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EFFECT OF THE POROUS STRUCTURE OF CATALYSTS ON THE PROCESS OF ACID HETEROGENEOUS ISOMERIZATION OF α-PINENE

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The isomerization of α-pinene in the presence of acids and acidic catalysts proceeds along two independent pathways. When the proton attacks the double bond of pinene, bi- and tricyclic terpenes are formed: camphene, tricyclene, fenchene; whereas when the cyclobutane ring is attacked, monocyclic terpenes are formed ([1]).

The action of numerous solid acidic catalysts on liquid pinene has been studied, and it has been shown that some of them direct the reaction mainly toward the formation of bi- and tricyclic terpenes, while others toward the formation of monocyclic terpenes ([2]); no explanation for this was given. Later, the action of certain acids deposited on catalytically inactive supports was studied. It turned out that the composition of the isomerizates depends not on the nature of the acids used as catalysts, but on the nature of the supports onto which these acids are deposited ([3]).

Table 1

Characteristics of silica gels from the chromatography set, used as supports

Silica gel grade	Bulk density, g/cm^3	Structure: surface area, m^2/g	Structure: true specific gravity, g/cm^3	Structure: apparent specific gravity, g/cm^3	Structure: pore volume, cm^3/g	Structure: mean pore radius, Å	Structure: porosity, %
KSK No. 2	0.39	338	2.240	0.611	1.19	70	72.7
KSK No. 2.5	0.46	376	2.244	0.706	0.971	51.6	67.4

Figure 1

Figure 1: Figure 1

Silica gel grade	Bulk density, g/cm^3	Structure: surface area, m^2/g	Structure: true specific gravity, g/cm^3	Structure: apparent specific gravity, g/cm^3	Structure: pore volume, cm^3/g	Structure: mean pore radius, Å	Structure: porosity, %
KSS No. 3	0.50	522	2.236	0.729	0.925	35.4	67.4
KSS No. 4	0.58	650	2.235	0.831	0.760	23.4	62.8
KSM No. 6p	0.87	527	2.255	1.353	0.296	11.2	40

The influence of the supports on the direction of the catalytic isomerization of pinene can be explained by the predominant orientation of pinene molecules, with either the double bond or the cyclobutane ring toward the surface of a support of a given composition in the sorbed layer ([4]), or by the different porous structure of the supports; since it may be assumed that, when pinene molecules move inside sufficiently narrow pores, the orientation of the molecules toward the surface disappears, which can lead to a change in the ratio between bicyclic and monocyclic terpenes in the reaction products. In this case, the transition of the reaction into the diffusion region is quite probable.

To determine the influence of the magnitude of the radius and volume of the pores of the supports on the process of α-pinene isomerization, the present work was carried out.

As supports we used catalytically inactive silica gels with different porous structures from a chromatography set, TU MSR No. 382-61 (Table 1), and "aerosil" silica gel, completely

devoid of pores, with a particle diameter of 18 mμ and a specific surface area of about 160 m^2/g*. Aluminosilicic acids deposited on their surface were used as catalysts. The action of these catalysts was compared with that of titanic acid, i.e., a solid catalyst whose acidic properties are inherent in its nature. The titanic acid was prepared by the usual method ([5]).

Fig. 1. Change in the composition of the isomerizate during the reaction. Catalyst: aluminosilicate, support: silica gel KSS No. 4.
I –α-pinene, **II** –camphene and tricyclene, **III** –limonene, **IV** –terpinolene, **V** –α-terpinene, **VI** –γ-terpinene.

The technical α-pinene used in the work (n_D^{20} 1.4665) contained 5-6% impurities (β-pinene, camphene, Δ^3-carene).

To prepare the catalysts, the silica gels were ground in a mortar, washed with water to a neutral reaction for ions, and then aluminum oxide was applied to them by impregnating the sample with a solution of aluminum nitrate containing the calculated amount of salt required to obtain the desired concentration of Al_2O_3 in the catalyst. After this, all samples were dried at room temperature to a free-flowing state, then for 4 hours in a drying oven at 200°, and finally calcined in a muffle furnace at 450° for 4 hours.

The experiments were carried out in a three-necked round-bottom flask with a stirrer, a reflux condenser, and a device for taking samples during the experiment.

Into the flask were placed 150 g of pinene and 0.015 g of hydroquinone (as an antioxidant). At a temperature of 100° the catalyst was added to the pinene. The mixture was then heated to the boiling point. Throughout the experiment samples were taken. Their composition was analyzed on a gas–liquid chromatograph. The detector was a katharometer with platinum coils. The stationary liquid phase was polyethylene glycol adipate. The column length was 2 m, diameter 8–9 mm, carrier-gas (hydrogen) flow rate 60–80 ml/min, temperature 120°. Gas–liquid chromatography made it possible to determine camphene, limonene, terpinolene, and terpinene in the isomerizates with sufficient reliability, whereas pinene and tricyclene gave a common peak. Therefore, when calculating the tricyclene content, it was assumed, on the basis of analytical distillation data, that it is formed in an amount of about 6% of its sum with camphene on aluminosilicate catalysts and about 16% on titanic acid.

It was shown that increasing the amount of Al_2O_3 deposited on the silica gel to 0.4% causes considerable polymerization. When the Al_2O_3 content is decreased to 0.1–0.2%, polymerization proceeds only to a slight extent, while the composition of the isomerization products is the same. We settled on an addition of 0.1% in order to minimize changes in the pore structure of the supports. The results of the study are summarized in Table 2.

The change in the composition of the isomerizate during the reaction (support: silica gel KSS No. 4) is shown in Fig. 1. For comparison, Fig. 2 shows the change in the composition of the isomerizate during the reaction in the presence of titanic acid, under the same temperature conditions.

From the data of Table 2 it is seen that the ratio between bicyclic and monocyclic terpenes in the reaction products is approximately constant and does not depend on the pore structure of the catalyst, the stirring rate, or, within known limits, the amount of the latter (1–2%). Kine-

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Table 2

Comparison of the action on pinene of silicate gels of different porous structure, at 155-160°

Experiment No.	Catalyst: silicate-gel grade	Catalyst: amount, %	Number of stirrer revolutions	Bicyclic and tricyclic terpenes, % of reacted substance	Monocyclic terpenes, % of reacted substance	Bicyclic + tricyclic / monocyclic
46	KSK No. 2	2.6	Without stirring	38.3	61.7	0.62
37	KSK No. 2.5	1.8	300	42.5	57.5	0.74
45	» » »	2.6	300	40.1	59.9	0.67
38	KSK No. 3	1.3	300	40.9	59.1	0.69
49	KSK No. 4	0.75	300	39.6	60.4	0.66
43	» » »	1	60	40.5	59.5	0.68
41	» » »	1	300	39.2	60.8	0.65
42	» » »	1	3000	40.6	59.4	0.68
40	» » »	2	300	38.8	61.2	0.63
44	KSK No. 6p	1.8	300	40.1	59.9	0.67
26	Aerosil	1.6	300	44	56	0.78

The kinetic curves (Figs. 1 and 2), however, indicate a zero order of reaction.

The data obtained make it possible to conclude that the reaction proceeds in the kinetic region, i.e., that the rate of diffusion of pinene to the catalyst surface considerably exceeds the rate of reaction.

Since the diameter and volume of the pores of the catalyst do not affect the ratio of the rates of the two reactions, it should be assumed that either the pinene molecules inside the catalyst pores are oriented toward the pore surface in the same way as toward the external surface, or that the reaction proceeds considerably more slowly than diffusion of pinene to the external surface, but considerably faster than diffusion into narrow pores; accordingly, the reaction proceeds practically quantitatively on the external surface of the catalyst and in wide pores, where the orientation of the molecules is not disturbed.

Fig. 2. Change in the composition of the isomerizate during the reaction. Catalyst: titanic acid. The designations are the same as in Fig. 1.

Fig. 2

Figure 2: Fig. 2

The kinetic curves show that the ratio between bicyclic and monocyclic terpenes is constant throughout the entire process, and the ratio among all reaction products (camphene, limonene, terpinolene, terpinene) at the initial stage of the process (until ~70–80% of the pinene has reacted) is also constant, which indicates their primary formation at this stage; only after the main mass of pinene has reacted do secondary transformations of limonene into terpinolene, and of the latter into terpinenes, begin.

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References

1. L. Ružička, *Pure and Appl. Chem.*, **6**, No. 4, 493 (1963).
2. G. A. Rudakov, *Chemistry and Technology of Camphor*, Moscow-Leningrad, 1961.
3. G. A. Rudakov, M. M. Shestakova, L. S. Ivanova, *DAN*, **162**, No. 6 (1965).
4. Ya. Kh. De-Boer, *The Dynamic Character of Adsorption, Catalysis, and Some Questions of the Theory and Technology of Organic Reactions*, collected translations, IL, 1959.
5. G. A. Rudakov, Z. S. Khomenko, *ZhOKh*, **24**, 337 (1954).

Note: Figure translations are in progress. See original paper for figures.