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Influence of the Titanium Content in the Ti-MCM-41 Catalyst on the Course of the α -Pinene Isomerization Process

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Abstract: Titanium-containing mesoporous silica catalysts with different Ti contents were prepared by the sol–gel method, whereby the molar ratios of silicon to titanium in the crystallization gel amounted to, respectively, 40:1, 30:1, 20:1 and 10:1. The produced Ti-MCM-41 materials were characterized by the following instrumental methods: XRD, UV-Vis, FT-IR, SEM, and XRF. Textural parameters were also determined for these materials by means of the N₂ adsorption/desorption method. The activities of these catalysts were investigated in the α -pinene isomerization process. The most active catalyst was found to be the material with the molar ratio of Si:Ti equal to 10:1, which contained 12.09 wt% Ti. This catalyst was used in the extended studies on the α -pinene isomerization process, and the most favorable conditions for this reaction were found to be temperature of 160 °C, reaction time of 7 h, with the catalyst composition of 7.5 wt% relative to α -pinene. These studies showed that the most active catalyst, at the best reaction conditions, allowed for the attainment of 100% conversion of α -pinene over a period of 7 h. After this time the selectivities (in mol%) of the main products were as follows: camphene (35.45) and limonene (21.32). Moreover, other products with lower selectivities were formed: γ -terpinene (4.38), α -terpinene (8.12), terpinolene (11.16), p-cymene (6.61), and α -phellandrene (1.58).

Keywords: Ti-MCM-41; isomerization; α -pinene; camphene; limonene; natural compounds; green chemistry

1. Introduction

Porous materials [1] have found applications in many fields, e.g., in catalysis [2], nanotechnology [3], medicine [4], in processes of liquid and gaseous sewage treatment [5], and in separation of mixture components [6]. Until the 1990s, the most commonly used materials in these fields were molecular sieves, especially zeolites. However, one of the few disadvantages of zeolites is their small pore diameter. The need to solve this problem prompted researchers to look for materials with a regular structure, such as zeolites, but with a larger pore diameter [7].

A breakthrough in this field occurred in 1990, when two independent research teams produced mesoporous silica with a strictly defined internal structure. Yanagisawa et al., using layered kanemite and surfactants, obtained mesoporous silica FSM-16 (folding sheet materials using C16 surfactant), which had excellent structural features [8].



The second method of producing mesoporous silica, known as MCM-41 (Mobil Composition of Matter No. 41), was presented by scientists from Mobil Oil [9]. The MCM-41 belongs to the M41S family and is one of the most-researched mesoporous materials. It is characterized by a hexagonal arrangement of cylindrical pores with a narrow diameter distribution and a large inner surface [10]. Despite the fact that the structure of the walls of the MCM-41 material is amorphous, it has a crystalline arrangement, which results from its ordered and periodically repeated structure [11]. This material is obtained by combining the sol–gel method with the method of templating, which allows for the production of materials with ordered, uniform pores. This process involves the use of surfactants or block polymers, which under appropriate conditions, form micelles on which polycondensation of silica monomers occurs. After completing the sol-gel process, the matrix is removed in the extraction or calcination process and a material with regular pores is obtained, the size of which corresponds to the size of the removed template [12]. The great advantage of the MCM-41 material is the easiness of its modification. One of these methods is based on the incorporation of titanium atoms into the silica structure, already at the stage of gel synthesis. For this purpose, a sufficient amount of the Ti-containing compound is added to the crystallization gel [13]. The Ti-MCM-41 materials produced in this way have found many applications as catalysts for reactions involving various organic compounds [14–16]. Mesoporous silica materials can also be modified by the grafting method. In this method, metal atoms are placed on the surface of the mesoporous material. Using both direct and grafting methods, MCM-41 materials containing the following metals were successfully synthesized: Mo [17], Ni [18], Co [19], Ga [20], Zr [21], Cu [22], Pd [23] or Fe [24]. In addition, studies were conducted on the conditions for obtaining the siliceous structure of MCM-41 (including Ti-MCM-41), so that the obtained material was characterized by greater stability in water at elevated temperatures and an ability to inhibit the phenomenon of metal leaching (Ti leaching in the case of Ti-MCM-41 catalysts) [25,26].

Alpha-pinene is a natural terpene found in the oils of coniferous trees, especially the pine, from which the compound's name is derived. Currently, the isomerization of α -pinene on an industrial scale is performed on TiO₂ modified with sulfuric acid at 140 °C. The main products of this reaction are bicyclic products, including camphene, bornylene, tricyclene, α -fenchene (formed with a total selectivity of 70 mol%), and monocyclic products, including limonene, α - and γ -terpinene, terpinolene, cymene and α -phellandrene [27]. These products are shown in Figure 1.



Figure 1. Main products of α -pinene isomerization process and paths of their formation.

The goal of the α -pinene isomerization process is to produce camphene with the highest selectivity. Camphene is an added value product due to its wide use and price. An interesting historical aspect is that in the middle of the 19th century, a related product—camphine (a mixture of turpentine dissolved in oil with some camphor)—was used as fuel for lamps [28], but due to its explosiveness and quick burning, its use was abandoned. Currently, camphene is mainly used as an intermediate in light organic synthesis, inter alia, in the production of toxaphene (an insecticide) [29]. In addition, in the reaction of camphene with acetic acid, isobornyl acetate is formed, which is an intermediate in the production of synthetic camphor [30]. Camphene is also used in the production of terpenecyclohexanols, which are an alternative to sandal oil and are widely used in the perfumery industry [31]. Camphene is also used as a fragrant and flavor substance. The mixture of camphene with pinene and cineole has medicinal properties and is used for kidney and hepatobiliary disorders [32]. Moreover, N. Girola et al. confirmed the anticancer properties of camphene [33].

In order to lower the temperature of α -pinene isomerization and to achieve the highest selectivity of transformation to the desired product, camphene, new catalysts for carrying out the α -pinene isomerization are sought. Chunhua Wu et al. applied the SBA-15 catalyst modified with phosphotungstic acid for the isomerization of α -pinene [34]. The reaction was performed at 130 °C for 2 h, after which the conversion of α -pinene was about 95%, while the camphene selectivity was about 48.5 mol%. J. Wu et al. examined Al-MCM-41 catalysts with different SiO₂ to Al₂O₃ ratios in the α -pinene isomerization process. The most active catalyst among the tested materials was the one with a molar ratio of 20:1 [35]. The reaction was accomplished at 160 °C, and the main products were camphene and limonene. Another team researching the isomerization of α -pinene using mesoporous catalysts is F. Launay et al. [36]. They applied the Ga/SBA-15 catalyst obtained by various methods (direct method and post-synthesis grafting method). At 80 °C, after 1 h, using the catalyst obtained by the direct method, they received camphene with a yield of 28%. G. Nie et al. used the MCM-41 catalyst modified by the wet impregnation method with tungstophosphoric acid [37]. They achieved the highest selectivity of transformation to camphene (40.6 mol%) and limonene (11.2 mol%), with 100% conversion of α -pinene, at 160 °C after 3 h.

In our previous work [38,39], we presented the isomerization of α -pinene over Ti-SBA-15 catalysts with different titanium contents. On the basis of the conducted tests, it was shown that the optimal titanium content in the Ti-SBA-15 catalyst is 1.1 wt% with the molar ratio of silicon to titanium in the crystallization gel of 20:1. In addition, the second stage of the research allowed for the selection of the most favorable conditions for the α -pinene isomerization process: temperature = 180 °C, catalyst content = 15 wt%, and reaction time = 6 h. The selectivities (in mol%) of the products were as follows: camphene 25.93, limonene 23.51, and γ -terpinene 18.74. Moreover, the formations (and selectivities) of the following products were also determined: α -terpinene (8.04), terpinolene (12.90), p-cymene (4.66), and α -phellandrene (2.05). During the research, it was noticed that a significant extension of the reaction time lead to subsequent reactions in which monocyclic terpenes are dehydrogenated to p-cymene [38,39].

Other micro- and mesoporous materials used as catalysts in the α -pinene isomerization process are: TCA/Y zeolite [40], desilicated ZSM-5, ZSM-12, MCM-22, and ZSM-12/MCM-41 [41], zeolite BETA [42], and SO₄/ZrO₂/HMS [43]. In addition, research was conducted on the use of natural materials (clinoptilolite, sepiolite, and montmorillonite) in the α -pinene isomerization process [44–48].

As shown above, mesoporous silicate catalysts, particularly those containing titanium, may be active catalysts in the α -pinene isomerization process, e.g., the Ti-SBA-15 catalyst. The Ti-MCM-41 catalyst, as compared with the Ti-SBA-15 material, is obtained in a simpler way (without the autoclaving step) and from cheaper raw materials, hence its synthesis is associated with the consumption of less energy and at the same time is more economical. Therefore, it was decided to determine whether the Ti-MCM-41 catalyst could also be used in the isomerization process of α -pinene. The purpose of this work was to investigate the effect of titanium content in the Ti-MCM-41 catalysts on the course of the α -pinene isomerization process. A series of studies on the α -pinene isomerization process

was conducted to select the most active catalyst. Subsequently, the influence of temperature, catalyst content, and reaction time were studied over the selected, best, catalyst. Our aim at this stage of tests was to determine the most favorable conditions for α -pinene isomerization over the Ti-MCM-41 catalyst. This was accomplished by quantitatively characterizing the main functions describing this process: selectivities of the appropriate products (mainly camphene) and the conversion of α -pinene. The Ti-MCM-41 materials were first characterized using the following instrumental methods: XRD, UV-Vis, FT-IR, SEM, and XRF. Also textural parameters were determined for these materials with the help of the N₂ adsorption/desorption method.

2. Results and Discussion

2.1. Characteristics of Catalysts

The relative titanium content in the Ti-MCM-41 catalysts was determined using the XRF method. The amount of Ti depends on the molar ratio of silicon to titanium in the crystallization gel. Thus the following compositions of Ti (in units of wt%) for the respective Si:Ti ratios were obtained: 3.12 for the 40:1 ratio; 4.51 for 30:1, 5.58 for 20:1, and 12.09 for 10:1.

Low-angle X-ray diffraction studies allowed for the confirmation that the MCM-41 structure for all tested materials was indeed obtained. Diffraction patterns presented in Figure 2 show one very intense peak corresponding to reflex (100), and in the case of the catalyst with the 40:1 Si:Ti molar ratio in the crystallization gel, two small peaks corresponding to reflexes (110) and (200). These data are consistent with the literature and confirm the hexagonal nature of the mesoporous silica with the MCM-41 structure. The maximum of the reflex (100) shifted to the higher 20 as the Ti content increased. This indicates that interplanar d100 spacing decreased because of the incorporation of Ti atoms, instead of Si atoms, into the MCM-structure. Because of the difference between the ionic radii of Ti⁴⁺ (0.068 nm) and Si⁴⁺ (0.041 nm), the substitution of Ti cations for Si ones distorts the tetrahedral coordination geometry around the Ti. The incorporation of Ti into the structure disordered the hexagonal arrangement in the Ti-MCM-41 materials, which increases with the amount of Ti. Moreover the intensity of the reflex (100) decreased with Ti content. This phenomenon has been previously reported [49]. These authors postulated that a lamellar phase is formed, which would cross-link and subsequently form the hexagonal phase.



Figure 2. Low-angle X-ray diffraction patterns for Ti-MCM-41 samples with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).

Figure 3 shows the high-angle XRD patterns of the Ti-MCM-41 materials. Each pattern exhibits a broad peak at 2 θ from 15 to 30°, which is typical for amorphous silica [50]. The peak corresponding to the anatase form of TiO₂ at 2 $\theta \approx 25^{\circ}$ was absent for all studied Ti-MCM-41 materials. This is in line with the results obtained by the UV-VIS method, which did not confirm the presence of anatase in the Ti-MCM-41 materials, as mentioned below.



Figure 3. High-angle X-ray diffraction data for Ti-MCM-41 samples with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).

In the UV-Vis spectrum of Ti-MCM-41 materials (Figure 4), a characteristic absorption band centered at the 215 nm wavelength is present, which confirms the coordinative inclusion of titanium (in the form of Ti^{+4}) in the silica structure. The band in the range of 225–260 nm is responsible for the occurrence of titanium in the form of dimers (Ti–O–Ti) on the surface of the catalyst [51]. In addition, in these spectra there is an absorption band at a wavelength of about 295 nm, which is derived from titanium having the coordination number of 5 or 6. The change in the coordination number of titanium can result from the coordination of water molecules by titanium included in the silica structure, which mainly occurs on the surface of the catalyst. The lack of a peak at 330–350 nm indicates the absence of TiO_2 in the form of anatase in the studied Ti-MCM-41 materials [52].



Figure 4. UV/Vis spectra of the Ti-MCM-41 catalysts with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).

In the IR spectrum of Ti-MCM-41 materials (Figure 5), the following main absorption bands can be observed: 440, 800, 960, 1000-1300, 1625-1650, 2350, and 3500 cm⁻¹. The band in the range of $1625-1650 \text{ cm}^{-1}$ is attributed to the bending vibrations of the -OH groups, coming from the water molecules adsorbed on the surface of the material. The bands at the 440 and 800 cm⁻¹ wavenumbers are attributed to the bending deformation vibrations of the Si–O–Si groups, which cause a change in the angle between the bonds, and symmetrical valence vibrations, which cause changes in the lengths of the bonds. The band in the range of $1000-1300 \text{ cm}^{-1}$ is attributed to the presence of Si–O–Si bonds, which exist in the siliceous structure and are characteristic for it. The 960 cm^{-1} band present in the materials is associated with the isomorphic substitution of Si by Ti ions and it is attributed to the stresses of the Si–O–Ti polar bonds or the presence of the titanyl group, >Ti=O. This band confirms the inclusion of titanium in the structure of silica [53]. It can be seen that as the titanium content increases, the intensity of this band increases. In addition, the 960 $\rm cm^{-1}$ band is attributed to the stretching vibrations of the Si–OH groups that are on the surface of the material [54]. The 3500 cm⁻¹ band is associated with the presence of hydroxyl groups on the surface of the catalysts, while the band at 2350 cm⁻¹ indicates the presence of carbon dioxide in the materials. The obtained spectra are in accordance with literature data [55].



Figure 5. FT-IR spectra of Ti-MCM-41 catalysts with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).

In the SEM photographs of the Ti-MCM-41 materials (Figure 6), well-formed spherical particles, with sizes in the range of $0.2-1 \mu m$, can be observed. These can combine into larger structures, which is typical for this type of material.



Figure 6. SEM pictures of Ti-MCM-41 catalysts with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).

Table 1 shows the specific surface area, S_{BET} , and the pore volume Vp of the catalysts. A slight decrease in the specific surface area of the materials along with the increase in the titanium content indicates small changes in the structure of the catalysts. In addition, similar Vp values suggest that pores are similar in size and are not blocked by TiO₂ molecules.

Table 1. Textural parameters for the Ti-MCM-41 catalysts with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).

Material	S_{BET} (m ² /g)	Vp (cm ³ /g)
Ti-MCM-41 10:1	902	0.839
Ti-MCM-41 20:1	1014	0.839
Ti-MCM-41 30:1	1071	0.826
Ti-MCM-41 40:1	1063	0.840

All synthesized Ti-MCM-41 materials exhibit a type IV isotherm with H1 hysteresis loops at intermediate relative pressures (Figure 7). This indicates well-shaped pores with a hexagonal shape. Similarly shaped isotherms also indicate similar pore sizes [56]. Thus, the similar position of the adsorption branch inflection of every isotherm suggests that all Ti-MCM-41 materials have similar pore sizes. The specific surface area for high Si content (Si:Ti 40:1 and 30:1) are nearly the same. However, further decreasing the Si content (Si:Ti 20:1 and 10:1) decreased the value of the specific surface area. The analysis of the pore size distribution curves obtained by means of the DFT method (Figure 8) showed that the pores of all the samples exhibited similar pore diameters (3–4.2 nm). The average pore diameter calculated by DFT was equal to 3.53 nm for all Ti-MCM-41 catalysts. Only the pore volume decreased with increasing Ti content. As was mentioned above, Ti was incorporated into the MCM-41 structure, and this inclusion invariably distorts the geometry around Ti from an ideal

tetrahedral coordination. The XRD patterns give evidence that the destruction was dramatic especially for materials with the higher Ti content. On the basis of the investigations performed by all the methods, one can conclude that the pores were not partially blocked but some of them were closed. The contribution of closed pores strongly depended on the Ti content in the structure.



Figure 7. N₂ adsorption–desorption isotherms of Ti-MCM-41 catalysts with different molar ratios of Si:Ti in the crystallization gel (respectively, 40:1, 30:1, 20:1, and 10:1).



Figure 8. Pore-size distribution for Ti-MCM-41 catalysts with different molar ratios of Si:Ti in the crystallization gel.

2.2. Studies on the Catalytic Activity of Ti-MCM-41 Materials

In the first stage of the research, the effect of the molar ratio of silicon to titanium in the crystallization gel (and of the resulting Ti composition) on the activity of the corresponding Ti-MCM-41 material was examined. The parameters of the α -pinene isomerization process were as follows: temperature 160 °C, catalyst content 7.5 wt% in relation to α -pinene, and reaction time 6 h. These parameters have been selected based on the results of our previous studies using Ti-SBA-15 catalysts [39].

The most active Ti-MCM-41 catalyst was used for further research to determine the most favorable conditions for the isomerization of α -pinene (the second stage of our research).

Figure 9 relates to the first stage of testing and shows that the highest conversion of α -pinene (97.08 mol%) was achieved after 6 h for the catalyst designated "Ti-MCM-41 10:1". The remaining catalysts showed significantly lower activity, which shows that increasing the amount of titanium introduced in the structure of silica significantly increases the catalytic activity of the materials. The shape of the curve representing the function of conversion of α -pinene can be approximated by a volcano-dependence presented by Frattini et al. [57]. In this work, similar volcano-dependency between W loading and catalyst activity was presented. For the highest Ti content, the highest conversion of α -pinene is achieved, 97.08 mol%. For three other Si/Ti molar ratios, this conversion function is considerably lower, and amounted to 49.48 mol% (Si/Ti = 20:1), 45.29 mol% (Si/Ti = 30:1) and 39.19 mol% (Si/Ti = 40:1). Higher levels of titanium in the crystallization gel (molar ratio Si:Ti < 10) could no longer be beneficial due to the possibility of anatase formation which would decrease the catalyst activity by blocking the pores. In addition, the number of closed pores could be increased, which would reduce the specific surface area of the catalyst; this tendency is noticeable in Table 1.



Figure 9. The influence of the molar ratio of Si:Ti in the crystallization gel on the conversion of α -pinene and on the selectivities of the appropriate products (temperature 160 °C, catalyst content 7.5 wt%, and reaction time 6 h).

The selectivities of the products were similar for the four tested Ti-MCM-41 catalysts. Among the products, the highest selectivities were achieved for camphene (35 mol%) and limonene (37 mol%). In the case of the Ti-MCM-41 10:1 catalyst, the lower selectivity of limonene results from the subsequent reaction–isomerization of the resulting limonene to terpinenes, terpinolene, and p-cymene.

The second stage of the studies consisted in determining the most favorable conditions for the isomerization of α -pinene over the most active Ti-MCM-41 catalyst. Taking into consideration the results from the first phase of the tests, the Ti-MCM-41 10:1 catalyst containing 12.09 wt% Ti was chosen for the second stage of tests. The influence of the following parameters was investigated: temperature 80–180 °C, catalyst content 2.5-15 wt% in relation to α -pinene, and reaction time from 15 min to 24 h.

Figure 10 shows the effect of temperature in the range of 80–180 °C on the isomerization of α -pinene in the presence of the Ti-MCM-41 10:1 catalyst. The reaction was carried out for 7 h in

the presence of 7.5 wt% of the catalyst. With increasing temperature, the conversion of α -pinene increased to a maximum (100 mol%) for a temperature of 160 °C—below this temperature this function of the isomerization process showed considerably lower values (80 °C–0.10 mol%, 100 °C–6.80 mol%, 120 °C–20.50 mol%, and 140 °C–63.90 mol%). Low values of α -pinene conversion at lower temperatures are most likely associated with limitations in diffusion to the pores of the catalyst. In addition, some pores are unavailable due to the fact that they have been closed. The isomerization reaction probably occurs only in the active titanium centers found on the surface of the catalyst. The increase in temperature causes the molecules of the organic compound to penetrate into the pores more easily and the isomerization reaction can also occur in the active titanium centers present in the catalyst pores. The main reaction products were camphene and limonene, which were formed with similar selectivities throughout the range of temperatures tested (80–160 °C). At 180 °C, the low selectivity of limonene indicates that it has been isomerized to terpinolene, terpinenes, and p-cymene.



Figure 10. The influence of temperature on the conversion of α -pinene and on the product selectivity over Ti-MCM-41 10:1 (catalyst content 7.5 wt% relative to α -pinene, reaction time 7 h).

The next examined parameter was the content of the catalyst involved in the reaction (Figure 11). For this purpose, a series of tests was performed at 160 °C. The tested range of catalyst content ranged from 2.5 to 12.5 wt% relative to α -pinene. With increasing catalyst content, the conversion of α -pinene increased to 100 mol% at the catalyst content of 7.5 wt%—for lower catalyst contents, the number of active titanium sites is insufficient to allow for all of the α -pinene to be consumed. Raising the catalyst content to values above 7.5 wt% did not significantly increase the selectivity of camphene, but contributed to the subsequent reaction, which is the isomerization of limonene.



Figure 11. The influence of the Ti-MCM-41 10:1 catalyst content on the α -pinene conversion and on the product selectivity (temperature 160 °C, reaction time 6 h).

Studies on the effect of reaction time on the course of isomerization of α -pinene were carried out using a larger amount of reaction mixture. In this case, 20 g of α -pinene was mixed with 1.5 g of the Ti-MCM-41 10:1 catalyst, and the samples of the reaction mixture for GC analyses were taken in the range of 15 min to 24 h. In the studied conditions, α -pinene almost completely reacted after 7 h (conversion of α -pinene equal to 97.97 mol%), as depicted in Figure 12. After this time, the main products formed with the highest selectivity are: camphene (35.45 mol%) and limonene (21.32 mol%). Moreover, other minor products (with their calculated selectivities in mol%) were produced: γ -terpinene (4.38), α -terpinene (8.12), terpinolene (11.16), p-cymene (6.61), and α -phellandrene (1.58). After 24 h, it can be noted that in the reaction mixture, limonene, which reacted mainly to form α -terpinene and p-cymene, was significantly reduced.



Figure 12. The influence of the reaction time on the conversion of α -pinene and on the product selectivity (temperature 160 °C, 7.5 wt% Ti-MCM-41 10:1 catalyst content relative to α -pinene).

3. Materials and Methods

3.1. Synthesis of Ti-MCM-41 Catalysts

Ti-MCM-41 catalysts with different molar ratios of silicon to titanium in the crystallization gel (40:1, 30:1, 20:1, and 10:1) were obtained by the method described by M. Grun et al. [58]. The samples of the Ti-MCM-41 catalysts produced in this manner are named respectively: "Ti-MCM-41 40:1", "Ti-MCM-41 30:1", "Ti-MCM-41 20:1", and "Ti-MCM-41 10:1". In the standard synthesis, 17.71 g of cetyltrimethylammonium bromide (99%, Fluka, Poznań, Poland) is dissolved in 324.1 g of deionized water and poured into a glass reactor equipped with a mechanical stirrer. Next, 132.02 g of ammonia (25% aqueous solution, POCh, Gliwice, Poland) is added to the previously prepared solution. In the next step, 422.1 g anhydrous ethanol (analytical grade, POCh, Gliwice, Poland) is added to the resulting mixture. The contents of the reactor are mixed for 15 min, and then a solution containing 33.11 g of tetraethyl orthosilicate, TEOS (98%, Aldrich, Poznań, Poland), is added dropwise. Following that, depending on the catalyst prepared, the appropriate amount of tetrabutyl orthotitanate, TBOT (99%, Fluka, Poland), is added to obtain the following molar ratios of Si/Ti: for 10:1, 5.421 g; for 20:1, 2.708 g; for 30:1, 1.755 g; and for 40:1, 1.354 g. The resulting crystallization gel is then stirred for 2 h and then left for 16 h without stirring at ambient temperature. After this time, the catalyst is filtered, washed with deionized water, and dried at 100 °C for 24 h and then calcined at 550 °C.

3.2. Characteristics of the Ti-MCM-41 Catalysts

The Ti content in each catalyst was calculated using an energy dispersive X-ray fluorescence (EDXRF) spectrometer (Epsilon 3, PANalytical, Almelo, The Netherlands).

For the produced catalysts, XRD analysis was performed in order to determine whether an MCM-41 structure was obtained for all tested materials. The X-ray diffraction (XRD) patterns of the catalysts were recorded by a X-ray diffractometer (Empyrean, PANalytical, Almelo, the Netherlands) using Cu K ($\lambda = 0.154$ nm) as the radiation source in the 2 θ range 0.1–10° with a step size of 0.013, and in the 2 θ range 10–40° with a step size of 0.05.

Textural properties were determined on the basis of nitrogen sorption at -196 °C (QUADRASORB evo Gas Sorption Surface Area and Pore Size Analyzer, Quantachrome Instruments, Boynton Beach, FL, USA). Prior to the sorption measurements all samples were outgassed at 250 °C for at least 20 h. The specific surface area was calculated on the basis of the Brunauer–Emmett–Teller (BET) equation and multi-point method. The relative pressure range was selected on the basis of the linear section of the BET plot, i.e., in the relative pressure range 0.05–0.2. Pore volume distribution, micropore volume V_{micro} , and the mean pore diameter (d_m) were calculated by the density functional theory (DFT) method. The total pore volume (V_{tot}) was obtained from the nitrogen volume adsorbed at a relative pressure of 0.98.

The scanning electron microscope (SEM) micrographs were obtained using ultra-high resolution field emission scanning electron microscope (UHR FE-SEM Hitachi SU8020, Tokyo, Japan) equipped with the secondary electron (SE) detectors and an energy dispersive X-ray detector (EDX).

The incorporation of titanium in the structure of silica was characterized by UV-Vis (V-650, Jasco, Tokyo, Japan) examinations in the wavelength range from 200 to 600 nm. Also, FT-IR spectra were obtained (Nicolet 380, Thermo Fisher Scientific, Waltham, MA, USA) in the range of wavenumbers from 400 to 4000 cm⁻¹.

3.3. Isomerization of α -Pinene

Studies on the influence of titanium content in the Ti-MCM-41 catalysts on the α -pinene isomerization process and the determination of the best conditions for the most active catalyst were carried out in a 25 cm³ glass reactor equipped with a reflux condenser and magnetic stirrer with a heating function. For studies on the isomerization, 4 g of α -pinene (98%, Aldrich, Poland) and the appropriate amount of catalyst were weighed into the reactor, which was then placed in an oil bath. The mixing speed was constant at 400 rpm.

In the first stage of the research, the activities of the Ti-MCM-41 catalysts with different molar ratios of silicon to titanium in the crystallization gel (10:1, 20:1, 30:1, 40:1) were investigated. The reaction temperature was 160 °C, the amount of catalyst amounted to 7.5 wt% relative to α -pinene, and the reaction time was 6 h. In the next stage, the most active catalyst was used to determine the most favorable conditions for the α -pinene isomerization. For this purpose the influence of the following parameters was studied: temperature in the range of 80–180 °C, catalyst content in the range of 2.5–12.5 wt%, reaction time from 15 min to 24 h. During the studies on the influence of reaction time, the amount of the reaction mixture was increased five-fold, and samples were taken at specific intervals.

The procedure for performing the qualitative and quantitative analyses of the post-reaction mixtures using the GC method was presented in our previous work [38]. The most active catalyst and the best conditions of the α -pinene isomerization process were determined on the basis of the mass balances according to which the main functions characterizing the process were determined: the conversion of α -pinene and selectivities of the main product camphene, as well as others (limonene, α -terpinene, γ -terpinene, terpinolene, α -phellandrene, and p-cymene). Selectivities were also determined for the remaining isomerization products that were formed in small amounts: tricyclene, α -fenchene, bornylene, polymer compounds, and oxidation products.

4. Conclusions

The studies show that Ti-MCM-41 catalysts are active in the α -pinene isomerization process, and that the increase in titanium content introduced into the silica structure significantly increases Ti-MCM-41 catalyst activity in this process. On the basis of the tests carried out, it was shown that the most active catalyst was the one with a Si:Ti molar ratio of of 10:1 in the crystallization gel, which contains 12.09 wt% Ti. In addition, the most favorable conditions for the isomerization of α -pinene were: temperature 160 °C, reaction time 7 h, and catalyst content of 7.5 wt% relative to α -pinene. It has also been shown that a significant increase in the reaction time leads to subsequent reactions in which monocyclic terpenes are transformed to p-cymene. The use of the optimal Ti-MCM-41 10:1 catalyst can yield 100% conversion of α -pinene, and, with the relatively high product selectivities, many useful intermediates (camphene, limonene, γ -terpinene, α -terpinene, terpinolene, p-cymene, and α -phellandrene) for various industries can also be formed in this process.

The Ti-MCM-41 catalysts, due to their morphology (higher amount of introduced titanium, higher specific surface area), showed better activity in the α -pinene isomerization process than Ti-SBA-15 catalysts. Their use significantly reduced the amount of catalyst used for 100 mol% substrate conversion, from 15 wt% for Ti-SBA-15 [39] to 7.5 wt% for Ti-MCM-41. The use of the Ti-MCM-41 catalyst also allowed for the reduction of the reaction temperature from 180 to 160 °C. In addition, the selectivities of the main products changed because camphene and limonene were produced with a total selectivity of more than 70 mol%. An additional advantage of using the Ti-MCM-41 catalyst in this process, in comparison with the Ti-SBA-15 catalyst, is that the Ti-MCM-41 catalyst is obtained in a simpler way and from cheaper raw materials, hence it is an economical heterogeneous catalyst.

A comparison of our results with the results presented in the literature [34–37] shows that similar results can be obtained over the Ti-MCM-41 catalyst as over SBA-15 and MCM-41 catalysts modified by the impregnation with phosphotungstic acid. Unfortunately, these catalysts are more expensive considering their synthesis and subsequently also the possibility of their regeneration. Similar results were also obtained over Al-MCM-41 and Ga/SBA-15 catalysts. However, these two catalysts may not be active in another process in which titanium silicates are used, namely in the epoxidation process, and this is our second direction of research on the possibilities of obtaining useful products from α -pinene.

The process described in the current study has industrial applications and should be developed. In the future, research on the influence of different solvents and their concentration on the α -pinene isomerization process should be performed. In this work we show a variant of this process without the use of a solvent, which is more ecological one. Further studies on the isomerization process should also be performed in the autoclave, which will most likely lead to lowering the temperature of this

process by conducting isomerization under autogenous pressure. We are also planning to prepare MCM-41 materials impregnated with various sources of titanium, perhaps they will be more active than the Ti-MCM-41 materials obtained by the direct method.

Author Contributions: A.W. prepared the conception of isomerization of α -pinene over selected titanium silicate catalysts. She had substantial contributions in the interpretation of research results. She critically corrected the preliminary version of this manuscript, including introduction, discussion of the results and conclusions. She translated the manuscript into English. P.M. prepared Ti-MCM-41 catalysts and performed α -pinene isomerization reactions in the laboratory. He prepared the GC analyses and took part in the calculations of the main functions describing the studied process and in the interpretation of data for the work. He prepared the first, preliminary version of this manuscript. J.T. took part in the calculations of the main functions describing the studied process and in the interpretation of data. J.S.-N. performed nitrogen adsorption at 77 K. Z.C.K. was involved in the discussions about the results, in the interpretation of the data, and in preparing the final version of the manuscript. B.M. made SEM pictures and was involved in discussions about results.

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