[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Adsorption of Gases on Palladium Oxide[1]

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Palladium oxide is reduced readily at room temperature by hydrogen, reacting as rapidly as the gas comes into contact with it. However, the reduction proceeds slowly even at 100° when carbon monoxide is used[2] and is difficult to carry to completion short of 156°. This is unusual, for the heat of formation of water is less than the heat of formation of carbon dioxide from the monoxide, and the reduction of other oxides proceeds at a lower temperature with carbon monoxide.[2] Since adsorption of the gases is certainly one of the important steps in the rate of heterogeneous reactions, the adsorption of oxygen, carbon dioxide and carbon monoxide have been determined on palladium oxide and on partially reduced palladium oxide, *i. e.*, on an interface between the oxide and palladium. Adsorption on palladium itself has been previously investigated.[3] A series of less reducible oxides was studied by Benton,[4] who determined the adsorption of carbon monoxide only up to 0°, thus obtaining very little information concerning the relationship of adsorption to reduction.

Experimental

Preparation of Material.—The palladium oxide was prepared by the method of Shriner and Adams,[5] that is, from the chloride in fused sodium nitrate, washed and dried over phosphorus pentoxide. For the adsorption studies it was evacuated for three days at 256°, and washed twice with nitrogen. The sample weighed 47.0 g., equivalent to 40.8 g. of palladium or 0.383 mole. All gases were purified by the usual methods; volumes are given corrected to standard conditions.

Apparatus.—The apparatus is that described in another connection[6] and was constructed so that the adsorption could be followed either in a constant volume, or at constant pressure. In the present case the entire process was by the latter method at 350 mm. pressure. It was completely glass sealed, connecting directly with the gas purification train and with the collecting pumps and the system for analysis over mercury.

The adsorption vessel was surrounded by suitable constant temperature baths. The traps were cooled continually by a carbon dioxide–ether mush, to prevent the access to the active surface, of mercury vapor from the pumps and manometer as well as vapors from the stopcock grease. It was found necessary to keep this trap freshly packed with dry ice in order to maintain a constant temperature. The collecting pumps consisted of a Toepler pump and a Sprengel pump. The mercury vapor pump was placed in series just before the Sprengel pump and also connected to the oil pump. Thus removal of strongly adsorbed gas could be made at the speed and vacuum of the mercury vapor pump and yet the gas could be collected. The manometer was a constant vol-

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(1) Paper presented at the Washington Meeting of the American Chemical Society, March, 1933.

(2) McKinney, THIS JOURNAL, **54**, 4498 (1932).

(3) (a) Taylor and Burns, *ibid.*, **43**, 1273 (1921); (b) Taylor and McKinney, *ibid.*, **53**, 3604 (1931).

(4) Benton, *ibid.*, **45**, 887, 900 (1923).

(5) Shriner and Adams, *ibid.*, **46**, 1683 (1924).

(6) McKinney, *J. Phys. Chem.*, **37**, 381 (1933).

ume instrument with electrical contact; however, the current was not used in the measurement with oxygen. The change in adsorption was observed by the change in level of the confining mercury in the buret. With this apparatus an adsorption isobar may be plotted directly.

Method.—The inert volume of the system was determined with nitrogen. There is sufficient evidence that it is not adsorbed. It had been previously shown to be inert to a palladium surface and it seemed reasonable to expect it to be inactive toward the oxide. The nitrogen was all recovered in the collecting system and a plot of the volume of the system against the temperature gives a smooth curve. The values obtained in three measurements with nitrogen spaced before and during the adsorptions are in agreement. Temperature equilibrium was attained rapidly over the entire range, with complete reversibility. The values are identical with the amount of oxygen required to fill the apparatus. The dead space of the apparatus to the master stopcock was 25.9 cc. with the bulb at 0°.

After the determination with nitrogen the order of study was oxygen, carbon dioxide and carbon monoxide. In each case the gas was admitted to the highly evacuated oxide at a low temperature and the rate of adsorption observed. The temperature was then changed and the process continued. Following a series of higher temperature measurements, the system was again cooled and the process observed for comparison with earlier results. The temperature range was from −78 to 218° for the adsorptions, with evacuation at 256° to recover the last trace of gas. In addition to the study of the adsorption isobar in the case of carbon monoxide, the rate of adsorption was measured at definite temperatures on a completely evacuated sample with analysis of the gas at suitable time intervals. Following each isothermal measurement the gas was collected until completely recovered, and the system pumped out at 256° with the mercury vapor pump for two to four hours.

Results

Adsorption of Oxygen.—This gas was measured over the temperature range −78 to 218° with a divergence of ±0.3 cc. from the nitrogen values. It is concluded that this is the order of accuracy of the individual measurement and that oxygen is not adsorbed by a palladium oxide surface. At each temperature there was no drift of the oxygen volume with time over a period of two hours. Actually 45.7 cc. of oxygen was admitted and 45.3 cc. recovered with less than 0.5% not adsorbed by alkaline pyrogallol solution.

Five adsorptions of oxygen were attempted, the first before the palladium oxide had been reduced differed by 0.3 cc. from the nitrogen volume, the last after the oxide was 2% reduced agreed within 0.05 cc. This is contrary to the results of Taylor and Burns,[3a] who found oxygen to be as strongly adsorbed as carbon monoxide on free palladium. However, the palladium they used had been reduced by hydrogen and it is difficult to remove all the hydrogen except by sintering the metal. The small amount of water would not have been observed since it is also strongly adsorbed by palladium.

Finally the partially reduced sample was heated in oxygen at 218°, and though ten minutes' contact showed no adsorption at this temperature, 2.13 cc. was adsorbed in four hours, and exactly this amount could not be recovered by the pumps, having reacted chemically. Metallic palladium reacts with oxygen at about 830°.[7]

Adsorption of Carbon Dioxide.—This gas, which Taylor and Burns have shown is not adsorbed by palladium black, is adsorbed normally by palladium oxide, Fig. 1. The adsorption is greatest at low temperatures and gradually evaporates with temperature increase becoming negligible at 218°. The observations are for a pressure of 350 mm. On a partially reduced surface, *i. e.*, one having perhaps Pd atoms and Pd–PdO interfaces, the adsorption of carbon dioxide is less as is shown by the lower curves.

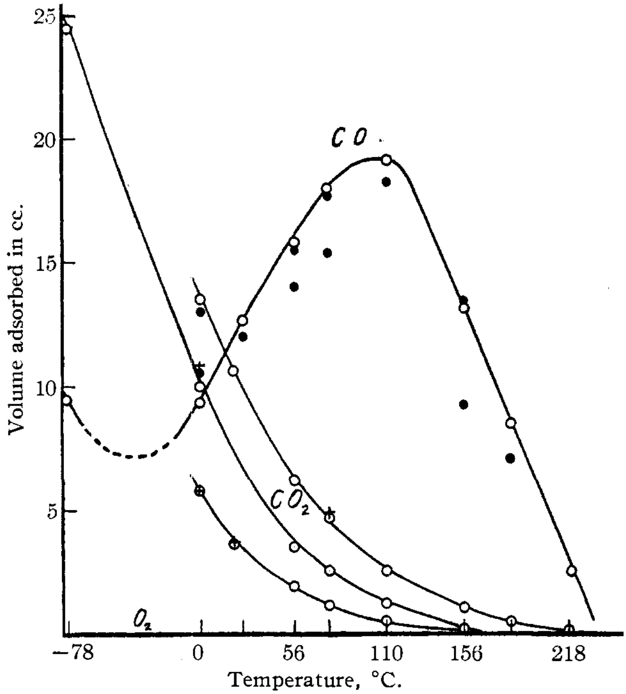

Fig. 1.—Adsorption on palladium oxide.

It is however similar in nature. Actually the original 0.383 mole of palladium oxide has been reduced by 0.0021 mole of carbon monoxide, *i. e.*, by only 0.5% before the second adsorption of carbon dioxide. Since the dioxide is not adsorbed by palladium itself, the decrease may represent either a decrease in the total extent of palladium oxide surface by the reduction or that the active palladium oxide spots have been removed to that extent. Values for the adsorption of carbon dioxide obtained on reducing the temperature are marked in Fig. 1 with +. Since it attains temperature equilibrium rapidly and is completely reversible, the adsorption of carbon dioxide by palladium oxide is entirely physical adsorption.

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(7) Lunde, *Z. anorg. allgem. Chem.*, **163**, 345 (1927).

Carbon Monoxide.—As we should expect the adsorption isobar with this gas is widely different. There is a moderate adsorption at low temperatures, increasing from room temperature to a maximum at about 110° and then decreasing. The values plotted are not equilibrium values as in the case of carbon dioxide but are those for an adsorption of thirty minutes at each temperature. If the process is continued longer there is a slight but significant change in the location of the points. At −78° the two values are identical, between that and the maximum the values for an adsorption at one hour all lie higher than for the thirty-minute periods. Beyond the maximum these points are lower.

Analysis of the gas removed by the pump following this isobar of carbon monoxide on palladium oxide gave 94% of carbon dioxide, the remainder being carbon monoxide. This is equivalent to 0.5% reduction of the entire sample of palladium oxide. When carbon monoxide was admitted to the partially reduced sample the adsorption was very similar to the previous case. However, the gas desorbed analyzed only 73% carbon dioxide. These measurements for thirty-minute adsorption at each temperature are plotted as dark circles in Fig. 1. A third set of values was obtained by the isothermal rate measurements of Fig. 3, and these are also plotted with the former. Analyses of the gas removed from the isothermal adsorption are collected in Table I.

TABLE I

ANALYSIS OF GAS REMOVED FROM CARBON MONOXIDE–PALLADIUM OXIDE SYSTEM

Volume in cc.; Time in hours; Carbon Dioxide Content in %

Method of removal		Toepler				Hg vapor pump		By heating
Temp. °C.		Time		Time		Time		
−78	Vol.	3.5	43.6					7.4
	CO_2		0					77
25	Vol.	4	32.04				3.3	10.8
	CO_2		0.5				37	82
56	Vol.	3	7.3	21	15.2		5.9	21.1
	CO_2		6		20		52	62
76	Vol.	3	4.3	15	24.4		10.5	9.6
	CO_2		2		18		19	75
156	Vol.	15 min.	2.8	2	3.6	5	30.2	6.2
	CO_2		1.8		13		61	78

The adsorption of carbon monoxide is not reversible. On cooling to 0 from 218° the amount of gas adsorbed greatly increased. If one assumes that on cooling the amount of carbon dioxide readsorbed will be equal to that adsorbed at 0° in the preceding experiment and that the amount of carbon monoxide readsorbed is that originally adsorbed in the present experiment then the total readsorbed gas may be calculated.

Readsorbed:	Expt. 4, 23.05 cc.;		Expt. 5, 19.00 cc.
CO_2	13.46	CO_2	9.97
CO	9.30	CO	10.44
Calculated readsorption	22.76		20.41

Discussion

Physical Adsorption.—The low temperature adsorption on palladium oxide is certainly of the physical type. At −78° there is no drift of the amount of gas adsorbed with time, Fig. 2, temperature equilibrium being established in about fifteen minutes. When the oxide has been partially reduced there is a slight drift in the adsorption at −78°. This is probably due to adsorption of carbon monoxide by the free palladium.[3b,8] The gas removed with the Toepler pump at −78° analyzed free from carbon dioxide; 7.4 cc. could not be removed even with the mercury vapor pump at this temperature. It seems reasonable to suppose that this represents carbon monoxide held by activated adsorption to palladium atoms. When this gas was removed at a higher temperature it analyzed 5.7 cc. of carbon dioxide and 1.7 cc. of carbon monoxide.

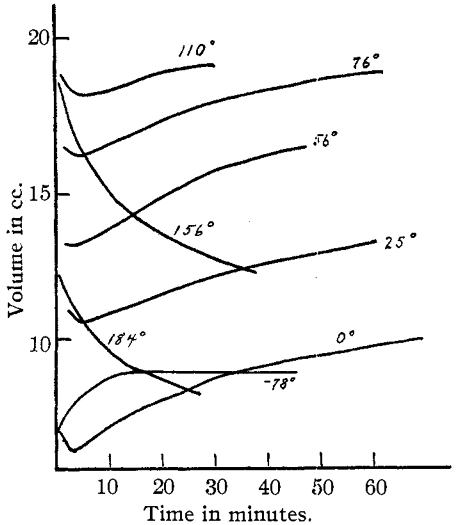

Fig. 2.—Rate of adsorption and desorption of carbon monoxide on palladium oxide.

Activated Adsorption and Reaction.—Between 0 and 100° the amount of carbon monoxide adsorbed increases with the temperature. Samples of the gas removed in this range showed varying amounts of carbon dioxide. On partial reduction the surface does not change much in extent and adsorption does not seem to penetrate the reduced material. However, certainly part of the adsorption in this case is on palladium. At 0° after each additional reduction the amount of adsorption increases, the dark circle lies higher, Fig. 1. At higher temperatures the values are not greater and in general less. This is reasonable since the maximum in the activated adsorption of carbon monoxide by palladium occurs at 0°, above which temperature the carbon monoxide rapidly evaporates from the free metal.

From the data of Fig. 3 activation energy of the process occurring in the rising portion of the curve of the adsorption of carbon monoxide may be calculated. The value of E for the volumes 8, 9 and 10 cc. between 0 and

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(8) On palladium the adsorption of carbon monoxide exhibited the same type of maximum. The low temperature process reached an equilibrium rapidly and reversibly. All the carbon monoxide was recovered. The activated or chemical process approached equilibrium more slowly. Above the maximum, the carbon monoxide may be completely recovered, but below this temperature it cannot be removed in any reasonable time even with the mercury vapor pump. We note that this activated adsorption begins on palladium around −78° and reaches a maximum about 0°.

25° is 2600 calories. Between 25 and 56° for 10 to 15 cc. adsorbed it varies from 3600 to 4800 calories. In the temperature range 56 to 76° the activation energy has again increased, ranging from 7800 calories for 10 cc. adsorbed to 10,000 calories for 15 cc. and 16,000 calories for 18 cc. adsorbed. The process occurring here must be complex since in the case of a simple activated adsorption the value of E should be constant. There is the adsorption of carbon monoxide on free palladium with its maximum below 25° which is decreasing in amount above this temperature although increasing in rate, as well as the adsorption of the monoxide on palladium oxide with a maximum above 76°. Reaction is occurring with some of the adsorbed molecules evaporating as carbon dioxide from palladium atoms, which introduces the heat of reaction into the observed value of E.

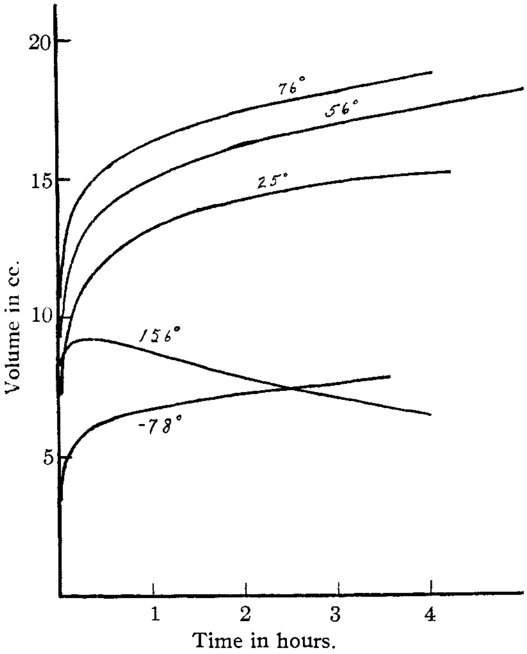

Fig. 3.—Rate of adsorption, carbon monoxide on palladium oxide.

Conclusion

The reduction of palladium oxide occurs through an adsorption step. However, unlike the case of most reducible oxides the process once begun is not autocatalytic and does not proceed to completion. The reduction in spite of the adsorption proceeds slowly. At −78° the carbon monoxide is adsorbed on palladium oxide physically and it may be recovered by evacuation. However, on a partially reduced sample even at this temperature the carbon monoxide is adsorbed strongly by the palladium atoms. Between room temperature and 110° the adsorption of carbon monoxide is chemical on palladium oxide. In this temperature range the analyses show that there is a slow evaporation of carbon dioxide but since the amount of adsorption continues to increase it is probably replaced by carbon monoxide, the dioxide being also adsorbed on palladium oxide but not on free palladium. In the higher temperature range the amount of adsorption decreases rapidly. Though the adsorption of carbon monoxide and carbon dioxide on palladium and of the dioxide on palladium oxide is negligible at 156° the carbon monoxide adsorbed on palladium oxide is quite strongly held at this temperature.

There are considerable data[9] which suggest that the reduction of platinum[10] oxide by carbon monoxide should be normal since it is adsorbed more strongly than hydrogen is by platinum, while the latter will displace carbon monoxide from palladium.[3a,11]

Summary

1. The adsorptions of oxygen, carbon dioxide and carbon monoxide on palladium oxide have been determined over the temperature range −78 to 218°.

2. Oxygen is not adsorbed by palladium oxide, nor by the oxide when partially reduced by carbon monoxide.

3. Carbon dioxide is adsorbed by palladium oxide reversibly, *i. e.*, by physical adsorption. The amount decreases with the extent of reduction of the surface of the oxide; on a sample only 2% reduced, the adsorption decreased by more than 50%.

4. The adsorption of carbon monoxide has a maximum about 100°. There is a physical adsorption at −78°. Activated adsorption increases slowly in amount between 0 and 100° and the gas is strongly held and evaporates only as carbon dioxide. Complete desorption occurs only above 218°.

5. The rates of adsorption on partially reduced samples and activation energies calculated from them indicate a complex process. Carbon monoxide is also adsorbed on the free palladium but so strongly that the further reduction of adjacent palladium oxide is not accelerated. The reaction does not occur at an interface, that is, it is not autocatalytic.

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[9] Langmuir, *Trans. Faraday Soc.*, **17**, 607, 621 (1921); THIS JOURNAL, **40**, 1361 (1918); Pollard, *J. Phys. Chem.*, **27**, 356 (1923); Harbeck and Lunge, *Z. anorg. Chem.*, **16**, 50 (1898).

[10] Baker and Company, Inc., Newark, New Jersey, have generously supplied a quantity of platinum for a similar investigation with that metal.

[11] Also De Hemptinne, *Z. physik. Chem.*, **27**, 429 (1898).