Catalytic Dehydration of Ethanol over Silica-Alumina

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On silica-alumina the dehydrations of ethanol into olefin and ether are parallel surface reactions. The kinetic law for ether production is $v = K\, ap^{1/2}/(1 + ap^{1/2})$; ethylene formation is zero order with respect to ethanol. The role of active sites has been investigated by poisoning the catalyst with pyridine, Na^+ ions, perylene, and tetracyanoethylene; both acids and bases inhibit dehydration. A mechanism is proposed assuming the intervention of basic and acidic sites for the dissociative adsorption of ethanol.

INTRODUCTION

The catalytic dehydration of alcohols on oxides has been extensively studied; two reviews were given on this subject by Winfield (*1*) and recently by Pines and Manassen (*2*), so we shall restrict ourselves to a few references.

For the dehydration of the four lower alcohols on alumina, Knözinger *et al.* (*3*) proposed a kinetic equation of the form $v = kap^{1/2}/(1 + ap^{1/2})$; this equation implies a dissociative adsorption of the alcohol, which is in good agreement with infrared data (*4*) identifying the surface compound on alumina as ethoxide ($C_2H_5O\text{-}Al\langle$).

DeBoer and co-workers (*5*) showed that both Langmuir-Hinshelwood and Rideal-Eley mechanisms occur simultaneously on alumina; their relative importance is connected with the hydration state of the surface: On a highly dehydrated solid like that used by the authors, the second process is predominant, but with a more hydrated catalyst the first one can be more important. Some disagreements in the literature may find here an explanation.

Our own work on the adsorption of ethanol on silica-alumina (*6*) supports the mechanism proposed by Knözinger, and recently (*7*) we proved that basic sites of alumina and silica-alumina play a major

role in dehydration, as previously suggested by Pines *et al.* (*8*).

This work is devoted to the kinetics of ethanol dehydration and correlatively to the nature of active sites of silica-alumina.

METHODS

Apparatus. The measurements were performed in a flow reactor described previously (*9*).

Catalysts. We used three solids without preheating; these were as follows: γ-Alumina—prepared from aluminum nitrate and ammonia. The alumina gel was washed until it was free of ammonia, then dried 24 hr at 120°C and calcinated at 500°C. X-Rays identified it as γ-alumina; surface area, 230 m²/g. Commercial silica-alumina (Ketjencat) with 13 wt % alumina, surface area 700 m²/g—it will be noted K 13. A solid obtained from K 13 by selective extraction of aluminum—the final product contained 2.1 wt % alumina and its surface area was 720 m²/g; it will be referred to as K2.1.

Poisoning of these catalysts was carried out in solution. For tetracyanoethylene and trinitrobenzene the experimental procedure was as follows: 0.5 g of catalyst was agitated overnight with 100 ml of a benzenic solution 0.01 M; after filtration, the solid

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was washed twice with 100 ml benzene, then dried. For perylene a saturated solution was used. A blank was made by the same procedure without addition of poison.

Na$^+$ ions were introduced by exchange; the experimental method was that described by Barthomeuf (15).

RESULTS

A. Kinetics of the Reaction

This study was mainly carried out with silica-alumina K 13.

1. Influence of the Partial Pressure of Ethanol

The products consist of ethylene as well as of ether. Figure 1 gives three sets of results obtained at 138°, 180°, and 220°C. This figure shows that ethylene production at 180°C tends to become a zero order reaction at ethanol pressures as low as 5 torr; in contrast, at 180°C ether production tends to zero order only at alcohol pressures greater than 50 torr. At 138°C, 20-torr partial pressure of ethanol is sufficient to reach a zero order in ether formation. Both reactions can be found with zero order. Even at low pressures, and at 220°C we never found
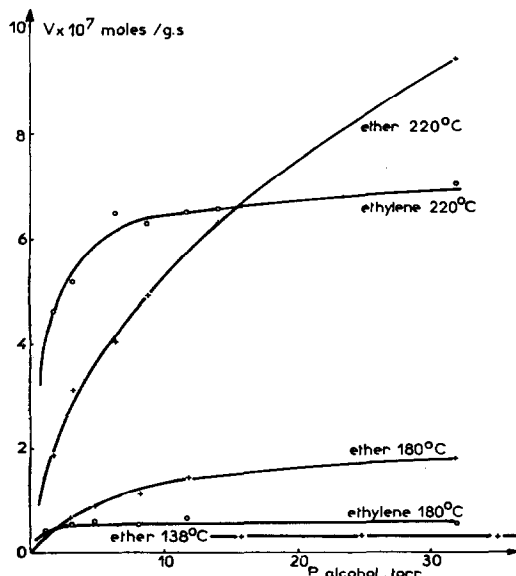
an order greater than 0.5. So the mechanism follows a Langmuir-Hinshelwood scheme on our silica-alumina catalyst.

The equation better fitting our experimental results for ether production is $v = k_1(ap)^{1/2}/[1 + (ap)^{1/2}]$ at 180°C, which reduces to $v = kp^{1/2}$ at 220°C. As said before, the first equation was proposed by Knözinger (3) for the dehydration of several alcohols on alumina, in the same range of temperature as ours. This equation implies a dissociative adsorption; we shall see later that this is consistent with the need for basic and acidic sites for dehydration. As ethylene production is zero order the relation between rate and pressure cannot be found directly; we shall obtain it from the study of the influence of water.

2. Influence of the Partial Pressure of Water

This permits check of the validity of the kinetic equation. It is known from the literature (10, 11) that water has a strong influence on the dehydration rate. Experiments were carried out under such conditions that the reaction be zero order. Figures 2 and 3 give the results obtained; from these we can conclude that alcohol and water compete for adsorption.

For ether at 138°C the equation $v = k_1(ap)^{1/2}/[(ap)^{1/2} + bp_w]$, where p_w is the water pressure, represents well the experimental data; this is a confirmation of the equation previously proposed.

For ethylene formation a similar equation is obtained at 180°C (Fig. 3), $v = k_2(cp)^{1/2}/[(cp)^{1/2} + dp_w]$; this equation was also proposed by Knözinger (3) for the dehydration of tert-butanol on alumina.

3. Influence of Ethylene

The rate is measured here by ether production; experimental results, listed in Table 1 show that addition of ethylene to

FIG. 1. Experimental results obtained at 138°, 180°, and 220°C with K 13 silica-alumina.

TABLE 1

INFLUENCE OF ETHYLENE PARTIAL PRESSURE
ON ETHER PRODUCTION RATE AT 185°C,
ALCOHOL PRESSURE, 32 TORR

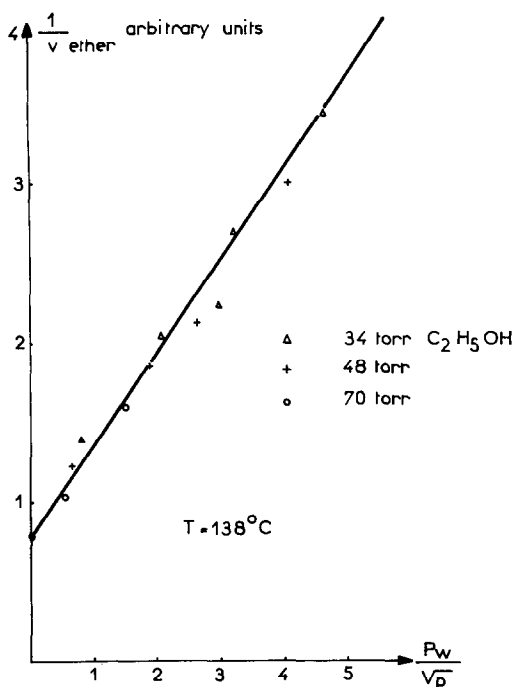| Ethylene pressure	0	10.6	21	31.5
Rate $\times 10^7$ (moles/sec g)	6.74	6.47	6.56	6.4

FIG. 2. Plot of the equation $v = k(ap)^{1/2}/[(ap)^{1/2} + bp_w]$, for ether formation rate at 138°C.

ethanol does not give any significant variation on the rate.

We can conclude that ethylene is not appreciably adsorbed under the reaction conditions.

4. Influence of Ether

We made some experiments in an attempt to obtain some results on the mechanism of ethylene formation from ether decomposition. This study is difficult because traces of water greatly inhibit ether decomposition (Table 2).

TABLE 2
RATE OF DEHYDRATION OF ETHER AND
INFLUENCE OF THE REAGENT PRESSURE

Ether pressure (torr)	63.6	180	400
$10^7 \times v_{170}C_2H_4$	0.66	0.67	0.47

The results in Table 2 are representative of a zero order reaction inhibited by water; the rate constant is 0.66×10^{-7} mole/sec g at 170°C. By comparison the rate constant obtained for ethanol dehydration, at the same temperature, is $k_{170} = 0.44 \times 10^{-7}$, so
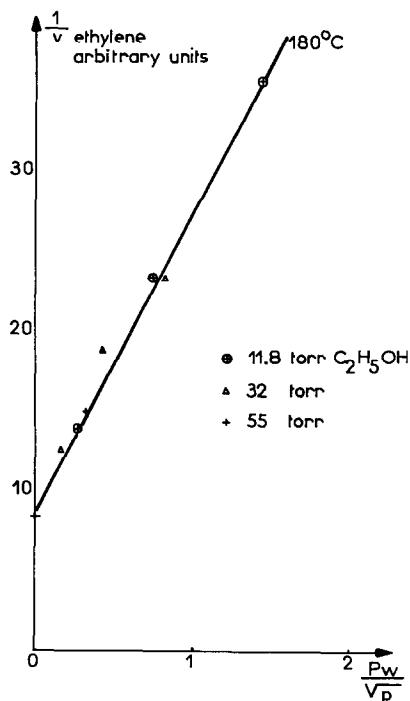
FIG. 3. Plot of the equation $v = k(cp)^{1/2}/[(cp)^{1/2} + dp_w]$, for ethylene production rate at 180°C.

pure ether decomposes slightly faster than ethanol.

Balaceanu and Jungers (11) have shown that dehydration is strongly inhibited by ethanol and water. From their results we can predict that the adsorption coefficient for ether at 170°C will be 10 times lower than the coefficient for ethanol and for water. We have seen that ether dehydration rate is of the same magnitude as alcohol decomposition rate; as ether coverage will be much lower than ethanol coverage, the decomposition of ether cannot explain the observed rate for ethylene formation, at least at low conversions. We are led to think that ether is not an intermediate for ethylene production in our temperature range.

5. Coefficients of the Kinetic Equations

These coefficients can be obtained from experimental results by plotting $1/v$ versus $1/p^{1/2}$; the slope gives $1/ka^{1/2}$ and the intercept at origin gives $1/k$ (Fig. 4). $b/a^{1/2}$ and $d/c^{1/2}$ are obtained from a similar plot of $1/v$ versus $p_w/p^{1/2}$ (Figs. 2 and 3). Table 3
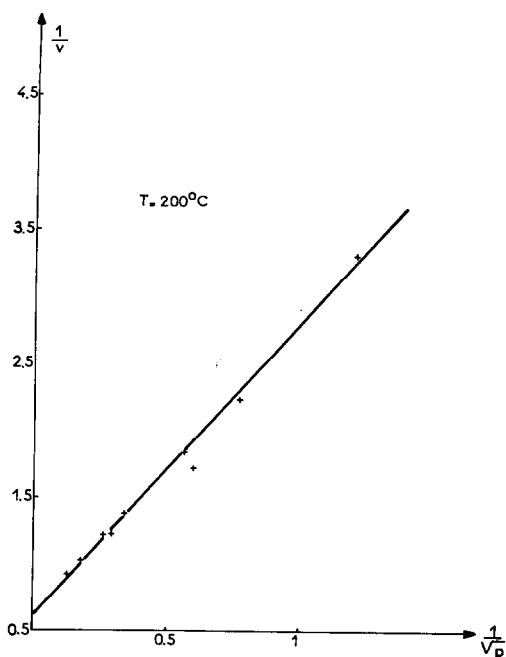
FIG. 4. Plot of the equation $v = k(ap)^{1/2}/[1 + (ap)^{1/2}]$, for ether formation rate at 200°C; calculation of k and $a^{1/2}$.

gives the set of values obtained at 180°C. These coefficients are equilibrium constants and can be written

$$a = \exp\left(\frac{-\Delta G}{RT}\right) = \exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right)$$

ΔG, ΔH, ΔS are the thermodynamic functions corresponding to the transfer of 1 mole from the gas phase to the adsorbed layer.

TABLE 3
ADSORPTION COEFFICIENTS AT 180°C

$a^{1/2}$	$b/a^{1/2}$	b	$d/c^{1/2}$
0.08	2.15	0.17	0.43

Making the usual assumption that the variation of ΔS with T is negligible we get

$$\frac{d \log a}{d(1/T)} = -\frac{\Delta H}{R} = \frac{Q_e}{R}$$

For $b/a^{1/2}$ we have

$$\frac{\log (b/a^{1/2})}{d(1/T)} = \frac{d \log b}{d(1/T)}$$
$$- \frac{1}{2}\frac{d \log a}{d(1/T)} = Q_w - \frac{1}{2}Q_e$$

The knowledge of a and ΔH at a particular temperature allows the calculation of ΔS since $\log a = (\Delta S/R) - (\Delta H/RT)$.

Results obtained from ether formation rate. (a) The heat of adsorption of ethanol on the sites producing ether is $Q_e = 25.6$ kcal/mole. Wade et al. (12) obtained 22 kcal/mole for the heat of adsorption of ethanol on alumina in the working state, so the heat encountered here is likely.

(b) The heat of adsorption of water is 18 kcal/mole, drawn from $Q_w - \frac{1}{2}Q_e = 5$ kcal/mole, as obtained from the coefficients. It is known from the literature (13) that the heat of adsorption of water on silica-alumina decreases steeply with coverage; the heat obtained here is a mean value, so 18 kcal/mole seems reasonable.

The internal coherence of these data can be checked by the calculation of the entropy differences in the adsorption of ethanol and water. We choose as standard state 1 atm. We get, for ethanol adsorption, $\Delta S = -51$ e.u., loss of 3 degrees of translational freedom corresponds to $\Delta S = -40$ e.u., for water adsorption, $\Delta S = -31.4$ e.u., complete loss of translational freedom gives $\Delta S = -32$ c.u.

The agreement is quite fair between experimental and theoretical values.

Results obtained from ethylene formation rate. We could only obtain the difference $Q_w - \frac{1}{2}Q_e = 8$ kcal/mole.

6. Effect of Temperature. Activation Energy

The determination of the rate constant k allows the calculation of the true activation energy. For ether this is $E_1 = 28.8$ kcal/mole and for ethylene formation $E_2 = 30$ kcal/mole. The activation energies of the two reactions are very near; this can suggest that the slow step is the same for both reactions.

7. Conclusions

The kinetic study shows that dehydration of ethanol on silica-alumina proceeds via a Langmuir-Hinshelwood scheme. The kinetic equation supposes the dissociation of ethanol on the surface; adsorption studies had led to the same conclusion.
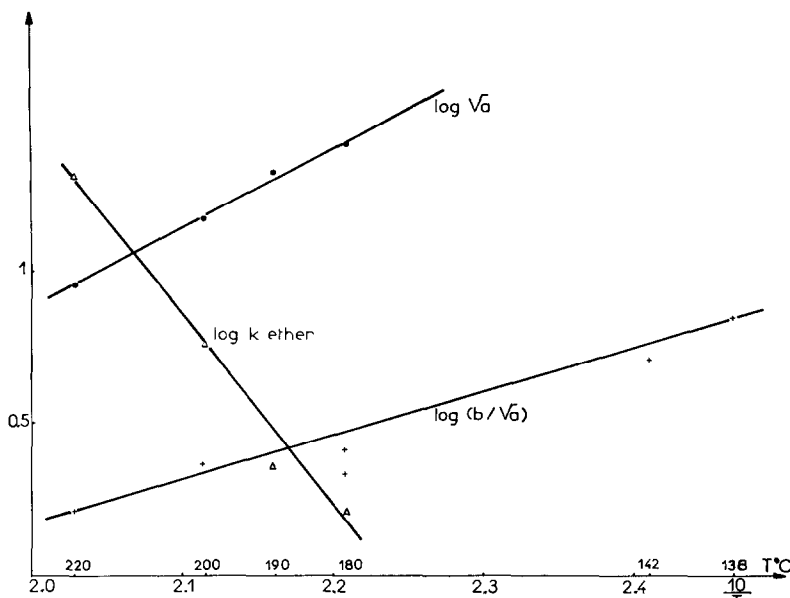
FIG. 5. Plots of $\log a^{1/2}$, $\log b/a^{1/2}$, and $\log k$ ether versus reciprocal temperature.

B. *Nature of Active Sites*

The simpler method for investigating the nature of active sites is to poison them selectively; we tried to do that for acidic and basic centers.

1. *Role of Acidic Sites*

Their importance in dehydration is well known and pyridine adsorption is a means to measure their number. From infrared studies on alumina and silica-alumina (14), it is known that pyridine is adsorbed reversibly on OH groups and irreversibly on acidic sites at temperatures around 200°C. So pyridine adsorption allows a distinction between the two sites; in Table 4 are given the rates obtained with the same catalyst, before adsorption, during adsorption, and after desorption of pyridine. For the measurements during adsorption pyridine was continuously fed to the catalyst under 3 torr together with ethanol.

For the three catalysts investigated, the conclusions are as follows:

The majority of active sites on alumina consist of OH groups, but the activity of silica-alumina is mainly connected with acidic sites, since the reversibility is very poor.

Ether can be produced on OH groups while ethylene is more tightly connected with acidic centers.

2. *Role of Lewis Acid Sites*

This was investigated in two complementary ways.

Poisoning by sodium ions. Na^+ ions exchange with protons and poison Brönsted acidity but not Lewis sites (15); activities and acidities of some exchanged catalysts are listed in Table 5.

As can be seen, Na^+ ions drastically inhibit dehydration, while Lewis acidity is nearly constant.

TABLE 4

INFLUENCE OF PYRIDINE ON DEHYDRATION RATES AT 200°C[a]

Catalyst	Product	Fresh	Adsorption equilibrium	Desorption equilibrium
K 13	Ethylene	2.14	0.14	0.25
	Ether	5.7	0.54	1.67
K 2.1	Ethylene	6.9	0.12	0.19
	Ether	6.17	0.23	1.03
γ-Al$_2$O$_3$	Ethylene	0.38	0.042	0.38
	Ether	7.5	3.95	7.5

[a] Rates $\times$ 10^7 (mole/sec g).

TABLE 5

INFLUENCE OF SODIUM AND PERYLENE ON ACTIVITIES

Catalyst	$v_{C_2H_4} \times 10^7$	$v_{ether} \times 10^7$	Temperature of measurement (°C)	Brönsted acidity	Lewis acidity
K 13 + NaCl	0.33	1.65	180	0.77	—
K 13 + CH₃COONa	0.047	0.043	180	0.5	1.3
K 13 + Na₂CO₃	0.14	0.3	240	0	1.1
K 13 + Na₃PO₄	2	2	340	0	1.2
K 13 + perylene	0.67	2.77	180	—	—
K 13 + benzene	0.6	2.1	180	—	—
K 13	0.51	2.75	180	0.8	1.4

Adsorption of Perylene. This hydrocarbon can adsorb on some Lewis sites (16) and poisoning the catalyst with perylene should shed light on the role of these centers. In fact, perylene has no effect (Table 5) though an EPR signal is obtained with the catalyst impregnated with perylene. So the sites on which this can adsorb do not play any role in the dehydration.

From this series of experiments we can conclude that Lewis acidity is not concerned with activity; this is mainly related to Brönsted acidity.

3. Role of Basic Sites

From a recent work on oxidizing–reducing properties of alumina and silica-alumina (17) it appears that tetracyanoethylene (TCNE) and trinitrobenzene (TNB) can adsorb on centers which can be identi-

TABLE 6

INFLUENCE OF ELECTRON ACCEPTOR ON ACTIVITIES[a]

Catalyst	$10^8 \times v$ ethylene production (moles/sec g)	$10^3 \times v$ ether production (moles/sec g)
K 13 + benzene	6	21
K 13 + TCNE	1.6	5.6
K 2.1 + benzene	13	23
K 2.1 + TCNE	2	7.8
γAl₂O₃ + benzene	0	3.2‡
γAl₂O₃ + TCNE	0	0.22‡
K 13 + TNB	10	36.5
PO₄Li₃	6.1*	4.4*

[a] Rates measured at 180°C, except ‡ at 220°C and * at 300°C.

fied as basic sites if the solid has not been heated at temperatures higher than 500°C. By adsorption of these compounds the role of basic sites can be proved; the activities for ethanol dehydration of the three catalysts at 180°C are listed in Table 6.

Adsorption of TCNE shows that basic centers are necessary for alcohol dehydration, as suggested by Pines (8); basic centers alone are not active since a purely basic solid like PO₄Li₃ is not a good catalyst. TNB does not inhibit the dehydration; it is a weaker electron acceptor than TCNE and reacts only on strong sites which are in small number on silica-alumina.

In conclusion, weakly basic centers are needed for dehydration.

DISCUSSION

Both kinetics and study of active sites support the hypothesis of ethanol dissociation on the surface of silica-alumina; adsorption studies reveal two sorts of ethanol molecules adsorbed:

(a) Very strongly adsorbed ones, in number equal to the number of acidic centers as measured by pyridine adsorption. Since this adsorption is closely related to acidic sites it can be thought to produce a carbonium ion firmly bound to the surface. Inhibition of ethylene production by TCNE supposes an intervention of the basic sites in the carbonium ion formation; a representation of this step could be
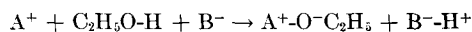
$$C_2H_5OH + A^+ + B^- \rightarrow A^+\text{-}OH^- + B^-\text{-}C_2H_5^+$$
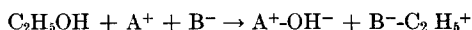
where A^+ is an acidic center and B^- a basic center. Further decomposition of the carbonium ion yields ethylene.

(b) Dissociatively and reversibly adsorbed ones, which we could represent as alcoholate groups, according to Arai *et al.* (*18*). This dissociation could be

$$A^+ + C_2H_5O\text{-}H + B^- \rightarrow A^+\text{-}O^-C_2H_5 + B^-\text{-}H^+$$

Diethyl ether could be formed either by interaction of two alcoholate groups or by reaction of a carbonium ion on an alcoholate, this second process being predominant on silica-alumina.

With the remark that the slow steps are the same for both dehydrations, we could add that carbonium ion formation should be the slow step; this would be in agreement with the mechanism proposed in the liquid phase (E1 mechanism).

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