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## Research Article

### CATALYTIC CONVERSION OF GERANIOL ON MICRO- AND MICRO-MESOPOROUS BETA-TYPE ZEOLITE

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#### ABSTRACT

The catalytic activities of beta-type microporous zeolites and their modified micro-mesoporous forms, with similar acid properties and differing in the characteristics of the porous structure, in reaction of conversion of acyclic monoterpene alcohol geraniol (C<sub>10</sub>H<sub>18</sub>O) was studied.

It was established using the GC/MS method that the dehydration, isomerization and cyclization reactions occur by the catalytic conversion of geraniol in a liquid phase in atmosphere of nitrogen or argon at 27-150°C.

Geraniol catalytic converting products contained mainly terpene hydrocarbons C<sub>10</sub>H<sub>16</sub>, linalool and nerol (C<sub>10</sub>H<sub>18</sub>O), sesquiterpene alcohols: C<sub>14</sub>H<sub>24</sub>O, (2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol and C<sub>15</sub>H<sub>26</sub>O, trans, trans-Farnesol, (2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol; stereoisomers are probably synthesized in chiral pore intersections of beta zeolites by the stereocontrolled synthesis.

Some correlations between catalytic properties of micro-and micro-mesoporous beta-type zeolites, their textural and acid characteristics are shown.

Over beta-type micro- and micro-mesoporous zeolites BEA-150 with  $n_{SiO_2}/n_{Al_2O_3}=150$  and RBEA-150 with  $n_{SiO_2}/n_{Al_2O_3}=176.4$ , respectively geraniol converted into the terpene alcohols C<sub>14</sub>H<sub>24</sub>O with the maximum selectivity of 50-52% and to C<sub>15</sub>H<sub>26</sub>O with about 33% and 27% selectivity on this catalysts, respectively.

The yields of isomerization products of geraniol in linalool and nerol were low (3-12 %).

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#### INTRODUCTION

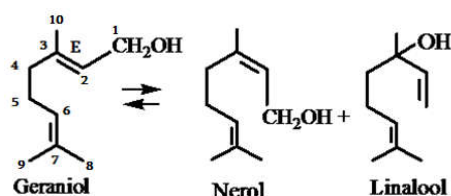
Geraniol ((2E)-3,7-dimethylocta-2,6-dien-1-ol) is monoterpene primary alcohol, Scheme 1; it has a wide application in perfumery, food industry, medicine and in organic synthesis [1].

Geraniol has high chemical activity and is used as starting material in organic synthesis of some linear and cyclic substances; geraniol is converted in many directions, particularly this is the reactions of dehydration, cyclization, isomerization, oxidation, C-C coupling etc [2]. Scientific and

practical interest have studies on the isomerization of geraniol in menthol, nerol and its conversion in other products e.g. citral; 50000 tons of terpenoid-containing aromatics with total value of 500 mln USD are produced worldwide every year; almost 10% of them falls on linalool, geraniol, nerol, citronerol and menthol [3].

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Scheme 1 Isomerization of geraniol into nerol and linalool

One pot one step isomerization reaction of geraniol to menthol on a Cu/Al<sub>2</sub>O<sub>3</sub> catalyst in 60% yield was performed [4]. Also with the catalytic transfer dehydrogenation of geraniol the citral is obtained in a yield of 50% when styrene was used as hydrogen acceptor on catalysts Cu/basic oxide [5].

Nerol has the best perfumery properties compared to geraniol. Nerol is prepared by isomerization of linalool in an acid medium or in the presence of aluminum benzylate, or by reduction of citral, and in the industry it is synthesized by isomerization of geraniol in the presence of NaOH [6].

Previously, the isomerization of terpene alcohols was carried out in the presence of acids: H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> or gaseous HCl and HBr, or mixture of acetic acid and acetic anhydride; then oxo-compounds of transition metals (V, Mo, W, Re, Nb) [7], catalytic system of alkyl orthovanadate (RO)<sub>3</sub>V=O and tetrabutylammonium hydroxide [(Bu)<sub>4</sub>N<sup>+</sup>] OH [8] and tungsten oxo (VI) alkoxides [9] were tested. The processes of isomerization on them are multi-stage, catalysts are toxic and there are problems with product separation, and a low regioselectivity for isomers.

Zeolites are deprived of many of these problems. However, the isomer selectivity is low; their acid properties are also responsible for the occurrence of side processes of dehydration and cyclization. In the conversion of linalool on the following catalysts: H- and dealuminated forms of zeolites FAU(Y), BEA, MOR, and OFF with large pores, as well as on mesoporous MCM-41 and micro- and micro-mesoporous Beta-type zeolites a low selectivity for geraniol and nerol was shown [10, 11].

By  $\gamma$ -irradiation of geraniol in the presence of air oxygen catalyst-free isomerization of geraniol into nerol and linalool was achieved; but geraniol conversion degree in nerol was 30% [12, 13].

Here we report about the catalytic conversion of geraniol in mild conditions over micro- and micro-mesoporous beta-type zeolites into isomerization products: linalool and nerol, and into C-C coupling compounds-sesquiterpene alcohols. Our goal was to determine the effect of the acidity and porosity of the beta type zeolite in the catalytic conversion of geraniol with the aim of revealing their isomerizing activity.

## Experimental

### Chemicals and Materials

Geraniol ( $\geq 97\%$ , FG, trans-3,7-Dimethyl-2,6-octadien-1-ol), Linalool (97-98 %, GC, ( $\pm$ )-3,7-Dimethyl-1,6-octadien-3-ol), Nerol (97%, cis-3,7-Dimethyl-2,6-octadien-1-ol); they were purchased at "Sigma-Aldrich"(USA). Nitrogen or argon (99.999% pure) was used as an inert medium during reactions.

### Catalysts preparation

Parent zeolites BEA-25 and BEA-150 (Zeolyst International, batches CP-814-E2200-19 and CP-811-E 1822-75) were used in NH<sub>4</sub>- and H-forms, respectively. The micro-mesoporous materials (RBEA-25 and RBEA-150) have been synthesized by recrystallization of the said initial zeolites in NaOH aqueous solution as described in [14, 15].

### Catalysts characterization

The chemical composition of the catalysts was established by X-ray fluorescence analysis (Thermo Scientific ARL PERFORM'X X-ray fluorescence spectrometer). Adsorption and acidic characteristics of catalysts were defined in detail earlier in [11]. The specific surface area, volume of micro- and mesopores of the investigated catalysts were determined from nitrogen adsorption-desorption isotherms at 77 K on an automated porosimeter ASAP 2000 Micromeritics, USA). The acid properties of catalysts were estimated using temperature-programmed desorption of ammonia (TPD NH<sub>3</sub>) (USGA-101 multipurpose sorption gas analyzer).

### Investigations of catalytic activity

The reaction of geraniol conversion was carried out in a liquid phase in a 50 ml three-necked round-bottomed glass flask with a reflux condenser, a thermometer and with an inlet for introducing of an inert gas; catalytic experiments were conducted on a magnetic stirrer with a heater under solvent free condition at temperatures in the range of 27-150 °C and under ambient pressure; duration of run was 1-2 h, catalyst mass-0.01-0.07 g, mass ratio of catalyst: geraniol was 1/133 -1/19 respectively, i.e. 0.86-0.12 mol geraniol/g of catalyst.

The catalyst and reaction products were separated from each other by centrifugation.

The progress of the geraniol conversion reaction and analysis of the reaction products in solvent-methanol was carried out by GC/MS method (Agilent Technologies GC/MS, 7890B/5977A, USA) in the EI mode, 70 eV. There were used helium as a carrier gas and capillary column HP-5ms, Ultra Inert, 30 m x 0.32 mm x 0.25  $\mu$ m. Analyzes were carried out in program mode: hold at 80 °C for 5 min, ramp to 210 °C at 30°/min, hold at 210°C for 10 min.

The content of the reaction products (C<sub>i</sub>, %) were determined by the internal standard method [16], internal standard was geraniol. Also the amount of linalool, geraniol and nerol was determined from their calibration curves. Conversion of geraniol (C<sub>geraniol</sub>), the yield (Y<sub>i</sub>), and selectivity to products (S<sub>i</sub>) were determined according to the formulas, respectively:

$$C_{\text{geraniol}}, \% = (\mathbf{m}_{\text{initial geraniol}} - \mathbf{m}_{\text{unconverted geraniol}}) \times 100 / \mathbf{m}_{\text{initial geraniol}}$$

$$Y_i, \% = C_i \times M_{\text{geraniol}} \times 100\% / 97\% \times M_i,$$

$$S_i, \% = 100 \times Y_i / C_{\text{geraniol}}$$

M<sub>geraniol</sub> is molar mass of geraniol, 97%-of its initial concentration, m is the mass of substance.

## RESULTS AND DISCUSSION

### Characteristics of the catalysts

From Table 1 it is visible that chemical compositions (i.e. molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) of the starting BEA zeolites with

microporous structure and corresponding recrystallized RBEA zeolites with the combined micro-mesoporous structure are nearly similar. The latter have a larger total pore volume and a larger proportion of mesopores with a diameter of about 3.5 and 3.9nm for samples RBEA-25 and RBEA-150, respectively.

**Table 1** Characteristics of catalysts

Catalyst	BEA-25	RBEA-25	BEA-150	RBEA-150
$n_{\text{SiO}_2}/n_{\text{Al}_2\text{O}_3}$	25.0	23.8	150.0	176.4
$S_{\text{BET}}, \text{m}^2 \text{g}^{-1}$	558	721	539	822
Total Pore volume	0.486	0.625	0.588	0.792
$V_{\text{cm}^3/\text{g}}$				
$V_{\text{micro}}/V_{\text{micro}} + V_{\text{meso}}$	0.340	0.200	0.260	0.180
$V_{\text{meso}}/V_{\text{micro}} + V_{\text{meso}}$	0.662	0.800	0.743	0.824
Acidity ( $a_0(\text{NH}_3)$ , $\mu\text{mol/g}$ ):				
Total	1200	1179	180	233
Weak acid center	725	704	97	95
Strong acid center	475	475	83	138

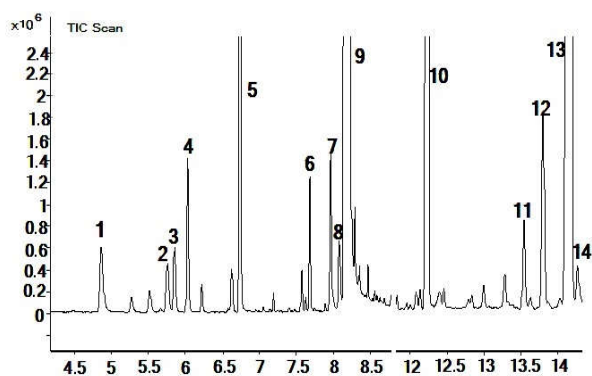
Their pores are more accessible for geraniol molecules with a maximum and minimum projection radii 0.643 and 0.379 nm [17], respectively than pores of original forms of zeolite beta with internal pore space of 3 dimensional channel 12-ring 0.668 nm [18].

According to the TPD of ammonia from samples of BEA and RBEA, the nature of the acid sites is the same; in each of them there are 2 types of acid centres, weaker and stronger, with maxima of the desorption temperature of ammonia approximately at 200 °C and 300 °C, Table 1 [11]. But these centres (both weak and stronger) in samples with high aluminium content (BEA-25 and RBEA-25) are significantly larger than in BEA-150 and RBEA-150. Accordingly, in the samples of BEA-25 and RBEA-25, the value of their total acidity is larger, as can be seen from Table 1.

### Catalytic activity

#### Composition of the reaction products

The composition of the reaction products using the example of the R-BEA-150 catalyst is shown in Figure 1.



**Figure 1** TIC Chromatogram of catalytic conversion products of geraniol on micro-mesoporous zeolite R-BEA-150 ( $m_{\text{cat}}/m_{\text{geraniol}}=1/26$ , reaction carried out in a nitrogen atmosphere at 80 °C): 1 -  $\beta$ -Mircene,  $\text{C}_{10}\text{H}_{16}$ , 2-D-Limonene,  $\text{C}_{10}\text{H}_{16}$ , 3-trans- $\beta$ -Ocymene,  $\text{C}_{10}\text{H}_{16}$ , 4- $\beta$ -Ocymene,  $\text{C}_{10}\text{H}_{16}$ , 5- $\beta$ -Linalool,  $\text{C}_{10}\text{H}_{18}\text{O}$ , 6- $\alpha$ -Terpineol,  $\text{C}_{10}\text{H}_{18}\text{O}$ , 7-Nerol,  $\text{C}_{10}\text{H}_{18}\text{O}$ , 8-cis-Isogeraniol,  $\text{C}_{10}\text{H}_{18}\text{O}$ , 9-trans-Geraniol,  $\text{C}_{10}\text{H}_{18}\text{O}$ , 10-trans, trans -Farnesol, (2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , 11- trans, trans, trans-Geranylgeraniol,  $\text{C}_{20}\text{H}_{34}\text{O}$ , (E,E,E)- 3,7,11,15-Tetramethyl-

2,6,10,14-hexadecatetraen-1-ol, 12-p-Camphorene,  $\text{C}_{20}\text{H}_{32}$ , 13-(2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol,  $\text{C}_{14}\text{H}_{24}\text{O}$ , 14- Unidentified isomer of trans-Geranylgeraniol,  $\text{C}_{20}\text{H}_{34}\text{O}$ .

**The main conversion products of geraniol on microporous BEA and micro-mesoporous RBEA samples are the following compounds:**

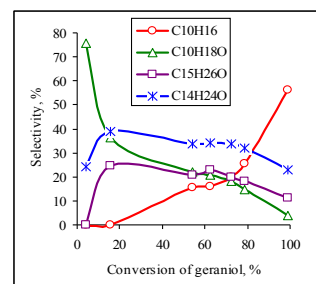
- Over 60 °C dehydration products with the formation of **terpene hydrocarbons**  $\text{C}_{10}\text{H}_{16}$  ( $\alpha$ -Mircene,  $\beta$ -Mircene,  $\alpha$ -Terpinolene, D-Limonene, trans- $\beta$ -Ocimene,  $\beta$ -Ocimene,  $\gamma$ -Terpinene, 1,1,2-Trimethyl-3-(2-methyl-1-propen-1-ylidene) cyclopropane,  $\alpha$ -Terpinene, (4E,6Z)-2,6-Dimethylocta-2,4,6-triene i.e. alloocimene).
- $\text{C}_{10}\text{H}_{18}\text{O}$ , Isomerization products**, (mainly the products of the double bond transfer in geraniol and, to a lesser extent, cis-trans isomerization)- $\beta$ -Linalool and Nerol, also a very small amount (up to 0.6%) of cis-Isogeraniol ((3Z)-3,7-Dimethyl-3,6-Octadien-1-ol) and **cyclised product**  $\alpha$ -Terpineol (up to 1.2%).
- Carbon chain-extending products with formation of **sesquiterpene alcohols**: trans,trans-Farnesol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , (2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol and  $\text{C}_{14}\text{H}_{24}\text{O}$ , (2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol.

Generally, up to 2-3% over the 40 °C was formed **diterpenoids (diterpene alcohols)**: trans, trans, trans-Geranylgeraniol,  $\text{C}_{20}\text{H}_{34}\text{O}$ , (E,E,E)-3,7,11,15-Tetramethyl-2,6,10,14-hexadecatetraen-1-ol and its other geometric isomers; (E,E)-geranylgeraniol,  $\text{C}_{20}\text{H}_{34}\text{O}$ , (6E, 10E)- 3,7, 11,15-Tetramethyl-1,6,10,14-hexadecatetraen-3-ol; only on the RBEA-25 and BEA-25 catalysts at 100-150 °C the formation of up to 1.0 - 1.5% **monocyclic diterpene alcohols**: thunbergol,  $\text{C}_{20}\text{H}_{34}\text{O}$ , isocembrol, (1R,2E,4S,7E,11E)-4-Isopropyl-1,7,11-trimethylcyclohexadeca-2,7,11-trienol and up to 0.3-0.6% **monocyclic terpene**, cembrene-(1E,3Z,6E,10E)-3,7,11-trimethyl-14-(propan-2-yl)cyclohexadeca-1,3,6,10-tetraene,  $\text{C}_{20}\text{H}_{32}$  is observed.

**Diterpene**: m- and p-Camphorene,  $\text{C}_{20}\text{H}_{32}$ , 4-(6-methylhepta-1,5-dien-2-yl)-1-(4-methylpent-3-enyl)cyclohexene.

#### Possible scheme of conversion of geraniol

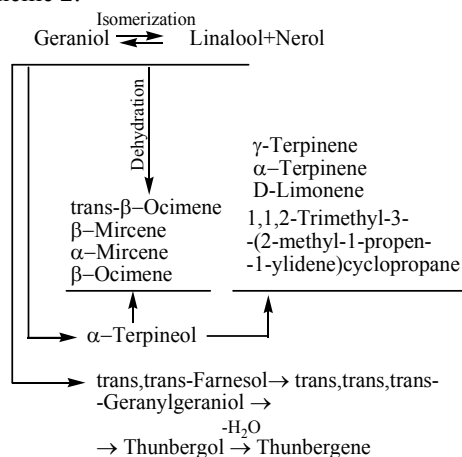
On all the catalysts investigated, the selectivity of the isomerization products ( $\text{C}_{10}\text{H}_{18}\text{O}$ -linalool, nerol, and slightly formed cis-isogeraniol and  $\alpha$ -terpineol) decreases with growing geraniol conversion, but the selectivity for the dehydration



**Figure 2** Selectivities in the geraniol conversion, catalysed by RBEA-25, run time-1 h, nitrogen atmosphere, mass of catalysts- 0.05 g, ratio of geraniol/catalyst - 0.17 mol/g.

products- the terpene hydrocarbons  $C_{10}H_{16}$  increases and an extreme dependence of selectivities of trans, trans-farnesol and  $C_{14}H_{24}O$  on the conversion of geraniol is observed.

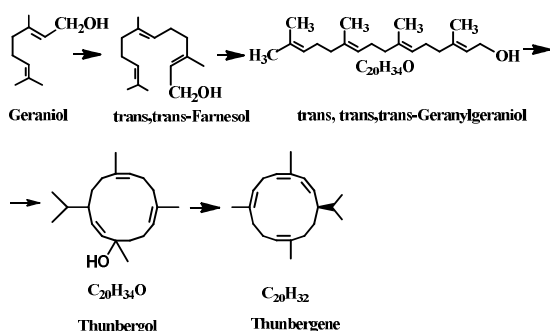
This is shown in Figure 2 using RBEA-25 as an example. Similar dependences of selectivities from conversion are observed in the case of complex parallel-consequent reactions [19]. With this in mind, possible ways of converting of geraniol on micro- and micro-mesoporous beta-type zeolite are shown on the Scheme 2.



**Scheme 2** Proposed directions for the conversion of geraniol on micro- and micro-mesoporous samples of the beta type zeolite.

The farnesols are sesquiterpene analogs of geraniol and they are probably obtained by extending one of the methyl groups in the 7 position of the geraniol [20].

Therefore, it can be assumed that by catalytic redistribution and extension of the carbon chain are formed two homologous terms of diterpene alcohols  $C_{14}H_{24}O$  and  $C_{15}H_{26}O$  (trans, trans - farnesol) from monoterpene alcohol geraniol, and from farnesol-  $C_{20}H_{34}O$  (trans, trans, trans-geranylgeraniol and its other isomers); the possibility of obtaining of geranylgeraniol from farnesol by allyl rearrangement under  $O = W(OR)_4 \cdot$  Ligand catalysts is shown in study [9].



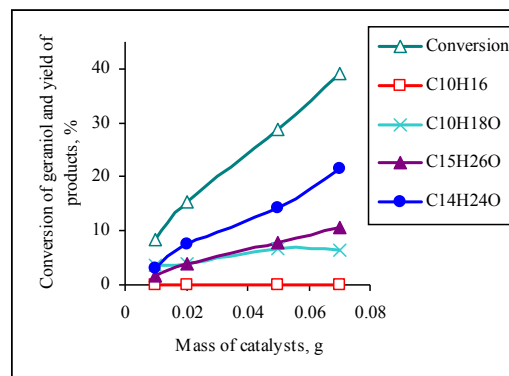
**Scheme 3** Ways of catalytic conversion of geraniol on micro- and micro-mesoporous zeolites.

Large molecules of cembrene (thunbergene,  $C_{20}H_{32}$ , Scheme 3) could be formed by cyclization of trans, trans, trans-geranylgeraniol between 1 and 14 carbon atoms, which was earlier shown in [21]. Cembrene is monocyclic 14-membered diterpene hydrocarbon with minimum and maximum projection radii 5.55 and 6.25 Å, respectively [22].

Cembrene can also be formed by dehydration of the resulting thunbergol  $C_{20}H_{34}O$  [23]. Usually thunbergol and its epimer are obtained by multistage regio- and stereoselective synthesis from dl-epimukulol and dl-mukulol, respectively [24].

**Effect of mass of catalyst, nonstoichiometric compound, temperature and acidity**

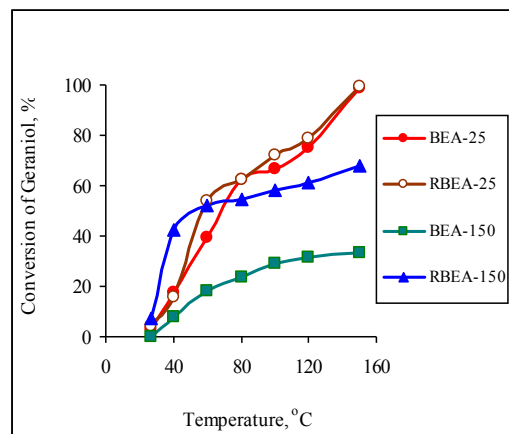
The dependence of the catalytic activity (conversion of geraniol, selectivity and yield of reaction products) on the nature of the inert medium ( $N_2$ , Ar), on the mass of the catalyst, on the temperature was studied. The optimum reaction time was chosen to be 1 h. To compare the activities of the catalysts, their mass was chosen equal to 0.05 g.



**Figure 3** The effect of mass of catalyst BEA-150 on conversion of geraniol and yield of products. Reaction conditions: geraniol - 0.0086 mole/h (1.5 ml/h), 100 °C, medium -  $N_2$ . Here the product  $C_{10}H_{18}O$  includes Linalool, Nerol, cis-Isogeraniol,  $\alpha$ -Terpineol.

As seen from Figure 3 the conversion of geraniol and the yields of diterpene alcohols  $C_{14}H_{24}O$  and  $C_{15}H_{26}O$  are increasing with the growth of catalyst mass in the range 0.01- 0.07 g; under BEA-150 at a catalyst mass of 0.07 g and 40% conversion of geraniol, the selectivity for these diterpene alcohols is 55% and 27%, respectively. It can be assumed that this one-stage synthesis of these alcohols with greater yield can be successful on the investigated micro- and micro-mesoporous zeolites of the beta type by selecting appropriate conditions. As is known, stereospecific syntheses of diterpene alcohols are multistage processes [20, 2].

It was shown that under the conditions studied in the atmosphere of nitrogen or argon the character of the transformation of geraniol is the identical.



**Figure 4** Effect of reaction temperature on the conversion of geraniol. Ratio of geraniol/catalyst was 0.17 mol/g,  $m_{catalyst} = 0.05$  g.

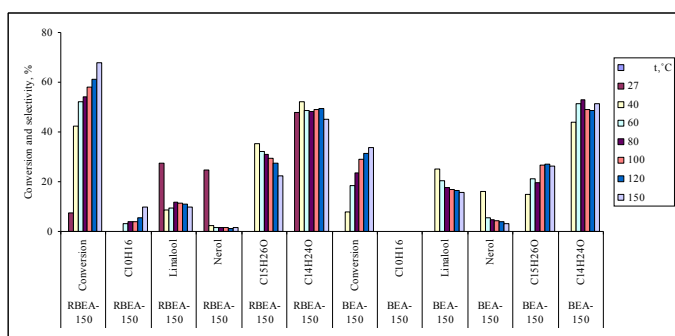


For the temperature region above 80 °C, probably less complicated by external diffusion, a comparison of the activities of catalysts by the conversion of geraniol at the same temperature and same load of catalysts shows the following relative series of their catalytic activity:

RBEA-25 ≥ BEA-25 > RBEA-150 > BEA-150, Figure 4; this sequence correlates with the values of their total acidity ( $a_0\text{NH}_3$ ), Table 1; the conversion of geraniol is greater on BEA-25 and RBEA-25 samples with a total acidity of 1179 and 1200  $\mu\text{mol NH}_3 / \text{g}$ , respectively, versus 180 and 233  $\mu\text{mol NH}_3 / \text{g}$ , respectively, versus 180 and 233  $\mu\text{mol NH}_3 / \text{g}$ , respectively, for the less active BEA-150 and RBEA-150, respectively.

#### Activity, acidity and porosity

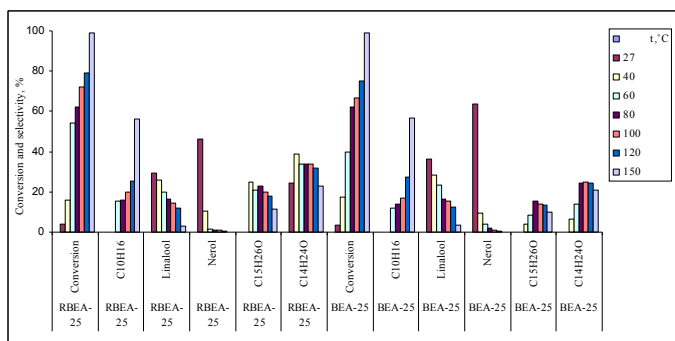
With the introduction of mesopores into the microporous zeolite and the increase of acidity of the catalyst, the conversion of geraniol increases from 33.6 and 67.7% for BEA-150 and RBEA-150, accordingly up to 99% for RBEA-25 and BEA-25, Figures 5, 6.



**Figure 5** Catalytic conversion of geraniol over micro- and micro-mesoporous BEA-150 and RBEA-150 zeolites and selectivity to some products. Reaction conditions: ratio of geraniol/catalyst was 0.17 mol/g, nitrogen atmosphere,  $m_{\text{catalyst}} = 0.05 \text{ g}$ .

From Figure 7 and Table 1 it can be seen that the selectivity of formation of terpenic hydrocarbons  $\text{C}_{10}\text{H}_{16}$  correlates with the acidity of the catalysts. On the catalyst with the lowest acidity (BEA-150) their formation is not observed. On BEA-25 and RBEA-25 samples with the highest acidity (1200  $\mu\text{mol} / \text{g}$ ) the selectivity of  $\text{C}_{10}\text{H}_{16}$  formation reaches 57%.

It is seen from Figure 8 that at low degrees of geraniol conversion there are the following series of selectivities for linalool and nerol: BEA-25 > RBEA-25 > RBEA-150 > BEA-150; this series shows that the effects of the acid factor and

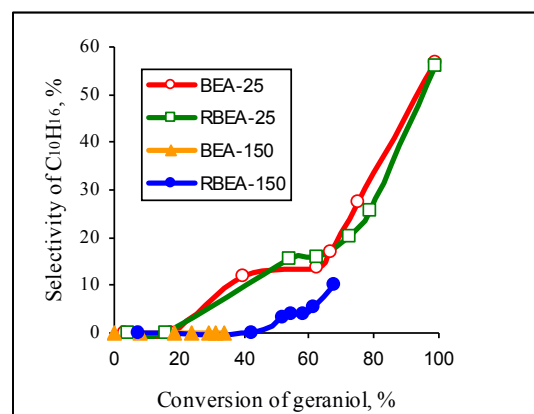


**Figure 6** Catalytic conversion of geraniol over micro- and micro-mesoporous BEA-25 and RBEA-25 zeolites and selectivity to some products. Reaction conditions: ratio of geraniol/catalyst was 0.17 mol/g, nitrogen atmosphere,  $m_{\text{catalyst}} = 0.05 \text{ g}$

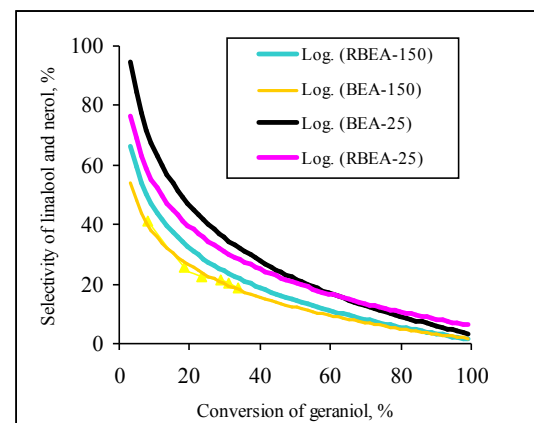
pore characteristics on the selectivity are intertwined; in particular, with the same acidity spectrum of BEA-25 and

RBEA-25 samples, it is likely that a large proportion of micropores in BEA-25 is responsible for its greater selectivity for linalool and nerol.

In the RBEA-150 and BEA-150 pairs, the high selectivity of the former is apparently associated with a large number of strong acid sites (138  $\mu\text{mol} / \text{g}$ ) in it. Comparing the selectivities of the micro-mesoporous RBEA-25 and RBEA-150 with the same characteristics of micro- and mesopores it can be seen that the high selectivity for RBEA-25 correlates with a large number of acid sites in RBEA-25 (1179  $\mu\text{mol} / \text{g}$ ) than in RBEA-150 (233  $\mu\text{mol} / \text{g}$ ), Table 1, Figure 8.



**Figure 7** Dependence of the selectivity of  $\text{C}_{10}\text{H}_{16}$  from conversion of geraniol over catalysts; ratio of geraniol/catalyst – 0.17 mol/g, nitrogen atmosphere,  $m_{\text{catalyst}} = 0.05 \text{ g}$ .



**Figure 8** Trends in the variation of total selectivity for both linalool and nerol on micro- and micro-mesoporous catalysts

At geraniol conversions up to about 20% of the selectivity for linalool and nerol are sharply reduced and then approach zero; at the same time, competitive reactions of formation of terpene hydrocarbons  $\text{C}_{10}\text{H}_{16}$  and  $\text{C}_{14}\text{H}_{24}\text{O}$  and  $\text{C}_{15}\text{H}_{26}\text{O}$  terpene alcohols are enhanced, Figure 2. With decrease of the selectivity of linalool and nerol the selectivity ratio of linalool/nerol increases, for example, from 0.6 to 20-25 and more for BEA-25 and RBEA-25, Figure 9. Thus the regioselectivity is achieved by linalool, i.e. in the migration of the double bond in the geraniol molecule, especially in the case of BEA-25 and RBEA-25; however, on these catalytic systems, the yields of linalool and nerol are low (3-12%), Figures 5, 6, 9.

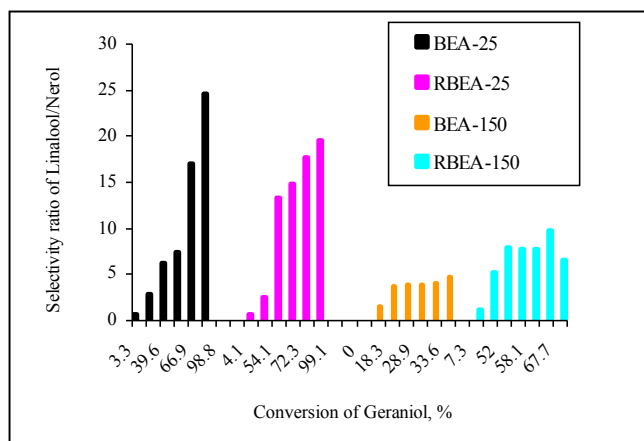


Figure 9 Effect of geraniol conversion over zeolite catalysts on the molar ratio of selectivity of linalool to nerol

In the transformation products of geraniol the content of stereoisomers of sesquiterpene alcohols:  $C_{14}H_{24}O$  ((2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol) and  $C_{15}H_{26}O$ , trans,trans-Farnesol, ((2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol), is probably due to the presence of the chiral pore intersections in the structure of zeolite beta.

With the approximately identical geraniol conversions on samples of RBEA-25 and BEA-25 with the highest acidity (1179 and 1200  $\mu\text{mol/g}$ , respectively), the selectivity to  $C_{15}H_{26}O$  and to  $C_{14}H_{24}O$  on the micro-mesoporous RBEA-25 is more due to its larger surface area, Figure 10.

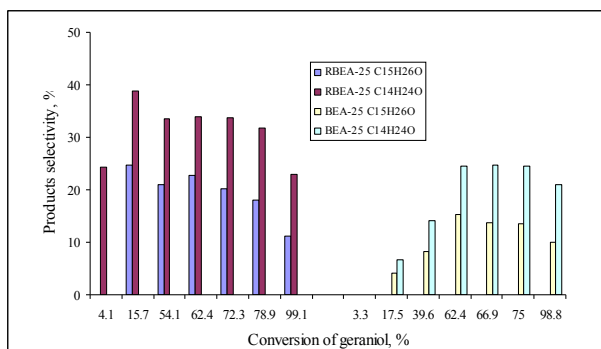


Figure 10 Dependence of the selectivity of  $C_{15}H_{26}O$  and  $C_{14}H_{24}O$  from the conversion of geraniol on BEA-25 and RBEA-25 catalysts; ratio of geraniol/catalyst – 0.17 mol/g, nitrogen atmosphere,  $m_{\text{catalyst}} = 0.05$  g.

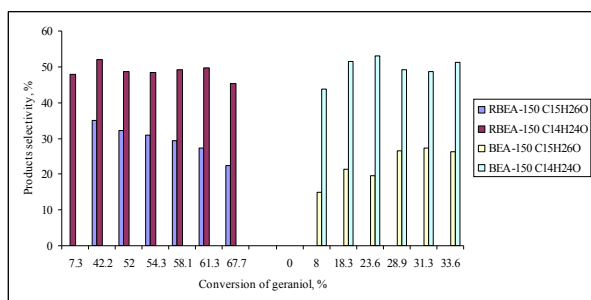


Figure 11 Dependence of the selectivity of  $C_{15}H_{26}O$  and  $C_{14}H_{24}O$  from the conversion of geraniol on BEA-150 and RBEA-150 catalysts; ratio of geraniol/catalyst – 0.17 mol/g, nitrogen atmosphere,  $m_{\text{catalyst}} = 0.05$  g.

It was established that on BEA-150 and RBEA-150 samples with a lower total acidity (180 and 233  $\mu\text{mol/g}$ , respectively) and with a large fraction of mesopores (0.82 and 0.74, respectively) the formation from geraniol of trans, trans isomers of sesquiterpene alcohols  $C_{14}H_{24}O$  and  $C_{15}H_{26}O$  takes

place with selectivity of about 50 and 30%, respectively. On BEA-25 and RBEA-25 samples with higher acidity (1200 and 1179  $\mu\text{mol/g}$ , respectively) and mesopore fractions of 0.66 and 0.80, the selectivity for  $C_{14}H_{24}O$  and  $C_{15}H_{26}O$  is less, Figure 11. These facts agree with the lowest dehydrating ability of the samples RBEA-150 и BEA-150, on which there is the least selectivity of formation  $C_{10}H_{16}$ , Figure 7.

## CONCLUSION

The catalytic conversion of the primary terpenic alcohol geraniol  $C_{10}H_{18}O$  was studied over the beta type microporous zeolites (BEA-25 and BEA-150 with  $n\text{SiO}_2/n\text{Al}_2\text{O}_3$  equal to 25 and 23.8) and their modified micro-mesoporous forms (RBEA-25 and RBEA-150 with  $n\text{SiO}_2/n\text{Al}_2\text{O}_3$  equal to 150 and 176.4). Using the GC/MS method it was shown that the dehydration, isomerization and cyclization reactions occur by the conversion of geraniol in a liquid phase in atmosphere of  $N_2$  or Ar at 27-150  $^{\circ}\text{C}$ .

On the investigated catalysts geraniol mainly forms terpenic hydrocarbons  $C_{10}H_{16}$ , isomerization products mainly linalool, nerol, and probably in chiral pore intersections of beta zeolites takes place the stereoselective synthesis of sesquiterpene alcohols:  $C_{14}H_{24}O$ , (2E,6E)-6,11-Dimethyl-2,6,10-dodecatrien-1-ol and  $C_{15}H_{26}O$ , trans,trans-Farnesol, (2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrien-1-ol; also in an insignificant amount diterpene camphorene and over RBEA-25 and BEA-25 diterpene alcohols  $C_{20}H_{34}O$  and monocyclic terpene cembrene  $C_{20}H_{32}$  are formed.

With the introduction of mesopores into the microporous zeolite and increasing acidity of the catalysts, the conversion of geraniol increases to a maximum of 99% for RBEA-25 and BEA-25.

The selectivity of formed terpenic hydrocarbons  $C_{10}H_{16}$  correlates with the total acidity of the catalysts. On the catalyst with the lowest acidity (BEA-150) their formation wasn't observed. On BEA-25 and RBEA-25 samples with the highest acidity (1200  $\mu\text{mol/g}$ ) the selectivity of  $C_{10}H_{16}$  formation reaches 57% at 150  $^{\circ}\text{C}$ .

The highest selectivity of nerol formation was 46% and 64% on samples of BEA-25 and RBEA-25 at low geraniol conversions (4-8%) at 27-40  $^{\circ}\text{C}$ . Yields of linalool and nerol were low (3-12%).

On samples of BEA-150 and RBEA-150 with a lower total acidity (180 and 233  $\mu\text{mol/g}$ , respectively) and with a large fraction of mesopores (0.82 and 0.74, respectively) the formation of trans, trans isomers of sesquiterpene alcohols  $C_{14}H_{24}O$  and  $C_{15}H_{26}O$  from geraniol with selectivity of about 52 and 33% at conversions 18-34 and 42-61%, respectively, was established. On BEA-25 and RBEA-25 samples with higher acidity (1200 and 1179  $\mu\text{mol/g}$ , respectively) and mesopore fractions of 0.66 and 0.80, the selectivity for  $C_{14}H_{24}O$  and  $C_{15}H_{26}O$  is less.

A comparison of the results obtained shows that the selectivity of the formation of molecules with a smaller size ( $C_{10}H_{16}$  and  $C_{10}H_{18}O$ ) is greater on RBEA-25 and BEA-25 catalysts with higher total acidity; and a larger molecules-sesquiterpene alcohols ( $C_{14}H_{26}O$  and  $C_{15}H_{26}O$ ) with greater selectivity are

formed on samples of catalysts RBEA-150 and BEA-150 with a lower total acidity.

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