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A. A. TOLSTOPYATOVA, Academician A. A. BALANDIN, and I. R. KONENKO

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Abstract

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A. A. TOLSTOPYATOVA, Academician A. A. BALANDIN, and I. R. KONENKO

CATALYTIC TRANSFORMATIONS OF ALCOHOLS AND CYCLIC HYDROCARBONS ON TITANIUM DIOXIDE

Although titanium dioxide is a sufficiently accessible catalyst, it belongs among the little-studied catalysts. The aim of the present work was to study the catalytic properties of TiO_2, prepared by various methods, in reactions with alcohols (ethyl, isopropyl, *n*-propyl) and hydrocarbons (cyclohexane, cyclohexene, 1,4-cyclohexadiene), and also to investigate the kinetics of these reactions and determine the binding energies of C, H, and O atoms with the TiO_2 surface. To study the catalytic reactions, the method of a differential thermocouple was used, which made it possible to overcome a number of experimental difficulties. The differential 20-junction thermocouple (chromel—copel) differed from that described earlier ([1]-[3]) in that all the junctions and the ordinary thermocouple were fastened on one half of a mica plate, while its other half remained free. The position of the catalyst relative to the differential thermocouple is shown in Fig. 1. The emf of the differential thermocouple was continuously recorded on an EPP-09 potentiometer, in which the zero position of the pointer needle was at the center of the scale; this made it possible to record endo- and exothermic heat effects of the processes. The apparatus and experimental procedure are described in detail in work ([4]). The use of the differential thermocouple made it possible to study changes in catalyst activity during each experiment, the conditions of their regeneration, and also carbon-deposition processes.

Using the differential thermocouple in combination with chemical methods of analysis, it was established that, in the case of isopropyl alcohol, during the initial 15–20 min the catalyst surface (each of the 4 samples) becomes covered with carbonaceous deposits; this is associated with a sharp change in the ratio of the rates of dehydrogenation and dehydration of the alcohol. During the first 2–5 min the alcohol practically undergoes only dehydrogenation; then dehydrogenation and dehydration proceed simultaneously, with the ratio of the rates of these reactions changing; and 20–25 min after the start of the experiment the alcohol undergoes only dehydration. At the same time, the total amount of gas evolved per unit time remains unchanged throughout the experiment. All this shows that the centers active toward dehydrogenation of the alcohol, after their carbonization, are poisoned with respect to this reaction, while at the same time acquiring the ability to dehydrate the alcohol at the same rate. The change in the ratio of the rates of the two reactions was established from the change in the heat effect (in relative divisions of the EPP-09 scale) during the first 15–20 min and was confirmed by analyses of gas samples taken during the experiment (Table 1).

Table 1

Change in the composition of gaseous products during an experiment with isopropyl alcohol

Time from the start of the experiment, min	ΔH in scale divisions	Gas composition, vol. %	Gas composition, vol. %
		propylene	hydrogen
2–4	1–2	1.0	99.0
8–10	5–11	43.8	54.5
15–16	12–15	61.7	38.2
18–20	15–16	72.5	26.8
22–24	17–18	98.0	2.0

With the aid of a differential thermocouple, the conditions for regeneration of the catalyst were found: after each experiment the carbonaceous film was removed by a strong stream of air, the catalyst first being heated to a temperature exceeding the experimental temperature by 40–50°. The end of regeneration was judged from the return of the EPP-09 pointer to the zero position. Regeneration usually lasted 20–30 min, depending on the conditions under which the experiment was carried out. To obtain reproducible results for the purpose of calculating the activation energies of dehydrogenation and dehydration, the gaseous and liquid products of the conversion of isopropyl alcohol were collected at different temperatures during time intervals corresponding to the same degree of carbonization of the catalyst, which was estimated from the magnitude of the t.d.s. of the thermocouple from a plot: t.d.s.—time from the beginning of the experiment.

The influence of the method of preparation of TiO_2 on its catalytic properties was studied using as an example 4 samples of TiO_2 obtained by precipitating hydroxides from $TiCl_4$ with water (No. 1); with ammonia (No. 2); by oxidation with air of freshly prepared $Ti(OH)_3$ precipitated from $TiCl_3$ with ammonia (No. 3); and by hydrolysis of orthoethyl titanate (No. 4). The $Ti(OH)_4$ hydroxides, washed free of Cl' ions, were dried for 6 h at 110° and dehydrated for 24 h with a gradual increase in temperature to 580°. The catalysts were formed as pieces 1 mm in diameter (No. 4 in the form of a powder). X-ray structural analysis of sample No. 1 showed that anatase was obtained. Table 2 gives the list of reactions studied in certain temperature ranges, the values of the activation energies ϵ and of the pre-exponential factors K_0 of the Arrhenius equation, and also indicates the degree of carbonization of the surface of each sample in the given reaction. The ethylene hydrogenation reactions indicated here were not studied, but since in all cases the reaction with ethyl alcohol forms a large amount

Table 2

Influence of the method of preparation and carbonization of the surface on the catalytic properties of TiO_2

Reaction	Surface state*	Temp. interval, °C, sample No. 1	Temp. interval, °C, sample No. 2	Temp. interval, °C, sample No. 3	Temp. interval, °C, sample No. 4	ϵ, kcal/mol, sample No. 1	ϵ, kcal/mol, sample No. 2	ϵ, kcal/mol, sample No. 3	ϵ, kcal/mol, sample No. 4	K_0, sample No. 1	K_0, sample No. 2	K_0, sample No. 3	K_0, sample No. 4
Dehydrogenation of C_2H_5OH	p.s.	299–340	334–404	392–457	340–398	22.8	20.4	9.4	12.4	$1.0\cdot 10^8$	$1.9\cdot 10^7$	$1.4\cdot 10^3$	$1.2\cdot 10^4$
Dehydration of C_2H_5OH	p.s.	299–370	334–444	392–457	340–398	25.0	25.4	9.0	12.5	$2.3\cdot 10^9$	$5.0\cdot 10^8$	$3.7\cdot 10^3$	$4.4\cdot 10^4$
Hydrogenation of ethylene	p.s.	299–340	334–404	392–457	340–398	21.2	22.2	13.0	16.8	$1.8\cdot 10^7$	$1.0\cdot 10^8$	$1.3\cdot 10^4$	$2.7\cdot 10^5$
Dehydration of iso-C_3H_7OH	p.s.	221–255	253–316	294–324	293–303	22.9	9.1	26.2	17.2	$3.7\cdot 10^9$	$9.1\cdot 10^0$	$1.0\cdot 10^{10}$	$2.8\cdot 10^7$
Dehydration of n-C_3H_7OH	p.s.	260–310	253–304			19.9				$3.7\cdot 10^8$	$2.2\cdot 10^4$		
Dehydrogenation of iso-C_3H_7OH	p.s.	266–310	253–304	480–518	454–505	9.1	10.4	21.6	15.0	$1.0\cdot 10^4$	$6.9\cdot 10^5$	$1.3\cdot 10^6$	$3.5\cdot 10^4$

Reaction	Surface state*	Temp. interval, °C, sample No. 1	Temp. interval, °C, sample No. 2	Temp. interval, °C, sample No. 3	Temp. interval, °C, sample No. 4	ϵ, kcal/mol, sample No. 1	ϵ, kcal/mol, sample No. 2	ϵ, kcal/mol, sample No. 3	ϵ, kcal/mol, sample No. 4	K_0, sample No. 1	K_0, sample No. 2	K_0, sample No. 3	K_0, sample No. 4
Dehydrogenation of n-C_3H_7OH	p.s.	316–316	253–304			25.4	15.3			$8.7 \cdot 10^9$	$1.1 \cdot 10^5$		
Dehydration of iso-C_4H_9OH	p.s.	443–498	460–528			19.6	14.7			$3.0 \cdot 10^6$	$5.1 \cdot 10^4$		
Dehydrogenation of C_6H_{12}	c.s.	446–470				22.2				$4.9 \cdot 10^7$			
Dehydrogenation of C_6H_{10}	p.s.	302–440				25.5				$6.2 \cdot 10^7$			
Dehydrogenation of 1,4-C_6H_8	p.s.	362–456				22.3				$2.4 \cdot 10^7$			
Isomerization of catalin C_6H_{10}	p.s.	300–420				26.1				$2.2 \cdot 10^9$			
Dehydration of tert-C_4H_9OH	p.s.	343–370				13.4				$6.3 \cdot 10^3$			
Dehydration of n-$C_5H_{11}OH$	p.s.	343–370				12.1				$4.5 \cdot 10^4$			

* p.s.—partly carbonized; c.s.—completely carbonized; n.c.—uncarbonized.

ethane (up to 40%); it is assumed that the latter can be formed during hydrogenation of ethylene on TiO_2 (5,6). It is seen from Table 2 that the method of preparation substantially affects the values of ε and K_0 for each reaction.

Fig. 1. Schematic of catalytic tube and thermocouple arrangement

Figure 1: Fig. 1. Schematic of catalytic tube and thermocouple arrangement

The kinetics of the catalytic conversion of isopropyl alcohol and cyclohexane was studied in detail on sample No. 1. The relative adsorption coefficients z of the reaction products were calculated from the dependence of the reaction rate on the composition of binary mixtures: alcohol—acetone, alcohol—hydrogen; alcohol—water, alcohol—propylene (dehydrogenation and dehydration of the alcohol), and cyclohexane—benzene, cyclohexane—hydrogen (dehydrogenation of cyclohexane), by the formula (7):

$$z = \left(\frac{m_0}{m} - 1\right) \Big/ \left(\frac{100}{P} - 1\right),$$

where m_0 and m are the amounts of reaction product formed (calculated for the vapor state under normal conditions), respectively

Table 3

Dependence of z on temperature and the values of ΔH°, ΔS°, and ΔF°

t, °C	z_{H2}	z_{acet}	$\Delta F^\circ_{\mathrm{acet}}$, kcal/mol	$z_{\mathrm{C_3H_6}}$	$z_{\mathrm{H_2O}}$	$\Delta F^\circ_{\mathrm{H_2O}}$, kcal/mol	t, °C	$z_{\mathrm{C_6H_6}}$	$z_{\mathrm{H_2}}$
282	0.9	2.4	−1090.0		1.9	−707.0	444	0.6	0.7
294	0.9	1.7	−665.0	0.2	1.4	−378.0	460	0.7	0.7
310	0.9	1.2	122.0	0.2	0.9	122.0	480	0.7	0.7

$$\Delta H^\circ_{\mathrm{acet}} = -23.1 \text{ kcal/mol}; \qquad \Delta H^\circ_{\mathrm{H_2O}} = -16.9 \text{ kcal/mol};$$

$$\Delta S^\circ_{\mathrm{acet}} = -39.7 \text{ cal/g-mol}; \qquad \Delta S^\circ_{\mathrm{H_2O}} = 29.2 \text{ cal/g-mol}.$$

for passage of the pure starting substance and its P-molar-percent mixture with the reaction product for which the relative adsorption coefficient z is determined. Table 3 presents, for different temperatures, the values of z for acetone, hydrogen, water, and propylene, as well as for benzene and hydrogen—the products of cyclohexane dehydrogenation.

Fig. 1. 1—ordinary chromel—copel thermocouple; 2—junction of the differential chromel—copel thermocouple; 3—catalytic tube; 4—leads of the differential thermocouple.

From the temperature dependence of $z_{\mathrm{CH_3COCH_3}}$ and $z_{\mathrm{H_2O}}$, using formulas (8,9), the changes in free energy ΔF° at $P = \text{const}$, the enthalpy ΔH°, and the entropy

ΔS° of the process of adsorption displacement of isopropyl alcohol by acetone and water from catalytically active centers were calculated.

The data obtained made it possible, by means of the kinetic method (10,11), to calculate the values of the bond energies $Q_{\mathrm{C-TiO_2}}$, $Q_{\mathrm{H-TiO_2}}$, $Q_{\mathrm{O-TiO_2}}$ for all four TiO_2 samples (Table 4).

It is seen from Table 4 that the method of preparation also affects the magnitudes of the bond energies.

Thus, in the present work, the detailed kinetics of the dehydrogenation and dehydration reactions of isopropyl alcohol and of the dehydrogenation of cyclohexane on titanium oxide have been studied for the first time. The influence of the method of preparation on catalytic activity has been investigated. For the first time, the influence of carbon deposition on the ratio of the dehydrogenation and dehydration reactions has been studied quantitatively; the values of the bond energies $Q_{\mathrm{C—TiO_2}}$, $Q_{\mathrm{H—TiO_2}}$, and $Q_{\mathrm{O—TiO_2}}$ have been calculated.

Table 4

Bond energies calculated by the kinetic method

Bond energy with TiO_2	On TiO_2 samples	On TiO_2 samples	On TiO_2 samples	On TiO_2 samples
Bond energy with TiO_2	No. 1	No. 2	No. 3	No. 4
$Q_{\mathrm{H—TiO_2}}$	57.1	60.5	53.1	57.1
$Q_{\mathrm{O—TiO_2}}$	35.7	32.8	59.3	47.0
$Q_{\mathrm{C—TiO_2}}$	20.7	20.3	23.0	23.4

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences of the USSR

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