JOURNAL OF CATALYSIS 6, 362–370 (1966)

Adsorption and Interaction of Hydrogen and Oxygen on Platinum

VLADIMIR PONEC

From the Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

Received May 9, 1966

Chemisorption and mutual interaction of hydrogen and oxygen has been measured on platinum films, the resistance changes have been followed simultaneously. By means of these experiments conditions have been found under which gases react on platinum. On the basis of the present results and of some data from the literature a model for the hydrogen chemisorption bond is suggested for transition metals.

Platinum forms an active component of catalysts belonging to the most active in widely different hydrogenation, dehydrogenation, and oxidation reactions. The metal is distinguished by its inertness and heats of adsorption of a number of gases (H_2, O_2, C_2H_4) are low (*1*). Platinum differs from other transition metals in that hydrogen adsorption causes a decrease of the film resistance below the initial value corresponding to the clean surface (*2*). It is remarkable, too, that the decrease of resistance with increasing adsorption (the so-called positive effect) starts on platinum [in contrast to Ni (*3–6*), Pd (*7, 8*), and Fe (*9, 10*)] with the initial stages of adsorption. The simultaneous existence of the "positive" and the "negative" effect at the adsorption of one gas belongs generally to those effects of adsorption on transition metals which have not been explained as yet. Since it eventually can indicate various kinds of chemisorbed species or various types of adsorption bonds, it is of great importance to exclude the possibility of a less "natural" positive effect being produced by some secondary sideaction, for example, by a reaction with impurities (oxygen) which could be present, in small quantities, even on the surface of films prepared under very clean conditions; platinum dissolves oxygen and the eventual liberation of the latter in the course of filament evaporation need not show in the rise of pressure. Furthermore, the high catalytic activity of platinum and the positive effect appearing at hydrogen adsorption from the very beginning of adsorption, could be interrelated in this respect.

In our Laboratory we have been studying the relation between adsorption and catalysis, the reactivity of adsorbed particles, and similar problems lying in the borderline between adsorption and catalysis. After a number of other metals had been studied (*6, 11*), platinum was selected as an example of a highly active metal.

EXPERIMENTAL

The high-vacuum apparatus in which the experiments were performed and the method of evaluation of the adsorption data are described in our preceding papers (*12, 13*). The adsorption vessel used also permits following the reactions of hydrogen atomized in the gaseous phase (*14*). The films were condensed in a vessel immersed in liquid nitrogen and, according to requirements, held at 298° or 330°K for at least 90 minutes. Platinum was evaporated from filament of 0.2-mm diameter (Safina, National Corporation, Czechoslovakia), heated during degassing by an electric current of 1.8–2.0 A, during evaporation by 2.3–2.5 A. After 3 days of degassing the apparatus and the filament, the pressure at evaporation was $\leqslant 1\text{–}2.10^{-8}$ torr. It is necessary to increase the filament temperature very slowly and cautiously to the evaporation temperature, because platinum melts very easily. Both adsorption and interaction were followed at two temperatures, 78° and 273°K.

RESULTS

Hydrogen and Oxygen Adsorption

Hydrogen is readily adsorbed on platinum at temperatures of 78° and 273°K and at pressures of up to 10^{-2} torr. The rate of adsorption is high in the course of adsorption of individual doses both before and after the minimum of the curves shown in Fig. 1. After a certain amount of hydrogen has been adsorbed at 78°K, a minimum resistance is reached and further addition of hydrogen causes an increase of the film resistance. At 78°K only a small part of the hydrogen ($\approx 5\%$), adsorbed after the minimum had been reached, is bound reversibly. At 273°K the reversible part (of hydrogen adsorbed) is substantially greater ($\approx 60\%$). If we cool the adsorption vessel from 273°K down to 78°K, a further amount of hydrogen is adsorbed. This hydrogen is accompanied at 78°K by an increase of the film resistance.

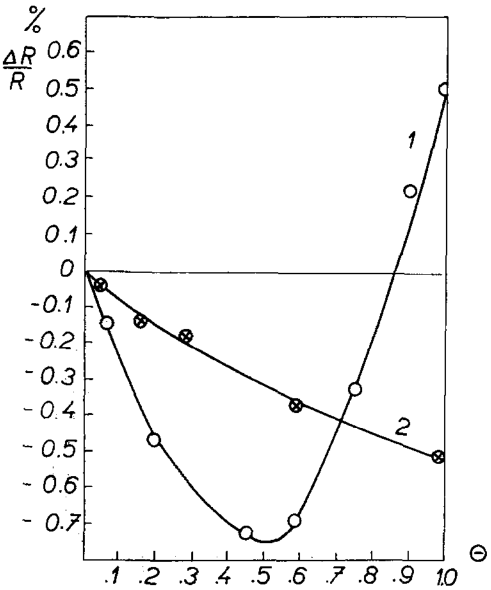

FIG. 1. Dependence of the relative resistance change $\Delta R/R$ (in percent) on the extent of hydrogen adsorption expressed in θ. $\theta = 1$ for adsorption extent corresponding to stationary state at given temperature and pressure of $1\text{–}2 \times 10^{-2}$ torr, 1–78°K, 2–273°K.

If the atomizing filament is switched on in the presence of gaseous hydrogen after the stationary state at 78°K has been reached, a further consumption of hydrogen takes place. However, the sorption of atomized hydrogen is of a lesser extent than, for instance, with nickel or iron.

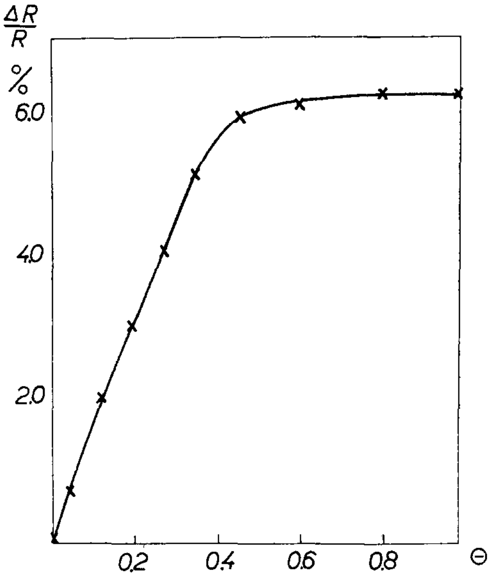

FIG. 2. Dependence of the relative resistance change $\Delta R/R$ (in percent) on the extent of oxygen adsorption expressed in θ. (For θ see Fig. 1 caption.)

Data concerning individual experiments together with some important information on the films used are listed in Table 1.

Oxygen is adsorbed, as is hydrogen, very rapidly, but there is, of course, a difference consisting in the film resistance only increasing at oxygen adsorption, as can be seen in Fig. 2. Similarly as with all other metals studied, the influence of oxygen up-

TABLE 1

SURVEY OF IMPORTANT DATA AND OF FILMS USED

Film No.	Film resistance before adsorption Ω	Maximum adsorption of H_2 at 78°K (μmole)	Maximum adsorption of O_2 at 78°K (μmole)	Maximum adsorption of H_2 or O_2 at 273°K (μmole)	$\left(\frac{-\Delta R}{R}\right)_{\max}$ (%)	Sequence of successive steps during individual experiments[a]
1	212.7	0.68	—	—	0.72	—
2	1000.	0.57	—	—	0.15	H_2 (78°K), pumping off at 78°K,
		—	0.43	—	0	O_2 (78°K)
3	23.6	—	1.11	1.01 (O_2)	−6.0 (78°K)	O_2 (78°K), O_2 (273°K), pumping off at 273°K,
		0.17	—	—	0	H_2 (78°K)
4	23.	0.76	—	—	0.05	H_2 (78°K), pumping off at 78°K,
		—	0.73	—	0	O_2 (78°K)
5	26.	0.65	—	—	0.5	H_2 (78°K), pumping off at 298°K,
		—	1.4	—	−5.0	O_2 (78°K)
6	45.	0.71	—	—	0.5	H_2 (78°K),
		0.3(at.)	—	—	−0.05	H atomized (78°K)
7	222.2	—	—	0.58 (H_2)	0.5	—
8	391.	—	—	0.38 (H_2)	3.0	H_2 (273°K), pumping off at 273°K,
		0.205	—	—	−0.45	H_2 (78°K)
9	39.	—	—	0.55 (H_2)	1.35	H_2 (273°K), pumping off at 273°K,
				0.33 (H_2)	0.05	H_2 (273°K)
10	12.6	—	—	0.6 (H_2)	0.35	—

[a] $\Delta R = 0$ at the beginning of measurements at particular temperatures.

on the film resistence is much higher than that of hydrogen, except when hydrogen dissolves as with Pd at 78°K.

Hydrogen–Oxygen Interaction

(a) If a platinum surface is completely* covered by oxygen at 78° or 273°K and if the gaseous phase is pumped off at these temperatures, only a very small amount of hydrogen is then adsorbed at 78°K (see Table 1) and the adsorption is not accompanied by a measurable film resistance change. If a film thus covered is exposed to hydrogen atomized by the tungsten filament, the uptake of hydrogen by the film takes place even at temperatures as low as 78°K. The slow decrease of the film resistance accompanying the time course of the slow hydrogen uptake from the gaseous phase, suggests that an interaction between atoms of hydrogen and preadsorbed oxygen takes place at this temperature. (Adsorption of hydrogen on a clean film is instantaneous.) The amount of hydrogen consumed is rather large and, as can be seen in Fig. 3, approaches the ratio $H_2/O_2 = 2$. Interaction of the preadsorbed oxygen with atomized hydrogen stops after a certain time and amount of hydrogen adsorbed; at this stage, the hydrogen adsorption just compensates the change in the resistance caused by the oxygen (Fig. 3). The surface on which reaction with atomized hydrogen had occurred also sorbed oxygen which did not react with atomic hydrogen subsequently admitted. Thus the behavior of platinum is the same, in this respect, as that of rhodium (*15*). It can be imagined that by the interaction of atomized hydrogen, surface atoms of the metal are to a

---

* The stationary state of adsorption attained at a constant pressure of oxygen in the gaseous phase within the range of $1\text{–}2.10^{-2}$ torr is considered as a complete coverage of the surface.

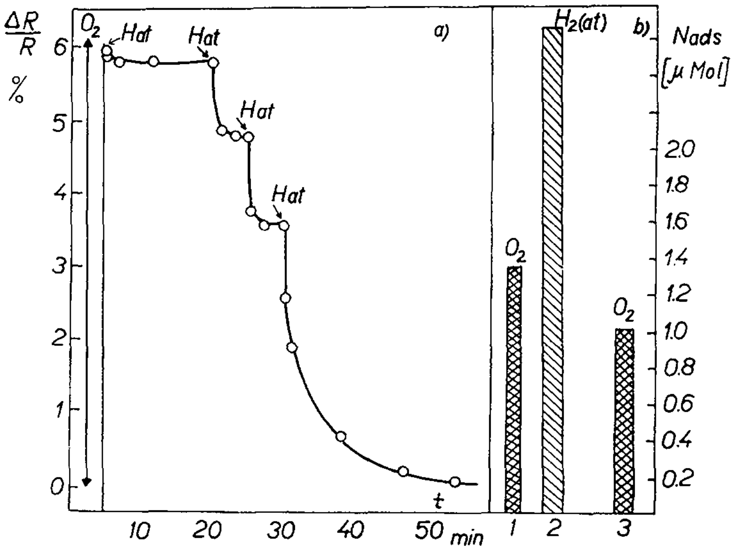

FIG. 3. Oxygen–hydrogen interaction at 78°K on surface completely covered with oxygen. (a) Film resistance change $\Delta R/R$ at oxygen adsorption (marked with arrow) and time change of $\Delta R/R$ at admission of doses of atomized hydrogen (arrow marks admission of a dose). Pressure drops to zero at the end of first three doses; at the end of the fourth dose the pressure (of 10^{-2} torr) is established, which changes further with time but very slowly. (b) Uptake of gases (at the attained stationary state); oxygen (1), atomized hydrogen (2), and oxygen after interaction (3).

certain extent made free for the further uptake of hydrogen and oxygen. However, a layer of sticking nondesorbing interaction products prevents further interaction.

(b) If the platinum surface was only partially covered by oxygen so that sites were left free for adsorption of hydrogen, the interaction of hydrogen with oxygen took place at 78°K [for 273°K see results under (c)]. The consumption of hydrogen from the gaseous phase was accompanied by a decrease in the film resistance,

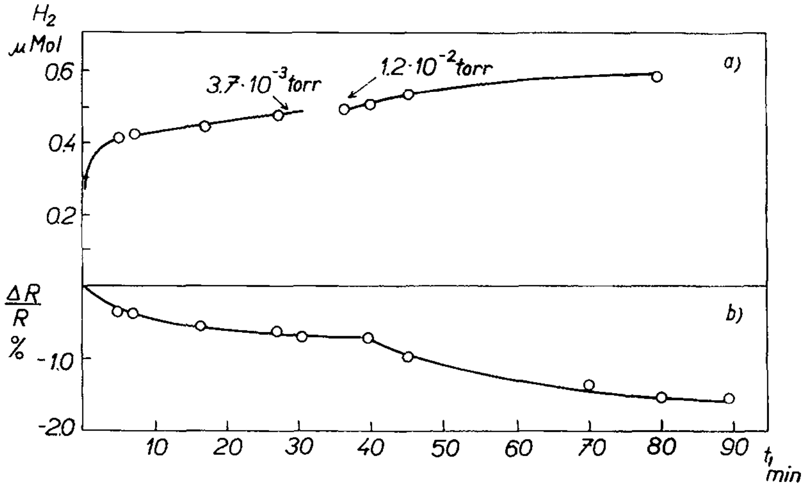

FIG. 4. Hydrogen–oxygen interaction at 78°K. Time dependence of hydrogen sorption (a) and film resistance change (b), at admission of gaseous hydrogen to film partly covered with oxygen (0.4, μmole; $\Delta R/R_{\max} = 5.2\%$). $\Delta R = 0$ at the beginning of hydrogen uptake.

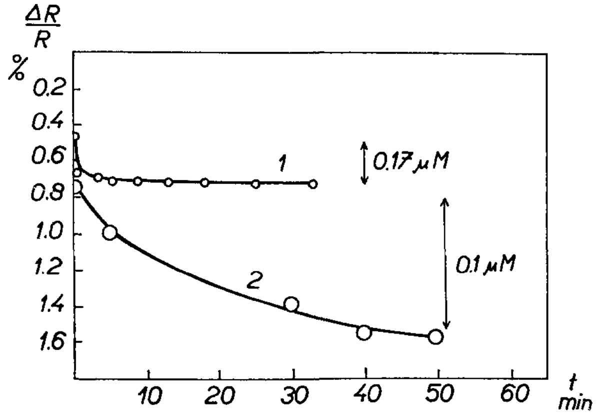

FIG. 5. Comparison of different time course of relative resistance changes at adsorption of one of the hydrogen doses admitted to a surface already covered by preceding adsorption of hydrogen only (1), or of both oxygen and hydrogen (2). Amounts of hydrogen sorbed in the course of mentioned doses are marked in the figure. Temperature in the course of sorption was 78°K. $\Delta R = 0$ at the beginning of the hydrogen uptake.

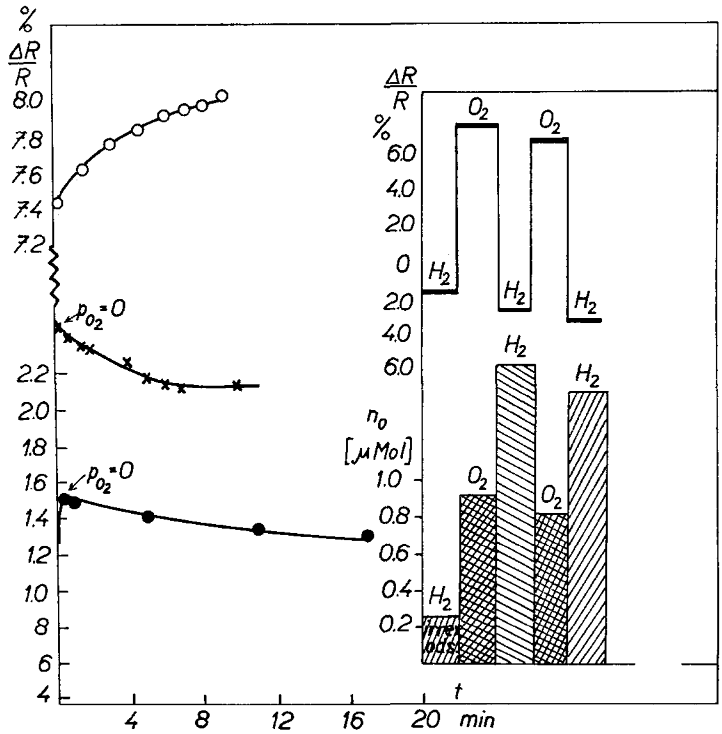

FIG. 6. Hydrogen–oxygen interaction at 273°K. Left: Time course of film resistance changes at admission of three doses of oxygen to surface covered by irreversible adsorption of hydrogen. Arrow marks the instant when pressure of oxygen in the gaseous phase drops to zero. Right: Uptake of hydrogen and oxygen at successively repeated sorption (uptake corresponds to the stationary state) and corresponding film resistance changes.

the time course of which was slower than on a clean surface, and no increase in film resistance was noticed after the minimum of curves on Fig. 1, as was the case on a clean surface. This suggests a reaction in the sorbed layer (see Figs. 4 and 5).

(c) If the surface of platinum is completely covered by hydrogen at 78°K, then —after the gas phase had been pumped out at this temperature—platinum takes up the admitted oxygen to a rather high extent (see Table 1). As distinguished from experiments (see Fig. 6) carried out at 273°K, this uptake of oxygen does not change the film resistance at all (Table 1), although on the same films it was possible also to observe resistance changes even by a small part of reversibly bound hydrogen. When, however, hydrogen had been partially pumped out at 273°K, then oxygen was adsorbed at 78°K on the freed portion with a large resistance change (Table 1).

At 273°K the reaction between hydrogen and oxygen proceeds with the formation of a product (most probably water), which is desorbed and sets the surface free. The extent of sorption of hydrogen and oxygen (Fig. 6) carried out successively, corresponds to the reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ and to the adsorption, on the freed surface, of the gas just being added. The time course of film resistance changes during the oxygen sorption, i.e., the decrease of resistance after the maximum when no oxygen is in the gaseous phase, suggests a reaction in the adsorbed phase.

On a surface that had been freed of oxygen by its reaction with hydrogen at 273°K, a rapid chemisorption of hydrogen takes place at 78°K, accompanied by a small increase of the film resistance.

Discussion

In the introductory remarks problems were mentioned connected with the characteristic difference of platinum from other transition metals. The different rate of the resistance change and of the gas uptake at the admission of hydrogen to a clean film and to a film partially covered with oxygen (Fig. 5) seems to exclude the possibility that the initial decrease of platinum film resistance, within the limits of the irreversible adsorption of hydrogen, is in fact caused by interaction with impurities. As contrasted with the paper of Sührmann and associates (*2*), we found on all the studied platinum films, at 78°K, besides hydrogen causing a positive effect, also hydrogen causing a negative effect.

If we consider the positive effect of hydrogen to be a proved result of interaction with the clean surface, the question which arises is: What is the cause of the platinum behavior differing from that of other transition metals, or what causes the positive effect of hydrogen generally?

Platinum, just as nickel and palladium studied before, has unpaired electrons in orbitals which are predominantly of *d* character; this fact is approximately expressed as the presence of holes in the *d* band (*16–20*). The predominating conductivity with the above-mentioned metals is electron conductivity caused by electrons of an incompletely filled *s* band (*17, 21*). Platinum has, moreover, a particularly low reactivity of its "*s* electrons" and its zero valence is obviously stabilized by the metal state (*22*). Platinum exhibits a low reactivity of its *s* electrons, as does gold which is close to it by its metallic state electron configuration, and thus platinum is less similar, in this respect, to other elements of its own group.

The simplest attempt to explain a simultaneous existence of the positive and negative effect at adsorption is based on the postulated presence of two kinds of differently charged species—ions on the surface. Such an explanation, however, meets also with other difficulties in addition to the slight probability of a simultaneous existence of two differently charged and at the same time mobile particles on the surface on the conductive metal (with a majority of metals, hydrogen in the adsorbed state becomes mobile at temperatures of about 150°K) (*24*). The strength of the adsorption bond (*26, 27, 28*) and its polarity are, for instance, close for nickel and iron, and the curve of dependence of the film resistance and of the work function on the extent of adsorption is at the same time of a very close character for both these elements (*3–6, 9, 10, 25, 29*). Since iron is a hole conductor and nickel an electron conductor, we should have to assume that a negative ion of hydrogen is formed on nickel at low coverages, while a positive ion is formed on iron; the latter ion would have, moreover, to be placed deeply under the level of the iron surface, which would enable us to explain also the measured work function changes. This prompts us to incline, for these and further metals, to the idea of covalently bound hydrogen, which always uses the "conductive" metal orbitals for its bond, giving rise to a double layer with the negative pole outside; the bond, for example, could be weakly polarized in the Me^+H^- sense* with all metals except platinum. The idea of hydrogen dissolution (*30*) cannot generally be used for explaining the positive effect, because the dissolved hydrogen, as for example in palladium, increases the film resistance (*7, 8*). Nor does the idea that hydrogen increases, at the expense of diffuse-scattered reflections of electrons from the metal surface, the share of mirror reflections and thereby diminishes the film resistance, seem justified just with platinum, the surface of which, covered sparsely by hydrogen, ought to reflect electrons better than a clean surface.

In the theory of transition metals, moreover, the following effects, contributing to the metal resistance, were suggested (*19, 20*):

I. the scattering of conductivity electrons on *d*-band holes;

II. electron mobility changes as the result of their interaction with unpaired spins of electrons occupying localized *d* orbitals.

Both these effects can be influenced by the bond of electrons of the adsorbed species and, consequently, the film resistance can be eventually reduced. Then the following explanation of effects found during adsorption on transition metals appears as a probable one.

Hydrogen is generally bound on metals by covalent bonds and uses for bonding, in the first place, on all metals except platinum, orbitals of predominatings (or *s–d*) character in the case of metals with a face-centered-cubic lattice (fcc) and orbitals of *s–p–d* character in the case of metals with a body-centered-cubic lattice (bcc). The same applies also to metals the electron structure of which is similar to these metal groups (Rh and Ir, fcc metals, are, for example, closer to bcc metals). Only with platinum, the *s* orbitals of which are very stable, hydrogen first uses orbitals of *d* character for a covalent bond for its adsorption. A strong and, at temperatures of up to the room temperature, irreversible adsorption, by means of *s* or hybridized *s–p–d* orbitals is, with all metals, connected with Me^+–H^- polarization. The only, already mentioned exception is platinum, which is the hardest metal to oxidize, with which a bond with *s* or *s–d* orbitals asserts itself as a weaker one and with which hydrogen always carries a slight positive charge [Pt^-–H^+ (*25*)]. Not until the adsorption proceeds up to a certain extent are orbitals with predominating *d* character also used for bonding (again except platinum), which leads to a decrease of the film resistance in accord with mechanism I or II. Since *d* orbitals of the metal atom extend to a shorter distance (*16*) than *s* orbitals of the higher main quantum number, it can be assumed that the bond with *d* orbitals of metal is combined with an immersion of the covalently bound hydrogen under the surface of metal, which leads, with a majority of metals, to a decrease of the work function of the metal and only with platinum to an increase of the same (this being the consequence of the presence of covalently bound $H^{\delta+}$ or $H^{\delta-}$, respectively, under the metal surface). With metals having completely empty orbitals which can carry electrons with a magnetic moment or with metals having no such orbitals (Ti, Mo, Rh, Mn, and obviously also further metals such as Ru, Ir, and Os), we find only one kind of

---

* This does not necessarily mean production of a free hole or localization of a conductivity electron in a two-electron bond Me–H.

chemisorption bond. Oxygen, which is bound more strongly than hydrogen, extracts platinum atoms out of the metal bond and at the same time binds electrons of both *s*- and *d*-character orbitals, whereby it brings about a great increase of the film resistance. Oxygen and other strongly bound gases behave in an analogous way on other metals, too. The fundamental possibility of this in the case of platinum is suggested, *inter alia,* by the existence of the oxide PtO_2.

The bond of gases to the surface of platinum is altogether weaker than with other metals (*1*). The high reversibly bound fraction of hydrogen (Table 1) also supports such a view. The high reactivity of species adsorbed on platinum is no doubt connected with this in the first place. Hydrogen reacts on platinum with oxygen even at 78°K, provided at least a part of the platinum surface is left unoccupied by oxygen for the adsorption of hydrogen. The condition that hydrogen must be adsorbed at low temperatures for a reaction with oxygen seems to be quite general, since it has already been proven also for Pd (*33*), Au (*34*), and Ni (*11*). As for oxygen, it has the ability to react in the adsorbed state. The time dependence in Fig. 6 shows that oxygen is sorbed by the film faster than it reacts. This seems to suggest that, as with hydrogen, oxygen always enters the reaction in the absorbed state.

With platinum, as in some experiments with Ni (*11*) and Pd (*8*), we again see that gas is adsorbed but does not change the film resistance as if it had been "screened off" by preadsorption of another gas. Those atoms which carry a strongly preadsorbed gas are therefore already excluded, to a certain extent, from the process of conducting electric current through the metal. These "nonconducting" metal atoms, however, are not excluded from their influence upon the resistance of the film, e.g., according to the model for hydrogen *d*-orbital interaction suggested above.

ACKNOWLEDGMENT

The author acknowledges the help extended to him by Dr. M. W. Roberts and Dr. B. R. Wells (Bredford University, England) during the preparation of the manuscript.

REFERENCES

1. TANAKA, K. I., AND TAMARU, K., *J. Catalysis* **2,** 366 (1963).

2. SUHRMANN, R., WEDLER, G., AND GENTCH, H., *Z. Physik. Chem.* (*Frankfurt*) **17,** 350 (1958).

3. SACHTLER, W. M. H., AND DORGELO, G. J. H., *Bull. Soc. Chim. Belg.* **67,** 465 (1958).

4. ODA, Z., AND ARATA, H., *J. Phys. Chem.* **62,** 1471 (1958).

5. SUHRMANN, R., MIZUSHIMA, Y., HERMANN, A., AND WEDLER, G., *Z. Physik. Chem.* (*Frankfurt*) **20,** 332 (1959).

6. PONEC, V., AND KNOR, Z., *Actes Intern. Congr. Catalyse, 2ᵉ, Paris, 1960,* p. 195 (1961).

7. SUHRMANN, R., WEDLER, G., AND SCHUMICKI, G., *in* "Structure & Properties of Thin Films" (Neugebauer *et al.,* eds.), p. 267. Wiley & Sons, New York, 1959.

8. KNOR, Z., PONEC, V., AND ČERNÝ, S., *Kinetika i kataliz.* **3,** 437 (1963).

9. ZWIETERING, P., KOKS, H. L. T., AND VAN HEERDEN, L., *J. Phys. Chem. Solids* **11,** 18 (1959).

10. CUKR, M., MERTA, R., ADÁMEK, J., AND PONEC, V., *Coll. Czech. Chem. Commun.* **30,** 2682 (1965).

11. PONEC, V., KNOR, Z., AND ČERNÝ, S., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* p. 353 (1965).

12. KNOR, Z., AND PONEC, V., *Coll. Czech. Chem. Commun.* **26,** 579 (1961).

13. KNOR, Z., AND PONEC, V., *Coll. Czech. Chem. Commun.* **31,** 1172 (1966).

14. PONEC, V., KNOR, Z., AND ČERNÝ, S., *Coll. Czech. Chem. Commun.* **29,** 3031 (1964).

15. PONEC, V., KNOR, Z., AND ČERNÝ, S., *Coll. Czech. Chem. Commun.* **30,** 208 (1965).

16. VONSOVSKIJ, S. V., AND IZJUMOV, JU. A., *Usp. Fiz. Nauk* Part I: **77,** 379 (1962); Part II: **78,** 4 (1962).

17. GOODENOUGH, J. B., *Phys. Rev.* **120,** 67 (1960).

18. MOTT, N. F., AND STEVENS, K. W., *Phil. Mag.* **2,** 1304 (1957).

19. COLES, B. R., *Advan. Phys.* **7,** 40 (1963).

20. MOTT, N. F., *Advan. Phys.* **13,** 325 (1964).

21. ZIMAN, J. M., "Electrons and Phonons." Clarendon Press, 1960.

22. BURWELL, R. L., JR., AND PERI, J. B., *Ann. Rev. Phys. Chem.* **15,** 131 (1964).

23. SUHRMANN, R., *Advan. Catalysis* **7,** 303 (1955).

24. GOMER, R., *Discussions Faraday Soc.* **28,** 23 (1955).

25. Culver, R. V., and Tompkins, F. C., *Advan. Catalysis* **11,** 67 (1959).
26. Černý, S., Ponec, V., and Hládek, L., *J. Catalysis* **5,** 27 (1966).
27. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
28. Hayward, D. O., and Trapnell, B. M. W., "Chemisorption." Butterworths, London, 1964.
29. Ponec, V., Knor, Z., and Černý, S., unpublished.
30. Sachtler, W. M. H., and Dorgelo, G. J. H., *Z. Physik. Chem. (Frankfurt)* **25,** 69 (1960).
31. Mizushima, Y., *J. Phys. Soc. Japan* **15,** 1614 (1960).
32. Meyer, H., "Physik Dünne Schichten." Wiss. Verlag, Stuttgart, Germany, 1955.
33. Sachtler, W. M. H., and de Boer, N. H., *J. Phys. Chem.* **64,** 1579 (1960).
34. Kazansky, V. B., and Voevodsky, V. V., *Dokl. Akad. Nauk SSSR* **116,** 633 (1957).