

The Preparation of Active Solids by Thermal Decomposition. Part VII.
The Calcination of (a) Ion-free and (b) Sulphate-contaminated, Pre-
cipitated Alumina Hydrates.*

By S. J. GREGG and K. H. WHEATLEY.

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The effect of sulphate ions on the activation and sintering of precipitated hydrated alumina is somewhat similar to that already reported for precipitated magnesium hydroxide (Part VI*). The influence appears to be indirect rather than direct, in that the part played by the flocculating ions during precipitation and washing of the starting material determines the texture of the solid and thus the behaviour of the solid on heating.

Two batches of alumina hydrate have been prepared, the first by hydrolysis of aluminium ethoxide so as to be virtually free from ionic impurity, and the second by precipitation from aluminium sulphate solution so that it would be contaminated with sulphate ions. A sample of each was first subjected to thermogravimetric analysis, and separate samples from each batch were then heated for 5 hours each at a fixed temperature, and a number of properties of the cooled product (specific surface, density, and lattice structure) were determined. The distinct difference found between the two series of products emphasises the important part played by ionic impurity in determining the properties of "active" oxides.

EXPERIMENTAL

Materials.—The first batch of alumina hydrate (Batch I) was prepared by the hydrolysis of aluminium ethoxide which had been obtained as a greyish powder by refluxing 27 parts of aluminium filings, 0.20 part of mercuric chloride, and several crystals of iodine with 276 parts of absolute alcohol; the excess of alcohol was removed by distillation on an oil-bath, and the residue rapidly distilled *in vacuo* through an air condenser, the pure ethoxide distilling over. A 3% solution of the ethoxide in alcohol was hydrolysed by dropping it into a large quantity of carbon dioxide-free water. The precipitate of hydrated alumina which was formed was washed by decantation, filtered off, and then "dried" by exposure to the atmosphere.

The second batch (Batch II) was prepared by precipitating aluminium sulphate solution with ammonia solution. The precipitation was carried out in three glass tanks each of about 15 l. capacity, and each contained 5 l. of water to which 2 l. of N-aluminium sulphate had been added; 2.5 l. of N-ammonia solution were then run into each with constant stirring, and after

* Part VI, *J.*, 1955, 51.

the precipitate had settled the supernatant liquid was siphoned off. The sludge was then washed several times with large quantities of distilled water, filtered at the pump, and "dried" as before by exposure to the atmosphere.

Procedure.—To throw light on the chemical composition of the two starting materials, they were both subjected to thermogravimetric analysis: each was placed in a crucible on a thermal balance and the temperature of the furnace was raised at the uniform rate of 3°/min., frequent readings of the weight being taken till the temperature reached 600° or so (cf. Gregg and Stephens, *J.*, 1953, 3951). For expulsion of the remainder of the volatile material in order to find the weight of the anhydrous sample, it would be necessary to raise the temperature to 1250°, but this was unattainable with the furnace. Accordingly, the temperature was raised only to 980° and was kept there till no further change in weight occurred. The correction corresponding to the further loss in weight which would have occurred on raising the temperature from 980° to 1250° was then determined in a further experiment in which a separate sample was calcined at 980° till no further loss in weight occurred, and was then heated for a further 6 hr. in a high-temperature furnace at 1250° and reweighed.

For preparation of the calcination series, separate samples (about 9 g.) from each batch were then heated for 5 hr. in a furnace each at a different fixed temperature T° lying between 200° and 1100°. The following properties of the cooled product were then determined: (a) sorption of nitrogen at -183° to find the specific surface (Gregg and Stephens, *loc. cit.*); (b) the density in carbon tetrachloride (*J. Phys. Chem.*, 1952, 56, 388); (c) the X-radiogram (kindly determined by Drs. H. Lipson and C. A. Taylor). The content of volatile matter had to be obtained indirectly: a separate sample was calcined as above, and the weight of the anhydrous material was determined exactly as in the thermogravimetric experiment.

RESULTS AND DISCUSSION

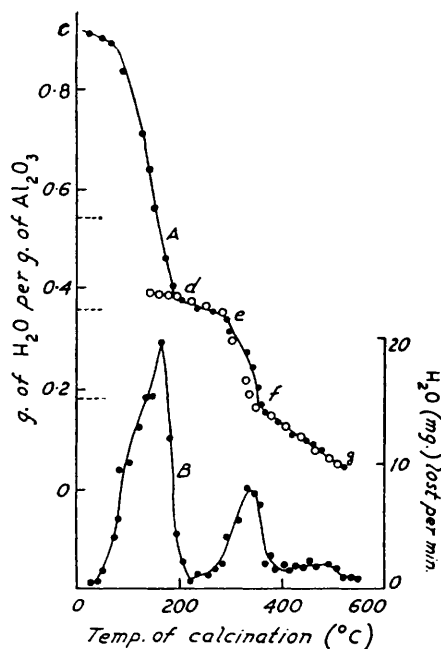
We deal first with the results of the thermogravimetric analysis. Those for Batch II are the simpler and are given in Fig. 2 both as a plot of water content w against temperature (Curve *A*) and as the derived curve $\Delta w/\Delta t$ against temperature, t being time (Curve *B*). The loss below 300° is most probably due to adsorbed water (which could persist at furnace temperatures much above 100° owing to the finite rate of loss of water). At point *c*, when the temperature is ca. 300° and the composition is $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, the rate of loss greatly increases and the weight falls continuously till the composition is close to $\text{Al}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ (point *d*); and, although this could represent a mixture in equal proportions of Al_2O_3 and $\text{AlO} \cdot \text{OH}$, the alternative possibility that the "water" is chemisorbed on a bulk material which is anhydrous, cannot be ruled out; for the water content, though so large, is still only of the order required to cover the surface of the micelles with chemisorbed OH groups. [Though the specific surface of the material at *d* was not determined directly, the specific surface of a material of corresponding composition in the calcination series (*viz.*, that at 300°, cf. Fig. 3) was about 400 $\text{m}^2/\text{g}.$; and one molecule of water being assumed to cover 15 \AA^2 of surface, the "water" content corresponding to $\text{Al}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ would cover 450 $\text{m}^2/\text{g}.$ of solid.]

Whatever the composition at *d*, however, it is clear that the original material had the composition $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and this is confirmed by the X-ray analysis which shows the presence of bayerite ($\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) only.

The results for Batch I are more complicated. As will be seen from Fig. 1, the initial water content is in excess of that required for the trihydrate, and there is no break in the curve at the composition $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. On the other hand, there is a distinct break in the region of $\text{Al}_2\text{O}_3 \cdot 2.2\text{H}_2\text{O}$ (*d*), the rate of loss of water becoming markedly slower until the composition is close to $\text{Al}_2\text{O}_3 \cdot 2.0\text{H}_2\text{O}$ (*e*). It is interesting and satisfactory that the curve *defg* was closely reproduced with a second sample.

The loss over the range *cd* would seem to represent adsorbed water; for a sample when outgassed for several hours at 25° (a procedure which should remove adsorbed water only) showed a loss in weight corresponding closely to *cd*; and when it was then subjected to thermogravimetric analysis it closely followed the curve obtained with the non-outgassed material (Fig. 1, circles). The fact that the composition at *e* is so close to $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ might seem to imply that the starting material at *c* consisted of a dihydrate along with adsorbed water; this, however, is not only unlikely on general grounds, but the alternative,

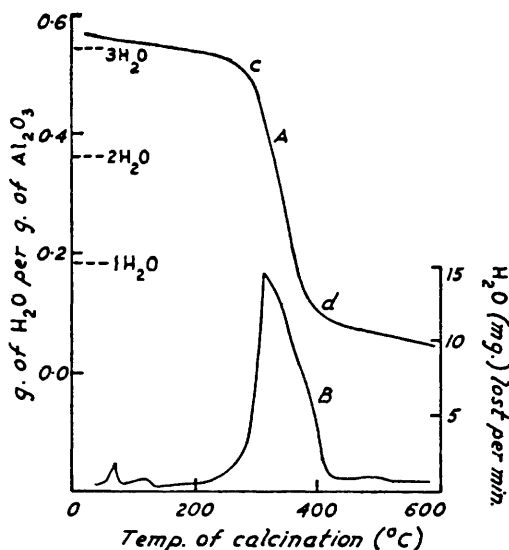
FIG. 1. Thermogravimetric analysis of Batch I of alumina hydrate (ion-free, from aluminium ethoxide), for a rate of rise of temperature of 3° per minute.



Curve A, The water content is plotted against temperature of calcination.

Curve B, The rate of loss of water is plotted against temperature of calcination.

FIG. 2. Thermogravimetric analysis of Batch II of alumina hydrate (ion-contaminated, from aluminium sulphate) for a rate of rise of temperature of 3° per minute.



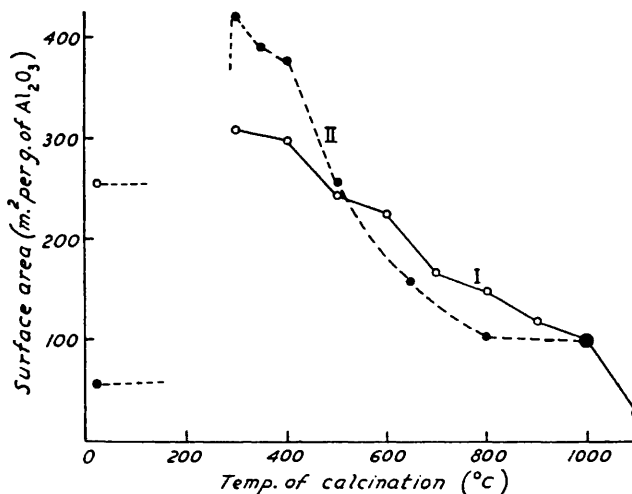
Curve A, The water content is plotted against temperature of calcination.

Curve B, The rate of loss of water is plotted against temperature of calcination.

FIG. 3. Surface area (expressed per g. of Al_2O_3) of the product obtained by calcining alumina hydrate for 5 hours at temperature T° , plotted against T° .

Curve I, for Batch I (ion-free).

Curve II, for Batch II (ion-contaminated).



and more plausible, view that it comprises an equimolecular mixture of the tri- and the monohydrate is supported by the X-ray data on the starting material, which showed lines corresponding to bayerite ($\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and boehmite ($\gamma\text{-AlO}\cdot\text{OH}$) only.

For each batch the curve of specific surface against temperature of calcination (Fig. 3) shows the characteristic increase in specific surface consequent on thermal decomposition followed by a decrease due to sintering (cf. Part I, *J.*, 1953, 3940). There is the marked difference between the two batches, however, inasmuch as with Batch I the surface (calc. per g. of Al_2O_3) increases relatively slightly when the water is driven off, whereas with Batch II the increase is at least seven-fold; also the fall due to sintering is considerably sharper both absolutely and relatively for Batch II till 800° is reached. The presence of a (quite small) percentage of sulphate ions (see Table) thus exercises a marked effect on the rate of sintering. This percentage is far too small to form a complete monolayer on the surface, and indeed is only enough to cover a little more than 1% of it; it would seem unlikely therefore that the ions are able to exert a *direct* influence on sintering, *e.g.*, by acting as a film which becomes mobile at elevated temperatures and so acts as a cement. More probably the ions dictate the structure of the starting material through their presence when it is being precipitated and washed. The starting material of Batch II is essentially a flocculated sol; the individual sol particles must have been built up from Al^{+++} and OH^- ions, giving a hydrated oxide, the lattice of which is no doubt very imperfect. The individual sol particles would be temporarily stabilised by an excess of Al^{+++} ions with SO_4^{--} and OH^- as counter-ions, and would then, as sufficient SO_4^{--} ions arrived by diffusion into the

*Certain properties of the products from calcining hydrated alumina for 5 hours at temperature T° .**

T°	S	Δw	ρ	SO_4	X-Ray pattern	T°	S	Δw	ρ	SO_4	X-Ray pattern
		Batch I	(ion-free)				Batch II	(ion-contaminated)			
15	—	91.1	—	—	ca. 50% ba, 50% bo	25	36	56.2	2.43	0.32	mostly ba
25	181	40.3 †	2.58	—	—	200	46	—	2.46	—	—
300	269	15.3	2.98	—	70% bo, 30% γ -type	300	386	9.26	3.15	—	η
400	281	6.9	3.18	—	γ or η	350	359	9.2	3.27	0.32	—
500	235	3.5	3.37	—	γ	400	353	6.0	3.28	—	γ
600	220	1.9	3.41	—	γ	500	246	3.7	3.41	—	γ -type
700	164	1.4	3.48	—	γ	650	154	1.5	3.49	0.32	γ
800	146	1.2	3.52	—	γ	800	103	0.8	3.58	0.24	γ -type; δ ?
900	117	0.8	3.51	—	γ -type; θ ?	1000	99	0.4	3.55	0.19	γ -type; θ
1000	98	0.6	3.54	—	γ -type; θ ?	1300	—	—	3.98	—	—
1100	27	—	3.56	—	α						

Cf. Corundum 3.98—4.01

* S = specific surface per g. of solid, measured by N_2 -sorption.
 ρ = apparent density in carbon tetrachloride.
 Δw = loss in weight at 1250° (g. per 100 g. of Al_2O_3).
 SO_4 = sulphate content (g. per 100 g. of Al_2O_3).
 ba = bayerite, $\alpha\text{-Al}(\text{OH})_3$; bo = boehmite, $\gamma\text{-AlO}\cdot\text{OH}$.
 $\alpha, \gamma, \delta, \eta, \theta$ are $\alpha\text{-Al}_2\text{O}_3, \gamma\text{-Al}_2\text{O}_3$, etc.
 † On prolonged evacuation.

electrical double layer, undergo flocculation. A compact precipitate would thus result, each grain of which would consist of an aggregate of the original sol particles, each of which in turn would carry its layer of SO_4^{--} ions; thus the grains of precipitate would have SO_4^{--} ions included within them and not merely located on the outer surface. By contrast, the starting material of Batch I, being formed by hydrolysis of the ethoxide, was precipitated in the virtual absence of ions; one pictures a polymerisation of molecular units of $\text{Al}(\text{OH})(\text{OEt})_2$, $\text{Al}(\text{OH})_2(\text{OEt})$, and $\text{Al}(\text{OH})_3$, probably occurring through hydrogen bonds, producing a solid with so low a degree of order as to be almost amorphous, and occluding a considerable amount of water. The X-ray examination (cf. Table), however, showed the solid to be an approximately equimolecular mixture of bayerite and boehmite; and this probably represents a secondary stage resulting from the recrystallisation at room temperature of the amorphous mass into a mixture of micelles of the two products with the elimination of much water and an increase in density. The consequent considerable

shrinkage of the solid would ensure that the component micelles would be in relatively loose contact, the bridges between neighbours being relatively few and weak; the specific surface would thus be large.

With both batches the thermal decomposition gives a product of increased density, and the resultant shrinkage would tend to weaken intermicellar contacts and to reduce their number; nevertheless, the higher degree of compactness of the starting material of Batch II should still persist in the product of calcination also, and so should give a greater tendency to sintering, as is actually found.

The process of crystallisation postulated for Batch I represents an activation of the first of the types discussed in Part I (*loc. cit.*), but occurring at room temperature. The unusually high magnitude of its specific surface shows that the micellar size of the starting material is small, a conclusion confirmed by the considerable degree of line-broadening in the X-ray photographs. This helps to explain why the specific surface of this batch increases relatively so little on decomposition: the micelles are so small that there would be a very small probability of a second nucleus in a given micelle being able to grow appreciably before the first nucleus had expanded to include the whole of the micelle.

A number of lattice changes of a minor nature occur when hydrated aluminas are heated over the range 400–900° or so (cf. Day and Hill, *J. Phys. Chem.*, 1953, **57**, 846). The general tendency of these (the occurrence of which in the present Series is supported by the X-ray evidence) would be, as already suggested in Part I, to produce further new surfaces and so to counteract sintering. This could happen by slight changes in density which would introduce strains in joints as yet rather weak and of small cross-section, and also because of imperfect alignment of lattices of contiguous micelles near joints; the latter effect would be intensified where one of the micelles had undergone rearrangement and its neighbour had not.

It will be noted that with Batch II the sintering becomes slower between 600° and 800°, and between 800° and 1000° the fall in specific surface almost ceases. The reason is not clear, but it is interesting and perhaps significant that the sulphate content of this batch first shows a decrease at 800° (Table); and since, as already argued, the SO_4^{--} ions are located on the *surface* of the original sol particles but *within* the grains of the precipitate itself, it may be inferred that these ions first become mobile at this temperature and so can move to the exterior of the grains of the precipitate and there volatilise. Such migration would disturb the junctions, already imperfect, between the sol particles, and so could lead to an increase in surface sufficient to counterbalance the reduction elsewhere due to the normal sintering process. It is unfortunate that no measurement of specific surface for Batch I was made for samples above 1000°, for it would be interesting to know whether an increase in sintering again appears corresponding to that found with Batch I.

The sudden fall in area between 1000° and 1100° with Batch II is associated with the fact that the Tammann temperature (*Z. anorg. Chem.*, 1928, **176**, 46) of aluminium oxide lies near 1000°, so that one would expect an acceleration in the rate of sintering to commence at this temperature. It seems that this acceleration can more than compensate for the increase in area that might be expected (cf. Part I) to result from the conversion of γ - into α -alumina which occurs between these two temperatures (Table).

We are grateful to Drs. H. Lipson and C. A. Taylor, of Manchester College of Technology, for kindly undertaking the X-ray examination of the starting material and the calcined specimens. One of us (K. W.) acknowledges receipt of a Further Education and Training Grant from the Ministry of Education.