



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 SiO₂/Al₂O₃ 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, 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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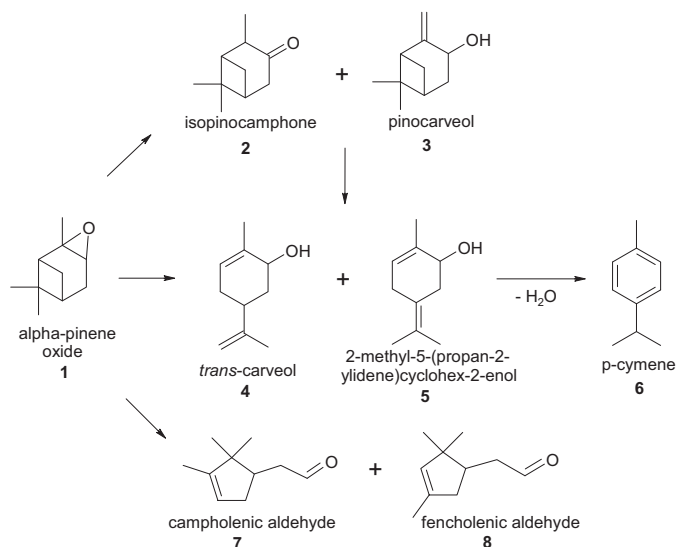


Fig. 1. Reaction scheme of α -pinene oxide **1** isomerisation to *trans*-carveol **4** and 2-methyl-5-(propan-2-ylidene)cyclohex-2-enol **5** and *p*-cymene **6** (product of subsequent dehydration), to isopinocampone **2** and pinocarveol **3** and to campholenic **7** and fencholenic **8** aldehydes.

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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 out-gassed 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 pre-treated 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 ($V_L = 100\text{ ml}$) at 140 °C. The kinetic experiments were performed under the following conditions to avoid external mass transfer limitation: the catalysts particle size below 90 μm 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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 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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