300. *The Production of Active Solids by Thermal Decomposition. Part VIII.* Calcination of Calcium Hydroxide.*

By D. R. Glasson.

The specific surface, *S*, of the product obtained by calcining calcium hydroxide (*a*) for a fixed time of 5 hours at different temperatures, (*b*) for various times at each of a number of fixed temperatures, has been measured by sorption of nitrogen (and occasionally of oxygen) at −183°. *X*-Ray powder photographs of certain calcined samples have been taken. At lower calcination temperatures, notably 350—500° *in vacuo*, the decomposition of the calcium hydroxide results in a several-fold increase in *S*; this is ascribed to the newly formed calcium oxide being activated when (according to the *X*-ray data) it recrystallises from a pseudo-lattice of calcium hydroxide to very small individual crystals having a more stable lattice structure. The specific surface ultimately decreases on further calcination because of sintering of the calcium oxide, which is enhanced by an increase in temperature. Recrystallisation of the calcium oxide is apparently inhibited by traces of chemisorbed carbon dioxide and water, particularly below 500° in air.

THERMAL decomposition of calcium hydroxide produces calcium oxide varying considerably in surface activity according to the temperature and time of calcination: the decomposition thus proves suitable for demonstrating changes in physical structure postulated in Part I[1] for the products of reactions of type: Solid A ⟶ Solid B + Gas. The specific surface areas and volatile-matter contents of the calcined samples were determined, and *X*-ray powder photographs of certain samples were taken. The results show that the calcium

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* Part VII, *J.*, 1955, 3804.

[1] Gregg, *J.*, 1953, 3940.

oxide, *i.e.*, solid B, is activated after its production from the calcium hydroxide, *i.e.*, solid A, probably through recrystallisation of a pseudo-lattice; the activated oxide sinters on further calcination.

EXPERIMENTAL

Materials.—The starting material was a batch of calcium hydroxide obtained from British Drug Houses, and contained small amounts of adsorbed water (1·10—1·13%) measurable by complete removal *in vacuo* below 200°. An additional weight loss of 24·43% occurred on calcination in air at 1000° on a thermal balance [2] corresponding to a composition of 99·5% of $Ca(OH)_2$ and 0·5% of $CaCO_3$ for the dried material. Its specific surface area was 4·9 and 5·2 $m.^2 g.^{-1}$, as measured by sorption of nitrogen and of oxygen respectively. Details of the nitrogen and oxygen used are given in Part II.[3]

Procedure.—Separate portions of the calcium hydroxide were calcined for 5 hr. at a succession of fixed temperatures either *in vacuo* on an electrical sorption balance [4] (at 350°, 450°, and 500°) or in air in an electrical furnace (at 450°, 500°, 600°, 700°, 800°, 900°, and 1000°). Further portions were calcined for varying periods *in vacuo* (at 200°, 250°, 300°, 350°, 400°, 450°, and 500°) and in air (at 450°).

To determine the specific surface, *S*, of the cooled samples, the sorption isotherms of nitrogen and of oxygen, both at $-183°$ and up to a maximum pressure of 1 atm., were first determined gravimetrically by using the electrical sorption balance; [4] the lower part of the limb of the balance was surrounded by a liquid-oxygen bath, the temperature of which (read by an oxygen vapour-pressure thermometer) remained constant within $\pm 0{\cdot}2°$; at least 1 hr. was allowed for the sample to attain this temperature. The oxygen isotherms, which extended to a relative pressure, p/p_0, near unity, were of type II (B.E.T. classifications [5]) with no hysteresis at $p/p_0 < 0{\cdot}3$; from these and the nitrogen isotherms, *S* could be calculated by the B.E.T. procedure [6] by use of values of 14·1 Å² and 17·0 Å² for the cross-sectional areas Am of oxygen and of nitrogen; this gave agreement within *ca.* 5% in the values of *S* obtained from both series of isotherms.

RESULTS and DISCUSSION

In Fig. 1*a* the specific surface, *S*, is plotted against the time of calcination for each of four temperatures of the "vacuum" experiments alongside the corresponding curves (Fig. 1*b*) for the percentage decomposition against time; *S* increases as the percentage decomposition increases, reaching a maximum when the decomposition is approximately complete (cf. *A* and *A'*, *B* and *B'*, *C* and *C'*, *D* and *D'*); thereafter it slowly decreases with increasing time of calcination. The system thus provides a further example of the first type of active solid described in Part I,[1] and the increase in surface area therefore constitutes an activation ascribed to an increase in the number of micro-regions * in the decomposition product as compared with the initial substance; and the decrease in area to a sintering of the product.

The maximum (*A*, *B*, *C*, *D*) moves progressively to the left and downward as the calcination temperature is raised, the first movement denoting that the rate of decomposition (and therefore of activation) increases with rise in temperature, and the second that the product is more extensively sintered; however, the *rate* of sintering, as measured by the slopes of the "sintering branches" of the specific surface–time graphs, does not greatly increase with rise in temperature.

In Fig. 2*a* the specific surface, *S*, and in Fig. 2*b* the percentage decomposition, is plotted against the temperature for samples calcined for fixed times; *S* always shows a maximum (*A*, *B*, *C*) located at about the temperature where decomposition is just complete in the given time (*A'*, *B'*, *C'*). In accord with Part I,[1] the surface area at first increases with rise in temperature, since increasing proportions of calcium hydroxide are decomposed in a

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* Crystallites having perfect or slightly imperfect lattices (cf. Part I, p. 3940).

[2] Gregg and Winsor, *Analyst*, 1945, **70**, 336.
[3] Gregg and Hill, *J.*, 1953, 3945.
[4] Gregg, *J.*, 1946, 561.
[5] Brunauer, Deming, Deming, and Teller, *J. Amer. Chem. Soc.*, 1940, **62**, 1723.
[6] Brunauer, Emmett, and Teller, *ibid.*, 1938, **60**, 309.

given time, but it decreases on further rise in temperature when the calcium oxide sinters more rapidly and for longer periods.

The plot of specific surface, S, against the percentage decomposition, m, in Fig. 3*a* reveals the interesting fact that, whilst S is approximately proportional to m for about the first 80% of the decomposition, yet S increases much more rapidly than m for the last 20%. The converse might have been expected in that the calcium oxide first formed has apparently had progressively longer in which to sinter, and a curve concave to the m axis would not be surprising. A similar anomaly was found during the decomposition of magnesium hydroxide [7] and may be similarly explained: the calcium oxide when first formed has a pseudo-lattice of calcium hydroxide, and recrystallises, but only at a limited rate, to true calcium oxide which subsequently sinters. Since the recrystallisation increases S, the time lag in the recrystallisation explains the fact that the production of new surface lags behind the decomposition.

FIG. 1. *Calcium hydroxide samples calcined* in vacuo *at various temperatures.*

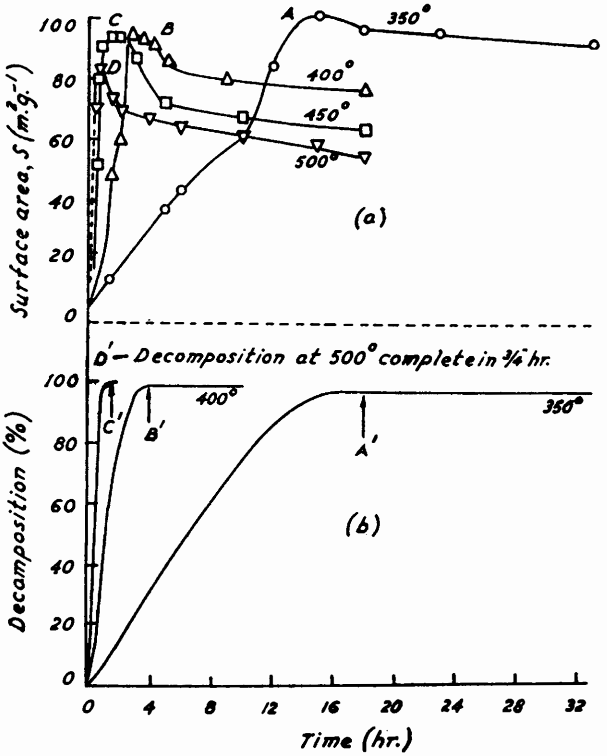
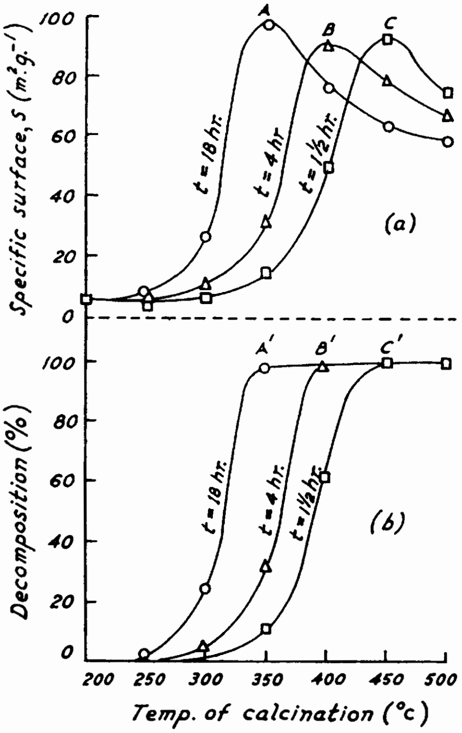


FIG. 2. *Samples calcined for periods t* in vacuo *at temperatures between* 200° *and* 500°



The state of affairs is strikingly illustrated in Fig. 3*b*, which plots the specific surface, S', of the calcium oxide itself (S' has been calculated from S by subtracting the area of the calcium hydroxide, assumed to be proportional to the weight present). During the decomposition of the last 20% of the calcium hydroxide, S' increases, corresponding to the expected recrystallisation of the pseudo-lattice.

This explanation is supported by X-ray data: a sample calcined *in vacuo* at 450° for ½ hr. and having the composition (calculated from the percentage decomposition) $Ca(OH)_2$ 40%; CaO, 60%, nevertheless showed the powder pattern corresponding to almost 100% $Ca(OH)_2$. (The X-radiograms of completely decomposed samples showed for various

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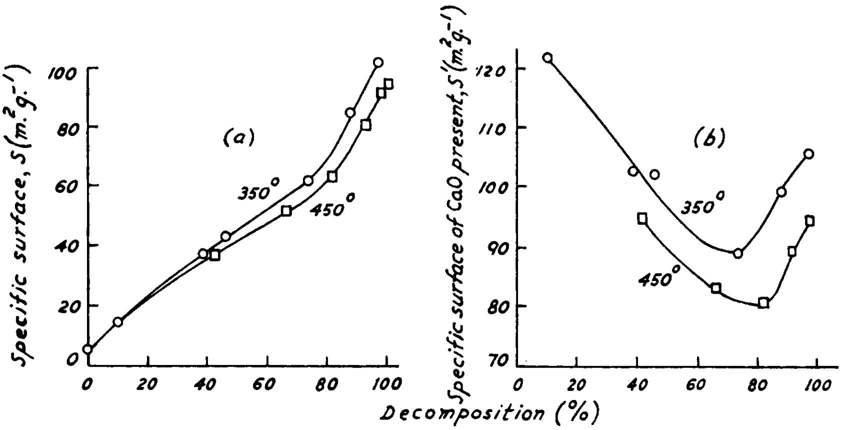
[7] Gregg, Packer, and Wheatley, *J.*, 1955, 46.

temperatures the weak and broadened lines to be expected for very small crystallites in random orientation, and thus qualitatively supported the specific-surface data.)

In Fig. 4, the specific surface, S, is plotted against the temperature for samples calcined for 5 hr. in air; S continuously decreases with increasing calcination temperature, so that as in the " vacuum " experiments, sintering of the calcium oxide is enhanced by increase in temperature. In calcinations between 550° and 900°, nearly all the calcium oxide is produced within the first few minutes, yet decomposition is not quite complete even after 5 hr., the volatile-matter contents of the samples generally showing temperature variations similar to those of S in Fig. 4. This suggests that, as for magnesium oxide, the rate of sintering is controlled by the removal of traces of water and carbon dioxide chemisorbed on the surface of the micro-regions; indications of a break in the specific surface curve at 700° are probably caused by the rate of sintering being mainly dependent on removal of water below this temperature and of carbon dioxide above (cf. Fig. 4), a larger energy of activation for the latter process causing greater proportionate decreases in S between 700° and 900°. The higher volatile-matter contents (w) of the samples calcined at 450° and 500° (Table 1) partly arise from carbonation of small amounts of the calcium oxide during calcination (since the dissociation pressure of calcium carbonate is less than the partial pressure of atmospheric carbon dioxide); these samples have remarkably *lower* specific surface areas than those calcined *in vacuo* for 5 hr., although over 97% of the calcium hydroxide is decomposed in all cases (Table 1). Similar differences in S are also shown

FIG. 3. *Samples heated* in vacuo *at* 350° *and* 450°.



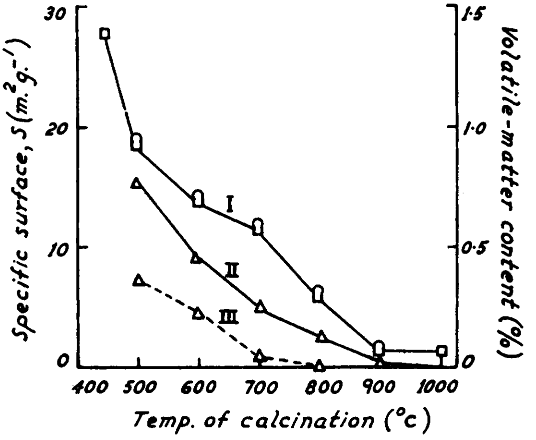


FIG. 4. *Calcination of calcium hydroxide heated for* 5 *hr. in air.*

I, Specific surface calc. from :

□ N_2 isotherms, ○ O_2 isotherms.

II, Total volatile-matter content.

III, Water content.

when the decomposition is far from complete, *e.g.*, at 40% decomposition in air and *in vacuo* at 450°, S = 14·1 and 35·5 m.^{2} g.$^{-1}$, respectively.

The last results appear contrary to expectation in that the calcium oxide is produced more slowly in air than *in vacuo* at the same temperature and subsequently has shorter time in which to sinter. During the decomposition in air, however, the water-vapour concentration gradients along the capillary passages in the product will probably be smaller, giving lower rates of nucleation in the recrystallisation of the calcium oxide pseudo-lattice, and thus smaller increases in the number of calcium oxide micro-regions and in S than in the " vacuum " experiments; the greater average micro-region size of the calcium oxide is indicated by the absence of line-broadening in the X-radiograms of the sample decomposed in air at 450°. Nucleation may also be inhibited in air by the surface layer of chemisorbed carbonate and of water (probably present as hydroxyl groups on the surface rather than as bulk calcium hydroxide). *In vacuo*, atmospheric carbon dioxide is excluded and the water vapour evolved is rapidly removed so that recombination with the newly formed calcium oxide is minimised. The last traces of water are, however, still held with considerable tenacity (Table 2). But the proportion of solid surfaces covered by this residual water, θ, is small and can have little effect on the rate of nucleation.

TABLE 1.

	S (m.^{2} g.$^{-1}$) for samples calcined in :		w (%) for samples calcined in :			
			air		vacuum	
Temp. of calcination	air	vacuum	H_2O (%)	CO_2 (%)	H_2O (%)	CO_2 (%)
450°	28·0	72·2	0·92	3·35	0·05	0·29
500	18·6	65·0	0·36	0·41	0	0·29

TABLE 2.

Temp. of calcination	350°	400°	450°	500°
Water content (%)	0·66	0·24	0·05	0
S * (m.^{2} g.$^{-1}$)	96·8	90·9	93·3	82·7
θ †	0·34	0·13	0·03	0

* Measured when the rate of decomposition first became inappreciable (<0·01% in 5 hr.).

† One molecule of residual water assumed to occupy the same area as 2 OH groups, *i.e.*, 15 Å^2.

Conclusion.—The calcination of lime is an example of the type of behaviour described in Part I,[1] in which the curves of specific surface against temperature of calcination for fixed times show maxima at or near the temperature for which decomposition is just complete. At temperatures below 500°, particularly *in vacuo*, the newly formed calcium oxide becomes activated by recrystallisation from a pseudo-lattice of calcium hydroxide to very small individual crystals having a more stable lattice. Calcination continued after complete decomposition always causes sintering, the extent of which is enhanced by increase in temperature at least up to 1000°; the sintering is concurrent with removal of chemisorbed water and carbon dioxide from the surfaces of the micro-regions, probably as they adhere.

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