JOURNAL OF CATALYSIS 87, 452–460 (1984)

Transient Behavior of the System Ethanol–Diethyl Ether–Water–Alumina

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Received May 31, 1983

The reactions of ethanol and diethyl ether on alumina have been studied by stopped-feed, started-feed, and pulse-flow techniques at 250°C. In pulse-flow experiments, the reactants were introduced both on a fresh alumina surface and on a surface covered by reaction components during steady-state operation. The results indicate that surface ethoxide is the reaction intermediate in all transformations. From the alcohol, it is formed by the substitution of the surface hydroxyl groups under liberation of water and then decomposes relatively slowly into ethylene; also 2-butanol and 2-methyl-2-propanol behaved in this way. A general scheme for reversible surface reactions of alcohols, ethers, and water with surface hydroxyl and alkoxide groups is proposed. The possibility of the participation of alkoxides in the steady-state dehydration of alcohols is discussed. The distinction between fresh and working surfaces of alumina is stressed.

INTRODUCTION

A number of authors (*1–14*) have proved by ir investigations that alcohols are adsorbed on alumina reversibly by hydrogen bridges and irreversibly as surface alkoxides or carboxylates. In respect to dehydration of alcohols to alkenes and ethers, the carboxylates constitute a dead-end pathway whereas the other two forms are possible reaction intermediates. Also ethers are adsorbed either molecularly, by hydrogen bridging, or dissociatively as two surface alkoxides (*7, 8*). The mechanism of ether formation from the alcohols has been studied mostly by Knözinger and co-workers (*7, 10, 15, 16*) who brought strong evidence that the key step is the reaction of a surface alkoxide with a weakly adsorbed alcohol. This conclusion is also supported by the pulse-flow experiments of Hattori and Murakami (*17*).

For the mechanism of alkene formation from the alcohol, two proposals have competed for a long time. Already before 1920 Sabatier (*18*) had suggested a two-step mechanism consisting in the formation of surface alkoxides which were considered to decompose to alkenes. A cyclic mechanism was later proposed by Eucken and Wicke (*19*) in which cooperation of an acidic and a basic surface center was regarded as being required for the splitting of the C_α-OH and C_β-H bonds, respectively. Some authors (*20–22*) prefer the latter mechanism, basing their views on strong stereochemical and other evidence. However, the alkoxide mechanism has also been advocated (*23–28*) and some newer observations support it. The surface alkoxides give alkenes by thermal treatment (*8, 26*). When a pulse of ethanol is led over alumina, ether formation stops with disappearance of the alcohol from the gas phase whereas the production of ethylene continues for some time (*17*). Koubek *et al.* (*27*) found that the rate of production of an alkene increases after stopping the alcohol feed and then decreases slowly for a long time; this finding can be explained by assuming that the "stored" form of the alcohol is identical with the well-evidenced surface alkoxides. Sadovnikov and Geffer (*28*) have observed rapid water release from the system when a pulse of 2-propanol was introduced in a carrier gas onto alumina, followed by a slower

0021-9517/84 $3.00

production of propene; this was interpreted as a proof of the formation of surface alkoxides by the reaction of the alcohol with surface hydroxyl groups and their slow decomposition.

The transient response techniques (pulse-flow and stopped-feed) have thus indicated their possibilities for the elucidation of the problem of the dehydration mechanism. Therefore, we have studied the system alumina–ethanol–diethyl ether–water using this approach with the aim to obtain more knowledge of the role of surface alkoxides. To the aforementioned methods we have added the perturbation of a steady-state process by a pulse of a product or another substance; this has yielded information on surface species and their reactivities in the situation when ethylene and diethyl ether are produced at constant rate. Also the transient behavior after starting the ethanol feed was briefly studied.

EXPERIMENTAL

Catalyst. Pure aluminum oxide Pural SB (Condea Chemie, FRG) calcined at 600°C, particle size 0.16–0.25 mm, has been used; surface area (BET) 206 m^2g^{-1}, the maximum on the pore size distribution curve around 4 nm, overall acid-site concentration by 1-butylamine titration 0.20 mmol g^{-1}, of sites with $H_0 > -8.2$ amounting to 0.075 mmol g^{-1}, basic-site concentration (according to (*30*)) 0.294 mmol g^{-1}, of strongly basic sites 0.129 mmol g^{-1}. Before experiments, each catalyst sample was standardized *in situ* by heating to 460°C for 5 h in a dry nitrogen stream.

Reactants. Ethanol (99.5%) was dried by Mg, distilled, and kept in sealed flasks; water content was 0.05 to 0.08 mol%. Methanol (Lachema, pro analysi) was dried in the same way. Diethyl ether was dried by sodium. Ethylene was of polymerization grade quality. Water sample, 99.9% ^{18}O (Ventron), was used as obtained.

Gases. Hydrogen was purified in a Deoxo unit and dried by molecular sieve 4 Å. Nitrogen was led over a reduced copper catalyst in order to remove oxygen and over molecular sieve 4 Å to remove water.

Apparatus. A flow apparatus was used which allowed both stationary and pulse experiments. Ethanol was fed from a syringe, and diethyl ether by saturation of the carrier gas. The reactor was a steel tube (i.d. 4 mm) with connections made from copper capillary tubing using Swagelok fittings. Great care was taken to minimize all dead space in order to achieve rapid concentration changes in transient experiments. The effluent from the reactor was led through a heated three-way sampling valve for direct introduction of the gaseous reaction mixture into the gas chromatograph. For pulse experiments, a septum was available at the top of the reactor.

Analysis. The products from the reactor were analyzed gas chromatographically, using a 2-m column with Porapak P and Q (1:4), hydrogen as the carrier gas, and a thermal conductivity detector (Gow-Mac, Model 40 05). The temperature of the column was 90°C. Quantitative evaluation of the chromatograms was based on peak height and preceding calibration. In experiments with $H_2{}^{18}O$, a quadrupole mass-spectrometer was used (Finigan, Model 3000).

Stopped-feed experiments. When the steady state was achieved by continuously introducing the reactants at 250°C, the feeding was stopped, a sample of the reactor effluent was taken at a required time after the stop and introduced into the chromatograph. Then the feeding was restarted and when the same steady-state composition was obtained, a new sample at a different time from the moment of the stop was taken and analyzed. This procedure was repeated until the dependences of the concentrations of individual compounds vs time were obtained. In some experiments, also the changes in the composition of the products in the starting period were measured.

Pulse-flow experiments. A small pulse (typically 5 μl) of the compound under study was introduced into the stream of nitrogen using a microsyringe and the products were analyzed at different times after injecting the pulse, using repeated measurements as in stopped-feed experiments. Good reproducibility was observed and the obtained concentration–time curves were smooth.

Experiments with pulses superposed on the steady state. A steady state was attained by feeding ethanol or diethyl ether and then it was perturbed by injecting a pulse of one of the reaction products or methanol into the feed. The change in composition of the reactor effluent and the relaxation to the original steady-state were monitored in the same way as in stopped-feed experiments.

RESULTS

Stopped feeding of ethanol. The interruption of ethanol feed resulted in a rapid disappearance of diethyl ether and water from the products and an increase of ethylene production which passed through a maximum and then slowly decreased (Fig. 1). Ethylene needed 30 to 40 min to reach trace concentration in the effluent. The total amount of ethylene formed after the stop was fairly reproducible and corresponded to 0.40 ± 0.02 mmol g^{-1} or 1.2 × 10^8 molecules m^{-2}. This value agrees well with that given by Koubek *et al.* (*27*) (1.4 × 10^{18} molecules m^{-2}) who have described the maximum on the ethylene curve and called it "stop-effect."

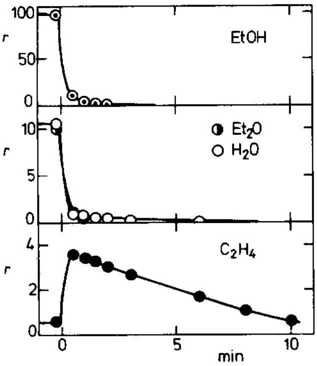


FIG. 1. Output rates of ethanol (EtOH), diethyl ether (Et_2O), water, and ethylene (in mmol h^{-1} g^{-1}) in stopped-feed experiments with ethanol at 250°C. Catalyst weight 314 mg, steady-state operation before stop at space velocity 170 mmol h^{-1} g^{-1}, partial pressure of ethanol 50 kPa, conversion 42%.

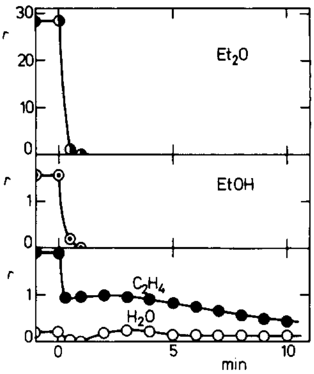


FIG. 2. Output rates of diethyl ether, ethanol, ethylene, and water (in mol h^{-1} g^{-1}) in stopped-feed experiments with diethyl ether at 250°C. Catalyst weight 95.4 mg, steady-state operation for 3 h before stop at space velocity 28.5 mmol h^{-1} g^{-1}, partial pressure of diethyl ether 20 kPa, conversion 7.6%.

Stopped feeding of diethyl ether. At the conditions of the steady state and 250°C, the disproportionation of the ether to ethylene and ethanol predominated (Fig. 2). After stopping the feed, diethyl ether and ethanol disappeared from the system rapidly and ethylene with water were washed out for a long time. When the steady state lasted several hours, a minimum on ethylene and water curves was observed, as depicted in Fig. 2; for shorter duration of the steady state, only a shoulder developed on the ethylene curve. The steep decrease of ethylene output after the stop to approximately half steady-state value and then its continuation in a form resembling that from stop-experiments with ethanol indicate that ethylene is formed from the ether in two different ways, one rapid and one slow.

Start-up of ethanol feed. When the feeding of ethanol was restarted after a pause in which only nitrogen was flowing through the catalyst bed at 250°C, a transient behavior was observed (Fig. 3). More water and less ethylene and diethyl ether are formed in the starting period than in the steady-state. This proves accumulation of alkene and ether precursors on the surface.

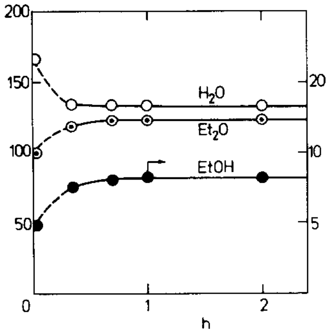


FIG. 3. Output rates of water, diethyl ether, and ethanol (in mmol h^{-1} g^{-1}) after starting the feed of ethanol. Temperature 250°C, 30 mg, partial pressure of ethanol 35 kPa, space velocity 476.5 mmol h^{-1} g^{-1}.

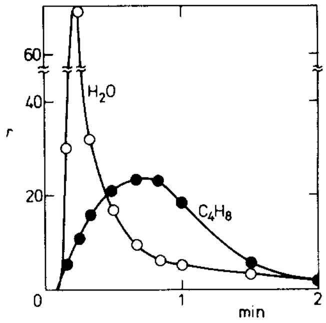


FIG. 5. Output rates (mmol h^{-1} g^{-1}) of water and butenes following a pulse of 2-butanol (5 μl) on 93.8 mg of alumina at 226°C. Flow rate of nitrogen 84 mmol h^{-1}.

Pulse of ethanol. Figure 4 demonstrates the positions of the peak maxima of individual components. Water formation was rapid, decreased steeply at first but then went on for a long time; similar behavior was observed when a pulse of water was introduced alone. The diethyl ether peak was slightly retarded in respect to the ethanol peak but soon reached, after removal of gaseous or weakly bonded ethanol from the system, zero value; a similar observation was reported by Hattori and Murakami (*17*). Ethylene emerged as the last product from the system. The relative positions of the water and ethylene peaks agree with the observation of Sadovnikov and Geffer (*28*) on 2-propanol dehydration. In order to ascertain that the shifting of the peaks is not an artefact, the experiments were repeated using a longer catalyst bed (95.4 mg) where any chromatographic separation would be more pronounced. The distance between the water and ethylene peaks was smaller and the ether peak preceded that of water; this shows that the chromatographic effect caused by higher adsorptivity of water shifts the peaks in reverse direction to the surface reaction. Separate pulse experiments with ethylene confirmed that this product is not adsorbed.

Pulses of other alcohols. Other alcohols behaved similarly to ethanol and 2-propanol (*28*). Experiments with 2-butanol (Fig. 5) and 2-methyl-2-propanol (Fig. 6)

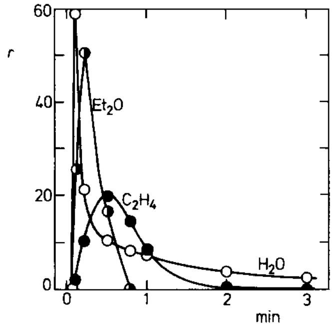


FIG. 4. Output rates (mmol h^{-1} g^{-1}) of water, ethylene, and diethyl ether following a pulse of ethanol (5 μl) on 285 mg of alumina at 250°C. Flow rate of nitrogen 62 mmol h^{-1}. The ethanol peak is omitted for simplification; its maximum coincided with that for water and the curve reached zero value at 0.5 min.

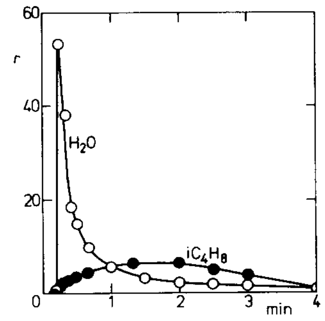


FIG. 6. Output rates of water and isobutene (mmol h^{-1} g^{-1}) following a pulse of 2-methyl-2-propanol (5 μl) on 93.8 mg of alumina at 167°C. Flow rate of nitrogen 84 mmol h^{-1}.

showed rapid output of water followed by slower production of butenes or isobutene, respectively.

Pulse of diethyl ether. In contrast to steady-state operation, in the pulse regime no ethanol was detected and only ethylene and water were formed (Fig. 7). Two distinct regions of ethylene production were observed; at first a sharp peak emerged, followed by a larger one which resembles that from experiments with ethanol. The curve for water production is positioned in the same time period as the second part of the ethylene curve; however, its maximum precedes slightly that of ethylene.

Pulse of water superimposed on the steady-state dehydration of ethanol. The perturbation by water is dramatic (Fig. 8). The formation of ethylene and diethyl ether is inhibited (however, their minima differ slightly) and large amounts of ethanol are displaced from the surface. In 20 min, the original steady state is almost restored. These experiments allow us to conclude that ethanol adsorbed during the steady state can be displaced by water and that no significant amounts of diethyl ether and ethylene are present on the surface.

Pulse of ethanol superimposed on steady-state dehydration of the same reactant. The output of water, ethylene, and diethyl ether was increased for a short time but the original steady state was restored to a great extent in 0.25 min and fully in 1 min.

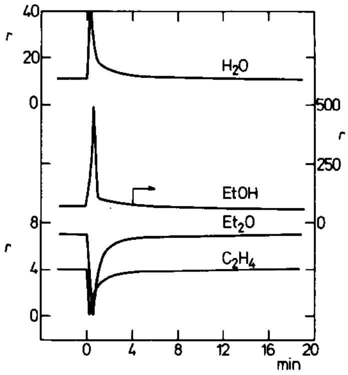


FIG. 8. Output rates of water, ethanol, diethyl ether, and ethylene (mmol h^{-1} g^{-1}) before and after perturbation of a steady-state dehydration of ethanol at 250°C by a pulse of water (5 μl). Catalyst weight 95.5 mg, space velocity 77.5 mmol h^{-1} g^{-1}, partial pressure of ethanol 5 kPa, total conversion approx. 15%. Experimental points are omitted for clarity.

Pulse of water superimposed on steady-state decomposition of diethyl ether. Also the reaction of diethyl ether was strongly perturbed by water pulses (Fig. 9). The formation of ethylene was almost suppressed but recovered rapidly. The curve for ethanol is rather complicated, exhibiting two maxima both reaching over the steady-state

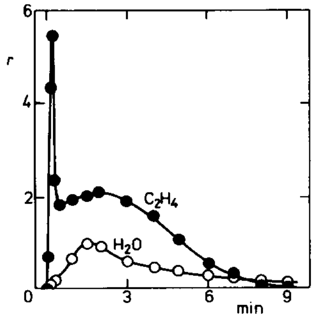


FIG. 7. Output rates of water and ethylene (mmol h^{-1} g^{-1}) following a pulse of diethyl ether (5 μl) on 31.4 mg of alumina at 250°C. Flow rate of nitrogen 114 mmol h^{-1}. The peak of diethyl ether is omitted for simplification; its maximum coincided with the first one of ethylene and the curve reached zero value at 0.5 min.

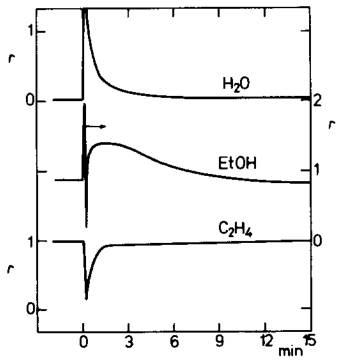


FIG. 9. Output rates of water, ethanol, and ethylene (mmol h^{-1} g^{-1}) before and after perturbation of a steady-state decomposition of diethyl ether at 250°C by a pulse of water (5 μl). Catalyst weight 95.4 mg, space velocity 3600 mmol h^{-1} g^{-1}, total conversion approx. 0.6%. Experimental points are omitted for clarity.

value. The first peak may be caused by displacement of the adsorbed alcohol, formed by disproportionation of the ether, and the second broad peak originated probably from the reaction of adsorbed water with continuously fed diethyl ether (ether hydrolysis).

Pulse of methanol superimposed on ethanol dehydration. Only qualitative analysis was made of the effluent sample taken about 10 s after a methanol pulse was injected. Three different moments of the stopped-feed experiments with ethanol were chosen for introducing a pulse of methanol (5 μl). The first was made at the steady state, the second at 7 min, and the third at 30 min after stopping the feed; the last one corresponded to the situation when no organic products could be detected in the effluent. The first reaction mixture contained, as could be expected, ethylene, water, methanol, dimethyl ether, diethyl ether, methylethyl ether, and ethanol. In the second sample, no ethylene was present and the concentration of the ethers was low but the mixed ether, methylethyl ether, was clearly detected. The third sample showed that methanol was able to displace water in large amounts and still ethanol in traces from the surface.

Exchange experiments with labeled water. The surface of the catalyst was hydrated by 99.5% ^{18}O water vapor at 250°C and, after 30 min purging with dry nitrogen, a pulse of ethanol was introduced onto it. The products were frozen out and analyzed by mass spectrometry; the produced water was labeled to 90%, ethanol to 5%, and diethyl ether to 1%. When the catalyst was heated for 1 h at 460°C in nitrogen, after rehydration with $H_2{}^{18}O$ at 250°C, the same result for water and diethyl ether was obtained and the ^{18}O content in ethanol decreased to 1%. A pulse of unlabeled water onto alumina previously hydrated by $H_2{}^{18}O$ at 250°C, led to only 10% exchange of oxygen with the surface. These experiments show that most water released from the catalyst following its interaction with ethanol comes from the surface and not from the OH groups of the alcohol.

Effect of catalyst activation time on response curves. In stopped-feed-of-ethanol experiments, the effect of catalyst pretreatment was also studied. The height of the ethylene peak increased slightly with the duration of heating the catalyst in a dry nitrogen stream at 460°C. However, the area under the curves, corresponding to the concentration of ethylene precursor, varied only slightly: for 0 h activation it was 0.45 mmol g^{-1}, for 1 h 0.38 mmol g^{-1}, and for 12 h 0.40 mmol g^{-1}. The descending parts of the curves can be correlated by the first-order rate equation in respect to surface concentration of ethylene precursor. Figure 10 shows that there are some deviating points at the beginning and at the end but in general the fit is satisfactory. The rate constants, determined as slopes of the lines in Fig. 10, are 7.5, 9.9, and 10.5 h^{-1}, respectively.

Comparison of output rates of ethylene and water. Also the tail parts of water curves could be correlated by the first-order rate equation with the rate constant of 3–5 h^{-1}, according to the activation and reaction conditions used. The logarithm of the ratio of the rates of ethylene and water production was linear in dependence on time, thus confirming the separate correlations.

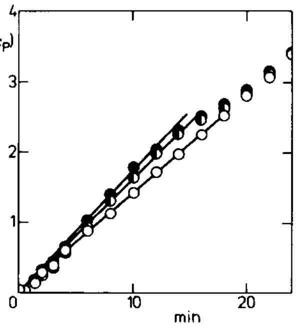


FIG. 10. Correlation of ethylene curves from stopped-feed experiments with ethanol at 250°C in the coordinates of the first-order rate equation. The c_P is the surface concentration of ethylene precursor, c_P^0 is the total concentration in the time of the stop. Activation of the catalyst at 460°C: (○) 0 h, (◐) 1 h, (●) 12 h.

The difference in rate constants shows that both products are formed in independent steps.

DISCUSSION

The interactions of alcohols, ethers, and water with the alumina surface are deep and can be explained only by assuming the formation of relatively stable surface species, that is, surface alkoxides and surface hydroxyl groups. Besides the relatively slow formation of ethylene from the strongly adsorbed alcohol, a number of rapid processes proceed which result in the exchange of hydrogen for alkyl or of hydroxyl for alkoxyl. These reactions can be described by the general reversible Scheme 1 where the surface species **I** and **III** are written according to Knözinger and Ratnasamy (*29*) as bridged structures. The species **II** is hypothetical but some short-lived intermediate must be assumed.

The symbols *X*, *Y*, *Z* denote hydrogen atoms or alkyl groups. The various reactions are summarized in Table 1.

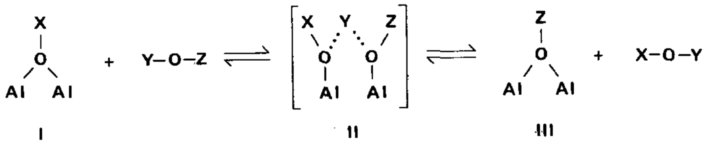
TABLE 1

Reactions Described by the General Scheme 1 [see Text]

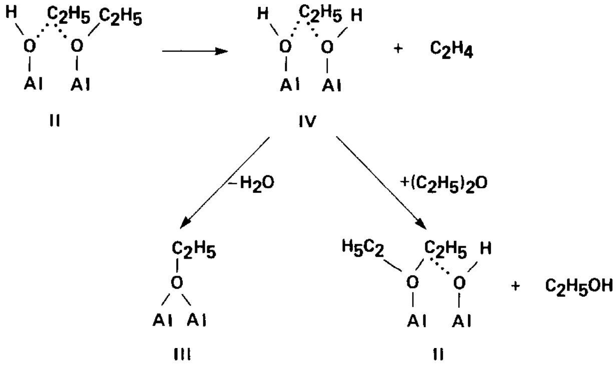
X	*Y*	*Z*	Type of reaction
H	H	H	(a) Exchange of oxygen in water
H	R	H	(b) Exchange of oxygen in alcohol
H	H	R	(c) Displacement of water by alcohol
R	H	H	(d) Displacement of alcohol by water
R^1	H	R^2	(e) Displacement of an alcohol by another alcohol
R^1	R^2	H	(f) Ether formation
H	R^1	R^2	(g) Ether disproportionation
R^1	R^2	R^3	(h) Ether transalkylation

According to this generalization, the strongly bonded form of an alcohol has the nature of a surface alkoxide, as suggested by previous authors (*1–16, 27, 28*). Evidence for individual reactions (Table 1) comes from the present work or from the literature. Oxygen exchange between water and alumina has been reported (*31, 32*) as well as between ethanol and alumina (*33*) (reactions (1a) and (1b)); our experiments confirm it. Displacement of water by an alcohol has been described by Sadovnikov and Geffer (*28*) (reaction (1c)) and observed by us (Figs. 4–6). The reverse reaction (1d) has been found by Treibmann and Simon (*4*) and our measurements show it clearly (Figs. 7 and 9). Krylov and Fokina (*34*) have found, using labeled 2-isopropanol, exchange between adsorbed and gaseous alcohol (reaction (1e)); it follows also from our experiments with methanol. The scheme for ether formation and disproportionation (reactions (1f) and (1g)) corresponds to the mechanism proposed by Knözinger and co-workers (*7, 10, 15, 16*) and is supported by our results (Figs. 2 and 7) which demonstrated the presence of surface alkoxide during ether decomposition.

However, both stopped-flow and pulse-flow experiments indicate that, besides the disproportionation (reaction (1g)), another reaction occurs which yields ethylene directly from the adsorbed ether, not via the relatively slow alkoxide route. In the steady state, this rapid pathway seems to be connected with the formation of ethanol, as ethylene and the alcohol are produced in almost stoichiometric amounts (Fig. 2); as only little water is formed, this reaction predominates. In pulse-flow experiments (Fig. 7) its contribution can be estimated from the area of the sharp peak which takes about 15% of the total ethylene area. If we assume that the second alkyl is split-off via



SCHEME 1



SCHEME 2

the alkoxide route, the rapid reaction makes only 30% of the total conversion. As to the nature of this rapid process we suggest that it is a side-reaction of the intermediate **II** in Scheme 1 which yields gaseous ethylene and molecularly adsorbed ethanol. This weakly bonded ethanol is either displaced from the surface by an ether molecule (in the steady state) or is transformed into surface alkoxide (in the pulse-flow regime). In this way, the difference between the product composition in the steady state and in the pulse-flow regime can be explained.

The high coverage of the surface by alkoxide species, already reported by Sadovnikov and Geffer (*28*) and Koubek *et al.* (*27*) has been confirmed also in this work; the stopped-feed measurements with ethanol yielded 0.40 mmol g^{-1}, the pulse-flow experiments 0.23 mmol g^{-1}. A difference is to be expected on the basis of start-up data which show a gradual build-up of full surface coverage by strongly adsorbed ethanol species. It may be caused by the heterogeneity of the surface hydroxyls originating from their location on various crystallographic planes.

We must now analyze whether the surface alkoxide can be the intermediate for ethylene formation at the steady-state dehydration. The descending part of the ethylene curve after stopping the alcohol feed was correlated by the first-order rate equation (Fig. 10) and the rate constant of the "monomolecular" surface reaction was estimated as $k = 10.5\ h^{-1}$. The total amount of ethylene produced after the stop was $c_P^0 =$ 0.40 mmol g^{-1}. From this, the rate $r_{max} = k \cdot c_P^0$ of ethylene formation shortly after the stop, when no ethanol, diethyl ether, and water are present in the catalyst bed, can be estimated as 4.2 mmol h^{-1} g^{-1}. This is by one order higher in value than the corresponding production of ethylene at stationary conditions when this reaction competes with the formation of ether. Thus, the potential of the decomposition of the surface alkoxide is higher than the steady-state rate and therefore there could not exist any serious limitation of this step to the overall rate at the reaction conditions used.

The decomposition of the surface ethoxide to gaseous ethylene leaves a proton on the surface with formation of a surface hydroxyl group which, at steady-state conditions, reacts with another alcohol molecule. The exact location of this renewed hydroxyl group is not important because Knözinger and co-workers (*35, 36*) have found high mobility of the protons on the surface of alumina. The assistance of neighboring surface oxygen atoms is probable.

Another problem is whether the alkoxide mechanism is consistent with the observed preference of antiperiplanar elimination on alumina (cf. Refs. (*21, 22*)). It seems that a suitable model for alkoxide decomposition can be found which will explain this observation (*37*).

A model of the working surface of alumina may be suggested which consists of oxygen atoms acting as basic centers, of hydroxyl groups and surface alkoxide groups. The concentration of free Lewis centers must be very low when water and alcohol are present in the system. The ratio of the -OH and -OR groups depends on the reaction conditions (temperature, partial pressures of water and alcohol over the surface). Besides that, alcohol and ether molecules are held weakly to the surface by hydrogen bonds. Water exhibits a higher affinity to the surface as the tailing of water curves in all nonstationary experiments shows. It seems that even water molecules released from the surface by reaction (1a) are partially readsorbed and strongly held.

A concluding remark seems appropriate, namely that the mechanism which assumes the formation of surface alkoxides predominantly by substitution of surface hydroxyl groups makes the distinction between Brønsted and Lewis sites for dehydration unnecessary: the original Brønsted hydroxyl centers act in fact as Lewis aluminum ion centers.

REFERENCES

1. Babushkin, A. A., and Uvarov, A. V., *Dokl. Akad. Nauk SSSR* **110,** 581 (1956).
2. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
3. Uvarov, A. V., *Zh. Fiz. Khim.* **37,** 1186 (1963).
4. Treibmann, D., and Simon, A., *Ber. Bunsenges. Phys. Chem.* **70,** 562 (1966).
5. Arai, H., Saito, Y., and Yoneda, Y., *Bull. Chem. Soc. Jpn.* **40,** 731 (1967).
6. Kagel, R. O., *J. Phys. Chem.* **71,** 844 (1967).
7. Knözinger, H., Bühl, H., and Ress, E., *J. Catal.* **12,** 121 (1968).
8. Arai, H., Saito, Y., and Yoneda, Y., *J. Catal.* **10,** 128 (1968).
9. Deo, A. V., and Dalla Lana, I. G., *J. Phys. Chem.* **73,** 716 (1969).
10. Knözinger, H., and Stolz, H., *Ber. Bunsenges. Phys. Chem.* **74,** 1056 (1970).
11. Deo, A. V., Chuang, T. T., and Dalla Lana, I. G., *J. Phys. Chem.* **75,** 234 (1971).
12. Chuang, T. T., and Dalla Lana, I. G., *J. Chem. Soc. Faraday Trans. 1* **68,** 773 (1972).
13. Knözinger, H., and Stübner, B., *J. Phys. Chem.* **82,** 1526 (1978).
14. Hattori, T., Shirai, K., Niwa, M., and Murakami, Y., *React. Kinet. Catal. Lett.* **15,** 193 (1980).
15. Knözinger, H., and Ress, E., *Z. Phys. Chem. (Frankfurt/Main)* **59,** 49 (1968).
16. Knözinger, H., Scheglila, A., and Watson, A. M., *J. Phys. Chem.* **72,** 2770 (1968).
17. Hattori, T., and Murakami, Y., *J. Catal.* **33,** 365 (1974).
18. Sabatier, P., "Catalyse en Chimie Organique," 2nd. ed., Paris, 1920.
19. Eucken, A., and Wicke, E., *Naturwissenschaften* **32,** 161 (1945).
20. Knözinger, H., *Angew. Chem. Int. Ed.* **7,** 791 (1968).
21. Noller, H., and Kladnig, W., *Catal. Rev. Sci. Eng.* **13,** 149 (1976).
22. Beránek, L., and Kraus, M., *in* "Comprehensive Chemical Kinetics" (C. H. Bamford, and C. F. H. Tipper, Eds.), Vol. 20, p. 263. Elsevier, Amsterdam, 1978.
23. Topchieva, K. V., and Yun Pin, K., *Zh. Fiz. Khim.* **29,** 2076 (1955).
24. Topchieva, K. V., Yun Pin, K., and Smirnova, I. V., "Advances in Catalysis," Vol. 9, p. 799. Academic Press, New York, 1957.
25. Notari, B., *Chim. Ind. (Milano)* **51,** 1200 (1969).
26. Arai, H., Take, J., Saito, Y., and Yoneda, Y., *J. Catal.* **9,** 146 (1967).
27. Koubek, J., Pašek, J., and Růžička, V., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 853, Kodansha, Tokyo, 1981.
28. Sadovnikov, V. V., and Geffer, A. M., *Izv. Akad. Nauk SSSR, Ser. Khim.* 1220 (1976).
29. Knözinger, H., and Ratnasamy, P., *Catal. Rev. Sci. Eng.* **17,** 31 (1978).
30. Nondek, L., Vít, Z., and Málek, J., *React. Kinet. Catal. Lett.* **10,** 7 (1979).
31. Mills, G. A., and Hindin, S. G., *J. Amer. Chem. Soc.* **72,** 5549 (1950).
32. Karpacheva, S. M., and Rosen, A. M., *Dokl. Akad. Nauk SSSR* **75,** 55 (1950).
33. Karpacheva, S. M., and Rosen, A. M., *Dokl. Akad. Nauk SSSR* **81,** 425 (1951).
34. Krylov, O. V., and Fokina, E. A., *Kinet. Katal.* **1,** 542 (1960).
35. Stübner, B., Knözinger, H., Conard, J., and Fripiat, J. J., *J. Phys. Chem.* **82,** 1811 (1978).
36. Clement, G., Knözinger, H., Stählin, W., and Stübner, B., *J. Phys. Chem.* **83,** 1280 (1979).
37. Morávek, V., and Ponec, R., to be published.