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H- and Fe-modified zeolite beta catalysts for preparation of *trans*-carveol from α -pinene oxide

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ABSTRACT

The isomerisation of α -pinene oxide has been intensively investigated for selective preparation of campholenic aldehyde, a compound used in the synthesis of fragrances. Selective preparation of another product of α -pinene oxide rearrangement, *trans*-carveol, still remains a challenging task. *Trans*-carveol is a highly valuable compound used in perfume bases, food flavour compositions and as an active pharmaceutical substance in chemoprevention of mammary carcinogenesis.

In the present work zeolite beta with different SiO_2/Al_2O_3 molar ratios was modified by iron, characterised and tested per se and in the modified form for *trans*-carveol preparation from α -pinene oxide. The isomerisation reaction was carried out in a polar basic solvent *N*,*N*-dimethylacetamide at 140 °C. The activities and selectivities of the catalysts were correlated with their acid properties and with the iron content.

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1. Introduction

Terpenes are a valuable natural resource for the production of fine chemicals. Turpentine, obtained from biomass and also as a side product of softwood industry, is rich in monoterpenes such as α -pinene and β -pinene, which are widely used as raw materials in the synthesis of flavour, fragrance and pharmaceutical compounds [1]. The rearrangement of their epoxides has been thoroughly studied in the recent years, as a method to obtain compounds which are further used in the fine chemical industry. The industrially most desired products of α -pinene oxide isomerisation are campholenic aldehyde and *trans*-carveol (Fig. 1) because they are highly valuable ingredients for the fragrances production. Campholenic aldehyde is an intermediate for the manufacture of sandalwood fragrances such as santalol. Trans-carveol is an expensive constituent of the Valencia orange essence oil used in perfume bases and food flavour composition. Furthermore it has been found to exhibit chemoprevention of mammary carcinogenesis [2,3]. Preparation of campholenic aldehyde has been intensively investigated throughout the years [4–9]. On the contrary few publications were focused on the preparation of trans-carveol.

The α -pinene oxide isomerisation can be homogeneously catalyzed by Lewis acids—ZnBr₂, ZnCl₂. A conventional process based on zinc bromide affords the selectivity to campholenic aldehyde of 85% [4–6]. Preparation of campholenic aldehyde is also possible using heterogeneous catalysts based on various metals—Fe, Ti. Several articles have been published focusing on the influence of Lewis and Brønsted acid sites of heterogeneous catalysts in this reaction [7,9]. The selectivity of about 78% to campholenic aldehyde has been achieved using strongly dealuminated H-US-Y zeolite at 0 °C in toluene [7]. Zeolite titanium Beta is found to be an effective catalyst for rearrangement of α -pinene oxide to campholenic aldehyde hyde, giving selectivities up to 89% [8]. The highest selectivity to campholenic aldehyde over iron modified catalysts was achieved using Fe-Y-12 being 68% at 78% conversion level [9].

Few heterogeneous catalysts were also studied for the selective preparation of *trans*-carveol. The selectivity to *trans*-carveol 73% at 98% conversion was achieved using cerium and tin supported catalysts in polar basic solvent, *N*,*N*-dimethylacetamide [10]. As reported, due to the leaching problems with Sn/SiO₂ and Ce/SiO₂ catalysts, the synthesis of *trans*-carveol was performed under homogeneous conditions using CeCl₃ or SnCl₂ [10]. Selectivity to *trans*-carveol of around 90% was obtained in *N*,*N*-dimethylformamide using silica supported hetero polyacids, however, this reaction was also performed under homogeneous conditions because of high solubility of phosphotungstic acids in polar solvents [11]. *Trans*-carveol was obtained in 45% yield using molecularly imprinted polymers as a protic catalyst with *N*,*N*dimethylformamide as a solvent [12]. High selectivity to the desired alcohol was achieved over ceria supported on Si-MCM-41 using

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Fig. 1. Reaction scheme of α -pinene oxide **1** isomerisation to *trans*-carveol **4** and 2-methyl-5-(propan-2-ylidene) cyclohex-2-enol **5** and *p*-cymene **6** (product of subsequent dehydration), to isopinocamphone **2** and pinocarveol **3** and to campholenic **7** and fencholenic **8** aldehydes.

N-methylpyrrolidone as a solvent being 46% at total conversion of α -pinene oxide [13].

The aim of the current work was selective synthesis of *trans*carveol over heterogeneous beta zeolites with different silica to alumina ratio in proton and iron modified forms.

2. Experimental

2.1. Catalyst synthesis and characterisation

The proton forms of zeolites with different silica to alumina ratio were supplied by Zeolyst International. The evaporation impregnation method using aqueous solutions of ferric nitrate was used for preparation of the catalysts: Fe-Beta-25, Fe-Beta-150 and Fe-Beta-300. The number in the catalyst code indicates the SiO_2/Al_2O_3 molar ratio in the zeolite structure. Water solutions of ferric nitrate were used for preparation of Fe modified beta zeolite catalysts. The mixtures were stirred for 24 h at 60 °C. The other steps of synthesis were evaporation, drying at 100 °C overnight and calcination at 450 °C for 4 h.

The characterisation of catalysts was carried out using scanning electron microscopy, energy dispersive X-ray microanalysis, nitrogen adsorption and FTIR spectroscopy using pyridine as a probe molecule.

The scanning electron microscope (Zeiss Leo Gemini 1530) was used for determining the crystal morphology of the proton forms and Fe-modified zeolites.

The surface area was determined by nitrogen adsorption using Carlo Erba Sorptomatic 1900 instrument. The samples were outgassed at 150 °C for 3 h. Dubinin's equation was used to calculate the surface areas. The pore size distribution was obtained from Barrett–Joiner–Halenda correlation.

The acidity of prepared catalysts was measured by infrared spectroscopy (ATI Mattson FTIR) using pyridine (\geq 99.5%, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The samples were pressed into thin self-supported wafers (10–25 mg). The pellets were pretreated at 450 °C for 1 h prior to the measurements. Pyridine was first adsorbed for 30 min at 100 °C and then desorbed by evacuation at different temperatures (250, 350, and 450 °C) to obtain distribution of acid sites strengths. All spectra were recorded at 100 °C with

Table 1

Iron loading determined by energy dispersive X-ray microanalysis.

Catalyst	Fe (wt%)		
	Nominal loading	SEM-EDXA	
Fe-Beta-25	5	4.1	
Fe-Beta-150	3	3.1	
Fe-Beta-300	2	1.1	

a spectral resolution equal to 2 cm^{-1} . Spectral bands at 1545 and 1450 cm⁻¹, were used to identify, respectively, Brønsted (BAS) and Lewis acid sites (LAS). The amounts of BAS and LAS were calculated from the intensities of the corresponding spectral bands using the molar extinction coefficients reported by Emeis [14].

2.2. Catalytic tests

Isomerisation of α -pinene oxide over the parent materials (H-Beta zeolites) and over Fe modified beta zeolites with varying SiO₂/Al₂O₃ ratios of 25, 150 and 300 was carried out in the liquid phase using a batch-mode operated glass reactor. In a typical experiment the initial concentration of α -pinene oxide and the catalyst mass were 0.02 mol/l and 75 mg, respectively, using *N*,*N*-dimethylacetamide as a solvent (*V*_L = 100 ml) at 140 °C. The kinetic experiments were performed under the following conditions to avoid external mass transfer limitation: the catalysts particle size below 90 μ m and the stirring speed of 390 rpm. The catalyst was activated in the reactor at 250 °C under an inert argon atmosphere for 30 min before the reaction. The samples were taken at different time intervals and analyzed by GC. The products were confirmed by GC–MS and NMR.

In order to study the reaction in the presence of trace amounts of a homogeneous catalyst, a few additional experiments were performed. As a homogeneous catalyst FeCl₃·6H₂O was applied in a typical experiment at 140 °C using 0.02 mol/l α -pinene oxide as a reactant in 100 ml of DMA. The amount of iron was 3.7 mmol in 100 ml of solution, which corresponds to about 9 wt% leaching of iron from 3 wt% Fe Beta-150.

3. Results and discussion

3.1. Catalyst characterisation results

The morphology (shape and size) of the parent and Fe modified zeolite catalysts was studied by scanning electron microscopy. The beta zeolites exhibit circular form. Fe modification of all three zeolites did not influence the parent crystal morphology. The energy dispersive X-ray micro analysis (EDXA) results shown in Table 1 are somewhat lower than nominal loading in case of Fe-Beta-300 and Fe-Beta-25 zeolite catalysts.

Iron loading was determined by EDX-microanalysis for catalysts Fe-Beta-150 after the isomerisation to test if leaching of iron occurred during the reaction. A slight decrease of iron content (below 9%) was observed in the spent Fe-Beta-150 (2.85 wt% of iron) in comparison to the fresh one (3.1% of iron) indicating that iron was not significantly leached during isomerisation of α -pinene oxide in DMA at 140 °C during 3 h reaction time.

The specific surface areas of the proton form zeolites and Fe modified zeolite catalysts determined by nitrogen adsorption and calculated by Dubinin's method are summarised in Table 2. The highest surface area of proton form zeolite was determined for H-Beta-25, being however comparable with surface area of H-Beta-300. The loading of iron on zeolites causes the decrease of the surface area. Among iron modified zeolites the highest specific surface area was determined for Fe-Beta-300, catalyst with the lowest content of iron.

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Table 2	
Main textural characteristics of the studied catalyst	s.

Catalyst	Metal content (wt%)	Specific surface area (m²/g)	Pore specific volume (cm ³ /g)
H-Beta-25	_	807	-
Fe-Beta-25	4.1	623	0.222
H-Beta-150	-	664	-
Fe-Beta-150	3.1	587	0.209
H-Beta-300	-	805	-
Fe-Beta-300	1.1	761	0.270

Table 3

Brønsted and Lewis acidities of the proton and Fe modified zeolites Beta.

Catalysts	Brønsted	Brønsted acidity (µmol/g)			Lewis acidity (µmol/g)		
	250°C	350°C	450°C	250°C	350°C	450°C	
H-Beta-25	269	207	120	162	128	113	
Fe-Beta-25	272	214	3	123	60	15	
H-Beta-150	176	161	72	43	23	10	
Fe-Beta-150	192	162	14	165	45	2	
H-Beta-300	82	67	10	30	4	4	
Fe-Beta-300	90	57	0	67	16	0	

Concentrations of Brønsted and Lewis acid sites were determined by FTIR using pyridine as a probe molecule.

The results of the FITR measurements of proton form zeolites and their iron modified counterparts are shown in Table 3. The Brønsted acidity increases with increasing of the alumina content in the Beta zeolites (decreasing values of the SiO₂/Al₂O₃ molar ratio from 300 to 150 and 25). The zeolite H-Beta-300 displays the lowest Brønsted acidity while still maintaining few strong Lewis acid sites. The introduction of Fe in the metal modification process decreases the concentration of strong Brønsted acid sites of the proton forms similar to previous reports on metal modified zeolites [15] and marginally increases the total amount of Brønsted acid sites. The highest total Brønsted acid sites concentration for iron containing catalysts was obtained for Fe-Beta-25, followed by Fe-Beta-150 zeolite catalyst. The trend of increasing of the concentration of Brønsted acid sites with decreasing SiO₂/Al₂O₃ ratio in Beta zeolite remains the same.

Similar to Brønsted acidity Lewis acidity increases with increasing of the alumina content in the proton form of beta zeolites. The highest concentration of Lewis acid sites for iron containing catalysts was determined for the Fe-Beta-150.

The introduction of Fe in beta zeolites decreases the concentration of strong Lewis acid sites. Total amount of Lewis acid sites (weak, medium and strong LAS) increases after iron modification of Beta-150 and Beta-300 zeolites, while introduction of iron in Beta-25 caused the decrease also in the total concentration of Lewis acid sites. It could be explained by the highest initial content of strong Lewis acid sites in H-Beta-25 which were eliminated during iron introduction.

3.2. Isomerisation of α -pinene oxide

Three beta zeolites with SiO_2/Al_2O_3 molar ratios 25, 150 and 300 were modified by iron and tested for selective *trans*-carveol preparation by α -pinene oxide (APO) isomerisation. Parent materials, proton forms of beta zeolites, were also tested for comparison. The activities and selectivities of the catalysts were correlated with their acid properties and iron content.

The results of the catalytic experiments focused on the preparation of *trans*-carveol by α -pinene oxide isomerisation over proton form of beta zeolites and their iron modified forms are shown in Table 4. The initial reaction rate was calculated according to

$$r_0 = \left(\frac{(c_0 - c_t)}{t} \frac{1}{m_{\text{cat}}}\right),\tag{1}$$

where c_0 , c_t are initial and actual concentration of APO (mmol/l), t is reaction time (3 min) and m_{cat} is mass of catalyst (g).

The total conversion of α -pinene oxide was obtained using all six materials within 180 min from the beginning of the reaction.

The highest initial reaction rate was achieved using H-Beta-25, the zeolites with the highest Brønsted acidity. The reaction rates for proton forms of zeolites were higher than for their iron modified forms. The highest initial reaction rate from iron modified materials was obtained using Fe-Beta-25, being 22 mmol/($l \min g_{cat}$), i.e. the Fe-modified catalyst with the highest Brønsted acidity. The initial reaction rate and activity of the Fe modified catalysts decrease with increasing SiO₂/Al₂O₃ ratio and decreasing of Brønsted acidity.

The highest selectivity to the desired *trans*-carveol at moderate (25%) and complete conversion of α -pinene oxide was obtained using H-Beta-300 and Fe-Beta-300, the catalysts with the lowest Brønsted and Lewis acidity.

Minor products are campholenic and fencholenic aldehyde, 2methyl-5-(propan-2-ylidene) cyclohex-2-enol and *p*-cymene. The product distribution varied over different beta zeolites as will be discussed below. Selectivity to the main by-product, campholenic aldehyde, is shown in Table 4. The highest selectivity to this product was achieved using proton and iron modified forms of zeolite Beta-25.

Conversion of α -pinene oxide as a function of the reaction time over Fe modified beta zeolites is depicted in Fig. 2a. Total conversion of α -pinene oxide was achieved within 80 min from the beginning of the reaction using Fe-Beta-25 and Fe-Beta-150 and in 150 min over Fe-Beta-300.

The selectivity to the desired *trans*-carveol as a function of α pinene oxide conversion is shown in Fig. 2b. As mentioned above, the highest selectivity to the desired alcohol was achieved using Fe-Beta-300, the catalysts with the lowest Brønsted and Lewis acidity and the lowest amount of iron. The selectivity to *trans*-carveol increases slightly during the reaction using all three catalysts being an indication of a consecutive parthway in *trans*-carveol formation.

Table 4

Initial reaction rate, conversion of α-pinene oxide and selectivities to *trans*-carveol and to campholenic aldehyde at 25% and 100% conversion of α-pinene oxide.

Catalyst	Metal content (wt%)	Initial reaction rate	Selectivity to TCV		Selectivity to CA	
		(mmol/(minlg _{cat}))	At 25% conversion of APO (%)	At 100% conversion of APO (%)	At 25% conversion of APO (%)	At 100% conversion of APO (%)
H-Beta-25	0	51.0	*31	32	*40	36
Fe-Beta-25	4.1	22.0	26	31	34	34
H-Beta-150	0	24.8	**32	35	**40	33
Fe-Beta-150	3.1	20.9	34	40	32	29
H-Beta-300	0	28.0	39	42	38	28
Fe-Beta-300	1.1	14.3	36	43	31	29

* At 70% conversion.

** At 40% conversion.

Reaction conditions: α-pinene oxide (0.02 mol/l), catalyst (75 mg), N,N-dimethylacetamide (V_L = 100 ml), 140 °C, 180 min.

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Fig. 2. (a) Conversion of α -pinene oxide as a function of time and (b) selectivity to *trans*-carveol as a function of conversion over Fe-Beta-25 (\blacklozenge), Fe-Beta-150 (X) and Fe-Beta-300 (\blacktriangle).

The conversion of α -pinene oxide as a function of the reaction time for proton forms of beta zeolites is depicted in Fig. 3a. Total conversion of α -pinene oxide was achieved within 20 min from the beginning of the reaction using H-Beta-25 and H-Beta-150 and within 60 min over H-Beta-300.

The selectivity to the desired *trans*-carveol as a function of α -pinene oxide conversion is illustrated in Fig. 3b. The highest selectivity to the desired alcohol was achieved using H-Beta-300. The selectivity to *trans*-carveol increases slightly with conversion using H-Beta-150 and H-Beta-300 being almost constant for H-Beta 25.

Selectivity to other encountered products (fencholenic aldehyde, 2-methyl-5-(propan-2-ylidene) cyclohex-2-enol and pcymene) is given in Table 5. The selectivity to fencholenic aldehyde, an aldehyde with cyclopentane framework, increases with increasing alumina content in case of parent zeolites and their Fe-modified forms. The formation of 2-methyl-5-(propan-2-ylidene)cyclohex-2-enol seems to be independent on catalysts properties being 7% using all Fe-modified catalysts and around 10% using parent zeolites at the total conversion of α -pinene oxide. The transformation of trans-carveol and 2-methyl-5-(propan-2-ylidene) cyclohex-2enol, products with *para*-menthene structure, to *p*-cymene is the same for all six tested catalysts. Other products, such as isopinocamphone and pinocarveol (Fig. 1, compounds 2 and 3), were present in the reaction mixture with selectivities around 1% using proton and Fe-modified forms of beta-zeolites. Furthermore, around 3% of undefined products were observed in the reaction mixture. The mass balance closure of compounds in 180 min is 100% using proton forms of beta zeolites and Fe-Beta-25 and 99% using Fe-Beta-150 and Fe-Beta-300.

Monocyclic products of α -pinene oxide isomerisation can be classified into two groups: compounds with 6-member carbon-ring

(*trans*-carveol, 2-methyl-5-(propan-2-ylidene)cyclohex-2-enol and *p*-cymene) and compounds with 5-member carbon-ring (campholenic and fencholenic aldehyde). The sum of the selectivities to these products is also depicted in Table 5. The same trend in formation of *trans*-carveol and C6 products and campholenic aldehyde and C5 products, respectively, is obvious. The formation of C5 products increases with increasing alumina content.

It should be noted that selectivity to C5 aldehydes was almost constant independent on conversion. Behaviour of C6 and bicyclic compounds was, however, different. The ratio between the concentrations of *trans*-carveol and campholenic aldehyde increases during the reaction over three Fe-Beta zeolites (Fig. 4a). The analogous formation of these products is obvious over H-beta zeolites (Fig. 5a). The same trend was observed for the concentrations of the products with 6-member carbon-ring (*trans*-carveol, 2-methyl-5-(propan-2-ylidene)cyclohex-2-enol and *p*-cymene) and 5-member carbon-ring (campholenic aldehyde and fencholenic aldehyde) (Fig. 4b). The ratio C6:C5 products increases from 0.5 to 0.7 over Fe-Beta-25, from 0.6 to 1 over Fe-Beta-150 and from 0.6 to 1.1 over Fe-Beta-300.

Such behaviour is an another evidence that C5 products on one hand and C6 and bicyclic compounds on the other hand are formed in the parallel fashion, at the same time C6 products are generated through bicyclic compounds. This is consistent with a decrease in selectivity to isopinocamphone and pinocarveol as the reaction proceeds.

The analogous formation of products is evident over H-beta zeolites (Fig. 6a and b). The ratio C6:C5 products increases from 0.6 to 0.7 over H-Beta-25, from 0.6 to 0.9 over H-Beta-150 and from 0.7 to 1.3 over H-Beta-300.

Fig. 6a and b show selectivity to *trans*-carveol and campholenic aldehyde at 100% conversion of α -pinene oxide as a function of the



Fig. 3. (a) Conversion of α -pinene oxide as a function of time and 4 (b) selectivity to *trans*-carveol as a function of conversion over H-Beta-25 (\Diamond), H-Beta-150 (\Box) and H-Beta-300 (\triangle).

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Table 5	5
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The selectivities to fencholenic aldehyde, *p*-cymene and 2-methyl-5-(propan-2-ylidene)cyclohex-2-enol) at 25% and 100% conversion of α -pinene oxide.

Catalyst	Selectivities (%) at 25% a (100%) conversion of APO					
	Fencholenic aldehyde	p-Cymene	2-Methyl-5-(propan-2-ylidene)cyclohex-2-enol)	C6	C5	
H-Beta-25	*23 ^a (22)	*2 ^a (1)	*4 ^a (9)	*37 ^a (42)	*61 ^a (58)	
Fe-Beta-25	22 ^a (22)	$2^{a}(2)$	4 ^a (7)	32 ^a (39)	58 ^a (56)	
H-Beta-150	**21 ^a (18)	**0 ^a (2)	**1 ^a (10)	**33 a(47)	**60 ^a (52)	
Fe-Beta-150	22 ^a (19)	$1^{a}(1)$	5 ^a (7)	41 ^a (48)	51 ^a (47)	
H-Beta-300	17 ^a (17)	3 ^a (1)	3 ^a (10)	44 ^a (53)	54 ^a (46)	
Fe-Beta-300	17 ^a (16)	$1^{a}(1)$	5 ^a (7)	40 ^a (51)	48 ^a (45)	

* At 70% conversion.

** At 40% conversion.

^a Selectivity at 25% conversion.

Reaction conditions: α -pinene oxide (0.02 mol/l), catalyst (75 mg), N,N-dimethylacetamide (V_L = 100 ml), 140 °C, 180 min.



Fig. 4. (a) The concentration of *trans*-carveol as a function of campholenic aldehyde concentration and (b) the concentration of C6 products (*trans*-carveol, *p*-cymene and 2-methyl-5-(propan-2-ylidene) cyclohex-2-enol) as a function of C5 products (campholenic and fencholenic aldehyde) over Fe-Beta-25 (\blacklozenge), Fe-Beta-150 (X) and Fe-Beta-300 (\blacktriangle).



Fig. 5. (a) The concentration of *trans*-carveol as a function of campholenic aldehyde concentration and (b) the concentration of C6 products (*trans*-carveol, *p*-cymene and 2-methyl-5-(propan-2-ylidene) cyclohex-2-enol) as a function of C5 products (campholenic and fencholenic aldehyde) over H-Beta-25 (◊), H-Beta-150 (□) and H-Beta-300 (△).

concentration of Brønsted (Fig. 6a) and Lewis acid sites (Fig. 6b) in case of proton forms of zeolites. Selectivity to *trans*-carveol decreases with increasing concentration of Brønsted acid sites while selectivity to campholenic aldehyde increases with increasing concentration of Lewis acid sites.

The same trends as shown in Fig. 6 for *trans*-carveol and campholenic aldehyde formation are observed for C6 and C5 products formation as a function of the concentration of Brønsted (Fig. 7a) and Lewis (Fig. 7b) acid sites. The selectivity to C5 products increases with increasing concentration of Brønsted and Lewis acidity.

Fig. 8a and b display selectivity to *trans*-carveol and campholenic aldehyde at 25%, 50% and 100% conversion of α -pinene oxide as a function of the concentration of Brønsted (Fig. 8a) and Lewis acid sites (Fig. 8b) in case of Fe-modified zeolites.

The selectivity to *trans*-carveol decreases, while selectivity to campholenic aldehyde increases with increasing concentration of Brønsted acid sites similar to proton forms. The dependence of the selectivity to *trans*-carveol and campholenic aldehyde on the amount of Lewis acid sites exhibits the minimum and maximum, respectively, which was somewhat different from the proton forms.

The trends for selectivity to C6 and C5 products as a function of the concentration of Brønsted and Lewis acid sites are given, respectively, in Fig. 9a and b. The selectivity to C5 products increases with increasing concentration of Brønsted acid sites at the expense of the selectivity to C6 products. The dependence of the selectivities to C6 and C5 products on the amount of all Lewis acid sites exhibits the minimum and maximum, respectively. Fig. 9c shows the selectivity to C6 and C5 products as a function of the

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Fig. 6. The selectivity to *trans*-carveol (line) and campholenic aldehyde (dashed line) at 100% conversion of APO as the functions of the concentration of (a) Brønsted and (b) Lewis acid sites at 140 °C in *N*,*N*-dimethylacetamide as a solvent.



Fig. 7. The selectivity to C6 (line) and C5 (dashed line) products at total conversion of α-pinene oxide as the functions of the concentration of (a) Brønsted and (b) Lewis acid sites at 140 °C in *N*,N-dimethylacetamide as a solvent for proton form zeolites.

concentration of the strong Lewis acid sites. The concentration of products with *para*-menthene structure decreases with increasing concentration of strong Lewis acid sites. On the contrary, the concentration of products with cyclopentane framework increases almost linearly. This trend could be explained by interactions of strong Lewis acid sites with oxygen atom of hydroxyl group causing

splitting of the adjacent C–C bond in 6-member carbon-ring forming thereby products with the C5 ring.

Based on the experimental observations a reaction mechanism of α -pinene oxide isomerisation accounting for formation of the major and minor encountered products can be proposed (Fig. 10). One route of *trans*-carveol **4** and 2-methyl-5-(propan-2-ylidene)



Fig. 8. Selectivity to *trans*-carveol (line) and campholenic aldehyde (dashed line) at 25% (♠), 50% (▲) and 100% (●) conversion of APO as the functions of the concentration of (a) Brønsted and (b) Lewis acid sites at 140 °C in *N*,*N*-dimethylacetamide as a solvent for Fe modified zeolites.







Fig. 9. The selectivity to C6 (\bullet) and C5 (\bigcirc) products at total conversion of α -pinene oxide as the functions of the concentration of (a) Brønsted and (b) Lewis acid sites at 140 °C in *N*,*N*-dimethylacetamide as a solvent. (c) The selectivity to C6 (\bullet) and C5 (\bigcirc) products at total conversion of α -pinene oxide as the functions of the concentration of strong Lewis acid sites for Fe modified zeolites.

cyclohex-2-enol 5 formation can be suggested to proceed through two intermediates, pinocaveol 3 and 2,6,6-trimethylbicyclo[3.1.1]hept-2-en-3-ol. The latter intermediate is an enol form of isopinocamphone 2. p-Cymene 6 is a product of subsequent transformation of the products with the para-menthenic structure. The other two routes explain the formation of campholenic 4 and fencholenic 5 aldehyde, i.e. aldehydes with the cyclopentane framework.



Fig. 10. Reaction mechanisms for formation of products during isomerisation of α -pinene oxide.

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Table 6

Initial reaction rate and selectivities to *trans*-carveol, campholenic aldehyde and to C6 and C5 products at 25% and 100% conversion of α-pinene oxide.

Solvent	Initial reaction rate	Selectivity at 25% and 100% ^a conversion of APO (%)					
	$(mol/(minlg_{cat}))$	TCV	CA	C6	C5		
DMA	14.3	36 ^a (43)	31 ^a (29)	40 ^a (51)	48 ^a (45)		
NMP	10.8	41 ^a (44)	30 ^a (29)	47 ^a (51)	50 ^a (46)		

Reaction conditions: α -pinene oxide (0.02 mol/l), Fe-Beta-300 (75 mg), solvent (V_L = 100 ml), 140 °C, 180 min.

^a Selectivity at 25% conversion.

The previous results on testing of heterogeneous catalysts for *trans*-carveol preparation discussed in the introduction of this article showed the problems with leaching of active components of supports under reaction conditions. The leaching of iron was studied in present study. As mentioned above, just slight decrease of iron content in spent catalyst Fe-Beta-150 was determined by EDXA method.

In order to study the reaction in the presence of trace amounts of a homogeneous catalyst, a few additional experiments were performed. As a homogeneous catalyst FeCl₃·6H₂O was tested in a typical experiment at 140 °C in 100 ml of DMA. The amount of iron corresponds to about 9 wt% leaching of iron from 3 wt% Fe Beta-150. The achieved conversion of α -pinene oxide was about 5% after 20 min under reaction conditions and obtained products were not the same as in a typical catalytic reaction discussed above. The results showed that contribution of homogenous catalysis by dissolved iron was negligible.

As reported in the literature, the reaction is strongly influenced by the basicity and the polarity of the solvent [11]. The optimal solvent for campholenic aldehyde preparation is toluene [9], a solvent without Lewis basicity. A polar basic solvent is necessary to be used for the selective preparation of *trans*carveol [11]. In this work activity and selectivity of Fe-Beta-300 in *N*,*N*-dimethylacetamide (DMA) were compared with the results obtained in *N*-methylpyrrolidone (NMP). The latter was chosen because of its higher Lewis basicity according to the Kamlet–Taft scale ($B_{\rm KT}$) [16].

The results of the catalytic experiments focused on testing of these solvents with Fe-Beta-300 are shown in Table 6.

Total conversion of α -pinene oxide was achieved using both solvents within 120 and 180 min from the beginning of the reaction using NMP and DMA, respectively. On the contrary, the initial reaction rate was higher using DMA.

The basicity of the solvent influences mainly the selectivity. Utilisation of NMP enhances selectivity to the desired *trans*-carveol as well as increases the formation of products with *para*-menthene structure. This fact confirms the expectation that polar basic solvent is necessary for formation of *trans*-carveol. Lower formation of the undesired C5 products can be caused by an interaction of oxygen atom of the Lewis basic solvent with Lewis acid sites of the catalysts, mainly with strong Lewis acid sites. As discussed above, strong Lewis acid sites cause a decrease of selectivity to *trans*-carveol and C6 products and thereby favouring formation of C5 products.

Experiments with the same catalyst at $70 \degree C$ in toluene gave *trans*-carveol and *p*-cymene in minor quantities at full conversion with predominant formation of fencholenic and campholenic aldehydes in almost equal amounts.

4. Conclusions

Synthesis of *trans*-carveol by α -pinene oxide isomerisation was done using proton form and Fe-modified zeolites beta with different SiO₂/Al₂O₃ molar ratios. Iron modified catalysts were prepared using impregnation evaporation method and characterised by various physico-chemical methods.

Reaction selectivity is strongly influenced by basicity and polarity of the solvent. The highest selectivity to the desired alcohol was achieved over Fe-Beta-300 (1.1 wt% of Fe) using *N*-methylpyrrolidone being 44% at total α -pinene oxide conversion. This result is comparable with selectivity obtained previously with molecularly imprinted polymers.

The total conversion of α -pinene oxide was achieved using all proton forms and Fe-modified zeolites within 180 min in *N*,*N*-dimethylacetamide at 140 °C giving selectivity to the desired alcohol of 30–43%. The highest selectivity to the desired *trans*-carveol being 43% was also obtained using Fe-Beta-300, the catalyst with the lowest iron content and the lowest Brønsted and Lewis acidity. The selectivities to *trans*-carveol achieved using proton forms of zeolites were similar or slightly lower than their Fe-modified forms.

Minor products are campholenic and fencholenic aldehyde, 2methyl-5-(propan-2-ylidene) cyclohex-2-enol and *p*-cymene. The selectivity to *trans*-carveol increases slightly during the reaction.

The selectivity to *trans*-carveol and campholenic aldehyde as well as selectivity to compounds with 6-member carbon-ring (*trans*-carveol, 2-methyl-5-(propan-2-ylidene)cyclohex-2-enol and *p*-cymene) and compounds with 5-member carbon-ring (campholenic and fencholenic aldehyde) were correlated with Brønsted and Lewis acidity of the tested catalysts. The selectivity to *trans*-carveol and generally to C6 products decreases with increasing concentration of Brønsted acid sites. The concentration of products with *para*-menthene structure (C6) also decreases with increasing concentration of strong Lewis acid sites with oxygen atom of hydroxyl group causing splitting of adjacent C–C bond in 6-member carbon-ring thereby forming products with C5 ring.

The previous results on testing of heterogeneous catalysts for *trans*-carveol preparation discussed in the introduction of this article showed the problems with leaching of active components of supports. The leaching of iron from Fe-Beta-150 was studied in present study under reaction conditions. The results showed that contribution of homogenous iron on the reaction course was negligible.

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