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Kinetics of the Dehydration of Alcohol on Alumina

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The dehydration of ethyl alcohol on η and γ alumina was investigated. The kinetics of the formation of ethylene obeyed the Langmuir-Hinshelwood mechanism, while the formation of ether occurred according to the Rideal-Eley mechanism and the Langmuir-Hinshelwood mechanism simultaneously. The rate constants obtained with η and γ alumina are correlated with their surface structures.

1. INTRODUCTION

The dehydration of alcohol to ether or to ethylene is known from about the 13th and 18th centuries, respectively.

In 1797 four Dutch chemists (*1*) (Bondt, Deiman, Paets van Troostwijk, and Lauwerenburgh) discovered the catalytic dehydration action of alumina on alcohol (at that occasion they introduced the name "olefine"). In 1901 Grigorieff rediscovered the catalytic dehydration action of alumina on alcohols (*2*). This induced Ipatieff to investigate systematically the catalytic dehydration in addition to the dehydrogenation which he was already studying at that time (*3*). This work induced again various studies by Sabatier, Senderens, and Mailhe (*4*) in the first decennium of this century.

As an excellent survey of these reactions was given in 1960 by Winfield (*5*) we shall restrict ourselves to the above historic introductory remarks.

The intermolecular dehydration of two molecules of alcohol to ether, on alumina as a catalyst, requires a lower activation energy than the intramolecular dehydration to ethylene. At temperatures below 260°C the production of ether is practically the only course (*6*), while at temperatures well above 300°C the products are almost entirely ethylene and water (*2*). As also ether may be catalytically dehydrated on alumina, either to ethylene and water or to ethylene and alcohol (*7*), ethylene may be produced by three catalytic reactions, viz. either directly or by two different consecutive reactions via ether. At about 300°C and with short contact times all these reactions may occur simultaneously on alumina as a catalyst (*8*).

As some authors (*9*) suggest that the catalytic dehydration of alcohol on alumina requires the formation of surface aluminum-alcoholate groups, while others (*10*) hold an oxonium–carbonium ion mechanism responsible for the reaction, a comparison of the catalytic behavior of different aluminum oxides might be helpful in studying the mechanism.

In the literature many authors have shown that aluminas differ significantly in their catalytic behavior when they have been prepared from different hydroxides or oxide-hydroxides. Pines and Pillai (*11*) studied the dehydration of menthol and neomenthol over different alumina cata-

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lysts. They showed that the activity depends on the method of preparation of the aluminas. Alumina catalysts prepared from sodium aluminate were found to be weakly acidic while those prepared from aluminum isopropoxide were strongly acidic. The dehydration of alcohols on the latter catalysts was accompanied by an extensive isomerization. The isomerization could be suppressed by poisoning of the strong acid sites of the alumina by bases like ammonia (*12*). In studying the relative acidities and catalytic activities of alumina samples prepared by various methods, Pines and Haag (*13*) found that the amine index showed good correlation with the catalytic activity for samples from the same source, but not for catalysts from different sources. Simon *et al.* (*14*) prepared a series of aluminum hydroxides by hydrolysis of amalgamated aluminum. Bayerite, boehmite, or a mixture of both hydroxides were obtained at various temperatures. After heating, the resultant oxides were tested on the dehydration of isopropanol. The catalytic activity was found the same for all oxides.

2. THE ALUMINA SAMPLES

In the majority of studies made in the field of dehydration with alumina as a catalyst, very little is known about the structure and the texture of the specific aluminas which have been used. From our studies (*15*) we know how narrow the pores in activated aluminas may be, if they have not been heated to sufficiently high temperatures. In order to avoid any disturbances from diffusion phenomena into or out of the pore system, we have to choose alumina preparations devoid of narrow pores.

In the present study two different species of alumina were used.

A. Alumina Prepared from Boehmite

Gelatinous boehmite was prepared (*16*) from alum (1 kg) which was added to a solution of 100 g of ammonium sulfate and 400 g of a 25% ammonia solution in 500 ml of water. After a few minutes the pH of the suspension had decreased to 9.2; this pH was kept constant during further reaction by adding a small portion of a 25% ammonia solution. Up to 50 g of this solution was required. The suspension was left overnight, then filtered and washed with water until no sulfate ion could be detected in the filtrate; it was finally dried at 120°C.

This gelatinous boehmite was then heated at 250°C for 6 hr with ten times its weight of water in closed glass tubes placed in an autoclave partly filled with water. The resultant microcrystalline boehmite was filtered and dried at 120°C. Its loss of water on heating to about 1100°C was 19.1 g/100 g Al_2O_3, somewhat higher than the theoretical value for AlO(OH), viz. 17.7 g/100 g Al_2O_3. As is usual with these microcrystalline boehmites the specific surface area is still rather high—63 m^2/g Al_2O_3 in our case—and somewhat more OH groups may be found on the surface than would correspond with the boehmite composition within. The adsorption of lauric acid showed the surface to be of a hydroxyl type (*17*).

The microcrystalline boehmite thus obtained was heated to 800°C, to convert it into γ-Al_2O_3. The specific surface area of this alumina was 55 m^2/g, its water content (loss on ignition) was 0.6 g/100 g Al_2O_3; all narrow pores had disappeared. Lauric acid adsorption showed it to be of oxidic character (*17*).

B. Alumina Prepared from Bayerite

Bayerite was prepared by the method given by Schmäh (*18*). Strips of very pure aluminum foil (99.99% purity) about 10 cm long, 1.5 cm wide, and 0.2 cm thickness, were degreased with acetone, etched with 2 *N* NaOH solution for 30 sec and then thoroughly rinsed in distilled water until neutral to methyl red indicator. Next they were amalgamated by immersion for 2 sec in a 1% mercurichloride solution and again thoroughly rinsed.

The strips were then placed in 5-liter beakers each containing 3 liters of water and brought to pH = 7 by adding some ammonia. After a 2 weeks exposure period at room temperature, during which the pH was kept constant by adding NH_3 (if necessary), all aluminum had reacted. The precipitate was filtered and dried at 120°C. Its loss of water on heating to about 1100°C was 53.0 g/100 g Al_2O_3. The theoretical value for $Al(OH)_3$ is, as well, 53.0 g/100 g Al_2O_3. The specific surface area of the bayerite was 18 m^2/g Al_2O_3. The adsorption of lauric acid showed the surface to be of a hydroxyl type (*17*).

The bayerite thus obtained was heated to 800°C for 24 hr, to convert it into η-Al_2O_3. The specific surface area of this alumina was 65 m^2/g Al_2O_3, its water content (loss on ignition) was 0.3 g/100 g Al_2O_3; all narrow pores had disappeared. Lauric acid adsorption showed it to be of oxidic character (*17*).

3. Experimental

A. *Ethyl alcohol*

The ethyl alcohol was prepared by keeping absolute ethyl alcohol over Linde molecular sieve IVa for several days, and then distilling it at a constant boiling point, 78.3°C (*19*). The distillate was kept over the molecular sieve until use.

B. *The Apparatus*

The catalytic reaction was carried out in a flow system with helium as a carrier gas. A schematic representation of the system is given in Fig. 1.

a. Controlling and measuring the carrier gas rate. Helium gas was passed through a rotameter after being controlled by a needle valve. Then the gas flow was measured accurately using a soap flow meter for which the volumes of the bulbs were calibrated. The pressure was recorded on a manometer. The gas was passed through a drying tower. The upper part of this tower is filled with KOH pellets and the lower part with clean steel wool. This part was, during the experiment, cooled with a carbon dioxide–ethyl alcohol freezing mixture.

b. Saturator. The saturator (*20*) consists of two parts. The first part is an evaporator which is equipped with a mariote vessel to keep the alcohol level in it rather constant. In an outer jacket water is circulated from a thermostat to keep the temperature constant. The helium gas passes through a sintered glass disc to bubble the gas through the alcohol in a uniform way. The second part is a condenser kept at a constant temperature as well, but lower than that of the evaporator. This ensures the complete saturation of the gas with alcohol vapor at the prevailing temperature.

c. Reactor. The glass reactor was kept at a constant temperature of 307° ±

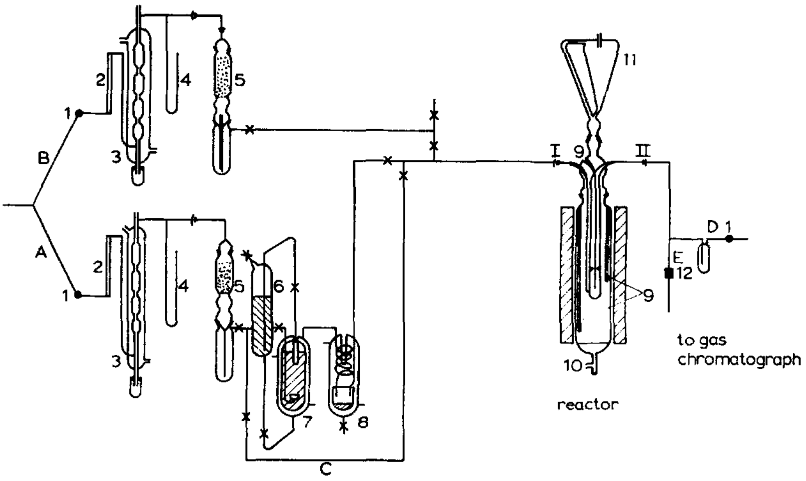

FIG. 1. The apparatus: 1, needle valve; 2, rotameter; 3, soap flow meter; 4, manometer; 5, drying tower; 6, mariote vessel; 7, evaporator; 8, condensor; 9, tube for thermocouple; 10, pressed air for fluidization; 11, cyclone to separate carborundum particles; 12, glass–copper joint.

0.5°C, using a fluid bed of carborundum as a heating medium. The fluidized carborundum is—if necessary—cycled back in the bed by a cyclone on the top of the reactor. The constant temperature in the bed was activated using a temperature control connected to a chromel-alumel thermocouple situated in the fluidized bed. The real reactor temperature was measured through another calibrated thermocouple situated in the middle of the reactor in a glass sheath. The catalyst granules (0.4–1.7 mm diameter) were supported in the reactor on glass beads of different diameter. About 50 mg of catalyst was sufficient to give about 20% conversion of the alcohol.

To prevent condensation of the products of the reaction all glass connections from the saturator to the gas chromatograph were heated by a resistance wire. The sampling tap of the gas chromatograph and its connections to the katharometer were heated in an air thermostat at 60°C.

During an experiment helium is passed through tract A (Fig. 1) to the saturator where the condenser is at a fixed temperature, then to the reactor, and further to the gas chromatograph for analysis. Tract B is used for dilution of the helium-alcohol current from A to obtain lower partial pressures of alcohol when required.

To remove air, before starting a run, helium was passed through the system by tract B or C. Side tract D after the reactor was used to control the rate of flow of the reaction product from the reactor to the katharometer by adjustment of a needle valve.

C. Analysis

After passing the reactor the gas stream is analyzed on a gas chromatograph, where ethylene, ether, water, and unreacted alcohol could be detected. A 2-m column of 20% Reoplex (polyester) on a silanized Embacel (60–100 mesh) was used (M & B-Dagenham, England). The column was kept at 100°C. The rate of helium gas flow, as a carrier gas, was about 40 ml/min. Calibrations showed linear relationships between the partial pressures of ethylene, ether, and alcohol and the areas of their peaks produced on the recorder.

D. Procedure

For a run, the first point is carried out by allowing the helium gas to flow through the alcohol at a rate of about 150 ml (STP)/min. The alcohol saturator is kept at about 25°C. This gives a partial pressure of alcohol of about 60 mm. Then, at the same alcohol temperature, the successive points are obtained by dilution of the helium-alcohol current with a helium flow from side tract B, until gradually a partial pressure of alcohol of nearly 10 mm is reached. Then the temperature of the alcohol is raised successively to higher temperatures, while a constant stream of helium is passed through. Each point takes about 1 hr, including exposure of alcohol stream to the catalyst as well as analysis.

4. CALCULATION

The rate of the helium flow ($F_{\mathrm{He}}{}^{\mathrm{A}}$) in tract A is calculated in the following way:

$$F_{\mathrm{He}}{}^{\mathrm{A}} = 0.359(p_1 F_{\mathrm{A}}/T_1)\ \mathrm{ml(STP)/min} \quad (1)$$

in which p_1 is the pressure in the soap flow meter; F_{A}, the flow as measured in the soap flow meter in ml/min; T_1, the temperature in the soap flow meter in °K; and 0.359, a factor for conversion to STP conditions.

In the same way the rate of the helium flow ($F_{\mathrm{He}}{}^{\mathrm{B}}$) in tract B is calculated, namely,

$$F_{\mathrm{He}}{}^{\mathrm{B}} = 0.359(p_2 F_{\mathrm{B}}/T_2)\ \mathrm{ml(STP)/min} \quad (2)$$

in which p_2 is the pressure in the soap flow meter; F_{B}, the flow as measured in the soap flow meter in ml/min; and T_2, the temperature in the soap flow meter in °K.

The rate of the alcohol flow (F_{alc}) is given by

$$F_{\mathrm{alc}} = p_s F_{\mathrm{He}}{}^{\mathrm{A}}/(p_3 - p_s)\ \mathrm{ml(STP)/min} \quad (3)$$

in which p_s is the saturation pressure of the alcohol at the fixed temperature; and p_3, the pressure after the saturator.

Because the total pressure in the

reactor is equal to p_3, the initial pressure of the alcohol in the reactor p_i is given by

$$p_i = \frac{F_{alc}}{F_{He}{}^A + F_{He}{}^B + F_{alc}} p_3 \text{ mm} \quad (4)$$

From the gas chromatographic analysis the partial pressures of alcohol (p_f), ethylene ($p_{ethylene}$), ether (p_{ether}), and water (p_{H_2O}) are known.

The conversion is then given by

$$\left[1 - \frac{p_f}{p_i}\frac{(p_3 - p_i)}{(p_3 - p)}\right] \times 100\% \quad (5)$$

the ethylene production by

$$\frac{F_{He}{}^A + F_{He}{}^B}{p_3 - p} p_{ethylene} \text{ ml(STP)/min} \quad (6)$$

and the ether production by

$$\frac{F_{He}{}^A + F_{He}{}^B}{p_3 - p} p_{ether} \text{ ml(STP)/min} \quad (7)$$

In the latter three formulas p is the total pressure of the reaction products.

5. Results

The dehydration products, under the conditions described above, consist of ethylene as well as of ether. It appears that the production of ethylene requires an initial period of 2 hr to arrive at its maximum and constant rate; the production of ether requires an initial period of about 1 hr. After the constant production of ethylene has been reached, the partial pressure of the alcohol may be raised or lowered, whereupon reproducible figures for ethylene as well as ether are obtained. Figure 2 gives a set of results obtained with γ-Al_2O_3; the figures for ether and ethylene are given in ml(STP) produced per minute and per m^2 of catalyst. Figure 3 gives a similar set of results obtained with η-Al_2O_3.

6. Discussion

A. Kinetics

Figures 2 and 3 show that the ethylene production tends to become a zero order reaction at partial pressures higher than about 30 mm alcohol pressure. We may, probably, conclude that a saturation of the surface with chemisorbed alcohol molecules has been reached under these circumstances, which certainly leads to a zero order reaction for the direct production of ethylene from alcohol.

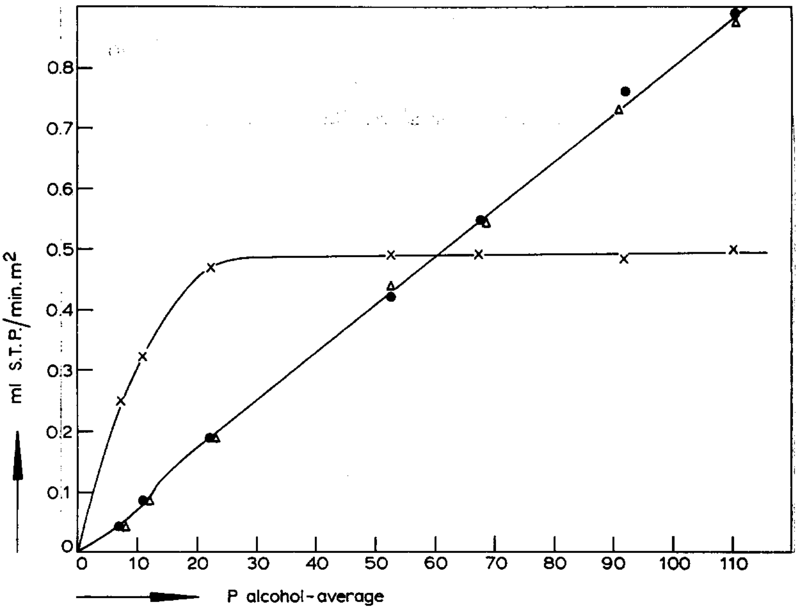

FIG. 2. Experimental results with γ-Al_2O_3.

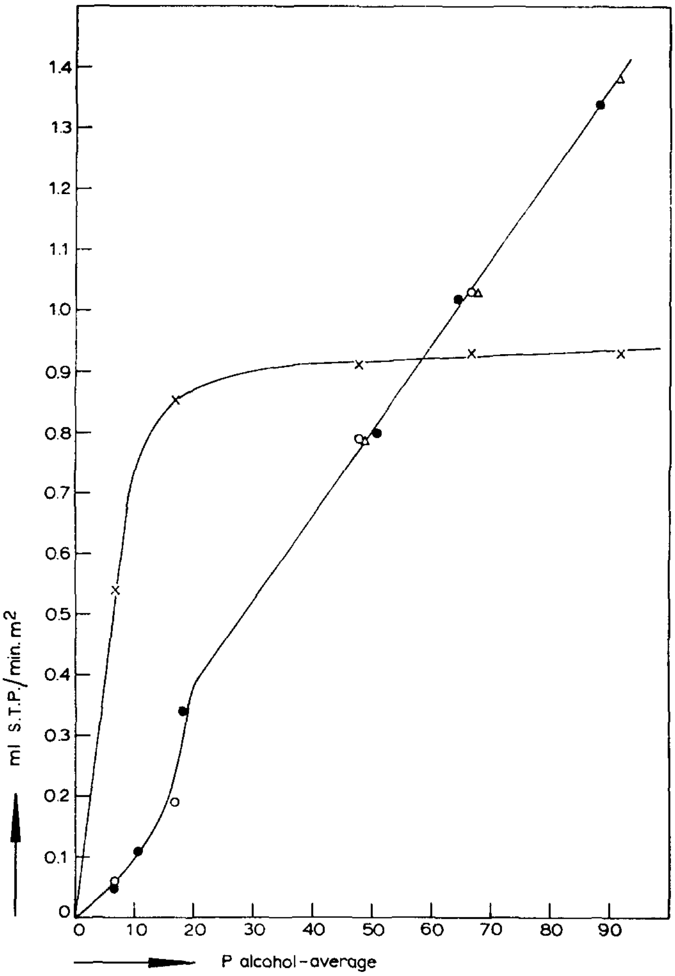

FIG. 3. Experimental results with η-Al_2O_3.

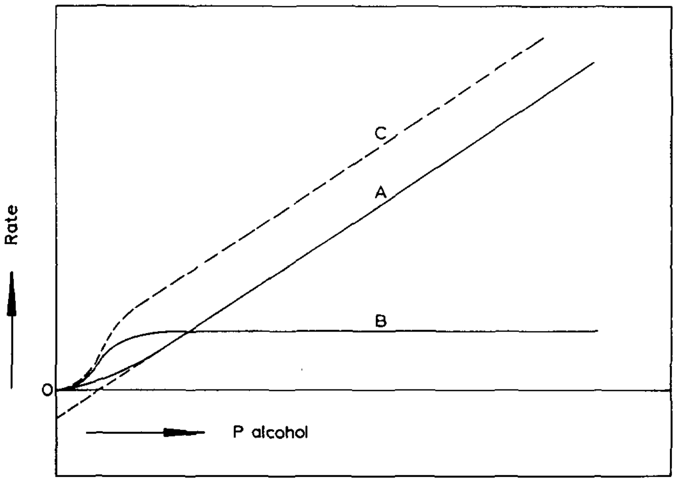

FIG. 4. Schemetical explanation of the curve of ether production.

Simultaneously ether is produced, involving a reaction between two alcohol molecules. Two reaction mechanisms may be considered. If the reaction would follow the Langmuir-Hinshelwood scheme, where both partners of the reaction would be adsorbed, the order of the ether production should also become zero at the same partial pressure as the ethylene production does, as indicated by curve B in Fig. 4. If, however, the reaction proceeds according to the Rideal-Eley scheme, where one molecule is adsorbed and the second molecule reacts from the gas phase, a curve such as curve A in Fig. 4 would result, starting with a second order reaction, changing into first order when the alcohol adsorption becomes saturated; extrapolating the straight part of the curve to zero pressure, it would cut the vertical axis below zero.

In reality the observed curve for the production of ether has the character of a second order reaction at low pressures and changes into a straight line at roughly the same pressure where the ethylene production becomes zero order. The extrapolations of the experimental curves to zero pressure, however, intersect the vertical axis above zero, as a combination of curves A and B to C in Fig. 4 does. We may, therefore, draw the conclusion that both the Langmuir-Hinshelwood and the Rideal-Eley mechanisms proceed simultaneously, the latter mechanism playing a more important role than the first-mentioned.

There is no indication of ethylene production from ether. Apparently all ether molecules produced on the surface desorb easily and do not get a chance for re-adsorbing. We may also expect that ethylene desorbs immediately and does not interfere with the reaction rates. In all reactions, however, water is also produced and we must expect water molecules to stay adsorbed or become adsorbed immediately after the reaction and we may even expect them to be more strongly adsorbed than the alcohol molecules of the feed. It is known from the literature that water is a strong inhibitor of these reactions. From the experimental results it is, nevertheless, clear that at a certain alcohol pressure a saturation of the surface with adsorbed molecules is reached and we may assume that

$$\theta_a + \theta_w = 1 \tag{8}$$

where θ_a is the degree of coverage with alcohol molecules and θ_w the degree of covering with water molecules. One might have expected the composition of this saturation to shift slightly to higher values of θ_a and correspondingly lower values of θ_w with increasing alcohol pressures. The strength of adsorption of water, however, will be higher than that of alcohol, which would lead to a less noticeable shift. The slight tendency of our experimental results to show somewhat higher figures for the ethylene production at higher alcohol pressures in the "saturation" area is too small to warrant conclusions.

From the "saturation" parts of our curves we may derive some numerical results. The equation for the ethylene production may be written as

$$v_{\text{ethylene}} = k_1\theta_a \tag{9}$$

which in the saturation area becomes

$$v_{\text{ethylene}} = k_1(1 - \theta_w) = k_{\text{I}} \tag{10}$$

The level of the "horizontal" part of the production curve gives k_{I}.

The production of ether is given by

$$v_{\text{ether}} = k_2\theta_p + k_3\theta_a p_a \tag{11}$$

where θ_p stands for the degree of occupation with such pairs of adsorbed alcohol molecules that reaction can take place. If there are n possible sites round every adsorbed alcohol molecule where another alcohol molecule can be adsorbed in a position favorable for reaction and the degree of occupation is θ_a, one may derive

$$\theta_p = \tfrac{1}{2}n\theta_a^2 \tag{12}$$

Substituting this in Eq. (11) and writing the equation for the "saturation" condition, where $\theta_a = 1 - \theta_w$, we obtain

$$\begin{aligned} v_{\text{ether}} &= k_2 \tfrac{1}{2}n(1 - \theta_w)^2 + k_3(1 - \theta_w)p_a \\ &= k_{\text{II}} + k_{\text{III}}p_a \end{aligned} \tag{13}$$

TABLE 1
VALUES OF THE RATE CONSTANTS OF ETHYL ALCOHOL DEHYDRATION ON γ- AND η-Al_2O_3 AT A TEMPERATURE OF 307°C[a]

	γ (Fig. 2)	γ (2nd expt.)	Average γ	η (Fig. 3)	η/γ(av.)
k_{I} (ml/m^2 min)	0.49	0.46_5	0.48	0.93	1.9
k_{II} (ml/m^2 min)	0.018	0.015	0.016_5	0.101	6.1
k_{III} (ml/m^2 min mm Hg)	0.0078	0.007	0.007_5	0.014	1.9
$k_{\text{I}}/k_{\text{III}} = k_1/k_3$ (mm Hg)	63	66.5	65	66	
$k_{\text{II}}/k_{\text{III}}$ (mm Hg)	2.3	2.15	2.2	7.2	

[a] k_{I} and k_{II} are the rate constants of ethylene and ether formation, respectively, according to the Langmuir-Hinshelwood mechanism; k_{III} is the rate constant of ether formation according to the Rideal-Eley mechanism.

k_{III} can be obtained from the slope and k_{II} from the vertical position of the straight part of the v_{ether} curve.

Table I gives the values of k_{I}, k_{II}, and k_{III} derived from the data of Fig. 2 and Fig. 3 and, moreover, from another set of curves obtained with a separate series of results with γ-Al_2O_3 of the same batch as those of Fig. 2.

With regard for the reactions (1) and (3) we see that η-Al_2O_3 is about 1.9 times as active as γ-Al_2O_3; with regard to reaction (2) (the Hinshelwood-Langmuir mechanism of the ether production) η-Al_2O_3 is more than six times as active as γ-Al_2O_3.

B. The Surfaces of the Two Aluminas

All kinetic results have been expressed per m^2 of active surface. Separate experiments have shown that the surface areas of these aluminas, both stabilized at 800°C, do not alter during this catalytic action.

Both η and γ aluminas crystallize in somewhat deformed spinel lattices. Due, however, to pseudomorphic relations with the parent hydroxide or oxide-hydroxide, respectively, their surfaces differ. The surface of η-Al_2O_3 made from bayerite is mainly formed by the (111) plane of the spinel, while the surface of the γ-Al_2O_3 from well-crystallized boehmite is formed by the (110) plane of the spinel (*21*). If, in the active aluminas with their large specific areas bringing roughly 15% of all oxygen ions in the surface, the same lattice constants still comply (the atomic distances will certainly not differ much) as in the compact spinel, there are 14.8×10^{18} oxygen atoms per m^2 of surface area in the (111) plane and 9.1×10^{18} oxygen atoms per m^2 of surface area in the (110) plane. Ignoring possible vacancies in the surface, these figures may be used for the oxygen packing of the last complete oxygen layers of the crystals.

Perpendicular to the (111) face of the spinel $[Al_8(Al_{13}\,\square_{2\frac{2}{3}})O_{32}]$ there are layers containing only oxygen alternating with layers containing only aluminum. If the last complete outside layer of the spinel is an oxygen layer its valencies (or ionic charges) are, on an average, only half compensated by the aluminum layer underneath. We may, consequently, expect a half-filled aluminum layer on top of the last complete oxygen layer, which aluminum atoms (ions) will be partly drawn into the cavities between the surface oxygen atoms (ions), but their centers are, nevertheless, situated in a plane *above* the positions of the centers of the last complete oxygen layer. We may, therefore, expect $\frac{1}{3} \times 14.8 \times 10^{18} = 4.93 \times 10^{18}$ aluminum atoms on top of the last oxygen layers of the (111) face.

The (110) face of γ-Al_2O_3 will be differently constituted. Perpendicular to the 110 face we find alternating layers, containing $29\frac{1}{3}$ aluminum atoms per 32 oxygen atoms and $13\frac{1}{3}$ aluminum atoms per 32 oxygen atoms, respectively, each compensating either unsaturated oxygen valencies or unsaturated aluminum valencies (or ionic charges) of the layers underneath and above. The last complete layer in this direction, therefore, has either 24 uncompensated aluminum valencies on every 32 oxygen atoms or 24 uncompensated oxygen valencies; hence on top of it we have to expect either a half layer containing 16 oxygen atoms together with $6\frac{2}{3}$ aluminum atoms or a half layer containing 16 oxygen atoms and $14\frac{2}{3}$ aluminum atoms. On the average we may also expect here a number of aluminum atoms equal to $\frac{1}{3}$ of the oxygen atoms, hence $\frac{1}{3} \times 9.1 \times 10^{18} = 3.03 \times 10^{18}$ aluminum atoms per m^2. These aluminum atoms are, however, surrounded by oxygen atoms of their own layer and they are, partly, incorporated in tetrahedral holes and in octahedral holes; their centers are situated in the same plane as those of the $\frac{1}{2} \times 9.1 \times 10^{18} = 4.55 \times 10^{18}$ oxygen atoms of this upper half layer.

These considerations warrant the conclusions that (1) η-Al_2O_3 has $4.93/3.03 = 1.6$ times as many aluminum atoms per m^2 of outside surface than γ-Al_2O_3 and (2) that the aluminum atoms on top of the surface of η-Al_2O_3 are in a more favorable position to act as an "acid" (Lewis-type) center than those of γ-Al_2O_3. The higher surface concentration together with the somewhat higher activity per center may account for the 1.9 times higher activity of η-Al_2O_3 for reactions I and III, while the higher surface density of the centers, probably involving far more suitable pairs of adsorbed alcohol molecules for reaction II, may account for the six times higher activity of η-Al_2O_3 for this reaction (see Footnote to Table 1).

If the reactions do not proceed via the acid Lewis-type centers, but via surface alcoholates, the higher density of η-Al_2O_3, with 1.6 as many oxygen atoms per m^2 surface area as compared with γ-Al_2O_3 might, perhaps, also be understood in this view. We know, however, from older work done in our research group (*22*) that χ alumina, prepared from gibbsite, gives a gradual decrease of activity during a run, which proved to be caused by a slow diffusion of sodium atoms—resulting from the gibbsite which always contains sodium—from the inside to the surface. This was the reason that we did not include this type of alumina in our present study and also that we prepared the γ-Al_2O_3 and η-Al_2O_3 for this study from completely sodium-free sources.

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