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Synergic Actions of BEA-Type Zeolites and Ultrasonic Irradiation in Conversion of Geraniol

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The geraniol conversion reaction was initiated by the simultaneous action of micro- and micro-mesoporous BEA-type zeolites and ultrasonic irradiation (UMR-300B hybrid reactor, 25 kHz, 100-900 W; SRF-1, 20-60 kHz, 100 W). Geraniol by ultrasonic irradiation at 27-100 ºC, had a low degree of conversion, upto 2 %. Geraniol was a resistant to ultrasound in argon atmosphere solutions of N,N-dimethylformamide and methanol. In methanolic solution, geraniol was actively converted to linalool and to methyl ethers of linalool and nerol with the selectivity of 80 % on zeolite BEA-25 under ultrasonic irradiation in air at 30 ºC. Using BEA-type zeolite/ultrasonic-assisted reaction was increased the degree of conversion of geraniol, the selectivity and yield to linalool and nerol on the most active RBEA-25 zeolite by prolonged ultrasonic irradiation (1.5-5 h) or under combined ultrasound and microwave irradiation (US 300 W/MW 550 W, 1.5 h, 80 ºC).

Keywords: Geraniol, BEA-type zeolite, Ultrasonic activation, Sinergic effect, Isomerization.

INTRODUCTION

The investigation of the process of isomerization of terpene alcohols *viz.* linalool ($C_{10}H_{18}O$) and its geometric isomer geraniol is of practical importance since the isomers of obtained equilibrium mixture are widely used in the perfumery, medicine and in cosmetic industry [1,2]. Many homogeneous and heterogeneous catalysts for the isomerization of geraniol are known *e.g.*, inorganic acids, oxo-compounds of transition elements, especially W, V and Mo [3,4]; catalytic system of alkyl orthovanadate $(RO)_3V=O$ and tetrabutylammonium hydroxide $[(Bu)_4N^+]OH$ [5].

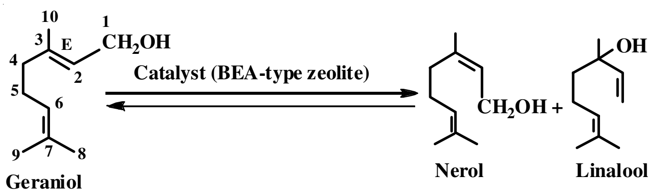
The mentioned active systems are environmentally harmful and not regioselective. In the case of "green" zeolite catalysts such as MOR OFF, zeolite beta (BEA), mesoporous MCM-41 and micro-mesoporous BEA, the yields of the isomers were low [6-8]. It is known that ultrasonic and microwave technologies have huge potential in the updating of many processes [9,10]. The ultrasound and microwave irradiation and the associated chemical and physical effects, provide more efficient chemical processes and the higher yields of products [9,11-13].

Today, more that 3000 chemical reactions are known, which are proceeded by specific activation during microwave and ultrasonic irradiation, assuming that they are based on mechanisms of fast dielectric heating of material [14] and acoustic cavitation [10,15]. From the viewpoint of fundamental studies, the chemical synthesis transformations by using ultrasound and microwave irradiations are considered as one of the relatively new "green" and progressive direction of chemistry similar to the use of high-effective catalytic systems micro-mesoporous composite zeolite materials; their mesoporous system (in contradistinction from zeolites) enables selective transformation of large-size molecules (diameter of section is more than 1 nm) used in pharmacy, perfumery, *etc*. industries.

In previous study [8], the investigation showed that the catalytic converting products of geraniol over BEA-type micro- and micro-mesoporous zeolites (BEA-25, BEA-150, RBEA-25 and RBEA-150) contained mainly terpene hydrocarbons $C_{10}H_{16}$, linalool and nerol ($C_{10}H_{18}O$), 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. The yields of isomerization products of geraniol in linalool and nerol were found to be low (3-12 %) at 80 ºC.

In present study, the reaction of geraniol conversion carried out under combined BEA-type zeolite and ultrasound (partly also microwave) irradiation to promote the activity of zeolites in the isomerization of geraniol (**Scheme-I**). The analysis showed that this influence of irradiation is ambiguous; synergistic effect is present in case of micro- and micro-mesoporous BEA-type zeolite samples with high acidity and a large pore surface. The combination of ultrasonic irradiation and BEA-type zeolite catalyst RBEA-25 allowed to obtain linalool and nerol in the isomerization of geraniol at 80 ºC with increased yields up to 31 % and selectivity up to 63.2 % at conversion of 49 %.



Scheme-I: Ultrasonically activated isomerization of geraniol into linalool and nerol

EXPERIMENTAL

The chemicals *viz*., geraniol ≥ 97 %, *trans*-3,7-dimethyl-2,6-octadien-1-ol, methanol for HPLC (≥ 99.9 %) were purchased from Sigma-Aldrich. The argon and nitrogen used were of 99.999 % purity (Metihbect, Ukraine). Geraniol was used without further purification, it contained up to 1 % *cis*-geraniol (nerol), small amount of *iso*-geraniol and 2 % α-citral.

Preparation of catalyst: The micro-mesoporous materials (RBEA-25 and RBEA-150) was synthesized by recrystallization [16,17], respectively of starting microporous zeolites NH_4-BEA ($nSiO_2/nAl_2O_3$ = 25) and H-BEA ($nSiO_2$/ nAl_2O_3 = 150) from Zeolyst International, USA.

Catalysts characterization: The chemical composition of the investigated catalysts and their specific surface area, volume of micro- and mesopores were previously determined by X-ray fluorescence analysis [7] and from nitrogen adsorption-desorption isotherms at 77 K on an automated porosimeter ASAP 2000 Micromeritics, USA. Acidic properties of catalysts were characterized using temperature-programmed desorption of ammonia (TPD NH_3) on USGA-101 multipurpose sorption gas analyzer [16].

The distribution sizes of crystallites of catalysts BEA-150 and RBEA-150, before and after ultrasonic irradiation of geraniol together with a catalyst were determined on the laser light scattering particle size analyzer (Laser-Particle Sizer Analysette 12-DynaSizer, Fritsch) as described earlier [18].

Catalytic and ultrasonic activation: The conversion of geraniol was carried out under undirect ultrasonic irradiation in nitrogen atmosphere in the Multi-frequency Sonoreactor SRF-1 (20/40/60 kHz, ultrasound output 100 W, Shinka, Japan) and under direct ultrasonic irradiation in Ultrasonic-Microwave (hybrid) Reactor UMR-300B (Shinka, Japan) by ultrasonic vibration probe of 18 mm diameter, US frequency 25 kHz and at ultrasound output 200-900 W; the reaction vessel consists of 50 mL three-necked glass ("Bomex") with a condenser.

The ultrasonic activation and conventional catalytic experiments were conducted in an atmosphere of argon, nitrogen or air. The convential catalytic conversion of geraniol was carried out at 30-80 ºC in a 50 mL round bottom flask with a reflux condenser containing the inlet for introducing of an inert gas [8], duration of run was 1.5-10 h, catalyst mass range 0.0094 -0.05 g, mass ratio of catalyst/geraniol was 1/26.7-1/142 respectively, *i.e*. 0.17 - 0.92 mol of geraniol/g of catalyst (1.5 mL-8 mL/0.05 g catalyst). The solid zeolite catalyst was removed by centrifugation. Geraniol conversion was performed in solvent-free conditions or in the presence of different polar solvents *e.g*., methanol, *N*,*N*-dimethylformamide and distilled water.

Catalytic activity: For the comparison of results of conventional thermocatalytic and ultrasonic conversions of geraniol on micro- and micro-mesoporous BEA-type zeolites experiments was carried out under identical test conditions and the same catalyst loading of 0.92 mol geraniol/g catalyst. The activities of studied zeolite catalysts were characterized by conversion of geraniol and selectivities to linalool and nerol. The selectivities were evaluated with respect to converted geraniol.

Analysis of reaction products: After completion of reaction and separation of catalyst, the reaction products were analyzed by GC/MS method (Agilent Technologies GC/MS, 7890B/ 5977A, USA), in the EI mode, 70 eV. Methanol was used as solvent, helium as a carrier gas and capillary column HP-5ms, Ultra Inert, 30 m × 0.32 mm × 0.25 µm; analyzes were carried out in program mode: hold at 80 ºC for 5 min, ramp to 210 ºC at 30º/min, hold at 210 ºC for 10 min.

The content of reaction products were determined by the internal standard method [19], where internal standard was 1-propanol. Also the amount of linalool, geraniol and nerol was determined from their calibration curves. The conversion degree of geraniol was calculated by the decreasing of its concentration in the final products. The calculations of conversion of geraniol, yield, selectivity of the products are described earlier [8].

RESULTS AND DISCUSSION

Physicochemical characteristics of BEA-type zeolite: Table-1 shows that the chemical compositions (*i.e*. molar ratio of SiO_2/Al_2O_3) of parent BEA zeolites with microporous structure and corresponding recrystallized (RBEA) zeolites with combined micro-mesoporous structure are nearly similar. The latter have a larger total pore volume and a larger proportion of mesopores with an average pore diameter (by BET) of about 3.5 and 3.9 nm for samples RBEA-25 and RBEA-150, respectively. The BEA-type microporous zeolites and their modified micro- mesoporous forms have similar acid properties and they differ in the characteristics of the porous structure.

The particle sizes distributions of parent (BEA-150) and ultrasound-irradiated catalysts (BEA-150 and RBEA-150) in geraniol as solvent are shown in Table-2. They were determined with Cumulant inversion algorithm in term of volume. Irradiation with ultrasound (350 W, 1.5 h, 40 ºC) in processor UMR-300B was carried out.

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF CATALYSTS USED IN GERANIOL CONVERSION [Ref. 8]

Catalyst	BEA-25	RBEA-25	BEA-150	RBEA-150
$n_{SiO_2}/n_{Al_2O_3}$	25.0	23.8	150.0	176.4
S_{BET} ($m^2 g^{-1}$)	558	721	539	822
Total pore volume (V) (cm^3/g)	0.486	0.625	0.588	0.792
$V_{micro}/V_{micro} + V_{meso}$	0.340	0.200	0.260	0.180
$V_{meso}/V_{micro} + V_{meso}$	0.662	0.800	0.743	0.824
Acidity ($a_0(NH_3)$, μmol/g):				
Total	1200	1179	180	233
Weak acid center	725	704	97	95
Strong acid center	475	475	83	138

TABLE-2
PARTICLE SIZE DISTRIBUTION IN SELECTED CATALYSTS

Catalysts	Average particle size (nm)	Cumulative volume (%)
BEA-150 (non-irradiated)	367	91
BEA-150	103	96
RBEA-150	240	90

Table-2 shows an almost homogeneous distribution of crystallites by their sizes and by the direct influence of ultrasound, the crystallites size decreased to the sizes of nanoparticles to 103 nm particularly for BEA-150.

Ultrasonic and conventional catalytic activity in geraniol conversion

Composition of reaction products: The qualitative composition of the products of geraniol conversion is almost the same in both for its purely catalytic and under combined ultrasonic irradiation/catalyst transformations (Fig. 1). Basically, reaction products of dehydration (terpene hydrocarbons are β-myrcene, *trans*-β-cimene, β-ocimene, pseudolimonene), isomerization (linalool and nerol) and carbon chain-extending (sesquiterpene alcohols: farnesol, (2*E*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrien-1-ol and (2*E*,6*E*)-6,11-dimethyl- 2,6,10-dodecatrien-1-ol.

Sonochemical transformation of geraniol and the effect of various solvents

Effect of ultrasonic and ultrasonic/microwave irradiations: Geraniol (0.0230-0.0461 mol) upon ultrasonic irradiation (argon atmosphere, run time 1.5 h, ultrasonic power 500-700 W, temperatures 40-100 ºC) and combination of ultrasonic and microwave irradiations (US 300 W/MW 550 W) was slightly converted up to 2 %, mainly to terpene hydrocarbons and also nerol with little yield was formed.

Effect of ultrasonic irradiation time and medium: With the increasing of the ultrasound power from 350 to 700 W and the irradiation time up to 1.5 h, the geraniol conversion degree increases imperceptibly. The ultrasound irradiation at 80 ºC, initiates oxidation processes with conversion degree of 2 %, a negligible amount of oxidation products were formed *viz.*, 2-isopropenyl-5-methylhex-4-enal ($C_{10}H_{18}O$), 4,8-dimethyl-3,7-nonadien-2-ol ($C_{11}H_{20}O$), oxacyclotetradeca-4,11-diyne. By increasing the irradiation time up to 10 h conversion of geraniol was 6.4 % at 80 ºC and synthesized the oxidation product α-citral with yield 1-2.5 % and terpene hydrocarbon β-myrcene. The reaction medium (argon, air) has practically no effect on the degree of conversion of geraniol when it is irradiated with ultrasound.

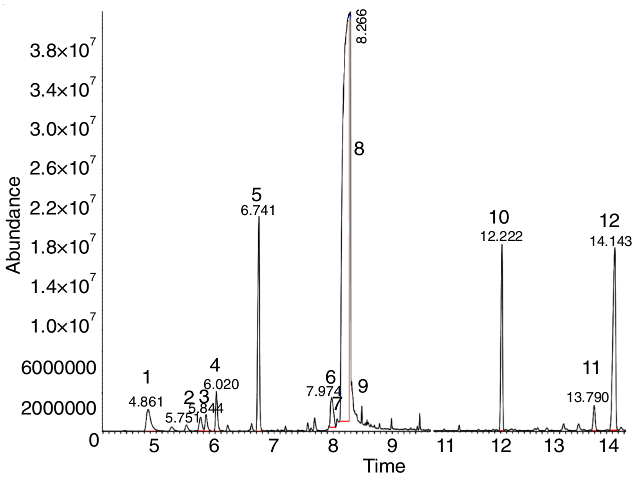


Fig. 1. TI chromatogram of catalytic conversion products of geraniol on micro-mesoporous zeolite R-BEA-25 ($m_{cat}/m_{geraniol}$=1/142, reaction carried out under simultaneous microwave and ultrasound irradiation (MW/US, 550 W/300 W, in a argon atmosphere at 80 °C, run time: 1.5 h): (1) β-myrcene, $C_{10}H_{16}$, (2) pseudo-limonene, $C_{10}H_{16}$, (3) *trans*-β-ocymene, $C_{10}H_{16}$, (4) β-ocymene, $C_{10}H_{16}$, (5) β-linalool, $C_{10}H_{18}O$, (6) nerol, $C_{10}H_{18}O$, (7) *cis*-isogeraniol, $C_{10}H_{18}O$, (8) *trans*-geraniol, $C_{10}H_{18}O$, (9) isopulegol, $C_{10}H_{18}O$, (10) *trans*,*trans*-farnesol, (2*E*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrien-1-ol, $C_{15}H_{26}O$, (11) succinic acid, di(neryl)ester, $C_{24}H_{38}O_4$, (12) (2*E*,6*E*)-6,11-dimethyl-2,6,10-dodecatrien-1-ol, $C_{14}H_{24}O$

Upon ultrasonic irradiation of geraniol itself, in contrast to the conversion of geraniol on BEA-type zeolite, the formation of any detectable quantities of sesquiterpene alcohols was not observed *viz.*, *trans,trans*-farnesol, ((2*E*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrien-1-ol) and (2*E*,6*E*)-6,11-dimethyl-2,6,10-dodecatrien-1-ol.

Effect of water and catalyst: The conversion of geraniol (8 mL, 0.046 mol) in the presence of water (2 mL, 0.11 mol) under the influence of ultrasound (300 W, 1.5 h, air and 71 ° C) showed a slight tendency to increase the conversion of geraniol and the yield of nerol to 4.5 % and 2 %, respectively.

The conversion of geraniol (0.046 mol) and the yield of linalool are increased respectively from 2 and 0.9 % to 10.4 and 7.0 % by the sonication (300W, 1.5 h, 71 ºC) in the presence of the microporous zeolite catalyst (BEA-25, 0.05 g) and water (0.11 mol).

Effect of DMF: There is no sonochemical transformation of geraniol at temperatures of 40 and 80 ºC, ultrasonic power 350 W, sonication time -1.5 h, in a dry solution of DMF and under argon atmosphere.

Effect of methanol: In methanol solution with molar ratio 1/38.7 in air under ultrasonic irradiation with power 200-900

TABLE-3
EFFECT OF METHANOL AND ZEOLITE CATALYST ON GERANIOL CONVERSION UNDER ULTRASONIC IRRADIATION

Entry	Content of reaction mixture (Molar ratio)	t,°C/medium/ US power, W/ Run time, h	Conversion of G, %	Yield/Selectivity (%)			
				β-Linalool	Nerol	Linalyl methyl ether	Neryl methyl ether
1*	4 mL G + 36 mL CH_3OH (0.023 /0.89)	25/Air/200-500-600-900/0.5-1.5	1-2	–	0.7	–	–
2	1.5 mL G + BEA-25 (0.17 mol/g cat)	27/N_2 or air/1.0	3.3	1.2/36.4	2.1/63.6	–	–
3	1.5 mL G + BEA-25 + 38.5 mL CH_3OH (0.17 mol/g cat/0.95)	30/Air/200/0.5	26.6	5.8/21.8	–	4.5/16.9	16.3/61.3
4	1.5 mL G + BEA-25 + 38.5 mL CH_3OH (0.17 mol/g cat/0.95)	30/Air/200/1.0	27.0	5.8/21.5	–	4.4/16.3	16.8/62.2
5	1.5 mL G + BEA-25 + 38.5 mL CH_3OH (0.17 mol/g cat/0.95)	40/Air/500/1.5	26.0	5.7/21.9	–	4.3/16.5	15.8/60.7

G-Geraniol; 1* - $C_{11}H_{18}O$, (3Z)-4,8-dimethylnona-3,7-dien-2-one, 0.5-0.9 %, α-citral and *cis*-iso-Geraniol, 0.4-0.4 %. In cases 2-5, a very small amount of terpene hydrocarbons ($C_{10}H_{16}$) was obtained.

W, geraniol converted slightly into the oxidation product (3*Z*)-4,8-dimethylnona-3,7-dien-2-one ($C_{11}H_{18}O$) and nerol. In argon atmosphere, the geraniol molecule is resistant to ultrasound.

Effect of methanol and catalyst: The system consists of catalyst, solvent and ultrasound, geraniol is actively converted to linalool and methyl ethers of linalool and nerol (Table-3, entries 3-5, Fig. 2). With the conversion of geraniol 27 %, the selectivity for esters was about 80 % and for linalool 21%.

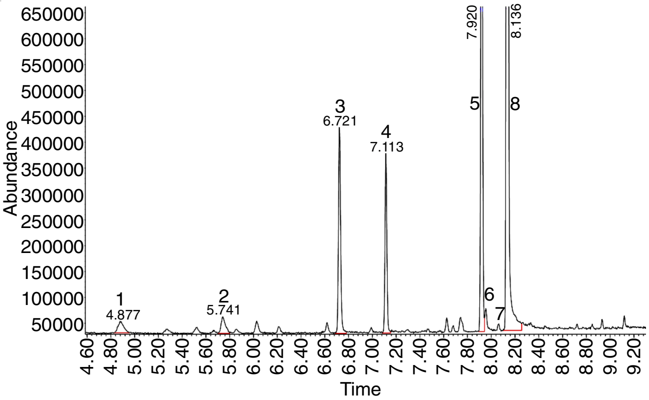


Fig. 2. TI Chromatogram of catalytic conversion products of geraniol on microporous zeolite BEA-25 ($m_{cat}/m_{geraniol}$ = 1/26.7, reaction carried out under ultrasound irradiation (US, 200 W, solvent – 38.5 mL methanol, medium–air, temperature 30 °C, run time–1 h). 1 – β-myrcene, $C_{10}H_{16}$, 2 – β-ocymene, $C_{10}H_{16}$, 3 – β-linalool, $C_{10}H_{18}O$, 4 – linalool, methyl ether, 5 – nerol, methyl ether, $C_{11}H_{20}O$, (2Z)-1-methoxy-3,7-dimethylocta-2,6-diene, 6 – nerol, $C_{10}H_{18}O$, 7 – *cis*-isogeraniol, $C_{10}H_{18}O$, 8– *trans*-geraniol, $C_{10}H_{18}O$

With the same quantity of BEA-25 (0.17 mol geraniol/g catalyst), the conversion of geraniol is small *i.e.* 3.3 % (Table- 3, entry 2) and increases nine times (entries 3-5) after the irradiation with ultrasonic.

Sonochemical conversion of geraniol on micro-and micro-mesoporous BEA-type zeolites

Effect of temperature under ultrasound irradiation: The conversion of geraniol was achived by using ultrasonic irradiation on micro- and micro-mesoporous beta-type zeolites at 40 ºC (Fig. 3). It is obvious from Fig. 3 that at 40 ºC, nerol is formed only on a microporous catalyst BEA-150 and the conversion of geraniol and yields of linalool and nerol on ultrasonic irradiated zeolite catalysts at 40 ºC were small, 4-10.5 and 1-2 %, respectively; mainly the dehydration reaction proceeds with the formation of terpene hydrocarbons of β-myrcene and *cis*-β-ocimene. Conventional catalytic activities of these zeolite catalysts were very small under the specified conditions.

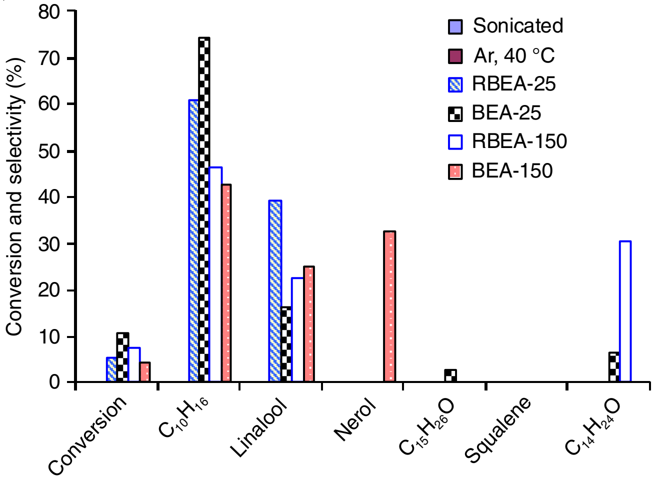


Fig. 3. Conversion of geraniol under US irradiation on microporous BEA-25, BEA-150 and micro-mesoporous RBEA-25, RBEA-150 zeolites, medium – Ar, catalyst loading –0.92 mol of geraniol/g catalyst. US power –350 W (UMR-300B), run time –1.5 h, temperature 40 °C

However, degree of conversion of geraniol on BEA-150 and RBEA-150 at 80 ºC by ultrasonic treated is significantly less than untreated samples (Fig. 4). The likely cause for this may be a negative effect of temperature increase on the energy of cavitation. It is a known existence of a temperature optimum of the cavitation intensity for a particular system [15,20,21].

By the conversion values of geraniol at 80 ºC (Figs. 4 and 5), the following relative series of activity are obtained:

(A) RBEA-25 (24.6 %) ≥ RBEA-150 (23.9 %) > BEA-25 (16.7 %) > BEA-150 (13.5 %), (conventional catalytic activity, run time: 1.5 h).

(B) RBEA-25 (42.0 %) > BEA-25 (28.4 %) > RBEA-150 (6.9 %) > BEA-150 (1.5 %), (ultrasonic activation, ultrasonic irradiation: 1.5 h).

Also conversion values for RBEA-25 was 49 %, (ultrasonic activation, ultrasonic irradiation: 5 h) and for RBEA-25 54.7 % (combined treated with microwave/ultrasonic 550 W/ 300 W, 1.5 h).

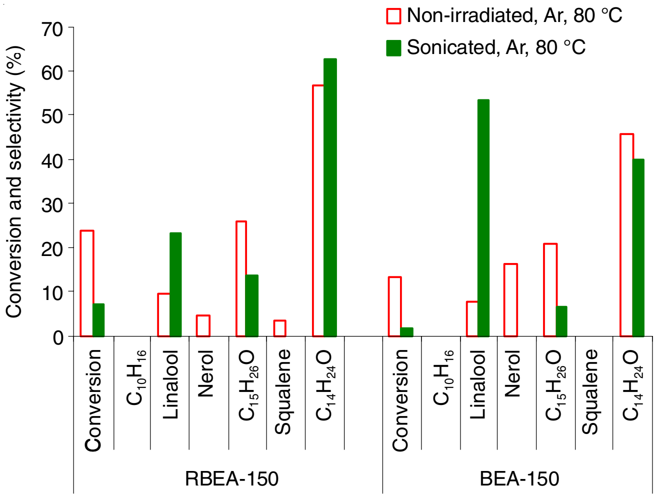


Fig. 4. Comparison of the conventional catalytic activity of zeolites (BEA-150 and RBEA-150) with activity in irradiated reaction of geraniol conversion; medium – US power –350 W (UMR-300B), Ar atmosphere, catalyst loading– 0.92 mol of geraniol/g catalyst, run time –1.5 h, temperature 80 °C

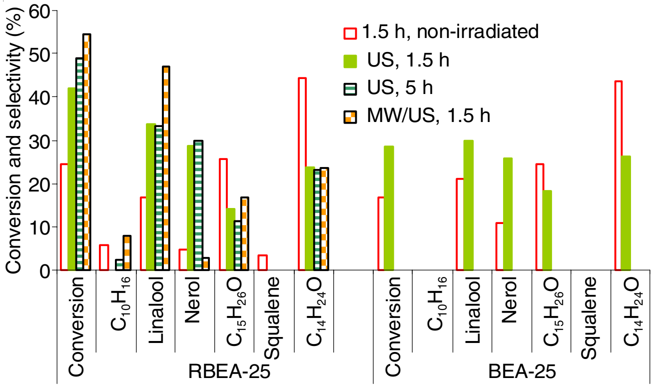


Fig. 5. Comparison of catalytic activities (at 80 °C, medium – Ar) of non-irradiated and irradiated with ultrasound zeolites (RBEA-25 and BEA-25) in reaction of geraniol conversion by • irradiation during 1.5 h, US power- 350 W, • irradiation during 5 h, • with combined US/MW irradiation during 1.5 h, US power - 300 W, MW power- 550 W

Under both conditions, the thermocatalytic conversion of geraniol and its ultrasonic activation on the investigated catalysts, the largest conversion of geraniol (42 % and 24.6 %, respectively) was on a micro-mesoporous catalyst RBEA-25 and the smallest on a microporous BEA-150 (13.5 and 1.5%, respectively). The first of them has the highest total acidity (1179 μmol/g) and a large pore surface (721 m^2/g) (Table-1).

The investigated zeolites easily dissolved in geraniol and after ultrasonic irradiation of geraniol/zeolite solution, a time-stable ultra-disperse systems of zeolite were formed. The sonication leads to an increase in the degree of dispersion of zeolite samples; for example, for BEA-150 and RBEA-150, grain sizes after sonication are reduced to 103 and 240 nm, respectively, whereas for non-irradiated BEA-150 sample they are 367 nm (Table-2). An established opinion in the literature that the cavitation can lead to a structural change in the catalytic centers of a solid and to change even the direction of the process [11].

Effect of ultrasonic and combined ultasonic/microwave irradiations on conversion and isomerization selectivity: On the most active catalysts RBEA-25 and BEA-25 in the case of irradiated reactions, selectivity of isomerization from conversion changes peculiarly; in particular with conversion growth the selectivity increases on micro-mesoporous catalysts (Fig. 6).

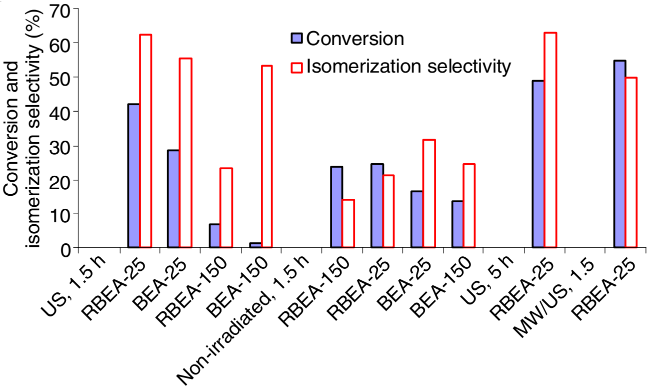


Fig. 6. Geraniol conversion under US (350 W, 1.5 and 5 h) and combined US/MW (300 W/550 W, 1.5 h) irradiation in the presence of micro- and micro- mesoporous beta-type zeolites. Effect of ultrasound irradiation time on degree of geraniol conversion and selectivity both to linalool and to nerol undividedly; reaction conditions: catalyst loading – 0.92 mol of geraniol/g catalyst, argon atmosphere, run time 1.5 h, 5.0 h, temperature 80 °C

As the irradiation time increases from 1.5 to 5 h on RBEA-25, the conversion of geraniol increases respectively from 42 to 49%, the isomerization selectivity almost does not change, ratio of selectivity of linalool to selectivity of nerol (L/N) was nearly same as 1.3 and 1.1, respectively (Figs. 6 and 7). At the simultaneous combined irradiation of geraniol by ultrasound and microwaves (US 300 W/MW 550 W) in case of RBEA-25, conversion increased to 54.7 % with isomerization selectivity up to 49.7 % with 47 % being the isomerization selectivity for linalool (Figs. 6 and 7).

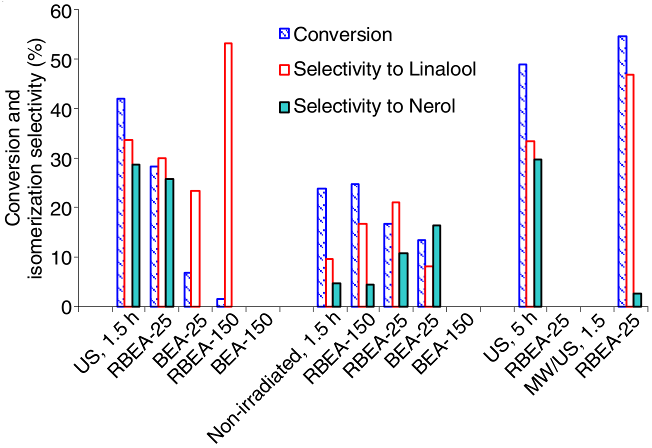


Fig. 7. Geraniol conversion under US (350 W) and combined US/MW (300 W/550 W) irradiations in the presence of micro- and micro-mesoporous beta-type zeolites. Effect of ultrasound irradiation time on degree of geraniol conversion and selectivity to linalool and to nerol; reaction conditions – catalyst loading –0.92 mol of geraniol/g catalyst, argon atmosphere, run time 1.5 h, 5.0 h, temperature 80 °C

In conventional catalytic conversion of geraniol on zeolites investigated at 80 ºC, the ratio L/N decreases from micro-mesoporous catalysts to the corresponding microporous samples;

upon the ultrasound irradiation of geraniol on zeolite catalysts there is a large tendency of growth of nerol selectivity; in particular, at a contact time of 1.5 h for non-irradiated reaction for RBEA-25 ratio L/N was 3.7 at conversion 24.6 % and selectivity for nerol 4.5 % at 80 °C. Under the same conditions by the sonicated reaction for this catalyst, the ratio L/N was less, equal 1.3, conversion 42 % and selectivity to nerol 28.8 %. By microwave/ultrasonce irradiation on RBEA-25 the ratio L/N was very large, equal to 17.4, however, accordingly the selectivity for nerol was less, equal to 2.7 and for linalool 47 %. Thus in this case there is regioselectivity by linalool (Figs. 7 and 8).

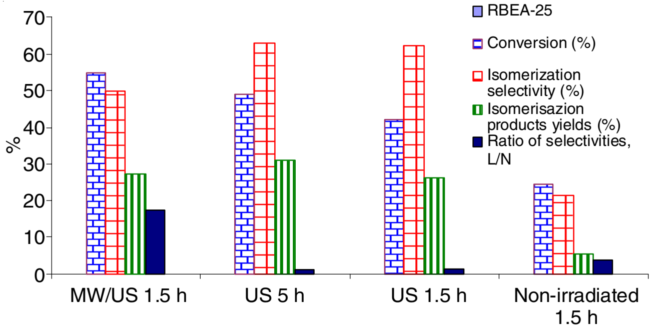


Fig. 8. Comparison of activities of different combined systems with micro-mesoporous zeolite RBEA-25 in the conversion of geraniol. Reaction conditions: catalyst loading – 0.92 mol of geraniol/g catalyst, argon atmosphere, run time –1.5 h, 5.0 h, temperature – 80 °C, US (350 W), US/MW (300 W/550 W)

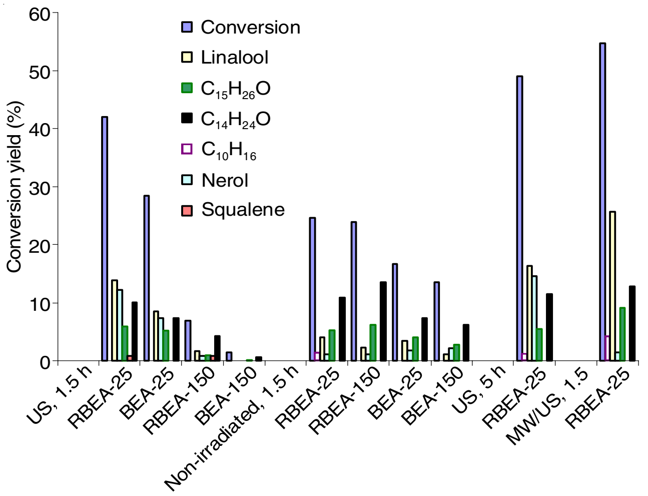


Fig. 9. Comparison of geraniol conversions and yields of products in reactions on beta-type zeolite catalysts. Reaction conditions: ultrasonic irradiation (350 W, 1.5 h; 5 h), without it (non-irradiated, 1.5 h) and simultaneous MW/US (550 W/300 W, 1.5 h) irradiation; catalyst loading – 0.92 mol of geraniol/g catalyst, argon atmosphere, run time –1.5 h, 5.0 h, temperature – 80 °C

Effect of ultrasonic and hybrid ultrasonic/microwave irradiations on yields of products of geraniol conversion: In case of irradiated reactions, the yields of linalool and nerol increased along with the conversion (Fig. 9). Yields of isomerization reaction products (linalool and nerol), under ultrasonic activation were higher on zeolites studied with a higher total acidity on RBEA-25 and BEA-25, 26 and 15.8 %, respectively, which is almost 3-5 times greater than in non-irradiated reaction. In case of RBEA-150 and BEA-150 yields of linalool and nerol were insignificant: 1.6 and 0.8 %. Under the same conditions, in non-irradiated reaction on RBEA-25 and BEA-25 yields of linalool and nerol were smaller: 5.2-5.3 %. On RBEA-25 and BEA-25 in non-irradiated and irradiated reactions yields of sesquiterpene alcohols ($C_{14}H_{24}O$ and $C_{15}H_{26}O$) were almost identical, 17 and 12 %, respectively.

With an increase in irradiation time from 1.5 to 5 h, the yields of linalool and nerol on RBEA-25 increased to 31 %, mainly due to the formation of linalool. By ultrasonic/microwave irradiation on RBEA-25 the yields of isomerization products increased to 27.2 % and of sesquiterpene alcohols ($C_{14}H_{24}O$ and $C_{15}H_{26}O$) to 21.9 % (Fig. 9).

Conclusion

The geraniol conversion reaction was initiated by the simultaneous action of micro- and micro-mesoporous beta-type zeolites and US irradiation with a power of 200-900 W and a ultasonic frequency of 25 kHz (UMR-300B hybrid reactor, Shinka, Japan) and in the ultrasonic reactor SRF-1(Shinka) with a US power of 100 W and a different frequency (20, 40, 60 kHz). Upon ultrasonic irradiation (100-900 W, 27-100 °C) geraniol was slightly converted up to 2 %, mainly in terpene hydrocarbons and also in nerol with little yield. The irradiation atmosphere (argon, nitrogen, air) does not affect the conversion degree of geraniol. In argon atmosphere and in DMF and methanol solutions, geraniol is resistant to ultrasound. Due to synergy of action in the system: zeolite catalyst BEA-25, solvent CH_3OH and ultrasound irradiation (200 W, 0.5 h, air, 30 °C), geraniol is actively converted (27 %) to linalool and linalyl and finally to neryl methyl ethers with the yields of 6 and 21 %, respectively at 30 °C. In the conversion of geraniol (0.9220 mol of geraniol/g catalyst) on the zeolite catalyst BEA-25 by presence of water and by sonication (300W, 1.5 h, air, 71 °C), the conversion and yield of linalool reached up to 10.4 and 7.0 %, respectively. The synergism between the action of ultrasonic irradiation (US power 350 W, 1.5 h, Ar, 80 °C) and BEA-type zeolite catalyst RBEA-25, caused to obtain increased yields up to 31 % and selectivity for linalool and nerol up to 63.2 % at conversion of 49 % in the isomerization of geraniol; while the yields of sesquiterpene alcohols $C_{14}H_{24}O$ and $C_{15}H_{26}O$ remain at the level of the non-irradiated reaction (about 15 %).

In comparison with non-irradiated reaction on RBEA-25, the combined action of ultrasound and zeolite, also increased selectivity towards nerol from 4.5 to 30 %. Due to the synergic effect between catalyst RBEA-25 and ultasonic/microwave (US 300 W MW 550 W/, 1.5 h, Ar, 80 °C), conversion to 54.7 %, yields of linalool and nerol to 27.2 and sesquiterpene alcohols to 21.9 % were increased; at the same time, the selectivity ratio linalool/nerol (L/N) increased to 17.4 and the regioselectivity for linalool is manifested. The combination of ultasonic irradiation separately with RBEA-150 and BEA-150 catalysts gives an inhibitory effect *i.e.* a decrease in the conversion and yields of reaction products, a strong increase in the L/N ratio. Under ultasonic irradiation on samples of micro- and micro-mesoporous zeolites of BEA-type with a higher acidity and a pore surface, activation of catalytic properties (conversion, selectivity, yields) in isomerization of geraniol is observed; on samples of the same catalysts with low acidity and pore surface, there is in the same reaction inhibition of the catalytic properties of the zeolite.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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