INVESTIGATION OF THE SELECTIVITY OF THE ACTION OF OXIDE CATALYSTS IN THE CONVERSION OF 2-PENTANOL

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The selectivity of the action of oxide catalysts in the decomposition of alcohols has been widely studied for the example of lower homologs – ethanol and isopropanol [1]. New data on the directing ability of catalysts may be given by investigations of the decomposition of more complex secondary alcohols, which react simultaneously along several pathways

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The available data on the conversions of 2-alkanols are scanty [1, 2], pertain chiefly to the catalytic action of aluminum oxide, and do not permit a judgment of the influence of the nature of the oxide on the direction of the process.

In this work, with the decomposition of 2-pentanol as an example, the selectivity of the action of 22 oxides of elements of groups II-VI of the periodic system with respect to dehydration and dehydrogenation reactions was studied.

EXPERIMENTAL METHOD

Oxides of Zn, La, Y, In, Nd, Sm, and Er were produced by calcination of the corresponding hydroxides were prepared by precipitation with ammonia from solutions of nitrates. Thorium dioxide was prepared by the decomposition of thorium oxalate at 400-450° [4], while MoO₃ and WO₃ were prepared by the decomposition of ammonium salts in a stream of nitrogen at 500° [5]. The remaining oxides (BaO, CaO, MgO, CdO, Sc₂O₃, CeO₂, Al₂O₃, Gd₂O₃, Dy₂O₃, ZrO₂, TiO₂, V₂O₅) were commercial preparations. The specific surface of the catalysts, determined according to the adsorption of air, was 3-25 m²/g, while that of Al₂O₃ was 240 m²/g.

| II | | | | |
|---|-----------------|--------------------------------|-------------------|----------------------|
| Oxide | A12O3 | Sc ₂ O ₃ | ¥2O3 | In ₂ O3 |
| Temperature, °C H ₂ O/H ₂ 1-Pentene/2-pentene | 185 * 0,7 | 350 0,6 7,0 | 280 1,6 8,5 | $245 \\ 0,12 \\ 5,1$ |

TABLE 1. Direction of the Decomposition of 2-Pentanol in the Presence of Oxides of Elements of Group

Selectively catalyzes dehydration.

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|---------------------------------------|------------------|------------------|---|------------------|-----|
| Oxide | TiO ₂ | ZrO2 | V205 | MoO ₃ | WO₃ |
| Temperature, °C | 300 180 | 3 00 5 | 210 17 | 200 | 150 |
| 1-pentene /2-pentene | 0,4 | 0,4 | 0,15 | 0,2 | 0,2 |
| Cis-/trans-2-pentene* | 1,2 | 1,1 | 0,7 | 1,3 | 0,8 |
| · · · · · · · · · · · · · · · · · · · | | | | | |

TABLE 2. Direction of the Decomposition of 2-Pentanol in the Presence of Oxides of Elements of Group IV-VI

* In the equilibrium mixture at 200-300°, the ratio of cis-/trans-2- pentene = 0.5-0.61 [2].

The experiments were conducted under flow-through conditions in the temperature range $180-450^{\circ}$ at volume velocities up to $10 h^{-1}$. The amount of the catalyst was 5 ml. The catalyst was regenerated by treatment with air at 400-450° for 1.5-2 h. The composition of the catalyzate was determined by the method of gas-liquid chromatography [2].

Selectivity of the Action of Metal Oxides with Respect to Reactions of Dehydrogenation and Hydrogenation. Cxides of metals of group II of the periodic system catalyze chiefly the dehydrogenation of the alcohol; dehydration proceeds to a negligible degree (2-6%). Their catalytic activity is manifested only at high temperatures (300-400°) and increases in the sequence: $CaO < BaO \le MgO \approx ZnO \approx CdO$.

The behavior of oxides of metals of group III is of interest. Oxides of aluminum and indium manifest substantial activity at only 200°, yttrium oxide at 280°, and scandium oxide at 350°. The relative rates of dehydration and dehydrogenation (H_2O/H_2) of 2-pentanol are cited in Table 1. From Table 1 it is evident that In_2O_3 catalyzes dehydrogenation with substantial selectivity, while Al_2O_3 selectively catalyzes dehydration. Y_2O_3 accelerates dehydrogenation to a greater degree, while Sc_2O_3 selectively accelerates the dehydration of the carbinol. Oxides of the lanthanides show activity at temperatures > 300° and catalyze the decomposition of the alcohol in both directions. With increasing temperature, the selectivity of the action of Y_2O_3 , Er_2O_3 , Gd_2O_3 , Sm_2O_3 is displaced in the direction of dehydration and dehydrogenation. With increasing atomic number of the element of the lanthanide group, the activity of its oxide in the dehydration of alcohol increases, while the activity in dehydrogenation decreases. Oxides of metals of group IV (TiO₂, ZrO_2) are active > 250° and catalyze chiefly dehydration; moreover, the activity and selectivity of TiO₂ are substantially higher than those of ZrO_2 (Table 2). Oxides of metals of group V and VI (V₂O₅, MoO₃, and WO₃) are already highly active at temperatures < 200°; they selectively catalyze the dehydration of 2-pentanol. Chromium oxide possesses a mixed effect [2].

Dependence of the Direction of Dehydration of 2-Pentanol on the Chemical Nature of the Oxide. In the presence of the tested catalysts, the α -olefin formed in the process of dehydration undergoes partial isomerization. This is confirmed by the fact that when the temperature is increased, the relative content of 1-pentene in the reaction products is reduced, while it increases with increasing volume velocity. Therefore, the direction of the elimination of water from the alcohol was judged according to the ratio of 1-pentene/2-pentene in the catalyzate, obtained at large volume velocities (9-10 h⁻¹), when the influence of the secondary reaction – displacement of the C = C bond – on the isomeric composition of the pentenes formed is negligible. With respect to selectivity of the action in the direction of dehydration, the oxides of metals of group II are clearly distributed in two subgroups. In the presence of oxides of the alkaline earth metals, the 1-pentene/2-pentene ratio in the catalyzate is 0.4-0.5, while on the catalysts ZnO and CdO it is 11 and 8, respectively. This ratio varied little when the volume velocity of passage of the alcohol is increased from 3 to 9 h⁻¹.

Of special interest are oxides of metals of group III. Almost all the tested oxides of elements of group III show high selectivity, catalyzing the dehydration of 2-pentanol primarily in the direction of formation of an α -olefin (see Table 1). In the series of lanthanide oxides, with increasing atomic number of the elements, the ability of its oxide to catalyze dehydration with the formation of an α -olefin decreases (Table 3).

Oxides of the actinides also show selectivity of action with respect to the dehydration of 2-alkanols with the formation of α -olefins [2, 6]. In our experiments with ThO₂ at 250°, the ratio 1-pentene/2-pentene = 11.

| Oxide | La ₂ O ₃ | Ce ₂ O ₃ | Nd ₂ O ₃ | Sm ₂ O ₃ | Gd2O3 | Dy ₂ O ₃ | Er2O3 |
|----------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------|--------------------------------|-------|
| | | | 1 | | | | |
| Tempera- | 420 | 425 | 400 | 425 | 410 | 350 | 350 |
| ture, °C | | | { | | | | |
| 1-Pen- | 9,0 | 8,9 | 2,7 | 6,8 | 4,3 | 1,8 | 4,2 |
| tene/2- | | | | | | | |
| pentene | 1 | | · · | | | | |

TABLE 3. Dependence of the Ratio 1-Pentene/2-Pentene on the Nature of Oxides of the Lanthanides

Great similarity in the direction of dehydration of 2-pentanol is shown by oxides of metals of groups IV-VI (TiO₂, ZrO₂, V₂O₅, MoO₃, WO₃): in their presence the ratio 1-pentene/2-pentene = 0.15-0.4 (see Table 2). The relative content of α - and β -olefins in the reaction products on these catalysts is determined by the direction of the process of dehydration of pentanol, and not secondary isomerization of the 1-pentene formed. Actually, lowering the reaction temperature from 400 to 250°, raising the volume velocity from 1 to 10 h⁻¹, and adding a base – pyridine (10% with respect to the alcohol) – do not change the ratios of α - and β -olefins in the reaction products. It was also established than when 1-pentene is passed, for example, over TiO₂ at 300°, the ratio 1-pentene/2-pentene=11, while over ZrO₂ at 350° it is 9.5, whereas in the process of dehydration of 2-pentanol under analogous conditions this ratio is equal to 0.4 in both cases.

Stereospecificity of the Dehydration of 2-Pentanol. In the dehydration of 2-pentanol in the presence of oxides of metals of groups IV-VI of the periodic system, a nonequilibrium mixture of cis- and trans-2-pentenes is formed (see Table 2). The predominance of cis-2-pentene is due to the stereospecificity of the dehydration of the alcohol and not to secondary isomerization of the initially formed 1-pentene to cis-2-pentene. Under similar conditions, in the presence, for example, of TiO_2 or ZrO_2 1-pentene isomerizes, forming an equilibrium mixture of cis- and trans-2-pentenes.

DISCUSSION OF RESULTS

The literature data on the quantitative composition of the isomeric olefins formed in the heterogeneous catalytic dehydration of secondary alcohols are contradictory: the formation both of equilibrium and of nonequilibrium mixtures of α - and β -olefins has been observed. Possibly the formation of mixtures of olefins of the equilibrium composition is explained by the fact that the conditions of the experiments (catalysts, temperature, time of contact) promoted the occurrence of a secondary reaction of displacement of the double bond [7].

The results obtained showed that in the presence of heterogeneous catalysts at moderate temperatures and high volume velocities, in the dehydration of a 2-alkanol, a nonequilibrium mixture of olefins is formed. The distance of the composition of the isomeric olefins from equilibrium depends on the chemical nature of the oxide.

The catalytic properties of metal oxides, determined by their chemical composition, may also be influenced by the peculiarities of the physical structure [8]. Despite this, the data that we obtained permit definite conclusions to be drawn on the similarity and peculiarities of the catalytic action of oxides.

Oxides of Zn and Cd, which selectively catalyze the dehydrogenation of 2-pentanol, direct the dehydrogenation chiefly toward the formation of an α -olefin. Oxides of elements of groups IV-VI (MoO₃, WO₃, TiO₂, V₂O₃, and ZrO₂) selectively accelerate the dehydration of the alcohol and direct the process toward predominant formation of a β -olefin. Oxides of metals of group III (Sc₂O₃, Y₂O₃, In₂O₃, oxides of the lanthanides and actinides), which catalyze both dehydrogenation and dehydration of a carbinol, accelerate the elimination of water preferentially with the formation of an α -olefin.

Thus, the selectivity of the action of oxide catalysts in reaction of decomposition of alcohols is associated with the position of the corresponding elements in the periodic system. The detected pattern agrees with the concept of the acid-base mechanism of the dehydration of an alcohol, with the acid character of the oxides of elements of groups IV-VI, and the basic properties of the active surface of oxides of elements of groups II and III of the periodic system. The established dependences confirm the chemical nature of the selectivity of catalysis.

CONCLUSIONS

1. The selectivity of the action of metal oxides in reactions of conversion of 2-pentanol is associated with the position of the corresponding elements in the periodic system.

2. Oxides of metals of group II selectively catalyze the dehydrogenation of the alcohol, oxides of metals of IV, V, and VI selectively catalyze dehydration, while oxides of metals of group III accelerate both processes.

3. In the presence of all the tested catalysts, the secondary alcohol is dehydrated with the formation of a nonequilibrium mixture of α - and β -olefins. The excess of the α -olefin concentration in the catalyzate over the equilibrium value depends on the chemical nature of the oxide. Oxides of elements of group II (with the exception of the alkaline earth oxides) and group III catalyze the dehydration of 2-pentanol primarily to an α -olefin, while oxides of elements of groups IV, V, and VI catalyze dehydration to a β -olefin.

4. The detected correlation confirms the concept of the chemical nature of catalysis.

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