

## Article

# Isomerization and Dehydroaromatization of R(+)-Limonene Over the Ti-MCM-41 Catalyst: Effect of Temperature, Reaction Time and Catalyst Content on Product Yield

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Received: 9 May 2019; Accepted: 3 June 2019; Published: 4 June 2019



**Abstract:** This work describes research on the isomerization of R(+)-limonene over the Ti-MCM-41 catalyst. The studies showed that the Ti-MCM-41 catalyst is an active catalyst in the isomerization of R(+)-limonene. As a result of the isomerization of this compound, it is possible to obtain  $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene and p-cymene. Terpinolene is the main product of this process, and p-cymene is formed by the  $\alpha$ -terpinene,  $\gamma$ -terpinene and terpinolene dehydrogenation. The aforementioned products are of great practical importance. The most favorable reaction conditions leading to the obtaining of limonene isomerization products is the use of the catalyst in an amount of 15 wt% and the temperature of 160 °C. Depending on whether the desired products are the isomers of limonene ( $\gamma$ -terpinene,  $\alpha$ -terpinene and terpinolene) or the product of their dehydroaromatization ( $\beta$ -cymene), it is possible to shorten or extend the reaction time. The method for the isomerization of limonene on the Ti-MCM-41 catalyst makes it possible to obtain a significant yield of both the limonene and p-cymene isomers. Longer reaction time is conducive to obtain larger quantities of other reaction products and less desirable products that constitute impurities (oxidized products and polymeric compounds).

**Keywords:** limonene; isomerization; Ti-MCM-41 catalyst; p-cymene; terpinenes; terpinolene

## 1. Introduction

Homogeneous catalysts typically dissolve in the reaction environment, allowing easy access of substrate molecules to active sites, and providing mild reaction conditions and high product selectivity. The disadvantage of these catalysts is their difficult and expensive separation from the post-reaction mixture. In addition, the reuse of these catalysts is associated with their costly recycling. Meanwhile, heterogeneous catalysts can be easily separated from the post-reaction mixture by centrifugation or filtration, and they can then be reused as catalysts for subsequent cycles of the process [1, 2]. An example of heterogeneous catalysts which currently enjoy great interest, both in industry and research institutes, are titanium-silicate catalysts, microporous (for example TS-1 or Ti-MWW) and mesoporous (for example Ti-MCM-41, Ti-SBA-15 or Ti-SBA-16). Generally, microporous materials, due to their pore diameter, which usually does not exceed 2 nm, can be used in catalytic processes involving organic molecules of small size, while mesoporous materials can be used in reactions involving larger and branched molecules (their pore diameter is in the range from 2 nm to 50 nm) [3]. Another important feature of the mesoporous materials is their very large specific surface, which allows a more even distribution of active centers, which are more easily available in larger pores [4].

Currently, among the mesoporous titanium-silicate catalysts, great attention is paid to the Ti-MCM-41 catalyst. This catalyst can be obtained in a simple way. 1) By the hydrothermal method, crystallization of Ti-MCM-41 in the autoclave from the crystallization gel, 2) by the direct precipitation of Ti-MCM-41 from the crystallization gel at ambient temperature without the crystallization in the autoclave, or 3) by the impregnation of the previously obtained MCM-41 structure with an appropriate titanium source [3]. The first two methods allow the introduction of titanium to the entire catalyst structure (including the pores), while the third method allows the introduction of titanium, only on the surface of this material [4].

Materials with MCM-41 structure (including Ti-MCM-41) are mesoporous materials having an ordered, two-dimensional structure with hexagonal pores. The MCM-41 structure resembles a honeycomb. These materials have a narrow pore size distribution (1.8 to 10 nm) that have  $p6mm$  symmetry. The size of the pores depends on the synthesis conditions, the composition of the crystallization gel, as well as on the length of alkyl chains of the surfactant used in the synthesis. The specific surface area of these materials is well developed and exceeds  $1000 \text{ m}^2/\text{g}$ . These types of materials have walls with a thickness of 1 nm, which are made of amorphous silica, and their structure is characterized by a close-range order [5–9]. Thanks to this structure, Ti-MCM-41 materials are used as effective catalysts in the processes of epoxidation, oxidation and isomerization of olefins, e.g., allylic compounds (allyl alcohol [10], diallyl ether [11], allyl-glycidyl ether [12], and allyl chloride [13]) or olefins of natural origin (limonene [14,15], alpha-pinene [16], eugenol [17], or geraniol [18]).

*R*(+)-limonene is the most common terpene found in nature. This compound is the main ingredient of orange oil obtained from orange peels (*R*(+)-limonene content up to 95–98%), which are a waste product after juice production. Its global production ranges from 50 to 75 million kg per year. *R*(+)-limonene is a very valuable compound with broad applications. It is used, among others, as a food additive, as well as a component of cleaning products, cosmetics and perfumes [19–21]. *R*(+)-limonene can also be used in medicine due to its antibacterial, antifungal and anti-inflammatory properties. Studies have shown that this monocyclic monoterpene is very effective in the prevention and treatment of cancer [22]. Good results have also been obtained using *R*(+)-limonene in the treatment of heartburn. *R*(+)-limonene covers the wall of the esophagus and thus protects it from acidic contents coming back from the stomach. In addition, *R*(+)-limonene dissolves gallstones, the compound can be used to treat cholelithiasis, which often involves the need for surgical intervention [23].

More and more scientists are focusing on the use of readily available and relatively cheap compounds of natural origin (renewable raw materials, biomass) in organic synthesis. Thanks to such a strategy, our dependence on the exhausting resources of petroleum resources decreases. These trends are perfectly suited to *R*(+)-limonene, which can be used as a substrate for the production of perillyl alcohol, carvone, carveol, 1,2-epoxylimonene, alpha- and gamma-terpinene, terpinolene, alpha-terpineol, uroterpenol, or dihydroperillic acid [24]. A particularly interesting reaction involving *R*(+)-limonene is its isomerization in the presence of titanium-silicate catalysts. The products of this reaction are valuable compounds such as gamma-terpinene, alpha-terpinene and terpinolene. Extending the reaction time also allows the obtaining of *p*-cymene (dehydroaromatization product formed from limonene isomers) [15]. The advantage of carrying out the *R*(+)-limonene isomerization process in the presence of titanium-silicate catalysts is that it is carried out without the use of organic solvents and without the need for waste disposal, which is indispensable in the traditional method of obtaining *p*-cymene by Friedel–Crafts reaction of toluene with isopropene [25].

*p*-cymene is used as a perfume additive for musky perfumes, as well as a masking fragrance in soaps [24]. In addition, it has been used as a solvent in dyes and varnishes, and as a heat transfer medium [26]. *p*-cymene is a substrate in the synthesis of compounds such as terephthalic acid, dimethylstyrene, thymol and carvacrol [27]. *p*-cymene is also a ligand of many olefin metathesis catalysts. It can also be used as a solvent in olefin metathesis reactions (it is less aggravating for the environment in comparison to chlorinated solvents) [28].

Terpinolene is used, among others, as a synthetic flavor and aroma additive to food [29]. Studies have also been carried out in which it has been shown to play a key role in inhibiting the development of tumors [30]. Other studies have shown that it has a calming effect, and that inhalations containing terpinolene have a relaxing effect [31]. Terpinolene is also an intermediate for the preparation of other compounds, e.g., terpinolic acid [32–34]. It has also been found that terpinolene has applications in radical polymerization of unsaturated monomers. A radical originating from terpinolene may take part in the initiation of the polymerisation reaction, or in its completion [35].

Alpha-terpinene is a compound that is a substrate for the synthesis of ascaridole, a compound used as an anthelmintic drug that also has sedative, analgesic and antifungal properties [36–38]. In addition, applications of alpha-terpinene and gamma-terpinene have been found in the cosmetics industry as an additive to perfumes, soaps, shaving foams and deodorants [39].

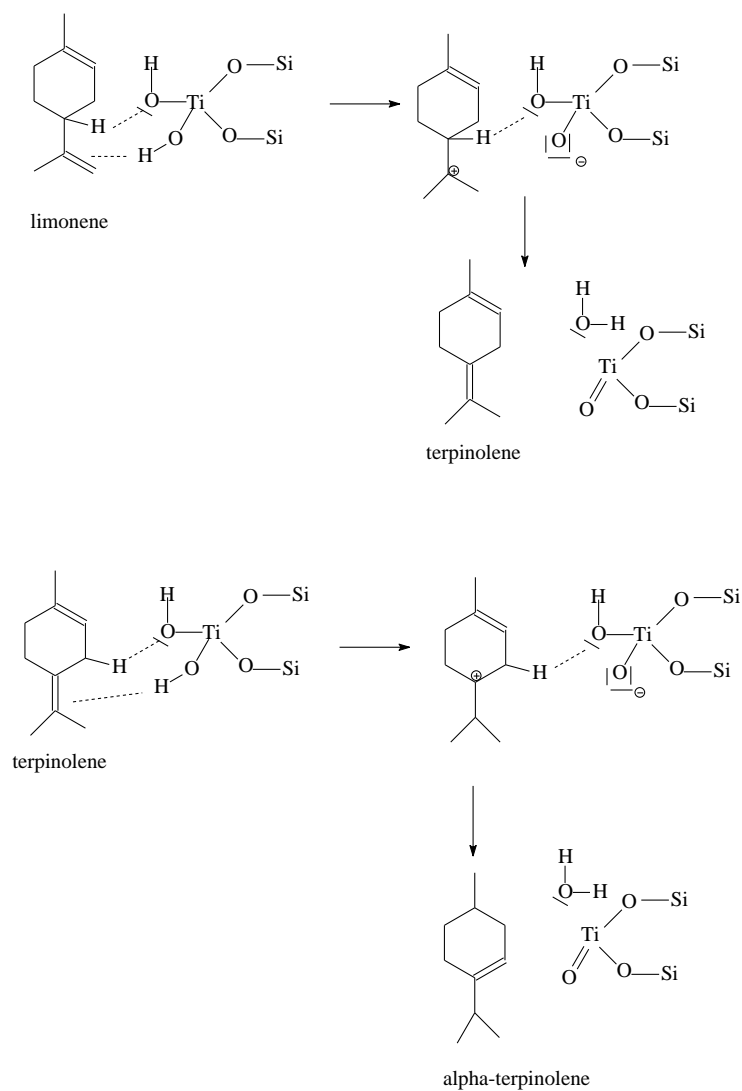
The aim of this work was to establish the best conditions (temperature, amount of the catalyst, and reaction time) for the *R*(+)-limonene isomerization process over the Ti-MCM-41 catalyst. The most favorable conditions for carrying out the isomerization process were chosen considering the yield of terpinolene (the main reaction product) and conversion of the organic substrate, *R*(+)-limonene. The conditions under which the highest yield of *p*-cymene, the product that forms in the follow-up reactions of the primary products of the limonene isomerization process, were also determined. An additional goal of the study was to compare the results obtained on the Ti-MCM-41 catalyst with the results previously described by us for the Ti-SBA-15 catalyst [15]. Both catalysts are titanium-silicate mesoporous catalysts. The Ti-MCM-41 catalyst is obtained without crystallization in an autoclave, which significantly shortens the synthesis time of this catalyst, as well as its manufacturing cost. The disadvantage of its synthesis is the use of hexadecyltrimethylammonium bromide as a template, so that the calcination of this catalyst is burdensome for the environment. In the synthesis of the Ti-SBA-15 catalyst, a biodegradable template is used, but its synthesis requires the use of an autoclave for crystallization, moreover it has more stages and is therefore more expensive.

## 2. Results

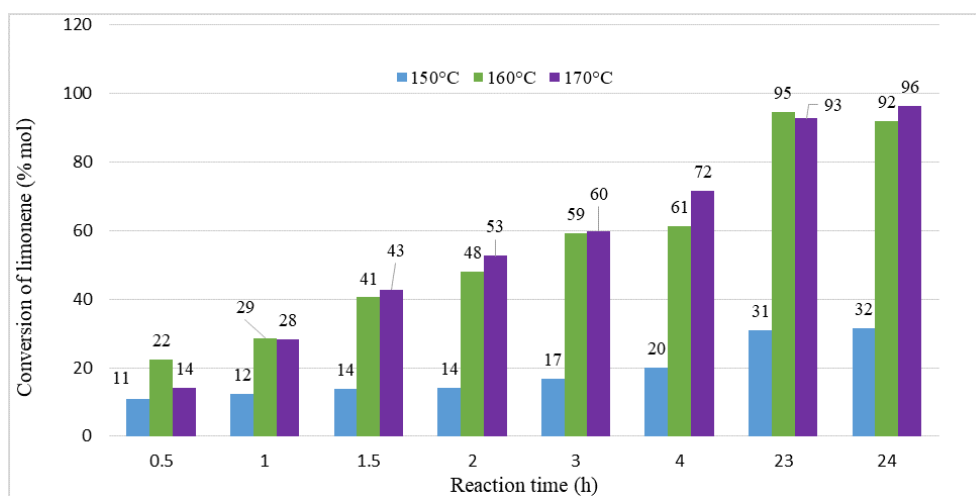
The studies showed that the Ti-MCM-41 catalyst is the active catalyst in the isomerization of *R*(+)-limonene. As a result of the isomerization of this compound, it is possible to obtain  $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene and *p*-cymene. Terpinolene is the main product of this process, and *p*-cymene is formed by the  $\alpha$ -terpinene,  $\gamma$ -terpinene and terpinolene dehydrogenation. Figure 1 presents the possible mechanism of the isomerization and dehydrogenation of limonene.

In the first stage of the presented mechanism, limonene is protonated at the double bond to give the cationic intermediate and the negatively charged Ti-O<sup>-</sup> species. Next, a hydrogen atom (at C4 atom) is shifted to the oxygen atom of the hydroxyl group, which results in the formation of a water molecule that detaches itself from the active complex of Ti. Simultaneously formation of T=O group in the active complex of Ti takes place. In an analogous way  $\alpha$ -terpinene and  $\gamma$ -terpinene are formed. The *p*-cymene, on the other hand, is obtained by the dehydrogenation of limonene and its isomers, which simultaneously leads to the reconstitution of the catalyst and its active form (hydroxyl group restoration at Ti).

Studies on changes in the conversion of *R*(+)-limonene showed that the longer the duration of the process of isomerization, the higher the amount of substrate that is converted into reaction products (Figure 2). At the same time, based on the conducted tests, it can be concluded that the higher the temperature of the isomerization process, the greater the amount of limonene being converted in a shorter time, which also translates into a shorter time needed to obtain valuable products. Moreover, increasing the temperature of the isomerization process from 150 °C to 170 °C, with the same catalyst content (15 wt%), allows for significantly higher substrate conversion for all tested reaction times (the highest increase in *R*(+)-limonene conversion was observed (about 60 mole%) for the reaction time of 24 hours).

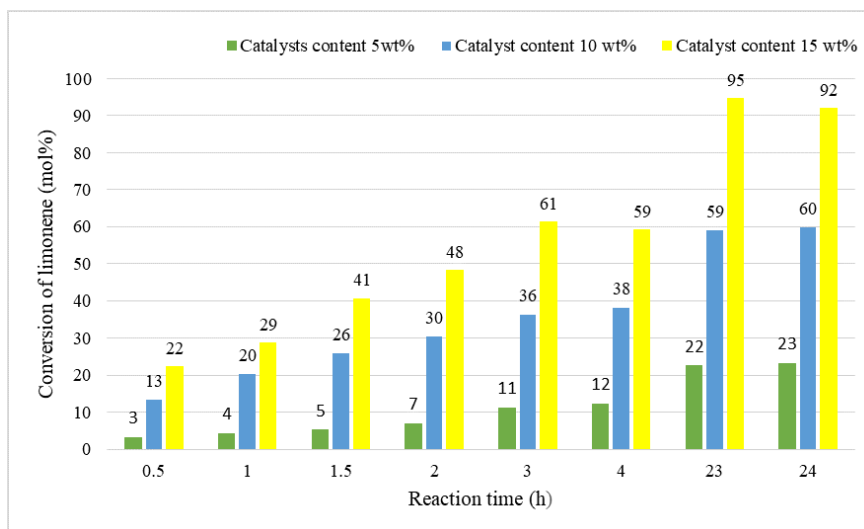


**Figure 1.** The mechanism of isomerization and dehydrogenation of limonene.



**Figure 2.** The influence of the isomerization temperature on the conversion of R(+)-limonene. The amount of the catalyst was 15 wt %.

Moreover, with the increase of the catalyst content in the reaction mixture, the conversion of *R*(+)-limonene increases for each tested reaction time. The described dependence of the substrate conversion on the catalyst content can be seen in the figure showing the dependence of limonene conversion on the catalyst content in the reaction mixture for isomerization at a temperature of 170 °C and for the catalyst content of 10 wt% and 15 wt%, respectively (Figure 3).



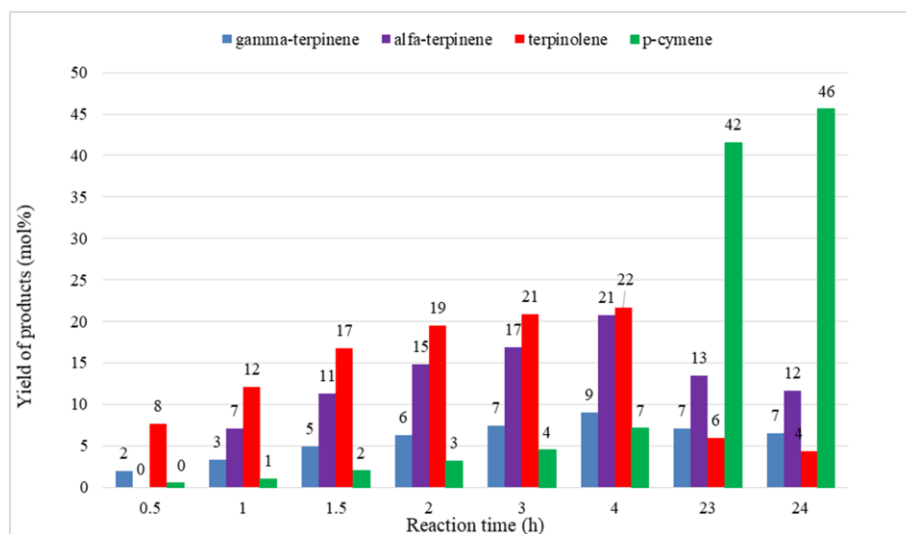
**Figure 3.** The influence of the catalyst content (10 wt% or 15 wt%) on the conversion of limonene for the reaction carried out at a temperature of 170 °C.

From Figure 3, results show that after 24 h of the isomerization process being carried out, the conversion of limonene for the catalyst content in the reaction mixture of 15 wt% is 30 mol% higher than for the catalyst content 10 wt%, and 60 mol% higher than for the catalyst content of 5 wt%. The process of the isomerization of limonene at a temperature of 170 °C amounted to 15 wt% for the catalyst content, and for the reaction time of 4 h, it is characterized by the highest yield of the three products (terpinolene, alpha-terpinene, and gamma-terpinene). At these conditions the conversion of limonene amounted to 71.7 mol% (Figure 4). The values of the yields of terpinolene, alpha-terpinene and gamma-terpinene for the reaction time of 4 h amounted to 21.67 mol%, 20.69 mol% and 9.05 mol%, respectively. After this reaction time, the yields of these limonene isomers decreased, while the yield of p-cymene increased. Hence the conclusion that these limonene isomers are intermediates in the process of obtaining p-cymene from limonene. At the 23rd hour of the isomerization process, the yield of p-cymene was significantly different from the yield of this compound at the 4th hour of the isomerization process, and amounted to 41.55 mol% at the conversion of limonene of 92.76 mol%. After 23 h of carrying out the limonene isomerization process, the yield of its individual products was similar to that obtained after 24 h of the isomerization process.

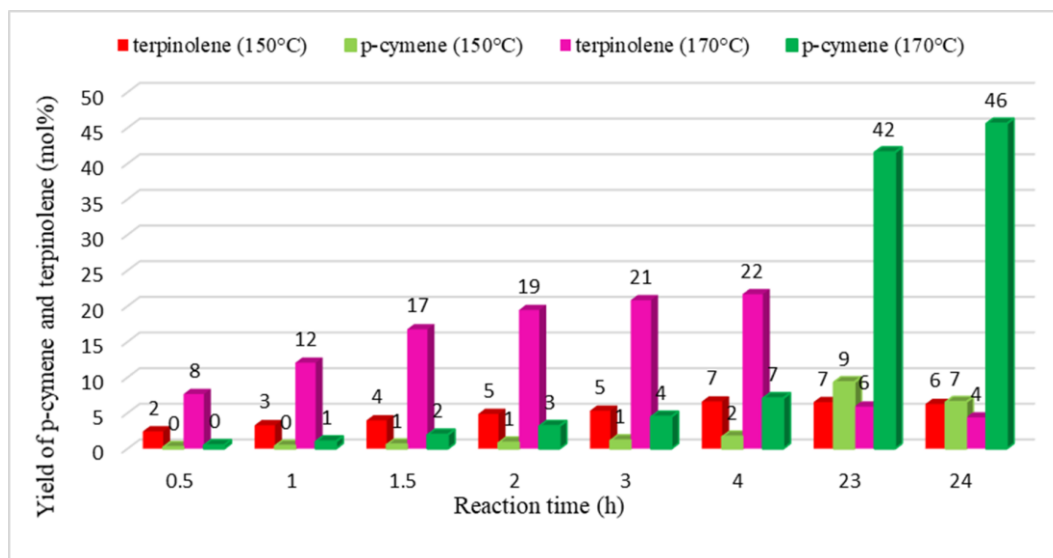
The reduction of the process temperature to 150 °C for the 15 wt% catalyst content, makes the conversion of limonene in the studied reaction time range much lower than in the case of isomerization of limonene at higher temperatures (160 °C and 170 °C) (Figure 2). The lower conversion of limonene also involves a significantly lower yield of individual products of the isomerization of limonene at a temperature of 150 °C (Figure 5).

Carrying out the isomerization of limonene at the catalyst content of 15 wt%, both at 160 °C and 170 °C allows obtaining a high and similar conversion of limonene at the same reaction time of the process (Figure 2). In addition, the yields of the two main isomerization products (terpinolene and p-cymene) are similar in the reaction time range studied up to a duration of 4 h of the process of isomerization (Figure 6). Extending the time of isomerization causes the differences in p-cymene yields

to increase significantly. The yield of p-cymene is significantly higher in the case of the isomerization of limonene at 170 °C.



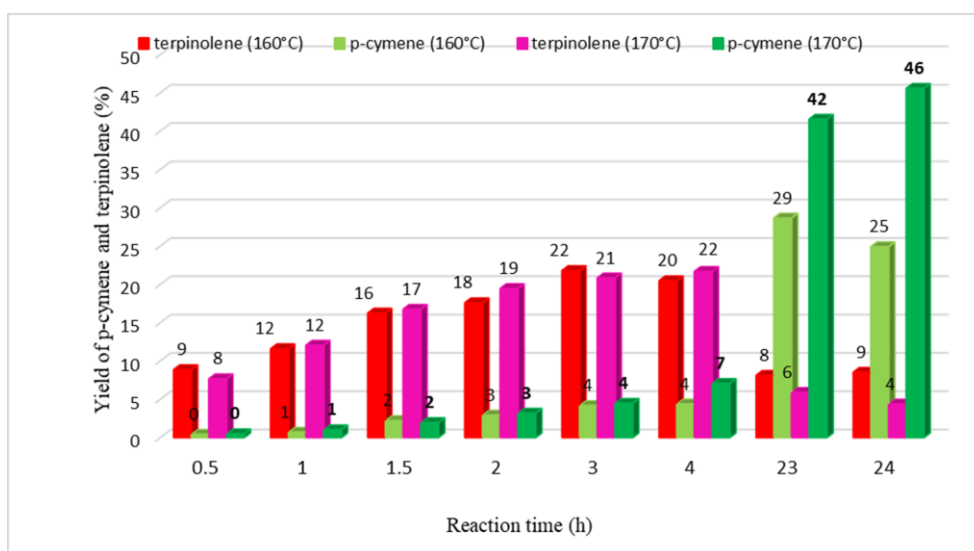
**Figure 4.** The influence of the reaction time on the yields of products of isomerization of limonene. The amount of the catalyst was 15 wt % and the temperature of the isomerization process was 170 °C.



**Figure 5.** The influence of temperature (150 °C or 170 °C) on the yield of the main products of the limonene isomerization process. The amount of the catalyst was 15 wt %.

In our previous studies on the isomerization of limonene, Ti-SBA-15 was used as the catalyst [15]. In the case of the isomerization of limonene carried out over the Ti-SBA-15 catalyst, the main reaction products were  $\alpha$ -terpinene and p-cymene. The comparison of the results obtained for both catalysts under the same process conditions (temperature 160 °C and catalyst content 15 wt%) shows that the Ti-SBA-15 catalyst is a more active catalyst in the process of isomerization of limonene because it allows to obtain higher product yields. However, Ti-MCM-41 acts more selectively towards the formation of terpinolene. After the reaction time of 3 h over the Ti-MCM-41 catalyst, the yield of terpinolene is nearly 22 mol% and at the conversion of limonene amounted to 59 mol%, while under the same isomerization conditions over the Ti-SBA-15 catalyst, the yield of terpinolene was 13 mol% and at the conversion of limonene amounted to 88 mol%. Simultaneously, over the Ti-SBA-15 catalyst, at that time the highest yield of  $\alpha$ -terpinene was obtained, which amounted to 31 mol%. In case of

the Ti-MCM-41 catalyst, the value of the terpinolene yield increases with the prolongation of the reaction time to 22 mol% after 3 h of reaction performing and then decreases. In the case of the Ti-SBA-15 catalyst, the yield of terpinolene increases to 17 mol% (at the conversion of limonene nearly 72 mol%) after 1.5 h, and then decreases. At the same temperature (160 °C), at the same catalyst content (15 wt%), and after 23 h of the process of limonene performing, the yield of p-cymene was 29 mol% and at the conversion of limonene amounted to 92 mol%, and 56 mol% and at the conversion of limonene amounted to 99 mol%, for Ti-MCM-41 and Ti-SBA-15, respectively.



**Figure 6.** The influence of the temperature (170 °C or 160 °C) on the yields of the main products (terpinolene, p-cymene). Amount of the catalyst was 15 wt% and the reaction time was 0.5, 1, 2, 3, 4, 23 and 24 hours.

In both cases, they were the highest values of the p-cymene yield in the studied time range under the given conditions. It can be concluded that in the case of the Ti-SBA-15 catalyst, the reaction of isomerization of limonene is faster, which is indicated by changes in the conversion value of limonene over time.

It is worth noting that the Ti-MCM-41 catalyst in comparison to the Ti-SBA-15 catalyst allows to obtain terpinolene with higher yield at lower conversion of limonene and at the same time. Higher selectivity in the transformation of limonene to terpinolene could be a good reason to use Ti-MCM-41 catalyst in the process of limonene isomerization. Unreacted limonene can be separated from the post-reaction mixture and returned to the process.

### 3. Materials and Methods

#### 3.1. Raw Materials

For the synthesis of Ti-MCM-41 catalyst and in the isomerization of limonene the following raw materials were used. R(+)-limonene (97%, Sigma, Poznań, Poland), hexadecyltrimethylammonium bromide (Sigma-Aldrich), tetraethyl o-silicate (TEOS, 98%, Aldrich, Poznań, Poland) as a silica source, and tetrabutyl orthotitanate (98%, Sigma Aldrich, Poznań, Poland) as a titanium source.

#### 3.2. The Synthesis of the Ti-MCM-41 Catalyst

The Ti-MCM-41 catalyst was obtained using the direct method described by Grün et al. [40]. The synthesis of the Ti-MCM-41 catalyst was performed as follows, 8.85 g of cetyltrimethylammonium bromide (99%, Fluka, Poznań, Poland) was dissolved in 161.95 g of deionized water and the obtained mixture was introduced into a glass reactor. Next, 65.97 g of ammonia (25% aqueous solution,



POCH, Gliwice, Poland) and 210.93 g of anhydrous ethanol (analytical grade, POCh, Gliwice, Poland) was added to this mixture. The resulting mixture was mixed for 15 min. Next, a solution containing 16.55 g of tetraethyl orthosilicate, TEOS (98%, Aldrich, Poznań, Poland) and 2.71 g of tetrabutyl orthotitanate, TBOT (99%, Fluka, Poland) was added dropwise (the molar ratio of Si/Ti amounted to 10:1). The resulting gel was then stirred for 2 h and then left for 16 h without stirring at ambient temperature. After this time, the catalyst was filtered, washed with deionized water, and dried at 100 °C for 24 h and then calcined at 550 °C. The full characteristic of the obtained Ti-MCM-41 catalyst was presented in our previous work [41]. In this work, 4 samples of Ti-MCM-41 catalysts with different molar ratio of Si:Ti were studied. The Ti-MCM-41 catalyst synthesized from the crystallization gel with the molar ratio Si:Ti (10:1) contained 12.09 wt% of Ti and was the most active in the alpha-pinene isomerization process. Thus we decided to use it in the full studies on the process of limonene isomerization presented in this work. In general, for materials such as Ti-MCM-41 the key methods are usually X-ray diffraction (XRD) and SEM, therefore, we only mention the results for these two instrumental methods in this paper. In the low-angle X-ray diffraction studies the diffraction pattern presented one very intense peak corresponding to reflex (100). These data were consistent with the literature and confirmed the hexagonal nature of the mesoporous silica with the MCM-41 structure. The high-angle XRD pattern of the Ti-MCM-41 material showed a broad peak at  $2\theta$  from 15 to 30°, which was typical for amorphous silica. The peak corresponding to the anatase (at  $2\theta \approx 25^\circ$ ) was absent for Ti-MCM-41 material. In the SEM photograph of the Ti-MCM-41 material, well-formed spherical particles, with sizes in the range of 0.2–1  $\mu\text{m}$ , were observed. These spherical particles formed larger structures, which is typical for this type of material.

### 3.3. The Method of the Isomerization of Limonene Over the Ti-MCM-41 Catalyst

The studies on the influence of reaction time, temperature and Ti-MCM-41 catalyst content on the course of limonene isomerization were performed according to the method showed in our last article [15]. Limonene isomerization's were carried out in a glass reactor with a capacity of 25 cm<sup>3</sup>. The reactor was equipped with a reflux condenser and a magnetic stirrer with the heating function. In the glass reactor, 5.00 g of limonene, and 0.5 g or 0.75 g of catalyst were introduced. The reactor was placed in the paw, then immersed in an oil bath and stirring was started (500 rpm). Limonene isomerization was tested at temperatures of 150 °C, 160 °C or 170 °C. Samples of the post-reaction mixture for analyses were taken at the following intervals of time 0.5 h, 1 h, 1.5 h, 2 h, 3 h, 4 h, 23 h and 24 h. To separate the catalyst from the sample, the reaction mixture was centrifuged.

### 3.4. Identification of the Products of Isomerization by the Gas Chromatography Method

The products were determined using the external standard method with the FOCUS (Thermo Electron) apparatus equipped with the FID flame ionization detector (Thermo, Warszawa, Poland) and ZEBRONZB-WAX plus capillary column (0.32 mm  $\times$  30 m  $\times$  0.5  $\mu\text{m}$ ), filled with polyethylene glycol.

Using an autosampler, 0.4  $\mu\text{L}$  of the sample was metered into the chromatography column. The parameters of the apparatus were as follows, helium pressure 60 kPa, sample chamber temperature 240 °C, detector temperature 250 °C. Thermostat temperature increased according to the following program, isothermal 60 °C for 2 min, temperature rise 10 °C/min, isothermally 240 °C for 4 min, cooling to 60 °C. Conversion of the substrate (limonene) and product yield at a given temperature (150 °C, 160 °C, or 170 °C), and at a given catalyst content were determined during the reaction. The most favorable process parameters were determined under such temperature conditions and at the catalyst content at which the product yields were the highest.

## 4. Conclusions

The catalyst content and process temperature have a significant influence on the conversion of limonene and at the same time on the yields of the resulting products. During the tests, it was observed that the best results of the isomerization reaction were obtained at a temperature of 170 °C



and with a catalyst content of 15 wt%. The above reaction conditions enable the highest product yield in the shortest time. Under such conditions of carrying out the process, it is also possible to obtain a significant yield of p-cymene. The use of a slightly lower reaction temperature (160 °C) at the same catalyst content allows similar yields of limonene isomerization products (terpinolene,  $\alpha$ -terpinene and  $\gamma$ -terpinene) to be obtained, however the dehydroaromatization yield is significantly lower compared to the reaction at 170 °C and for the same catalyst content (15 wt%). Hence, the most favorable reaction conditions leading to the obtaining of limonene isomerization products are the catalyst in an amount of 15 wt% and a temperature of 160 °C, which requires less energy than the reaction carried out at 170 °C. Depending on whether the desired products are the isomers of limonene ( $\gamma$ -terpinene,  $\alpha$ -terpinene and terpinolene) or the product of their dehydroaromatization ( $\beta$ -cymene), it is possible to shorten or extend the reaction time. The method for the isomerization of limonene over the Ti-MCM-41 catalyst makes it possible to obtain a significant yield of both the limonene and p-cymene isomers. The lower catalyst content (10 wt%) has a significant effect on the conversion of limonene and at the same time on the yields of the resulting products. It should also be noted that longer reaction time is conducive to obtaining larger quantities of other reaction products and less desirable products that constitute impurities (oxidized products and polymeric compounds). This means that improving the isomerization reaction, by finding the best conditions to conduct it and the ideal catalyst that would ensure high selectivity of products, remains a challenge for the world of science.

**Author Contributions:** M.R. made isomerization's in the laboratory. She prepared the GC analyses, calculated the main functions describing the studied process and took part in the interpretation of data for the work. She prepared the preliminary Polish version of this manuscript. A.W. prepared the conception of isomerization of limonene over selected titanium-silicate catalysts. She took part in the interpretation of data for the work and in the selection of appropriate parameters for next stages of studies. She critically corrected the preliminary version of this manuscript, including introduction, discussion of the results and conclusions. She has prepared the final English version of this manuscript.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflict of interest.

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