

Mechanism of Dehydration of Ethanol over γ Alumina

by

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ABSTRACT

The dehydration reaction of ethanol to ether and ethylene was kinetically investigated in a flow system using γ -alumina. Pyridine was found to inhibit the formation of ethylene and ether. The rate of ethylene formation was investigated under steady state and non-steady state conditions and it was found to be zero order. The bimolecular ether formation is described by a first order equation of the Langmuir-Hinshelwood type. The activation energies for ethylene and ether formation were determined. A mechanism based on the participation of a common alkoxide intermediate for both reactions is proposed.

دراسة ميكانيكية نزع الماء من الايثانول باستخدام

جاما - الومينا

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تضمن البحث دراسة كيناتيكية نزع الماء من الايثانول وتكوين الاثير او الاثيلين باستخدام جاما - الومينا . واتضح من الدراسة ان البيريدين يقلل من تكوين الاثيلين في ظروف ثابتة وغير ثابتة ووجد انها تفاعلات من مرتبة الصفر .

وتعد دراسة وتحديد طاقة التنشيط لتكوين كل من الاثير والايثيلين واتضح ان الميكانيكية تعتمد على مشاركة الالكوكسيد كعامل وسيط للتفاعلين في حالة الاثير والايثيلين .

Introduction

The dehydration reaction of ethanol is commonly studied to investigate the catalytic activity of a given alumina. Although a considerable amount of research has been done on this subject, little was concerned with its kinetics. Different mechanisms have been proposed for the dehydration reaction of ethanol. De Boer *et al.* [1] assumed that ether is formed principally by a Rideal-Eley mechanism with a small contribution by the Langmuir-Hinshelwood mechanism. They also concluded that ethylene formation is zero order above 30 torr. Knözinger [2] proposed that ether formation is described by the Langmuir-Hinshelwood mechanism whereas ethylene formation proceeds via an alcohol molecule joined to the surface by two angular H-bonds.

The condensation of two adjacent alkoxide groups to form ether was proposed by Topchieva *et al.* [3], whereas the dissociation of an isolated alkoxide group yields ethylene. The simultaneous formation of ethylene and ether via a common intermediate was proposed by Solomon *et al.* [4]. The effect of pyridine was found by Jain and Pillai [5] to inhibit the formation of ethylene and ether, whereas Beranek *et al.* [6] and Misono *et al.* [7] found that pyridine has no effect on ethylene formation.

This study was carried out to contribute in explaining the mechanism of ether and ethylene formation from ethanol over γ -alumina.

Experimental

Apparatus

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

Materials

1. Catalyst. γ -alumina was prepared by precipitating aluminium hydroxide by aqueous ammonia solution from 10% aluminium nitrate solution. The precipitate was dried at 120°C for two hours and activated at 450°C in air for five hours. The particle size used was 0.4 - 0.6 mm. The BET surface area was found to be 180m².
2. Ethanol. The quality used was Merck absolute which was further distilled in the presence of magnesium and iodine and kept over molecular sieves until used.
3. Nitrogen. A technical product of the IGC in Doha which was purified from the contaminated oxygen by passing over heated copper catalyst.

Procedure

The catalyst was activated at the beginning of each run at 450°C for four hours then it was allowed to cool in a stream of dry and oxygen-free nitrogen. The temperature of the catalyst bed was kept constant during measurements in the range $\pm 0,5^\circ\text{C}$. Ethanol was introduced to the reactor by two different ways. The calibrated burette (B) was used for measurements at relatively high partial pressures and the saturator (C) was used to obtain low partial pressures. In both cases the calculated amount of nitrogen was passed at a constant flow rate. The partial pressure of ethanol was varied by changing both rates of alcohol and nitrogen flow, while keeping their total flow constant. The condensable reaction product was collected in the receiver (F) and was analysed chromatographically. The

noncondensed product was introduced to the chromatograph (G) via gas sampling valve. Standards of ether and ethylene were prepared and analysed with the reaction product.

Analysis

Analysis was carried out using Pye Unicam GCD gas chromatograph with flame ionisation detector. The column used was 0,4 X 180 cm packed with Diatomite (Q.80 - 100 mesh) coated with 10% dinonyl phthalate DNP. Both ethylene and ether were analysed isothermally at 100°C.

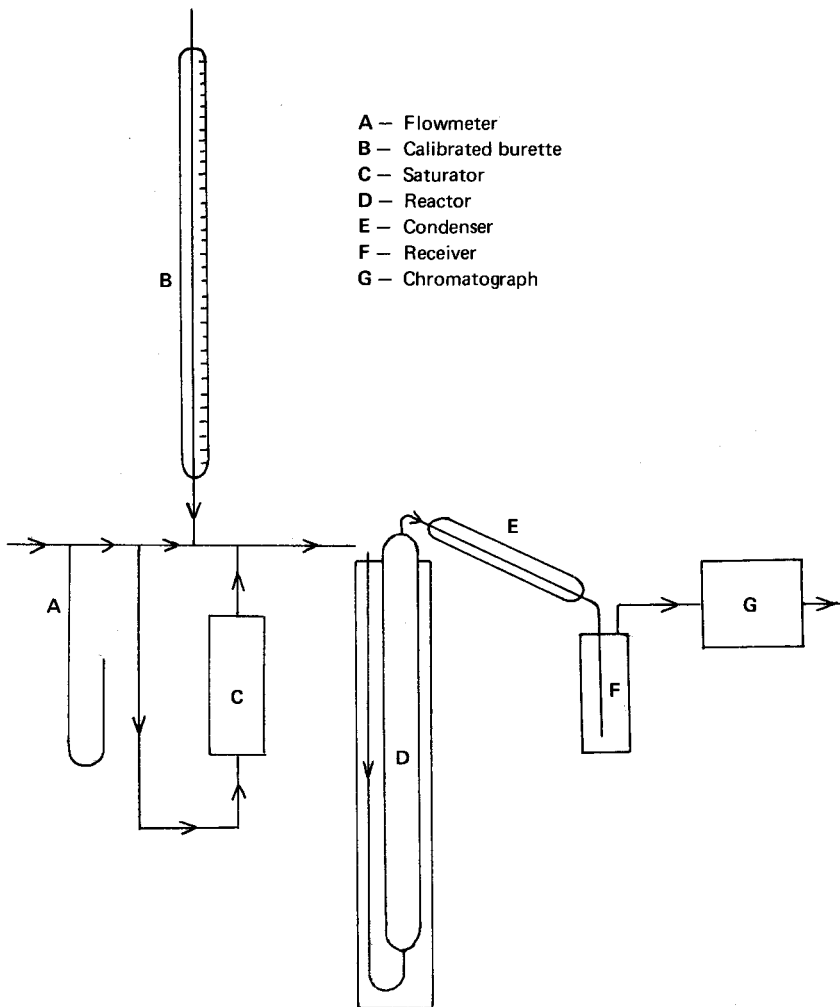


Fig. 1: Schematic diagram of the apparatus.

Results

1. Differentiability

The reactor was operating differentially towards ether formation in the temperature range 185-205°C and towards ethylene formation between 215° and 235°C. The data obtained are given in Table 1.

TABLE 1
Data obtained for reactor differentiability at constant partial pressure of ethanol

Product	Temp °C	Flow Rate Mole/h	Reaction Rate Mole/h l	Conversion %
Ether	185	0,229	0,096	0,419
		0,342	0,102	0,301
		0,445	0,100	0,225
Ethylene	235	0,229	0,056	0,122
		0,342	0,053	0,077
		0,445	0,057	0,064

2. Formation of Ether

In the temperature range 185-205°C using 5 ml. catalyst, the rate of ether formation was measured at different partial pressures of ethanol. The data given in Fig. 2 show that the rate of ether formation is directly proportional to the partial pressure of ethanol up to about 200 torr; then it remains constant above this value. Moreover, the rate is doubled every 10°C in the reaction temperature.

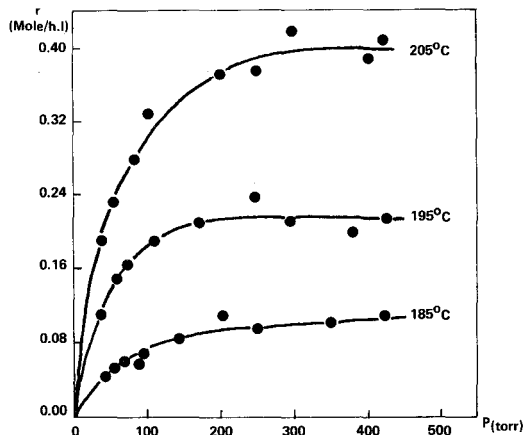


Fig. 2: Rate of ether formation at different partial pressures of ethanol.

The validity of the Langmuir-Hinshelwood models (1) and (2) for explaining the experimental data was tested.

$$r = k_1 \frac{K_1 P}{1 + K_1 P} \quad (1)$$

$$r = k_2 \left(\frac{K_2 P}{1 + K_2 P} \right)^2 \quad (2)$$

The values of k and K were calculated from both models, Table 2:

TABLE 2
Rate constants and adsorption coefficients calculated from models (1) and (2) for ether formation

$^{\circ}\text{C}$	k_1	k_2	K_1	K_2
185	0,12	0,12	0,016	0,032
195	0,21	0,26	0,021	0,034
205	0,43	0,51	0,022	0,038

The experimental data obtained for the rate of ether formation at different partial pressures of ethanol at 205°C were compared with the values calculated from models (1) and (2).

It is observed from Fig. 3 that no conclusion could be made as to whether model (1) or (2) is applicable. However, from measurements carried out at low partial pressures of ethanol (Fig. 4) it is observed that the experimental data conform to a great extent with model (1).

The activation energy for ether formation as calculated from the Arrhenius plot (Fig. 5) is 27,8 kcal/mol./

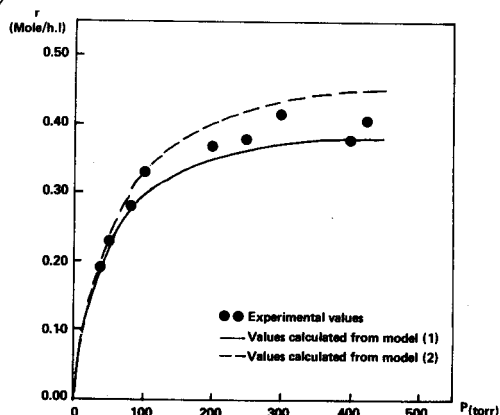


Fig. 3: Rate of ether formation at 205°C and different partial pressures of ethanol.

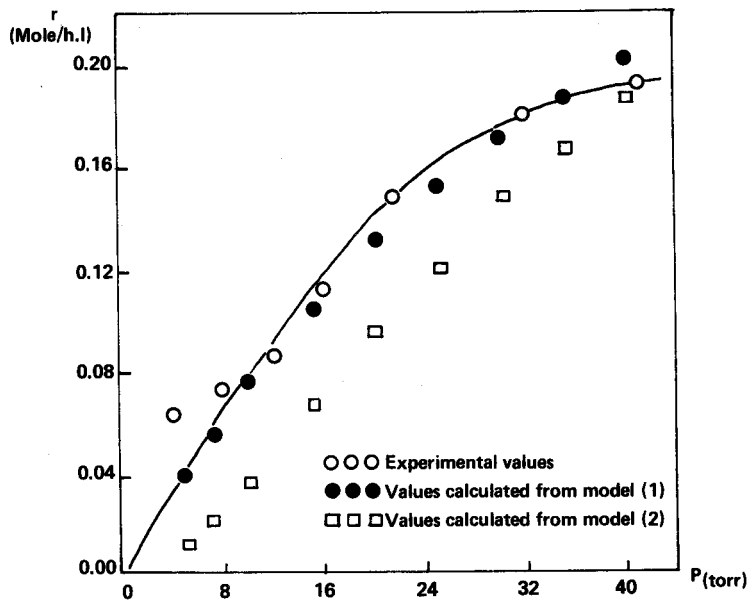


Fig. 4: Rate of ether formation at 205°C and low partial pressures of ethanol.

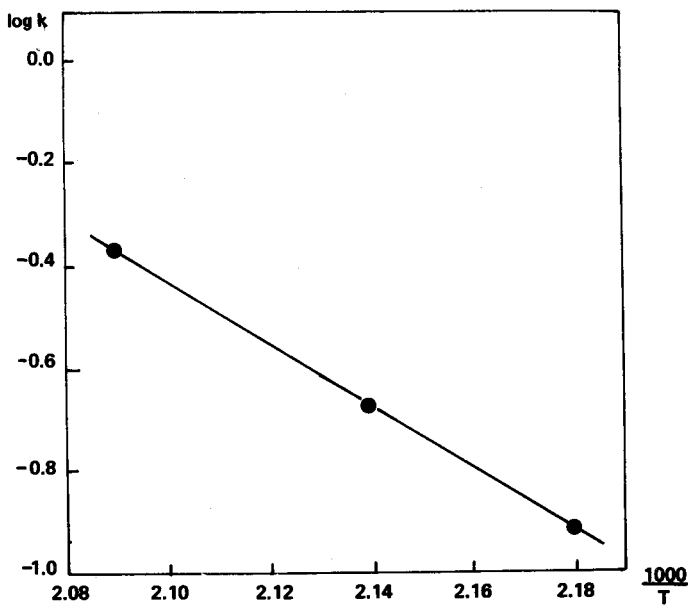


Fig. 5: Arrhenius plot for ether formation.

3. Formation of ethylene

The decomposition of ethanol to ethylene was investigated in the temperature range 215-235°C at different partial pressures of ethanol. The data obtained are given in Fig. 6. It was observed that the rate of ethylene formation is independent of the partial pressure of ethanol and could be considered as a zero order reaction. The effect of temperature on the reaction rate is that, for every 10°C rise in the reaction temperature, the rate is doubled. From the Arrhenius plot (Fig. 7) the activation energy for ethylene formation is 45.8 kcal/mol.

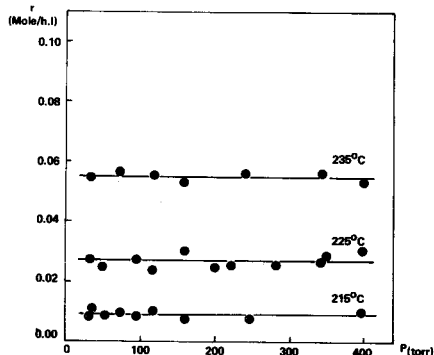


Fig. 6: Rate of ethylene formation at different partial pressures of ethanol.

4. Formation of ethylene in the non-steady state

To investigate the reaction order of ethylene formation at very low partial pressures of ethanol, the reaction was carried out with preadsorbed alcohol. It is observed from the data given in Fig. 8, that the rate of ethylene formation from preadsorbed ethanol remains constant for 50 minutes at a value which equals that obtained at higher partial pressures of ethanol (Fig. 6). The sudden increase in the reaction rate soon after stopping the alcohol feed is explained elsewhere [8].

5. Effect of pyridine

The formation of ether and ethylene was inhibited in the presence of pyridine. The data obtained in Table 3 show that the rate of ether formation was inhibited by 36% of the rate measured in absence of pyridine. The magnitude of inhibition of ethylene formation by pyridine, 69% is nearly double the effect on ether formation.

TABLE 3

Effect of pyridine on the formation of ether and ethylene at 195° and 235° respectively and 195 torr partial pressure of ethanol.

r Mole/h. l	Molar conc. of pyridine in feed		Magnitude of Inhibition
	0%	10%	
Ethylene	0,055	0,017	69%
Ether	0,072	0,049	36%

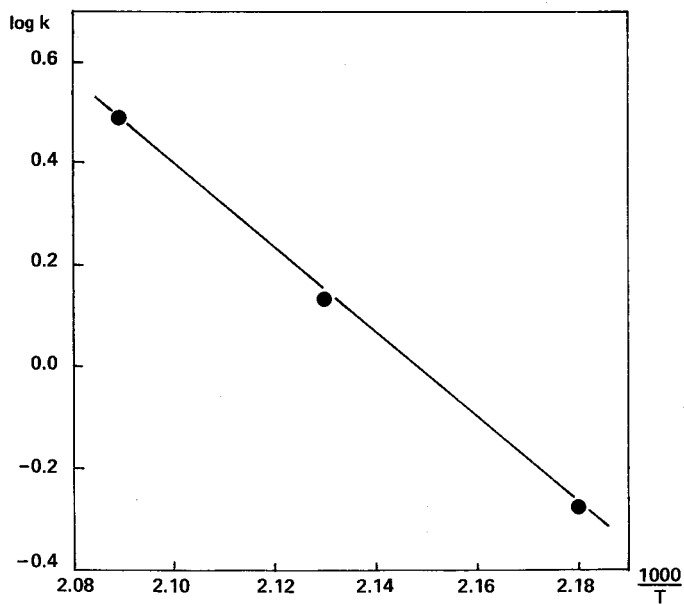


Fig. 7: Arrhenius plot for ethylene formation.

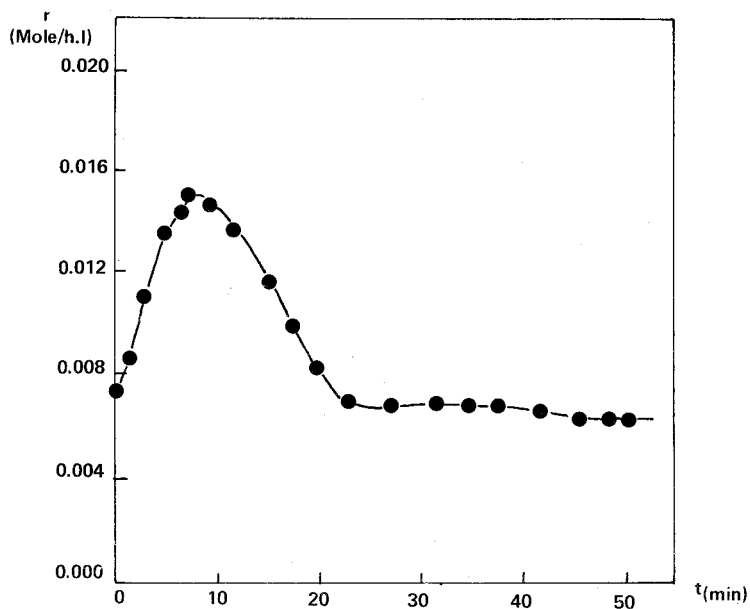


Fig. 8: Rate of ethylene formation from preabsorbed ethanol at 215°C.

Discussion

The data obtained in Table 3 show that pyridine inhibits both ethylene and ether formation. The rate of ether formation is inhibited by 36% of the rate measured in the absence of pyridine whereas the rate of ethylene formation is inhibited by 69%. The inhibition of both products by pyridine may be explained by assuming the existence of a common intermediate which participates in ethylene and ether formation. The surface concentration of this intermediate is decreased in the presence of pyridine in the reaction mixture. However, the great effect of pyridine on ethylene formation compared with its effect on ether formation indicates that ethylene formation depends greatly on the concentration of this common intermediate, whereas for ether formation the participation of another alcohol species is obvious. If ether is formed via the condensation of two adjacent alkoxides the magnitude of inhibition by pyridine would be the same for both reactions.

As pyridine is selectively adsorbed on the incompletely coordinated aluminium [9], it is likely to assume that the formation of this common intermediate takes place over the Lewis acidic aluminium ion centre. The secondary olefin formation is unlikely because of the low concentration of ether produced.

The alkoxide structure has been detected in the IR spectra of ethanol over aluminium oxide [10-14]. Treibmann and Simon [11] concluded from displacement reactions that the alkoxide formation involves incompletely coordinated aluminium ions. Kagel [15] reached the same conclusion on the basis of mass spectroscopic residual gas analysis after adsorption. It follows from the above discussion that the common intermediate required for ethylene and ether formation is the alkoxide group formed on the incompletely coordinated aluminium ion.

The rate of ethylene formation at different partial pressures of ethanol is constant (Fig. 6) and equals the rate measured from preadsorbed ethanol (Fig. 8) which remains constant for about one hour. These results may be explained by assuming that ethylene is formed from a strongly adsorbed ethanol intermediate, alkoxide, the surface concentration of which is independent of the partial pressure of ethanol.

The rate of ether formation as described by the first order equation model (1) requires, in addition to the alkoxide intermediate, a weakly adsorbed alcohol molecule whose concentration depends on the partial pressure of ethanol up to 200 torr. This weakly adsorbed molecule, as assumed to be H-bonded [16], has a nucleophilic oxygen atom which upon attacking the positively charged α -carbon of an adjacent alkoxide by S_N2 mechanism leads to ether formation. It is expected that the nucleophilicity of this oxygen atom will reduce the activation energy required for the cleavage of the C - O, if compared with the energy required for the cleavage of the C - O bond of an isolated alkoxide group. The first case that leads to ether formation requires an activation energy of 27,8 kcal/mol., whereas in the second case ethylene is formed with 45,8 kcal/mol.

Conclusions

1. Ether formation is described by a first order equation of the Langmuir-Hinshelwood type up to 200 torr, whereas ethylene formation is a zero order reaction at any partial pressure of ethanol.
2. Both ethylene and ether are surface reactions in which the alkoxide species is a common participant.
3. Pyridine inhibits both ethylene and ether formation; the first reaction being largely inhibited, indicates its great dependence on the surface concentration of the alkoxide species.

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