Physical Chemistry

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1965

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Abstract

Full Text

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CATALYTIC PROPERTIES OF ZIRCONIUM PHOSPHATE

Using model reactions of intra- and intermolecular dehydration, isomerization, alkylation, and dehydrogenation, the catalytic properties of zirconium phosphate were studied—an inorganic polyfunctional ion exchanger possessing exchange capacity in acidic, neutral, and alkaline solutions (^{1}).

The catalytic activity of two catalysts was compared: K1—a commercial preparation ($S_{\text{sp}} = 2.9$ m^2/g; total acidity 0.05 meq/g), and K2—zirconium phosphate prepared by the method of (^{1}) ($S_{\text{sp}} = 335$ m^2/g; total acidity 1.2 meq/g). By physicochemical methods used in our laboratory, the kinetics of dehydration of C_2–C_4 alcohols of the paraffin series and of cyclohexanol were studied. In the presence of zirconium phosphate (K1 and K2), the alcohols are dehydrated practically quantitatively—by 93-94% at 390-400°—with formation of olefins, which are immediately isomerized; moreover, in the presence of K2 the isomerization proceeds almost twice as fast as on K1. It was established that during dehydration of cyclohexanol, as the experimental temperature is increased from 350 to 450°, the amount of isomeric methylcyclopentenes increases almost twofold (from 10 to 17% on K1). For isomerization, $\varepsilon_{\text{app}} = 11.2$ kcal/mol.

Table 1

Values of the apparent activation energy ε_{app} and temperature intervals of the dehydration reaction of alcohols on zirconium phosphate prepared by different methods

Catalyst	Total acidity, meq/g	S_{sp}, m^2/g	Quantities determined	Ethanol	Propanol-1	Butanol-1	2-Methylpropanol-1	Propanol-2	Butanol-2	2-Methylpropanol-2
K1	0.05	3.1	ε, $\frac{\text{kcal}}{\text{mol}}$	33.3	28.0	31.6	23.6	17.8	21.3	11.9
K1	0.05	3.1	T, °C	326 – 355	338 – 374	344 – 384	232 – 252	242 – 276	322 – 346	114 – 148
K2	1.2	230.0	ε, $\frac{\text{kcal}}{\text{mol}}$	22.9	16.5	19.4	15.0	10.3	16.8	11.8

Reaction scheme

Figure 1: Reaction scheme

Catalyst	Total acidity, meq/g	S_{sp}, m^2/g	Quantities determined	Ethanol	Propanol-1	Butanol-1	2-Methylpropanol-1	Propanol-2	Butanol-2	2-Methylpropanol-2
K2	1.2	230.0	T, °C	237 – 310	258 – 290	296 – 322	258 – 290	155 – 176	182 – 204	100 –12

The apparent activation energies ε_{app} were determined under conditions in which the conversions of the alcohols do not exceed 20-25% (^{2}) and the isomerization of olefins is small. As is seen from Table 1, the values of ε for K2 are considerably lower than for K1. In the case of zirconium phosphate, regularities are observed similar to those published earlier (^{3}).

In the products of dehydration of ethyl alcohol, in addition to the principal reaction product—ethylene—the formation of a simple ether is observed; at the same time, on the acidic sample K2 the yield of diethyl ether is twice as great as on K1, and at 310° reaches 21%. In the dehydration of C_3-, C_4-alcohols, higher simple ethers were not detected.

The specificity of K2 is also manifested in the formation of esters in the vapor phase. If the maximum yield of amyl butyrate is 56% at 240° on K2, then on K1 it is only 16%. It is possible that the decrease in the ether yield on K1 is connected with the decrease in its acidity and surface area.

As follows from the literature (4), ion exchangers possessing a high exchange capacity are active in the esterification reaction.

Ketonization of butyric acid in the presence of K1 and K2 is difficult and proceeds with low yields in the high-temperature region, although ZrO_2 is an active catalyst for this reaction (5). Consequently, in the case of zirconium phosphate the specificity of the metallic component is not manifested.

The work has shown the fundamental possibility of using K2 in the reaction of alkylation of benzene with haloalkyls under static conditions.

The experimental material presented convincingly shows that zirconium phosphate is active in reactions accompanied by redistribution of hydrogen (isomerization, alkylation, esterification). According to the multiplet theory, schemes of reaction indices can be proposed for the isomerization reaction of olefins proceeding in the presence of catalysts containing mobile surface-active hydrogen.

When the index group of an olefin is superposed on the active center of the catalyst $A_1, A_2(H)$, containing hydrogen capable of exchange, interaction of the olefin is observed with rupture of the C—H bond and transfer of hydrogen to the active centers A_1. At the same time, under the influence of surface-active hydrogen supplied by the catalyst A_2, redistribution of electron density occurs in the reacting olefin molecule with formation of a new π-electron bond, while the β-rule is not violated (6). The question of the structure of the active center remains open.

Using the dehydrogenation of ethylbenzene as an example, the dehydrogenating ability of zirconium phosphate was investigated. It was established that, on zirconium phosphate after acid treatment (K2), the styrene content in the catalyzate at 650° is somewhat lower (26%) than on the factory preparation (29%), while hydrogenolysis of ethylbenzene proceeds to a greater extent—the amounts of benzene and toluene are, respectively, 24 and 19%. Thus, an increase in the acidity of the catalyst causes an increase in its cracking action.

Zirconium phosphate may be recommended as a catalyst exhibiting high activity in various catalytic reactions. By changing the method of its preparation, one can control the specificity of its catalytic action in reactions associated with the redistribution of hydrogen.

However, in the dehydrogenation reaction of ethylbenzene, a change in acidity has no effect. Evidently, this reaction is carried out on other active centers.

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Received
25 XII 1964

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