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ADSORPTION ISOTHERMS FOR OXYGEN CHEMISORBED ON SILVER POWDER*

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ABSTRACT

Adsorption isotherms have been measured on cleaned silver powder from 178 to 339°C at oxygen pressures of 0.226 Pa to 40 kPa using a vacuum ultramicrobalance. Adsorption equilibrium was found at all temperatures and pressures studied. The surface was prepared for the reproducible chemisorption studies using an established method of cyclic outgassing, oxygen adsorption and reduction in carbon monoxide. Seven isotherms were measured that spanned fractional surface coverages from 0.17 to 1.1. The isosteric heat of adsorption q was determined at constant values of θ. After decreasing from 42 to 17.7 kcal mol^{-1} at the lower coverages, q remains constant at 18.4 ± 0.8 kcal mol^{-1} from θ of 0.33 to about 0.90 and then decreases to zero at the highest coverages and temperatures. The initial drop in q is attributed to the formation of islands of a two-dimensional surface silver oxide. The constant value of q results then from the completion of the oxide layer and molecular adsorption on and/or through the oxide. The decrease in q to zero at the highest coverages results from repulsions in the adlayer at $T \leq 275$°C and absorption into silver at $T > 302$°C.

INTRODUCTION

The magnitude of the isosteric heat of adsorption q is an important quantity in an adsorption. The functional relationship of $q(\theta)$ with surface coverage and/or surface structure may provide information about the gas–surface bond, the factors responsible for high catalytic activity, and the nature of the chemisorbed species. Silver is unique in its ability to catalyze the oxidation of ethylene to ethylene oxide and, in commercial reactors, oxygen partial pressures of the order of 40 kPa (300 Torr) are used. Thus, the determination of a reliable heat of adsorption is important for

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understanding the silver–oxygen adsorbate–adsorbent system as well as for the epoxidation of ethylene.

Measured values of the heat of adsorption of oxygen on silver 67(16)[1], 71–105 (17–25)[2], 75–79(18–19)[3], and 67(16)[4] kJ(kcal) mol^{-1} and calculated ranges of 67–142 (16–34)[5] and 46–88(11–21)[6] kJ(kcal) mol^{-1} have been reported. The range in these values could result from measurements made at different coverages, on samples of varying surface purity, or a combination of both of these factors. Where adsorbate–adsorbent equilibrium exists, the isosteric heat of adsorption can be readily determined. The mass m of the gas adsorbed per unit area of the pure adsorbent depends on the pressure, temperature and, on some systems, the surface structure. For a particular stable surface structure, q may be obtained at a constant amount of gas adsorbed from the relationship $(\mathrm{d} \ln P/\mathrm{d}T)_m = q/RT^2$. If the value of m can be related to the surface area, the $q(\theta)$ can be determined where θ is the fractional coverage.

Although the specific surface area of cleaned silver is small, the vacuum ultramicrobalance[7] can be used to measure the adsorption equilibrium from 10^{-3} Torr to superatmospheric pressures. It is particularly suitable for studying the silver–oxygen system where weak chemisorptive bonds are obtained at high adsorbate coverages and less than atmospheric pressures of oxygen. In fact, an ultramicrobalance, with UHV capabilities is one of the few measuring methods in surface science that may be applied in situ for studying chemisorption on surfaces from the "ideal" conditions in UHV to regions of practical interest.

EXPERIMENTAL

Silver powder, suspended from a vacuum ultramicrobalance, was exposed to oxygen at pressures of 0.266 to 4 × 10^4 Pa (2 mT to 300 Torr) and temperatures of 178 to 339°C. Details about the purity of the silver powder[8, 9] and the procedure for processing the powder to a cleaned surface[10, 11] with reproducible chemisorptive behavior[8–11] and a constant BET surface area[10] have been published. In this study, a 0.75 g silver sample had a surface area of 920 cm^2 g^{-1} based on nitrogen adsorption at 78 K.

The ultramicrogravimetric apparatus[8, 12], the vacuum system[8], the preparation of the gases[8–11], the measurement and control of the temperature[8], the determination of the surface area[7], and the specialized procedure for obtaining adsorption isotherms[13] at the temperatures and pressures of this study have been reported. The adsorption isotherms were obtained in pure oxygen above 1.33 kPa; below this pressure, oxygen–nitrogen mixtures were used because Knudsen forces decrease the precision of the measured mass[14].

Adsorption isotherms were measured at temperatures of 178, 199, 217, 245, 275, 302 and 339°C. The mass gained at equilibrium was measured at the pressure intervals (1.33, 2.37, 4.12 and 7.98) in each decade of pressure over the range from 0.226 to 4 × 10^4 Pa. The actual oxygen pressure was measured to an accuracy of 5 per cent at the lowest pressures and to 0.05 per cent at the highest pressure. Equilibrium was generally attained in less than ten minutes as deduced from observing the time base chart recording of the automatically operated ultramicrobalance.

Adsorption isobars were obtained over the same temperature and pressure regions as for the isotherms. After the amount adsorbed was monitored at 339 °C, the temperature was decreased in several decrements to 178 °C and reheated in increments to 339 °C. Corrections for buoyancy effects were made from similar exposures to nitrogen and argon. When a constant coverage was obtained in oxygen for at least four hours at any temperature, the temperature was changed to a new value. The cycle, 339–178–339 °C, was repeated at least three times at each pressure. Adsorption isobars were not measured below 1.33 Pa because the partial pressure of oxygen in the closed system could be altered by the amount adsorbed or desorbed from the sample. Adsorption isobars were measured from 1.33 Pa to 1.33 kPa of oxygen in oxygen–nitrogen mixtures[12].

RESULTS

The amount adsorbed on increasing or decreasing the pressure or temperature was reproducible and reversible, as expected for equilibrium adsorption. The data from the adsorption isobars were replotted as isotherms since $m(P, T)$ has only two independent variables. The detail of the composite isotherms is shown at the higher pressures in Fig. 1 and at the lower pressures on the log–log plot in Fig. 2. The best smooth curves are plotted to avoid confusion. Typical scatter of the data points around a given isotherm, as shown in Fig. 1 for the adsorption at 245 °C, was always within a precision of $\pm$ 0.25 ng cm^{-2} or better than $\pm$ 1 % of a monolayer. Although the scatter of the data between 0.078 and 7.8 Torr (10 to 1000 Pa) was at the limits of uncertainty, the isotherms in this region are nearly linear on a log P versus m plot and were smoothed easily by using a modified least squares method. The values from

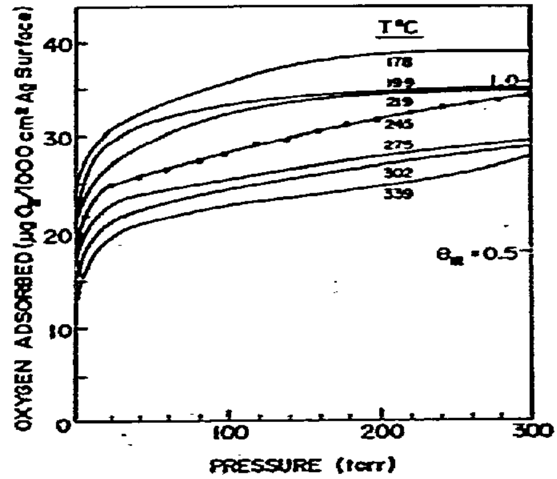

Fig. 1. Adsorption isotherms for oxygen on silver powder. The surface coverages θ were calculated assuming all the exposed silver atoms are in a $\langle 111 \rangle$ configuration.

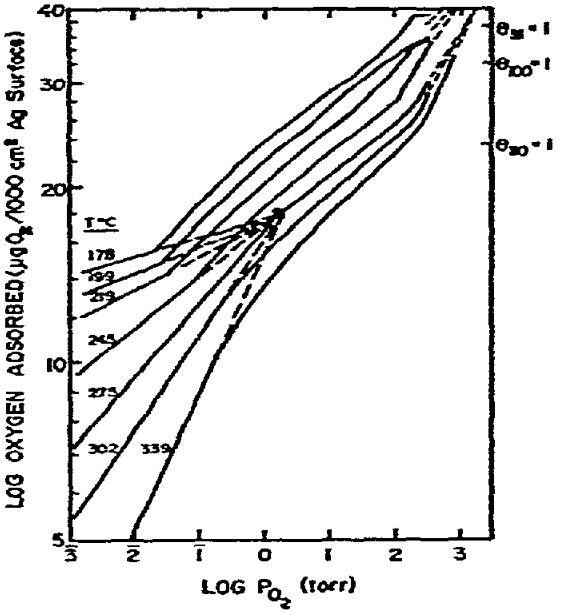

Fig. 2. Log–log plot of the isotherms shown in Fig. 1 showing low-pressure detail. The low coverage part of the isotherms extrapolate to a common point of 17.8 ng cm^{-2} and 266 Pa.

TABLE I

ISOSTERIC HEATS FOR OXYGEN ADSORBED ON SILVER AT VARIOUS SURFACE COVERAGES

Mass adsorbed (ng cm^{-2})	q_1 *(kcal mol^{-1})*	*T range of validity of* q_1	q_2 *(kcal mol^{-1})*	*T range of validity of* q_2	θ_{111}, *surface coverage for* ⟨*111*⟩ *Ag*
6	40.5–43.5	$T>260$	—	—	0.162
8	31.5–35.5	$T>260$	—	—	0.216
10	24.2–26.2	$T>260$	41.0–43.0	$T<245$	0.270
12	17.8–18.5	$T>260$	40.0–43.5	$T<245$	0.324
14	17.9–18.5	$T>260$	28.0–34.0	$T<245$	0.378
16	17.6–17.8	178–339	17.6–17.8	178–339	0.432
18	17.6–17.8	178–339	17.6–17.8	178–339	0.486
20	17.6–18.7	178–339	17.6–18.7	178–339	0.540
22	13.5–15.0	$T>302$	18.3–19.1	178–302	0.595
24	9.5–11.5	$T>302$	18.3–20.3	178–302	0.649
26	8.0–10.0	$T>302$	18.7–19.5	178–302	0.703
28	4.0– 5.5	$T>302$	17.6–19.9	178–302	0.757
30	18.6–18.8[a]	$199<T<245$[a]	13.0–15.0[b]	$T<199$[b]	0.811
32	17.6–18.5[a]	$199<T<245$[a]	9.4–11.4[b]	$T<199$[b]	0.865
34	12.5–13.5[a]	$199<T<245$[a]	4.0– 6.0[b]	$T<199$[b]	0.919

[a] Double values in q here more likely a continuation of q_2.
[b] Double values in q here more likely result from a "q_2".

the smoothed curves were used for calculating q at each mass of oxygen adsorbed.

The q at any θ was obtained from the data used to construct Figs. 1 and 2 by plotting ln P vs. $1/T$ at a constant mass adsorbed, e.g., a constant θ. The resulting slope is q/R as deduced from the defining relationship[7]. The values of q obtained at various masses of oxygen adsorbed are given in Table 1. The ranges give the maximum variation in q for data points falling $\pm$ 0.25 ng cm^{-2} away from the smoothed curve. When the determination for q included data from all seven isotherms, and was single valued (Table 1, at 16, 17, 18, 19 and 20 ng cm^{-2} of oxygen adsorbed), the deviations in the slope led to uncertainties of $\pm$ 0.2 kcal mol^{-1} or approximately $\pm$ 1% of the measured value. Larger uncertainties necessarily resulted when q's had to be determined from only two or three available isotherms at a constant mass adsorbed. The increased uncertainty results, in part, from the error in the measured temperature as well as from the probable changes in the adsorption. The raw data used for the plots in Figs. 1 and 2 are available on request from the author.

A surface structure must be assumed to obtain fractional coverages θ from the mass of oxygen adsorbed. If it is assumed one oxygen atom will be associated with one silver atom at $\theta = 1$, then for the ⟨111⟩, ⟨100⟩ and ⟨110⟩ surfaces, 37, 32, and 22.7 ng of oxygen per cm^2 of silver surface will comprise a monolayer, corresponding to 7.2, 8.31 and 11.75 Å^2 for the average area of a silver atom on these three surfaces. The θ's computed are also listed in Table 1 and the appropriate coordinate labels are attached to Figs. 1 and 2.

DISCUSSION

The textbook interpretation of the $q(\theta)$'s in Table 1 could be as follows: The "linear" decrease of q up to m = 12 ng cm^{-2} is characteristic of a Temkin isotherm, with or without dissociative adsorption, on a heterogeneous surface[16]. A constant value of q from 12 to 32 ng cm^{-2} is adequately described as an adsorption without dissociation, without lateral interactions, with surface uniformity and with an immobile layer, e.g., a simple Langmuir interpretation. The decrease in q to zero at the higher coverages and/or higher temperatures results from a mobile adsorbed species or weak lateral interactions. The complexities of the silver–oxygen system are ignored by the textbook interpretation.

Numerous investigators have concluded that oxygen adsorbs on silver in both atomic and molecular forms[2–5, 8–11], as is adequately referenced in recent reviews[17, 18]. Direct confirmation of the existence of the molecular form has been demonstrated by Clarkson and Cirillo using electron spin resonance[19] and by Kilty et al.[5] using infrared spectroscopy. Rovida et al.[20, 21] have provided evidence for the existence of an *ordered* atomic species, using low energy electron diffraction. They postulated[21] that a two-dimensional surface oxide of ⟨111⟩Ag_2O is formed on ⟨111⟩ Ag to explain 4 × 4 LEED patterns, basing their interpretation on the lattice constants of Ag_2O and Ag. Evidence for the well-known absorption of oxygen into silver has been detected at temperatures as low as 100°C with FEM[22], 150–200°C microgravimetrically[8], and 200°C by thermal desorption[20]. These thresholds of absorption are considered to be small amounts that penetrate only the first few atomic layers. Thus, oxygen adsorbed on silver includes oxygen adions and admolecule ions, where the adions may form an ordered two-dimensional "oxide" or diffuse into the bulk at higher temperatures. The likely possibilities that could unravel the complexities of $q(m)$ in Table 1, will now be attempted.

The drop in the isosteric heat from 42 to 18 kcal mol^{-1} at low coverages is associated with the formation of a two-dimensional surface oxide rather than surface heterogeneity. A drop in q can result from charged ions if they are close together[16]. This could be accomplished by the surface diffusion of oxygen adions to form two-dimensional islands of silver oxide. Large stable nuclei of Ag_2O on silver have been reported at super-atmospheric pressures[23]; the partially ionic character of oxygen in bulk silver oxide is well known. If the drop in q results from repulsions of "oxide ions" in a two-dimensional Ag_2O, is it then reasonable also to assume the surface of the silver powder is uniform?

Excellent agreement exists between the surface coverages given by Rovida et al.[21] for a ⟨111⟩ single crystal (Fig. 4, ref. 21) and those listed in Table 1, which were calculated on the assumption that the silver powder is composed primarily of ⟨111⟩ microfacets. Whenever quantitative comparisons have been possible, the results obtained on single crystals[20, 21] and OAOR cycled silver powder[8, 10] have shown good agreement. One is led to the conclusion that either the adsorption of oxygen is not sensitive to surface structure or the initially polycrystalline powders assume low-index plane microfacets. In either case, the decrease in q with the amount adsorbed should not be attributed to surface heterogeneity. Furthermore, additional comparisons between the data on silver powders and single crystals can be made that do not appear to be especially speculative.

Rovida et al.[20, 21] reported the upper bounds of stability of a 4 × 4 superstructure range from about 200 to 260°C between 10^{-2} to 10^{-1} Torr, respectively, e.g., the 4 × 4 is stable at higher pressures (higher coverages) and lower temperatures. Thus, the drop in q at $T < 245$°C and m from 10–16 ng cm^{-2} could be associated with the formation of ordered 4 × 4 arrays of silver oxide; the drop in q at $T > 260$°C and m from 6–12 ng cm^{-2} then could be associated with the formation of islands of silver oxide not detectable by LEED. If this assignment is correct, the mass of oxygen adsorbed along the boundary of 4 × 4 stability is about 13 ng cm^{-2} or $\theta_{111} = 0.35$.

Additional arguments can be advanced to support the hypothesis for the formation of a surface silver oxide. The plots of log m versus log P, shown in Fig. 2, produce straight lines, at the lower pressures, that converge to a point where the mass gain is 17.8 ± 0.8 ng cm^{-2} and the pressure is 266 Pa. (At higher pressures, the log–log plot does not exhibit a discernible convergence.) The point of convergence of isotherms on log–log plots can be interpreted as the limiting coverage of a particular chemisorbed state[16]. If this state is the surface oxide Ag_2O, as is suggested by comparing this work with that of Rovida et al.[21], the limiting coverage should be $\theta =$

0.50; $m = 17.8$ ng cm^{-2} corresponds to $\theta = 0.48$ for the model of a ⟨111⟩ surface, which is in good agreement with a θ of 0.5 for a surface Ag_2O.

Finally, Rovida et al.[20] reported the 4 × 4 structure is formed on exposure to 0.01 Torr of O_2 at 200°C for 10 min and that the oxygen coverage for this exposure of the Ag ⟨111⟩ is about half the maximum value they obtained by exposing at 1 Torr for 10 min at 200°C. An equilibrium coverage can be obtained in 10 min at 200°C based on the kinetic studies of Czanderna[8], so further comparisons are not unreasonable. In Fig. 1, 22.2 ng cm^{-2} of oxygen will be obtained at 1 Torr and 199°C; half this amount, 11.1 ng cm^{-2} should correspond to the lower bound where the 4 × 4 could be formed and is in reasonably good agreement with the lower bound of about 13 ng cm^{-2} deduced above from the temperature and pressure limits of stability of the 4 × 4.

Interpretation of $q(m)$ for m exceeding 12–16 ng cm^{-2} is rather straightforward once the hypothesis of forming a surface oxide is accepted. The "constant" value of 17.7 kcal mol^{-1} (m from 12–19 ng cm^{-2}) is associated with the heat of formation of the surface oxide at the lower coverages and the value of 19 kcal mol^{-1} at higher coverages is attributed to the heat of adsorption of molecularly adsorbed oxygen onto the surface oxide. The gradual drop in q at the lower temperatures and highest coverages is ascribed to repulsive interactions between the charged adsorbed molecules.

The apparent drop in q at $T > 302$°C results from measurable amounts of oxygen absorption into the subsurface regions. For absorption, the amount of uptake increases with increasing temperature, which is an endothermic rather than an exothermic process. The threshold deviations from each isotherm from the converging linear plots (dashed lines, Fig. 2) provide detectability limits for absorption into silver at pressures of 266, 53 and 20 Pa for 275, 302, and 339°C, respectively.

Although direct evidence for forming ⟨111⟩ microfacets (~ 20–35 Å in size) has not been produced, Kollen[24] did show facets, several hundred angstroms in size, can develop on a small part of the surface during OAOR cycling. Recently, Ekern[25] demonstrated the activation energy for desorption of oxygen from thermally etched (facetted) and polycrystalline wire become identical when the latter is subjected to outgassing and oxygen adsorption cycling, similar to that used on single crystals[20, 21]. Furthermore, Rovida et al.[20] reported the same adsorption is obtained when silver single crystals are cleaned by cyclic outgassing and oxygen adsorption or by ion bombardment and annealing. Thus, there is persuasive evidence now available, in addition to previous arguments[10], that adds considerable credibility to the suggestion that ⟨111⟩microfacets form during the OAOR cycling of silver powder.

The sum of $q + E_A$ should equal E_D, where E_A and E_D are the activation energies of adsorption and desorption, if entropy effects are negligible. By adding Czanderna's values of 22–24 kcal mol^{-1} for E_A with the q's reported in Table 1 at normalized coverages, an E_D of 41 ± 3 kcal mol^{-1} is obtained. This value compares favorably with reported values of E_D of 41.8 ± 3.5, 37.8, and 35 to 45 kcal mol^{-1} given for silver powders[9], filaments[25] and single crystals[20], respectively. An E_D of 41 ± 3 kcal

mol^{-1} is also quite interestingly within the probable uncertainty of the activation energy for the dissociation of silver oxide[26] of 36 kcal mol^{-1}. For the model given in this paper, the E_D would result from the desorption of molecular oxygen at higher coverages and the dissociation of silver oxide at lower coverages.

At the lower coverages, E_A must decline towards zero as $q(m)$ rises to 42 kcal mol^{-1} to maintain a constant E_D of $\sim$ 41 kcal mol^{-1}. An E_A of 3 kcal mol^{-1} has been reported at normalized coverages below $\theta = 0.4$ but these were measured below 65°C.

CONCLUSIONS

In summary, adsorption equilibrium was found for the silver–oxygen system from 178 to 339°C at pressures of 0.226 to 40,000 Pa. Favorable comparisons between this work, where silver powders were used, and that on single crystals[20, 21] provide a basis for assuming a ⟨111⟩ facetted surface is developed on the powder during extensive and repeated outgassing and oxygen adsorption cycling. The mass adsorbed was then related to surface coverages on ⟨111⟩ silver. A decrease in the isosteric heat from 42 to 17.7 kcal mol^{-1} at coverages from 0.17 to 0.33 is attributed to the formation of islands of a two-dimensional surface oxide composed of charged anions. At higher coverages, the variation of the heat from 17.7 to 19 kcal mol^{-1} is attributed to growth of the surface oxide to form a monolayer of Ag_2O and to adsorption of molecular oxygen by and/or through the oxide. Repulsions in the molecularly adsorbed oxygen at the coverages of about 0.9 produces a decrease in the isosteric heat at low temperatures; at higher temperatures, a decrease in q at θ of 0.6 results from the onset of absorption of oxygen into the silver.

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