808. *The Production of Active Solids by Thermal Decomposition. Part III.* The Calcination of Kaolinite.*

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Samples of kaolinite have been calcined for a fixed time at a succession of fixed temperatures between 50° and 1400°, and the specific surface S measured by the sorption of nitrogen and of oxygen. The value of S varies but little over the range 0—800°; in particular, S does not increase appreciably when the structural water is lost in the region of 400—500°, though the " holes " corresponding to the lost water are large enough to admit hydrogen ions, as shown by the greatly increased rate of dissolution of the 500° sample in acid. The fall in apparent density shows that the structure shrinks to a considerable extent when the water is lost, and the X-ray data show it to be highly disordered. Above 900° the apparent density and the bulk density sharply increase, and the specific area decreases, corresponding to the sintering and the conversion into mullite of the product. From 50° to 800° slight but definite sintering occurs.

WHEN kaolinite is heated to *ca.* 450° in air it loses nearly 14% of water and might, therefore, be expected to show a considerable increase in specific surface. The detailed study reported here shows, however, that the surface area of the product—usually termed metakaolinite—is little different from that of the undecomposed solid, though the gaps in the structure corresponding to the lost water are not completely closed up and indeed are large enough to admit hydrogen ions, as indicated by an enhanced rate of dissolution in acid.

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* Part II, preceding paper.

The general method adopted was to calcine separate samples for a fixed period and then determine, for the cooled product, adsorption isotherms of oxygen and of nitrogen at low temperatures (to yield the specific surface), the apparent density in carbon tetrachloride, the bulk density in vacuum, and X-ray powder photographs; also the rate of dissolution in acid (three samples only). In addition two dehydration experiments were done with the original material: one sample was subjected to a steadily rising temperature *in vacuo* on the sorption balance, and the curve of loss of weight against time thus obtained; and a second sample was heated to constant weight at a succession of fixed temperatures.

EXPERIMENTAL

Materials.—The kaolinite was kindly provided by the Research Laboratories of English Clays, Lovering, Pochin Ltd., and was described as "finest commercial grade." It was estimated to be 95% pure, the chief impurity being mica, with small quantities of quartz, tourmaline, and montmorillonite. Analysis of the Andreasen curve obtained by gravity sedimentation showed it to be all <5 μ, *ca.* 80% <1 μ, 40% $<0{\cdot}5$ μ, and all $>0{\cdot}05$ μ, in equivalent Stokes's diameter.

The details of the oxygen, nitrogen, and carbon tetrachloride have been given in Part II.

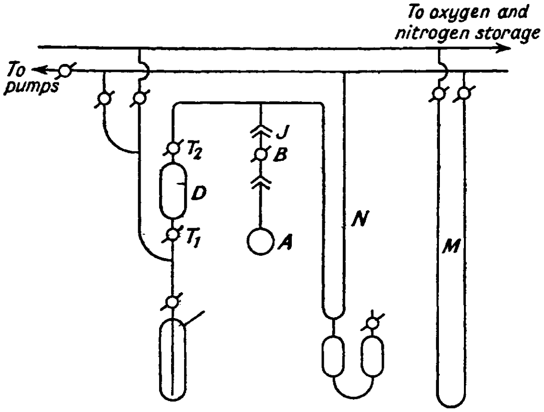

FIG. 1. *Apparatus for measurement of the sorption of nitrogen and of oxygen at* −183°.

Methods.—The determination of the adsorption isotherm on a non-porous solid like kaolinite constitutes a somewhat more difficult problem than with porous solids such as ferric oxide gel, in that the total adsorption is relatively small, and if a volumetric apparatus is used it must have a small "dead-space." The apparatus used was a modification of that described by Tompkins and Young (*Trans. Faraday Soc.*, 1951, **47**, 77) and is illustrated in Fig. 1. The sample was contained in the bulb A which was attached to the main apparatus by means of an adaptor B, and which after being outgassed was detached at J to determine the loss of weight. After being replaced in position, A was immersed in liquid oxygen to a definite mark, and a charge of gas was admitted to the doser D, and its pressure measured on the wide-tube manometer M by means of a cathetometer. The doser was then isolated by closing tap T_1, and the connecting tubes were pumped out. The charge of gas was next admitted to the bulb A by opening T_1 and raising the mercury to the tap T_2; and when the pressure had become constant it was read accurately on the manometer N, the mercury on the left-hand side being adjusted accurately to a mark C so as to define the dead-space volume. Further charges of gas were admitted until the equilibrium pressure had reached approximately 76 cm. The manometer N and the remainder of the "equilibrium" portion of the apparatus were constucted of narrow tubing (3-mm. bore). The volume of the doser and of the bulb was determined by weight of mercury, and the remainder of the apparatus was calibrated for volume with helium. The whole apparatus was contained in a constant-temperature room ($\pm 0{\cdot}25°$). The amount adsorbed, x moles, was then calculated by the formula:

$$x = \frac{(\Sigma P_D) V_D}{\mathbf{R} T_R} - \frac{p}{\mathbf{R}}\left[\frac{V}{T_R} + \frac{V_0}{T_0}\right]$$

Here $\Sigma\ P_D$ is the sum of successive doser pressures in mm.; V_D, V, V_0, are respectively the volumes (cm.^{3}) of doser, dead space, and bulb immersed in liquid oxygen; p is the equilibrium pressure (mm.); ***R*** the gas constant, and T_R and T_0 the temperature (°K) of the room and of liquid oxygen, respectively. The specific surface was calculated from the adsorption isotherm by application of the B.E.T. method, and the measurements of density in carbon tetrachloride were carried out, both as described in Part II (*loc. cit.*). The bulk density in vacuum was determined by the method of Gregg and Behrens (*J. Appl. Chem.*, 1951, **1**, S 139—141).

The *X*-ray powder photographs were kindly taken by Mr. E. K. Cundy of the laboratories of English Clays, Lovering, Pochin Ltd.

The rate of dissolution in acid, determined conductometrically, was studied at 93° because at room temperature it is inconveniently slow even with the most active sample; the cell was fitted with a stirrer and a reflux condenser (to avoid loss by evaporation). It contained 200 ml. of N-hydrochloric acid, and when this had come to constant temperature a sample of the clay (*ca.* 4 g.) was introduced and readings of the resistance were taken until it became nearly constant (usually 12—24 hr.).

In the dehydration experiments, two types of treatment were adopted, *viz.*, " isothermal " and " rising temperature." The latter was *in vacuo* on the electrical sorption balance (Gregg, *J.*, 1946, 561), the sample being subjected to a nearly constant rate of rise of temperature of approx. 3°/min. over the range 100—950°, the temperature being controlled by hand adjustment of a " Variac " variable transformer. For the former, two sets of experiments were done, (*a*) " in air " on the thermal balance, and (*b*) *in vacuo* on the electrical sorption balance. Separate samples were taken for both (*a*) and (*b*), and were heated to a succession of fixed temperatures until further loss in weight was negligible; in air this required 3 hr. or less at temperatures below 450° and above 600°, and 6—7 hr. at temperatures between 450° and 600°; *in vacuo* constancy was reached in 2—3 hr. at all temperatures.

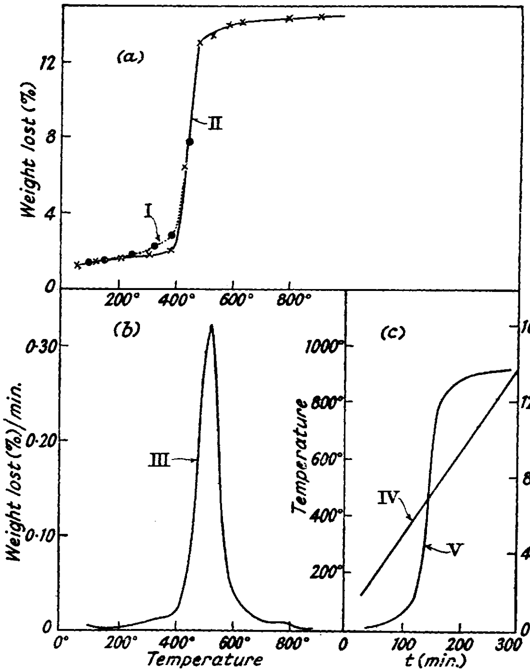

FIG. 2. *Loss of weight of kaolinite on heating.*

(*a*) *Heating to constant weight at each temperature*: *I, in vacuum*; *II, in air*; (*b*) *III, percentage weight lost per min., based on data of* (*c*); (*c*) *heating with steadily rising temperature*; *plot against time, of IV, temperature, and V, percentage weight lost.*

The calcination of the samples was carried out *in situ* for temperatures up to 400°, a small tubular furnace being placed around bulb *A*, or the density bulb, or the bulk density cylinder, as the case might be: the sample was heated at the required temperature for 5 hr. under a vacuum of 10^{-4} mm. For higher temperatures the calcination was in air, either on the thermal balance (500—1000°) or in a platinum-wound furnace (above 1000°), again for 5 hr. All samples were outgassed at 100° before being subjected to the relevant technique.

Results.—The isothermal dehydration data are plotted in Fig. 2*a*, where the continuous line refers to the results " in air " and the broken line to those *in vacuo*. The former agree substantially with the results of other workers (cf. Grim and Rowland, *Amer. Min.*, 1942, **27**, 746, 801), and the deviation between the two curves of Fig. 2*a* in the region 300—400° is in the sense expected, *i.e.*, the loss of weight commences at a lower temperature *in vacuo*.

The " rising-temperature " dehydration curve is shown in Fig. 2*c*, and a derived curve of percentage loss in weight per min. against temperature in Fig. 2*b*. The latter is analogous to the curves of differential thermal analysis, and it shows a marked peak with its maximum at *ca*. 510°, and corresponding to the loss of " structural " water. This loss is already noticeable at 350°, a temperature again definitely lower than that noted in the experiments " in air." It is interesting that a small but definite loss continued up to a temperature of 750° or more, in agreement with the finding by Brindley *et al.* (*Min. Mag.*, 1952, **29**, 963) that nacrite (a mineral similar to kaolinite) retained traces of water up to *ca*. 800° in air. The small loss below 200° is of course due to adsorbed water.

The curves for surface area plotted in Fig. 3 show that little if any increase in specific surface accompanies the loss of water. Curve V has been calculated from the nitrogen, and Curve VI from the oxygen, isotherms; the two agree satisfactorily with each other and also with the curves (not shown) based on " preliminary " sets of isotherms of nitrogen and of oxygen.

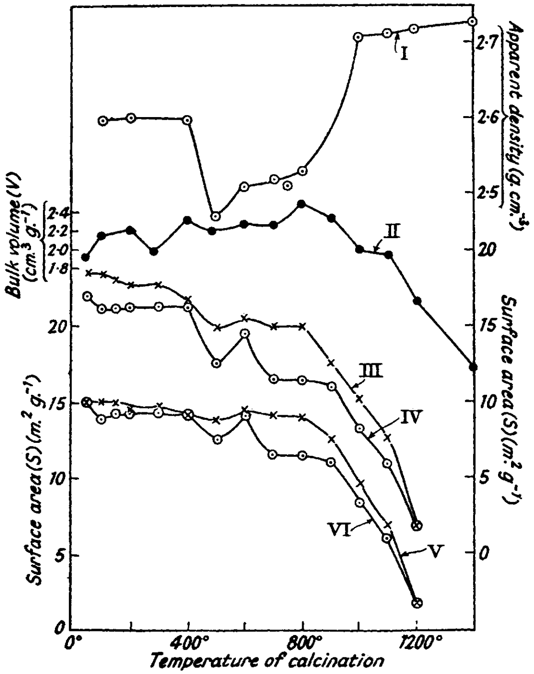

FIG. 3. *Various properties of calcined kaolinite plotted against temperature of calcination.*

I, Apparent density. II, Bulk volume. III, IV, Surface area by nitrogen and by oxygen sorption, per g. of non-volatile material. V, VI, Surface area by nitrogen and by oxygen sorption, per g. of calcined sample.

To obtain a more intimate picture of the effect of heat on the surface area one may plot the surface, say S', per g. of non-volatile material present in the product. This is readily calculated as $S' = S\ (1 - w/100)$, where w is the percentage of water lost when the sample was prepared by calcination. The curve of S' against temperature of calcination then represents the way in which one and the same sample of kaolinite, originally *ca*. 1·16 g., would change in area when heated for 5 hr. at each temperature, if the effect of all previous heating could be ignored. As will be seen, S' from both nitrogen (III) and oxygen (IV) sorption drops as the temperature rises from 50° to 800°, with a suggestion of a slight rise at 600° in the nitrogen curve, and a rather more pronounced drop and subsequent rise in the region 400—600° in the oxygen curve.

The *X*-ray photographs have been interpreted by Mr. Cundy as follows: 200°, 400°, kaolinite; 500°, 600°, 750°, 800°, lines due to mica impurity only, no kaolinite lines left; 900°, faint lines of γ-alumina also; 1100°, γ-alumina plus some mullite; 1200°, 1400°, mullite.

The results for apparent density in carbon tetrachloride are plotted in Fig. 3; in Curve I the fall of some 4% between 400° and 500°, corresponding to the loss of water, will be noted, as will the steady rise up to 900°; and the gentle rise thereafter corresponds to the gradual formation of mullite.

Owing to lack of time, the study of the rate of dissolution in hydrochloric acid at 93° had to be restricted to three samples, *viz.*, the original material, and samples which had been heated at 500° and 1000°. Neither the original nor the 1000° sample dissolved appreciably even after 26 hr. in the hot acid, whereas the 500° sample dissolved extensively; calculation from the final conductivity of the solution showed that some 37% of the solid had gone into solution.

Finally, the data for bulk volume V ($= 1$/bulk density) are plotted in Fig. 3, Curve II.

Of main interest is the fact that V changes only very slightly for the wide range 50—900°, and then decreases sharply from 900° to 1400°, *i.e.*, in the range where mullitisation is taking place.

DISCUSSION

From the viewpoint of the present series, the most significant feature of the results is the absence of an appreciable increase in specific surface when the kaolinite loses its structural water, in contrast to the rise of several-fold encountered with solids such as magnesium hydroxide or aluminium hydroxide. As might be expected from the fact that hydroxyl ions are involved, the lattice becomes greatly disturbed in the process, and the product at 500—800° is *not* a mere pseudo-lattice of kaolinite (cf. Part I, *J.*, 1953, 3940). The values for apparent density ρ support this conclusion, for if a perfect pseudo-lattice were formed when dehydroxylation occurs, ρ would fall by the same percentage as the weight (since the volume would be unchanged), *i.e.*, by 13·6%; the actual fall is only *ca.* 4%, indicating that the structure is much more compact than the pseudo-lattice would be. The small but definite fall in ρ signifies the presence of holes that are too small to admit carbon tetrachloride molecules; and since there is no rise in the specific surface the holes must also be too small to admit nitrogen or oxygen molecules. Since they were formed by the elimination of H atoms and OH groups, however, it might be expected that the holes they leave behind would be large enough to admit hydrogen ions. This inference is supported by the very considerable solubility of the 500° sample in acid.

The rapid fall in area from 800° or 900° onwards corresponds to the crystallisation of the solid to give first some γ-alumina and then increasing amounts of mullite; it is interesting that this sintering should first occur when the temperature is in the region of the Tammann temperatures of alumina and of silica (*ca.* 960° and 760°, respectively), and also when the last traces of water appear to have been driven off (cf. Part I, *loc. cit.*).

The fact that the sintering occurring below 800° is so slight at first seems anomalous, for according to the mechanisms outlined in Part I considerable sintering would be expected at temperatures below the Tammann temperature, because of adhesion and surface diffusion. The reason for the smallness of the effect lies in the coarseness of the starting material—it was all coarser than 500 Å, and 40% was coarser than 5000 Å—which would not only militate against adhesion (cf. Andreasen *et al.*, *Kolloid-Z.*, 1939, **86**, 70; Gregg, " Surface Chemistry of Solids," Chapman and Hall, London, 1951, p. 56) but would restrict the scope of surface diffusion, inasmuch as the areas of good fit of neighbouring grains would be small. Above the Tammann temperature, where lattice diffusion of ions can occur, both crystallisation within a grain and movement of matter across grain boundaries (leading to grain growth) would be possible.

The data for bulk volume V fit satisfactorily into the general picture : between 50° and 100° V rises because the adsorbed water, which had reduced adhesion, is driven off and the grains adhere together more firmly so that the mass acquires an elementary " structure " with an enhancement in volume (cf. Gregg and Behrens, *J. Appl. Chem.*, 1951, **1**, S 139). From 100° to 900° V shows little alteration (the fall at 300°, which has been confirmed by duplicate measurement, is unexplained) because neither the size nor the true density of the grains changes very much; but from 900° onwards V falls rapidly because the grains are becoming much larger and the proportion of intergranular space is correspondingly diminishing, from *ca.* 83% of the total volume at 700° to *ca.* 54% at 1400°.

Conclusion.—Kaolinite does not significantly increase or decrease in specific surface when it loses a volatile product by thermal decomposition. Expressed in the terms of Part I (*loc. cit.*), this is because the solid remaining (meta-kaolinite) is relatively stable and shows no marked tendency to break up into crystallites of a more stable form. Such stability is compatible with our knowledge of the structure of kaolinite (cf. Brindley and

Robinson, *Min. Mag.*, 1946, **27**, 242) : the conversion of each pair of hydroxyl ions into a single oxygen ion could leave the remainder of the aluminosilicate sheet still intact, though greatly distorted; the tetrahedral co-ordination of the oxygen around the silicon ions need not be greatly affected, the aluminium ions suffering a change from an octahedral (4OH plus 2O) to a tetrahedral (4O) disposition; the latter would, as Tscheidschwili has pointed out (*Ber. deut. keram. Ges.*, 1939, **20**, 249) be stabilised by the neighbouring SiO_4 network.

Our cordial thanks are offered to Mr. C. K. Cundy for kindly undertaking the *X*-ray examination of the samples, to Dr. N. O. Clark and Mr. T. W. Parker for valuable discussions, and to the Agricultural Research Council for a grant.

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