

Catalytic isomerization of α -pinene oxide in the presence of acid-modified clays

A.Yu. Sidorenko^{a,*}, A.V. Kravtsova^a, A. Aho^b, I. Heinmaa^c, T.F. Kuznetsova^d, D.Yu. Murzin^b, V.E. Agabekov^a

^a Institute of Chemistry of New Materials of National Academy of Sciences of Belarus, 220141, Skaryna str. 36, Minsk, Belarus

^b Åbo Akademi University, 20500, Biskopsgatan 8, Åbo-Turku, Finland

^c National Institute of Chemical Physics and Biophysics, 12618, Akadeemia tee 23, Tallinn, Estonia

^d Institute of General and Inorganic Chemistry of National Academy of Sciences of Belarus, 220072, Surganov str. 9/1, Minsk, Belarus

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ABSTRACT

Isomerization of α -pinene oxide was studied at 20–50 °C in the presence of commercial montmorillonites K-10 and K-30, acid-treated illite clay as well as synthetic aluminosilicate AS-36 using cyclohexane as a solvent. The catalysts were characterized by XRD, XRF, FTIR, MAS NMR, thermal analysis and N₂ low-temperature sorption methods. The main reaction products at 99.9% conversion of the substrate are campholenic and *iso*-campholenic aldehydes, the largest amount of which (68.1 wt.%) is formed on illite clay treated by 10% HCl. The *iso*-campholenic/campholenic aldehydes ratio decreases from 0.7 to 0.25 with an increase of acidity of the catalyst from 47 to 153 $\mu\text{mol/g}$. The content of products with *p*-menthane structure (*trans*-carveol, *trans*-sorberol, *p*-cymene, pinol) reaches a maximum (33.0 wt.%) in the presence of medium-acid (104.0 $\mu\text{mol/g}$) K-10 clay. The amount of campholenic aldehyde in reaction mixture increases from 34.3 to 48.2 wt.%, and content of *iso*-campholenic aldehyde decreases from 33.7 to 17.7 wt.% with increasing the drying (calcination) temperature of illite clay from 50 to 600 °C respectively. The scheme for the formation of reaction products on clays was proposed.

1. Introduction

Oxygen containing derivatives of terpene hydrocarbons, isolated from turpentine and essential oils, are widely used in the synthesis of various fragrant and biologically active compounds. Thus, α -pinene oxide (2,3-epoxypinane) is a highly labile terpenoid and can be converted to various valuable products [1–18] (Fig. 1). In industry, isomerization of the α -pinene oxide is carried out in the presence of zinc halides as homogeneous catalysts to form campholenic aldehyde (I), from which a range of substances with sandalwood odor are obtained [1–4]. This process has several drawbacks, such as the formation of toxic waste, and the difficulty of separating the catalyst from the reaction mixture [2,3].

Recently, a number of studies to develop new heterogeneous catalytic systems for 2,3-epoxypinane isomerization to campholenic aldehyde, as well as other valuable products (*trans*-carveol, pinocarveol, *iso*-pinocamphone, etc.) have been performed. A special attention was given to investigations of influence of the nature and strength of the acid sites (a.s.) on the yield of reaction products [6–18].

Relatively high selectivity to campholenic aldehyde was exhibited

B₂O₃/SiO₂ (69%), HY (66.0%) and Al-MSU-S (86%) zeolites, which is explained by a large amount of Lewis acid sites (L) [10]. The physico-chemical and catalytic properties of iron-modified Beta-75 and ZSM-5 zeolites, MCM-41 silicate, as well as Al₂O₃ and SiO₂ were studied in [7]. In the presence of toluene as a solvent, Fe-MCM-41 was the most selective towards campholenic aldehyde (66%), which can be explained by the predominance of L sites in the catalyst. A high concentration of weak and medium Brønsted (B) acid sites in Fe-Beta-75 afforded formation of up to 23% of *iso*-campholenic (fencholenic) aldehyde (III). When N,N-dimethylacetamide was used as a solvent, the α -pinene oxide isomerization on H- and Fe- forms of Beta zeolites proceeded to form 31–43% *trans*-carveol (VI), which finds application in perfume compositions [8].

In the presence of Fe₂O₃-TiO₂ mixed oxides, synthesized by the sol-gel method, the main product of 2,3-epoxypinane conversion was campholenic aldehyde (selectivity 42%), which is explained the presence of strong L sites in the solids, whereas over TiO₂ a predominant (40%) formation of pinocarveol (IV) was observed [11]. An increase in the yield of aldehyde (II) from 25 to 38% was caused by gold deposition on TiO₂ (> 70% anatase). In smaller amounts, the formation of

* Corresponding author at: Institute of Chemistry of New Materials of National Academy of Sciences of Belarus, 220141, Skaryna str, 36, Minsk, Belarus.
E-mail addresses: camphene@gmail.com, mixa@ichmn.basnet.by (A.Y. Sidorenko).

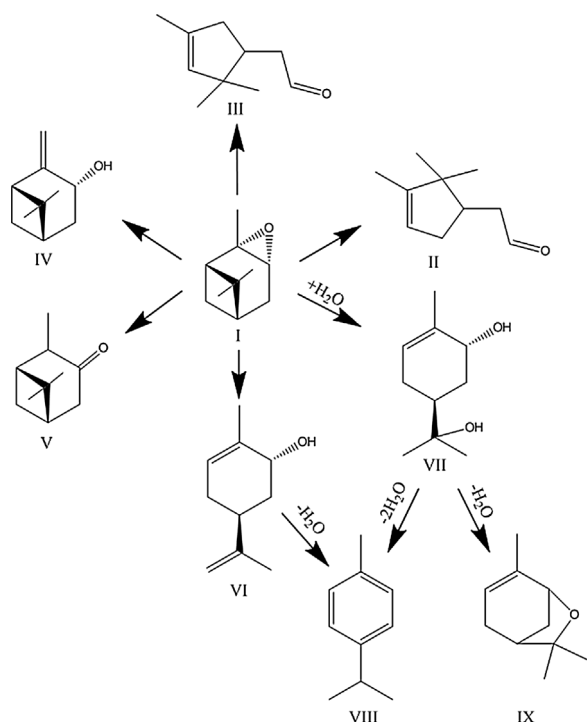


Fig. 1. Scheme of α -pinene oxide isomerization I – α -Pinene oxide; II – Campholenic aldehyde; III – *iso*-Campholenic (fencholenic) aldehyde; IV – Pinocarveol; V – *iso*-Pinocamphone; VI – *trans*-Carveol; VII – *trans* – Sorberol; VIII – *p*-Cymene; IX – Pinol.

compounds (IV) and (V) from Fig. 1 occurred on this catalyst [12]. The grafting of Fe^{3+} ions on SiO_2 surface resulted in a catalyst with Lewis acidity, allowing selectivity to compound (II) of 56–72% [13].

The effect of various solvents on the yield of α -pinene oxide isomerization products on heteropoly acids was investigated in [9]. In a non-polar and non-basic solvent (cyclohexane), the formation of aldehyde (II) was predominant, while in polar and basic media (DMF, DMA) *trans*-carveol (VI), and in weakly basic solvents (PhNO_2 and others) *trans*-sorberol (VII) and pinol (IX) were formed. In supercritical isopropanol selectivity to campholenic aldehyde reached 59.4% at 465 K and 13.5 MPa [14].

The porous structure of the catalysts can have a significant effect on selectivity. Thus, isomerization of α -pinene oxide was studied at 30 °C in the presence of porous metal-benzenetricarboxylates, such as MIL-100 (Al, Fe and Cr), MIL-110 (Al) and MIL-96 (Al). The highest selectivity for campholenic aldehyde (51–61%) at the substrate conversion of 96–98% was achieved on MIL-100 series, which is presumably due to their unique structure [15]. In the presence of US-Y zeolites having a three-dimensional large pore system (7.4 Å) with supercages of 12 Å and a large amount of mesopores, selectivity to campholenic aldehyde was 75% at 0 °C [16]. A very high selectivity to this product (89–94%) was observed in the presence of Ti-Beta zeolites, which may be in result of comparable sizes of pores, reagents and intermediates [17].

Formation of *iso*-campholenic aldehyde (III) from α -pinene oxide was first observed in the presence of *p*-toluenesulfonic acid in a quinoline solution. The combined aldehyde yield was 30% with the ratio of products (II) and (III) equal to 17:3 [18]. Compound (III) can be obtained from pinocarveol by addition of HBr addition forming bromo-*isofenchol*, which in the presence of an equimolar amount of AgNO_3 gives the desired product [19]. In the presence of $\text{BF}_3\cdot\text{Et}_2\text{O}$ *iso*-campholenic aldehyde was obtained from α -pinene oxide with a yield of 51% [20].

Clays predominantly composed of layered silicates are effective catalysts for various terpenes and terpenoids transformations [25,26]. These reactions often occur along routes that are not characteristic for

other types of catalysts [25]. An effective way to improve the catalytic activity and selectivity of clays is their treatment (modification) by mineral acids, most often HCl and H_2SO_4 . Depending on the process conditions (temperature, concentration and amount of a modifier), the specific surface area, volume and pore diameter as well as acidity of clays can vary over a wide range [26–31]. Note that in clays with a high CaO content, the use of sulfuric acid as a modifier is undesirable, because this leads to formation of sulphates, which impair the porous structure of the solids [27].

The acid-modified clays produced in industry, for example, montmorillonites KSF, K-10 and K-30 (Germany), can be used as catalysts for various organic reactions [25,31,32]. Isomerization of α -pinene oxide on commercial montmorillonite clays K-10, Filtrol-105 and Tonsil LF-80 was studied in [5]. The main products were campholenic (27–40 wt.%) and *iso*-campholenic (11–19 wt.%) aldehydes. The influence of type, features of the crystal structure, nature and strength of the acid sites, conditions of chemical and thermal modification of clays on the composition of α -pinene oxide isomerization products remain unexplored. Therefore, the establishment of such quantitative dependences and investigated of a possibility to apply such modified clays for α -pinene oxide isomerization is an important task.

2. Experimental

Commercial K-10 and K-30 montmorillonites (Germany), as well as a clay from Belarusian “Lukoml-1” mine (L-1) were applied. An amorphous aluminosilicate catalyst AS-36 (Russia) was used for comparison.

Acid treatment (modification) of L-1 was carried out by 1–30% solutions of HCl. A clay sample (10–15 g) was ground and placed in a 250 ml three-necked flask, thereafter 5 ml per g (5 ml/g) of the acid solution was added, heated to 90 °C and stirred at this temperature for 3 h. Then the solid was washed by decantation until the complete absence of Cl^- in the wash water (test with AgNO_3) and dried (50–300 °C) or calcined (350–600 °C) for 2 h. For all studies the fraction of solids below 100 μm was used to avoid mass transfer limitation.

The chemical composition of the samples was determined by X-ray fluorescence using JED 2201 equipment (analyzed elements from B to U, minimum detectable concentration – 0.1%).

The porous structure of aluminosilicates was measured by ASAP 2020 MP (Micromeritics) analyzer. The samples (50 mg) were previously evacuated (residual pressure 0.013 Pa) for 1 h at a 200 °C. The specific surface area was calculated by the BET equation. The volume and average diameter of pores were determined by the BJH method using the desorption branch of isotherm [33].

The phase composition of L-1 clay was elucidated on a DRON-3 X-ray diffractometer (CuK α radiation, $2\theta = 5\text{--}70^\circ$).

The FTIR spectra were recorded in the 4000–400 cm^{-1} region using a Bruker Tensor 27 spectrometer. The samples were prepared by pressing 2.0 mg of an air-dry clay with 400 mg of KBr.

Thermogravimetric analysis of L-1 was carried out on a Netzsch 449 F3 Jupiter thermal analysis system. The sample (50 mg) was heated from 30 to 900 °C at a ramping rate 10 °C/min in a nitrogen medium, TG and DTG curves were recorded.

^{29}Si MAS NMR spectra were recorded on Bruker AVANCE-II spectrometer in 8.5 T magnetic field using MAS probe for 10 mm zirconia rotors. Single pulse spectrum were accumulated with 6 μs pulse excitation at 71,43 MHz with a repetition time of 100 s at 5 kHz sample spinning speed. The chemical shifts are given in TMS scale. ^{27}Al MAS NMR spectra were recorded at 208.49 MHz on Bruker AVANCE-III with 18.8 T external field using Bruker MAS probe and 3.2 mm zirconia rotors. The spectra were collected by single 0.6 μs pulse excitation with repetition time 30 ms and 22 kHz sample spinning frequency. The spectra are referenced to the frequency of $\text{Al}(\text{NO}_3)_3$ solution.

The acid properties of aluminosilicates were determined by FTIR spectroscopy using pyridine as the probe molecule [34]. The samples were calcined at 350 °C for 1 h, then cooled to 100 °C, and saturated by

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