The Production of Active Solids by Thermal Decomposition. Part VI. The Calcination of Magnesium Hydroxide.*

By S. J. GREGG and R. K. PACKER.

[Reprint Order No. 5577.]

Two batches of magnesium hydroxide were precipitated, one almost ion-free and the other containing 1·22% of sulphate ion. Separate samples of each were then calcined for two hours at a succession of fixed temperatures, and a number of properties of the resultant active magnesium oxide were measured after cooling, including the specific surface area (S), the heat of immersion (H_L), and the density. The curves of specific surface and of heat of immersion against the temperature of calcination show a marked maximum corresponding to the chemical decomposition; the maximum is displaced towards higher temperatures, and its height is greater, for the sulphate-contaminated material. The rate of fall of S and of H_L with temperature of calcination is greater, denoting enhanced sintering, for this same material.

THE production of active magnesium oxide by the thermal decomposition of magnesium hydroxide offers certain advantages for studying the preparation of active solids by thermal decomposition: magnesium hydroxide is a definite stoicheiometric compound, a *hydroxide*, and not a mere hydrated oxide of indefinite composition; and the product of decomposition, magnesium oxide, exists in one modification only and undergoes no polymorphic transformation. Moreover it can be deliberately contaminated with ions during preparation, or obtained nearly pure, thus permitting a study of the effect of impurity on the production and on the subsequent sintering of an active solid.

EXPERIMENTAL

Materials.—Two batches of magnesium hydroxide were prepared by precipitation, Batch A from magnesium chloride under conditions likely to minimise contamination, and Batch B from magnesium sulphate under conditions likely to favour adsorption of sulphate ions. Both precipitations were conducted in a closed aspirator X of 25 l. capacity fitted with an electrical stirrer entering through a mercury seal; two other aspirators Y and Z were fitted with delivery tubes drawn down at the end so as to form jets terminating near the bottom of X. The contents of Y and Z could thus be run into X at a rate controlled by screw-clips. All the distilled water used in making up solutions and in washing precipitates was boiled before use to expel carbon dioxide and stored in vessels protected by potassium hydroxide guard tubes. The outlet from X to the atmosphere was similarly guarded.

For Batch A, 10 l. each of N-magnesium chloride and of N-potassium hydroxide were run from the two aspirators Y and Z into X, which initially contained enough water to cover the jets; the precipitate was then allowed to settle, and after the supernatant liquor had been sucked off was washed repeatedly with distilled water (about 20 l. each time), and then with 0·025N-ammonia solution. There were twenty-eight washings in all, though even after the fifteenth a minute reaction for chloride ions was obtained. The sludge was then transferred to Winchester bottles and most of the water removed by warming in a water-bath at 65° and evacuation with a filter pump; the Winchesters were then cut open and the solid was dried (P_2O_5) in a vacuum desiccator, and stored in screw-topped bottles. The granular product was pure white and its chloride content—determined photometrically—was 0·015%, its loss in weight at 1000° being 30·93% [Calc. for $Mg(OH)_2$, 30·88%].

For Batch B, 10 l. of N-ammonia solution were added from aspirator Y to 10 l. of N-magnesium sulphate in X. The precipitate was washed as before, the last washings still giving a slight precipitate with barium chloride, and dried, also as before, to a more powdery product which, by analysis, contained 1·22% of sulphate ion. Its loss on ignition at 1000° was 31·83% [Calc. for $Mg(OH)_2$, if all the sulphate were lost as SO_3, 31·74%].

---

* Part V, preceding paper.

Procedure.—A " calcination series " was prepared from each batch by heating separate samples to each of a succession of fixed temperatures for 2 hr. : preliminary experiments on the open thermal balance (Gregg and Winsor, *Analyst*, 1945, **70**, 336) had shown that at 400° and 500° the rate of loss of weight became very small (though not zero) after 2 hr. The properties of the products were then examined as in Part V (*loc. cit.*), *viz.*, measurement of (1) sorption of oxygen and of nitrogen at 90·2° K and of nitrogen at 77·4° K; (2) sorption of carbon tetrachloride at 25° C; (3) the apparent density in carbon tetrachloride and in decalin; (4) the heat of immersion in carbon tetrachloride; (5) the loss on ignition (by raising to 980° on the thermal balance); (6) the sulphate content by gravimetric analysis, weighing as barium sulphate. The sorption isotherm of nitrogen at 77·4° K was also measured in some cases, by use of a low-temperature cryostat (cf. Tompkins and Young, *Trans. Faraday Soc.*, 1951, **47**, 77) with liquid oxygen, boiling under reduced pressure, as the refrigerant.

Results.—The isotherms of nitrogen, both at 90·2° K and 77·4° K, and of oxygen at 90·2° K were of Type II (B.E.T. classification) and the specific surface area *S* could be readily calculated from them by the usual B.E.T. procedure; the three values of *S* (cf. the table) corresponding to the three sets of isotherms agreed satisfactorily, usually within 10% or so and often better.

Temp. of calcination	Specific surface area *			Density, ρ †			Content of volatile matter, w (%)	θ ‡	Pore volume v (cm.^{3} g.$^{-1}$)
	S_1	S_2	S_3	1	2	3			
Batch *A*									
15°	56	—	—	2·38	—	—	30·93	—	0·385
300	47	—	—	2·36	—	—	—	—	—
340	106	110	—	2·42	2·88	2·55	25·14	—	—
350	—	—	—	2·58	3·32	3·02	11·49	—	—
365	162	165	—	2·72	2·72	2·83	16·30	—	—
400	169	179	—	3·33	—	3·45	2·32	0·64	0·865
500	171	115	—	3·40	3·30	3·53	1·64	0·71	0·865
600	94	95	—	3·43	3·37	3·56	0·51	0·28	0·863
700	74	71	—	3·48	3·37	3·56	0·28	0·20	0·840
900	30	31	—	3·44	3·48	3·57	0	—	0·646
1400	—	—	—	3·47	2·88	—	0	—	0·007
Batch *B*									
15	32	33	34	2·36	—	2·39	31·83	—	0·057
365	40	38	38	2·91	—	3·06	10·53	—	0·059
400	118	123	129	3·31	—	3·43	2·93	—	0·155
425	—	196	—	3·37	—	3·46	2·04	—	—
450	—	209	197	3·42	—	3·51	1·14	—	—
500	166	171	185	3·45	—	3·55	0·46	—	0·226
600	75	84	80	3·45	—	3·56	0·29	—	0·169
700	—	38	—	3·47	—	3·57	0·15	—	—
900	9·3	11	11	3·46	—	—	0	—	0·015

* S_1, S_2, S_3 = specific surface area (m.^{2} g.$^{-1}$) from sorption of oxygen at 90·2° K, of nitrogen at 90·2° K, and of oxygen at 77·4° K.

† 1, In CCl_4; 2, in decalin (cm.^{3} g.$^{-1}$); 3, calc. from w and true densities of MgO and of $Mg(OH)_2$ (cm.^{3} g.$^{-1}$).

‡ θ = fraction of surface covered with OH groups.

In Fig. 1 (*a*) the surface area (say S') has been calculated per gram of non-volatile material (MgO) from the values of S (say S_2) obtained with nitrogen at 90·2° K. The two quantities S_2 and S' are not in general identical because the content of volatile matter is usually appreciable; and the plot of S' against the temperature of calcination (Curves I and II) represents the change in the surface area of a given sample when heated for two hours at a given temperature if the effect of all previous heating could be ignored. Comparison with Curve III of Fig. 1 (*b*) which gives the percentage decomposition (calculated from the loss on ignition) as a function of temperature shows that with both batches there is a marked increase in area when water is expelled; but with the pure sample the increase is very marked whilst the decomposition is still far from complete, whereas with the sulphated sample there is much closer correspondence between the extent of decomposition and the increase in surface area. The relative increase in surface area from *B* to *C* is greater for the sulphated than for the pure material, being some five-fold as against some three-fold.

The values obtained for the percentage of sulphate for Batch *B* are : 15°, 1·76; 550°, 1·73; 600°, 1·54; 650°, 1·63; 900°, 1·35; the variation in sulphate content with temperature is thus relatively and surprisingly small. The data for loss on ignition are given in the Table and for Batch *A* require little comment, for they clearly represent the " water " content of the samples; for Batch *B*, the values quoted contain an unknown contribution from the portion of sulphate volatilised at 980° and at the higher temperatures are particularly uncertain.

As will be noted, the sulphate content varies comparatively slightly with temperature and at 900° is still approximately three-quarters of its original value. It is interesting that the sulphate content of the unheated material is just sufficient to form a completed monolayer on the surface of the micelles if it be assumed that each sulphate ion covers an area of 30 Å^2, *i.e.*, four times that of an oxygen ion : the total area occupied by 1·76% of sulphate would then be 33 m.^{2}, exactly the specific surface area of the unheated material.

The data for density are also recorded in the Table, where they are compared with the density calculated for a mixture of magnesium oxide and magnesium hydroxide (true density **3·576** and 2·39 respectively) in proportions given by the water content. The experimental value is, at all temperatures and for both batches, distinctly below that calculated; even with 5 hours' heating at 1400° the measured density in carbon tetrachloride is some 3% lower than

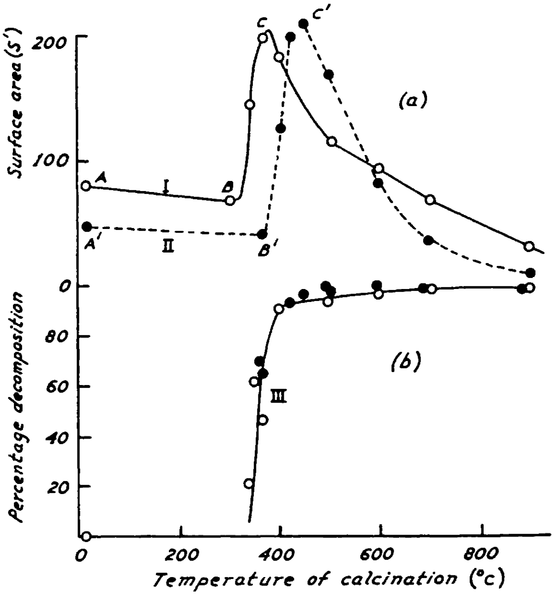


FIG. 1. *Calcination of magnesium hydroxide.*

(*a*) *Plot of* S', *the surface area in square metres per gram of non-volatile material, against the temperature of calcination ; I, Batch* A ; *II, Batch* B.

(*b*) *Plot of percentage decomposed against the temperature of calcination for both Batches* A *and* B. *Open circles, Batch* A ; *solid circles, Batch* B.

the accepted figure for true density (3·576), determined on magnesium oxide crystals formed from the melt (Durand, *Phys. Review*, 1936, **50**, 451). In decalin the 1400° sample showed a density which is unaccountably low.

The heat of immersion H_L in carbon tetrachloride when plotted against the temperature of calcination (Fig. 2) gives a curve very similar in shape, for both batches, to that for specific surface area (Fig. 1); and the sorption isotherms of carbon tetrachloride are probably all of Type IV (B.E.T. classification), though in one or two instances it is difficult to decide between Type II and Type IV, owing to paucity of data near saturation. The data both for the isotherms and for the heat of immersion will be discussed in detail elsewhere.

From the carbon tetrachloride isotherms on Batch *A* and the oxygen isotherms on Batch *B* an approximate value of the pore volume of each sample has been calculated (by dividing the total number of grams adsorbed at the saturated vapour pressure by the ordinary liquid density at the temperature of the experiment). The values obtained (Table) differ strikingly for the two series, being at all temperatures up to and including 900° far smaller for the sulphated than for the pure material.

DISCUSSION

The results clearly demonstrate the effect of an ionic impurity on the curve representing activity as a function of temperature (cf. Fig. 1, curves I and II, and Fig. 2).

As explained in Part I, curves of this kind may be interpreted in terms of two opposing effects : an *activation* due to the decrease in the size and an increase in the number of micelles consequent on a chemical decomposition, and a *sintering* of the product resulting in an increase in size and a decrease in the number of micelles. The sudden increase in the value of the area S' (BC and $B'C'$ of curves I and II, Fig. 1) corresponds to a sharp increase in the percentage decomposition m (curve III) but neither S' nor S is proportional to m, particularly with the pure batch. It is likely (cf. Part V) that the increase in the number of micelles is brought about by the recrystallisation—proceeding from nuclei—of the magnesium oxide from a pseudo-lattice of the hydroxide to the stable lattice, periclase; if there is an average of n nuclei per micelle of the " pseudo " oxide, the specific surface will increase n-fold.

From Fig. 1 it may be inferred that the presence of the sulphate ions affects the rate of recrystallisation rather than the rate of decomposition; for whereas the curves of percentage decomposition are very close to one another, the curve for specific surface area of the " sulphated " is considerably displaced from that for the " pure " batch, in the direction of higher temperature. This could be explained by the assumption that the rate of formation of nuclei follows a law of the form $dn/dt = Be^{-E/RT}$ and that both B and E are higher for the sulphated batch; for the higher E would mean that n and therefore the increase in S first become appreciable at higher temperatures for this batch, whilst the higher B would result in a proportionately higher maximum value for n and therefore for S. Data are too few and the system too complicated to permit B and E to be estimated quantitatively at present; nor is it possible to put forward a precise model for the effect of sulphate ions on these quantities, though one can see how the presence of such ions could distort the lattice in their neighbourhood in their own favour and so render more difficult the formation of nuclei of magnesium oxide.

FIG. 2. *Plot of the heat of immersion H_L in carbon tetrachloride against the temperature of calcination; I, Batch* A*; II, Batch* B.

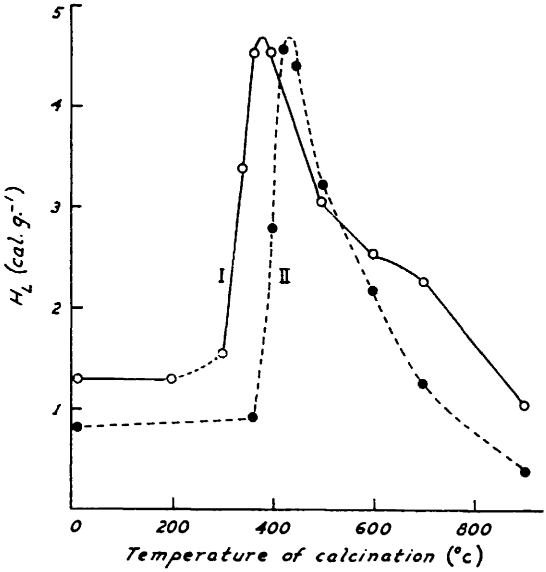
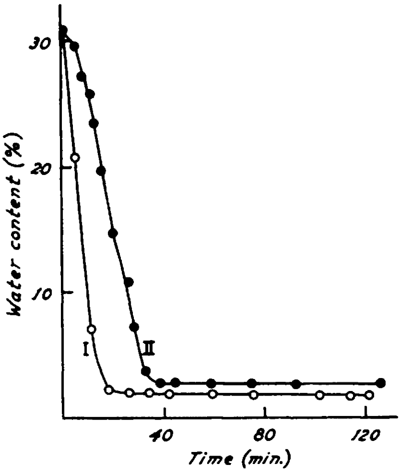


FIG. 3. *Isothermal decomposition of magnesium hydroxide* (*Batch* A) *on the thermal balance.*



Plot of water content against time: I, 500°; II, 400°.

From the fact that the curve for Batch B above 500° or so falls more sharply than that for Batch B, one infers that the presence of the sulphate ion promotes sintering; and a possible explanation suggests itself from a consideration of the pore volume (Table). That these are so low for the sulphated material is probably due to the fact that this material was produced, in essence, by flocculation of a sol by sulphate ions; this process would tend to produce a compact precipitate of low pore volume in which micelles are touching over relatively large areas, a condition which would tend to promote sintering. This picture is supported by the fact that the specific surface of the hydroxide of the sulphated batch before calcination was distinctly lower than that of the pure batch, where the flocculating effect would, of course, be less.

A second factor, which could operate alongside the first, is the surface diffusion of Mg^{2+} and SO_4^{2-} ions which would result in a filling-in of cracks and fissures (places of low adsorption potential to which mobile ions would tend to drift) and a consequent reduction in specific surface area. Such diffusion might perhaps be expected to become appreciable at temperatures near the Tammann temperature of bulk magnesium sulphate (*ca.* 430°), and could therefore be present over the whole of the " sintering " branch of curves I and II of Fig. 1 or of Fig. 2.

Attention should again be drawn to the extraordinary tenacity with which the last traces of " water " are held (cf. Gregg and Hill, *J.*, 1953, 3945; Gregg and Sing, *J. Phys. Coll. Chem.*, 1952, **56**, 1388; also Britton, Gregg, and Winsor, *J. Appl. Chem.*, 1952, **2**, 693, for traces of carbon dioxide in carbonates). It is difficult to believe that water, which is only released at temperatures of a hundred or more degrees above the decomposition temperature of the material, can represent bulk magnesium hydroxide which has eluded decomposition: the graphs of weight against time obtained on the thermal balance (Fig. 3) show that the " water " content falls sharply to a figure which varies only very slowly with time and points to a mode of combination distinct from the rest. It is reasonable to suppose that this " water " is present as hydroxyl groups on the surface, and assuming each " molecule of water " to cover 15 $Å^2$, values for the fraction θ of the surface covered with hydroxyl are readily calculated (Table). At 400° θ is not greatly below unity; it falls as the temperature rises, as expected, partly because of direct evaporation and partly because of sintering (cf. Part V), both of which processes would be accelerated by rise in temperature.

The fact that the experimental values for density are, in general, lower than those calculated, signifies the presence of lattice strain, or of an appreciable volume composed of holes too small to admit molecules of the immersing fluid, or of both factors together. That the second effect is relatively unimportant is indicated by the absence of appreciable drift in the density determinations, and of abnormally long times of equilibrium at low pressures in the carbon tetrachloride isotherms, both of which would be expected if holes were present of a size such that carbon tetrachloride molecules could enter only with difficulty.

Conclusion.—The formation of active magnesium oxide by the calcination of the hydroxide provides a clear example of the first type of behaviour described in Part I of this series in that the curve of specific surface against temperature of calcination shows a very definite maximum. The location of the maximum is affected appreciably, and the extent of sintering at any one temperature markedly, by the presence of sulphate ions in the original hydroxide precipitate.

Our thanks are offered to the London University Research Fund for the loan of a galvanometer, and to the Imperial Chemical Industries Research Fund for the loan of apparatus. One of us (R. K. P.) acknowledges receipt of a maintenance grant as a student-in-training from the Department of Scientific and Industrial Research.

UNIVERSITY COLLEGE, EXETER. [*Received, July* 21*st*, 1954.]