

Epoxidation of natural limonene extracted from orange peels with hydrogen peroxide over Ti-MCM-41 catalyst

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The paper presents the oxidation of natural limonene (extracted from waste orange peels) by 60 wt% hydrogen peroxide, in the presence of Ti-MCM-41 catalyst and in methanol as the solvent. The aim of the research was to develop the most favorable technological parameters for the process of limonene oxidation (temperature, molar ratio of limonene to hydrogen peroxide, methanol concentration, Ti-MCM-41 catalyst content and reaction time) by analyzing changes in the main functions describing this process: the conversion of limonene, selectivities of appropriate products, the conversion of hydrogen peroxide and the effective conversion of hydrogen peroxide. The process is environmentally friendly process and it uses renewable raw material - limonene and a safe oxidant - hydrogen peroxide. During the study, very valuable oxygenated derivatives of limonene were obtained: 1,2-epoxylimonene, its diol, carvone, carveol, and perillyl alcohol. These compounds are used in medicine, cosmetics, perfumery, food and polymers industries.

Keywords: limonene, Ti-MCM-41 catalyst, hydrogen peroxide, 1,2-epoxylimonene and its diol, carveol, carvone, perillyl alcohol.

INTRODUCTION

Nowadays, performing chemical processes that use waste as a raw materials for their management and for reduction of the emission of pollutants are desirable. An example of this type of process is the limonene epoxidation over the Ti-MCM-41 catalyst by 60 wt% aqueous solution of hydrogen peroxide and in methanol as the solvent. In this process natural limonene was used as raw material. Limonene was obtained by the simply distillation of orange peels, which are very valuable waste from the fruit juice industry. Limonene oxidation was carried out to obtain its valuable oxygen derivatives such as: 1,2-epoxylimonene, its diol, carvone, carveol and perillyl alcohol. These compounds are used for the production of paints, lacquers and protective coatings. Due to their high biological activity, they are also used for drug synthesis. In addition, they are also used in the cosmetic industry (as ingredients of fragrances) and food industry (for flavoring food)^{1–8}.

The first research on mesoporous siliceous materials was carried out in 1968⁹. A breakthrough in research occurred in the 1990s, when first surfactants for synthesis as a template were used. In this way researchers from Mobil company received a series of M41S mesoporous materials including: hexagonal MCM-41 (A), layered MCM-51 (B) and cubic MCM-48 (C)¹⁰ (Fig. 1).

This discovery was very important because when zeolites are used as catalysts in chemical reactions, the particle size of the organic compound involved in the reaction can not exceed 10 Å, whereas the mesoporous material

have pore size in the range of 2–50 nm and they allow to break this barrier and conduct chemical reactions involving much larger, often branched molecules¹¹. MCM-41 material has an ordered hexagonal pore structure whose surface area exceeds 1000 m² g^{−1}, while the pore size is in the range of 5–10 nm. The parameters for obtaining mesoporous silica allows to change the size of the pores, grain sizes and even the way they are organize¹² (Fig. 2).

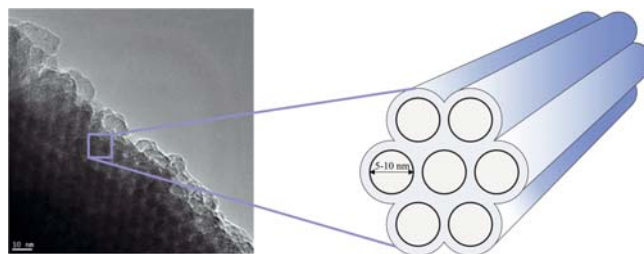


Figure 2. Hexagonal structure of MCM-41 material

MCM-41 material is obtained by two-stage method. The first stage of the synthesis is the sol-gel method, whereby the surfactant forms a suitable micellar structure that is then enclosed by a silicon precursor. In order to increase the crystallites, the resulting crystallization gel is allowed to stand for specified time and at a suitable temperature. The last step in obtaining the mesoporous material is removing the organic matrix from the pores (template)¹³. One of the modifications of the MCM-41 material is the incorporation of titanium atoms into the silica structure. Two methods of obtaining of the Ti-MCM-41 catalysts are known: direct method and impregnation method.

As we shown above the Ti-MCM-41 catalyst is characterized by specific, mesoporous structure containing moreover Ti atoms (active centers for epoxidation reactions) and this caused us to choose this catalyst for studies on limonene epoxidation. The aim of this research was to

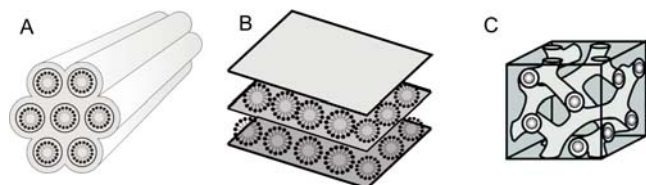


Figure 1. Different structures of the M41S family: hexagonal, layered, cubic

determine the most favorable technological parameters of the limonene epoxidation process with 60 wt% hydrogen peroxide over Ti-MCM-41 catalyst and in methanol as the solvent. For this purpose, a number of syntheses were made in which the influence of the following technological parameters was investigated: temperature (0–120°C), molar ratio of limonene to hydrogen peroxide (from 1:2 to 5:1), methanol concentration (from 65 to 95 wt%), content of catalyst (from 0.125 to 6 wt%) and reaction time (from 15 minutes to 240 hours). In the description of the course of the limonene epoxidation process, the following main functions were described: limonene conversion, selectivities of the appropriate products, hydrogen peroxide conversion and effective conversion of hydrogen peroxide. During the studies, very valuable oxygenated derivatives of limonene were obtained, such as: 1,2-epoxylimonene, its diol, carvone, carveol and perillyl alcohol.

EXPERIMENTAL

Extraction of limonene from orange peels by the simple distillation method

Limonene extraction from orange peels was carried out by the simple distillation method. A 500 cm³ round bottom flask was filled with 100 g of shredded orange peels and with 100 cm³ of deionized water, after that the contents of the flask were brought to the boil and the distillation was continued for 120 min. After the process, the condensate collected in the receiver was centrifuged on the centrifuge for 15 minutes to separate the organic layer from the aqueous one. The separated upper organic layer was collected with a syringe and then dried with a suitable amount of 4A molecular sieves to remove water molecules.

Determination of water content by the Karl-Fischer method

Water content in natural limonene was determined by the Coulometer 831 KF (Metrohm), using coulometric method, in the presence of the reagent – HYDRANAL – Coulomat AG (Fluka).

Identification of limonene by the gas chromatography method

The qualitative and quantitative identification of limonene was performed by the gas chromatography method, using the following separation parameters: helium pressure 50 kPa, sample chamber temperature 200°C, detector temperature 240°C, the oven temperature was increased according to the following program: isothermally at 60°C for 1 minute, temperature increase at 15°C/min, isothermally at 200°C for 3 minute, and cooling up to 60°C, detector sensitivity 10, volume of dosed sample 4 µl. Chromatographic analyzes were performed with the gas chromatograph FOCUS equipped with flame ionization detector (FID), using a capillary column (Quadrex 30 m × 250 µm × 0,25 µm, filled with methylsiloxane modified with phenyl groups) and autosampler. In order to determine the composition of the post-reaction mixtures the method of an external standard was used. For establishing the amounts of products and the unreacted

substrate, calibration curves were made for eight measurement points within a concentration range of 0–33 wt%.

Synthesis of Ti-MCM-41 catalyst

The Ti-MCM-41 catalyst was obtained by the modified method, published by Grun et al.¹⁴. The detailed characteristics of this material are presented in our previous paper¹⁵.

Epoxidation of natural limonene on Ti-MCM-41 catalyst

Research on the determination of the most favorable technological parameters of the epoxidation of natural limonene with hydrogen peroxide over Ti-MCM-41 catalyst and in presence of methanol as the solvent was carried out in a 100 cm³ glass reactor (equipped with a reflux condenser and a magnetic stirrer with a heating function to precisely determine the process temperature). Substrates were placed into reactor in the following order: Ti-MCM-41 catalyst, limonene (99.9%), methanol (99.9% POCH Gliwice) and H₂O₂ (60 wt% water solution, POCH Gliwice). The reactor was then placed in the paw, immersed in an oil bath and reaction was running for a specified period of time. After the completion of the process, the post-reaction mixture was separated from the catalyst particles by the centrifugation and then post-reaction mixtures were analyzed to prepare mass balances. Unreacted hydrogen peroxide was determined by the iodometric method¹⁶ and the limonene oxidation products were analyzed by the gas chromatography method (GC).

Identification of limonene oxidation products by the gas chromatography method

Chromatographic analyzes were performed with a Thermo FOCUS device equipped with a flame ionization detector and a Restek Rtx-WAX capillary column filled with polyethylene glycol. The operating parameters of the GC were as follows: helium pressure 45 kPa, sample chamber temperature 200°C, detector temperature 250°C, the oven temperature has increased according to the following program: isothermally at 60°C for 2 minute, temperature increase at 15°C/min, isothermally at 240°C for 4 minute and cooling up to 60°C, detector sensitivity 10, volume of dosed sample 0.1 µl. The influence of the following technological parameters was investigated in the limonene epoxidation process: temperature (0, 20, 40, 60, 80, 100 and 120°C), molar ratio of limonene to hydrogen peroxide (1:2, 1:1, 2:1, 3:1, 4:1, and 5:1), methanol concentration (65, 70, 75, 80, 90 and 95 wt%), Ti-MCM-41 catalyst content (0.125, 0.166, 0.25, 0.5, 1, 2, 3, 4, 5 and 6 wt%) and reaction time (15, 30, 45, 60, 120, 180, 240 and 300 min.). The studies on the temperature was conducted for the following initial parameters: molar ratio of limonene: H₂O₂ 1:1, methanol concentration 80 wt%, Ti-MCM-41 content 3 wt% and reaction time 180 min. The studies on the influence of others parameters was performed at the value of the tested parameter considered to be the most favorable in the previous stage of the test and while maintaining the remaining reaction parameters. The progress of the limonene oxidation process has been described with such main functions as: the conversion of limonene (C_L), selectivities of appropriate products ($S_{\text{product/limonene}}$), the

conversion of hydrogen peroxide ($C_{H_2O_2}$) and the effective conversion of hydrogen peroxide ($E_{H_2O_2}$). The way of calculation of these functions was presented below:

$$C_L = \frac{\text{amount of moles of limonene consumed}}{\text{amount of moles of limonene introduced into reactor}} \cdot 100 \text{ (mol\%)}$$

$$C_{H_2O_2} = \frac{\text{amount of moles of hydrogen peroxide consumed}}{\text{amount of moles of hydrogen peroxide introduced into reactor}} \cdot 100 \text{ (mol\%)}$$

$$S_{\text{product/limonene}} = \frac{\text{amount of moles of product}}{\text{amount of moles of limonene consumed}} \cdot 100 \text{ (mol\%)}$$

$$E_{H_2O_2} = \frac{\text{amount of moles of } H_2O_2 \text{ used for synthesis of organic compounds}}{\text{total amount of moles of } H_2O_2 \text{ consumed}} \cdot 100 \text{ (mol\%)}$$

RESULTS AND DISCUSSION

In the process of the extraction of natural limonene from orange peels by the simple distillation method, orange oil was obtained. The main component of this oil was limonene, moreover oil contained 0.033% of water.

Figure 3 and Figure 4 summarize the results of the studies on the influence of temperature on the oxidation process of natural limonene and the corresponding values of the main function describing the process. The study of the influence of temperature on the limonene oxidation process shows that the conversions of limonene and hydrogen peroxide increased as the process temperature increased throughout the examined range of this parameter (Fig. 3). The first function increased from 8

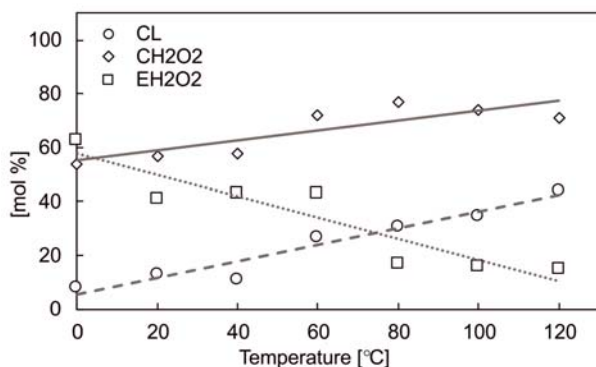


Figure 3. The influence of the temperature on the conversion of limonene (C_L), the conversion of H_2O_2 ($C_{H_2O_2}$) and the effective conversion of H_2O_2 ($E_{H_2O_2}$). Constant parameters: the molar ratio of limonene/ H_2O_2 =1:1, the methanol concentration of 80 wt%, the Ti-MCM-41 catalyst content of 3 wt%, the reaction time 3 h, and the intensity of stirring 500 rpm

to 44 mol%, while the second increased from 54 to 71 mol%. In the case of effective conversion of hydrogen peroxide, the values of this function decreased from 63 to 15 mol%. The main product that was formed in the process of limonene oxidation was perillyl alcohol (Fig. 4). The highest selectivity to this compound was obtained at 20°C–79 mol%. During the studies, the following compounds were also formed: 1,2-epoxylimonene (the highest selectivity of this compound was 8 mol%, it was reached at the temperature of 0°C), 1,2-epoxylimonene diol (the highest selectivity of this compound was 26

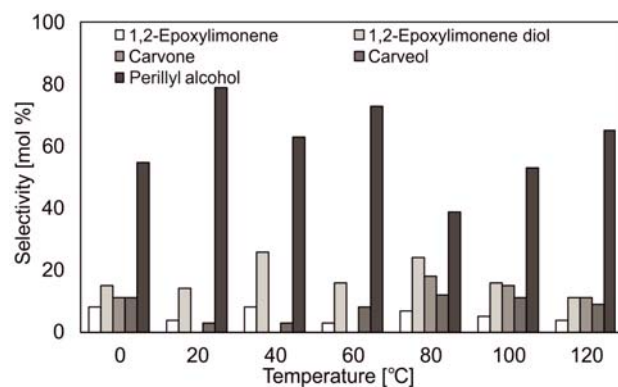


Figure 4. The influence of the temperature on the selectivities of the main products of limonene oxidation. Constant parameters: the molar ratio of limonene/ H_2O_2 =1:1, the methanol concentration of 80 wt%, the Ti-MCM-41 catalyst content of 3 wt%, the reaction time 3 h, and the intensity of stirring 500 rpm

mol%, it was reached at the temperature of 40°C), carvone (the highest selectivity of this compound was 18 mol%, it was reached at the temperature of 80°C) and carveol (the highest selectivity of this compound was 12 mol%, it was reached at the temperature of 80°C). Taking into account the results of the studies on the influence of temperature on the oxidation of limonene (mainly high value of efficiency of hydrogen peroxide conversion), the temperature of 60°C was considered to be the most advantageous at this stage of research. All products forming in the process are shown on Figure 5.

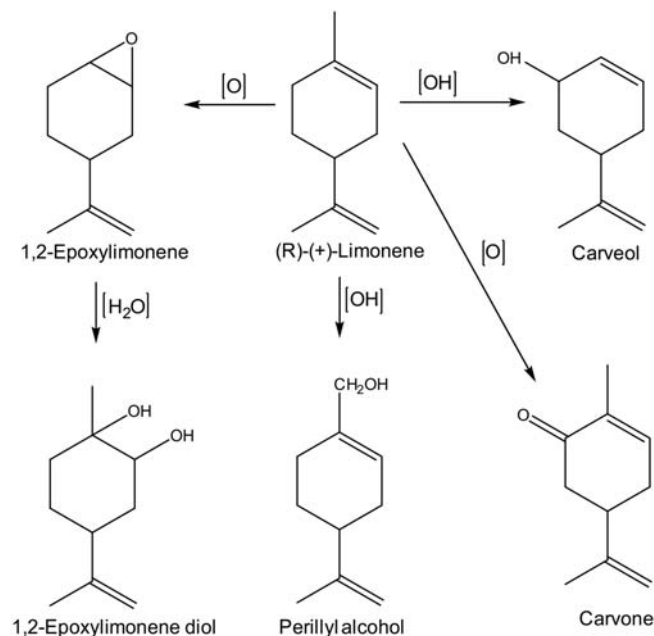


Figure 5. Reaction scheme of limonene oxidation over Ti-MCM-41 catalyst

Figure 6 and Figure 7 shows the results of studies on the influence of the molar ratio of limonene to hydrogen peroxide on the course of limonene oxidation and the values of the main functions describing of the process.

From the research on the effect of the molar ratio of reactants, it was found that as the molar ratio of the limonene to the oxidant increased, the conversions of limonene and hydroperoxide decreased, the first

function from 47 to 12 mol%, and the second from 78 to 65 mol% (Fig. 6). On the other hand, the effective conversion of hydrogen peroxide increased from 31 to 99 mol%. There was also visible an increase in the selectivity of 1,2-epoxylimonene (from 2 to 10 mol%) and a decrease in the selectivity of its diol (from 18 to 11 mol%) over the entire range of the tested parameter (Fig. 7). However, independent of the molar ratio of the reagents, the perillyl alcohol selectivity remained almost constant and amounted about 73 mol%. Moreover, the formation of carvone was not observed. Taking into account the results obtained in this stage of research (mainly conversion of limonene and hydrogen peroxide and also safety considerations), the equimolar ratio of reactants was chosen as the most favorable for further studies.

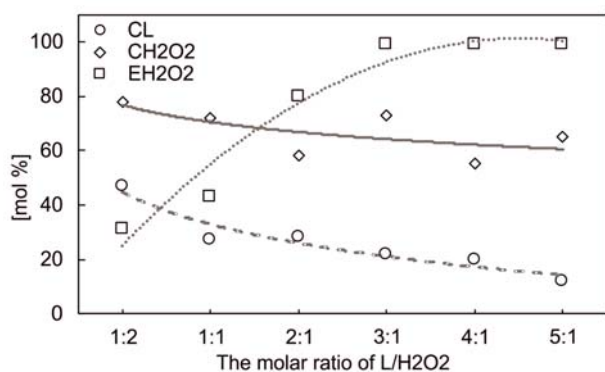


Figure 6. The influence of the molar ratio limonene/hydrogen peroxide on the conversion of limonene (C_L), the conversion of H_2O_2 ($C_{H_2O_2}$) and the effective conversion of H_2O_2 ($E_{H_2O_2}$). Constant parameters: temperature 60°C , the methanol concentration of 80 wt%, the Ti-MCM-41 catalyst content of 3 wt%, the reaction time 3 h, and the intensity of stirring 500 rpm

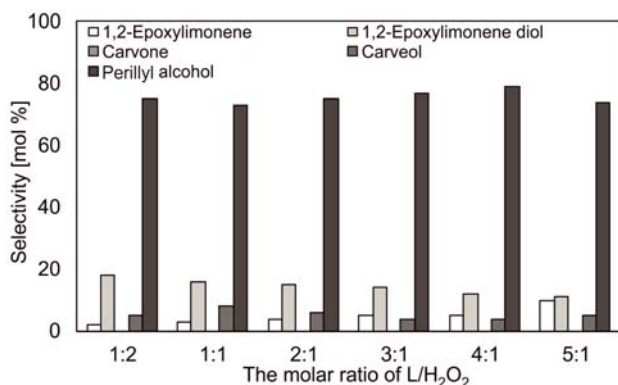


Figure 7. The influence of the molar ratio limonene/hydrogen peroxide on the selectivities of the main products of limonene oxidation. Constant parameters: temperature 60°C , the methanol concentration of 80 wt%, the Ti-MCM-41 catalyst content of 3 wt%, the reaction time 3 h, and the intensity of stirring 500 rpm

The results of studies on the influence of methanol content (solvent very commonly used in epoxidations over titanium silicate catalysts, which is involved in the creation of active sites in pores of the catalyst) on oxidation of limonene and appropriate values of the main

functions of the process are summarized on Figure 8 and Figure 9.

The studies on the effect of methanol concentration showed that as the amount of solvent increased, the conversion of the limonene increased from 4 to 20 mol% and then decreased to 4 mol% (Fig. 8). The effective conversion of hydrogen peroxide increased from 12 to 83 mol% at methanol concentration of 80 wt%, and then decreased to 8 mol% at methanol concentration of 90 wt%. The conversion of hydrogen peroxide over the entire range of tested concentrations was about 50 mol%. The selectivity to 1,2-epoxylimonene amounted to 4 mol% for the first three concentrations of methanol (65, 70 and 75 wt%), and then slightly decreased to 3 mol% (Fig. 9). As the methanol concentration increased, the selectivity of perillyl alcohol increased from 62 to 98 mol%. The selectivity of the other products decreased when the methanol concentration increased and usually was very small. The most preferred concentration of methanol was taken the concentration of 75 wt%.

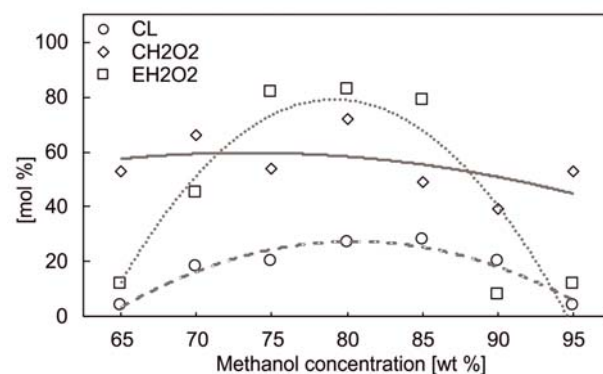


Figure 8. The influence of methanol concentration on the conversion of limonene (C_L), the conversion of H_2O_2 ($C_{H_2O_2}$) and the effective conversion of H_2O_2 ($E_{H_2O_2}$). Constant parameters: temperature 60°C , the molar ratio of limonene/ H_2O_2 = 1:1, the Ti-MCM-41 catalyst content of 3 wt%, the reaction time 3 h, and the intensity of stirring 500 rpm

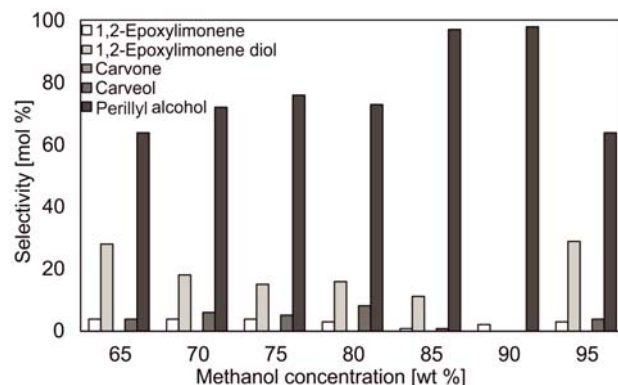


Figure 9. The influence of methanol concentration on the selectivities of the main products of limonene oxidation. Constant parameters: temperature 60°C , the molar ratio of limonene/ H_2O_2 = 1:1, the Ti-MCM-41 catalyst content of 3 wt%, the reaction time 3 h, and the intensity of stirring 500

Figure 10 oraz Figure 11 summarize the effect of Ti-MCM-41 catalysts content on the process of oxidation of natural limonene and the appropriate values of the main functions of the process.

Studies on the effect of Ti-MCM-41 content on the epoxidation process showed that the amount of the catalyst used significantly influenced on the oxidation process. As a result of using too little amount of Ti-MCM-41 in the range of 0.125–0.5 wt% no one oxidation products was observed. The oxidized derivatives of limonene were formed when the amount of catalyst was $\geq 1\%$ wt%. From this catalyst content the increase in values functions describing process was observed – in the conversion of limonene and in the efficient conversion of hydrogen peroxide (Fig. 10). The first of function reached its highest value for the catalyst content amounted to 5 and 6 wt% (23 mol%), while the effective conversion of hydrogen peroxide reached the highest value for the catalyst content 4 wt% (97 mol%). The conversion of hydrogen peroxide also increased, reaching it's the highest value (58 mol%) for the catalyst amount of 6 wt%. The highest selectivity of 1,2-epoxylimonene (equal to 38 mol%) was noted for Ti-MCM-41 content of 1 wt% and that is the amount of catalyst considered to be the most favorable at this stage of the studies, since the further increase in the catalyst content caused the increase in the selectivities of 1,2-epoxylimonene diol and perillyl alcohol (Fig. 11).

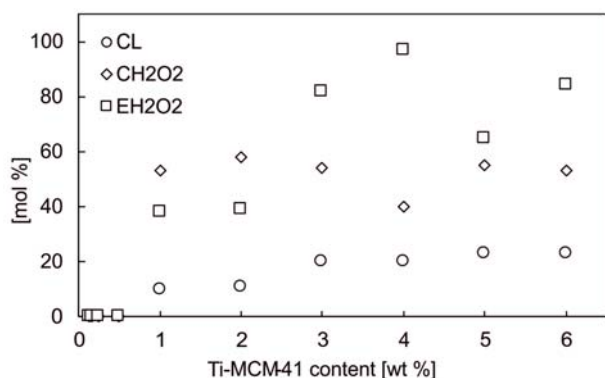


Figure 10. The influence of the Ti-MCM-41 catalyst content on the conversion of limonene (C_L), the conversion of H_2O_2 ($C_{H_2O_2}$) and the effective conversion of H_2O_2 ($E_{H_2O_2}$). Constant parameters: temperature 60°C , the molar ratio of limonene/ H_2O_2 =1:1, the methanol concentration of 75 wt%, the reaction time 3 h, and the intensity of stirring 500

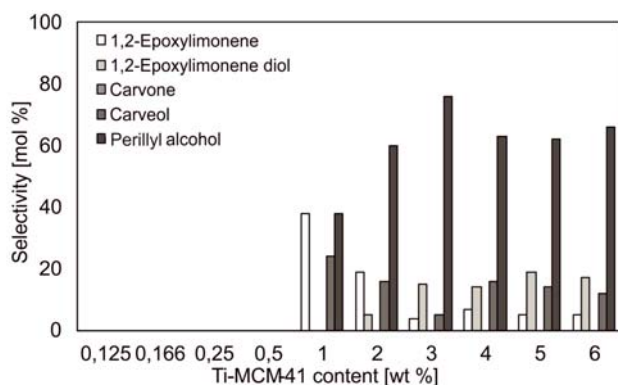


Figure 11. The influence of the Ti-MCM-41 catalyst content on the selectivities of the main products of limonene oxidation. Constant parameters: temperature 60°C , the molar ratio of limonene/ H_2O_2 =1:1, the methanol concentration of 75 wt%, the reaction time 3 h, and the intensity of stirring 500

Figure 12 and Figure 13 summarize the results of the studies on the influence of the reaction time on the oxidation of limonene and the appropriate values of the main functions of this process.

The studies on the influence of the reaction time on the oxidation of limonene showed that with the an increase in the reaction time, the conversion of limonene increased from 9 to 20 mol%, the effective conversion of hydrogen peroxide also increased from 87 to 99 mol%, while the conversion of hydrogen peroxide increased from 20 to 42 mol% (Fig. 12). The formation of 1,2-epoxylimonene was observed after 3 h of reaction (Fig. 13). The highest selectivity of this compound (7 mol%) was obtained for the reaction time of 168 minutes. Moreover, the research showed that with the increase in reaction time, the selectivity of perillyl alcohol decreased from 85 to 68 mol%. The results showed that the most advantageous reaction times was the reaction time of 3 h.

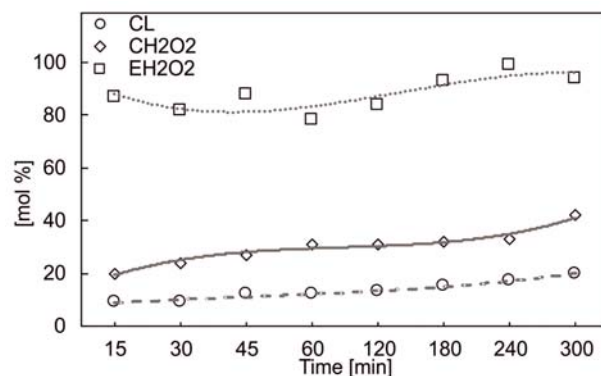


Figure 12. The influence of the reaction time on the conversion of limonene (C_L), the conversion of H_2O_2 ($C_{H_2O_2}$) and the effective conversion of H_2O_2 ($E_{H_2O_2}$). Constant parameters: temperature 60°C , the molar ratio of limonene/ H_2O_2 =1:1, the methanol concentration of 75 wt%, the Ti-MCM-41 catalyst content of 1 wt%, and the intensity of stirring 500

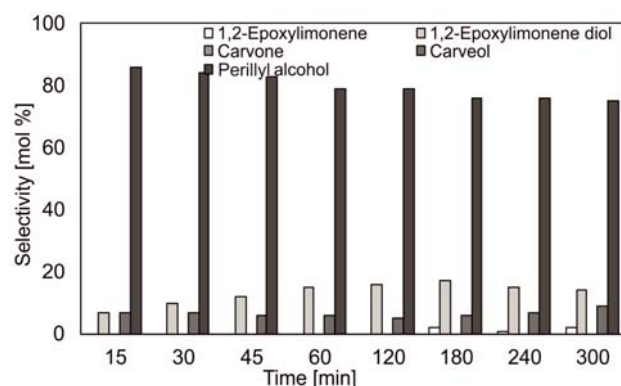


Figure 13. The influence of the reaction time on the selectivities of the main products of limonene oxidation. Constant parameters: temperature 60°C , the molar ratio of limonene/ H_2O_2 =1:1, the methanol concentration of 75 wt%, the Ti-MCM-41 catalyst content of 1 wt%, and the intensity of stirring 500

CONCLUSIONS

Research on the influence of technological parameters on the natural limonene epoxidation showed that valuable oxygenated derivatives of limonene were formed in this

process, such as: 1,2-epoxylimonene, its diol, carvone, carveol and perillyl alcohol. There was mainly observed the allylic oxidation in direction of perillyl alcohol. Taking into account the numerous and valuable applications of perillyl alcohol this direction of conversion of limonene, which is a component of biomass, is very desirable and it is worth further investigation, for example, to increase the conversion of the raw material. Taking into account the results of the studies, the most favorable reaction conditions reaction are as follows: temperature 60°C, molar ratio of limonene to hydrogen peroxide 1:1, methanol concentration 75 wt%, catalyst content 1 wt% and reaction time of 180 min. For these parameters, the main functions of the process achieved the following values: the conversion of limonene – 15 mol%, the conversion of hydrogen peroxide – 31 mol%, the effective conversion of hydrogen peroxide – 93 mol%. The products at these conditions achieved the following selectivities: 1,2-epoxylimonene – 2 mol%, 1,2-epoxylimonene diol – 17 mol%, carvone – 0 mol%, carveol – 6 mol% and perillyl alcohol – 75 mol%.

The established process parameters are mild, allow to reduce the amount of waste, and the use of a recyclable Ti-MCM-41 catalyst is environmentally friendly. In addition, the use of natural limonene (waste and renewable compound derived from biomass) is an additional positive aspect in this environmentally friendly process.

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