The Production of Active Solids by Thermal Decomposition. Part V. The Sintering of Active Magnesium Oxide.*

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Two series of experiments have been performed to test the reality of the sintering of active solids postulated in Part I (*J.*, 1953, 3940). In the first the starting material was pure precipitated magnesium hydroxide, and in the second a sample of active magnesium oxide prepared from the same hydroxide by calcining for six hours at 534°; separate samples of both starting materials were calcined for varying periods at a number of fixed temperatures and the specific surface, the heat of immersion, the density, and certain other properties of the cooled products examined. The results confirm that sintering does occur and that it is promoted by an increase in either time or temperature. They also indicate that sintering may be accompanied by progressive elimination of chemisorbed water (or of chemisorbed carbon dioxide for the older specimens) from the surface of the micelles. It is further shown that the " activation " of the solid may occur after the decomposition of the parent substance rather than simultaneously with it.

In Part I (*J.*, 1953, 3940) it has been postulated that active solids prepared by thermal decomposition of a parent substance at elevated temperatures begin to sinter as soon as they have been formed. The process of sintering should, from its very nature, depend on time as well as on temperature, so it was considered desirable to demonstrate directly, the progress of sintering with time. The solid chosen was magnesium oxide, as we had already acquired some knowledge on this substance (Gregg and Razouk, *J.*, 1949, S36; Britton, Gregg, and Winsor, *Trans. Faraday Soc.*, 1952, **48**, 63; Gregg and Packer, see Part VI, following paper). Separate samples were calcined for varying periods at fixed temperatures, and, on cooling, the content of volatile matter, the apparent density, the specific surface area, and, for certain samples, the heat of immersion were determined. The results show clearly the reality of the sintering, but that the problem is complicated and requires further study before a fully quantitative model can be formulated.

EXPERIMENTAL

Materials.—The magnesium hydroxide (Batch A), which is more fully described in Part VI, was prepared from the chloride by precipitation with aqueous ammonia. Its chloride-ion content was only 0·015%; its " water " content was 30·93 (Calc., 30·88%), and the specific surface area, measured by nitrogen sorption at −183°, was 56 $m.^2 g.^{-1}$.

Procedure.—The experiments fell into two separate Series. In Series I the starting material was magnesium hydroxide and separate samples were calcined for varying periods at 400°, 700°, and 750°, the products being examined on cooling. In Series II, carried out some months later, it was desired that the starting material should be such that any heat treatment it received would bring about no further activation but only sintering; accordingly a portion of the same batch of hydroxide as that used in Series I was first heated to 534° ± 5° for 6 hr. to become the starting material for Series II. (Preliminary experiments had shown that the rate of loss of weight after 6 hr. at this temperature was exceedingly slow.) Separate samples of this already calcined material were then further calcined on the thermal balance (Gregg and Winsor, *Analyst*, 1945, **70**, 336) for varying times at 534° ± 5°, 561° ± 5° and 592° ± 5°, and the products were examined after cooling.

Details of the tests employed have been, or will be, described elsewhere, *viz.*, specific surface by nitrogen sorption at −183° (Gregg and Sing, *J. Phys. Coll. Chem.*, 1951, **55**, 592); the apparent density ρ in carbon tetrachloride (*idem, ibid.*, 1952, **56**, 388); the heat of immersion

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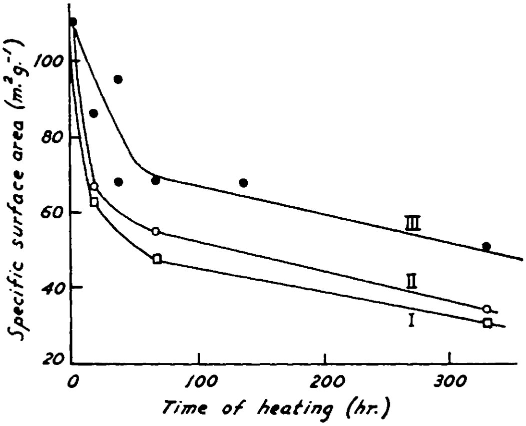
* Part IV, *J.*, 1954, 3887.

in carbon tetrachloride (Asher, Gregg, and Hill, unpublished work); content *w* of volatile matter, by heating the material to 980° on the thermal balance (Gregg and Hill, *J.*, 1953, 3945).

RESULTS AND DISCUSSION

The results for Series II will be presented first. In Fig. 1 the specific surface area *S* is plotted against time; the points do not lie even approximately on a straight line, the rate of fall of *S* being far greater in the early stages than in the later. If, however, the quantity $1/S_\rho (= r$, say) be plotted against the square root of the time the points, including that for zero time, fit with some scatter along a straight line (Fig. 2). The quantity S_ρ is actually the surface area per cm.^{3} of the solid material, so that $1/S_\rho$ is essentially the ratio of the true volume to the surface area of the solid; it may perhaps be made more concrete by means of the simplifying (though obviously very crude) assumption that the material exists as equal cubelets, or micelles, of length *l*; for then $l = 6/S_\rho$ and the use of the right-hand scale of Fig. 2 gives the rate of growth of micellar length with time. The equation to the straight lines may be written as

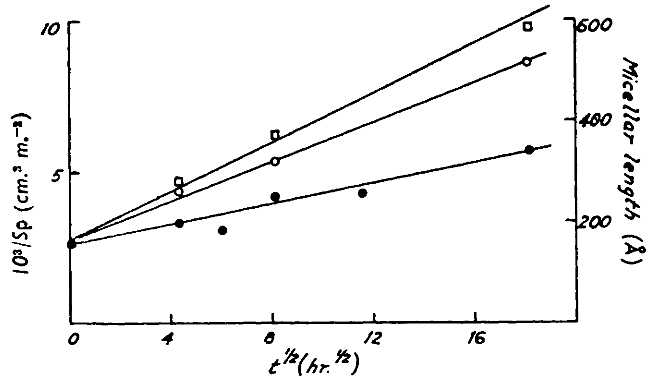
FIG. 1.



FIGS. 1 and 2. *Effect of time of heating on the sintering of active magnesium oxide prepared by heating the precipitated hydroxide for 6 hours at 534°.*

I, 592°; II, 561°; III, 534°.

FIG. 2.



$$l - l_0 = kt^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or as

$$r - r_0 = 6kt^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where l_0 is the micellar length, and r_0 is the value of the volume-to-surface ratio, at the commencement of the experiment, *k* being a constant at constant temperature. A relationship identical with (1) is followed in the oxidation of certain metals with l as the thickness of the oxide layer; the resemblance is purely formal, however, for, whereas the oxide layer increases in thickness as a result of a net transport of matter (oxygen) from the outside, in sintering, the reduction is brought about by a mere rearrangement of material already present without any increase in the total quantity.

Differentiation of equations (1) and (2) gives

$$\mathrm{d}l/\mathrm{d}t = \tfrac{1}{2}kt^{-\frac{1}{2}} = \tfrac{1}{2}k^2/(l - l_0) \qquad (3)$$

and

$$\mathrm{d}r/\mathrm{d}t = k^2/[72(r - r_0)] \qquad (4)$$

respectively. These imply that the rate of increase in micellar length or in the volume-to-surface ratio is inversely proportional not, as might have been expected, to l or to r but rather to the *change* in each quantity which has occurred since the beginning of the experiment.

No simple and plausible model has emerged so far for the quantitative interpretation of these deceptively simple relations. The temperature range is so low when referred to the absolute melting point T_m—it corresponds to an α-value of some 0·25 only—that both surface diffusion and bulk diffusion seem to be ruled out and adhesion alone can remain; and adhesion is promoted when one or more of the dimensions of the adhering bodies is small ($\alpha = T/T_m$). Relations (3) and (4) are, qualitatively at least, in accordance with such a picture, in that as l or r increases, the tendency to adhere should diminish.

The existence of a large temperature coefficient for k (see Table 1 and Fig. 2) indicates, however, that simple adhesion cannot represent the whole truth, for the temperature coefficient of k should then be of the order of the temperature coefficient of rigidity, and this is small; and, as will be shown shortly, it is quite likely that the rate of sintering is controlled by the rate of removal of a chemisorbed layer from the surfaces about to adhere, a process for which an energy of activation and therefore an appreciable temperature coefficient is to be expected.

TABLE 1.

T	592°	561°	534°	400°
k (Å hr.$^{-\frac{1}{2}}$)	24·0	20·0	11·0	5·0
Series	II	II	II	I

TABLE 2.

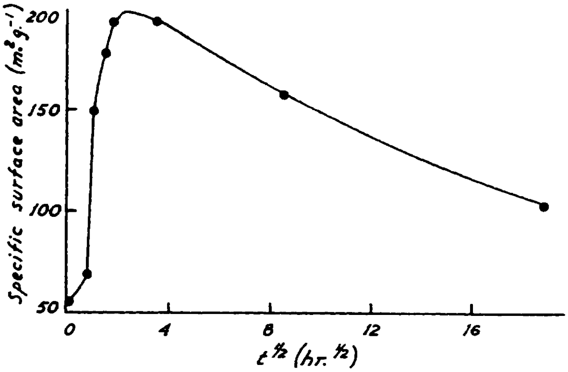
T	t (hr.)	S (m.^{2} g.$^{-1}$)	w (%)	MgO (%) (m)	A_{CO_2}	Density in CCl_4 (g. cm.$^{-3}$)
			Series I			
400	0	56	30·93	0·0	—	—
	0·5	69	6·45	79·2	—	—
	1	151	2·94	90·5	—	—
	2	179	2·32	92·5	—	—
	3	189	1·89	93·9	—	—
	12	190	1·79	94·2	—	—
	72	168	1·70	94·5	—	—
	356	107	1·42	95·4	—	—
			Series II			
534	0 *	111	3·1	—	26	3·43
	18	87	2·4		26·5	3·34
	36	94, 68	2·3, 1·8		30, 27	3·44, 3·50
	66	69	1·8		27	3·50
	136	68	1·8		27	3·51
	330	51	1·8		21	3·58
			Series II (*contd.*)			
561	18 *	67	1·4		35	3·46
	66	55	1·3		31	3·50
	330	34	1·1		23	3·55
592	18 *	63	1·6		29	3·44
	66	47	1·4		24	3·48
	330	30	1·3		17	3·55

* The material had been heated for 6 hours at 534° before the commencement of the experiment.
w = content of volatile matter. A_{CO_2} = area occupied per molecule of chemisorbed CO_2(Å^2).

The results of Series I, where the starting material was uncalcined magnesium hydroxide, may now be considered. In Fig. 3 the specific surface S has for convenience been plotted against $t^{1/2}$ for the experiment at 400°, and as is seen it first increases to a maximum and then slowly decreases. Comparison with the values of percentage decomposition m (calculated from the loss on ignition) given in Table 2 reveals that S is by no means proportional to m; thus whereas S increases only slightly whilst m increases from 0 to 79%, a further 10% decomposition sees the area increased by more than two-fold, and the next 2% conversion is accompanied by no less than 18% increase in area. Clearly, the production of new surface must result from some process which either occurs *after* the decomposition or at any rate proceeds more slowly than the decomposition; and a reasonable postulate is that the magnesium hydroxide decomposes to give the oxide in the form of a pseudo-lattice of the hydroxide, which later recrystallises to the stable form of the oxide (periclase). The recrystallisation would proceed from nuclei, each one giving rise to a micelle of oxide, the increase in specific surface being thus decided by the number of micelles present per original micelle of hydroxide (Gregg, Part I *loc. cit.*); the surface would be largely located on the walls of fine cracks produced by the shrinkage associated with the recrystallisation process. Once formed, the oxide would immediately sinter, probably by an adhesion mechanism as already indicated, the fine cracks giving place to a smaller number of wide cracks with a lower surface area.

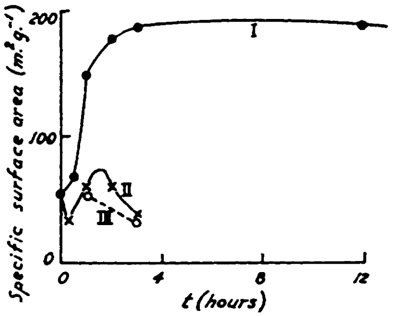
FIG. 3.

Calcination of precipitated magnesium hydroxide.



At 400°.

FIG. 4.



I, 400°; II, 700°; III, 750°

In Fig. 4 the value of S is plotted against t for the early part of the experiment at 400° and for the whole of the experiments at 700° and 750°. The initial dip in the curve for 700° is probably real and due to the sintering of the unchanged magnesium hydroxide, the rise and subsequent fall being explained by activation and sintering just as before; the curve for 750° has two readings only, but there is little reason to doubt that its form would have been identical with that for 700° had more readings been taken in the first hour.

The data for content of volatile matter w are given in column 4 of Table 2. Since in the experiments of Series II the material had already been heated for 6 hours at 534° before commencing the experiment proper, it is clear that for comparable total times of heating w is consistently higher than in Series I at 400°—an unexpected result in view of the higher temperatures of Series II. The most likely explanation is that the whole, or most, of w in Series II represents combined carbon dioxide derived from the atmosphere during storage of the specimen, despite the use of a screw-topped bottle; and since w is (very roughly) proportional to the specific surface, a chemisorbed layer of carbonate on the surface is indicated. The values for the area A per molecule of carbon dioxide, calculated from S and w, are given in column 6. They are only approximate because of the difficulty of measuring w accurately, but are consistent with the reasonable assumption that each chemisorbed molecule of carbon dioxide covers *three* ions of oxygen in the surface of the magnesium oxide, *i.e.*, two in addition to the one which is directly linked to the carbon atom; for the area occupied per molecule of carbon dioxide would thus be at least 3 × 7·8 Å^2, *i.e.*, 23 Å^2—and perhaps somewhat greater for any isolated oxygen ion lying between neighbouring chemisorbed carbon dioxide molecules would have to remain vacant. According to this picture, when sintering occurs, chemisorbed carbon dioxide will be expelled from the surfaces as they adhere; and if this expulsion with its rather large energy of activation be assumed to control the overall rate of sintering, the high temperature coefficient already remarked on is qualitatively explained.

In the language of reaction kinetics it seems then that the " energy factor " controlling the rate of sintering may be determined by the expulsion of carbon dioxide, and the " frequency factor " by the micellar dimensions.

The volatile matter in Series I, for reasons already indicated, probably represents water only; and if the area per molecule is calculated (for the sintering branch of the curve for 400°, since bulk hydroxide may then be assumed absent), it comes to 32 Å^2 for 12 hr., 30 Å^2 for 32 hr. and 23 Å^2 for 23 hr. If one molecule of chemisorbed water is assumed to cover *two* oxygen ions in the surface of the solid, the proportion of surface covered with chemisorbed water is 0·49, 0·50, and 0·67 respectively. The results are too scanty to allow unequivocal conclusions to be drawn, but they do suggest that the sintering of Series I is accompanied by the elimination of chemisorbed water; the energy of activation for this process would be lower than for the elimination of chemisorbed carbon dioxide, and this may explain why the increase in rate of sintering (measured by the slope k of the " sintering branch "), *e.g.*, from 400° for Series I to 534° of Series II is so small compared with that from 534° to 561° or 561° to 592° in Series II (see Table 1).

Referring finally to the results for the density ρ (Table 2) it is seen that ρ gradually rises with increasing time of heating, denoting either a progressive destraining of a strained lattice or a gradual elimination of holes inaccessible to the molecules of the immersing liquid, or, of course, to both factors operating together. The density of crystals of magnesium oxide cut from the melt is 3·5761 at 25° (Durand, *Phys. Review*, 1936, **50**, 451) and it therefore appears that only after long heating, for periods of the order of 330 hr., at temperatures upwards of 530°, does the measured density of active magnesium oxide approach closely that of the unstrained, non-porous material.

Conclusion.—The work here reported provides a direct demonstration of the reduction of the specific surface of an active solid by the action of heat; and it shows that the extent of the reduction is increased by an increase in either the temperature or the time of heating. It also shows that " activation " of the solid need not coincide with the decomposition of the parent substance, but may follow it in time, being probably due to recrystallisation of a pseudo-lattice. The sintering is accompanied by an increase in apparent density and probably also by progressive elimination of chemisorbed water (or of chemisorbed carbon dioxide in older specimens) from the surface of the micelles.

The formulation in fully quantitative terms of a detailed mechanism for the sintering of active solids must, however, await further experimental and theoretical work.

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