

## 65. *Alumina Catalysts for Vapour-phase Organic Dehydrations, Deaminations, etc.*

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The publications dealing with the properties of  $\gamma$ -alumina and with the use of alumina catalysts for certain vapour-phase reactions are reviewed. These lead to the conclusions that  $\gamma$ -alumina is the catalytically active species, that purer specimens are more active catalysts, and that active catalysts can be prepared from precipitates that are initially granular: it is not necessary to precipitate gels. Experiments are described that confirm these conclusions: the activities of the catalysts being measured by the rate of dehydration of ethanol to ethylene, under such conditions that the finite rates of diffusion of the reagents in the vapour phase do not seriously affect the rate of the reaction. The effect of crystal size has not been thoroughly studied, but in general, methods of preparation that would be expected to give small crystals give the most active catalysts. The time required to dehydrate boehmite to  $\gamma$ -alumina varies enormously from sample to sample, and care must be used in catalyst testing to ensure that the dehydration is complete: methods for doing this and the difficulties that arise are discussed.

CATALYSTS made from natural or artificial hydrated aluminas are widely used in the temperature range between about 200° and 400° for organic reactions in the vapour phase that involve amino- and hydroxyl radicals (Sabatier and Reid, "Catalysis in Organic Chemistry", London, 1923, pp. 690—818). At higher temperatures they are also used for reactions between hydrocarbons, but these processes are not considered here. The reactions considered include hydrations and dehydrations [alcohols to ethers and olefins; ammonium formate to hydrogen cyanide (Johnson, B.P. 220,771)]; deaminations [aniline to diphenylamine (Hill and Hill, B.P. 473,739)]; hydrolyses of arylamines to phenols (Cross, B.P. 584,241); ammonolyses of alcohols to amines, alkylations of primary and secondary to secondary and tertiary amines and many others (Sabatier and Reid, *op. cit.*).

The object of the work described here was to discover which form of alumina was catalytically active and how it should be prepared. Information from the literature indicates that the active species is  $\gamma$ -alumina, and this conclusion is supported by experimental work.

*Properties of  $\gamma$ -Alumina.*—The name " $\gamma$ -alumina" is applied to the isometric form of anhydrous alumina,  $Al_2O_3$  (Chatt, *Chem. and Ind.*, 1946, 65, 78). The only known way of preparing this substance is by dehydration of the orthorhombic ( $\gamma$ ) form of the monohydrate,  $AlO(OH)$ , which is known as boehmite (Biltz and Lemke, *Z. anorg. Chem.*, 1930, 186, 373; Fricke, *Kolloid Z.*, 1934, 69, 312; Klever, *Trans. Ceram. Soc.*, 1930, 29, 149; Rooksby, *ibid.*, 1929, 28, 399; Weiser and Milligan, *J. Physical Chem.*, 1934, 38, 1175). This change is reversible (Bentley and Feachem, *J. Soc. Chem. Ind.*, 1945, 64, 148). Boehmite is prepared by the dehydration of either of the trihydrates bayerite or gibbsite (Fricke; Rooksby; Weiser and Milligan; *loc. cit.*), and also by precipitation of alumina from solution under certain conditions (Biltz, Lehrer, and Meisel, *Z. anorg. Chem.*, 1928, 172, 292; Boehm, *ibid.*, 1925, 149, 203; Magarschek, *Leg. Met.*, 1938, No. 2, p. 12; *Chem. Abs.*, 1939, 33, 2403; Milligan and Weiser, *J. Physical Chem.*, 1936, 40, 1095; Rooksby, *loc. cit.*; Weiser and Milligan, *Chem. Rev.*, 1939, 25, 1; Weiser, Milligan, and Purcell, *Ind. Eng. Chem.*, 1940, 32, 1487; Weiser, Milligan, and Purcell, *ibid.*, 1941, 33, 669). The conversion of gibbsite into boehmite is reversible, and freshly precipitated boehmite is hydrated on contact with water, becoming first bayerite and then gibbsite (Biltz, Lehrer, and Meisel; Fricke; Weiser and Milligan, 1939; *loc. cit.*).  $\gamma$ -Alumina can be converted (presumably through boehmite) into gibbsite (Bentley and Feachem, *loc. cit.*).

$\gamma$ -Alumina is not formed from the orthorhombic monohydrate diaspore, which changes into the hexagonal  $\alpha$ -alumina (corundum) on heating (Fricke, *loc. cit.*; Laubengayer and Weisz, *J. Amer. Chem. Soc.*, 1943, 65, 247): this change is reversible (Laubengayer and Weisz, *loc. cit.*).  $\gamma$ -Alumina also changes into corundum on prolonged heating at high temperatures: this change has not, as far as we know, been reversed experimentally.

$\gamma$ -Alumina is most conveniently recognised by X-ray diffraction, and the spacings and intensities of the lines on the powder photograph have been published by many workers and will be found in the A.S.T.M. card index. All the identifications quoted below were obtained in this way, and there is no other established method. If  $\gamma$ -alumina were obtained in large crystals, it could be distinguished from boehmite because the latter would lose water on heating. In practice, however,  $\gamma$ -alumina is always obtained in very small crystals, which adsorb water vapour very strongly. Some adsorptions have been measured on typical specimens of  $\gamma$ -alumina, and these show that this water cannot be driven off by heating in conditions in which boehmite is not decomposed. Below about 200°, boehmite decomposes only very slowly (Bentley and

Feachem, *loc. cit.*), and it is suggested that water adsorbed on  $\gamma$ -alumina might be displaced by a hydrocarbon in an apparatus such as that described by Dean and Stark (*Ind. Eng. Chem.*, 1920, **12**, 486) : preliminary experiments showed that some water could be recovered in this way, but the authors were able to obtain X-ray powder spectrograms of all their specimens, and this was sufficient, so that investigation was not pursued.

The conversion of boehmite into  $\gamma$ -alumina proceeds reasonably fast at about 400° and it has been observed at temperatures down to 256°, where it was very slow (Bentley and Feachem, *loc. cit.*). Results quoted below show that the rate depends on the previous history of the alumina, and that some specimens of boehmite are only dehydrated very slowly, even at 450°. Any short-period test of catalytic activity is therefore of doubtful validity unless the state of the catalyst is certainly known. The conversion of  $\gamma$ -alumina into corundum usually occurs at about 1200°, but it has been observed down to 800° at atmospheric pressure (Biltz and Lemke, *loc. cit.*; Klever, *loc. cit.*; Parravano and Onorato, *Atti R. Accad. Lincei*, 1929, **10**, 475; *Chem. Abs.*, 1930, **24**, 4681; Rooksby, *loc. cit.*) and at 415° in the presence of a high pressure of steam (Laubengayer and Weisz, *loc. cit.*). The lowest temperature at which this change will occur is not known, but at normal pressures it appears to occur so slowly below about 600° that it is not likely to affect the type of work discussed here.

*Alumina Catalysts.*—Most of the aluminas described in the literature as dehydration catalysts were made by washing and drying precipitated alumina. The dried solid was then very often heated between about 300° and 500°; *i.e.*, it is likely to have been brought into the  $\gamma$ -condition (Alekseevskii, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 221,817; *Chem. Abs.*, 1930, **24**, 4442; 1931, **25**, 1138; Alekseevskii and Belotzerkovskii, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 370, 382; *Chem. Abs.*, 1936, **30**, 5481; Alexander, Horn, and Munro, *Canadian J. Res.*, 1937, **15B**, 438; *Chem. Abs.*, 1938, **32**, 910; Fricke, Niermann, and Feichtner, *Ber.*, 1937, **70**, 2318; Griessbach and Eisele, U.S.P. 1,775,640; Guichard, *Compt. rend.*, 1934, **193**, 573; Johnson, B.P. 220,771; Mackert, D.R.-P. 486,597, 1926; Patrick, U.S.P. 1,682,241). Other experimenters prepared hydrated forms of alumina, but tested them above about 250° or 300°, so that they were probably converted into  $\gamma$ -alumina during the tests (Alvarado, *J. Amer. Chem. Soc.*, 1928, **50**, 790; Boehringer, D.R.-P. 569,842; *Chem. Abs.*, 1933, **27**, 3788; Burda, *Coke and Chem. U.S.S.R.*, 1932; No. 12, p. 50; *Chem. Abs.*, 1934, **28**, 2321; Spinoglio, *Atti Accad. Padova*, 1935, **51**, 25, *Chem. Abs.*, 1937, **31**, 7733). Taking all these published results together, it seems clear that the species that is catalytically active for dehydrations and related reactions is  $\gamma$ -alumina, and that therefore to obtain an active catalyst it should only be necessary to prepare  $\gamma$ -alumina with a large specific surface. The only method available for this preparation is the dehydration of boehmite, which may be either precipitated directly or obtained by dehydration of either of the trihydrates. The observations of Senderens (*Ann. Chim. Phys.*, 1912, **25**, 449) and of Clark, Graham, and Winter (*J. Amer. Chem. Soc.*, 1925, **47**, 2748) suggest in addition that purification of the alumina will increase its catalytic activity.

There is no reason to suppose that there is any advantage in controlling the conditions of precipitation to produce boehmite directly : the boehmite can equally well be obtained by dehydration of either of the trihydrates. Precipitates of boehmite are usually gelatinous, and so might be expected to have large specific surfaces, but the work of Kearby and Swann (*Ind. Eng. Chem.*, 1940, **32**, 1607) and observations made in this laboratory (Bentley and Feachem, *loc. cit.*) show that the gelatinous form is not necessary : active catalysts can be obtained from granular precipitates. The experiments now to be reported provide further evidence that  $\gamma$ -alumina is the active species and that its activity increases with its purity. They also show that specimens that are likely (from their methods of preparation) to have larger specific surfaces are more active : this point is not conclusively proved, because the exact estimation of crystal sizes (and so of surface areas) from X-ray diffraction patterns is too laborious.

Certain precautions are necessary in the dehydration and testing of alumina catalysts. It was observed in preliminary trials that the activity of a catalyst sometimes rises during the first few days of its life, and then settles down to a steady value. There may be several reasons for this : the slow completion of the dehydration to  $\gamma$ -alumina, a change to some other crystalline form by combination with one of the reagents used in the test, or the release of strongly held adsorbed water and the adsorption of other substances. A fall in activity, which would be expected to result from crystal growth or from the formation of corundum, has not been observed in a working catalyst below about 600°. It follows from this that any test lasting for only a few hours may not be reliable, so tests should if possible be continued for long enough to show that the activity is steady.

In addition to this precaution, it is also desirable to complete the dehydration to  $\gamma$ -alumina

before beginning the test, otherwise it will occur during the test and (as the results quoted below show) it may take several days.

If the particular alumina that is being used dehydrates reasonably rapidly at the temperature of the test, then there is no point in dehydrating it at a higher temperature, and so incurring a risk of reducing the active surface by crystal growth. Otherwise the optimum temperature must be found empirically: temperatures of 500° have been used (Fricke, Niermann, and Feichtner, *loc. cit.*; Griessbach and Eisele, U.S.P. 1,775,640; Guichard, *loc. cit.*), and one particular specimen of  $\gamma$ -alumina has been heated to 1000° for an hour without any detectable formation of corundum (Chirnside and Dauncy, B.P. 563,636): this observation has been repeated in this laboratory. It is shown below that the temperature of activation can affect the behaviour of the catalyst, but the effect is small and is not likely to be of much practical importance.

#### EXPERIMENTAL.

(A) *Apparatus and Method for Catalyst Testing.*—The catalyst activities quoted below were measured with samples of catalyst occupying about 200 c.c. To ensure constant temperature, the catalyst space was surrounded by mercury vapour condensing at atmospheric pressure. The apparatus was arranged to run continuously, day and night, for a week or more with each sample, to ensure that the condition of the catalyst was constant. The reaction was the dehydration of ethanol to ether and ethylene, and under the conditions used, ethylene was the principal product.

The reactant mixture was a solution of ethanol in water, containing 93% of ethanol by weight. This was stored in a reservoir under constant head, and allowed to drip through a fine jet into a short tube of about 4 mm. bore, which was connected by a U-seal of about 2 mm. bore to the evaporating coil. The jet was protected from air-borne solid particles by a sintered-glass filter, and this arrangement made it possible to control the rate of feed down to 20 c.c. per hour. The evaporating coil led into the vapour jacket in which the catalyst tube was situated, so that the reactant solution was slowly warmed and evaporated, and the vapour superheated to approximately the temperature of the catalyst. After passing over the catalyst, the vapour was cooled, first by tap water to about 12°, when most of the water and unreacted ethanol condensed, and then by solid carbon dioxide, when the ether condensed.

The specific gravity of the first condensate was measured, and its difference from unity was regarded as being due to unchanged ethanol. There was never sufficient ether present to form a separate layer and the effect of a little ether on the specific gravity of a dilute ethanol solution is about the same as the effect of an equivalent quantity of ethanol (I.C.T., 1928, 3, 126). The second condensate was measured and regarded as ether: a guard trap, also cooled by solid carbon dioxide, collected no condensate.

These methods for estimating ether and unchanged ethanol were only approximate: it was not practicable to make accurate analyses, because of the large numbers of tests involved. The errors due to ether in the first condensate and ethanol in the second would tend to compensate each other, and the method would be expected to arrange a series of results in the right order. The results can therefore properly be used to support qualitative conclusions.

The results are expressed either as the pass conversion of the ethanol (the fraction converted into ethylene and ether) or as the pass yield of ethylene (the fraction of the ethanol converted into ethylene), and either of these, usually the latter, is plotted against the feed space velocity (the volume of solution fed to unit volume of the catalyst vessel per hour). The graphs naturally slope down from left to right as the conversion decreases with increasing space velocity, but the curves do not all belong to one family. Some of them cross each other, indicating that the kinetics of the process are different with different catalysts. There is thus no single quantity that can be used to express the activity of a catalyst, and this is best shown as a graph.

Most of the catalysts were tested either as granules passing through a 5/16" mesh and retained on a 3/16" mesh or as right circular cylindrical pellets of 3/16" length and diameter. An approximate calculation was made of the order of magnitude of the differences between the concentrations of the reagents at the solid surface and those in the bulk of the gas phase. For this purpose, the diffusivities were estimated by the method of Gilliland (*Ind. Eng. Chem.*, 1934, 26, 516). For particles of these small sizes, and for the rates of reaction actually observed, the differences are negligible, so the observed rates can be taken as measures of the activities of the catalysts.

(B) *Time Required for Dehydration of  $\gamma$ -Alumina.*—The following three experiments illustrate the different behaviours of specimens of boehmite of different origins.

(1) *Boehmite from precipitated bayerite.* An alkaline solution of sodium aluminate (65½ kg. of Na<sub>2</sub>O, 45 kg. of Al<sub>2</sub>O<sub>3</sub>, 213½ kg. of water) was added slowly to a stirred solution of 152 kg. of sodium hydrogen carbonate in 1850 kg. of water. The precipitate was washed 41 times with distilled water between 19° and 25°, the ratio of the volume of settled slurry after decantation to the volume after the addition of wash water being 0.7. The slurry was then filtered off, and the cake was dried at 110° and broken into granules, which were sufficiently strong to withstand ordinary laboratory handling. X-Ray examination showed that the solid was mainly bayerite, the unstable form of Al(OH)<sub>3</sub>, containing a little boehmite.

Several specimens of this batch were sieved through 5/16" on to 3/16" sieves and heated in air in an electric muffle furnace at 350° for various times: one specimen (denoted by an asterisk in the table) was heated at 460°. The specimens heated at 350° were X-rayed, and the phases identified are tabulated below. Some of the specimens were tested for catalytic activity: these are indicated in the table and the activities are shown in Fig. 1. The catalytic activity of the alumina was greatest after it had been heated at 350° for just long enough to convert it all into  $\gamma$ -alumina: further heating caused a small but significant reduction of activity. Heating at 400° gave a catalyst of comparable activity, for which the relation between conversion and space velocity was different from that of any of the catalysts heated at 350°.

Activity tested.	Duration of heating, hrs.	X-Ray diagnosis.
—	0	Bayerite and a little boehmite
×	1	Boehmite and a trace of $\gamma$ -alumina
—	2	$\gamma$ -Alumina and a little boehmite
×	3 $\frac{1}{2}$	} $\gamma$ -Alumina and a trace of boehmite
—	4	
—	5	
×	6	
—	9	
×	12	} Only $\gamma$ -alumina
×	24	
×	69 *	Not X-rayed

FIG. 1.

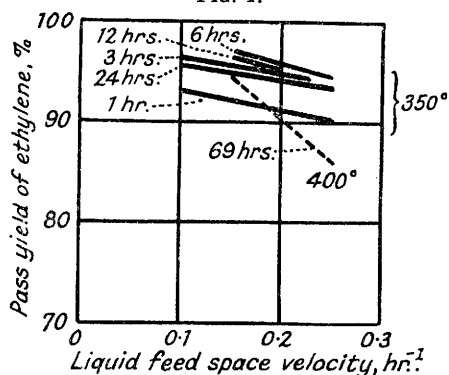


FIG. 2.

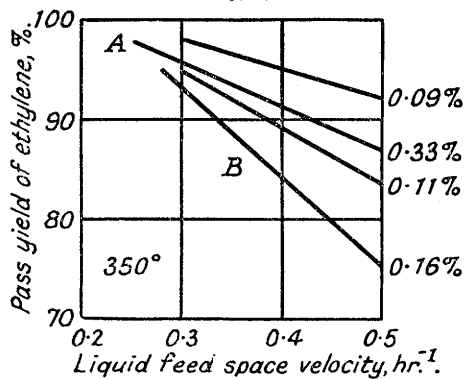


FIG. 3.

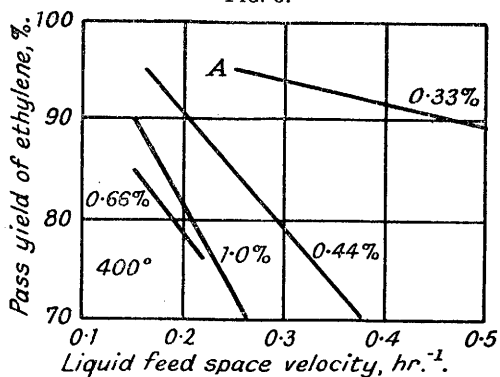


FIG. 4.

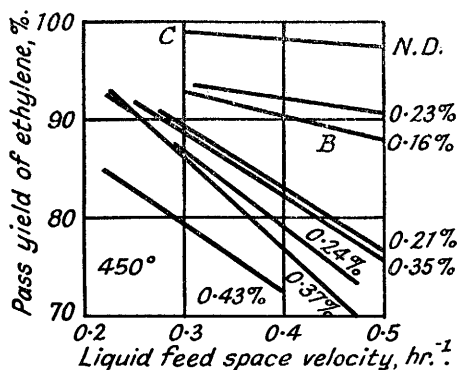
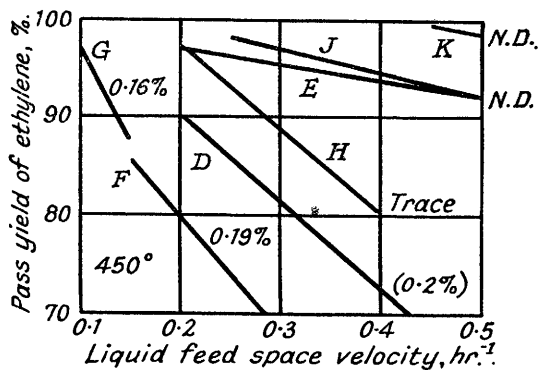


FIG. 5.



The figures against the lines in Figs. 2—5 are the sodium contents of the catalysts, expressed as  $\text{Na}_2\text{O}$ . Figures in parenthesis are typical of the materials concerned; the remaining figures were determined by analysis ("N.D." means not detected). The temperatures are those at which the catalysts were dehydrated.

(2) *Boehmite from (purchased) precipitated gibbsite.* Four specimens were taken from two different batches of "Aluminium Hydroxide", purchased from the British Aluminium Co. Ltd. This material is a crystalline powder of gibbsite, the stable form of  $\text{Al}(\text{OH})_3$ , believed to have been made by slow precipitation in the Bayer process, and therefore likely to be composed of relatively large crystals. These specimens were heated in the electric muffle for various times at various temperatures with the following results :

<i>First batch.</i>	<i>Second batch.</i>
420°, 12 hrs. : boehmite still present.	400°, 18 hrs. : boehmite still present.
440°, 6 hrs. : boehmite not detected.	450°, 12 hrs. : " " "
490°, 3 hrs. : trace of boehmite.*	" 18 & 24 hrs. : trace of boehmite.*
" 6 hrs. : boehmite not detected.	500°, 1½ hrs. : " " " *
550°, 1 hr. : " " "	

\* These samples showed the last disappearing traces of the strongest line of the boehmite pattern.

(3) *Boehmite grown under pressure.* Another specimen of this gibbsite was heated in water under pressure at 200° for 60 hours : it was converted into boehmite that was remarkably stable to heat, as follows :

- 5 days at 360° : only boehmite detected.
- 8 days at 360° : only boehmite detected.
- 5 days at 450° (in addition to the 8 days at 360°) :  $\gamma$ -alumina and a small amount of boehmite.

These three sets of results illustrate the very different behaviours on heating of specimens of boehmite of different origins, and also the differences that can occur between batches made apparently by the same method. The ultimate crystal sizes of the boehmite used were not estimated, but qualitatively (from the methods of preparation) the crystal sizes would be expected to be in the same order as the observed times required for dehydration. The activities of catalysts made from gibbsite treated as described in paragraphs (2) and (3) are mentioned in the following section.

(C) *Effect of Purity on Catalytic Activity.*—Bentley and Feachem (*loc. cit.*) recently described a method for preparing an active alumina catalyst from purchased gibbsite by repeated alternate washing (which is accompanied by hydration to boehmite) and dehydration. The increase in activity was attributed to two causes, *viz.*, increasing purity, due to the washing, and decreasing crystal size, due to the repeated changes of phase. In the experiment now to be described the latter cause was absent : several specimens of alumina were precipitated from sodium aluminate and bicarbonate, generally as described in section B(1), but with various concentrations of the reagents, and washed with various degrees of thoroughness. The resulting catalysts were analysed for sodium by the method of Haslam and Beeley (*Analyst*, 1941, 66, 185). An examination of test results on duplicate samples showed that differences of 0.06% (of the sample) were probably significant, and this figure is taken as the limit of accuracy of the method. The sodium ( $\text{Na}_2\text{O}$ ) contents ranged from 1% down to below the above limit, and these are used as an approximate criterion of purity. The specimens were dehydrated at 350°, 400°, and 450° and tested, and their activities are shown in Figs. 2, 3, and 4. The letters *A* and *B* at the left-hand ends of four of the lines identify the same specimens dehydrated at different temperatures : the numbers at the right-hand ends are the sodium contents determined by analysis. In general the purer catalysts are the more active. There is little crossing of the lines for catalysts dehydrated at any one temperature, but if the three graphs are superimposed many of the lines cross each other, again illustrating the change in kinetics caused by a change in the temperature of dehydration.

The line *C* on Fig. 4 shows the activity of a catalyst made by precipitation with ammonia from a solution of aluminium chloride and nitrate. The purest possible reagents were used, and the amounts of sodium and other impurities present in the catalyst were below the limits detectable by analysis.

It is interesting to compare these activities with those of some industrially useful catalysts shown in Fig. 5. Line *D* shows the activity of a catalyst made by dehydrating a commercially available "Activated Alumina" at 450°. The particular batch was not analysed, but a typical value of the sodium content is 0.2% as  $\text{Na}_2\text{O}$ . Before dehydration "Activated Alumina" consists of boehmite, and its crystals are usually small enough to give blurred *X*-ray patterns. The catalytic activity of the dehydrated material can be increased by alternate washing and heating : three such treatments gave line *E* in Fig. 5.

Catalysts made from purchased gibbsite were considerably less active at the same sodium content : this would be expected because they are likely to have been more coarsely crystalline. Lines *F* and *G* on Fig. 5 show the activities of two specimens of boehmite grown under pressure, as described in section B(3). They were made as follows :

	Heated in water at 200° for (hrs.) :	$\text{Na}_2\text{O}$ , %.	Dehydrated at 450° for (days) :
Line F .....	16	0.19	5
Line G .....	60	0.16	3½

In the previous publication (Bentley and Feachem, *loc. cit.*) a pelleted catalyst was described, made by dehydrating purchased gibbsite at 450°. The  $\text{Na}_2\text{O}$  content of the starting material is normally about 0.3%, but the catalytic activity was extremely small (off the scale of Fig. 5). Three cycles of washing and heating raised the activity successively to *H*, *J*, and *K* on Fig. 5, no sodium being detectable after the second treatment.

#### DISCUSSION.

These results support the conclusion derived from the literature, that  $\gamma$ -alumina is the catalytically active species and that activity is increased by increasing freedom from alkali

impurities and by decreasing crystal size. It is difficult to be certain that in changing either the purity or the crystal size the other is not altered, but the results displayed in Figs. 2, 3, and 4 and the effect of alternate washing and heating on " Activated Alumina " (which is already of small crystal size but not particularly pure), when taken all together, seem to show the effect of increased purity.

The effect of crystal size is less definitely demonstrated, because the crystal sizes were not estimated. But the three catalysts made from gibbsite, which were far less active than their purities would suggest, were made in ways that would be expected to give larger crystals and smaller surface areas. The alternate washing and heating process is likely to break up these crystals and to increase their areas, exactly as alternate oxidation and reduction do with metallic catalysts, and lines *H*, *J*, and *K* on Fig. 5 show how this treatment brings the activity nearer to that of the catalysts precipitated in the laboratory, which are likely to have had smaller crystals initially.

The results illustrate one point of practical importance : to get the greatest activity it is necessary to make  $\gamma$ -alumina, and the times and temperatures required for the dehydration of boehmite to  $\gamma$ -alumina vary greatly from one specimen of boehmite to another. Some of the specimens of boehmite used in this work were dehydrated after 6 hours at 350°, while others needed more than 5 days at 450°. This variation is surprisingly large.

The catalyst activity tests show that the kinetics of the reaction that the catalyst is promoting are changed by a change in the temperature at which the alumina is dehydrated. This is not unexpected, because any heterogeneous catalytic reaction is the result of a series of processes such as adsorption, diffusion in the catalyst and reaction, and this particular reaction—the dehydration of ethanol to ethylene—can go by either of two routes, directly and by the intermediate formation of ether. Alekseevskii (*loc. cit.*, 1930) has observed that the temperature of dehydration of the alumina affects its adsorbing power, low temperatures favouring the adsorption of alcohols and higher temperatures that of olefins. It would not be surprising if this temperature affected the diffusion or the reaction stages in the dehydration of ethanol, as well as the adsorption, and small differences in any of these would alter the balance of the complex system of processes and so alter the observed kinetics.

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