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Abstract

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Mutual Influence of Reacting Molecules on the Surface of Dehydration Catalysts

In investigating the mechanism of dehydration of lower aliphatic alcohols in the adsorbed layer on Al_2O_3 catalysts of various origins ([1]), we showed the existence, under certain conditions, of a coupled surface reaction of dehydration of isopropyl and ethyl alcohols. Thus, at 120–150°, adsorption of C_2H_5OH in amounts of 1–5 cm^3 (NTP)/g (i.e., at most up to 40–70% of a monolayer) proceeds practically to completion, without any noticeable pressure in the gas phase. Under these conditions the dehydration reaction either does not occur at all or proceeds very slowly. If, after this, a relatively small amount (0.3 cm^3 (NTP)/g, i.e., 2–4% of a monolayer) of iso-C_3H_7OH is adsorbed, also completely absorbed by the catalyst, then an increase of pressure in the gas phase is observed, indicating the course of the reaction. In this case the rate of decomposition of the standard amount of iso-C_3H_7OH was always found to be considerably lower than in the absence of previously adsorbed C_2H_5OH. The rate of dehydration of C_2H_5OH, on the other hand, in a number of cases increased markedly, as could be judged both from the considerable increase in the total pressure of the reaction products and from their ethylene content.

Further experiments carried out by us showed that the course of the coupled dehydration reaction described in ([1]) represents a special case of a more general relationship, namely the mutual influence of reacting molecules on the rate of their decomposition in the adsorbed layer.

The characteristics of the alumina catalysts used by us are given in Table 1; for the experimental procedure see ([1]).

Table 1

Characteristics of the Al_2O_3 catalysts used

No.	Method of preparation	Specific surface area, m^2/g ads.	Catalytic activity in the dehydration reaction in the adsorbed layer: iso-C_3H_7OH, E, kcal/mol	Catalytic activity in the dehydration reaction in the adsorbed layer: iso-C_3H_7OH, t^*_{20}, °C	Catalytic activity in the dehydration reaction in the adsorbed layer: C_2H_5OH, E, kcal/mol	Catalytic activity in the dehydration reaction in the adsorbed layer: C_2H_5OH, t^*_{20}, °C
1	Precipitated with NH_4OH at 20° from a solution of aluminum nitrate at constant pH 6.3	176	24.3	126	28.7	217
2	Obtained by hydrolysis of aluminum isopropylate at 20°	210	24.5	110	29.0	218

No.	Method of preparation	Specific surface area, m^2/g ads.	Catalytic activity in the dehydration reaction in the adsorbed layer: iso-C_3H_7OH, E, kcal/mol	Catalytic activity in the dehydration reaction in the adsorbed layer: iso-C_3H_7OH, t^*_{20}, °C	Catalytic activity in the dehydration reaction in the adsorbed layer: C_2H_5OH, E, kcal/mol	Catalytic activity in the dehydration reaction in the adsorbed layer: C_2H_5OH, t^*_{20}, °C
3	Precipitated by gaseous CO_2 from a solution of sodium aluminate at 0°	220	26.1	126	27.5	213
4	Precipitated from a solution of aluminum nitrate with aqueous ammonia at 90°**	195	14.2	110	26.0	217

No.	Method of preparation	Specific surface area, m^2/g ads.	Catalytic activity in the dehydration reaction in the adsorbed layer: iso-C_3H_7OH, E, kcal/mol	Catalytic activity in the dehydration reaction in the adsorbed layer: iso-C_3H_7OH, t^*_{20}, °C	Catalytic activity in the dehydration reaction in the adsorbed layer: C_2H_5OH, E, kcal/mol	Catalytic activity in the dehydration reaction in the adsorbed layer: C_2H_5OH, t^*_{20}, °C
5	Precipitated with bromine water from a solution of sodium aluminate at 60°	290	26.7	117	–	–
6	$Al_2O_3 + Fe_2O_3$ (7%) precipitated from a solution of nitrates with aqueous ammonia	–	not amenable to determination	not amenable to determination	–	–
7	Same as No. 3, another preparation	220	30.0	108	–	–

Fig. 1. Dehydration of *iso*-C_3H_7OH in the adsorbed layer on catalyst No. 7 at 110°. 1 –pure *iso*-C_3H_7OH, 2 –*iso*-C_3H_7OH + C_2H_5OH (0.3 cm^3 (N.T.P.)/g), 3 –the same (5.3 cm^3 (N.T.P.)/g), 4 –*iso*-C_3H_7OH + $(C_2H_5)_2O$ (0.3 cm^3 (N.T.P.)/g)

Figure 1: Fig. 1. Dehydration of *iso*-C_3H_7OH in the adsorbed layer on catalyst No. 7 at 110°. 1 –pure *iso*-C_3H_7OH, 2 –*iso*-C_3H_7OH + C_2H_5OH (0.3 cm^3 (N.T.P.)/g), 3 –the same (5.3 cm^3 (N.T.P.)/g), 4 –*iso*-C_3H_7OH + $(C_2H_5)_2O$ (0.3 cm^3 (N.T.P.)/g)

* t_{20} is the temperature at which the half-decomposition period $\tau_{0.5} = 20$ min.

** The catalyst was obtained from A. A. Tolstopyatova, for which the authors express their gratitude.

On the indicated catalysts, the kinetics of dehydration in the adsorbed layer was studied for the following binary systems and the corresponding individual components (the numbers in parentheses denote the catalyst Nos.): a) *iso*-C_3H_7OH–ethyl alcohol (1,2,3,4,5,6,7); b) *iso*-C_3H_7OH–ethyl ether (3,5,7); c) *iso*-C_3H_7OH –methyl alcohol (1,2,3,4,5,7); d) *iso*-C_3H_7OH–water (1,2,3,5,7); e) *iso*-C_3H_7OH –diisopropyl ether (1); f) *iso*-C_3H_7OH–dimethyl ether (5,7); g) (*iso*-$C_3H_7)_2O$ –ethyl ether (1,2,4,7); h) (*iso*-$C_3H_7)_2O$–methyl alcohol (4); i) C_2H_5OH–*tert*-butyl alcohol (1, 2, 3); k) C_2H_5OH–trimethylcarbinol (1, 2, 3).

In all these binary systems the amount of the first component I was constant–0.3 cm^3 (N.T.P.)/g, and the reaction rate in the mixture was compared with the rate of its decomposition in the pure state at the same filling density. The amount of component II in different cases was varied from 0.3 to 5.3 cm^3 (N.T.P.)/g.

Fig. 1. Dehydration of *iso*-C_3H_7OH in the adsorbed layer on catalyst No. 7 at 110°.
1 –pure *iso*-C_3H_7OH, 2 –*iso*-C_3H_7OH + C_2H_5OH (0.3 cm^3 (N.T.P.)/g), 3 –the same (5.3 cm^3 (N.T.P.)/g), 4 –*iso*-C_3H_7OH + $(C_2H_5)_2O$ (0.3 cm^3 (N.T.P.)/g).

In **system a)** the rate of decomposition of I in the mixture always decreases strongly, whereas the rate of decomposition of II in some cases increases noticeably (by 4-6 times), and sometimes remains unchanged. In this, a substantial influence is exerted both by the nature of the catalyst and the reaction temperature, and by the conditions of regeneration of the catalyst between experiments –sometimes the rate of decomposition of II is anomalously high from the very beginning and no longer increases after the introduction of I. After thorough regeneration–heating in a stream of air at 400° and then many hours of evacuation to a vacuum of the order of 10^{-5} mm Hg at 400°–the phenomenon of coupled dehydration of II is observed again. If C_2H_5OH is introduced not before but after the introduction of *iso*-C_3H_7OH, when dehydration of I is complete, then the ethylene-formation reaction either does not proceed at all or proceeds at as small a rate as on a fresh catalyst sample. The amount of adsorbed ethyl alcohol also plays a very substantial role. Thus, on catalysts Nos. 5 and 7,

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

at small amounts of C_2H_5OH (0.3 and 1.2 cm^3 (N.T.P.)/g, respectively) the phenomenon of coupled dehydration is not observed, and only a slowing of the decomposition of *iso*-C_3H_7OH is detected, whereas at fillings with C_2H_5OH of the order of 5.3 cm^3 (N.T.P.)/g a clearly expressed coupling occurs—the rate of ethylene formation increases noticeably (Fig. 1).

The phenomenon of coupled dehydration was found on catalysts Nos. 1, 2, 3, 4, 5, 7 (in the latter case only at 120°, but not at 150°). On catalyst No. 6, during dehydration of the mixture I + II, not only the rate changes but also the entire character of the course of the reaction: the pressure curve of the reaction products during dehydration of I and I + II at 120° is shown in Fig. 1. The fall in pressure in the second part of curve 1 is evidently explained by polymerization of the propylene initially formed. In the mixture I + II, coupled dehydration of C_2H_5OH to C_2H_4 does not occur, but polymerization of C_3H_6 also ceases. The decomposition of I is strongly slowed, and the half-decomposition period is $\tau_{0.5}$ = 40-60 min, depending on the amount of II.

In **system b)** a very strong mutual inhibition is observed—the addition of the relatively more rapidly decomposing I not only does not increase the rate of decomposition of the mixture I + II, but even sometimes makes this rate lower than for pure ether.

In **system c)** the presence of CH_3OH decreases the rate of decomposition of I —the value of $\tau_{0.5}$ at 120° increases from 13-14 min to 22-24 min (for catalyst No. 4) or from 25 to 38 min (for No. 5). It is interesting to note that on catalyst No. 4, at identical surface coverages, methyl alcohol exerts a smaller inhibiting effect than ethyl alcohol, whereas on all the other catalysts the opposite relation is observed. Evidently, on this catalyst the methanol-isopropanol complexes (I) formed as intermediates are less stable than on the others.

Water (**system d**) at moderate surface coverages (up to 1.5 cm^3 (N.T.P.)/g) does not slow the rate of dehydration of iso-C_3H_7OH at all, while at high coverages (5.3 cm^3 (N.T.P.)/g) it leads to an increase of $\tau_{0.5}$ by a factor of 1.3-1.5. Apparently, water simply blocks the most catalytically active centers, displacing iso-C_3H_7OH onto the remaining unoccupied regions of lower

Fig. 2. Dehydration of iso-C_3H_7OH on catalyst No. 6 at 120°:
1 —pure iso-C_3H_7OH, 2 —iso-$C_3H_7OH + C_2H_5OH$ (5.3 cm^3 (N.T.P.)/g), 3 —the same (3 cm^3 (N.T.P.)/g)

Fig. 3. Inhibiting effect in the system ethyl ether—diisopropyl ether on catalyst No. 1 at 100°

adsorption and catalytic activity, but does not exert an inhibiting effect.

For **system d)** at 120° the following half-decomposition periods were found: for I, $\tau_{0.5}$ = 9 min; for II, 20 min; and for I + II, 12 min. The kinetic curve of the pressure of the reaction products in the system I + II is almost exactly the additive sum of the curves obtained for I and II separately, and in this case there is evidently neither mutual inhibition nor acceleration.

Dimethyl ether (**system e**), which by itself, as was to be expected, does not decompose at all under the reaction conditions in the adsorbed layer, exerts a very strong inhibiting influence on the rate of dehydration of iso-C_3H_7OH. Thus, for example, already at a surface coverage of about 1 cm^3 (N.T.P.)/g on catalyst No. 7 at 110°, the values of $\tau_{0.5}$ increase to 60 min, instead of 14–18 min for pure I.

A quite striking example of strong mutual inhibition of two reactions, each of which separately proceeds at a relatively high rate, is the case of the joint dehydration of $(C_2H_5)_2O$ and $(iso\text{-}C_3H_7)_2O$ (**system g**). On all the catalysts studied, $(iso\text{-}C_3H_7)_2O$ dehydrated considerably faster than ethyl ether; therefore, when the reaction for I and II was carried out separately, the total pressure of the olefin formed over a given interval of time was greater for $(iso\text{-}C_3H_7)_2O$, although the initial amount of this ether on the catalyst was considerably smaller than that of ethyl ether. In the dehydration of the mixture I + II, however, with the same amounts of the initial ethers, the reaction was inhibited so strongly that its rate did not exceed the rate for pure II. On catalyst No. 1, for the mixture I + II, after approximately one and a half hours the increase in pressure ceased altogether (see Fig. 3), i.e., the two reactions mutually suppressed one another. In this connection it should be taken into account that $(iso\text{-}C_3H_7)_2O$, the amount of which

on the surface did not exceed 2–3% of a monolayer, completely inhibited the decomposition of a sevenfold larger amount of diethyl ether.

The presence of CH_3OH during the dehydration of isopropyl ether (**system d**) does not lead to any noticeable decrease in the reaction rate: at 110° the corresponding values are 9 and 11 min. The different action of CH_3OH in mixtures with iso-C_3H_7OH and $(iso\text{-}C_3H_7)_2O$ (**systems c and d**) on one and the same catalyst confirms the opinion expressed by us earlier ([2]), namely that ethers are not intermediate products in the dehydration reaction of alcohols, and that the corresponding processes proceed by different mechanisms and through different elementary stages.

In **system i**, in a number of cases, some coupled dehydration is observed, although it is more weakly expressed than in system a): the values of $\tau_{0.5}$ for sec.-C_4H_9OH increase from 2–4 to 10–16 min, while the rate of increase of the ethylene pressure rises from 0.02 to 0.03–0.04 mm/hr.

Finally, the presence of C_2H_5OH during the dehydration of trimethylcarbinol (**system k**) does not lead to the coupled formation of ethylene, but causes only an increase in the limiting pressure of isobutylene formed from I. This phenomenon, especially pronounced on catalysts Nos. 1 and 2, is close to that

described above for system a) on catalyst No. 6. Evidently, on these catalysts a considerable part (up to 50%) of the isobutylene formed during the dehydration of pure trimethylcarbinol is not desorbed, but polymerizes on the surface. The presence of the second component, as in case a) for No. 6, inhibits the parallel polymerization reaction.

Thus, the results of this work confirm the conclusion made earlier ([1]) that, in the dehydration reaction, the reacting molecules cannot be regarded as isolated structures whose character of change does not depend on the nature and number of other molecules simultaneously present in the adsorbed layer. If other substances are present there which are also capable of undergoing the dehydration reaction (various alcohols and ethers), or at least of forming, under the given conditions, surface intermediate forms analogous to those formed during dehydration (methyl alcohol, dimethyl ether), then the rate of decomposition of isopropyl, ethyl, and sec.-butyl alcohols, as well as of diethyl and diisopropyl ethers, changes strongly. In this case the dehydration rate of the more rapidly decomposing component always decreases, whereas that of the more stable component either increases (the case of coupled dehydration) or decreases (the case of mutual inhibition). This phenomenon, in contrast to the known cases of inhibition of catalytic reactions in the liquid phase by reaction products or foreign substances, is not due to competition for a place on the catalyst surface (since in our case all components are already present in the adsorption layer), but is probably explained by the interaction of surface complexes with the formation of mixed complexes which, under the reaction conditions, possess greater or lesser stability in comparison with the initial ones.

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