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Catalytic Conversions of Linalool and Linalyl Acetate over Large-Pore Zeolites and Mesoporous MCM-41

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Abstract—The dehydration, condensation, and isomerization of linalool and linalyl acetate occur over the H- and dealuminated forms of zeolites FAU(Y), BEA, MOR, and OFF and mesoporous aluminosilicate MCM-41 at 373–453 K. The yields of linalool isomerization to geraniol and α- and β-terpineols are low. The use of linalyl acetate enhances isomerization; the highest yields of the products of linalyl acetate rearrangement (geranyl acetate and terpinyl acetate) are achieved over DeAlBEA(277). Dehydration produces various $C_{10}H_{16}$ terpenic hydrocarbon isomers.

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INTRODUCTION

Primary terpenic alcohols—geraniol (3,7-dimethyl-*trans*-2,6-octadien-1-ol) and nerol (3,7-dimethyl-*cis*-2,6-octadien-1-ol)—are valuable fragrant compounds. They are used in perfumery, soap fragrances, and synthetic detergents; they are also used for preparing geranyl acetate and other fragrant esters, intermediates for organic synthesis [1], citronellol, and citral [2]. Geraniol now accounts for 10% (10000 t/a) in the world-wide production of fragrances [3].

Hydrolysis, followed by fractional distillation, is used to isolate geraniol and nerol, which are contained as esters in palmarosa oil (70–89%), geranic oil, and citronella oil (30%) [3]. Full-scale processes for geraniol and nerol production include multistage synthesis from isoprene [1] and β-pinene [4], as well as the homogeneous isomerization of linalool (a tertiary terpenic alcohol, 3,7-dimethyl-1,6-octadien-3-ol) or its acetate or borate esters [5–13]. Linalool is prepared from renewable natural sources: coriander oil (containing up to 80% linalool) [14] or α-pinene, which is isolated from turpentine (a woodworking product) [15].

Allyl rearrangement to isomerize linalool to geraniol and nerol is carried out in the presence of acids (H_2SO_4, H_3PO_4, or CH_3COOH mixed with acetic anhydride) [5, 6] or gaseous HCl and HBr [7] (process temperatures are 25–135°C; geraniol and nerol yields are 40–55%)), or in the presence of oxometallic derivatives (esters) and ammonium salts of some transition-metal (V, Mo, W, Re, or Nb) acids [8–10], especially orthovanadates, in particular ammonium metavanadate [9]. Alkyl orthovanadates $(RO)_3V{=}O$ [8] are also used in the pure form or mixed with tetrabutylammonium hydroxide [15, 16]. These catalysts increase the linalool conversion and the selectivity of formation of primary alcohols (geraniol and nerol). For example, over triisobutyl orthovanadate (200°C, N_2, 3 h), the yields increase up to 42 and 96%, respectively [10]; over the catalysts claimed in [15, 16], the respective yields are up to 40 and 95–99% (140–220°C). Weaknesses of the state-of-the-art catalysts for linalool isomerization are their environmental hazard, difficult separation from reaction products, nonrenewability, and complexity of preparation.

This work studies the conversions of linalool and linalyl acetate intended to isomerize them over heterogeneous catalysts (zeolite and mesoporous molecular sieves); these catalysts have acidic properties but have no drawbacks intrinsic to the aforementioned homogeneous catalysts of linalool isomerization. The use of micro- and mesoporous molecular sieves in the isomerization of linalool to geraniol and nerol has not been documented in the scientific or patent literature [14].

EXPERIMENTAL

Catalysts. Catalysts were prepared from the following large-porous zeolites and mesoporous MCM-41 aluminosilicate (AS) (Table 1): NH_4BEA (Si/Al = 42) and NaMOR (Si/Al = 5) (from Zeolyst). NaFAU(Y) (Si/Al = 1.95) and colloidal TMA-OFF (Si/Al = 3) were synthesized from natural clinoptilolite (the Khekordzula deposit, Georgia) as described previously [17]. Scanning electron microscopy (magnification 10000) showed that colloidal TMA-offretite had submicron crystallites with one dimension equal to 100 nm.

Aluminum-containing MCM(Al)-41 (Si/Al = 42.5) and siliceous MCM(Si)-41 mesoporous materials were prepared by the hydrothermal treatment at 373 K for 24 h of aluminosilicate and silicate hydrogels, respectively, in the presence of cetyltrimethylammonium bro-

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Table 1. Physical–chemical parameters of the test catalysts

Catalyst	Si/Al, mol/mol	S_{BET}, m^2/g	V, cm^3/g	V_{micro}/V	Unit cell composition
NaFAU(Y)	1.95	–	–	–	$Na_{43.94} \cdot Ca_{2.59} \cdot Al_{66.37} \cdot Si_{129.76} \cdot O_{384} \cdot 196.49H_2O$
HFAU(Y)	1.95				
NH$_4$BEA	42.0	557	0.678	0.228	$(NH_4)_{1.44} \cdot Na_{0.06} \cdot Al_{1.48} \cdot Si_{62.5} \cdot O_{128} \cdot 28H_2O$
DeAlBEA	277.0	565	0.335	0.510	$H_{0.23} \cdot Al_{0.23} \cdot Si_{63.77} \cdot O_{128} \cdot 9H_2O$
NaMOR	5.0	–	–	–	–
DeAlMOR	97.0	–	–	–	–
TMA-OFF	3.0	–	–	–	$0.48K_2O \cdot 0.33Na_2O \cdot 0.16(TMA)_2O \cdot 0.15CaO \cdot 0.09MgO \cdot Al_2O_3 \cdot 5.94SiO_2 \cdot 3.91H_2O$
HOFF	3.0	–	–	–	–
MCM(Al)-41	42.5	1048	1.000	–	$0.04Na_2O \cdot 0.96H_2O \cdot Al_2O_3 \cdot 85SiO_2 \cdot 30H_2O$
MCM(Si)-41*	–	1222	–	–	$SiO_2 \cdot 0.07H_2O$
MCM(Al)-41**	25.0	–	–	–	–
HMCM(Al)-41***	25.0	–	–	–	–

Notes: * Pore size of 2.5 nm.
** Pore size of 2.8 nm.
*** Crystallite size of 100 nm.

mide [18]. The TMA forms were precalcined at 813 K for 3 h in an inert gas flow, then in air. Aluminum-containing mesoporous MCM(Al)-41 (Si/Al = 25) with the pore diameter equal to 2.8 nm was prepared at 373 K from deeply acid-leached clinoptilolite (from the Khekordzula deposit) in the presence of a decyltrimethylammonium bromide template. The tested acidic H-forms of large-porous FAU(Y), OFF, and BEA and mesoporous MCM(Al)-41 were prepared through their ammonium species by decomposing them in a dry air flow at 773 K.

This work also studies deeply dealuminated large-porous zeolites DeAlBEA (Si/Al = 277) and DeAlMOR (Si/Al = 97). High-silicon DeAlBEA and DeAlMOR were prepared by boiling the starting H-forms with 2 M oxalic acid. The total acidities as determined by the TPD-NH$_3$ method were 378 and 365 μmol/g for HBEA and DeAlBEA, respectively.

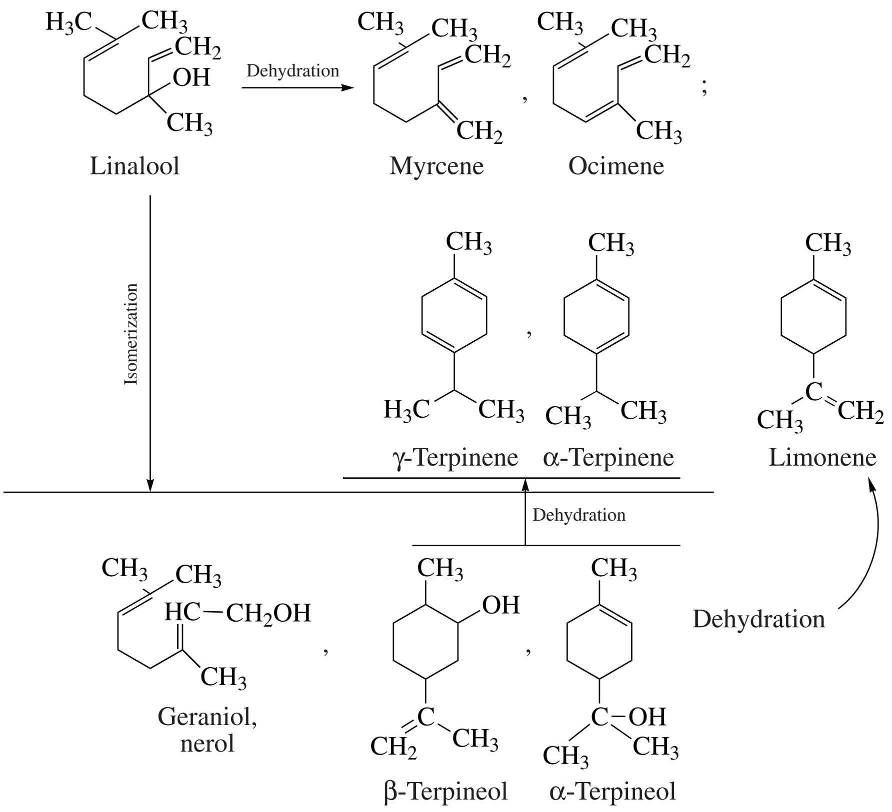
Catalytic experiments and product analysis. The catalytic conversion of linalool and linalyl acetate was carried out at 373–453 K using 0.1–0.3 g of the catalysts and 3 mL of the substrate in a batch mode either in a four-necked flask (equipped with a refluxer, a magnetic stirrer, a thermometer, and a knee for the admission of the reagent and inert gases (Ar or He)) or in a specially designed titanium autoclave of a small capacity (20 mL).

The reaction products were separated from the catalysts by centrifuging. They were identified by chromatography/mass spectrometry on a VG 7070 instrument (a quartz capillary column (25 m × 0.2 mm) packed with SE-30). The liquid reaction products were analyzed on an LKhM-8MD model 2 chromatograph equipped with a catharometer installed on a steel column (5 m × 3 mm) packed with 20% Tween-85 on acid-washed Chromaton-N-AW. The analysis parameters were as follows: carrier gas, helium; carrier-gas rate, 40 mL/min; and evaporator temperature, 443 K. Analysis was carried out in a programmed mode: first, temperature was increased from 323 to 413 K at 8 K/min; then, it was maintained at 413 K for 20 min. Chromatographic peaks were identified by the retention time of individual components. The products appeared in the following order: α-pinene, camphene, myrcene, α-terpinene, limonene, ocimene, γ-terpinene, linalool, camphor, linalyl acetate, β-terpineol, α-terpineol, terpinyl acetate, nerol, geraniol, and geranyl acetate. Quantitative chromatographic analysis was performed by the standard additions techniques [19, 20]. The standard used was the starting compound (linalool or linalyl acetate). Product yields (B) were derived from the concentrations of reaction products (C_i). The concentration of chromatographically undetectable condensation products (C) was derived from

$$C = 100 - \sum C_i.$$

The reagent conversion (Y, wt %) and product selectivity (S, %) were, respectively, calculated from

$$Y = Q_1 - Q_2/Q_1 \times 100\%,$$

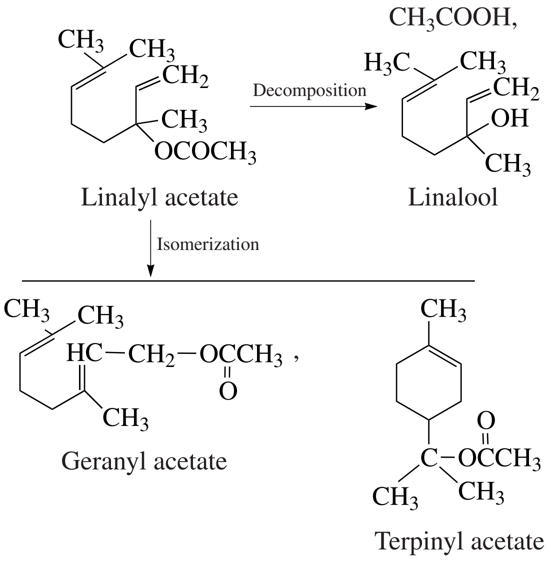


Scheme 1.

$$S = B \times 100\%/Y,$$

where Q_1 and Q_2 were peak areas due to the reagent (linalool or linalyl acetate), obtained under identical conditions during calibration and product analysis.

Chemicals. Racemic linalool and linalyl acetate (from Aldrich, 97–98%) was used. In some cases, d-linalool isolated by the fractional distillation of coriander oil (T = 50–60°C, p = 3 mm, 88.1% linalool) was used.



Scheme 2.

RESULTS AND DISCUSSION

The composition of the conversion products of linalool and linalyl acetate over the tested acidic forms of zeolites and MCM-41 (Tables 2, 3) implies that we are dealing with multipath processes; the main paths are presented by Schemes 1 and 2. The conversion products of linalool and linalyl acetate over the tested zeolites and MCM(Al)-41 are yellowing liquids with a characteristic smell.

Linalool conversion. Linalool over the tested zeolites and MCM-41 is mainly dehydrated and cyclized to form acyclic and monocyclic terpenic hydrocarbons (HCs), namely, myrcene, ocimene, α- and γ-terpinenes, and limonene, with total yields of 18–81% and conversions equal to 21–100%. Linalool also forms condensation products with the lowest yields at 380 K over DeAlMOR and the highest yields at 413 K over MCM(Al)-41, these yields being equal to 4 and 36%, respectively (Table 2).

The data contained in Table 2 show that the degree of linalool isomerization to geraniol is insignificant: geraniol yields over zeolites HFAU(Y), HBEA, and DeAlMOR are as low as 1–3%. The selectivity of

Table 2. Catalytic activity of zeolites and MCM-41 in linalool conversion (substrate volume, 3 mL; reaction duration, 2 h)

Catalyst (Si/Al, mol/mol)	MCM(Si)-41	HMCM(Al)-41 (25)*•	MCM(Al)-41 (42.5)**	HFAU(Y) (1.95)*•	HBEA(42)		DeAlBEA(277)	HOFF(3.0)		DeAlMOR(97)	
T (K), medium	413, Ar	413, He	413, air	413, He	380, Ar	413, Ar	413, Ar	373, air	413, air	380, Ar	413, Ar
Catalyst weight, g	0.1–0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.10	0.13	0.2	0.2
Conversion, %	0.0	79.8	100	48.6	89.6	100	44.8	85.7	100	42.7	81.1
Selectivity, %											
α-Pinene	–	12.1	17.3	1.4	2.8	4.4	12.9	–	–	3.5	19.9
Camphene	–	–	1.5	–	–	1.2	–	–	–	–	–
Myrcene	–	–	22.0	–	15.6	15.6	11.2	3.1	10.0	–	–
α-Terpinene	–	3.0	–	11.9	–	–	–	–	31.6	27.4	18.9
Limonene	–	–	7.7	–	54.2	43.7	28.8	58.7	20.0	44.7	14.2
Ocimene	–	20.6	12.8	48.6	1.1	13.8	–	3.2	12.5	Trace	Trace
γ-Terpinene	–	23.8	1.0	Trace	–	7.6	–	Trace	5.0	Trace	Trace
Unidentified	–	–	1.9	–	–	2.0	–	–	–	–	–
Camphor	–	12.8	–	9.3	1.8	Trace	–	–	–	–	3.8
β-Terpineol	–	Trace	–	0.6	–	–	–	5.1	–	Trace	4.3
α-Terpineol	–	9.2	–	0.8	6.3	2.8	6.3	7.0	–	7.9	8.2
Nerol	–	Trace	–	Trace	–	–	–	–	–	–	–
Geraniol	–	Trace	–	2.5	1.8	–	–	–	–	6.9	3.1
Condensation products	–	18.5	35.8	24.9	16.4	8.9	40.8	22.9	20.9	9.6	27.6
Total HC selectivity	–	47.5	43.5	60.5	70.9	80.7	40.0	65.0	79.1	72.1	33.1
HC yield, %	–	37.8	43.5	29.4	63.5	80.7	17.9	55.8	79.1	30.8	26.8

• Linalool (88.1%).

* Runs carried out in a flask, otherwise in an autoclave. HC stands for myrcene, ocimene, α- and γ-terpinenes, and limonene.

** Obtained by calcining of the TMA form at 813 K.

Table 3. Catalytic activity of zeolites and MCM-41 in linalyl acetate conversion (substrate volume, 3 mL; reaction duration, 2 h)

Catalyst (Si/Al, mol/mol)	MCM(Si)-41		HMCM(Al)-41(25)*	HFAU(Y)(1.95)*		DeAlBEA(277)			OFF(3.0)**	HOFF(3.0)	
T (K), medium	413, air	453, Ar•	413, He	380, CO_2	413, He	413, air	413, air	453, Ar•	373, air	373, air	413, air
Catalyst weight, g	0.20	0.20	0.20	0.20	0.20	0.13	0.20	0.10	0.10	0.10	0.10
Conversion, %	100	100	90.2	34.9	55.7	44.1	96.4	100	21.2	89.9	94.7
Selectivity, %											
α-Pinene	–	–	0.8	–	–	–	–	–	–	–	–
Myrcene	5.6	–	–	13.8	8.8	9.1	7.2	12.9	4.7	9.7	11.4
α-Terpinene	29.6	6.7	8.3	–	–	–	–	–	12.3	44.3	50.3
Limonene	–	18.1	–	36.4	28.9	30.6	25.5	16.7	–	–	9.1
Ocimene	3.7	2.9	25.0	–	–	3.6	1.6	3.3	–	–	8.1
γ-Terpinene	1.9	6.7	2.9	–	–	–	–	–	Trace	Trace	5.4
Linalool	–	–	0.2	–	–	Trace	Trace	Trace	–	–	–
Terpinyl acetate	–	2.4	11.6	2.3	7.9	14.3	11.3	–	–	Trace	Trace
Geranyl acetate	–	13.7	21.3	12.6	21.8	39.5	34.3	–	4.7	22.0	Trace
Condensation products	59.2	49.5	29.9	34.9	32.6	2.9	20.1	67.1	78.3	24.0	15.7
Total HC selectivity	40.8	34.4	37.0	50.2	37.7	43.3	34.3	32.9	17.0	54.0	84.3
HC yield, %	40.8	34.4	33.3	17.5	21.0	19.1	33.1	32.9	3.6	48.5	79.8

• Run duration, 0.5 h; the other notations as in Table 2.

isomerization to α- and β-terpineols is also insignificant. Their yields are 1–10%, including HMCM(Al)-41 (Si/Al = 25), unlike over the MCM(Al)-41 sample (Si/Al = 42.5): over MCM(Al)-41, which bears less acidic sites, isomerization either to geraniol or α- and β-terpineols does not occur. A linalool molecule is large (9 × ~5.8 Å); during its conversion over zeolites and MCM(Al)-41, the intracrystallite space should be accessible only in mesoporous MCM-41 due to its large pore sizes (2.8 nm). Indeed, linalool conversion at 413 K over MCM(Al)-41 and HMCM(Al)-41 occurs with high extents (100 and 80%, respectively).

In the presence of MCM(Si)-41 (a catalyst with very weak acidic sites), linalool is not converted under the same conditions, indicating a need for the involvement of stronger acidic sites in this process; another indication is that the reaction does not occur over DeAlBEA pretreated with aqueous KOH.

Over zeolite catalysts with window sizes (MOR and BEA) or pore sizes (FAU(Y)) ranging from 6.5 to 7.7 Å [21], linalool conversion also proceeds with high extents (43–100%). Presumably, linalool conversion occurs at the acidic sites of the outer grain surfaces; however, the involvement of the reactive sites and intracrystallite space of zeolites cannot be ruled out with the provision that the orientation of linalool molecules favors the interaction of their OH groups with the reactive sites of the zeolite. The same is indicated by the different linalool-dehydration selectivities over different zeolite types studied. In particular, the highest ocimene selectivity (48.6%) is achieved over HFAU(Y) and the highest limonene selectivity is over DeAlMOR, HBEA, and HOFF (44.7, 54.2, and 58.7%, respectively).

In the progress of BEA dealumination, i.e., as the Si/Al ratio increases from 42 to 277 or as the BEA acidity decreases with changing strength of acidic sites [22], the dehydration–cyclization yield (hydrocarbon yield) decreases from 80.7 to 17.9%. The linalool conversion decreases in association from 100 to 44%, while the isomerization selectivity (to α-terpineol, β-terpineol, geraniol) does not change significantly (Table 2).

Over HMCM(Al)-41, HFAU(Y), and DeAlMOR, camphor ($C_{10}H_{16}O$, a terpenic ketone) is also formed, with the highest yield over HMCM(Al)-41 being equal to 10.2% (Table 2).

Linalyl acetate conversion. The catalytic properties of zeolites and MCM-41 in linalyl acetate conversion were studied in order to avoid dehydration and to obtain geranyl acetate as the isomerization product. The OH group in linalyl acetate is shielded, unlike in linalool. The data in Tables 2 and 3 demonstrate that, under commensurable conditions, the degrees of conversion and the condensation yields for linalyl acetate conversion are higher than for linalool conversion, with the dehydration and cyclization selectivity being decreased almost over all types of catalysts studied. The isomerization selectivity for terpinyl acetates and geranyl acetates over these catalysts is higher during linalyl acetate conversion than the selectivity of linalool isomerization to geraniol, nerol, and α- and β-terpineols; at 373–380 and 413 K, the selectivity for terpinyl acetates and geranyl acetates is, respectively, 2.3–14.3 and 4.7–39.5% (Table 3). The highest geranyl acetate yield is over DeAlBEA and colloidal HOFF. The geranyl acetate yield is 17.4–33.1% over DeAlBEA at 413 K and 19.8% over HOFF at 373 K (Table 3).

The finding of terpenic hydrocarbons (myrcene, ocimene, α- and γ-terpinenes, and limonene) in the conversion products of linalyl acetate shows that linalyl acetate over the tested zeolites and MCM-41 partially decomposes to linalool and acetic acid. Recall that, in the presence of MCM(Si)-41 at 413 K, linalool is not converted, while linalyl acetate fully decomposes to terpenic hydrocarbons and condensation products (Table 3). Therefore, we can suggest that acetic acid has a promoting effect on linalyl acetate conversion over zeolites and MCM-41.

Over colloidal HOFF at 373 and 413 K, a high selectivity for α-terpinene is observed, equal to 44.3 and 50.3% for conversions equal to 90 and 95%, respectively (Table 3).

CONCLUSIONS

We can conclude that, in a liquid phase at 373–453 K over acidic and dealuminized zeolites (FAU(Y), BEA, OFF, and MOR) and over mesoporous AS MCM-41, linalool isomerizes to geraniol and α- and β-terpineols in low yields equal to 1–3 and 1–10%, respectively. Linalyl acetate, an acetylated linalool derivative, makes it possible to avoid some side reactions. Over the same catalysts, linalyl acetate isomerizes to a greater degree, yielding geranyl and terpinyl acetates with the highest yields at 413 K. These yields over DeAlBEA are equal to 33.1 and 10.9%, respectively.

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