemisorption isotherm at 100, 150, or 170°C. For copper this approach could not be followed because bulk oxidation goes very fast here; in silver, however, bulk oxidation does not occur as a rule. Where it does occur, one can clearly differentiate between the chemisorbed part and the absorbed part of oxygen, as is evident from Fig. 6. In Fig. 8 the amount of oxygen chemisorbed per gram of silver at 150°C is plotted as a function of the BET surface area. The measurements were performed on four silver powders of high purity. It can be concluded from Fig. 8 that 0.27 cm^3 of chemisorbed oxygen corresponds to 1 sq.m of silver.

Results obtained with the nitrous oxide and oxygen method at 150°C are collected in Table 3. Here $\bar{d}_{v.s.}$, the mean volume-surface diameter, is calculated from

$$\bar{d}_{v.s.} = 6V/S \tag{1}$$

where V is the volume of 1 g of silver and S the surface area per gram of silver.*

Equation (1) is valid for cubes, in which case $\bar{d}_{v.s.}$ represents the mean edge of the cubes, or for spheres, with $\bar{d}_{v.s.}$ denoting the mean value of the sphere diameter. $\bar{d}_{v.s.}$ is defined by

$$\bar{d}_{v.s.} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2 \tag{2}$$

where n_i is the number of particles of d_i. X-ray line broadening gives the weight-mean diameter $\bar{d}_w$.

$$\bar{d}_w = \Sigma n_i d_i^4 / \Sigma n_i d_i^3 \tag{3}$$

As shown in Table 3, there exists rather good agreement between the results of the various independent methods for determining the metallic dispersion.

CONCLUSION

Both nitrous oxide adsorption–decomposition and oxygen chemisorption can be used for determining free-silver surface areas. With oxygen, bulk oxidation may sometimes occur (cf. Fig. 6), but the sharp knee in the isotherm at low oxygen pressures (1 to 5 mm Hg) makes it possible to differentiate between surface coverage and bulk oxidation. Calculation of the free-silver surface area from the extent of the chemisorbed monolayer is hampered by the inadequacy of our knowledge about the distribution of the exposed crystal planes (i.e., the number of sites per unit surface area) and the surface stoichiometry (i.e., the number of sites needed per chemisorbed

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* In Eq. (1) it is assumed that the area of the particle is totally accessible for chemisorption.

TABLE 3

Mean Sizes of Silver Crystallites in Silver-on-Carrier Catalysts, as Calculated from the Free-Silver Surface Area, Compared with the Results of Electron Microscopy and X-ray Line Broadening

No.	Sample	Silver content (wt%)	Free-silver surface area (S) from O_2 chemisorption at 150°C (m^2 Ag/g Ag)	from N_2O-adsorption–decomposition at 150°C (m^2 Ag/g Ag)	from N_2O-adsorption–decomposition at 200°C (m^2 Ag/g Ag)	$\bar{d}_{v.s.}$ calculated from (S) in column 5 (Å)	$\bar{d}_w$ from X-ray line broadening (Å)	d from electron microscopy (Å)
5	Raney silver from Degussa	98.7	0.98	0.86		6,000	—	particles between 5000 and 15 000
6	Raney silver from Degussa	98.7	1.15	1.15	1.16	5,000	—	particles between 5000 and 15 000
7	Silver on γ-Al_2O_3 (Degussa P110)	10.6		7.2		800	650	particles between 500 and 1000
8	Silver on γ-Al_2O_3 (Degussa P110)	10.5	24.4	24.2		235	300	particles between 250 and 500
9	Silver on α-Al_2O_3 (Alcoa A3)	9.3	18.5	18.0	16.3	320	250	particles between 200 and 500, particles of 300 dominate
10	Silver on α-Al_2O_3 (Alcoa A3)[a]	10.1	22.5	19.9	22.0	285	190	particles between 100 and 500, particles between 200 and 250 dominate
11	Silver on SiO_2 (aerosil 200 V from Degussa)[2]	11.9	19.5	24		240	280	particles between 300 and 400

[a] The large difference between the mean crystallite sizes found from chemisorption and from X-ray line broadening or electron microscopy might be due to the fact that this sample contained a relatively large amount of barium oxide promoter (1%). Assuming 30% of the surface to be covered by barium oxide, one finds the total surface area of the silver particles to be 30% higher than indicated in the table, and $\bar{d}_{v.s.}$ becomes 200 Å.

oxygen atom). In the present and earlier work (*9, 21*) we obviated these difficulties by measuring, on pure metal samples, both the BET-surface area and the extent of the chemisorbed layer. The chemisorption on a metal-on-carrier catalyst can thus be expressed in terms of the BET surface area of the metallic part of the catalyst. It is then tacitly assumed, however, that the crystal plane distribution and the surface stoichiometry of the coarse crystallites in the silver powder are equal to those of the small crystallites in the silver-on-carrier catalysts.

Since the smallest silver crystallites encountered in this research are about 180 Å in diameter, we think that a "crystallite-size effect" need not be feared. If, however, the crystallites are smaller than, say, 50 Å the assumption made above may be less correct.

In the study of the adsorption-decomposition of nitrous oxide a maximum oxygen coverage of 0.2 cm^3 per sq.m of silver was arrived at (see Fig. 8), whereas exposure to oxygen gave 0.27 cm^3 of adsorbed oxygen per sq.m of silver (see Fig. 8). It is known (Sachtler (*22*)) that oxygen is adsorbed on silver in both atomic and molecular forms, and that it is the molecular form to which the epoxidation activity is to be ascribed. Nitrous oxide, however, gives rise to only the atomic species and, indeed, a very low epoxidation activity is found with this gas (*23*). We conclude from our figures that oxygen and nitrous oxide at 150°C both give full coverage of the silver surface, but that the amount of oxygen adsorbed from O_2 is 0.07 cm^3 per sq.m greater than the amount adsorbed from nitrous oxide. This must be due to the fact that in the former case part of the oxygen adsorbed (viz. 25%) is in the molecular form.

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REFERENCES

1. GORDON, J., *Hydrocarbon Process. Petrol. Refiner* **40,** 159 (1961).

2. LAW, G. H., AND CHITWOOD, H. C., U.S. Pat. 2,279,469 (1942).

3. BORESKOV, G. K., *et al., Kinet. Katal.* **3,** 214 (1962).

4. VOGE, H. H., AND ADAMS, C. R., *Advan. Catalysis* **17,** 161 (1967).

5. THOMAS, C. L., "Catalytic Processes and Proven Catalysts," Academic Press, New York, 1970, p. 208.

6. CZANDERNA, A. W., "Clean Surfaces" (G. Goldfinger, Ed.), Dekker, New York, 1970, p. 142.

7. HAYWARD, D. O., AND TRAPNELL, B. M. W., "Chemisorption," 2nd ed. Butterworth, London, 1964, p. 75.

8. WEDLER, G., "Adsorption." Verlag Chemie, Weinheim, 1970, p. 179.

9. SCHOLTEN, J. J. F., AND KONVALINKA, J. A., *Trans. Faraday Soc.* **65,** 2465 (1969).

10. BARDEEN, J. W., BRATTAIN, W. H., AND SHOCKLEY, W., *J. Phys. Chem.* **14,** 714 (1946).

11. KEYES, F. G., AND HARA, H., *J. Amer. Chem. Soc.* **44,** 479 (1922).

12. SMELTZER, W. W., TOLLEFSON, E. L., AND CAMBRON, A., *Can. J. Chem.* **34,** 1046 (1956).

13. CZANDERNA, A. W., *J. Phys. Chem.* **68,** 2765 (1964).

14. KHOLYAVENKO, K. M., RUBANIK, M. YA., AND CHERNUKHINA, N. A., *Kinet. Katal.* **5,** 505 (1964).

15. SANDLER, Y. L., AND HICKAM, W. M., *Proc. 3rd Int. Congr. Catal.* 1964, 227 (1965).

16. FARKAS, A., *Z. Phys. Chem. B* **22,** 344 (1933).

17. French patent 844,145 (19-7-1939).

18. Dutch patent application 68.18.337.

19. Dutch patent application 68.16.777.

20. SUNDQUIST, B. E., *Acta Met.* **12,** 67 (1964).

21. SCHOLTEN, J. J. F., AND VAN MONTFOORT, A., *J. Catal.* **1,** 85 (1962).

22. SACHTLER, W. M. H., *Catal. Rev.* **4,** 27 (1970).

23. HERZOG, W., *Ber. Bunsenges. Phys. Chem.* **74,** 216 (1970).