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## Abstract

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# CONJUGATE DEHYDRATION OF ALCOHOLS IN THE ADSORBED LAYER ON ALUMINA CATALYSTS

In studying the mechanism of the dehydration reaction of alcohols on $Al_2O_3$ from the kinetics of the reaction in the adsorbed layer on the catalyst ([1],[2]), we showed that, on a series of catalysts of different genesis, the reaction rates for different alcohols differ greatly ([3]). In the present work, carried out on other samples of $Al_2O_3$ catalysts (No. 1—precipitated from nitrate with caustic soda at constant pH 6.3; No. 2—obtained by hydrolysis of aluminum isopropylate; and No. 3—precipitated from a solution of aluminate with gaseous $CO_2$ at 0°), this difference in the dehydration rates of $C_2H_5OH$ and *iso*-$C_3H_7OH$ was confirmed.

By adsorbing small amounts of vapors of these substances on a sample of $Al_2O_3$ trained in a high vacuum and measuring the kinetics of the increase in olefin pressure above the catalyst, we found that comparable values of the half-life periods $\tau$ (and, consequently, of the rate constants of the reactions) for $C_2H_5OH$ and *iso*-$C_3H_7OH$ are reached only when the reaction is carried out in the temperature intervals 180–240° and 120–150°, respectively.

Extrapolation of the Arrhenius straight lines for the dehydration of $C_2H_5OH$ in the adsorbed layer to a temperature of 150° leads to values of $\tau = 1000$–$1300$ min, i.e., 2-3 orders of magnitude higher than those experimentally obtained for *iso*-$C_3H_7OH$. Proceeding from the fact that at temperatures of 120–150° the dehydration of *iso*-$C_3H_7OH$ in the adsorbed layer proceeds at an appreciable rate ($\tau = 1$-$20$ min), whereas ethanol under these conditions should be practically stable, we decided to use $C_2H_5OH$ as a readily adsorbed but chemically inert substance in studying the character of the heterogeneity of the surface of catalysts by the method of progressive blocking proposed in ([3]).

This method consists in investigating the decomposition of a standard small amount (2-4% of a monolayer) of a substance on a catalyst on which an increasing, from experiment to experiment, amount of an inert substance that blocks the surface for the catalytic reaction has been preadsorbed. In this case, because of the displacement of the reacting substance to surface regions that are less active with respect to adsorption, the reaction rate constant should decrease or increase, depending on the relative catalytic activity of the given group of regions. In this way it is possible to determine the differential (and not integral ([1],[2])) distribution curve of regions according to catalytic activity.

Fig. 1

Figure 1: Fig. 1

In carrying out this study, a different effectiveness of the action of $H_2O$, $CH_3OH$, and $C_2H_5OH$ was unexpectedly found—adsorbed in equal amounts, they reduced the rate of dehydration of *iso*-$C_3H_7OH$ to different extents, and differently on $Al_2O_3$ samples of different genesis. Water had the least effect—it almost did not reduce the rate of alcohol decomposition up to very high filling densities; ethyl and methyl alcohols, however, inhibited the reaction very substantially, and on some samples methanol inhibited more strongly, on others ethanol did. This clearly did not fit within the framework of a simple explanation by blocking; therefore we investigated in greater detail the kinetics of decomposition of *iso*-$C_3H_7OH$ and $C_2H_5OH$ in

adsorbed layer on several samples of $Al_2O_3$ when they were present together in amounts of 0.3 $cm^3/g$ (N.T.P.) (i.e., 2-4% of a monolayer) and 5.3 $cm^3/g$ (N.T.P.), respectively.

**Fig. 1.** Coupled dehydration of $C_2H_5OH$ + *iso*-$C_3H_7OH$ on catalyst No. 1 at 150°:
1 –$C_2H_5OH$ + *iso*-$C_3H_7OH$; 2 –$H_2O$ + *iso*-$C_3H_7OH$; 3 –*iso*-$C_3H_7OH$ (control experiment). The vertical dotted line indicates the moment of admission of isopropyl alcohol for curve 1 and the start of the experiment for curves 2 and 3.

The experiments were carried out as follows. First, ethanol was adsorbed at 120-150°, and for some time (from 40 min to 2.5 h) the change in pressure in the gas phase was measured. Since the amount of $C_2H_5OH$ is also relatively small, during the first minutes the alcohol is practically completely adsorbed by the catalyst without residual pressure in the gas phase. Thereafter the pressure over the catalyst remains constant or, in some experiments, slowly increases because of dehydration (see, for example, Figs. 1-3). Then *iso*-$C_3H_7OH$ was adsorbed and the kinetics of the increase in olefin pressure were measured.

In all cases it was found that the reaction proceeded more slowly than in control experiments with pure *iso*-$C_3H_7OH$ or than in *iso*-$C_3H_7OH$ + $H_2O$ systems. Further, in a number of cases it was found that the pressure in the apparatus considerably exceeded the value calculated on the assumption of 100% decomposition of the entire adsorbed amount of *iso*-$C_3H_7OH$ (and, in cases where the decomposition of $C_2H_5OH$ at the start of the experiment proceeded at a noticeable rate, the value calculated on the assumption of additivity of the rates of decomposition of ethanol and *iso*-$C_3H_7OH$).

This value $p_{\infty\,\mathrm{theor}}$ should have been equal to 0.6-0.7 mm Hg; in practice, during decomposition of pure *iso*-$C_3H_7OH$ the values of $p_{\infty\,\mathrm{expt}}$ were somewhat lower, and for catalysts Nos. 1, 2, and 3 averaged 0.50, 0.40, and 0.35 mm Hg, respectively; whereas in the simultaneous presence of $C_2H_5OH$ and *iso*-$C_3H_7OH$ in the adsorbed layer, $p_{\infty\,\mathrm{theor}}$ reached 1.1-1.6 mm and continued to increase.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

The rate of this pressure increase at 4-6 h of reaction became constant and considerably exceeded (by a factor of 3-7) the rate of pressure increase due to dehydration of pure $C_2H_5OH$ during the first period of the experiment (in those cases where this dehydration occurred at any appreciable rate).

**Fig. 2.** Coupled dehydration of $C_2H_5OH$ + *iso*-$C_3H_7OH$ on catalyst No. 1 at 120°:
1 –$C_2H_5OH$ + *iso*-$C_3H_7OH$; 2 –*iso*-$C_3H_7OH$ (control experiment). Half-decomposition period $\tau = 18$ min. 3 –kinetic curve for the decomposition of *iso*-$C_3H_7OH$ in a mixture with ethanol, calculated taking into account the rate of decomposition of ethanol, taken as equal to the constant rate on the last rectilinear segment of curve 1. Half-decomposition period $\tau = 30$ min. 4 –rate of decomposition of $C_2H_5OH$ in a mixture with *iso*-$C_3H_7OH$ (calculated from the last rectilinear segment of curve 1). 5 –rate of decomposition of $C_2H_5OH$ before admission of *iso*-$C_3H_7OH$ (extrapolated initial segment of curve 1).

The results of these experiments show unambiguously that, when ethyl and isopropyl alcohols are simultaneously present in the adsorbed layer on the catalyst, their coupled dehydration can occur, and the rate of the slower reaction (dehydration of ethanol) strongly

increases, while the rate of the faster reaction (dehydration of isopropanol) decreases.

It follows from this that the multiplet complex (a molecule of the reacting substance adsorbed on an active site of the catalyst) in the dehydration reaction of alcohols on $Al_2O_3$ is not an isolated structure whose character of change along the reaction coordinate is independent of the properties of molecules adsorbed on neighboring centers.

A similar multiplet complex should rather be regarded as a radical that can react with neighboring molecules, giving more or less stable intermediate formations. Thus, molecules of iso-$C_3H_7OH$ adsorbed on the catalyst (the case of dehydration of pure iso-$C_3H_7OH$) apparently form intermediate complexes that decompose relatively rapidly into olefin and water, whereas mixed ethanol-isopropanol (or methanol-isopropanol) complexes decompose more slowly.

**Fig. 3.** Coupled dehydration of $C_2H_5OH$ + iso-$C_3H_7OH$ on catalyst No. 3 at 150°:
1 –$C_2H_5OH$ + iso-$C_3H_7OH$; 2 –iso-$C_3H_7OH$ (control experiment); 3 –iso-$C_3H_7OH$ in a mixture with $C_2H_5OH$; 4 –$C_2H_5OH$ in a mixture with

iso-$C_3H_7OH$; 5 –$C_2H_5OH$ before introduction of isopropanol. 3–5 calculated.

The formation of such less reactive mixed complexes makes it possible to understand the reason for the difference in the action of preadsorbed molecules of $H_2O$, $CH_3OH$, and $C_2H_5OH$. Obviously, water simply blocks the surface, whereas $CH_3OH$ and $C_2H_5OH$, in addition, bind the relatively more reactive radical-like multiplet complexes of isopropyl alcohol, which leads to an additional decrease in the rate of the dehydration reaction.

The data are still insufficient for judging the nature of the surface radicals formed; however, the phenomenon we observed, in any case, cannot be reduced simply to the formation of intermediate mixed ethers, since this cannot explain either the slowing of the decomposition reaction of iso-$C_3H_7OH$ (as was shown by us ([3]), the rate of dehydration in a monolayer for ethers is approximately twice as high as for the corresponding alcohols), or the character of the kinetic curves obtained: constancy of the rate during the period when all the introduced iso-$C_3H_7OH$ should already have decomposed completely.

Further, it is evident from our data that coupled dehydration, and consequently also the surface-radical mechanism of the reaction, is most clearly expressed on catalyst No. 3, then on Nos. 1 and 2, whereas in catalytic activity in the decomposition reaction of pure iso-$C_3H_7OH$ in a monolayer at 150° these catalysts can be arranged in the series $1 < 3 < 2$. This shows that the surface-radical mechanism apparently is not the only possible pathway for the dehydration reaction of alcohols in a monolayer, and that alongside it this reaction may also proceed by the usual mechanism, the ratio of these two reaction directions being different on different catalysts.

In conclusion, we note that the proposed radical mechanism of the dehydration reaction probably underlies intermolecular dehydration reactions.

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*Note: Figure translations are in progress. See original paper for figures.*