



The studies on the limonene oxidation over the microporous TS-1 catalyst



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ABSTRACT

The studies on the oxidation of limonene with 60 wt% hydrogen peroxide over the titanium silicalite TS-1 catalyst were carried out. The influence of the following parameters was examined: the temperature 0–120 °C, the molar ratio of limonene/H₂O₂ = 1:2–5:1, methanol concentration 60–95 wt%, TS-1 content 0.25–8 wt% and the reaction time 15 min to 11 days. The studies showed that the most beneficial conditions for the obtaining of high selectivity of 1,2-epoxy limonene, at simultaneously high values of the conversion of reactants and the efficiency of hydrogen peroxide, are as follows: the temperature 80 °C, the molar ratio of limonene/H₂O₂ = 1:1, the methanol concentration 80 wt%, the TS-1 content 3 wt% and the reaction time 10 days. Moreover, the research showed that the process of limonene oxidation is very complicated, because during this process also other very useful oxygenated derivatives of limonene can be obtained, for example: perillyl alcohol, carveol, carvone and 1,2-epoxy limonene diol. The studies on the reuse of the TS-1 catalyst showed that it is very stable catalyst at the studied conditions and it can be recycled to the oxidation process at least three times.

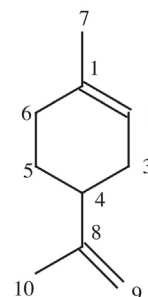
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1. Introduction

Terpenes are renewable natural resources which are readily available in the large scale. The examples of the compounds which belong to the terpene family are: limonene, camphene, pinene, vitamin A, steroids, carotenoids and natural rubber. Nowadays, a special attention is directed to limonene, a natural, cheap and easy available compound. This compound can be obtained in large quantities from the orange peels (biomass and renewable source), which are the waste product from the orange juice industry. The purity of limonene obtained from orange peels reaches 97% and its world production amounts to 110–165 million pounds per year. Limonene can be used as a fragrance, flavor, insecticide or renewable solvent for coatings – replacing aromatic or mineral oils. But the main application of limonene is the utilization of this compound as a very valuable intermediate for organic syntheses.

The high reactivity of limonene is mainly connected with the presence in the molecule of this compound two double bonds: one vinylene group allocated in the cyclic ring (the position 1–2) and

one vinylidene side group (the position of 8–9) [1–6]. The positions of these unsaturated bonds are presented below:



limonene

One of the main ways of transformation of limonene to valuable compounds is its oxidation (including epoxidation) with hydrogen peroxide or t-butyl hydroperoxide (TBHP) in the presence of various heterogeneous catalysts, especially, titanium silicate catalysts. But the literature shows that the limonene oxidation process is very complicated and during this process it is possible to obtain a lot of products. The main reaction is the epoxidation of the unsaturated bond at the position of 1–2 in the limonene molecule and

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formation of 1,2-epoxylimonene. During the secondary reactions the formation of the following by-products is observed (very often at the appropriate conditions these reactions can be the main reactions of this process): 1,2-epoxylimonene diol – the product of the hydration of the epoxide ring in 1,2-epoxylimonene molecule, 8,9-epoxylimonene and its diol (epoxidation and next hydration of the epoxide ring at the position 8–9), carveol – the product of the allylic oxidation at the position 6, carvone – the product of the oxidative dehydrogenation of carveol molecule, 1–2,8–9-diepoxydiol and its diol, perillyl alcohol – the product of the allylic oxidation at the position 7 of limonene molecule, perillyl aldehyde and acid-products of the oxidation of perillyl alcohol [4,5,7–11]. However, the formation of perillyl alcohol as the predominant product was observed mainly during oxidation of limonene in the presence of bacteria, fungus and yeasts [12–15]. The possibility of the obtaining the products of the cyclic allylic hydrogen abstraction and the acyclic allylic hydrogen abstraction during the oxidation of terpenes (3-carene and α -pinene – compounds with the structure similar to limonene) and especially limonene was described by Rothenberg [16] and Wróblewska [17], respectively. Not only 1,2-epoxylimonene but also other oxygenated derivatives of limonene have a great advantage for many branches of the organic industry. 1,2-Epoxy limonene, its diol, carvone, carveol and perillyl alcohol are very valuable intermediates which are applied in the production of: flavors, perfumes, cosmetics, food additives [4,6,7], agrochemicals, special fragrant polymers [18,19] and drugs used in the curing of various kinds of cancer [20,21].

There are few reports about utilization of the titanium silicate catalysts in the liquid phase oxidation of limonene with hydrogen peroxide or *t*-butyl hydroperoxide (TBHP). Until now the following titanium silicate catalysts were used in this process: Ti-MCM-41 [8,22–24], Ti-MMM-2 [10], Ti-SBA-15 [17,25,26] and TS-1 [17,26]. The studies on the oxidation of limonene over the Ti-MCM-41 catalyst were performed with such oxidizing agents as: hydrogen peroxide and TBHP. Ti-MCM-41 catalyst used in the oxidation of limonene was synthesized by the direct sol-gel method [8], and also by grafting (Ti-grafted MCM-41) [22] or wetness and wet impregnation [24]. The structure of the Ti-MCM-41 catalyst obtained by the direct sol-gel method was silylated [23]. The studies over the Ti-MCM-41 catalysts were performed at the temperatures in the range of 70–85 °C, for the molar ratio of limonene/H₂O₂ = 3.7:1 and for the reaction time in the range of 0.5–7 h (in one case from 1 h to 24 h [22]). Over the direct synthesized Ti-MCM-41 catalyst the selectivity of the epoxide compounds (the sum of 1,2- and 8,9-epoxylimonene) was about 60 mol%. Carveol and carvone were formed with the selectivity of 20 mol%, diepoxy limonene with the selectivity of about 10 mol% and glycols about 10 mol%. The conversion of limonene changed from 36 to 80 mol%. Over the silylated Ti-MCM-41 catalyst the results of limonene epoxidation were very close, and the only one difference was a higher value of the hydrogen peroxide efficiency [23]. The two other methods of Ti-MCM-41 preparation (wetness and wet impregnation) do not cause important changes in the catalyst activity, only a slight decrease in the epoxides selectivity was observed [24]. The utilization of TBHP in the oxidation of limonene caused that after the reaction time of 24 h the conversion of limonene was 62 mol% and the selectivity of 1,2-epoxylimonene amounted to 75 mol%. Over the Ti-MMM-2 catalyst the oxidation of limonene was performed in acetonitrile as the solvent, at the temperature of 60 °C and for the molar ratio of limonene/H₂O₂ = 1:2 [10]. These studies showed that the amount of the obtained epoxide compound was three times higher than the other products and the amount of carvone was higher than carveol. Moreover, in the post-reaction mixtures also perillyl alcohol was detected [10]. During the studies over the Ti-SBA-15 catalyst synthesized by grafting titanium on a SBA-15 structure two oxidizing agents

were used: hydrogen peroxide and TBHP [25,26]. The reaction was performed in acetonitrile as the solvent and for the reaction time to 24 h. The following molar ratios of limonene/oxidizing agent were used in these studies: the molar ratio of limonene/H₂O₂ = 1:1.3 and the molar ratio of limonene/TBHP = 1:1.6. For the reaction with H₂O₂ the temperature of 70 °C and for TBHP the temperature of 80 °C were applied. For all investigated oxidizing agents the selectivity of 1,2-epoxylimonene was 100 mol%, but the conversion of limonene amounted to 40 mol% for H₂O₂, and 60 mol% for TBHP.

The preliminary studies on the oxidation of limonene over the TS-1 and Ti-SBA-15 catalysts (both catalysts were hydrothermally synthesized by the sol-gel method) were performed in the glass reactor with the capacity of 25 cm³ equipped with the reflux condenser, the thermometer and the magnetic stirrer and at the following constant starting conditions: the temperatures of 0 °C, 40 °C, 80 °C and 120 °C, the molar ratio of limonene/H₂O₂ = 1:2, methanol (solvent) concentration 80 wt% and the catalyst content 3 wt% [17]. The reaction time changed from 0.5 to 24 h. These studies were only the preliminary studies which showed the possibility to perform the oxidation of limonene over the microporous TS-1 catalyst (in spite of small pore size of this catalyst) and over the Ti-SBA-15 mesoporous catalyst (it was possible to obtain high selectivity of 1,2-epoxylimonene at the low selectivity of 1,2-epoxylimonene diol). Moreover, these studies allow to propose the possible mechanism of the formation of the appropriate products of this process. It was observed during these studies that in almost syntheses the main product of limonene oxidation process was not 1,2-epoxylimonene but perillyl alcohol.

The aim of this work is the detailed studies on limonene oxidation with 60 wt% hydrogen peroxide over the TS-1 catalyst – the titanium silicate zeolite type material. This work is a continuation of the paper [17], where were presented the preliminary studies for the process of limonene oxidation over TS-1 catalysts but over this catalyst the broad studies on limonene oxidation have not been performed yet. It will be very interesting to describe the full influence of the following technological parameters on the course of limonene oxidation: the temperature, the molar ratio of limonene/H₂O₂, methanol (solvent) concentration, the TS-1 catalyst content, and the reaction time. It will be also helpful in the establishing of the most beneficial conditions of 1,2-epoxylimonene obtaining, taking into account the values of the main functions describing this process. Also very important is the presentation the conditions of the formation the by-products of this process, because these by-products very often can be the main products of limonene oxidation process and they have a lot of applications. Also the possibility of the reuse of the TS-1 catalyst was examined on this work.

2. Material and methods

The TS-1 catalyst was prepared according to the method described by Thangaraj et al. [27]. The molar ration of Si/Ti in the gel before crystallization was 64:1. The Ti content in this catalyst was 3.01 wt%, the specific surface area amounted to 372 m²/g, the size of the pores achieved 0.5 nm and the crystal size amounted to 0.5 μ m. The full characteristic of this catalyst was presented in our previous articles [17,28].

In the studies on the oxidation of limonene the following raw materials were used: R-(+)-limonene (97%, Sigma), hydrogen peroxide (60 wt% water solution, Chempur), and methanol (solvent) (analytical grade, Chempur). During these studies the influence of the following parameters was tested: the temperature in the range of 0–120 °C (the concentration of limonene amounted to about 13.7 wt% and hydrogen peroxide 3.4 wt%), the molar ratio of limonene/H₂O₂ = 1:2–5:1 (the values of limonene and hydrogen peroxide concentration in relation to the appropriate molar

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