Synthesis, Characterization, and Catalytic Applications of the Ti-SBA-16 Porous Material in the Selective and Green Isomerizations of Limonene and S-Carvone

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Abstract: This work presents studies on the activity of the Ti-SBA-16 (SBA—Santa Barbara Amorphous) catalyst in the isomerization of limonene and S-carvone. The Ti-SBA-16 catalyst was synthesized by a two-step method: first, the SBA-16 material was produced, and then it was impregnated with the titanium source. The Ti-SBA-16 catalyst was subjected to detailed characterizations by means of instrumental methods: XRD (X-ray Diffraction), UV-Vis (Ultraviolet–Visible) spectroscopy, FTIR (Fourier-Transform Infrared) spectroscopy, SEM (Scanning Electron Microscopy) with EDX (Energy Dispersive X-ray) spectroscopy, and EDXRF (Energy Dispersive X-ray Fluorescence). Both limonene and S-carvone underwent isomerization over the Ti-SBA-16 catalyst. In the isomerization of limonene, the main product was terpinolene, and its highest yield amounted to 39 mol% after 300 min at 170 °C with a catalyst content of 15 wt%. Under these conditions, the conversion of limonene reached 78 mol%. In contrast, the highest yield of carvacrol (65 mol%) was obtained with the catalyst content of 15 wt%, at 200 °C, and with the conversion of S-carvone reaching 79 mol%.

Keywords: Ti-SBA-16; limonene; S-carvone; isomerization

1. Introduction

The methods of producing olefinic compounds from natural sources for organic syntheses not only allow for an ecological waste management protocol but simultaneously also enable the production of important and relatively inexpensive intermediates. These latter compounds can be used as flavors in the food industry, fragrances in the perfume and cosmetics industries, and as drugs in medicine. Porous materials can serve as efficient heterogeneous catalysts in the transformation of such compounds from natural sources. The characteristic features of heterogeneous catalysts are usually their significant specific surface, uniform distribution of pores, as well as the ability to modify their surface. Titanium silicate catalysts belong to this group of catalysts and are currently widely studied due to their high activity. New synthesis routes for these materials are constantly being sought and new porous materials are being discovered in this group. The Ti-SBA-16 (SBA - Santa Barbara Amorphous) catalyst studied in this research belongs to the latest titanium-silicate catalysts. The processes of the isomerizations of limonene and S-carvone over this catalyst have not yet been studied and described. In general,
isomerizations of limonene and S-carvone are rarely described in the literature, regardless of the catalyst used. This work is a continuation of our previous research on the isomerization of compounds of natural origin over porous heterogeneous catalysts, both synthetic and of natural origin [1–3]. The isomerization of limonene leads to such valued products as terpinolene, α-terpinene, γ-terpinene, and p-cymene (a dehydroaromatization product)—Figure 1.

![Isomerization of limonene and S-carvone](image)

Figure 1. Products of the isomerizations of limonene and S-carvone.

Due to their properties, the above-mentioned compounds have found wide applications in many industries. Terpinolene can be used as a raw material for the synthesis of terpineol and 1-methyl-4-isopropylidene-cyclohexanol-1. Terpinolene is also a terminating factor in some polymerization reactions in an aqueous medium [4]. Terpinolene, with its refreshing fragrance, is widely used as a fragrance in cosmetics and household products. In addition, this compound shows a calming effect as inhalations of terpinolene affect the autonomic nervous system and the human psyche, increasing a feeling of relaxation. Therefore, this compound can be used in the treatment of mental disorders, e.g., depression [5]. Terpinolene, similar to γ-terpinene, can be used in the treatment of atherosclerosis because this compound, in combination with β-carotene and α-tocopherol, effectively prevents LDL oxidation, which plays a key role in the formation of arteriosclerosis [6]. Terpinolene also prevents the oxidation of riboflavin in food products, a compound that produces an unpleasant aftertaste of milk. This compound is also used as an additive in food products, such as fruit, baked products, ice cream, soft drinks, and candies [7,8].

α-Terpinene is used as a food, medicine, and cosmetics additive, as it provides these products with oxidative stability. This compound is also a component of many essential oils, e.g., tea tree oil, and is responsible for the antioxidant properties of these oils. Due to this property, tea tree oil can be used topically as an antibacterial and anti-inflammatory agent, and to treat skin ailments, such as acne or mycosis [9].

p-Cymene is the only naturally occurring form of cymene, and it is a monoterpenic compound containing a benzene ring. P-Cymene is the raw material for the synthesis of cresols, and it can also be converted to aromatic monomers such as terephthalic acid or dimethylstyrene. P-Cymene is also used in the synthesis of olefin metathesis catalysts, and the precursor for the preparation of such catalysts is obtained from α-terpinene. As a result of the reaction of α-terpinene with hydrated ruthenium chloride, dichloro(p-cymene)ruthenium dimer is obtained with a 92% yield [10,11]. From p-cymene, p-cymenesulfonic acid can also be obtained, which has similar properties to p-toluenesulfonic acid, used in the Fischer esterification reaction [12]. P-Cymene is also used as an additive to mask odors in soaps and in other industrial products. This compound is also used as a solvent for dyes and varnishes, as a heat transfer agent, and as a component of fragrance compositions and musk perfumes [13].
γ-Terpine has antibacterial properties. In addition, as also mentioned above, this compound can be used in the treatment of atherosclerosis, because its antioxidant property prevents LDL oxidation. It was also found that γ-terpinene is one of the two components of pine oil that have acaricidal properties, and, thus, this oil can be used to protect food against mites during storage [14–16].

The product of S-carvone isomerization is carvacrol (Figure 1). This compound is a biologically active monoterpene belonging to the group of phenols. Carvacrol has been touted as a near-panacea because of its many healing properties. It exhibits antibacterial, antifungal, analgesic, antioxidant, and antiparasitic properties, which were confirmed in numerous scientific papers. Studies in animals (mice) have shown that carvacrol reduces weight gain and fat mass, and, therefore, it can be used to treat obesity [17]. In addition, this compound has been shown to have a strong effect on S. aureus granulomas, on Escherichia Coli rods, as well as on Mycobacterium tuberculosis bacteria that cause tuberculosis [18,19]. Carvacrol also has antioxidant and anti-cancer properties for colorectal, melanoma, lung, and cervical cancers [20,21].

Until now, the SBA-15 material, which has an ordered, hexagonal and two-dimensional structure with p6mm symmetry, has been given the most attention among the mesoporous materials of the SBA structure. The successor to SBA-15 is the SBA-16 material, which is characterized by a highly ordered, cubic, three-dimensional structure, showing Im3m symmetry. Mesoporosity in this material results from the presence of a non-interpenetrating three-dimensional channel system and the spherical cavities that divide these channels [22–26]. The structure of SBA-16 can be described using a regular, internally centered structure and is depicted in Figure 2. The spherical, or rather twelve-walled, internally centered mesopore is in a cubic arrangement, with each mesopore connected to eight adjacent ones. Three-dimensional 12-wall channels run towards the corners of the cube. This structure allows for easier mass transfer with a significant reduction in the risk of pore blockage [27].

![Figure 2. Structure of the SBA-16 (SBA—Santa Barbara Amorphous) material and scheme of Schoen’s I-WP (WP—wrapped package) minimal surface.](image)

The diameter at the entrance from one mesopore to the other is usually much smaller than the diameter at any segment of the mesopore (cage diameter). Internally centered mesopores, about 10 nm, go into channels of about 2 nm. The average surface of mesopores in SBA-16 resembles Schoen’s I-WP (WP - wrapped package) minimal surface (Figure 2), which is repeatable in three directions of space. However, this arrangement of silica walls has not been confirmed by tests [28,29].

The Ti-SBA-16 catalyst has so far been used in limonene epoxidation, in cyclohexene oxidation, and in the preparation of aminoalcohols [30–32]. To date, no studies have been reported in the literature on the isomerization of limonene and S-carvone using the Ti-SBA-16 catalyst. In our previous works, we described research on the isomerization of limonene in which we used Ti-SBA-15 and Ti-MCM-41 (Mobil Crystalline Material) catalysts, and in both cases we obtained satisfactory results. In the case of the Ti-SBA-15 catalyst, with a 15 wt% catalyst content in the reaction mixture, for the reaction times of 30–1380 min and at 160 °C, the yield of p-cymene of over 50 mol% was obtained, while substrate
conversion was close to 90 mol%. The use of the Ti-MCM-41 catalyst in the amount of 15 wt% in the reaction mixture, for the reaction times of 30–1440 min at 170 °C, made it possible to obtain p-cymene with the yield of 46 mol% and with the conversion of limonene amounted to over 90 mol% [1,2].

The purpose of this work was to investigate the activity of the new titanium silicate catalyst, Ti-SBA-16, in the isomerization processes of two olefinic compounds, limonene and S-carvone. These can be obtained from waste plant material, such as orange peels and from the processing of caraway fruit seeds, by the simple distillation or steam distillation methods. Because these two olefinic compounds can be obtained from waste, they are relatively inexpensive and are easily available raw materials. The purpose of this work was to obtain high-yield valuable products from the isomerizations of limonene and S-carvone, and to determine the most favorable conditions (such as, temperature, content of the catalyst, and reaction time) for obtaining these products. The tests were performed in mild conditions, i.e., under air atmospheric pressure, and without the use of any organic solvents, which is in accordance with current environmental protection requirements. It should be emphasized that the Ti-SBA-16 catalyst is one of the newest titanium-silicate catalysts and its use in the process of limonene and S-carvone isomerizations has not been described in the literature so far. Taking into account its structure, it may emerge to be a more active catalyst in the investigated reactions than the older generation of titanium-silicate catalysts.

2. Results and Discussion

2.1. Characteristics of the SBA-16 and Ti-SBA-16

The N₂ adsorption–desorption isotherms at 77 K are presented in Figure 3. They are very similar and belong to type IV according to the IUPAC classification [33]. Between relative pressures of 0.35 and 0.7, capillary condensation steps were observed, which indicates the presence of mesopores. The hysteresis loop H2 was identified. On the basis of the N₂ isotherms the presence of cage-like mesopores connected by relatively narrow openings can be postulated in two materials [34].

![Figure 3. Nitrogen adsorption–desorption isotherms at 77 K of SBA-16 and Ti-SBA-16.](image-url)
The N₂ adsorption on SBA-16 at low relative pressures was quite higher than on Ti-SBA-16. The reason was the higher surface area of pristine material. The specific surface areas calculated using the Brunauer–Emmett–Teller (BET) method were equal to 727 and 663 m²/g for SBA-16 and Ti-SBA-16, respectively. However, the pore volume was identical and was equal to 0.540 cm³/g for both materials. These values are typical for SBA-16 materials also containing Ti [30,34].

As was shown in Figure 2, the SBA-16 has two types of pores with different diameters: cage and entrance to the cage. The pore size distribution of cage diameters was calculated on the basis of the adsorption branch in Figure 3 and is presented in Figure 4. The pore size distribution of diameters at the entrance to the cage was calculated from the desorption branch in Figure 3 and is presented in Figure 5. We previously presented more details of this method [35]. The diameters of the entrances to the cages were slightly narrower after impregnation. The bimodal shape of the cage size distribution for Ti-SBA-16 was observed (Figure 4), and the second peak for Ti-SBA-16, with a maximum at 6.3 nm, appeared. The reason for this was that Ti was partially incorporated into the silica structure. The ionic radius of Ti⁴⁺ (74.5 pm) is considerably higher than that of Si⁴⁺ (54 pm). The incorporation of Ti was also confirmed by the XRD (X-Ray Diffraction) results (moving of the maximum of 110 peak to lower angle—Figure 6) and from the UV-Vis (Ultraviolet-Visible spectroscopic results (presence of absorption bands at 220 and 249 nm—Figure 7).

The small XRD angles of SBA-16 and Ti-SBA-16 are shown in Figure 6. Three diffraction peaks indexed as 110, 200, and 211 are characteristic for mesoporous materials and therefore also for SBA-16 [36]. They indicate a cubic structure with space group Im3m. Only the 110 peak is clearly seen (2θ = 0.83° for SBA-16 and 0.78° for Ti-SBA-16) in Figure 6. The very weak reflections at 2θ equal to 1.2° (200) and 1.5° (211) can only be observed at high magnification. One can conclude that the pore properties were slightly affected by the insertion of titanium. On the basis of the XRD spectra in the wide-angle region it was concluded that the pore paths in the sample are partially filled with TiO₂.

**Figure 4.** Cage diameter distribution calculated by the Barrett–Joyner–Halenda (BJH) method from the adsorption branch for the SBA-16 and Ti-SBA-16.
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![Figure 5. Diameter at the entrance to the cage distribution calculated by the BJH method from the desorption branch for the SBA-16 and Ti-SBA-16.](image)

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![Figure 6. XRD (X-ray Diffraction) patterns of the SBA-16 and Ti-SBA-16 materials.](image)

Ultraviolet and visible (UV-Vis) light spectroscopy enabled confirmation of the introduction of titanium in the catalyst structure (Figure 7). In the UV-Vis spectrum, characteristic absorption bands can be observed at 220 and 249 nm, which confirm the incorporation of titanium into the silica structure. In addition, the wide band at 312 nm indicates the presence of titanium oxide (anatase) in the pores of the catalyst. The UV-Vis spectrum for the Ti-SBA-16 catalyst is consistent with the literature data [37].

![Figure 7. UV-Vis (Ultraviolet–Visible) spectrum of the Ti-SBA-16 material.](image)

The FTIR (Fourier-Transform Infrared) spectroscopy analysis confirmed the structure of the synthesized material. The FTIR spectrum of Ti-SBA-16 (Figure 8) shows the absorption bands characteristic for titanium silicate materials. The band at 445 cm⁻¹ is attributed to deformation bending vibrations of the Si–O–Si groups during which the angle between bonds changes, and symmetrical valence vibrations during which the bond lengths change. The band at 789 cm⁻¹ indicates the presence of amorphous silica. Another band (962 cm⁻¹) confirms the incorporation of titanium into the silica structure. It is associated with the isomorphic substitution of Si by Ti ions and is attributed to the stress of polar Si-O-Ti bonds or the presence of the Ti=O group (titanyl group) in the silica material. The band at 1062 cm⁻¹ is attributed to the presence of Si-O-Si bonds occurring in the

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SEM (Scanning Electron Microscope) images revealed that the particles of Ti-SBA-16 have non-uniform particle morphology; spherical particles were also observed (Figure 9).

The Si and Ti contents were estimated on the basis of the XRF (X-ray Fluorescence) method, and were equal to 36.8 and 9.6 wt%, respectively. The Ti content determined by the EDX (Energy Dispersive X-ray) spectroscopic method was 4 wt%. The different values for Ti indicates that about 60% of titanium is placed inside pores and about 40% on the surface of the SBA-16, which is consistent with XRD results.
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Figure 8. FTIR spectrum of the Ti-SBA-16 material.

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Figure 9. SEM (Scanning Electron Microscope) image of the Ti-SBA-16 catalyst.

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2.2. Studies on the Isomerization of Limonene over the Ti-SBA-16 Catalyst

The studies showed that, in the process of isomerization/dehydroaromatization of limonene over the Ti-SBA-16 catalyst, the main products were: terpinolene, α-terpinene, γ-terpinene, and p-cymene. Figures 10–12 show that, in general, as the reaction time increased, the yield of these products, as well as the conversion of limonene, also increased. The major product is usually terpinolene, except for the reaction time of 1440 min, where p-cymene predominates in the post-reaction mixture at 150 and 170 °C (Figures 10 and 12). The largest increase in the conversion of limonene was observed for short reaction times. At the lowest processing temperature (150 °C) and for the reaction time of 120 min, the conversion of limonene was 30 mol%, while after 1440 min it reached a value of 56 mol% (Figure 10). Among the limonene isomerization products, the highest...
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![Figure 10](image1.jpg)

**Figure 10.** Influence of reaction time on the yield of products of the isomerization of limonene. Amount of the catalyst 0.75 g (15 wt% in relation to mass of limonene). The reaction was performed at 150 °C. (The experimental error was 1 mol%).

![Figure 11](image2.jpg)

**Figure 11.** Influence of reaction time on the yield of products of the isomerization of limonene at 160 °C. Amount of the catalyst 0.75 g, which is 15 wt% in relation to mass of limonene. (The experimental error was 1 mol%).
which indicates the small presence of by-products in the final mixture. The highest yield of carvacrol while a reduction in the yield of terpinolene to 12 mol% is observed. (48 mol%) at 190 °C was also obtained for this reaction time. It is also worth noting that for the reaction time of 300 min the value of the conversion of limonene and the sum of the yields of the main products are similar in value, which indicates the small presence of by-products in the post-reaction mixture. Further extending the time of the process leads to the increase in the conversion of limonene to 92 mol%, as well as an increase in the yield of its isomerization/dehydroaromatization products (Figure 12). A comparison of the results shows that it is possible to obtain a yield of 39 mol% for terpinolene after 300 min of processing time, while the conversion of limonene after this time reached the value of 78 mol%. A high yield of α-terpinene (20 mol%) was also obtained for this reaction time. It is also worth noting that for the reaction time of 300 min the value of the conversion of limonene and the sum of the yields of the main products are similar in value, which indicates the small presence of by-products in the post-reaction mixture. Further extending the time of the process leads to the increase in the conversion of limonene to 92 mol%, and simultaneously the yield of p-cymene increased to 34 mol% (for the reaction time of 1440 min), while a reduction in the yield of terpinolene to 12 mol% is observed.

2.3. Studies on the Isomerization of S-Carvone over the Ti-SBA-16 Catalyst

Our research results showed that the main product of the isomerization of S-carvone over the Ti-SBA-16 catalyst is carvacrol. Figures 13–15 show that, as the duration of the isomerization process is extended, the conversion of S-carvone and the yield of carvacrol increase, regardless of the amount of the catalyst used. Moreover, increasing the content of the catalyst in the reaction mixture increases the value of these two properties. At lower catalyst contents (5 and 10 wt%) and in the studied temperature range, the values of the conversion of S-carvone and the yield of carvacrol are similar, which indicates the small presence of by-products in the final mixture. The highest yield of carvacrol (48 mol%) at 190 °C was obtained at the highest content of the catalyst in the reaction mixture. At the
same temperature, but with three times lower catalyst content (5 wt%), the yield of this product was only 6 mol%.

**Figure 13.** Influence of the reaction time and catalyst content on the conversion of S-carvone and the yield of carvacrol at 190 °C. (The experimental error was 1 mol%.)

**Figure 14.** Influence of the reaction time and catalyst content on the conversion of S-carvone and the yield of carvacrol at 200 °C. (The experimental error was 1 mol%.)

**Figure 15.** Influence of the reaction time and catalyst content on the conversion of S-carvone and the yield of carvacrol at 210 °C. (The experimental error was 1 mol%.)
Figure 14 shows that an increase in temperature by 10 °C (up to 200 °C) causes an increase in the conversion of S-carvone and also an increase in the yield of product (carvacrol) in the range of the studied reaction times. This is especially noticeable at lower catalyst contents (5 and 10 wt%). A comparison of Figures 11–13 shows that the highest yield of carvacrol (65 mol%) was obtained at 200 °C and at the highest content of catalyst in the reaction mixture. However, at the higher process temperature and with the highest catalyst content (15 wt%), the difference between the values of the conversion of S-carvone and the yield of carvacrol increases, which indicates the greater presence of by-products in the final mixture.

An increase in the temperature of S-carvone isomerization to 210 °C (Figure 15) causes an increase in substrate conversion for all catalyst contents in the reaction mixture (5, 10, and 15 wt%), as well as an increase in the yield of the main product for lower catalyst contents (5 and 10 wt%). At these lowest catalyst contents, the values of the conversion of S-carvone and the yield of carvacrol are similar, indicating the small proportion of by-products in the final mixture. At the highest catalyst content (15 wt%), only a slight increase in the yield of carvacrol is observed; however, at these processing conditions, the yield of by-products increases.

It is worth noting that both limonene and S-carvone undergo isomerization over the Ti-SBA-16 catalyst synthesized in this work. However, a comparison of these two processes shows that the isomerization of limonene is a more complicated process, which is carried out in many stages (one of which is the dehydroaromatization of isomerization products to p-cymene) and produces several products whose yield changes during the process. This then requires that the post-reaction mixture after the isomerization of limonene be separated in order to obtain compounds of high purity, which involves additional processing costs. In contrast, the isomerization of S-carvone is a selective process and leads to one main product of high purity—carvacrol. In the isomerization of limonene, the main product was terpinolene, and its highest yield was 39 mol% after 300 min of process time at 170 °C with the catalyst content of 15 wt%. Under these conditions, limonene conversion reached 78 mol%. In contrast, the highest carvacrol yield (65 mol%) was obtained for the catalyst content of 15 wt% at 200 °C, and with S-carvone conversion of 79 mol%. When comparing the processes of isomerizations of limonene and S-carvone, one should also pay attention to the differences in boiling points of the tested olefinic compounds (limonene 176 °C, S-carvone 231 °C), so that tests for limonene could be conducted at lower temperatures than for S-carvone. However, this could have a slightly negative effect on the results for S-carvone if mainly taking into account the raw material conversion.

3. Materials and Methods

3.1. Raw Materials for the Synthesis of the Ti-SBA-16 Catalyst

For the synthesis of the Ti-SBA-16 catalyst the following raw materials were used: hydrochloric acid (HCl, 37%, Hartim, Szczecin, Poland), Pluronic F127 (Aldrich, MW = 5800, St. Louis, MO, USA) as a template, tetraethyl o-silicate (TEOS, 98%, Aldrich, St. Louis, MO, USA) as a silica source, and tetraisopropyl o-titanate (TiPOT, >98%, Merck, Schuchardt OHG Hohenbrunn, Hohenbrunn, Germany) as a titanium source.

3.2. The Synthesis and Characterization of the Ti-SBA-16 Catalyst

In the first stage, the SBA-16 material was produced, and then, in the second stage, this material was impregnated with the titanium source to obtain the Ti-SBA-16 catalyst.

The SBA-16 material was produced by the method described by Kleitz et al. [39]. A solution of 288.00 g of deionized water and 11.88 g of a 35–38% aqueous hydrochloric acid was prepared, into which 6.00 g of the template (Pluronic F127) was added at 45 °C. After 30 min of intensive stirring, 18.00 g of butan-1-ol, which acts as a co-surfactant, was added to this mixture. The mixture was maintained under vigorous stirring in a glass reactor for 60 min after which 28.40 g of tetraethyl o-silicate was added. This mixture was kept at 45 °C for 24 h, and then transferred to the autoclave.
where it stayed for another 24 h at 100 °C (without stirring). The resulting mixture was filtered, dried in an air atmosphere at 100 °C for 24 h, and then calcined for 6 h at 550 °C (using a temperature rise of 2 °C/min) to remove the template from the SBA-16 channels.

The impregnation of the SBA-16 material with titanium was performed with an alcohol solution of tetraisopropyl titanate. First, the SBA-16 material, which was produced as mentioned above, was crushed in a mortar and then introduced into the 250-cm³ glass reactor. A mixture of tetraisopropyl o-titanate and butanol was prepared in a 1:10 molar ratio, respectively, and then added dropwise into the reactor. The mixture thus obtained was kept at 45 °C for 24 h with vigorous stirring. Subsequently, the precipitate was filtered, washed on the filter with about 5 L of deionized water, dried in an air atmosphere at 100 °C for 24 h, and then calcined at 550 °C for 6 h (temperature rise of 2 °C/min) [40].

The synthesized Ti-SBA-16 catalyst was characterized by various instrumental methods. X-ray powder diffraction (XRD) investigations were performed using the Empyrean, PANalytical diffractometer, and the measurements were collected at ambient conditions using copper radiation (Kα1 = 0.154056 nm), and the X’Pert HighScore software used to analyze the patterns.

Confirmation of the inclusion of titanium in the SBA-16 structure was examined using the UV-VIS method in the wavelength range from 200 to 600 nm with a JASCO V-650 spectrophotometer. The FTIR analysis was performed by a Thermo Nicolet 380 spectrophotometer.

The textural parameters were calculated on the basis of N₂ adsorption-desorption isotherms at 77 K by means of the Quantachrome QUADRASORB evo Autosorb Automated Gas Sorption System. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) equation. The total pore volume was calculated on the basis of the N₂ volume adsorbed at a relative pressure p/p₀ = 0.99. The Barrett–Joyner–Halenda (BJH) method was applied for mesopore volume calculations and the range of dominant pores.

Elemental analysis was performed with the Epsilon3 (Malvern Panalytical, Malvern, UK) energy dispersive X-ray fluorescence (EDXRF) spectrometer.

Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4700 microscope (Hitachi, Tokyo, Japan) equipped with the secondary electron detector and an energy-dispersive X-ray analyzer (EDX) for elemental analysis of the surface.

3.3. Raw Materials for the Isomerization Processes

For the isomerization of limonene and S-carvone, the following raw materials were used: R- (+)-limonene (>93%, Sigma, St. Louis, MO, USA), and S- (+)-carvone (>96%, Acros Organics, Morris Plains, New Jersey, USA).

3.4. The Method of the Isomerization of Limonene and S-Carvone over the Ti-SBA-16 Catalyst

Studies on the influence of temperature, content of the Ti-SBA-16 catalyst, and reaction time on the course of the isomerizations of limonene and S-carvone were performed in the 25-cm³ glass reactor under air atmospheric pressure. The catalyst in the amount of 5 to 15 wt% (in relation to amount of limonene or S-carvone) was first introduced into the glass reactor equipped with a reflux condenser and a magnetic stirrer with heating function. Then, the organic raw material was introduced into the glass reactor and heating commenced. The process was performed from 60 to 1440 min for the isomerization of limonene and from 60 to 300 min for the isomerization of S-carvone. The isomerization of limonene was performed in the temperature range of 150–170 °C, while the isomerization of S-carvone was performed in the temperature range of 190–210 °C. Studies were also carried out over the unmodified SBA-16 material, but it turned out to be inactive. Moreover, the blank experiment in which no catalyst was used showed that no products were formed in the reaction mixture.

3.5. The Identification of Products by the Gas Chromatography Method

The samples for the analysis by means of gas chromatography (GC) were prepared in the following way: first, the catalyst was separated from the post-reaction mixture by centrifuging, and next 0.250 g
of the resulting solution was diluted with 0.750 g of acetone. The qualitative analyses were performed with the help of reference substances by the external standard method. The chromatographic analysis for each post-reaction mixture was performed three times.

The GC system consisted of a FOCUS apparatus (Thermo Company, Waltham, MA, USA) equipped with a flame-ionization detector (FID), a capillary column (ZEBRON ZB-WAXplus type, 0.32 mm × 30 m × 0.5 μm, filled with polyethylene glycol), and an autosampler. The conditions of analyses were as follows: helium pressure 60 kPa, temperature of the sample chamber 240 °C, and detector temperature 250 °C. The thermostat temperature was raised according to the following program: isothermally to 60 °C for 2 min., increase in temperature at a rate of 10 °C/min to 240 °C, isothermally at 240 °C for 4 min, and finally cooling to 60 °C.

The method of calculating the yield of products and the conversion of raw materials used in the studies is shown in Figure 16.

\[
W_{\text{product/limonene or S-carvone}} = \frac{\text{amount of moles of product}}{\text{amount of moles of limonene (or S-carvone) introduced into reactor}} \times 100 \text{ [mol%]}
\]

\[
C_{\text{limonene (or S-carvone)}} = \frac{\text{amount of moles of limonene (or S-carvone) consumed}}{\text{amount of moles of limonene (or S-carvone) introduced into reactor}} \times 100 \text{ [mol%]}
\]

**Figure 16.** Method of calculating the yields of products and the conversions of raw materials.

4. Conclusions

The Ti-SBA-16 catalyst is effective for the isomerizations of limonene and S-carvone. The isomerizations of these olefinic compounds of natural origin lead to valuable products with numerous applications, especially in organic syntheses, as well as in the food and cosmetics industries and in medicine.

In our previously published studies, we have described in detail the isomerization of limonene only over Ti-SBA-15 and Ti-MCM-41 catalysts and also over natural zeolite—clinoptilolite [1–3]. In the isomerization with the Ti-SBA-15 catalyst, the main products of the process was p-cymene and α-terpinene. p-Cymene was obtained with the yield of 51 mol% at 160 °C, with the catalyst content of 15 wt%, and after the reaction time of 1380 min. Simultaneously, at the same temperature and with the same catalyst content, but for the shorter reaction time of 180 min, the high yield value of 31 mol% for α-terpinene was obtained. The main products of the isomerization of limonene over the Ti-MCM-41 catalyst were p-cymene and terpinolene. The highest yields of these products were obtained at the temperature of 170 °C with the catalyst content of 15 wt%. After 1440 min of process time, the yield of p-cymene reached 46 mol%. However, after the reaction time of 240 min, and at the same temperature and catalyst content, the highest yield of terpinolene amounted to 22 mol%. The use of natural clinoptilolite as the catalyst also led to high yields of terpinolene and p-cymene. Already after 30 min, the yield of terpinolene amounted to 39 mol% at the process temperature of 175 °C with the catalyst content of 15 wt%. Under the same temperature and catalyst content, the highest p-cymene yield was obtained after 1440 min and it amounted to 45 mol% with the limonene conversion of 63 mol%.

In comparison with previous studies on the isomerization of limonene (Ti-SBA-15 and Ti-MCM-41 catalysts) at the same catalyst content (15 wt%), the use of the new Ti-SBA-16 catalyst allowed for better results for terpinolene. This compound was obtained with the same yield (39 mol%, at the temperature of 170 °C) as when clinoptilolite was used (39 mol%, at the temperature of 175 °C) and with higher yield than isomerization with the previous Ti-SBA-15 catalyst. With the latter-mentioned catalyst, the highest yield of terpinolene amounted to only 16 mol% at 160 °C. In contrast, the highest yield of terpinolene (22 mol%) was obtained over the Ti-MCM-41 catalyst and at the temperature of 170 °C. In addition, the isomerization of limonene with the new Ti-SBA-16 catalyst under the same temperature conditions...
(170 °C) and catalyst content (15 wt%) allowed for the production of significant yields of p-cymene (34 mol%) and α-terpinene (32 mol%), after the reaction times of 1440 and 300 min, respectively.

In the case of S-carvone isomerization over the Ti-SBA-16 catalyst, the highest carvacrol yield (65 mol%) was obtained at 200 °C and at the highest catalyst content of 15 wt%. A similar yield (61 mol%) was obtained with the same catalyst content (15 wt%), but at a higher process temperature of 210 °C. It should be noted that at higher temperatures, the yield of carvacrol increased faster for shorter reaction times. However, the yield of by-products was higher, as evidenced by the difference between the value of the conversion of S-carvone and the value of the yield of the main product.

Comparison of the processes of isomerization of limonene and S-carvone shows that isomerization of limonene is a more complex process that leads to three products, which are then dehydroaromatized to p-cymene. In contrast, the isomerization of S-carvone is a more selective process, resulting mainly in the formation of carvacrol. The isomerization process is an example of heterogeneous catalysis, its use allows easy separation of the catalyst from the post-reaction mixture, and provides the possibility of its reuse (directly or after regeneration). Raw materials for isomerization processes (limonene and S-carvone) were obtained from plant waste (orange peels and caraway processing), which offers double benefits. Firstly, it allows for the obtainment of relatively inexpensive olefinic compounds for the isomerization process, and secondly, it allows for waste management. The isomerization of S-carvone seems to be particularly profitable for countries involved in the processing of oranges and caraway due to the high selectivity of this process. In addition, this isomerization does not require the use of organic solvents, which means that it does not place a heavy burden on the environment. Research shows that titanium silicate materials are active and very effective catalysts that can be used in many other olefinic isomerization processes. As a result, it will be cost-effective to produce compounds that will find applications in cosmetics, perfumery, and the food industries, as well as in medicine.

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