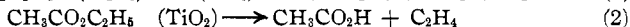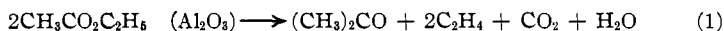# THE SELECTIVE ACTIVATION OF ALUMINA FOR DECARBOXYLATION OR FOR DEHYDRATION[1]

BY HOMER ADKINS

The selective or preferential activation of catalysts has in general only been accomplished by such means as changing the temperature, pressure or state of the catalyst. These factors bear no easily discernible relationship to the mechanism of the catalytic activity. Recently Rosemund[2] has been able by the use of "sulfurized quinoline" to influence a palladium catalyst so that the reduction of benzoyl chloride to benzaldehyde was accomplished while the catalytic activity for the further reduction of the aldehyde to the alcohol was inhibited. This discovery while of great theoretical and practical importance seems to add little to our understanding of the mechanism of the catalytic reaction because of the complex nature of the substance used to influence the activity of the catalyst. It has seemed to the author that progress in understanding the mechanism of organic reactions and the role of catalysts might be more easily made if types of reaction could be related to simple surface conditions of the catalyst rather than to the much studied but little understood phenomena which are met in solutions.

Alumina, titania and thoria at temperatures in the vicinity of 400° cause the formation from ethyl acetate of varying proportions of ethylene, carbon dioxide, acetic acid, acetone, alcohol and water. Sabatier[3] summarizes the action of these catalysts in three equations.

$$2CH_3CO_2C_2H_5 \quad (Al_2O_3) \longrightarrow (CH_3)_2CO + 2C_2H_4 + CO_2 + H_2O \qquad (1)$$
$$CH_3CO_2C_2H_5 \quad (TiO_2) \longrightarrow CH_3CO_2H + C_2H_4 \qquad (2)$$
$$2CH_3CO_2C_2H_5 \quad (ThO_2) \longrightarrow (CH_3)_2CO + CO_2 + C_2H_4 + C_2H_5OH \qquad (3)$$

It has been shown in a previous article[4] of this series that these equations do not completely express the facts and that the type of reaction which a given oxide induces is dependent not only upon the metallic element present in the catalyst but is primarily dependent upon its method of preparation. It seemed probable that the character of the surface of the catalyst rather than the stability of hypothetical intermediate compounds

[2] Rosemund, Ber., 54B, 425, 638 (1921).

[3] Sabatier, "La Catalyse en Chemie Organique," Van Nostrand Co., 1920, p. 341.

[4] Adkins and Krause, THIS JOURNAL, 44, 385 (1922).

was the determining factor in establishing the relative efficiency of the catalyst for decarboxylation or for dehydration. An idea obtained from an article by Briggs[5] made it possible to test this matter experimentally.

Briggs considers that the activation of charcoal for adsorption of gases is dependent upon interstices of molecular dimensions formed by the elimination of carbon atoms from the carbon molecule or space lattice. It must be understood that this has reference to the cavities of molecular size not to those *much* larger, microscopically visible pores or capillaries which apparently have little to do with adsorption. If Briggs is correct, and it is assumed that catalytic activity in heterogeneous systems is conditioned by adsorption, or is due to the same causes as adsorption, then it should be possible to activate a catalyst selectively towards one of two reactions by modifying the size of the pores which are of molecular dimensions, for it is unlikely that two dissimilar reactions would meet their optimum conditions for reaction in the same sized molecular pores.

An alumina catalyst is prepared, or activated, by heating aluminum hydroxide, thus expelling water molecules. The molecular porosity, that is, the pores of molecular dimensions of the catalyst may then be supposed to be dependent upon the size of the water molecules, which are eliminated.

If one could make an alumina catalyst from aluminum ethoxide according to the following reaction, $2Al(OC_2H_5)_3 + heat \longrightarrow Al_2O_3 + 3C_2H_5OC_2H_5$, the size of the pores would be increased, for the molecule eliminated (ether) would be about 4 times as large as in the former case. This is not feasible, however, because the aluminum alkoxides derived from the primary and secondary alcohols are quite stable towards heat and do not decompose quantitatively in the sense of the equation given. It is also true that these alkoxides melt at relatively low temperatures, and hence one would be comparing the decomposition products of the liquid alkoxides with that of the solid aluminum hydroxide. This difficulty can be avoided in working with the non-fusible magnesium alkoxides, and it is intended to study the selective activation of magnesia by the use of these compounds.

Alumina catalysts have been selectively activated by preparing them from the aluminum alkoxides by an indirect method. In the solid aluminum ethoxide, for example, it may be assumed that there is a definite space lattice formation and that the distance between the aluminum atoms is a certain definite value. If aluminum ethoxide, in the solid state, is allowed to react with water vapor (or absorbed water) the reaction, $Al(OC_2H_5)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3C_2H_5OH$, takes place.

Aluminum hydroxide is formed but the distance between the aluminum atoms and the size of the cavity now occupied by the hydroxyl group is determined not by the volume of that group but by the volume of the ethyl (or ethoxyl) group whose place was taken by the hydrogen (or hy-

[5] Briggs, *Proc. Roy. Soc. London*, **100A**, 88 (1921).

droxyl). In other words, the size and shape of the alkyl group would be a determining factor in the size of the interstice left in the catalyst when the hydroxyl group is later eliminated as water during the heating of the aluminum hydroxide.

Assuming the above as a working hypothesis, 11 different alumina catalysts were prepared and their effects upon the reactions of ethyl acetate in the gas phase determined.

## Experimental Part

**Apparatus.**—The apparatus described in the previous article of this series[4] is not particularly satisfactory. It is difficult to maintain an even flow of the vapors and it is not feasible to modify greatly the rate of the flow without changing the size of the capillary tube, temperature of the bath, etc. A vaporizer was made which was essentially the same as that described by Taylor.[6] This type of apparatus is efficient, but for the purposes of this work unnecessarily complicated. A simple set-up was devised which is very satisfactory. The substance to be passed over the catalyst was placed in a pint size vacuum "food jar" having a mouth of such a size as to hold a 50 mm. rubber stopper. A heating coil consisting of B. and S. No. 26 platinum wire having a resistance of 1.5 ohms was placed in the bottom of the jar, the leads from the heating coil being sealed into 5mm. glass tubes which passed through the stopper of the jar. A few drops of mercury were placed in each tube and contact made with the source of current by introducing bare copper wires into the tubes. Ethyl acetate was distilled at the rate of 40 g. in an hour by the use of 1.45 amperes current. The rate of distillation was readily modified by regulating the current passing through the heating coil. The vapor of the ethyl acetate passed up through the stopper by means of a 7mm. glass tube sealed to the catalyst tube. This latter consisted of a Pyrex glass tube 15 mm. in diameter and 48 cm. in length. The tube bore 42 indentations within a length of 37 cm. of the inlet. These were of the type used in the still head described by Noyes and Skinner.[7] The indentations serve to break up and heat the current of vapor to the temperature of the furnace. A layer of glass wool was laid against the last pair of indentations and the catalyst placed against this and held by a second plug of glass wool. The position of the catalyst in the furnace, the condensing system and gas collector, were essentially the same as those illustrated on p. 386 of Ref. 4.

**Temperature Control.**—The temperature of the outside of the catalyst tube was recorded and controlled at 465° ± 2° by means of a Leeds and Northrup potentiometer recorder and controller, the end of the thermocouple being in an indentation of the tube so placed that it was at the point where the vapors of ethyl acetate first struck the catalyst.

[6] Taylor, THIS JOURNAL, **43**, 2060 (1921).

[7] Noyes and Skinner, *ibid.*, **39**, 2718 (1917).

The temperature was of course more constant within the tube than was indicated by the recorder. It is also 15–20° lower than that recorded in making these runs. These facts were established by controlling the furnace with one controller and recording the temperature in the center of the catalyst tube by placing there the head of a second thermocouple connected to a second recorder. The variations in temperature are much greater when the temperature of the furnace is controlled by a thermocouple placed within the catalytic mass than with one on the outside of the catalyst tube.

## Preparation of the Aluminum Alkoxides

The aluminum alkoxides were prepared by the method of Wislicenus[8] and Hillyer[9] which involves the action of amalgamated aluminum upon the anhydrous alcohols. Amalgamated aluminum was prepared as follows. The metal in the form of narrow curled strips cut from sheets was washed with dil. hydrochloric acid and dil. sodium hydroxide solution at least twice. It was then thoroughly rinsed with water and covered with a $1/2\%$ solution of mercuric chloride for $1^1/_2$ minutes, washed with water, alkali, and water again, and amalgamated as before. After washing it thrice with water, then with alcohol and finally with ether, it was then quickly transferred to the flask containing the alcohol to prevent oxidation in the air.

**Aluminum Methoxide.**—One hundred cc. of methyl alcohol dried over quicklime was heated under a reflux condenser with 10 g. of the amalgam. After 24 hours or more the infusible, non-volatile methoxide may be extracted with hot xylene, and the solvent removed by distillation. As in all cases it is most essential that the alcohol be *thoroughly* dried over quicklime.

**Aluminum Ethoxide.**—The preparation was carried out as above, but in this case the ethoxide was purified by distillation. A pure white product melting at 140° was obtained after 3 distillations. It distilled at about 175–180° at 3 mm., or 200° at 6–8 mm. The yield was 70%. It seemed impossible to have all the metal react even with a large excess of alcohol.

**Aluminum Propoxide.**—The preparation was carried out as for the ethoxide. The product melted at 106° and distilled at 240° at 5 mm. The yield was 80%.

**Aluminum *Iso*propoxide.**—This alkoxide is the easiest of all to prepare. The reaction went to completion due to the solubility of the *iso*propoxide in the excess of alcohol. It was essential to distil all the excess alcohol before attempting to distil the alkoxide. It boiled at 125–130° at 4 mm. and the distillate solidified slowly. The crystals melted at 118°. The yield was 95%.

[8] Wislicenus, *Ber.*, **28**, 1325 (1895).

[9] Hillyer, *Am. Chem. J.*, **19**, 41 (1897).

**Aluminum Butoxide.**—The reaction was violent even in the cold. The preparation must be watched very carefully when it is later refluxed for the completion of the reaction. The excess of alcohol was difficult to remove, and was best accomplished under diminished pressure. The butoxide distilled at 290° under 12 mm. pressure, and melted at about 100°.

**Aluminum _Iso_butoxide.**—The reaction was quite brisk upon heating, and went to completion in a few hours. The _iso_butoxide was soluble in the excess alcohol. It was extremely difficult to distil the product because of the closeness of the melting and boiling points, but distillation was effected at 250° at 12 mm. pressure; the substance melted at 215° and upon cooling solidified to a paraffin-like mass.

**Aluminum _Tertiary_-butoxide and _Tertiary_-pentoxide.**—Negative results were obtained when attempts were made to prepare these alkoxides.

## The Preparation of the Catalysts

The catalysts were used in two forms. In the one case a given weight of an aluminum alkoxide was melted in contact with a known weight of ignited pumice which had been cut into lumps about 3–4 mm. in diameter. After cooling, the pumice impregnated with the solid alkoxide was exposed to the air of the laboratory for 18 hours or longer. In some cases the catalyst was treated with steam.

In the second case the aluminum alkoxide was broken into small pieces and exposed in thin layers to air for a week or more. At the end of this time the fine powder was dried at 100° and pressed into pellets with a pill machine. These pellets were of such a size that 15 of them weighed about 2 g.

## The Analysis of the Products of the Reaction

Carbon dioxide, ethylene and acetic acid were determined as previously described.[10] The saponification of ethyl acetate was carried out in an aqueous rather than in an alcoholic solution of alkali. Considerable quantities of alcohol were normally present in the distillates analyzed for acetone, and since experiments showed that under the conditions outlined in Ref. 4, p. 387, the alcohol reacted with the iodine so that the apparent acetone content was increased several per cent., the method was modified by shortening the time allowed for the reaction of the acetone and iodine. It was found to be impractical to lower the temperature of the reaction, for this greatly increased the time necessary for the reaction of the acetone. The method adopted after considerable experimentation was as follows. About 0.4 g. of distillate was added to 100 cc. of water in a glass-stoppered bottle to which had been added 50 cc. of a 0.5 $N$ solution of sodium hydroxide. A 0.4 $N$ solution of iodine in potassium iodide was then slowly added in an amount at least 25% in excess of the amount required by the

[10] Ref. 4, p. 386.

acetone. The solution was allowed to stand 2 or 3 minutes and then neutralized with 0.5 $N$ hydrochloric acid and the excess of iodine titrated with 0.4 $N$ sodium thiosulfate solution using soluble starch as an indicator. The method was shown to give results accurate within 1% for acetone. The iodine solution was standardized against acetone purified by sodium iodide. Redistilled U. S. P. acetone may be used for the standardization without introducing any errors greater than those inherent in the method.

CATALYSTS

| No. | Source Quantity G. | Material Aluminum | Quantity of catalyst G. | Preparation |
|---|---|---|---|---|
| 1 | 4 | ethoxide | ... | Melted on 3 g. of dry pumice and exposed to moist air for 18 hrs. or longer. |
| 2 | 4 | *iso*propoxide | ... | As in No. 1. |
| 3 | | methoxide | 2.0 | By action of moist air. Contained small amounts of mercury. |
| 4 | | amalgam | 2.5 | By interaction with water. |
| 5 | | ethoxide | 2.5 | Precipitated by water from a cold dil. xylene solution. |
| 6 | 4 | *iso*butoxide | ... | As in No. 1. |
| 7 | 4 | propoxide | ... | As in No. 1. |
| 8 | 5 | butoxide | ... | As in No. 1. |
| 9 | | ethoxide | 2.0 | Pills from powder resulting from action of moist air. |
| 10 | | nitrate | 2.5 | Pills from powder obtained by action of NH$_4$OH on dilute water solution. |
| 11 | | ..... | 2.5 | Pills from precipitate by HCl on solution of sodium aluminate. |

TABLE I

RESULTS WITH ETHYL ACETATE

| Catalyst | AcOEt introduced | AcOEt in distillate | Distillate | CO$_2$ | C$_2$H$_4$ | CH$_3$COCH$_3$ | CH$_3$COOH | AcOEt Eq. CO$_2$ | AcOEt Eq. CH$_3$COCH$_3$ | AcOEt Eq. C$_2$H$_4$ | AcOEt Eq. CH$_3$COOH | C$_2$H$_4$ efficiency (CO$_2$) | C$_2$H$_4$ efficiency (CH$_3$COCH$_3$) | Determinations |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| 1 | 37 | 14.8 | 29.7 | 4.57 | 2.46 | 6.14 | 0.60 | 18.3 | 18.6 | 7.74 | 0.89 | 42 | 41 | 7 |
| 2 | 36 | 15.5 | 29.0 | 4.5 | 1.95 | 5.81 | 0.53 | 18.0 | 17.6 | 6.12 | 0.77 | 34 | 35 | 6 |
| 3 | 41 | 18.3 | 33.5 | 4.4 | 2.30 | 5.7 | 1.00 | 17.6 | 17.3 | 7.10 | 1.47 | 40 | 41 | 1 |
| 4 | 38 | 16.1 | 29.0 | 3.1 | 5.95 | 3.8 | 5.00 | 12.4 | 11.6 | 18.7 | 7.35 | 150 | 161 | 3 |
| 5 | 26 | 2.6 | 16.0 | 3.75 | 6.75 | 4.6 | 3.6 | 15.0 | 14.4 | 21.2 | 4.8 | 142 | 153 | 1 |
| 6 | 46 | 23.0 | 40.0 | 4.3 | 2.1 | 5.7 | 0.92 | 17.2 | 17.3 | 6.6 | 1.36 | 38 | 38 | 1 |
| 7 | 40 | 14.7 | 31.9 | 4.9 | 2.5 | 6.2 | 0.68 | 19.7 | 18.8 | 7.85 | 1.01 | 40 | 42 | 3 |
| 8 | 37 | 13.7 | 28.9 | 4.6 | 2.9 | 5.9 | 1.14 | 18.4 | 17.9 | 9.16 | 1.64 | 50 | 51 | 5 |
| 9 | 34 | 13.1 | 26.0 | 4.1 | 2.8 | 5.2 | 1.14 | 16.4 | 15.8 | 9.0 | 1.64 | 55 | 57 | 1 |
| 10 | 36 | .. | 26.0 | 3.2 | 5.9 | .. | 3.8 | 12.8 | .. | 18.5 | 5.58 | 144 | .. | 1 |
| 11 | 43 | 18.0 | 34.0 | 3.7 | 5.0 | .. | 4.2 | 14.8 | .. | 15.7 | 6.17 | 107 | .. | 2 |

TABLE II

RESULTS WITH ETHYL ALCOHOL AND ACETIC ACID

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Distilled, g............ | 40 | 29 | 42 | 33 | 29 | 28 | 28 |

|  | AcOH | AcOH | AcOH | EtOH | EtOH | EtOH | EtOH |
|---|---|---|---|---|---|---|---|
| Distillate, g............ | 32 | 21 | 33 | 16 | 20 | 19 | 16 |
| Catalyst | 4 | 1 | 2 | 4 | 1 | 2 | 9 |
| Product, g............ | 7.0 | 7.4 | 7.8 | 15.6 | 7.5 | 6.6 | 10.3 |
|  | $CO_2$ | $CO_2$ | $CO_2$ | $C_2H_4$ | $C_2H_4$ | $C_2H_4$ | $C_2H_4$ |

**Explanation of the Tables.**—The headings of Cols. 1–8 in Table I are self-explanatory. Cols. 9–12 give the ethyl acetate equivalent of the various products of the reaction, 1 molecule of carbon dioxide and of acetone being considered equivalent to 2 molecules of ethyl acetate, and 1 molecule of acetic acid and of ethylene as equivalent to 1 molecule of the ester. In Cols. 13 and 14 are given certain percentages which are labeled "ethylene efficiency." The figures in Col. 13 are calculated as follows. The ethyl acetate equivalent of the ethylene formed in Run 1, for example, is 7.74 g. (Col. 11). The ethyl acetate equivalent to the carbon dioxide produced is 18.3 g. (Col. 9). In other words the fraction 7.74/18.3 or the percentage 42 (Col. 13) represents the number of molecules of ethyl acetate that gave ethylene as compared with the number that were the source of carbon dioxide. The percentages given in Col. 14 are based upon the production of acetone as the ones in Col. 13 are based upon the amount of carbon dioxide formed. Barring experimental errors and side reactions, these two sets of figures should be the same. The number of runs which were made and averaged to obtain the figures given in other columns of Table I is indicated in Column 15. The duration of the runs was 1 hour.

The headings for Table II are self-explanatory.

## Discussion of Results

Three of the catalysts whose activities in the formation of acetone, carbon dioxide and ethylene have been studied, are evidently quite similar, as would be expected from their method of preparation (Nos. 4, 5 and 10). They were all precipitated from neutral or alkaline solutions. The catalysts are evidently derived from hydrated colloidal alumina; that is, they are all precipitated as the so-called colloidal aluminum hydroxide, which is not an hydroxide at all though it is the substance obtained by treating aluminum salts with ammonium hydroxide. The drying curve of this product is a regular function of the temperature[11] from 15° to 300° and shows no definite hydrate at any temperature. The distinction between this colloidal aluminum hydroxide and the true crystalline aluminum hydroxide obtained by the action of acids upon solutions of sodium aluminate was made by Bremmelen and substantiated by E. Martin.[12] Catalyst 11 was derived from the true hydroxide. Recently Lowell Milligan[13]

[11] van Bremmelen, *Rec. trav. chim.*, **7**, 75 (1888).

[12] Martin, *Mon. Sci.*, [5] **5**, 225 (1915).

[13] Milligan, *J. Phys. Chem.*, **26**, 247 (1922).

has shown that this compound, Al(OH)₃, is stable up to about 145°. Between this temperature and 200° it loses most of its water of constitution.

Alumina derived from the colloidal hydrated aluminum hydroxide precipitated by ammonium hydroxide (Catalyst 10) is one that has been used in previous work. It is very efficient in the production of ethylene but comparatively inefficient in the production of acetone and carbon dioxide; 144% as many molecules of ethyl acetate give ethylene as produce carbon dioxide. A catalyst prepared by the action of amalgamated aluminum upon water (No. 4) is very similar in activity to that precipitated with ammonium hydroxide. It is slightly more efficient as an ethylene producer because by its method of preparation it can contain no occluded salts. The gas from such a catalyst does not contain the 2–3% of hydrogen and saturated hydrocarbons that characterize the gas produced over catalysts such as No. 10. On the average, $1^1/_2$ times as many molecules of ethyl acetate give ethylene as produce carbon dioxide. (The ethylene efficiency calculated on the acetone found is erroneously high due to condensation or loss of acetone.) A catalyst prepared from the precipitate, obtained by adding water to a xylene solution of aluminum ethoxide, gives results similar to those obtained with the other 2 catalysts noted above (Catalyst 5). Its ethylene efficiency is apparently slightly lower. The catalyst (11), derived from the true aluminum hydroxide, is quite different in its activity toward ethyl acetate. Its ethylene efficiency is much lower, the value being 107%. The reaction induced corresponds within 6.5% to the equation given by Sabatier (Eq. 2).

The catalysts prepared by melting aluminum alkoxide upon pumice and then causing the formation of alumina by exposing the pumice impregnated with the alkoxide to moist air are markedly different in their activities from the other catalysts whose activities are described above. They are similar to Sabatier's thoria catalysts. They are good catalysts for the production of acetone and carbon dioxide but are inefficient in the production of ethylene. They produce ethylene from only 35% to 50% of the molecules of ethyl acetate from which comes carbon dioxide. Alumina from the colloidal aluminum hydroxide produces ethylene from about $1^1/_2$ times as many molecules of ethyl acetate as it does carbon dioxide and acetone. The ethylene efficiency is thus less than $^1/_3$ as great with these catalysts derived from the alkoxides as it is with catalysts derived from the hydrated alumina. (It should be noted that the figure representing ethylene efficiency by its method of calculation indicates the relative activity of the catalyst towards the two reactions involved.) The 5 different catalysts of this group show considerable differences in activity among themselves. The average of 7 runs in which alumina (1) derived from the ethoxide was used shows an ethylene efficiency of 42% based upon the carbon dioxide determinations, and 41% based upon the analysis for

acetone. The average ethylene efficiencies of the catalysts derived from the propoxide show a close agreement with the above. The averages are 40% and 42%. The average ethylene efficiencies for catalysts derived from *iso*propoxide (2) are much lower, being 34% and 35%. The catalysts (8) from the *normal*-butoxide in an average of 5 runs show a considerably higher ethylene efficiency, the figures being 50% based on the carbon dioxide analysis, and 51% based upon the determination of acetone. The catalyst derived from the branched-chain *iso*butoxide shows a lower ethylene efficiency of only 38%.

Attention should be called to 2 other catalysts which are not of any of the chief types noted above. Catalyst 9 prepared by the exposure to moist air of aluminum ethoxide, shows an ethylene efficiency higher than that obtained when pumice is impregnated with ethoxide, but much lower than that obtained by the catalysts prepared by precipitation methods. In general it has been found that much more uniform catalysts are obtained when the alkoxide is impregnated on pumice than when it is exposed to moist air and then pressed into pellets. The use of the pumice as a support for the catalyst at first was made because of the ease of preparation of the catalyst and because of the economy in the quantities of alkoxide needed. Its use was continued both for these reasons and because catalysts of uniform activity could thus be easily obtained. Catalyst 3, obtained by the exposure of crude aluminum methoxide to moist air, was similar in activity to the catalysts derived by the impregnation of the ethoxide upon pumice.

In Table II are given the results of some experiments in which the activity of the catalysts towards acetic acid and absolute alcohol was determined. The results indicate that the most efficient catalyst for the production of acetone is the one derived from the *iso*propoxide, less efficient is the one derived from the ethoxide and least efficient is the one derived from hydrated alumina. The order of efficiency for ethylene is exactly the reverse, the precipitated catalyst being more than twice as efficient as those derived from the alkoxides. These results are in entire harmony with those obtained by the use of the same catalysts with ethyl acetate. Not as much reliance should be placed, however, upon the quantitative aspects of determinations of the order of efficiency of catalysts for different reactions when the determinations are made in different experiments at different times, with different samples of catalysts, as upon determinations made under conditions which are automatically identical for the two reactions. The latter conditions are met in the study of the reactions of ethyl acetate. The experiments whose results are given in Table II are cited only as evidence that the reactions observed in the decomposition of the esters are the same as those that take place in the decarboxylation of acids and in the dehydration of alcohols.

To summarize, it may be said that the order of efficiency for ethylene

production by alumina catalysts is as follows. (1) By far the most efficient are those catalysts derived by the formation of hydrated alumina from water and aluminum amalgam, or from aqueous solutions of inorganic salts with ammonium hydroxide or by the action of water upon a xylene solution of aluminum ethoxide. The numerical value for the ethylene efficiency of these catalysts is about 150%. In these catalysts the size of the molecular pores is least because it is determined by the size of the water molecules which are driven from the alumina nuclei during heating. (2) The ethylene efficiency of the alumina derived from the true aluminum hydroxide is much lower, having a value of about 107%. While the suggestion that this is due to an increase in molecular porosity of the catalyst is not so strongly made by the method of preparation, as in the case of the alumina from the alkoxides, yet its behavior is entirely in accord with the hypothesis advanced in the introduction of this paper. It seems that larger pores nearer to the central aluminum atoms would be formed by the elimination of the elements of water from aluminum hydroxide than by the expulsion of water of hydration from the colloidal form. (3) Of much less efficiency are those catalysts derived by the formation of aluminum hydroxide from the *solid* aluminum alkoxides, without destroying the space relationships of the aluminum atoms or attached groups. Of these the alumina derived from the *normal*-butoxide is most efficient as an ethylene producer, that from the ethyl and propyl alkoxides less so, and that from the branched-chain *iso*butyl and *iso*propyl alkoxides least efficient of all. Of these last two catalysts the less efficient is the one derived from the *iso*propoxide in which the branching takes place from the carbon atom which is attached to the oxygen that holds the aluminum atom. In this case the branching is nearest the central aluminum atom, and hence gives the maximum size of pore within atomic distances of the central atom. If this hypothesis is correct, that increase in the size of the molecular pores decreases ethylene efficiency, the alumina derived from the alkoxides of the tertiary alcohols should be least efficient. As yet it has not been found possible to prepare these alkoxides, although repeated attempts have been made using both *tertiary*-butyl and amyl alcohols. The long, straight butyl chain may be considered to give the smallest or narrrowest pore and hence the catalyst is more efficient as an ethylene producer than the catalysts derived from the other shorter or branched chain alkoxides.

Alumina catalysts have been prepared which split ethylene from about 32% to 97% of the molecules of ethyl acetate actually decomposed. These same catalysts varied in the reverse order with respect to their ability to decarboxylate the acid residue. The variation may be expressed numerically by saying that carbon dioxide and acetone were formed from 95% to 60% of the molecules of ethyl acetate actually decomposed

by the catalyst. According to the hypothesis advanced, increase in the size of the molecular pores or of the distances between aluminum atoms increases the activity of the catalyst for decarboxylation.

Certain anticipated results have been obtained. The author realizes quite well that the hypothesis on the basis of which they were anticipated is not, therefore, *necessarily* correct. Evidence for or against the hypothesis is being sought in this laboratory by the use of the different types of alumina in the catalysis of various organic reactions. If the hypothesis be true, it is hoped to relate the size of the molecular pores of the catalyst to the type of reaction induced. Two problems suggested by this work which are outside the scope of a laboratory of organic chemistry would involve a study by means of X-rays of the space lattices of the different types of alumina and also a study of their absorption of various gases.

The paper of Lowell Milligan[13] upon the "Dehydration of Crystalline Aluminum Hydroxide" is of great significance. It is shown that when the water is expelled from the crystalline aluminum hydroxide at temperatures above 275°, and it is then allowed to "rehydrate," the water is adsorbed and is not *chemically* combined in the sense that the word was used in pre-Langmuirian times. If water does not chemically combine with alumina it seems unreasonable to assume that ethyl alcohol would react to form the aluminum ethoxide as is postulated by Sabatier to account for the formation of ethylene from ethyl alcohol under the influence of catalysts. Milligan quotes Professor Warren J. Mead of the University of Wisconsin to the effect that heating crystalline aluminum hydroxide at 325° changes the X-ray pattern of the hydroxide (this pattern is identical with that of the mineral, gibbsite) to another pattern which, however, is that of a crystalline state of aggregation. The latter pattern is not that of diaspore or of corundum. This is evidence then that the catalyst obtained for the crystalline hydroxide was crystalline. "Rehydration" of this alumina does not affect the X-ray pattern of the dried (above 325°) alumina, which is again evidence that chemical combination does not take place between the alumina and the water. Heating the alumina from 600–1000° destroys the crystalline condition as shown by the X-ray pattern. Alumina is inactivated for catalysis by exactly this treatment. This is evidence that much that has been written concerning inactivation because of crystallization is perhaps not based upon fact.

Palmer[14] explains the fact that copper electrolytically deposited is inactive, while copper by reduction is active in the dehydrogenation of alcohol, by considering that the activity is due to a kind of copper produced from cuprous compounds. There would, of course, only be "cupric" copper in the deposit on an electrode and hence, according to Palmer, this would be inactive. The result could be explained on the basis of the hypothesis

[14] Palmer, *Proc. Roy. Soc. London*, **98A**, 13, 412 (1921).

here advanced by considering that the copper ions when discharged at the electrode are free to take up positions which will most completely satisfy the secondary fields of force about the copper atoms. This means that the copper atoms will be closely packed and that there will be a weak "field of force" at the surface. Copper prepared by reduction of the oxide on the contrary will have a pitted surface in which the interstices are possibly of the dimensions of oxygen atoms. In these molecular interstices those forces which condition adsorption and catalytic activity will exert their influence.

## Summary[15]

1. Alumina has been preferentially activated for decarboxylation or for dehydration by modifying its method of preparation. This has been accomplished by obtaining aluminum hydroxide and hydrated alumina by precipitation from its salts or esters in water or xylene solution and by preparing it by the action of water vapor upon aluminum alkoxides in the pure state and when the latter are impregnated upon pumice.

The extent to which selective activation has been accomplished is indicated by the series of figures, 34, 38, 41, 50, 107, 150, which represent the "ethylene efficiency" of the different catalysts.

2. An hypothesis has been advanced in which it is considered that the catalytic acitivity of alumina is conditioned by its molecular porosity or the distances between the aluminum atoms and that this in part is determined by the size, shape and position of the radicals attached to the aluminum when the aluminum compound goes into the solid state. All of the experimental evidence obtained with alumina catalysts is in complete harmony with this hypothesis.

3. In terms of this hypothesis it is held that decarboxylation is favored by large pores in the alumina and that ethylene formation is favored by small pores. Large and small in this case refer to units of molecular dimensions.

4. The work of Milligan and Mead upon the dehydration and X-ray pattern of crystalline aluminum hydroxide is discussed in its relation to catalytically active alumina.

5. The results obtained by Palmer, in the use of electrolytic copper and copper by reduction for the dehydrogenation of alcohol, are explained on the basis of the hypothesis noted above.

MADISON, WISCONSIN

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[15] After this paper had been submitted to the Editor, 't was learned through a reprint from the Transactions of the Faraday Society, 17, 617, May, 1922, that Dr. Irving Langmuir had spoken in September, 1921, at Edinburgh, of the probable importance in heterogeneous catalysis of the spacing of the atoms on the surface of the solid. The foregoing paper has been written in terms of "molecular porosity," as the catalyst was thought of as a 3-dimensional mass. Dr. Langmuir for the sake of simplicity considered only one of the innumerable planes which go to make up the solid. It is believed that the work described in this paper is experimental verification of the speculation first made by Dr. Langmuir.