PHYSICAL CHEMISTRY

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1961

SovietRxiv

Abstract

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INHIBITION OF SURFACE REACTIONS ON CATALYSTS AND THE MOBILITY OF ADSORBED MOLECULES

In studying the mechanism and elementary stages of the dehydration reaction of lower aliphatic alcohols on Al_2O_3 catalysts ($^{1-3}$), we showed that the molecule of the reacting substance at the moment of reaction on the active center of the catalyst is not an isolated structure incapable of interaction with neighboring molecules. Thus, in work (^{1}) a conjugated dehydration reaction of isopropyl and ethyl alcohols in the adsorption layer was described, and the assumption was made that radical-like intermediate forms are formed on the catalyst surface under conditions of catalytic dehydration. This assumption was subsequently confirmed experimentally in work (^{4}) for the case of dehydration of iso-C_3H_7OH on magnesium sulfate. In work (^{3}) cases of dehydration of binary mixtures of various alcohols and ethers in an adsorption layer on the catalyst surface were considered, and it was shown that in mixtures the rates of decomposition of the individual components are, as a rule, lower than for the individual substances at the same filling density.

In the present work the kinetics of dehydration of iso-C_3H_7OH and trimethylcarbinol was studied in the presence of certain substances located in the adsorption layer on the catalyst surface but incapable (in general or under the given conditions) of undergoing the dehydration reaction. The catalysts used were Al_2O_3 precipitated by bromine from an aluminate solution, $Al_2O_3 + Fe_2O_3$, and Al_2O_3 precipitated by CO_2 from an aluminate solution (catalysts Nos. 5, 6, 7 from work (^{3})), as well as W_2O_5*. For the characteristics of the Al_2O_3 catalysts and the method of investigation, see work (^{3}); the W_2O_5 catalyst had a specific surface area (from the nitrogen adsorption isotherm) of 14 m^2/g, dehydration activation energies in the adsorption layer of 17.8 and 31.2 kcal, and values of t°_{20}** = 76 and 187° for isopropyl and ethyl alcohols, respectively.

On alumina catalysts, in order to study the influence of adsorbed foreign substances on the reaction rate, dehydration of iso-C_3H_7OH adsorbed on the catalyst in an amount of 0.3 cm^3 (N.T.P.)/g was used as the standard reaction; this corresponds, for different samples, to a filling density of 2–4% of a monolayer. The influence of the following substances was investigated (the figures in parentheses denote catalyst numbers): acetone (5), dioxane (5, 7), acetonitrile (5), ethyl acetate (5), and nitrogen oxide (5, 6, 7). On W_2O_5, dehydration was studied in an adsorption layer of C_2H_5OH, iso-C_3H_7OH, $(CH_3)_3COH$, and the systems C_2H_5OH + iso-C_3H_7OH, $(CH_3)_3COH + CH_3OH$, $(CH_3)_3COH + C_2H_5OH$, $(CH_3)_3COH$+ iso-C_3H_7OH, $(CH_3)_3COH + H_2O$.

It turned out that acetone, which by itself does not decompose at all on the catalyst used and, as is known, is incapable of combining with iso-C_3H_7OH under ordinary conditions, exerts a strong inhibiting effect during the dehydration of isopropyl alcohol in the adsorption layer (Figs. 1, 3). As the amount of adsorbed acetone decreases, this inhibiting effect weakens, but it remains clearly expressed even at a coverage density of about 4-6% of a monolayer (Fig. 2, 1-4). Dioxane, already at coverages of about 2-4% of a monolayer, practically completely suppresses the dehydration of iso-C_3H_7OH both on catalyst No. 5 (see Fig. 1, 6) and on catalyst No. 7.

Acetonitrile has a somewhat weaker inhibiting effect (see Fig. 1, 4), so that to achieve a comparable effect it is necessary to use relatively high coverage densities (4–5 cm^3 (N.T.P.)/g).

Nitric oxide had no appreciable effect on the reaction, but this may be explained by the fact that its adsorption on the catalyst is relatively small and, with the same inlet amounts as the other substances studied, the resulting coverage density is small.

Fig. 1. Inhibition of the decomposition of iso-C_3H_7OH on catalyst No. 5 in the adsorbed layer at 120°.
1 –pure iso-C_3H_7OH; 2 –iso-C_3H_7OH + ethyl acetate (1.2 cm^3 (N.T.P.)/g); 3 –iso-C_3H_7OH + CH_3COCH_3 (0.3 cm^3 (N.T.P.)/g); 4 –iso-C_3H_7OH + acetonitrile (5.3 cm^3 (N.T.P.)/g); 5 –iso-C_3H_7OH + nitric oxide; 6 –iso-C_3H_7OH + dioxane (0.3 cm^3 (N.T.P.)/g).

Experiments on the dehydration of ethyl and isopropyl alcohols in the adsorbed layer on W_2O_5 showed that on this catalyst the reaction proceeds at temperatures considerably lower than on Al_2O_3. Thus, at a coverage density of about 20-30% of a monolayer, the half-decomposition period $\tau_{0.5}$ of iso-C_3H_7OH at 120° is less than 1 min, and at 100° is 6-7 min. For C_2H_5OH at 150°, practically complete absence of reaction was observed, while at 170 and 190° the values of $\tau_{0.5}$ were, respectively, 70 and 18 min. For the system iso-C_3H_7OH + C_2H_5OH, the coverage density with respect to iso-C_3H_7OH was the same, and the amount of C_2H_5OH introduced was 5.3 cm^3 (N.T.P.)/g, which, because of

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* Obtained from A. A. Tolstopyatova, to whom the authors express their gratitude.

** t°_{20} is the temperature at which the half-decomposition period $\tau_{0.5}$ is equal to 20 min.

Fig. 3

Figure 1: Fig. 3

the small value of the specific surface area, should have led to a degree of coverage close to a monolayer. Under these conditions it was first of all observed that already at 100–120° pure C_2H_5OH exhibits an unexpectedly high absolute rate of decomposition, manifested in an increase in the ethylene pressure in the gas phase, although the extent of decomposition (owing to the large initial amounts of alcohol) remains insignificant.

Fig. 2. Effect of the amount of acetone on the rate of decomposition of iso-C_3H_7OH on catalyst No. 5 in the adsorbed layer at 130°.
1 —pure iso-C_3H_7OH; 2 —the same + 3.0 cm^3 (N.T.P.)/g acetone; 3 —the same + 0.6 cm^3 (N.T.P.)/g acetone; 4 —the same + 5.3 cm^3 (N.T.P.)/g acetone; 5 —iso-C_3H_7OH + C_2H_5OH (5.3 cm^3 (N.T.P.)/g) —case of coupled dehydration.

Trimethylcarbinol on W_2O_5 at 30–80° (and higher) does not form gaseous products: the isobutylene formed evidently undergoes polymerization on the catalyst. That, in this case, unchanged initial alcohol does not remain on the catalyst was demonstrated by heating the catalyst after—

after adsorption to 300°, and in this case the alcohol should have been completely dehydrated with liberation of butylene, which was not observed (Fig. 3).

However, if the adsorption layer on the catalyst contains considerable amounts of previously adsorbed C_2H_5OH, iso-C_3H_7OH, or H_2O (but not *n*-pentane), then already at temperatures of 25—40° trimethylcarbinol undergoes the normal dehydration reaction with formation of isobutylene, which desorbs from the catalyst surface into the gas phase (Fig. 3). Thus, the presence of hydroxyl-containing substances in the adsorbed layer practically completely suppresses the polymerization reaction. A similar influence of C_2H_5OH on the decomposition reaction of iso-C_3H_7OH over the $Al_2O_3 + Fe_2O_3$ catalyst was noted in work (3).

The results of the present work, as well as of works (2,3), show that the dehydration of alcohols on oxide catalysts in the adsorption layer at low temperatures is not a simple monomolecular reaction of one-stage elimination of water, but has a more complex mechanism. The facts we have found concerning the mutual influence of molecules in the adsorption layer may be explained on the basis of two different assumptions: 1) a change in the electronic properties of the catalyst as a result of adsorption of the second component of the mixture and 2) direct interaction of adsorbed molecules or active components on the catalyst surface. The first of these two possibilities seems considerably less probable, since such a change in electronic properties is substantial only for semiconductors, whereas Al_2O_3 at the temperatures of our experiments is a dielectric. In addition, this assumption does not explain the reasons for the different, sometimes even opposite, action of additives of the same type—alcohols, ethers, etc.

Fig. 3. Decomposition of trimethylcarbinol on W_2O_5 at 40°.
1 –pure trimethylcarbinol; 2 –trimethylcarbinol $+C_2H_5OH$ (high surface coverage density); 3 –the same $+C_2H_5OH$ (low surface coverage density); 4 –the same $+CH_3OH$ (high surface coverage density)

On the other hand, by many formal criteria—by the presence of an accelerating or inhibiting influence of foreign substances, by the dependence of this effect on the reaction temperature and on the concentration of additives, by the presence of a critical concentration of the initial substances for attainment of a definite reaction rate (as, for example, in the case of dehydration of C_2H_5OH on W_2O_5 at 100–120°), etc.—these processes resemble chain reactions involving free radicals in the gas phase. Although the existence of flat chains cannot yet be regarded as established, the presence of radical-like surface forms under the conditions of our experiments was experimentally proved by us from the occurrence of the para-ortho conversion reaction of hydrogen at the moment when the dehydration process proceeds ([4]). On the other hand, this is in agreement with the fact of exchange of hydrocarbon radicals under dehydration-reaction conditions, established by us by a radiochemical method ([5]). The considerations presented make the second explanation—through direct interaction of adsorbed molecules with formation of intermediate transition complexes—considerably more probable.

The question of the nature of these complexes still remains unresolved; attention is drawn to the circumstance that all the additives used (except *n*-pentane, which had no inhibiting effect) contain atoms possessing lone electron pairs, which is manifested, in particular,

in the considerable polarity of the corresponding molecules. The absence of a dipole moment in dioxane is only an apparent exception, since it is explained by internal compensation of the charges of two oxygen atoms with unshared electron pairs. It is known that such compounds have a considerable capacity for addition reactions and can, as, for example, NO, serve as traps for free radicals. Indeed, all of them inhibit dehydration in the adsorbed layer. The absence of an effect of nitrous oxide is apparently connected with the fact that it is very weakly adsorbed on Al_2O_3.

A similar inhibiting influence of neighboring adsorbed molecules can apparently, along with simple adsorption displacement caused by differences in relative adsorption coefficients, serve as the reason for the influence, observed by many authors (see, for example, ([6],[7])), of the nature of the solvent on the rate of the catalytic hydrogenation reaction.

Along with the collective mechanism of dehydration in the adsorbed layer considered here, a simple single-step mechanism with immediate desorption of the reaction products cannot be regarded as excluded. At low temperatures and with a relatively long lifetime of intermediate surface forms, as was the case under the conditions of our experiments, the collective mechanism should play a large role. At high temperatures, characteristic of dehydration under ordinary flow conditions at atmospheric pressure, more favorable conditions may be created for the single-step mechanism. This difference in the mechanisms of the process may serve to explain the difference, noted in work (1), in the values of the activation energy of the dehydration reaction in the monolayer and under ordinary conditions.

Finally, the facts found by us, in our opinion, make it possible to draw one more conclusion. Both for the interaction of molecules of two different substances in an adsorbed layer and for the polymerization of an olefin formed from an alcohol, it is necessary that these molecules, initially located far from one another owing to the low initial degree of filling (up to 6–8% of a monolayer), be able to come closer to a distance permitting the action of chemical forces. The question of the possibility of diffusion over the catalyst surface, which is of fundamental importance for understanding the mechanism of catalytic processes, has repeatedly been discussed in the literature (see, for example, the review (8)), but in different cases it has been resolved differently. The judgments expressed by various authors on this question are based either on indirect experiments or on general thermodynamic considerations about the possible nature of the adsorbed layer. Our experimental data unambiguously show the possibility of surface diffusion on Al_2O_3 and W_2O_5 catalysts even of relatively firmly bound chemisorbed molecules already at temperatures of 60–150°.

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
19 V 1961

CITED LITERATURE

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