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ON THE MECHANISM OF THE ACTION OF MODIFYING ADDITIVES ON THE SELECTIVITY OF ZINC OXIDE WITH RESPECT TO THE DEHYDROGENATION AND DEHYDRATION OF ISOPROPYL ALCOHOL

(Presented by Academician M. M. Dubinin, March 21, 1960)

In earlier studies ([1–5]) it was established that zinc oxide, upon sorption of microimpurities from electrolyte solutions, is capable of markedly changing its catalytic activity and selectivity with respect to the decomposition of isopropyl alcohol. It was of interest to investigate in greater detail the nature of the action of modifying additives on the processes of dehydrogenation and dehydration of isopropyl alcohol by comparing the kinetic, chemisorption, and electronic characteristics of the catalyst samples under study.

Modified samples of the zinc oxide catalyst were prepared by the measured introduction of additives mainly onto the surface of zinc oxide. Additives of sodium and lithium oxides were introduced by impregnating zinc oxide with oxalic-acid salts, followed by carrying out the topochemical process of their decomposition at relatively low temperatures (450–500°C). Additives of zinc sulfate were introduced by chemical sorption from solutions containing various concentrations of the given electrolyte ([4,5]).

The specific surface areas of the catalyst samples studied were determined from the adsorption of *n*-heptane, developed in the catalysis laboratory of the Institute of Physical Chemistry of the Academy of Sciences of the USSR, by a chromatographic method ([6]), and, for some samples, from krypton adsorption at $T = 196^{\circ}$ by BET. The two methods gave concordant results.

The catalysts were tested in an adsorbed layer.

It was established that the kinetics of dehydrogenation and dehydration of isopropyl alcohol obeys the bilogarithmic equation characteristic of a heterogeneous surface:

Fig. 1. Kinetic curves for the dehydrogenation of isopropyl alcohol on samples of modified zinc oxide:
I –ZnO + 0.114% Na_2O;

Figure 1. Kinetic curves for the dehydrogenation of isopropyl alcohol on samples of modified zinc oxide: I –ZnO + 0.114% Na2O; II –ZnO + 0.38% Na2O; III –ZnO + 3.1% Li2O; IV –ZnO + 6.2% Na2O; V –ZnO without additives; VI –ZnO + 14.5% ZnSO4.

Figure 1: Figure 1. Kinetic curves for the dehydrogenation of isopropyl alcohol on samples of modified zinc oxide: I –ZnO + 0.114% Na2O; II –ZnO + 0.38% Na2O; III –ZnO + 3.1% Li2O; IV –ZnO + 6.2% Na2O; V –ZnO without additives; VI –ZnO + 14.5% ZnSO4.

II –ZnO + 0.38% Na_2O;
III –ZnO + 3.1% Li_2O;
IV –ZnO + 6.2% Na_2O;
V –ZnO without additives;
VI –ZnO + 14.5% $ZnSO_4$.

$$q = At^{1/n}, \tag{1}$$

where q is the amount of alcohol that has reacted, and $1/n$, A are constants.

As a characteristic of the activity of the catalysts studied, the initial rates were chosen, corresponding to the rate in the first minute of the process. The activation energy was calculated from the values of the initial rates, and also according to the formula:

$$E = -\frac{4.57\left(\ln t_{1q} - \lg t_{2k}\right)}{1/T_2 - 1/T_1}, \tag{2}$$

Table 1

Dependence of the kinetic characteristics of the dehydrogenation and dehydration of isopropyl alcohol on the introduction of modifying additives into zinc oxide

Catalyst	S, m^2/g	$V_{sp} \cdot 10^{-3}$, cm^3/min, 130°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 150°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 180°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 200°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 220°	E, kcal/mol (from initial rate)	$\lg V_0$
Dehydrogenation								
ZnO without additives	2.1	–	–	0.4	0.87	3.3	23	7.6

Catalyst	S, m^2/g	$V_{sp} \cdot 10^{-3}$, cm^3/min, 130°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 150°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 180°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 200°	$V_{sp} \cdot 10^{-3}$, cm^3/min, 220°	E, kcal/mol (from initial rate)	$\lg V_0$
ZnO + 0.114% Na_2O	3.0	–	7.0	20	–	–	17.7	6.8
ZnO + 0.38% Na_2O	3.0	–	2.3	14	24	–	18.0	6.7
ZnO + 6.2% Na_2O	3.0	–	1.7	8.0	13.3	–	17	6.0
ZnO + 3.1% Li_2O	4.9	–	1.2	10.2	22.4	–	27	10.8
ZnO + 14.5% $ZnSO_4$	7.9	–	–	0.27	1.9	4.8	32	12.1
Dehydration								
ZnO without additives	2.1	–	–	2.3	7.9	22	26	9.9
ZnO + 14.5% $ZnSO_4$	7.9	–	–	4.6	16.5	51	27	10.7

where q is the amount of alcohol that has reacted, or the percentage of the catalyst surface filled with chemisorbed alcohol.

Figure 1 presents kinetic curves for the dehydrogenation of isopropyl alcohol on zinc oxide samples with introduced additives. The reaction was carried out at 180°. The entire series of samples was prepared on luminescent zinc oxide, characterized by both dehydrogenating and dehydrating properties ([7]). The rate of dehydrogenation increases sharply upon introduction of sodium and lithium oxides and decreases upon introduction of zinc sulfate additives. Detailed kinetic

Fig. 2. Kinetic isotherms of acetone desorption from zinc oxide: I —at 120°; II —at 150°; III —at 190°

Figure 2: Fig. 2. Kinetic isotherms of acetone desorption from zinc oxide: I —at 120°; II —at 150°; III —at 190°

data are given in Table 1. As follows from Table 1, the introduction of 0.114% sodium oxide increases the specific dehydrogenation rate, i.e., the rate referred to 1 m^2 of surface, by a factor of 50. At the same time, the activation energy of dehydrogenation decreases. The introduction of 0.38 and 6.2% sodium also leads to a significant increase in specific catalytic activity, although these points apparently lie below the optimum concentration of this modifying additive. A significant increase in specific catalytic activity is also caused by introduction of a lithium oxide additive. Conversely, the introduction of zinc sulfate lowers the specific dehydrogenation constant and increases the activation energy of this process. As for the dehydration of isopropyl alcohol, the introduction of 0.114% sodium into a sample of luminescent zinc oxide almost completely suppressed this process. The specific rate of dehydration increases with increasing zinc sulfate content, while the activation energy of dehydration remains practically unchanged.

It was of interest to investigate the kinetic regularities of adsorption and desorption of isopropyl alcohol and of the product of its conversion—acetone—on samples of pure and modified zinc oxide. It was established that chemisorption of isopropyl alcohol at temperatures close to the catalytic temperatures, and chemisorption of acetone at catalytic temperatures, proceed practically instantaneously. Desorption of chemisorbed isopropyl alcohol and acetone proceeds slowly. Characteristic kinetic isotherms of acetone desorption from zinc oxide at different temperatures are presented in Fig. 2. These isotherms do not become linear in semilogarithmic coordinates, as would be characteristic of a homogeneous surface. The activation energy of acetone desorption from zinc oxide at a coverage of ~2% of a monolayer, calculated by formula 1, is 32 kcal/mol. Introduction of an additive of 14.5% $ZnSO_4$ leads to an increase in the activation energy to 41 kcal/mol (at approximately the same coverage), while an additive of 6.2% Na_2O leads to a decrease in the activation energy to 10.0 kcal/mol.

Figure 3 presents curves characterizing the change in work function in electron-volts as a function of the content of modifying additives in zinc oxide. The electron work function was determined from the contact potential difference by the vibrating-capacitor method (8). The measurements were carried out by E. Kh. Enikeev. The accuracy of the measurements was 0.01 V. As follows from Fig. 3, with increasing content of sodium and lithium oxide additives in zinc oxide, the work function decreases. With increasing zinc sulfate content, the work function increases.

Fig. 2. Kinetic isotherms of acetone desorption from zinc oxide: *I* —at 120°; *II* —at 150°; *III* —at 190°.

Fig. 3. Dependence of the electron work function of zinc oxide on the content of modifying additives

Figure 3: Fig. 3. Dependence of the electron work function of zinc oxide on the content of modifying additives

According to electronic concepts, additives of sodium and lithium oxides are donor additives, shifting the Fermi level at the surface toward the conduction band. These additives charge the surface of zinc oxide positively. Additives of zinc sulfate and thorium dioxide are acceptor additives, shifting the Fermi level toward the valence band and impeding the transition of electrons into the conduction band. In this case the surface of zinc oxide becomes negatively charged. It should be noted that donor additives are characterized by basic properties, and acceptor additives by acidic properties.

Fig. 3. Dependence of the electron work function of zinc oxide on the content of modifying additives.

To study the influence of chemisorption of isopropyl alcohol and of the products of its conversion on the charging of the surface of the investigated zinc oxide samples, simultaneous measurements were made of the electrical conductivity and work function in an atmosphere of vapors of alcohol, acetone, and water, as well as of hydrogen and propylene (pressure 10 mm Hg), at temperatures close to the catalysis temperature (100°). It had previously been established that under these conditions significant chemisorption of isopropyl alcohol and acetone takes place (~60% of a monolayer).

It was established that chemisorption of isopropyl alcohol at temperatures close to the catalysis temperature leads to a decrease in the work function by 0.1 eV both on the initial zinc oxide sample and on samples with additives of sodium oxide and zinc sulfate. Chemisorption of acetone leads to the same effect. Consequently, isopropyl alcohol and acetone are electron donors, and their chemisorption is accompanied by the transfer of electrons from the adsorbed molecules to the conduction band of zinc oxide. Chemisorption of water vapor, even on samples possessing maximum dehydrating ability (for example, zinc oxide containing 14.5% zinc sulfate), at 20° does not change the electrical conductivity or the work function. At a temperature of 100° small fluctuations of the work function were observed, lying within the limits of measurement accuracy. The presence of hydrogen and

propylene had no effect on any of the above-mentioned electronic characteristics. The data obtained by us are in good agreement with the results of F. I. Vilesov and A. N. Terenin [9], as well as with the data of E. Kh. Enikeev, L. Ya. Margolis, and S. Z. Roginskii [10].

On the basis of the results obtained, one can draw a conclusion about the mechanism of the dehydrogenation process and about the character of the influence of modifying additives on the stages of this process.

Apparently, dehydrogenation consists of the following three stages:

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CHOH^+ + \ominus, \quad \text{(I)}$$

$$(CH_3)_2CHOH^+ \rightarrow (CH_3)_2CO^+ + H_2, \quad \text{(II)}$$

$$(CH_3)_2CO^+ + \ominus \rightarrow (CH_3)_2CO. \quad \text{(III)}$$

The first stage—chemisorption of isopropyl alcohol—is a donor stage and is accompanied by displacement of an electron from the chemisorbed molecule into the conduction band of zinc oxide. The chemisorbed molecule of isopropyl alcohol becomes positively charged. This stage, according to our data, proceeds at a very high rate, practically instantaneously. In the second stage, chemisorbed acetone, also positively charged, is formed, and gaseous hydrogen is evolved. The third stage—desorption of chemisorbed acetone—is an acceptor stage, requiring the transfer of an electron from the conduction band of zinc oxide to the chemisorbed acetone. As was shown (see Fig. 2), acetone desorption proceeds extremely slowly. Acetone desorption is evidently the limiting stage of the dehydrogenation process of isopropyl alcohol.

The activation energy of acetone desorption decreases upon introduction of a donor additive—sodium oxide. Conversely, introduction of an acceptor additive —zinc sulfate—increases the activation energy of acetone desorption. This agrees with the established fact that the activation energy of dehydrogenation decreases upon introduction of sodium oxide additives and increases upon introduction of zinc sulfate additives (see Table 1).

Thus, the totality of the data obtained permits one to suppose that dehydrogenation of isopropyl alcohol is an electronic (donor-acceptor) process, in which the role of the limiting stage is played by the acceptor stage of acetone desorption. The results obtained by us do not confirm the supposition of Hauffe [12], Schwab [13], and Garner [14] concerning the limiting role of the donor stage of dehydrogenation of isopropyl alcohol on zinc oxide.

Dehydration of isopropyl alcohol can apparently be interpreted as an acid-type process, proceeding by transfer of protons from the catalyst to the reacting molecule and back.

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