Dehydration of Ethanol over HF-treated Al_2O_3 using the GC-column as Chemical Reactor

by

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ABSTRACT

The effect of treating γ-alumina with hydrofluoric acid on the dehydration reaction of ethanol was investigated at 325°C. The gas chromatographic column was used as a chemical reactor. The rate of formation of ethylene and ether was found to increase by such a treatment. The data obtained were explained by assuming that HF-treated alumina has exclusively Lewis acidity.

نزع الماء من الكحول الايثيلي باستخدام اكسيد الالمنيوم المعالج بحامض الايدروكلوريك بجهاز كروماتوجرافيا الغاز كوسيط كيميائي

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(ملخص البحث)

تستخدم الالومينا كعامل حفاز في تفاعلات الكحول الايثيلي الى الاثيلين والاثير والغرض من هذا البحث هو اختيار تأثير معالج الالومينا بحمض الهيدروفلوريك على معدل تكون الايثيلين في درجة ٣٢٥م .

وتدل نتائج هذه الدراسة على ان معالجة الالومينا بحمض الهيدروفلوريك تساعد على زيادة معدل تكون الاثيلين والاثير ، قد فسرت هذه النتائج على اساس ان حمض الهيدروفلوريك يزيد نسبة مراكز لويس الحمضية على سطح الألومينا .

استخدم في هذه الدراسة عمود كروماتوجرافيا الغاز كمفاعل كيميائي ووسيلة تعليل نواتج التفاعل في نفس الوقت .

Introduction

The importance of acid catalysts in the petroleum industry has stimulated a considerable amount of research on the adsorptive and acid properties of solid surfaces, and the correlation of these properties with catalytic activity. In the last few years the reactions of alcohols over acid catalysts has received much attention. From the industrial point of view, the dehydration of alcohols has no importance because alcohols are produced by the hydration of olefins. However, the importance of studying the dehydration of alcohols arises from the fact that it is considered as a model reaction, as well as the reaction of amines, for investigating the nature of active centres present on the surface of acid catalysts and hence their catalytic activities may be explained.

Reactions of alcohols and amines over alumina have been studied from different points of view:

1. Kinetics of dehydration and deamination reactions.
2. Investigation of the nature of the chemisorbed molecules by spectral analysis.
3. Measurement of heats of adsorption.
4. Effect of alcohol and amine structure on the reaction rates.
5. Effect of catalyst preparation, poisons and promoters on the course of the reaction.

In spite of this intensive study there is no agreement in the literature about the mechanism of the dehydration of ethanol. Although the majority of authors [1, 2] agree that both acidic and basic sites are involved in the dehydration of ethanol over alumina, some of them [3, 4] suggest that only the surface hydroxyl groups are responsible for such a reaction.

Topchieva and co-workers [3] suggested that ethanol reacts through the formation of an alcoholate intermediate with the surface hydroxyl groups.

Pines and Manassen [1] suggested that both acidic and basic sites on alumina surface are involved. The formation of ethylene proceeds via the abstraction of the β-proton, from a strongly adsorbed alcohol molecule, by a basic site.

Knözinger [2] proposed that ethanol molecules are adsorbed on the surface of alumina in two different forms, a strongly adsorbed molecule with a positive alkyl group and a weakly adsorbed molecule through H-bond. At higher temperatures the positively charged alkyl group decomposes to ethylene. The reaction of diethylamine over alumina was proposed by Fikry and Pašek [5] to proceed in a way similar to that of ethanol. The strongly adsorbed ethanol was suggested by Jain and Pillai [6] to form intermediate carbonium ions which give rise to olefin.

The effect of treating alumina with HCl and HF on its catalytic properties was investigated. Both Fikry [7] and Ogasawara et al. [8] suggested that HCl-treated alumina has exclusive Lewis acidity. Parera [9] reported that HF-treated alumina presents protonic acidity.

In the light of the foregoing review it was thought that by increasing the Lewis acidity on the surface of alumina the rate of both olefin and ether formation would be increased. Such a result would be in agreement with the mechanism proposed by Knözinger [2].

In this work the effect of treating γ-alumina with HF on the dehydration of ethanol was investigated.

Experimental

Apparatus
The reaction was carried out on the two columns of the Pye Unicam G.C.D. gas chromatograph with thermal conductivity detector. The HF-treated alumina catalyst was placed in the heated zone of the measuring column and the fresh alumina catalyst was placed in the same zone of the reference column. The amount used of both samples was 0.25 gm. which occupied a length of 2 cm. The rest of the column length was left for analysis of the reaction products. The catalyst temperature was adjusted by the temperature control knob which was previously calibrated by measuring the actual temperature of the heated zone.

Catalyst
γ-alumina was prepared according to the standard procedure [10]. Treatment with HF was carried out by impregnating 2.0 gm. alumina with 75 ml. of 0.1 N HF for 20 hours; it was then filtered, dried at 120°C and sieved to remove the fine particles produced by such procedure. The amount of HF taken by alumina was found to be 0.6 mg/g. alumina.
    Fresh alumina was impregnated in distilled water under the same conditions.

Chemicals
Ethanol: BDH of the distillation range 78 to 78.5°C, purity 99.7% : 100% v/v.
Hydrofluoric acid: 4% analar of BDH company.
Nitrogen: The nitrogen used was produced by IGC, Doha, with purity 99%.

Procedure
The same volume of ethanol was injected in the two columns simultaneously. The peaks of the reaction product components eluted from both columns were compared on the basis of their heights. Any factors, external or internal, that might have interfered in the course of the whole reaction were compensated for by such an arrangement. The difference in the peak height of a certain component was then attributed to the presence of HF on the surface of alumina in the measuring column only.
    The volume of ethanol injected ranged from 1 to 9 ul. Every sample was injected at least five times and the mean peak height was considered as a measure of the relative reaction rate. The data obtained were highly reproducible.

Analysis
As described above the reaction was carried out and the product was analysed in the same chromatographic column. Two glass columns were used each 1.98 m. long and 4 mm. internal diameter. They were packed with Diatomite (Q. 80-100 mesh) coated with 10% PEG. Column preparation was done according to the standard procedure reported [10]. The flow velocity of the nitrogen carrier was 17 ml./min. The chromatograms were recorded on a Philips recorder PM 8251. The reaction products are shown in the chromatogram Fig. 1, whereas a chromatogram showing a mixture of ethylene, ether, ethanol and water is given in Fig. 2. The analysis was carried out isothermally at 100°C and sensitivity 10/8.
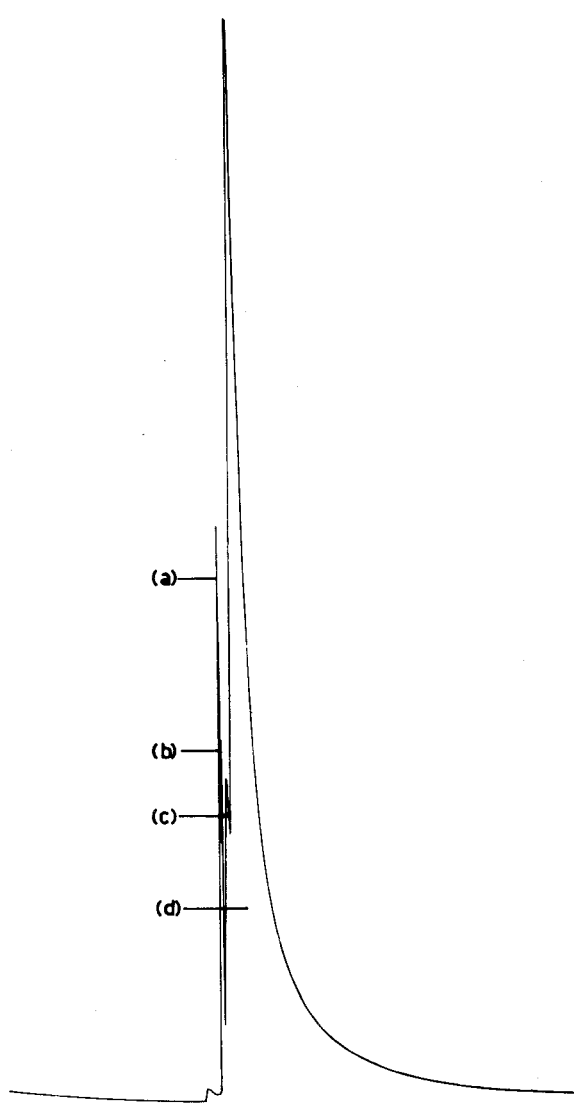
Fig. 1: Chromatogram of the reaction mixture containing (a) ethylene, (b) ether, (c) ethanol and (d) water.
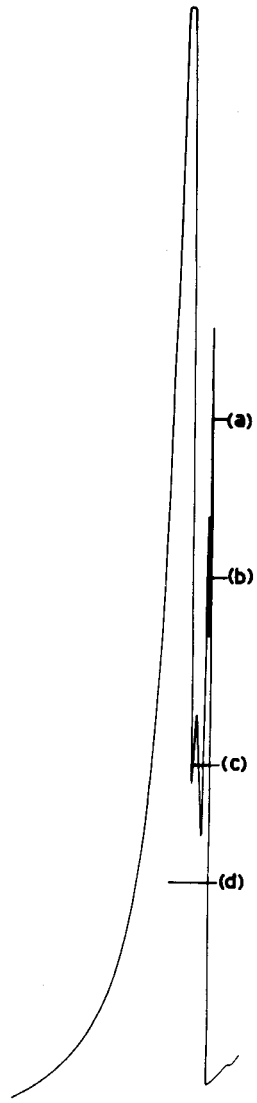
Fig. 2: Chromatogram of a mixture containing the same components as the reaction mixture (a) ethylene, (b) ether, (c) ethanol and (d) water.
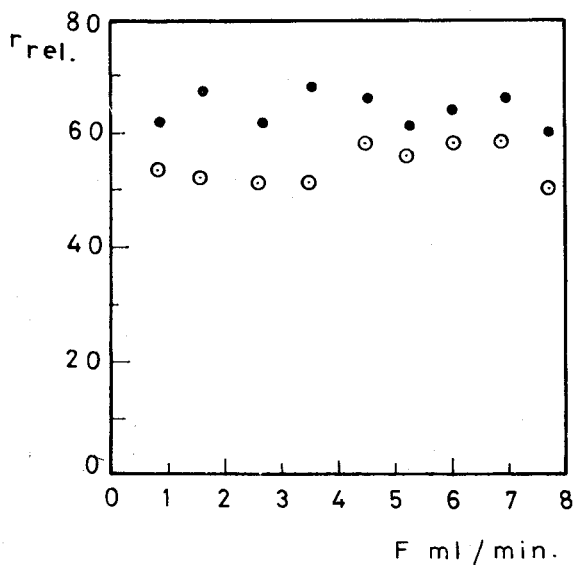
Fig. 3: Effect of flow velocity of ethanol
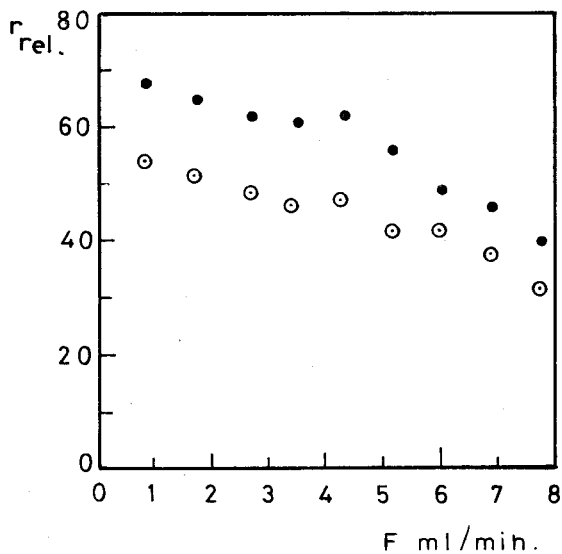vapour on the rate of ethylene formation over
alumina ⊙ and HF-alumina ●

Fig. 4: Effect of flow velocity of ethanol
vapour on the rate of ether formation over
alumina ⊙ and HF-alumina ●

Results and Discussion

The dependence of the rate of ethylene formation, expressed in terms of peak height, on the flow velocity of ethanol vapor was investigated at 325°C. The data obtained over HF-treated alumina and fresh alumina are given in Fig. 3.

It is observed that the rate of ethylene formation over both catalysts is constant under the whole range of the operating flow velocities. This may be explained by the existence of a strongly adsorbed alcohol molecule whose concentration is constant irrespective of the operating flow velocity of ethanol vapor. This strongly adsorbed form decomposes to olefin after receiving the required activation energy for the cleavage of the C-O bond. This result is in agreement with the S_N1 mechanism proposed by Knözinger [2] and Fikry *et al.* [11] for the formation of olefin from ethanol and diethylamine respectively.

The rate of ether formation over both catalysts was investigated under the same experimental conditions. The data obtained in Fig. 4 are for fresh alumina and HF-treated alumina.

It is observed that the rate of ether formation decreases over both catalysts as the flow velocity increases while such relation is not observed in the formation of ethylene. This behaviour could be explained by the S_N2 mechanism adopted by Knözinger [2] for ether formation and proposed by Fikry *et al.* [11] for the formation of triethylamine from diethylamine. This proceeds via the interaction of a weakly adsorbed molecule with another molecule which is strongly adsorbed. The concentration of the first species decreases as the flow velocity increases i.e. as the contact time increases. If the concentration of the strongly adsorbed species is also decreased by increasing the flow velocity the rate of ethylene formation over both catalysts (Fig. 3) would be decreased too.

By comparing the results obtained for ethylene and ether formation over both catalysts, it is observed that HF-treated alumina is more active for both reactions than fresh alumina. This result may be explained on the basis that HF-treated alumina has more Lewis acidity than fresh alumina. Lewis acid centres were supposed to be responsible for the strong adsorption of alcohol and amines over alumina [2, 11]. Ogasawar *et al.* [8] from the infrared of the adsorbed state of aniline on alumina and HCl-treated alumina concluded that HCl-treated alumina has exclusively Lewis acidity.

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