JOURNAL OF CATALYSIS 64, 68–73 (1980)

Calorimetric Studies of Oxygen Adsorption on Silver Powder and of CO and CO_2 Interactions with Preadsorbed Oxygen on Silver

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Received January 5, 1979; revised July 16, 1979

The initial heat of adsorption and the variation of the heat of adsorption of oxygen with coverage were measured at room temperature on silver powder. The heats of interaction of carbon monoxide and of carbon dioxide with preadsorbed oxygen on silver powder were measured. A mechanism involving the formation of CO_3(ads) complex on the silver surface is suggested.

INTRODUCTION

The high ability of silver to catalyze ethylene oxidation to ethylene oxide accounts for the continuing importance given to the oxygen–silver system, and oxygen adsorption on silver has been regularly and thoroughly reviewed (*1*, *2*).

A wide spectrum of values is found in the literature for the heats of adsorption of oxygen on silver: 130–80 kcal $mole^{-1}$ from calorimetric measurements on powders (*3*, *4*); 25–16 kcal $mole^{-1}$ from kinetic measurements at high coverages on powders (*1*, *2*) and Ag(111) (*5*); 42–40 kcal $mole^{-1}$ from equilibrium measurements at high coverages on powders (*6*) and on Ag(110) (*7*). The differences are usually attributed to differences in preparation of silver samples and to the conditions of measurements of the heats of adsorption.

Investigations of the oxidation capacity of silver have shown on Eley–Rideal mechanism in the carbon monoxide oxidation (*8*). The existence of a CO_3(ads) complex has also been suggested (*9*).

The aim of the present work was to make use of thermochemical data for further proving the formation of a CO_3(ads) complex in the interaction of CO and CO_2 with rapidly adsorbed oxygen. For this purpose we used the calorimetric method which can give important information on the mechanism of processes taking place at surfaces (*10*). The results obtained are used in a thermochemical cycle devised for the assumed CO_3(ads) complex. A good agreement between calculated and measured heats of adsorption has been found.

EXPERIMENTAL

Calorimeter

The study has employed a glass twin calorimeter of the isoperibol type adapted for working in high vacuum, a modification of the Gale, Haber and Stone type (*11*).

Details of the apparatus, which consists essentially of two independently operating high vacuum systems, are given in Fig. 1. One system evacuates the inside part of the calorimeter and gas-dosing system and the other one the calorimeter jackets. A normal evacuation–baking procedure gives pressures of $1.5 \cdot 10^{-6}$ Pa.

The calorimeter is shown in Fig. 2. Our setup attempts to improve the gas diffusion in the sample and to simulate better by calibration the heat-evolving process during adsorption. Instead of a Dewar-type seal (*11*) we have a thin-walled tube T containing a concentric thin-walled tube E with many lateral holes. Tube E supports a calibration resistance and is covered with a glass fiber mesh to prevent powder penetration into tube T. The resistance thermometer and calibration resistance are anti-in-

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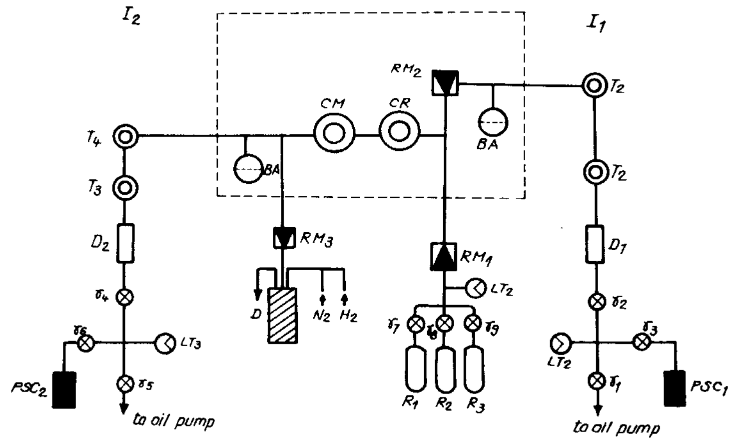

FIG. 1. Schematic diagram of the calorimetric apparatus. (CM) Measuring cell of the calorimeter; (CR) reference cell of the calorimeter; ($D_{1,2}$) oil diffusion pumps; (T_{1-4}) liquid-nitrogen traps; (r_{1-9}) glass greased stopcocks; ($RM_{1,2}$) metallic leak valves (Granville–Phillips); (RM_3) metallic valve (Granville–Phillips); (D) palladium thimble; (LT_{1-3}) thermocouple gauges; (BA) Bayard Alpert gauges; ($PSC_{1,2}$) sorption pumps.

ductively wound, and the thickness of the sample layer is about 2 mm. The reference cell has an identical structure.

The temperature of the measuring cell was measured by a Wheatstone bridge, with a circuit sensitivity of $8 \cdot 10^{-4}$ deg/10 mm. The temperature drift before a measurement was better than $8 \cdot 10^{-5}$ deg/min.

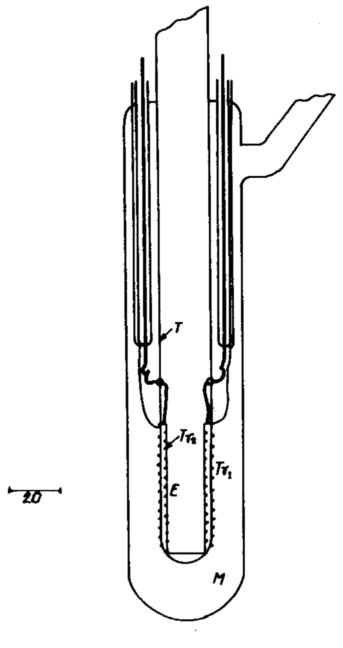

FIG. 2. Measuring cell of the calorimeter. (M) Vacuum jacket; (T) thin-walled tube; (E) thin-walled tube with lateral holes; (Tr_1) resistance thermometer; (Tr_2) calibration heater.

Preparation of Silver Powder

The silver powder was prepared by the method described by Gruver and co-workers (*12*, first method) from spectroscopically pure silver. A silver powder with grains between 0.3 and 0.7 mm in diameter was introduced into the measuring cell of the calorimeter. To eliminate traces of carbon, the oxidation procedure described by Boreskov and co-workers (*4*) was used. The final reduction with hydrogen was carried out for at least 48 h, the hydrogen being replaced periodically. The specific area of the silver powder, determined by the BET method using Kr, was 0.15 m^2/g.

Calibration of the Calorimeter and Procedure for Heat Measurements

The pulse method (*13*) was used since the temperature course was then similar to the temperature evolution during adsorption. The applied heat pulses were similar to the heat of adsorption values.

The constants of the calorimeter filled with silver powder were:

$$\frac{K}{C} = 1.58 \pm 0.015\ \mathrm{s}^{-1}$$

$$C = 7.12 \pm 0.11\ \mathrm{cal/deg},$$

where K is the constant in the Newton law of cooling and C is the heat capacity of the calorimeter.

A calorimetric measurement consisted of simultaneous determination of the evolved heat and of pressure changes inside the calorimeter vessel. The heat was evaluated from thermograms by the method of adiabatic correction (*13*). The amount of adsorbed gas was determined from the pressure measured in the calibrated volumes by a thermocouple gauge (LT_2, Fig. 1) coupled with a recorder.

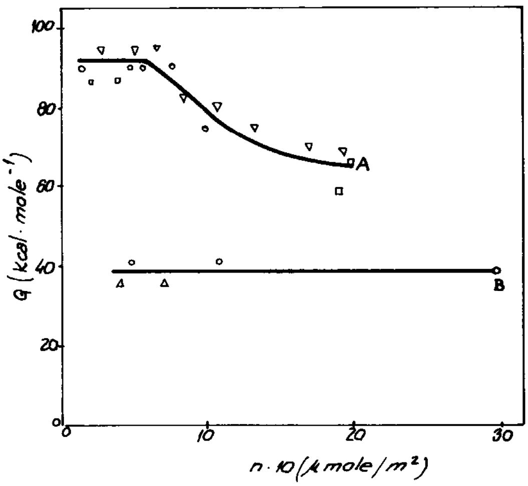

FIG. 4. Heats of adsorption of CO (curve A) and CO_2 (curve B) on preadsorbed oxygen.

RESULTS

Adsorption of Oxygen on Silver Powder

The first doses of oxygen were rapidly adsorbed. After the adsorption of 2.1 μmole O_2/m^2 Ag, the rate of adsorption decreased and the process could be described by the Elovich equation. Since our calorimeter is suited for the study of rapid processes, the measurements were carried out in the range of rapid adsorption only. The most probable curve (Fig. 3) of the heat of adsorption versus the amount of adsorbed oxygen was obtained by applying to the primary experimental values a nonlinear regression based on the least squares method.

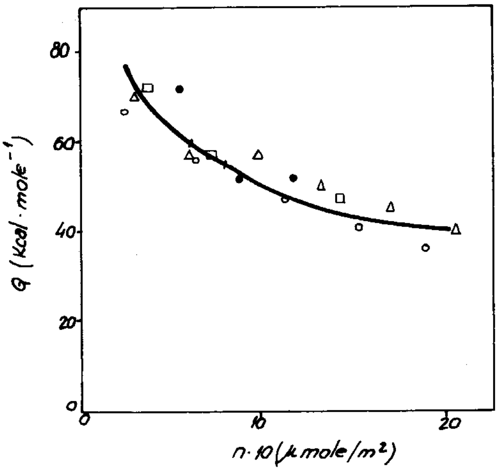

FIG. 3. Heat of adsorption of oxygen on silver powder.

Adsorption of Carbon Monoxide on Preadsorbed Oxygen

The silver surface was covered by 2.1 μmole O_2/m^2 Ag from successive doses. Then doses of CO were introduced and the heat of interaction measured. The doses of CO were adsorbed completely and rapidly on preadsorbed oxygen (CO is not adsorbed on silver at room temperature (*14, 15*).

The experimental results and the most probably curve of the heat of adsorption versus the amount of adsorbed CO are shown in Fig. 4. The initial heat of adsorption is relatively large ($\approx$90 kcal mole^{-1}) and after adsorption of 0.6 μmole CO/m^2, the heat of adsorption diminished progressively from 90 to 70 kcal mole^{-1}.

Adsorption of Carbon Dioxide on Preadsorbed Oxygen

The silver surface was covered with oxygen in the same way. All doses of CO_2 were adsorbed completely and rapidly on preadsorbed oxygen (silver does not adsorb CO_2 at room temperature (*8, 15, 16*). Volumetric measurements showed that the number of adsorbed CO_2 molecules corresponded to 0.75 of the number of preadsorbed oxygen atoms.

The results presented in Fig. 4 show a relatively high but constant heat of adsorption (Q = 38 kcal mole^{-1}) for all the range.

DISCUSSION

Adsorption of Oxygen

The values of the heat of adsorption of oxygen on silver powder measured by us are in good agreement with the results of Boreskov and co-workers (*4*) but differ from others (*3*).

There is good proof (*2, 5, 7, 18*) that the rapidly adsorbed oxygen is of a O^{2-} type. Kilty and co-workers (*2, 17*) found that the rapid adsorption of oxygen can be inhibited by covering a fourth of the silver surface by chlorine atoms. Our results suggest a similar conclusion: the ratio of surface silver atoms to adatoms of oxygen is $1.15 \cdot 10^{19}/2.1 \cdot 10^{-6} \cdot 6.023 \cdot 2 = 4.6$ ($1.15 \cdot 10^{19}$ is the number of silver atoms per square meter). Hence, only a fourth of the bare silver surface can accommodate rapidly adsorbed oxygen. The actual position of adsorbed oxygen on silver is still a debated matter even on single crystals and cannot be inferred only from volumetric measurements.

Interactions of CO and CO_2 with Preadsorbed Oxygen

The stoichiometry of CO adsorption on oxygen-covered silver surface suggests the following equation:

$$CO(g) + 2O(ads) \rightarrow CO_3(ads) \qquad (1)$$

Evidence for the existence of a CO_3(ads) complex comes from the adsorption of CO_2 on Ag_2O (*18, 19*) and on other oxides (*20, 21*) leading to a carbonate-type structure. Our results give further supporting evidence for CO_3(ads) complex formation. Indeed the following thermochemical equations can be written:

$$O_2(g) \rightarrow 2\,O(ads) + Q_1 \qquad (2)$$

$$CO(g) + 2O(ads) \rightarrow CO_3(ads) + Q_2 \qquad (3)$$

$$CO(g) + O_2(g) \rightarrow CO_3(ads) + Q_1 + Q_2 \qquad (4)$$

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) + Q \qquad (5)$$

$$CO_2(g) + O(ads) \rightarrow CO_3(ads) + Q_3 \qquad (6)$$

$$\tfrac{1}{2}O_2(g) \rightarrow O(ads) + \tfrac{1}{2}Q_1 \qquad (7)$$

$$CO(g) + O_2(g) \rightarrow CO_3(ads) + Q + Q_3 + \tfrac{1}{2}Q_1 \qquad (8)$$

where Q_1 is the heat of adsorption of oxygen, Q_2 is the heat of adsorption of CO on preadsorbed oxygen, Q_3 is the heat of adsorption of CO_2 on preadsorbed oxygen, and Q is the heat of oxidation of CO in homogeneous phase (68 kcal-mole^{-1}).

From Eqs. (4) and (8) we have:

$$Q_3 = \tfrac{1}{2}Q_1 + Q_2 - Q. \qquad (9)$$

By inserting into this equation the measured values of Q_1 and Q_2 and assuming that the first doses of CO react with low-heat-adsorbed oxygen, the heat of interaction of CO_2 with preadsorbed oxygen can be calculated. The calculated values are in good agreement with the experimental results, within the range of experimental errors (Table 1).

TABLE 1

Thermochemical Check of the Formation of CO_3(ads) Complex on Silver[a]

$10 \cdot n_{CO}$ (μmole/m^2)	Q_2 (kcal mole^{-1})	$10 \cdot n_{O_2}$ (μmole/m^2)	Q_1 (kcal mole^{-1})	Q_3 (kcal mole^{-1})	
				calculated	determined
3	91	20–18	41–42	44	
6	91	18–14	42–43	44	
9	85	14–11	43–50	38–41	38
12	74	11–8	50–56	31–34	
14	71	8–6	56–62	31–34	
16	68	6–4	62–70	31–35	
17	66	4–3	70–72	32–34	

[a] n_{CO} and n_{O_2} are the amounts of adsorbed CO and O_2 respectively; Q_1, Q_2, and Q_3 are the heats of adsorption of O_2, CO, and CO_2, respectively.

A similar numerical result is obtained by inserting into relation (9) the values of integral molar heats. Using the curves from Figs. 3 and 4 and assuming that the first doses of CO react with low-heat-adsorbed oxygen, the following integral molar heats are obtained: $Q_1 \simeq 49.5$ and $Q_2 \simeq 82$ kcal mole^{-1}. A value of $\simeq$39 kcal mole^{-1} is then obtained for Q_3 from relation (9), in good agreement with the experimental results.

CONCLUSION

Our results confirm the existence of two domains of oxygen adsorption on silver, namely, a rapid one (heats larger than 40 kcal mole^{-1}) which can account for covering a fourth of the silver surface and a slow domain with heats lower than 40 kcal mole^{-1}.

At room temperature, CO and CO_2 are rapidly adsorbed on preadsorbed oxygen with relatively high heats of adsorption.

A thermochemical cycle using measured heats gives good evidence for the formation of a CO_3(ads) complex during CO and CO_2 interactions with preadsorbed oxygen on silver.

ACKNOWLEDGMENTS

The authors are grateful to Dr. S. Černý from the J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Prague, Czechoslovakia, for helpful comments and for a critical reading of the manuscript and to Mr. B. Constantinescu from the Institute of Physical Chemistry, Bucharest for computer processing of the experimental data.

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