MECHANISM OF THE DEHYDRATION OF SECONDARY ALCOHOLS IN THE PRESENCE OF OXIDE CATALYSTS

L. Kh. Freidlin, V. Z. Sharf, and V. Sh. Abdumavlyanova UDC 542.97+542.936:547.26

The dehydration of 2-alkanols can proceed in two directions, with the formation of either the α - or the β -olefin.

 $\begin{array}{c|c} R-CH_{2}-CH-CH_{3} \xrightarrow{-H_{9}O} & \xrightarrow{} R-CH-CH=CH_{3} \\ & & & \\$

We established that the oxides of the elements of Groups IV, V, and VI of the periodic system catalyze the conversion of an alcohol predominantly to the β -olefin. In contrast to this, the oxides of the elements of Groups II (ZnO, CdO) and III (Sc₂O₃, Y₂O₃, In₂O₃, lanthanides and actinides) accelerate the dehydration mainly with the formation of the α -olefin.

In the present paper was studied the mechanism for the decomposition of a secondary alcohol on oxides of an acid and basic nature. In connection with this, we also studied the effect of acid and basic additives on the change in the activity and selectivity of action of these catalysts.

EXPERIMENTAL METHOD

The preparation of the catalysts, the experimental procedure and conditions, and the chromatographic analysis were described in [1]. From Table 1 it can be seen that the addition of pyridine to 2-pentanol (in the experiments with TiO₂, ZrO₂, V₂O₃, MoO₃, and WO₃), and the deposition of alkali (on ZrO₂, V₂O₅), leads to a reduction in the activity of the catalyst. In the presence of pyridine the degree of dehydration of the alcohol on TiO₂ at 300°C dropped from 89 to 35%. After the addition of alkali (3%) to V₂O₅ the degree of dehydration of the alcohol at 210° dropped from 90 to 40%. The deactivating effect of pyridine and alkali confirms the acid nature of the activity of those catalysts on which 2-pentanol is selectively dehydrated. It is interesting to mention that under the influence of pyridine, alkali or phenol the direction of the process (ratio of 1-pentene :2-pentene in the catalyzate) hardly changed.

The addition of pyridine to 2-pentanol does not lower the activity of ThO_2 , whereas when phenol is added (5%) the degree of dehydration of the alcohol at 370° dropped from 91 to 21%. Phenol simultaneously lowers both the catalytic activity of La_2O_3 and Nd_2O_3 and the 1-pentene :2-pentene ratio in the catalyzate, while pyridine has no effect on the direction of the process.

The obtained data and the results of the preceding paper [1] both show that the direction of the dehydration of an alcohol depends on the acid – base nature of the catalyst.

Regarding Two Mechanisms for the Dehydration of a 2-Alkanol. The selectivity of the catalytic decomposition of alcohols was discussed mainly in the literature on the score of their dehydrogenation and dehydration, and most frequently on the example of isopropanol [2]. The mechanism of both intra- and intermolecular dehydration was studied predominantly on the example of the transformations of ethanol to either ether or ethylene in the presence of Al_2O_3 [2, 3]. The dehydration of 2-alkanols (2-butanol and 2-pentanol) on Al_2O_3 [4] proceeds with the formation of the β -olefin. The selective dehydration of secondary alcohols to α -olefins in the presence of ThO_2 was regarded as an exception [5].

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Catalyst	Т, °С	Amount added to al cohol, %		Degree of conversion, %		1-Pentene
		pyridine	phenol	total	dehydration	:2-pentene
$\begin{array}{c} {\rm Ti}O_2 \\ {\rm Ti}O_2 \\ {\rm Zr}O_2 \\ {\rm V}_2O_5 \\ {\rm V}_2O_5 \\ {\rm V}_2O_5 \\ {\rm V}_2O_5 \\ {\rm W}O_3 \\ {\rm WO}_3 \\ {\rm U}a_2O_3 \\ {\rm L}a_2O_3 \\ {\rm N}d_2O_3 \\ {\rm N}d_2O_3 \\ {\rm N}d_2O_3 \\ {\rm N}d_2O_3 \\ {\rm Th}O_2 \end{array}$	$\begin{array}{c} 300\\ 300\\ 300\\ 300\\ 350\\ 350\\ 210\\ 210\\ 210\\ 200\\ 150\\ 150\\ 150\\ 150\\ 440\\ 440\\ 380\\ 380\\ 350\\ 370\\ \end{array}$	$ \begin{array}{r} 10 \\ 10 \\ $		$ \begin{array}{r} 89 \\ 35 \\ 16 \\ 5 \\ 60 \\ 12 \\ 90 \\ 69 \\ 40 \\ 31 \\ 8 \\ 27 \\ 4 \\ \\ $	$ \begin{array}{r} 89 \\ 34 \\ 13 \\ 4 \\ 50 \\ 52 \\ 67 \\ 35 \\ 31 \\ 22 \\ 18 \\ 7 \\ 16 \\ 8 \\ 91 \\ \end{array} $	$\begin{array}{c} 0,4\\ 0,4\\ 0,5\\ 0,5\\ 0,6\\ 0,2\\ 0,2\\ 0,2\\ 0,2\\ 0,2\\ 0,2\\ 0,2\\ 0,2$
ThO_2 ThO_2	370		5	92 73	89 21	5,2

TABLE 1. Effect of Pyridine and Phenol on Direction of Transformations of 2-Pentanol (space velocity $3 h^{-1}$)

* Amount of KOH added to catalyst = 3%.

In our studies [1, 6] we were the first to establish that, together with thorium dioxide, the oxides of the elements of Groups II (ZnO, CdO) and III (including lanthanides) and Cr_2O_3 also catalyze the dehydration of a 2-alkanol mainly toward the formation of the α -olefin.

The dehydration of an alcohol, accelerated by catalysts of an acid nature, is usually considered to belong to reactions of the heterolytic type. Common to the heterolytic mechanisms of dehydration (carboniumion [3, 7], coordination [2], bicentric [8]) is the formation of an unstable intermediate form, bearing a positive charge. Taking into consideration the acid nature of oxides that catalyze the dehydration of a secondary alcohol preferentially toward the formation of a β -olefin, it is necessary to adopt the carbonium-ion mechanism 1 for this direction of the process.

$$\begin{array}{c} R-CH_{2}-CH-CH_{3} & \xrightarrow{-OH^{\ominus}} R-CH_{2}-CH - CH_{3} & \xrightarrow{-H^{\oplus}} R-CH = CH - CH_{3} \\ \downarrow \\ OH & \xrightarrow{1} R-CH_{2}-CH - CH_{3} & \xrightarrow{-H^{\oplus}} R-CH_{2}-CH = CH_{2} \\ \xrightarrow{2} -H^{\oplus} & R-CH_{2}-CH - CH_{3} & \xrightarrow{-OH^{\ominus}} R-CH_{2}-CH = CH_{2} \\ \xrightarrow{0} OH & \xrightarrow{0} OH \end{array}$$

The predominant formation of the β -isomer indicates the greater lability of the hydrogen of the methylene group of the carbonium ion when compared with methyl. It is natural to assume that the selective dehydration of a 2-alkanol to the α -olefin in the presence of oxides of the elements of Groups II and III proceeds by a different mechanism. The reactions, catalyzed by solid bases, proceed via the intermediate step of the carbanion [9]. Apparently, also on oxides of basic character the dehydration of an alcohol goes by the carbanion mechanism 2. Here the selectivity with respect to the formation of the α -olefin is caused by the greater stability of the primary carbanion when compared with the secondary.

The carbanion mechanism explains the high activity of ThO_2 in aldol condensation reactions [10] and its efficiency in the dehydration of ethanol to ethylene, but not to the ether [11]. It also becomes understandable why 2,3-butanediol is converted to methylvinylcarbinol in the presence of ThO_2 , and to methyl ethyl ketone [12] on other dehydration catalysts.

$$\begin{array}{c} CH_{3}-CH-CH-CH_{3} \xrightarrow{-H_{2}O} & \begin{array}{c} ThO_{2} \\ CH_{2}-CH-CH-CH_{3} \\ OH \\ OH \\ OH \end{array} & \begin{array}{c} H_{2}O \\ OH \\ Al_{2}O_{3} \end{array} & \begin{array}{c} CH_{2}-CH-CH-CH_{3} \\ OH \\ OH \\ OH \end{array} \\ \end{array}$$

In all of these cases the ThO_2 activates the hydrogen of the methyl group (adjacent to the -C-OH), thus catalyzing the process by the carbanion mechanism, due to the basic character of its active surface.

CONCLUSIONS

1. The catalytic dehydration of a 2-alkanol on metal oxides proceeds in two directions by different mechanisms.

2. In the presence of catalysts of a basic nature, namely oxides of the metals of Groups II and III of the periodic system of elements, the dehydration of a secondary alcohol apparently goes by the carbanion mechanism toward the formation of the α -olefin.

3. On catalysts of an acid nature, namely the oxides of the metals of Groups IV, V, and VI, the dehydration of the carbinol proceeds by the carbonium-ion mechanism with the predominant formation of the β -olefin.

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