

SHORT COMMUNICATIONS

SINTERING OF SILVER(I) OXIDE POWDER AT 173°*

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In view of the importance of particle size on the rate of chemisorption of carbon dioxide on silver oxide and on the rate of decomposition of silver carbonate,^{1,2} a study of the rate of sintering of silver oxide powder at 173° was undertaken. Allen³ has shown that the method of preparing silver oxide powder has a significant effect on the surface area. It was therefore of interest in this work to study the effect of reagent concentration and method of preparation on initial surface area as well as on the rate of sintering.

Experimental

Silver oxide was prepared by precipitation from solutions of analytical reagent grade silver nitrate with carbonate-free sodium hydroxide according to a method previously described.⁴ The concentrations of the reagents used for precipitation and the order in which they were added are shown in Table 1.

TABLE 1
REAGENT CONCENTRATIONS AND ORDER
OF ADDITION

Preparation	Reagents
A and D	0.048N NaOH to 0.050N AgNO ₃
B and E	0.050N AgNO ₃ to 0.48N NaOH
C and F	0.048N NaOH to 0.50N AgNO ₃

Samples were initially dried over CaSO₄ at ambient temperature (c. 25°) and under vacuum (<0.1 torr) for no less than 4 days. They were then dried for 24 hr in a vacuum oven at 47°, followed by 48 hr at about 75°. Preparations D, E, and F were lightly ground, in a dry-box under a helium atmosphere, during the final drying procedure to hasten drying. No silver was detected by X-ray powder photographs in samples prepared by this method.

Sample handling was carried out in daylight, but to minimize exposure to atmospheric CO₂, the Ag₂O samples were transferred to adsorption vessels in a dry-box under a helium atmosphere.

After the initial surface area measurements were made, subsequent heating of the samples was carried out under vacuum on the surface area analyser with heating mantles (temperature

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¹ Spencer, W. D., and Topley, B., *J. chem. Soc.*, 1929, 2633.

² Spencer, W. D., and Topley, B., *Trans. Faraday Soc.*, 1931, 27, 94.

³ Allen, J. A., *Aust. J. Chem.*, 1960, 13, 431.

⁴ Gregor, L. V., Rep. No. UCRL-9723, Univ. of California, Lawrence Radiation Laboratory, May 31, 1961.

control $\pm 2^\circ$). B.E.T. surface areas were determined with nitrogen at various intervals during the heat treatment. Particle size analyses, using electron micrographs, and X-ray powder photographs were made before and after heat treatment on the analyser.

Results and Discussion

The results of surface area measurements on silver oxide are shown in Table 2. The percentage error, calculated for the first data point⁵ of the B.E.T. isotherms, ranged from 1.62 to 4.49% with a mean of 2.41% for the six samples. The significant increase in surface area after preparations A, B, and C were heated under vacuum at 110° is apparently due to a loss of adsorbed water.

TABLE 2
SURFACE AREA AND WEIGHT LOSS OF SILVER OXIDE HEATED IN VACUUM

	Sample					
	A	B	C	D	E	F
B.E.T. surface area (m ² /g)*						
Initial	1.58	1.64	1.87	4.00	3.83	3.08
After 15 hr at 110°	3.25	3.37	3.33	3.67	3.49	3.37
After 150 hr at 173°	3.02	3.05	2.79	3.23	3.29	3.26
After 250 hr at 173°				3.32	3.71	3.08
Surface area from particle size (m ² /g)†						
Initial	2.6	2.4	3.3			
Final	2.0	2.3	2.0			
Weight loss (%)	0.8160	0.9085	1.198	0.2932	0.2567	0.2601
Oxygen loss (%)‡				4.248	3.719	3.768

* Calculated using $15.8\text{\AA}^2$ as the area of the nitrogen molecule. † Calculated using 7.243 g/ml as the density of silver oxide. ‡ Loss of adsorbed water did not warrant this calculation for A, B, and C.

Allen's data³ indicate that the amount of oxygen lost by silver oxide after heating for about 20 hr at 180° was $5.6 \pm 0.6\%$. This value is in fair agreement with the oxygen losses found in this work for preparations D, E, and F.

The final X-ray powder patterns of samples A through F did not show a pattern of silver metal, presumably due, as mentioned elsewhere,³ to a lack of agglomeration of silver nuclei. Both the initial and final X-ray powder photographs revealed the silver carbonate pattern in samples A, B, and C but not in D, E, and F. Since the greater weight loss and significant increase in surface area of A, B, and C after heating at 110° indicates adsorbed water and as adsorbed water accelerates the reaction between carbon dioxide and silver oxide,^{1,2,6} silver carbonate would be expected to form more rapidly on samples A, B, and C than on D, E, and F. The suggestion of Herley and Prout⁷ that earlier investigators who studied the kinetics of silver oxide decom-

⁵ Loebeinstein, W. V., and Deitz, V. R., *J. chem. Phys.*, 1947, **15**, 687.

⁶ Culbertson, W. J., Jr., Rep. No. AMRL-TR-64-119, Denver Research Institute, 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio, December 1964.

⁷ Herley, P. J., and Prout, E. G., *J. Am. chem. Soc.*, 1960, **82**, 1540.

position did not take adequate precautions to prevent carbonate formation during sample handling appears, from this work, to be especially true of those samples that are poorly dried.

Although samples A, B, and C behave similarly to Allen and Scaife's silver oxide preparation which contained coprecipitated⁸ silver carbonate, it is difficult to see how coprecipitation could have occurred in A, B, and C and not in D, E, and F when the same reagents were used for both.

It is apparent (Table 2) that after 250 hr of heating silver oxide powder at 173° under vacuum no significant decrease in surface area had occurred, which indicates that the degree of sintering or agglomeration was negligible. This is substantiated by the particle size data. Furthermore, the different reagent concentrations and order of addition employed in sample preparation did not result in a significant difference in sample surface area either initially or after heating at 173° for several days. The good agreement between the surface area calculated from particle size data and the B.E.T. isotherms further suggests that the internal surface area of the silver oxide powder is small.

In summary, surface area measurements have shown that sintering of silver oxide at 173° in vacuum is negligible. Furthermore, reagent concentration and order of addition have no apparent effect on the rate of sintering of silver oxide or on the surface area of the precipitated powder. X-ray powder photographs revealed that moist silver oxide samples contained silver carbonate which formed by reaction with atmospheric carbon dioxide. Adequately dried samples, however, contained no detectable silver carbonate. The amount of dry silver oxide which decomposed when heated in vacuum for 250 hr at 173° is less than 5%.

⁸ Allen, J. A., and Scaife, P. H., *Aust. J. Chem.*, 1966, **19**, 715.