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Table 1

1958

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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE FREE ENERGY, HEAT, AND ENTROPY OF ADSORPTIVE DISPLACEMENT OF ALCOHOLS BY WATER FROM THE SURFACE OF AN OXIDE CATALYST

In works ([1]) the kinetics of dehydrogenation of a series of alcohols over a mixed oxide catalyst was investigated. It was shown that the dehydrogenation reaction proceeds on the catalyst without appreciable formation of products of decomposition and dehydration of the alcohols. The relative adsorption coefficients of the reaction products were determined. It was found that the relative adsorption coefficient of hydrogen is practically equal to zero, while the relative adsorption coefficients of aldehydes are a function of temperature and decrease with increasing temperature.

Table 1

Dehydrogenation of binary alcohol–water mixtures

Run no.	Temperature, °C	Amount of H_2, NTP, l, in 5 min	Gas analysis (vol. %)	Gas analysis (vol. %)	Gas analysis (vol. %)
			CO_2	C H_2	H_2
n-Propyl alcohol–water	*n*-Propyl alcohol–water	*n*-Propyl alcohol–water	*n*-Propyl alcohol–water	*n*-Propyl alcohol–water	*n*-Propyl alcohol–water
534	307	10.9	none	none	99.9
535	320	19.4	0.4	0.2	99.4
538	326	20.7	0.4	0.2	99.4
536	342	36.1	1.2	0.2	98.6
537	357	52.2	1.4	0.2	98.4
n-Butyl alcohol–water	*n*-Butyl alcohol–water	*n*-Butyl alcohol–water	*n*-Butyl alcohol–water	*n*-Butyl alcohol–water	*n*-Butyl alcohol–water
539	302	8.6	none	none	99.9
540	322	15.5	0.4	none	99.6
541	340	30.5	0.8	0.2	99.0

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Run no.	Temperature, °C	Amount of H_2, NTP, l, in 5 min	Gas analysis (vol. %)	Gas analysis (vol. %)	Gas analysis (vol. %)
542	360	51.0	0.8	0.6	98.6
n-Hexyl alcohol–water	*n*-Hexyl alcohol–water	*n*-Hexyl alcohol–water	*n*-Hexyl alcohol–water	*n*-Hexyl alcohol–water	*n*-Hexyl alcohol–water
550	302	11.5	none	none	100
547	320.5	26.0	0.6	”	99.4
548	340	52.0	0.8	”	99.2
549	360	83.0	0.8	0.2	99.0

In the present work the kinetics of dehydrogenation of binary mixtures of primary alcohols of normal structure with water over the same oxide catalyst was investigated. The aim of the work was to determine the relative adsorption coefficients of water and to study the dependence of these quantities on the length of the carbon chain of the alcohol. Investigation of the adsorption coefficients is of interest from the point of view of the orientation of molecules on the surface. The following alcohols were taken for the work: *n*-propyl, *n*-butyl, and *n*-hexyl. Before the experiment the alcohols were dried with magnesium methylate ([2]) and fractionated on a column. The alcohols had the following constants: *n*-propyl alcohol, b.p. 97–97.2°, d_4^{20} 0.8044, n_D^{20} 1.3858; *n*-butyl alcohol, b.p. 117–117.5°, d_4^{20} 0.8098, n_D^{20} 1.3992; *n*-hexyl alcohol, b.p. 155.1–155.8°, d_4^{20} 0.8196, n_D^{20} 1.4188.

The initial alcohol–water mixtures were obtained by adding water to a weighed amount of alcohol. In preparing the mixtures, the limited mutual solubility of the components imposed a limit on the choice of concentrations. In the experiments with *n*-propyl and *n*-butyl alcohols the mixtures contained 34.2 mol.% water, and in the experiments with *n*-hexyl alcohol, 17.1 mol.% water. The experiments were carried out by the flow method under the same conditions as in works ([1]). The reaction rate was determined from the evolution of hydrogen, which occurred

at a constant rate; as analysis showed, the gas evolved contained a small amount of CO_2 and unsaturated hydrocarbons, not exceeding 2% (Table 1). The experiments were carried out in the temperature range 300–360° with a mixture flow rate of 1.05 ml in 5 min for mixtures of propyl and butyl alcohols, and 1.4 ml in 5 min for mixtures of hexyl alcohol.

Table 2

Dehydrogenation of binary alcohol–water mixtures. Relative adsorption coefficients of water, calculated by formula (1)

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Mixtures	Temperature, °C	m_0 (p = 100 mol. %)	m (p = 65.8 mol. %)	z	$-\Delta F$, cal/mol	$-\Delta H$, kcal/mol	$-\Delta S$, cal/(deg·mol)
n-Propyl alcohol—water	307	31	10.9	3.5	1440	16.2	26.0
n-Propyl alcohol—water	326	45	20.7	2.25	960	16.2	26.0
n-Propyl alcohol—water	342	60	36.1	1.27	290	16.2	26.0
n-Propyl alcohol—water	357	77	52.2	0.9	130	16.2	26.0
n-Butyl alcohol—water	302	25	8.6	3.6	1460	16.4	26.0
n-Butyl alcohol—water	320	35	15.5	2.42	1040	16.4	26.0
n-Butyl alcohol—water	341	52	30.5	1.34	360	16.4	26.0
n-Butyl alcohol—water	360	75	51.0	0.9	130	16.4	26.0

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Mixtures	Temperature, °C	m_0 (p = 100 mol. %)	m (p = 65.8 mol. %)	z	$-\Delta F$, cal/mol	$-\Delta H$, kcal/mol	$-\Delta S$, cal/(deg·mol)
n-Hexyl alcohol–water	302	28	14.5	3.7	1490	16.4	26.1
n-Hexyl alcohol–water	320.5	43	26.0	2.48	1070	16.4	26.1
n-Hexyl alcohol–water	340	70	52.0	1.36	370	16.4	26.1
n-Hexyl alcohol–water	360	102	83.0	0.9	140	16.4	26.1

The data obtained are given in Table 1 and arranged in order of increasing temperature. Table 2 gives the values of the relative adsorption coefficients of water, z_4, calculated from the experimental data by formula (3):

$$z_4 = \left(\frac{m_0}{m} - z\right) \Big/ \left(\frac{100}{p} - 1\right). \quad (1)$$

As can be seen from the data presented, the relative adsorption coefficient of water depends on temperature; as the temperature rises, its value decreases. Comparing the rates of alcohol dehydrogenation at the same temperature, observed with alcohol-water mixtures, with the rates obtained with pure alcohol (m and m_0, Table 2), one can see that the addition of water reduces the rate of alcohol dehydrogenation by more than 45% at a temperature of 320°. With increasing temperature the inhibiting effect of water gradually decreases. Thus, one may conclude that water vapors are adsorbed by the catalyst, and the more strongly the lower the temperature. The adsorption coefficients of water on the active centers of the catalyst in the temperature interval studied prove to be 3.5-1.3 times greater for water than for alcohol. Figure 1 shows the values of z_4 for the alcohols studied at different temperatu–

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Figure 1. Value of z4 as a function of temperature for mixtures of different alcohols with water: 1 —n-propyl alcohol; 2 —n-butyl alcohol; 3 —n-hexyl alcohol

Figure 1: Figure 1. Value of z4 as a function of temperature for mixtures of different alcohols with water: 1 —n-propyl alcohol; 2 —n-butyl alcohol; 3 —n-hexyl alcohol

Fig. 1. Value of z_4 as a function of temperature for mixtures of different alcohols with water: 1 —*n*-propyl alcohol; 2 —*n*-butyl alcohol; 3 —*n*-hexyl alcohol.

···vapors. As is seen from Table 2, the values of the relative adsorption coefficients of water, calculated from the experimental data for *n*-propyl, *n*-butyl, and *n*-hexyl alcohols, have values close to one another. Applying to the data obtained the formula derived earlier [4,5]

$$\Delta F = -RT \ln z_4, \tag{2}$$

we find the free energy of the adsorption displacement of alcohol by water from the active surface of the catalyst (see Table 2). In the coordinates $\lg z_4$—$1/T$ (Fig. 2), the experimental points lie on a straight line. From this, the changes in heat content ΔH and entropy ΔS during the adsorption displacement of alcohols by water vapor from the active surface of the catalyst were calculated (see Table 2).

Fig. 2. Dependence of $\lg z_4$ on the reciprocal absolute temperature

Since

$$z_4 = \frac{a_{\text{w}}}{a_{\text{sp1}}} = \frac{a_{\text{w}}}{a_{\text{sp2}}}, \tag{3}$$

where a_{w}, a_{sp1}, and a_{sp2} are the adsorption-equilibrium constants, respectively, of water, of one alcohol, and of another alcohol, then

$$\frac{a_{\text{sp2}}}{a_{\text{sp1}}} = 1 \tag{4}$$

and, consequently, the adsorption coefficients of the alcohols in this case are identical. The equality of the adsorption coefficients, in turn, indicates the identical orientation of the molecules of the alcohols studied with respect to the active centers of the catalyst surface.

On the basis of the experimental data obtained by us, it may be concluded that the reaction of alcohol dehydrogenation on an oxide catalyst is appreciably inhibited by water; moreover, the absolute adsorption coefficients water—alcohol

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for primary alcohols of normal structure are a function of temperature and do not depend on the length of the carbon chain of the alcohol.

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Received
23 VIII 1957

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