CCVIII.—*The Nature of the Sintering of Active Copper Catalysts.*

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THE conceptions of Taylor (*Proc. Roy. Soc.*, 1925, *A*, **108**, 106) and of Armstrong and Hilditch (*ibid.*, p. 111) concerning the structure of active metallic surfaces seem to have progressed very far in such a direction as to attribute to the centres of activity a quantity of energy that would approach the heat of vaporisation of the metallic atoms (see Constable, *ibid.*, p. 355). Armstrong and

Hilditch have assumed that the nickel atom responsible for hydrogenation reactions is actually gaseous at the instant of the chemical change. Pease (*J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2238, 2297) and Constable (*Proc. Roy. Soc.*, 1926, *A*, **110**, 283), while fully convinced of the existence of centres of activity, do not attribute to them such great energy, the facts being much more in accord with the assumption that they consist of groups of atoms frozen in such a manner that they can still possess intense fields of external force, while being far removed from the condition of vapour.

Taylor (*loc. cit.*) laid considerable stress on the sensitiveness of the surface to heat treatment: "A granule of the catalyst must therefore possess, in part, the ordered arrangement of the atoms found in crystals of the metal. The sensitivity of the product to even moderate heat treatment, whereby marked sintering occurs, suggests that this completely ordered arrangement of the atoms has not been attained, and that here and there, on the surface of a mainly crystalline granule, there are groups of atoms in which the processes of crystallisation are not yet complete." In reality the process of sintering is more complicated than this,* for the boundaries of individual grains are in contact, and therefore the granular structure is itself capable of such a growth as to reduce the area of the exposed surface in a marked degree. Thus, evidence that heat treatment reduces catalytic activity is valueless by itself as a criterion that some of the active centres on the surface have collapsed owing to the increased thermal agitation, for the total active surface has also been reduced in a marked manner. It is therefore essential for the solution of the problem to measure both the surface area of the catalyst and its catalytic activity.

The investigations of Dunn (*ibid.*, 1926, *A*, **111**, 210) provide a means of elucidating this problem. If the course of oxidation of a metal be followed, both by measurements of the electrical conductivity of the metal–oxide mixture, and by estimation of the thickness of the surface film of oxide by means of its colour in normally reflected light, a direct measure of the surface area of the catalyst can at once be obtained. Unfortunately, it is only possible to estimate the equivalent air thickness of the oxide film, *i.e.*, the thickness of a film of air that would produce the same colour effects, and thus the absolute measurement of the area of the surface is not possible by this method, without introducing very distinct assumptions as to the refractive index and nature of the oxide. It is, however, possible to measure the fractional decrease in the

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* There are at least two variables: the number of centres of activity per unit area of the surface, and the relative rate of reaction on each individual centre of activity.

surface area when the catalyst is exposed to a high temperature. Let S be the surface area of the catalyst, C the conductivity of the film of metal supported on a China-clay rod, a the thickness of the oxide film, t the time the metal has been exposed to oxidation, and ρ the density of the oxide of mass W. Then, assuming that the electrical conductivity of the film is a measure of its metallic content (compare Palmer, *Proc. Roy. Soc.*, 1921, *A*, **103**, 444),

$$\rho S(da/dt)/W = -(dC/dt)/C \quad . \quad . \quad . \quad . \quad (1)$$

As the oxidation proceeds, the value of S must become smaller, and as its *initial* value only is important, it is necessary to measure da/dt and dC/dt at the commencement of the reaction. According to Dunn (*loc. cit.*; his conclusions are confirmed by the present work), the process is controlled by the rate of diffusion of oxygen through the protecting layer, and if W is the weight of the oxide formed in time t, then

$$W^2 = Kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K is a constant. It was found that both the fall in the conductivity and the equivalent air thickness follow the law quoted above for the weight of oxide formed in time t, when the catalysts are rendered inactive by sintering. But for the most active catalysts the value of K obtained fell considerably with increasing time. Dunn showed this to be due to the influence of time on the oxide film : some hardening process apparently takes place which causes the film to become less permeable to oxygen. Therefore, in the case of active catalysts it is necessary to find the *initial* value of K in equation (2).

If c be the fall in conductivity, *i.e.*, $c = C_0 - C_t$, then $c^2 = K_c t$. Hence $dc/dt = \frac{1}{2}\sqrt{K_c/t}$; similarly $da/dt = \frac{1}{2}\sqrt{K_a/t}$. Thus equation (1) becomes

$$\rho S\sqrt{K_a}/W = \sqrt{K_c}/C \quad . \quad . \quad . \quad . \quad (3)$$

Let the symbols with suffix 1 relate to the active catalysts, and those with suffix 2 to the sintered catalyst; then dividing the two equations of type (3) for the active and sintered catalysts, respectively, after the same small time interval t from the commencement of the oxidation of each at the same temperature, we obtain

$$S_2\sqrt{K_{a_2}}/S_1\sqrt{K_{a_1}} = \sqrt{K_{c_2}/K_{c_1}} \quad . \quad . \quad . \quad . \quad (4)$$

The ratio of the area of the catalyst in its two states (*i.e.*, S_2/S_1) can thus be measured and compared with the fall in catalytic activity, without assuming any particular value for the refractive index of the copper oxide.

EXPERIMENTAL.

The films used were prepared as described previously (*Proc. Roy. Soc.*, 1924, *A*, **106**, 251). They were rendered active by alternate oxidation and reduction at 210°, and the nature of the departure from the parabolic law was studied, together with the effect of arrested oxidation. The fractional conductivities of the film of copper and the constants of the parabolic law are shown in Table I.

TABLE I.

t (mins.).	Fraction of original metal remaining.	c (ohm^{-1}).	$c^2/t = K_c$.
0	1·000	0·000	—
1	0·747	0·149	0·0222
2	0·671	0·193	0·0183
3	0·600	0·236	0·0159
4	0·558	0·261	0·0170
5	0·525	0·281	0·0157
6	0·494	0·299	0·0149
10	0·422	0·342	0·0117
15	0·349	0·385	0·0099

The fall in the initial conductivity noticed by Dunn was confirmed, some 18% being lost in five alternate oxidations and reductions. The fractions of the initial conductivities were plotted against time, so that each curve should be strictly comparable. If the arrested oxidation follows the same law, then the value of the constant so obtained would be of importance as a characteristic of the hardened oxide film produced in the second experiment. A difficulty arises in calculating the value of K_c for all curves after the first, because the origin of the later curves is not the point $t = 0$, $c = 1{\cdot}00$; this can be removed by considering later curves as part of a parabolic curve of the form $c^2 = K_c(t + \tau)$, and deriving K_c from the relation $2c.dc/dt = K_c$. The results so obtained are recorded in Table II.

The value of K_c is thus the same whether the oxidation has been arrested for 20 or 70 minutes; hence the sintering and hardening of the oxide is moderately rapid. The oxide formed during continuous oxidation has, however, a higher permeability to oxygen, since it does not have time completely to attain the final state, owing to the constant formation of a fresh layer. The result nevertheless confirms that the fall in the constant for the most active catalysts can be accounted for by the hardening of the newly formed oxide layer; thus it is necessary for the solution of equation (4) to compare the values of K in the initial stages of the oxidation.*

* It is fortunate that the values of K, both for the equivalent air thickness curves and for the fall in conductivity compared with time, fall in the same manner for the most active catalysts. Hence the average values may be used for comparison, and for solution of equation (4).

Table II.

The constant in the parabolic law for catalysts whose oxidation has been arrested and then continued.

t.	Fall in conductivity.	Mean c over interval.	Time interval.	Δc.	$K_c \times 10^3$.
		A. Oxidation arrested for 20 mins.			
0	0·000				
2	0·198				
5	0·229	0·233	10 − 2 = 8	0·069	4·00
10	0·267	0·260	15 − 5 = 10	0·063	3·27
15	0·292	0·290	20 − 10 = 10	0·047	2·73
20	0·314				
		B. Oxidation arrested for 70 mins.			
2	0·216				
5	0·254	0·248	10 − 2 = 8	0·064	3·96
10	0·280	0·288	15 − 5 = 10	0·068	3·92
15	0·322	0·310	20 − 10 = 10	0·059	3·76
20	0·339				

The same film of metallic copper was studied by simultaneously measuring its conductivity and comparing its colour with a standard. An activated film, prepared at 210°, was sintered at 440° for 10, 50, 100, and 200 minutes, and its rate of oxidation studied immediately after each sintering. (After each experiment the film was reduced at 210° by carbon monoxide, and sintered for the requisite time for the next experiment.) It was more convenient to use an old rod coated with copper which had been oxidised and reduced a large number of times; there was thus less volatilisation of copper during the series of experiments than would have been found with a freshly prepared rod.

The results obtained with the old rod are recorded in Table III, which shows the validity of the parabolic law; α represents the equivalent air-thickness of the oxide film (in cm. $\times 10^{-5}$), and K_a is the corresponding constant ($K_a = \alpha^2/t$).

The mean values of K_c and K_a are used, since it is evident from Tables III A and B that the fall in the constants for the fully activated catalysts occurs in the results of both methods and to a strictly comparable extent (see footnote, p. 1581). The surface area is reduced to about one-third while the catalytic activity is reduced to about one-seventh; thus the reduction in the surface is somewhat more effective in reducing the catalytic activity than is the collapse in the actual centres existing on the surface.

It has therefore been shown that the active centres collapse when exposed to temperatures considerably in excess of those at which the surface was formed, and hence that these centres of activity are in a state of strain. But the coarse structure seems to collapse even more easily, suggesting that the energy present in the centres

TABLE III.

The oxidation of active and sintered catalysts at 210°.

A. Measurements by the conductivity method.

Time of sintering at 440° (mins.).

	0·0		10		50		100	
t.	*c*.	$100K_c$.	*c*.	$K_c \times 10^3$.	*c*.	$K_c \times 10^3$.	*c*.	$K_c \times 10^4$.
0	0·000	—	0·000	—	0·000	—	0·000	—
1	0·142	2·02	0·086	7·41	0·045	2·01	0·030	9·00
2	0·191	1·82	0·122	7·45	0·066	2·18	0·036	6·48
3	0·234	1·82	0·150	7·50	0·079	2·08	0·048	7·68
4	0·249	1·55	0·171	7·30	0·092	2·12	0·055	7·56
5	0·272	1·48	0·184	6·76	0·103	2·13	0·068	9·23
6	0·287	1·37	0·203	6·86	0·108	1·95	0·071	8·38
7	0·303	1·31	0·225	7·23	0·123	1·80	0·078	8·68
8	0·312	1·22	0·241	7·26	0·134	2·22	0·083	8·61
10	0·338	1·14	0·259	6·71	0·149	2·21	0·101	10·2
12			0·276	6·34	0·162	2·62	0·112	10·4
14			0·299	6·38	0·178	2·63	0·126	11·3

Mean value of K_c.

$1{\cdot}52 \times 10^{-2}$ $7{\cdot}02 \times 10^{-3}$ $2{\cdot}18 \times 10^{-3}$ $8{\cdot}76 \times 10^{-4}$

B. Measurements by the colour method.*

Time of sintering at 440° (mins.).

	0·0		10		50		100	
t.	*a*.	$K_a \times 10^{10}$.	*a*.	$K_a \times 10^{10}$.	*a*.	$K_a \times 10^{10}$.	*a*.	$K_a \times 10^{10}$.
0	0·0	—	0·0	—	0·0	—	0·0	—
1	2·0	4·0	1·5	2·2	1·3	1·7	1·2	1·4
2	2·4	2·9	2·1	2·2	1·9	1·8	1·6	1·3
3	2·8	2·6	2·6	2·3	2·2	1·6	2·2	1·6
4	3·1	2·4	3·0	2·3	2·5	1·6	2·3	1·3
5	3·3	2·2	3·2	2·0	2·9	1·7	2·6	1·4
6	3·6	2·2	3·5	2·0	3·0	1·5	2·9	1·4
7	3·9	2·2	3·8	2·1	3·3	1·6	3·2	1·5
8	4·1	2·1	4·0	2·0	3·6	1·6	3·4	1·4
9	4·3	2·0	4·2	2·0	3·9	1·7	3·7	1·5
10							3·9	1·5

Mean value of K_a.

$2{\cdot}50 \times 10^{-10}$ $2{\cdot}12 \times 10^{-10}$ $1{\cdot}63 \times 10^{-10}$ $1{\cdot}43 \times 10^{-10}$

* Estimated from Rollett's table (*Sitzungsber. K. Akad. Wien*, 1887, **57**, 229) of the colours of Newton's rings in transmitted light.

TABLE IV.

Comparison of fall in catalytic activity in the dehydrogenation of alcohol with the decrease in surface area.

Time of sintering (mins.)	0·0	10	50	100	200
$K_c \times 10^4$	152	70·2	21·8	8·76	8·19
$K_a \times 10^{10}$	2·50	2·12	1·63	1·43	1·33
Fractional surface area	1·00	0·72	0·468	0·32	0·33
Rate of dehydrogenation observed with six rods similarly prepared	3·21	1·71	0·47	0·43	0·43
Fractional reaction velocity	1·00	0·53	0·146	0·134	0·134
Reaction velocity per unit area of catalyst	1·00	0·74	0·31	0·42	0·40

of activity is not very greatly in excess of that possessed by the regular arrangement of the surface atoms. Thus the theory in the form advanced by Taylor, and by Armstrong and Hilditch, seems to be too drastic, and the more moderate views of Pease and Constable accord better with the experimental facts.

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