

PERTURBATION OF STEADY-STATE CATALYTIC DEHYDRATION OF ALCOHOLS BY PULSES OF WATER AND OTHER SUBSTANCES*

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Received October 5th, 1984

The dynamic behaviour of systems consisting of 2-propanol or tert-butanol and of a solid dehydration catalyst has been studied by means of pulses of the alcohols, water, nitrogen or carbon dioxide, respectively, introduced onto fresh catalyst surface in a stream of nitrogen, or onto the working surface. The catalysts employed were alumina, alumina modified by fluoride, sulphate or sodium ions, respectively, thoria, silica-alumina, phosphotungstic acid and a sulphonated styrene-divinylbenzene copolymer. The positions and shapes of the response curves allowed to distinguish between catalysts operating by formation of surface alkoxides or of protonated alcohols as surface intermediates in the transformation of the alcohols into alkenes.

This paper is a continuation of the preceding study¹ on dynamic behaviour of the system ethanol-diethyl ether-water-alumina in which the pulse-flow, stopped flow and started flow experiments have shown that surface ethoxide is formed as the intermediate in all transformations of ethanol to diethyl ether and ethylene and of diethyl ether into ethylene. In preliminary experiments, reported also in the paper¹, other alcohols behaved similarly.

In the present paper, we extended this approach to characterization of different dehydration catalysts in respect to reaction mechanisms by which they operate. As probes, 2-propanol and tert-butanol have been used in place of ethanol, in order to simplify the system, as these two alcohols do not form ethers under conditions of our experiments (gaseous phase, 110–250°C).

EXPERIMENTAL

Materials. The catalysts are summarized in Table I. 2-Propanol (Lachema, *p.a.*) was dried by calcium chloride and rectified. Tert-butanol (Reanal, *p.a.*) was rectified and twice crystallized. Water content in both reactants was under 0.1%. Nitrogen was purified by a copper absorption mass and by molecular sieve; oxygen and water content was lower than 20 ppm.

Procedure. The experiments were performed in a flow reactor, consisting of a 4 mm i.d. stainless-steel tube. The volume of the catalyst sample was 0.05 to 0.15 ml, its grain size 0.16 to 0.25 mm. The samples were dried at 300°C, with exception of phosphotungstic acid and Amberlyst, for

* Presented at the CHISA '84 International Conference, Prague, September 1984.

which 120°C was applied. The following types of pulse-flow measurements were made (their symbols consist of a letter denoting the substance of the pulse and a letter under the slash denoting the continuously fed substance): *a*) a pulse of an alcohol introduced into a stream of nitrogen (experiment A/I); *b*) a pulse of water superposed on steady-state flow of an alcohol–nitrogen mixture (W/A); *c*) a pulse of an alcohol superposed on steady-state flow of a mixture of the same alcohol and nitrogen (A/A); *d*) a pulse of nitrogen, interchanged for steady-state flow of an alcohol–nitrogen mixture (I/A); *e*) a pulse of carbon dioxide interchanged for steady-state flow of an alcohol–nitrogen mixture (C/A). The pulses of the alcohols or water were introduced by injecting the liquid from a microsyringe into the reactor. For the gases, a three-way stopcock was used. The forms of the pulses, obtained in blank experiments in the reactor packed with an inert material are shown in Fig. 1. The pulse sizes of 2-propanol, tert-butanol, water, nitrogen and carbon dioxide were 65, 53, 27, 150 and 150 μmol , respectively. Steady-state feed rates were 52 $\mu\text{mol/s}$ N_2 , 5 $\mu\text{mol/s}$ 2-propanol and 4 $\mu\text{mol/s}$ tert-butanol. The response curves were obtained by repeated analyses of the reactor effluent in different times after perturbation. The reproducibility of the measurements was better than 4%. The primary data were transformed into rates of production from the reactor $R_i = F_i/W$, where F_i is the molar flow rate of component i at the reactor exit ($\mu\text{mol/s}$) and W is catalyst weight (g); the rates are thus given in $\mu\text{mol/s g}$.

RESULTS AND DISCUSSION

The response to a perturbation of a reacting system by an interacting substance is connected to the reaction mechanism. The dehydration of alcohols requires the split-

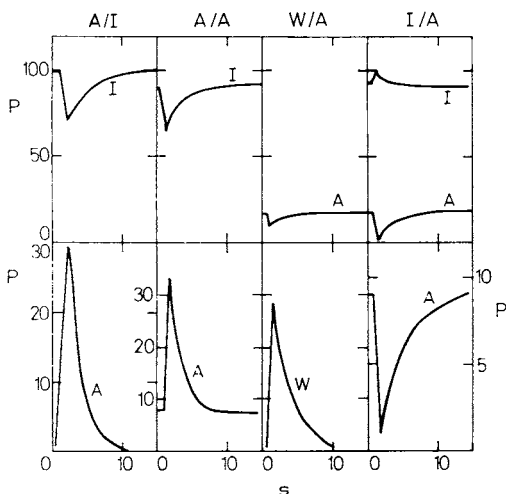


FIG. 1

Response curves in blank experiments. The concentrations are given in kPa. A denotes 2-propanol, W water, I nitrogen. The symbols of experiments (A/I, A/A, W/A, I/A) are explained in the text

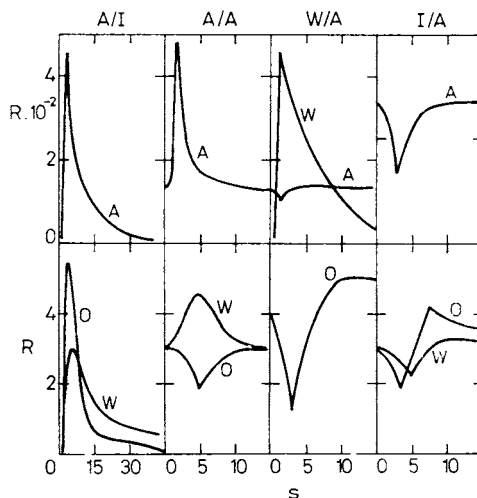
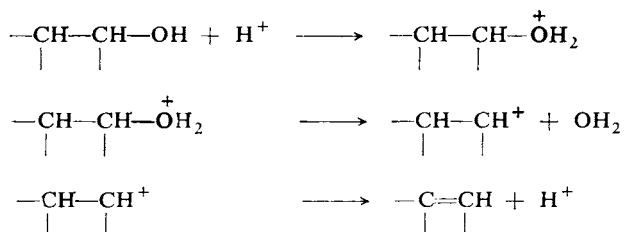


FIG. 2

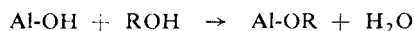
Response curves for experiments with 2-propanol on phosphotungstic acid. 23.3 mg of the catalyst, 110°C. The meaning of the symbols as in Fig. 1, O denotes propene

ting of the C_{α} -OH and C_{β} -H bonds and the basic differences in various mechanisms are the timing of this two steps and the activation of the alcohol by the catalyst. The mechanisms have been discussed in a number of publications (*e.g.*²⁻⁴). For the purpose of this work, three limiting cases are of interest, in spite of the most probable existence of a spectrum of intermediate situations in timing of the steps. The first type of dehydration mechanism is characterized by protonation of the hydroxyl group, splitting off the water molecule and simultaneous or delayed fission of the C_{β} -H bond



The last step must be assisted by a basic species (or surface centre) which accomodates the proton. The mechanism is called acidic or protonic. Its counterpart starts with splitting off the proton from the C_{β} -H group in the first step, catalyzed by a basic species (or surface centre). An acidic species must give assistance to the splitting off the OH group; this mechanism is called basic.

The third mechanism is specific for certain oxides (like alumina) and comprises the formation of a surface alkoxide by substitution of a surface hydroxyl group



The surface alkoxide decomposes then into an alkene and the proton from C_{β} -H bond is accomodated by a surface basic site (a surface oxygen atom); *cf.*^{1,5}.

The first two examined catalysts were of the type which we assumed to operate by the acidic mechanism. The experiments with phosphotungstic acid and with poly(styrene-divinylbenzenesulphonic acid) confirmed this expectation. Fig. 2 shows the response curves for different perturbations of the reaction of 2-propanol on phosphotungstic acid. The upper part of the figure contains the exit curves of the injected substance and the lower part the curves of the products. The strong retention of water and 2-propanol on the surface (or in the bulk of the catalyst, *cf.*⁶) is evidenced by the tailing. The pulse of 2-propanol (experiment A/A) inhibits the formation of propene; it is possible that this effect is caused by water released in the reaction. The dehydration of 2-propanol on this catalyst is partially inhibited by water (experiment W/A), probably due to competitive adsorption. The reaction products, water and propene, leave the reactor almost simultaneously (experiment A/I), in contrast to previously

observed behaviour of alumina where the alkene was released very slowly¹. Water activates temporarily the catalyst (experiment W/A), probably by creating additional protonic sites which are later destroyed again by loss of water from the catalyst. Nitrogen and carbon dioxide (experiments I/A and C/A) behave similarly, both causing some decrease in propene production, probably due to dilution of the reaction mixture. The measurements with tert-butanol gave similar picture.

The polymeric sulphonic acid (Amberlyst) sorbs water strongly; this is indicated by the retention and widening of its peaks. In contrast to phosphotungstic acid, propene formation is enhanced by water at first, then slightly suppressed. Water seems to have complex role in the mechanism; again, tert-butanol behaved as 2-propanol.

In the dehydration of alcohols on alumina, a relatively stable intermediate is formed which has the structure of surface alkoxide^{1,5,6}. In the pulse regime (Fig. 3), this mechanism manifests itself by the peak of water preceding the peak of propene (experiment A/I). The dehydration is almost completely inhibited by water (experiment W/A) and water peak shows extensive tailing. From the response to a pulse of 2-propanol (experiment A/I), the mean life time of adsorbed molecules can be estimated as the difference between the first moments of 2-propanol and propene

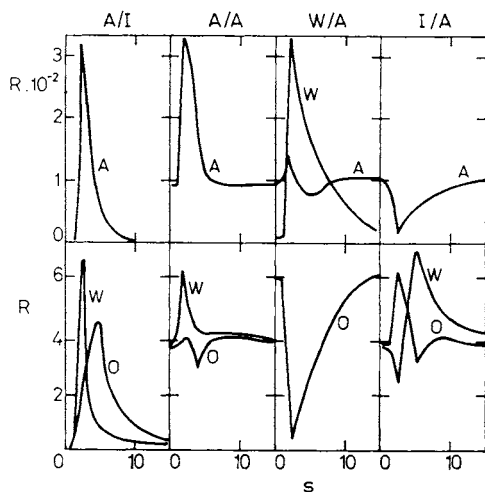


FIG. 3

Response curves for experiments with 2-propanol on pure alumina (34.2 mg) at 200°C

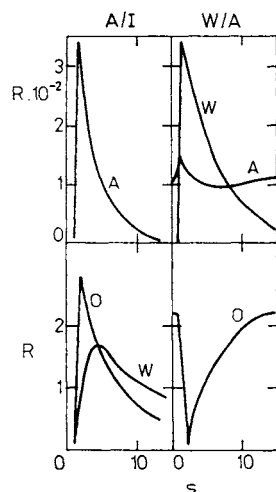


FIG. 4

Response curves for experiments with 2-propanol on alumina modified by F⁻ (32.8 mg) at 200°C

peaks

$$t = t_{\text{alkene}} - t_{\text{alcohol}} \quad (1)$$

For 166°C, $t \approx 60$ s. The rate constant of the decomposition of surface isopropoxide, estimated from the right hand arm of the propene peak using the formula¹

$$k = \ln(c_1/c_2)/(t_2 - t_1) \quad (2)$$

(indices 1 and 2 denote suitable points on the curve) is $k = 0.0069 \text{ s}^{-1}$ at 166°C. As $1/k = 37$ s, the mean life time of the alcohol and the alkoxide is different, indicating the presence of other reaction steps preceding the formation of propene from the alkoxide. With increasing temperature, the difference diminishes; this shows that the activation energies of the steps are different.

The experiment A/A results in autoinhibition of the dehydration by the alcohol. An explanation of this observation can be found in our previous work¹. The bridged surface alkoxide is transformed into transient surface compound containing two alkoxide groups and being unable to dehydrate to an alkene. Also the I/A experiment shows different phasing of water and propene liberation.

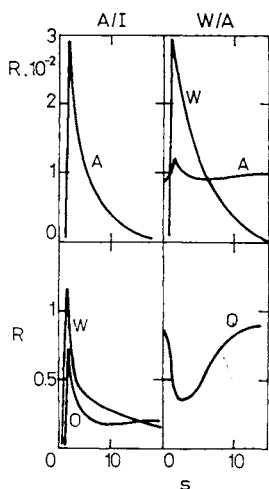


FIG. 5

Response curves for experiments with 2-propanol on alumina modified by SO_4^{2-} (35.5 mg) at 175°C

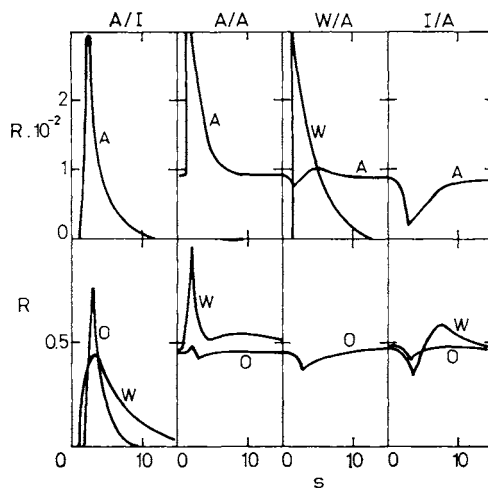


FIG. 6

Response for experiments with 2-propanol on alumina modified by Na^+ (80 mg) at 200°C

The next point of interest was the effect of modification of alumina by different foreign ions. We had at our disposal a series of aluminas, prepared and studied by Jiráťová and Beránek⁷, containing F^- , SO_4^{2-} and Na^+ . Increased protonic activity of alumina containing fluorine has been reported in the literature^{8,9}. Our fluorided alumina behaved qualitatively in the same way as the parent alumina and with only small quantitative differences but with one important exception. In the A/I experiment propene was leaving the reactor before water (Fig. 4). We connect this fact to the observed decrease of the concentration of surface hydroxyl groups (Table I). With this catalyst, the surface alkoxide groups are formed not by substitution of the hydroxyl groups but probably by interaction with a fluorine bridged structure.

Similar effect as fluoridation had the introduction of the SO_4^{2-} ions. Qualitatively, all response curves remained the same as with pure alumina but in the A/I experiment, propene and water peaks emerged together (Fig. 5). The propene curve seems to be composed from two peaks, one sharp coinciding with the water peak and one broad peak. We suggest two mechanisms operating simultaneously, one characterized by protonation of the alcohol (sharp peak) and the second broad peak by alkoxide formation.

The changes in response curves, caused by sodium hydroxide added to alumina, are extensive. Most significant is the simultaneous release of the alkene and water

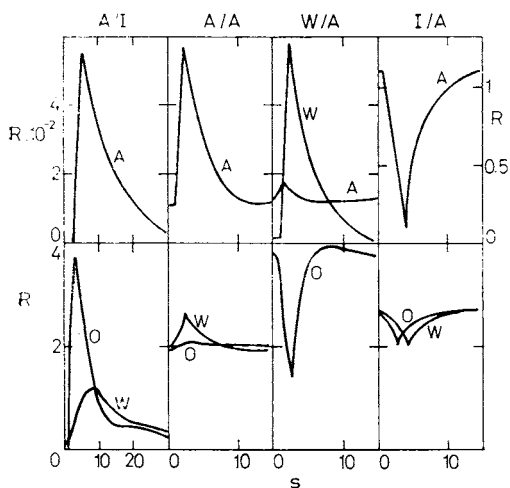


FIG. 7

Response curves for experiments with 2-propanol on silica-alumina (32.6 mg) at 150°C

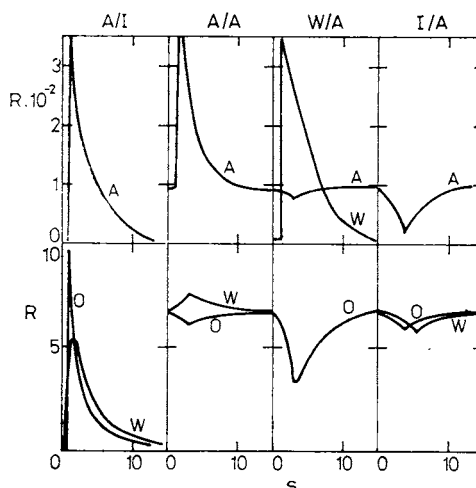


FIG. 8

Response curves for experiments with tert-butanol on thoria (23.6 mg) at 200°C

in the A/I experiment (Fig. 6) and very small perturbation of the dehydration by a water pulse (experiment W/A). The activity of the catalyst is also lowered. All this indicates a major change in reaction mechanism; we believe that the alkoxide mechanism is almost suppressed by the presence of Na^+ and the basic type of elimination is predominating. Such influence of sodium was observed previously in a study of structure effects on rate of dehydration of secondary alcohols¹¹.

The measurements with tert-butanol on pure alumina gave different results than in our previous work¹ where this alcohol showed all features of alkoxide mechanism. In the present work, tert-butanol behaved according to protonic mechanism: in the experiment A/I, water and isobutene were released almost at the same time and a water pulse (experiment W/A) liberated no alcohol from the catalyst. The reasons for this difference are not clear; the catalyst samples were prepared from the same stock of aluminium hydroxide by seemingly the same procedure of peptization with acetic acid, extrudation and calcination at 600°C. However, the protonation mechanism is not surprising with tert-butanol in view of the nature of tertiary alcohols²⁻⁴. On alumina modified by Na^+ ions, the responses of tert-butanol resemble strongly acidic centres are neutralized by sodium and that the alkoxide mechanism can operate.

Silica-alumina (Fig. 7) behaved like phosphotungstic acid and Amberlyst, as could be expected with this strongly acidic cracking catalyst.

Thoria is regarded as a basic catalyst for dehydration^{3,12,13}. Our measurements are in accord with this view. Tert-butanol was used as the probe because the catalyst was not active enough with 2-propanol and higher temperatures were necessary for achieving sufficient conversion. The isobutene curve in the experiment A/I shows (Fig. 8) a small second maximum which may indicate a slight contribution

TABLE I
Catalysts used

Catalyst	Origin	Composition	Surface area m^2/g	Conc. of OH groups nm^{-2} (ref. ¹⁰)
Phosphotungstic acid	laboratory	13% on C	600	0.5
Amberlyst XN-1010	Rohm Haas (USA)	capacity 2 mmol/g	—	—
Alumina Pural SB	Condea (GFR)	—	250	6.4
Alumina + F^-	ref. ⁷	2.6% F	183	3.4
Alumina + SO_4^{2-}	ref. ⁷	4.85% SO_4^{2-}	239	6.3
Alumina + Na^+	ref. ⁷	0.62% Na	208	6.4
Silica-alumina	USSR	11% Al_2O_3	372	2.1
Thoria	laboratory	—	15	—

of the alkoxide mechanism. Of interest is the response to a pulse of carbon dioxide. Whereas with other catalysts the response curves of nitrogen (I/A) and carbon dioxide (C/A) practically coincided, in this case they differed, carbon dioxide exhibiting larger influence in suppressing the dehydration. This fact can be regarded as further proof of the basic mechanism.

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Translated by the author (M. K.).