

*Physical Chemistry*

## Catalytic Conversion of Linalool on Micro-Mesoporous BEA-Type Zeolite

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**ABSTRACT.** The catalytic conversion of the tertiary terpenic alcohol linalool ( $C_{10}H_{18}O$ ) on samples of the beta type microporous zeolites (BEA-25 and BEA-150 with  $n(SiO_2)/n(Al_2O_3)$  equal to 25 and 150) and on their modified micro-mesoporous forms (RBEA-25 and RBEA-150 with  $n(SiO_2)/n(Al_2O_3)$  equal to 23.8 and 176.4, and transport mesopores with pore diameters 3.5 and 3.8 nm, respectively) was studied.

The micro-mesoporous materials were synthesized by recrystallization of initial commercial BEA-zeolites in NaOH aqueous solutions. The chemical composition of the catalysts was determined using X-ray fluorescence analysis. The micro- and mesopores volumes and specific surface areas of catalysts were defined by nitrogen adsorption-desorption. The acid properties of catalysts were estimated using temperature-programmed desorption of ammonia. The catalytic conversion of linalool was carried out in a static system in the liquid phase. The analysis of products of catalytic reactions was carried out by the GC-MS.

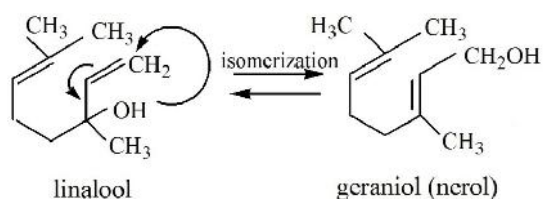
The reactions of isomerization, dehydration, cyclization and condensation of linalool take place on the studied micro- and micro-mesoporous zeolites by the conversion of linalool in an atmosphere of nitrogen or argon in a liquid phase at 60–170 °C.

The conversion of linalool (4-40%) and the selectivity (45-12 %) of the formation of nerol and geraniol as products of linalool isomerization are low. The introduction of mesopores in the microporous BEA-type zeolite catalysts leads to a significant increase in conversion of linalool and a slight growth in selectivity towards nerol and geraniol. Comparatively high amount of weak acid sites in microporous BEA zeolites contributes to enlarge in selectivity. ©2017 Bull. Georg. Natl. Acad. Sci.

**Key words:** Linalool, Beta-type zeolite, Micro-Mesoporous material

Geraniol (3,7-dimethyl-**trans**-2,6-octadiene-1-ol) and nerol (3,7-dimethyl-**cis**-2,6-octadiene-1-ol) are valuable aromatic substances, which have subtle perfume of rose aroma and are used in perfumery, as well as strategic raw materials – “building units” in syntheses of A, E and K vitamins, carotenoids, ionones and methyl-ionones [1, 2]. Approximately 10% of worldwide production of aromatics falls on geraniol and equals to 10000 tons per year [2].

Commercial production of geraniol and nerol generally is based on the catalytic liquid-phase isomerization of linalool (3,7-dimethyl-1,6-octadiene-3-ol), extracted from *Lavandula* flowers, *Coriandrum sativum* seeds, or  $\alpha$ - and  $\beta$ -pinene obtained from coniferous wood, as well as received using multistage chemical ways. Both isomers – geraniol and nerol are obtained from linalool due to 1,3-migration of the OH-group and appropriate shift (allylic rearrangement) of the double bond, Scheme 1.



**Scheme 1.** Allylic rearrangement in linalool

Today there are no regioselective catalysts of linalool isomerization to geraniol or nerol; only the possibility of geraniol receipt from linalool via microbial transformation is known [3]. Catalytic isomerization of linalool in the mixture of geraniol and its geometric isomer nerol is a reversible process; initially it was conducted in the presence of homogenous catalysts  $H_2SO_4$ ,  $H_3PO_4$  or gaseous HCl and HBr, or else in the presence of mixture of acetic acid and acetic anhydride; afterwards allylic rearrangement was realized in the presence of oxo-compounds of transition metals (V, Mo, W, Re, Nb) [4], and catalytic system of alkyl orthovanadate  $(RO)_3V=O$  and tetrabutylammonium hydroxide  $[(Bu)_4N^+] OH$  was testified as the most stable and having high selectivity at 100-240 °C temperature [5]. In comparison with

vanadium-containing catalysts, complexes of tungsten oxo (VI) alkoxides [6] are less toxic, but product yield is low and hydrolysis of catalysts easily occurs. In manufacturing process nerol is obtained via geraniol isomerization by heating with alkali.

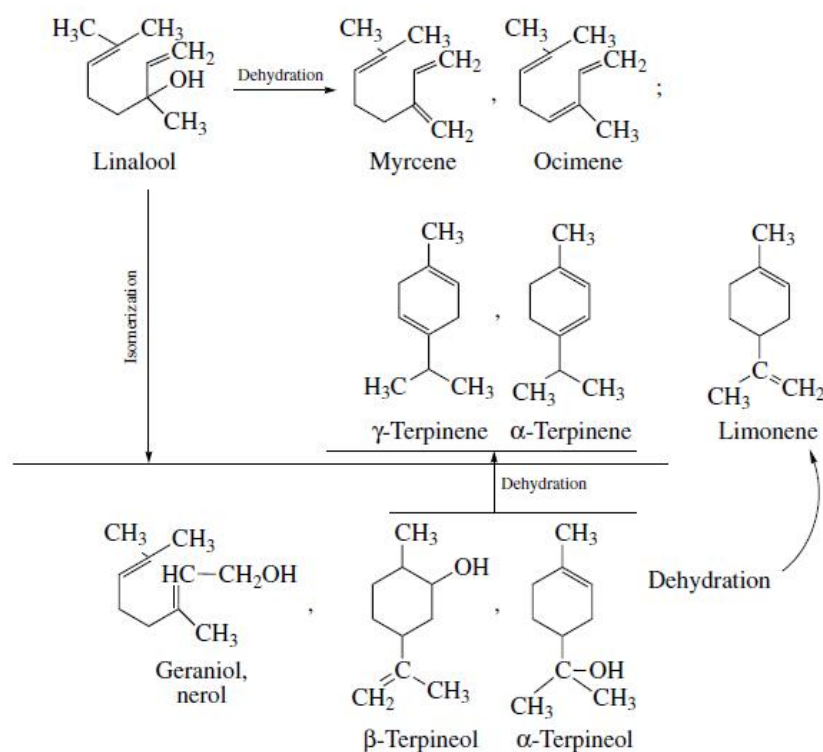
Negative aspects of the above mentioned catalytic processes of linalool isomerization reactions: namely, multistaging of processes, low regioselectivity, problem with products' separation, abundance of waste waters, excessive expenses for neutralization of alkalis and acids, difficulties related to preparations of catalysts and their multiuse, as well as their toxicity are among biggest challenges.

The allyl rearrangement of linalool on H- and dealuminated forms of zeolites FAU(Y), BEA, MOR, and OFF with large pores, as well as on mesoporous MCM-41 at 100–180 °C is complicated by linalool dehydration, cyclization and condensation [7, Scheme 2].

Low selectivity for geraniol and nerol on zeolitic catalysts by linalool's bulky molecules (e.g., for linalool molecular sizes are 9.0 x ~5.8 Å) isomerization is explained with the fact that reaction takes place at the acid sites of the outer surfaces of zeolites crystallites [7].

The wide-pore, high-silica zeolite beta (UPAC formula  $[Na_7] [Al_7Si_{57}O_{128}]^*BEA$ ) was first synthesized in 1967, today it is a commercial product and an excellent catalyst for a wide number of acid-catalyzed reactions. It is known, that the catalyst is more effective when the crystals are small or when a secondary porous network exists in the material, thereby allowing shorter diffusion paths. Several studies have demonstrated the beneficial effect of steaming and acid leaching on the performance of zeolite beta, and it was concluded, that hydrothermal treatment of a macrocrystalline BEA results in the formation of secondary mesoporous structure [8, 9].

We used the micro-mesoporous zeolite materials synthesized from the BEA type zeolites [10] for the catalytic conversion of tertiary terpene alcohol linalool (( $\pm$ )-3,7-Dimethyl-1,6-octadien-3-ol). The goal



**Scheme 2.** Linalool conversion reactions on zeolites.

was to establish the relationship between the porosity and acidity and the selectivity of the formation of linalool isomerization products— primary alcohols geraniol and nerol.

## Materials and Methods

**Reagents.** Racemic linalool (97-98%, FG containing 1.12% 1,2-dihydrolinalool), geraniol (97%), nerol (97%) and methanol (for HPLC,  $\geq 99.9\%$ ) were purchased from Sigma-Aldrich. Argon and nitrogen (99.999 % pure) were used as the reaction medium.

**Catalyst preparation.** Starting zeolites BEA-25 and BEA-150 (Zeolyst International, batches CP-814-E2200-19 and CP-811-E 1822-75) were used in  $\text{NH}_4$ - and H- forms, respectively. The micro-mesoporous materials (RBEA-25 and RBEA-150) were synthesized by recrystallization of said zeolites in NaOH aqueous solution as described in [11, 12].

**Characterization of catalysts.** The chemical composition of the catalysts was determined using X-ray fluorescence analysis on a Thermo Scientific ARL

Perform'X instrument equipped with a 3.5-kW rhodium tube.

Nitrogen adsorption-desorption isotherms were measured at 77 K on an automated porosimeter ASAP 2000 (Micromeritics, USA). Specific surface area was measured from the obtained nitrogen adsorption isotherms with the BET method; the micropore volume was determined using the  $t$ -plot method. The pore volume, which takes into account adsorption in micropores and mesopores and on the external surface, was calculated from the amount of nitrogen sorbed at a relative pressure of  $p/p_0 = 0.95$ .

The acid properties of catalysts were estimated using temperature-programmed desorption of ammonia (TPD  $\text{NH}_3$ ) on a USGA-101 multipurpose sorption gas analyzer.

**Catalytic activity, analysis of reaction products.** Experiments were carried out on the H-forms of BEA-zeolites preliminary calcined for 2 hours at 550 °C in a stream of purified air, and the  $\text{NH}_4$ -form – under the same conditions, but 6 hours in the program mode.

**Table 1. Characteristics of catalysts**

Catalyst	$n_{\text{SiO}_2}/n_{\text{Al}_2\text{O}_3}$	$S_{\text{BET}}$ [ $\text{m}^2 \text{g}^{-1}$ ]	Pore volume $V$ [ $\text{cm}^3/\text{g}$ ]	$V_{\text{micro}}$ [ $\text{cm}^3/\text{g}$ ]	$V_{\text{meso}}$ [ $\text{cm}^3/\text{g}$ ]	$V_{\text{micro}}/$ $V_{\text{micro}} +$ $V_{\text{meso}}$	$V_{\text{meso}}/$ $V_{\text{micro}}$ $+ V_{\text{meso}}$	Total acidity $a_0(\text{NH}_3)$ [ $\mu\text{mol}/\text{g}$ ]
BEA-25	25.0	558	0.486	0.164	0.322	0.34	0.662	1200
RBEA-25	23.8	721	0.625	0.125	0.500	0.20	0.800	1179
BEA-150	150.0	539	0.588	0.151	0.437	0.26	0.743	180
RBEA-150	176.4	822	0.792	0.139	0.653	0.18	0.824	233

Catalytic conversion of linalool was performed in the liquid phase in a 50 ml three-necked round bottomed glass flask with a reflux condenser, thermometer and a port for input of an inert gas. In the presence of solvents (methanol and ethanol), the conversion of linalool is complicated by side processes, so following experiments were carried out under solvent-free condition at temperatures in the range of 60–170 °C and in an atmosphere of inert gases (nitrogen or argon); duration of run was from 0.5–3 h, the catalyst mass 0.010–0.050 g, mass ratio of catalyst: linalool was from  $1/_{129}$  to  $1/_{26}$  (0.84–0.17 mole of linalool per gram of catalyst). Reagent and catalyst were stirred by a magnetic stirrer with heater. The catalyst was separated from the reaction products using centrifugation. The catalytic properties was characterized by the conversion of linalool and the selectivity of the formation of isomerization products.

The analysis of products of catalytic reactions was carried out by the GC-MS method (Agilent Technologies, 5890B/5977A, capillary column HP-5ms, Ultra Inert, 30 m x 0.32 mm x 0.25 μm), analyzed in program mode. The amounts of linalool, geraniol and nerol was determined from the calibration data.

## Results and Discussion

### Characterization of catalysts

Determined characteristics of initial (BEA) and recrystallized (RBEA) samples of beta-type zeolites are given in Table 1.

Chemical composition [ $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ] of the parent microporous and corresponding micro-mesoporous samples is nearly similar (recrystallization results both in decreasing (BEA-25) and increasing (BEA-150) of the silicon content), they generally differ in the porous structure – total pore volume  $V$  =

$V_{\text{micro}} + V_{\text{meso}}$ , and shares of the micro- ( $V_{\text{micro}}/V$ ) and meso-pores ( $V_{\text{meso}}/V$ ).

The adsorption-desorption isotherms of nitrogen for initial zeolites BEA-25 and BEA-150 represent a combination of type I and IV curves (according to IUPAC classification); at a low relative pressure ( $p/p_0 \leq 0.2$ ) high adsorption of nitrogen is observed which is typical for adsorption in micropores; in the range of  $p/p_0 = 0.7-1.0$  a long hysteresis loop begins, which is associated with the filling of the intercrystalline pores [13, 14]. On the isotherms of recrystallized samples RBEA-25 and RBEA-150 there is a jump (at  $p/p_0 = 0.3-0.4$ ) indicating the presence of mesopores with average pore diameter of 3.47 and 3.85 nm, respectively. According to Table 1, in recrystallized samples (micro-mesoporous materials) the total pore volume and proportion of mesopores volume increase, and the fraction of micropores decrease in comparison with the parent micropores zeolites.

It is evident from Fig. 1 that the thermo-programmed desorption (TPD) curves of ammonia have two maxima, corresponding to the presence in the catalysts of two types of acid sites – weak acid sites with ammonia desorption temperature maximum approx. at 200 °C, and stronger sites with desorption temperature over 300 °C. Catalysts with high aluminum content (BEA-25 and RBEA-25) have a large number of weak acid sites, for catalysts with high silicon content (BEA-150 and RBEA-150) amount of weak and strong sites is nearly the same. As it is seen from Fig. 1 and Table 1, the parent and the corresponding recrystallized samples differ little from each other in terms of their total acidity ( $a_0$ ) and the strength of the acid sites.

### Catalytic activity

The catalytic reaction products were the light yellow

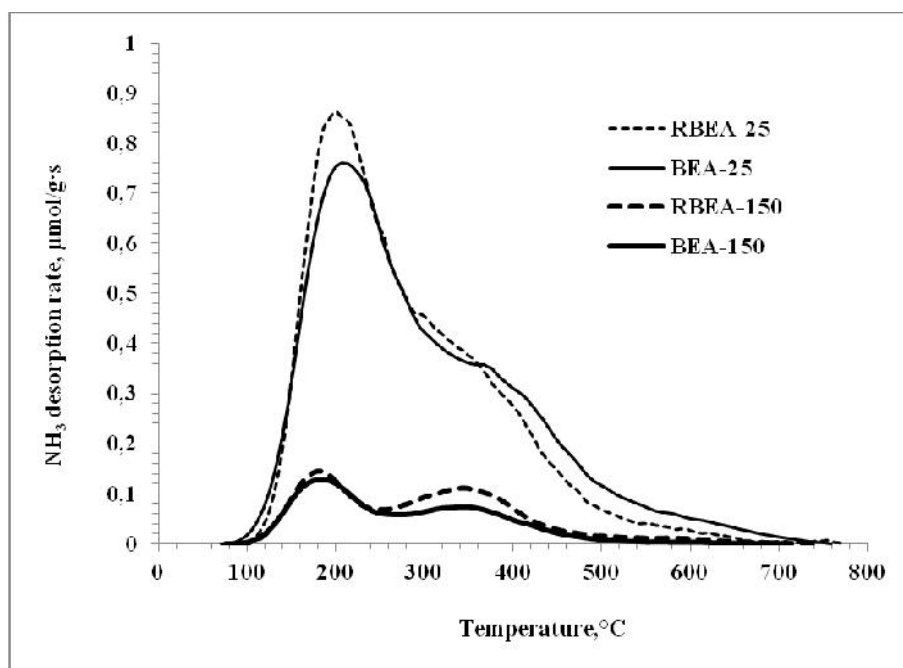


Fig. 1. Ammonia temperature desorption spectra for micro- and micro-mesoporous catalysts.

liquids with a characteristic smell. After catalytic conversion from the reaction products the catalyst was separated by centrifugation. It contained in adsorbed form a significant part (up to 25-35% volumetric) of reaction products. Their washing was carried out with methanol and their composition was identical with the main reaction product.

Catalytic activity of surveyed catalysts was compared for their 0.05 g masses; for 0.04-0.05 g masses the catalytic activity for all surveyed catalysts is not depended on mass of the latter. Optimum time of reaction conduct – 1 hour was selected for the experiment.

It was shown that the nature of astehiometric components of reaction (nitrogen and argon) has no influence on running of the linalool conversion process on surveyed catalysts. Linalool conversion reaction runs in many, but identical routes on both microporous BEA-25 and micro-mesoporous RBEA-25 catalysts with nearly the same values of total acidity ( $a_0(\text{NH}_3)$  is 1200 and 1179  $\mu\text{mol/g}$ , respectively).

These are basically the processes running on acid sites: reactions of dehydration, cyclization and condensation, as well as isomerization; and the qualitative content of reaction products is identical.

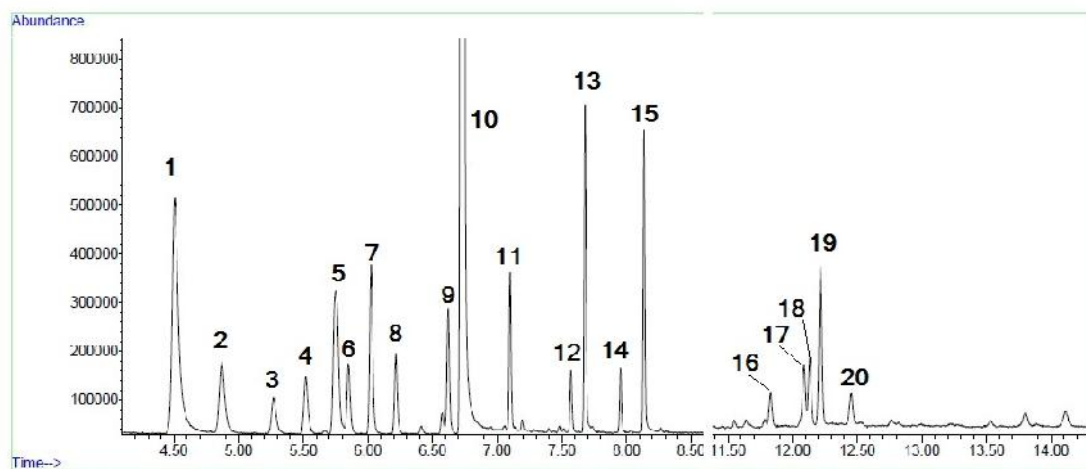
Typical chromatogram of the products of linalool conversion on the investigated catalysts is shown in Fig. 2.

In conditions under study, linalool is mainly dehydrated and cyclized to form terpenic hydrocarbons (mircene, ocymene, terpinenes, d-limonene), converted into 3-Cyclohexen-1-ol, 3,7-octadiene-2,6-diol, 2,6-dimethyl,  $\text{C}_{10}\text{H}_{18}\text{O}_2$  (on BEA-25), trans-Geranyl geraniol, condensed to Squalene  $\text{C}_{30}\text{H}_{50}$ , cyclic alcohol Thunbergol ( $\text{C}_{20}\text{H}_{34}\text{O}$ ), 2,6,10-Dodecatrien-1-ol ( $\text{C}_{15}\text{H}_{26}\text{O}$ ), isomerized into  $\pm$ -Terpineol (monoterpene alcohol), Geraniol, Nerol.

As is seen from Table 2, in case of identical loads on catalyst ( $m_{\text{catalysator}}/m_{\text{linalool}} = 1/26$ ), linalool conversion on micro-mesoporous RBEA-25 is higher than on microporous BEA-25, apparently due to bigger share of mesopores in the first one ( $(V_{\text{meso}}/V_{\text{micro}} + V_{\text{meso}}) = 0.800$ ). Product yields of linalool isomerization into geraniol/nerol are low (3-5%) and they do not depend on temperature, as well as on the mole ratio of geraniol/nerol, which approximately equals to 2. Product yields for other processes on BEA-25 and RBEA-25 are 7-17% and 19-39%, respectively, when linalool conversion is 10-42%. The same takes place in a case of BEA-150 and RBEA-

**Table 2. Catalytic properties of microporous BEA-25 and micro-mesoporous RBEA-25 zeolites in linalool conversion reaction. Medium- Ar,  $m_{\text{catalyst}}/m_{\text{linalool}} = 1/26$ , catalyst mass - 0.05 g, run-1 h**

Catalyst	BEA-25			RBEA-25		
Temperature, °C	60	80	130	65	80	130
Conversion, %	10.4	12.9	22.5	22.9	28.0	42.0
Yield, %						
of geraniol	2.4	2.4	2.7	3.3	2.2	2.0
of nerol	1.2	1.2	1.3	1.4	1.2	1.1
Selectivity, %						
of isomerization	34.6	27.9	17.8	20.8	12.1	7.4
on geraniol	23.1	18.6	12.0	14.4	7.8	4.8
on nerol	11.5	9.3	5.8	6.4	4.3	2.6



**Fig. 2. Chromatogram of catalytic conversion products of linalool on micro-mesoporous zeolite R-BEA-150 ( $m_{\text{cat}}/m_{\text{linalool}} = 1/26$ , reaction carried out in a nitrogen atmosphere at 80 °C): 1 – Pinene, 2 –  $\beta$ -Mircene, 3 –  $\alpha$ -Phellandrene, 4 –  $\alpha$ -Terpinene, 5 – D-Limonene, 6 – trans- $\beta$ -Ocymene, 7 –  $\alpha$ -cis-Ocimene, 8 –  $\gamma$ -Terpinene, 9 – Terpinolene, 10 – Linalool, 11 – 1,2-dihydrolinalool (impurity in initial linalool), 12 – 3-Cyclohexen-1-ol, 13 –  $\alpha$ -Terpineol, 14 – Nerol, 15 – Geraniol, 16 – trans-Geranyl geraniol, 17 – Squalene ( $C_{30}H_{50}$ ), 18 – Thunbergol ( $C_{20}H_{34}O$ ), 19 – 2,6,10-Dodecatrien-1-ol ( $C_{15}H_{26}O$ ), 20 –  $\pm$ -Springene ( $C_{20}H_{32}$ ).**

150 (see Table 3), but linalool conversion and product yields of isomerization into geraniol and nerol are lower – 4-30% and 2-4%, respectively.

Based on data of Tables 2 and 3 we obtain the following relative series of linalool conversion values: RBEA-25 > RBEA-150 > BEA-25 > BEA-150; there are nearly identical shares of micropores (0.20–0.18) and mesopores (0.80) in micro-mesoporous samples of RBEA-25 and RBEA-150, though the number of acid sites in RBEA-25 is bigger (1179  $\mu\text{mol/g}$ , basically represented by weak acid centers) than in RBEA-150 (233  $\mu\text{mol/g}$ , shares of soft and strong acid sites are nearly equal). In both microporous and micro-mesoporous samples prevailing role in linalool conversion belongs to acid factor – activity of sample RBEA-25 with bigger value of total acidity and weaker acid sites is higher.

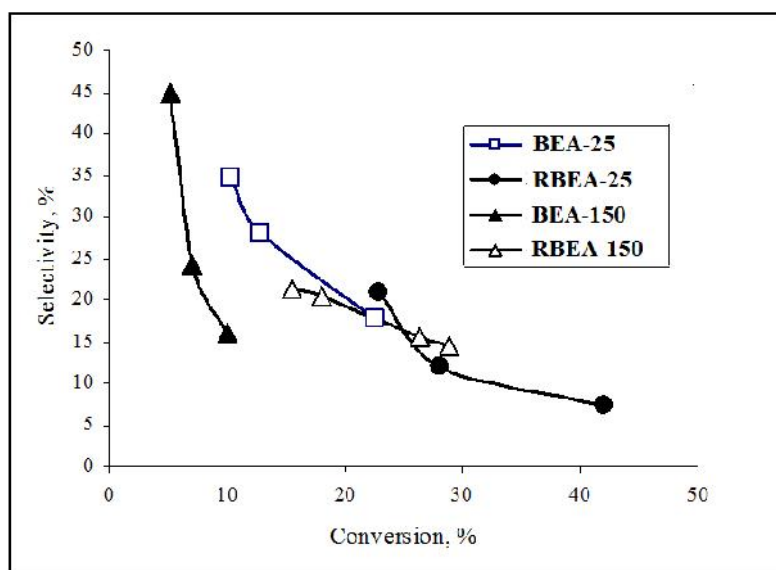
This is also indicated by the character of the change in selectivity; approximately at the same conversions of linalool (Tables 2 and 3, Fig. 3), there is the following relative selectivity series of isomerization of linalool to geraniol and nerol: RBEA-25  $\geq$  BEA-25 and RBEA-150 > BEA-150; the sample RBEA-150 contains a greater number of strong acid sites than in RBEA-25 characterized by less selectivity associated with such sites. Increase in the share of weak acid centers (BEA-25 compared to BEA-150) contributes to the enhancement of selectivity.

## Conclusion

The catalytic conversion of tertiary terpenic alcohol linalool ( $C_{10}H_{18}O$ ) has studied on samples of the beta type microporous zeolites and on their modified micro-mesoporous forms having transport mesopores

**Table 3.** Catalytic properties of microporous BEA-150 and micro-mesoporous RBEA-150 zeolites in linalool conversion reaction carried out in argon,  $m_{\text{cat}}/m_{\text{linalool}} = 1/26$ , catalyst mass - 0.05 g, run - 1 hour

Catalyst	BEA-150				RBEA-150			
Temperature, °C	80	100	130	150	80	120	150	170
Conversion, %	3.7	5.1	7.0	10.0	15.5	18.0	26.4	28.9
Yield, % of geraniol of nerol	slight slight	1.5 0.8	1.0 0.7	1.0 0.6	2.1 1.2	2.4 1.3	2.7 1.4	2.7 1.4
Selectivity, % of isomerization on geraniol on nerol	- - -	45.0 29.4 15.6	24.3 14.3 10.0	16.0 10.0 6.0	21.4 13.6 7.8	20.5 13.3 7.2	15.5 10.2 5.3	14.4 9.4 4.9

**Fig. 3.** Dependence of selectivity of linalool isomerization into geraniol and nerol on the conversion of linalool on micro- and micro-mesoporous zeolites.

with pore diameters 3.5 and 3.8 nm, respectively. Micro-mesoporous catalysts have nearly identical porous structure, but they differ by nature and strength of acid sites like initial microporous BEA zeolites. Creation of the mesoporosity does not cause a noticeable change in the acidity.

Linalool transformation on micro- and micro-mesoporous zeolites of the beta type under investigated reaction conditions (in atmosphere of inert gases  $N_2$  or Ar, at 60-170°C) proceeds many ways; reactions of dehydration, cyclisation, condensation and isomerization take place resulting in several products with rather low yield, including target geraniol and nerol (2–5%); linalool conversion is not high (4–40%).

Comparison of values of conversion and selec-

tivity with textural and acidic properties of catalysts allows us to make conclusion that the introduction of mesoporosity in Beta-type catalyst leads to significant increase in the conversion of linalool and to slight increase in selectivity. High share of weak acid sites in microporous sample (BEA-25 compared with BEA-150) contributes to enhancement of selectivity for geraniol and nerol.

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ფიზიკური ქიმია

## ლინალოლის კატალიზური გარდაქმნა მიკრო-მეზოფოროვან BEA ტიპის ცეოლითზე

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# ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, ფიზიკური და ანალიზური ქიმიის დეპარტამენტი, თბილისი, საქართველო

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. ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, ზუსტ და საბუნებისმეტყველო მეცნიერებათა ფაკულტეტი, თბილისი, საქართველო

შესწავლილია ტერაპენული მესამეული სპირტის – ლინალოლის კატალიზური გარდაქმნები მიკროფოროვან BEA ტიპის ცეოლითებსა და მათ მოდიფიცირებულ მიკრო-მეზოფოროვან ფორმებზე. ამ კატალიზატორებზე ინერტულ გარემოში და 60-170 ° ტემპერატურებზე ლინალოლი მრავალი მიმართულებით გარდაიქმნება; ხდება მისი დეჰიდრატაციის, ციკლიზაციის, კონდენსაციის და იზომერიზაციის რეაქციები; ამ დროს ლინალოლის გარდაქმნის ხარისხი მცირეა (4-40%), წარმოიქმნება მრავალი ნივთიერება, მათ შორის სამიზნე პროდუქტები გერანიოლი და ნეროლი – მცირე გამოსავლიანობით (2 - 5%).

მეზოფორების შეყვანით BEA ტიპის ცეოლითებში შესამჩნევად იზრდება ლინალოლის გარდაქმნის ხარისხი და უმნიშვნელოდ, სელექტურობა გერანიოლის და ნეროლის მიმართ; ეს უკანასკნელი მიკროფოროვან BEA ტიპის ცეოლითების შემთხვევაში მით მეტია, რაც უფრო დიდია მათში სუსტი მჟავური ცენტრების რაოდენობა.



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