



# Article The Application of Clinoptilolite as the Green Catalyst in the Solvent-Free Oxidation of $\alpha$ -Pinene with Oxygen

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Abstract: In this work, we present the catalytic application of the naturally occurring zeolite, clinoptilolite, in the oxidation of  $\alpha$ -pinene, a natural terpene compound. Clinoptilolites with different average particle sizes, designated as (in µm) clin\_1 (20), clin\_2 (50), clin\_3 (200), and clin\_4 (500-1000), were used as the green catalysts in the solvent-free oxidation of  $\alpha$ -pinene with oxygen. Prior to their application in catalytic tests, the catalysts were characterized by the following methods: nitrogen sorption at 77 K, EDXRF, XRD, SEM, UV-Vis, and FTIR. The effects of the temperature, amount of the catalyst, and reaction time on the product's selectivity and  $\alpha$ -pinene conversion were determined. At the optimal conditions (a temperature of 100 °C, catalyst content (clin\_4) in the reaction mixture of 0.05 wt%, and 210 min reaction time), the following compounds were obtained as the main products:  $\alpha$ -pinene oxide (selectivity 29 mol%), verbenol (selectivity 17 mol%), and verbenone (selectivity 13 mol%). The conversion of  $\alpha$ -pinene under these conditions amounted to 35 mol%. Additionally, the kinetic modeling of  $\alpha$ -pinene oxidation over the most active catalyst (clin\_4) was performed. The proposed method of oxidation is environmentally safe because it does not require the separation of products from the solvent. In addition, this method allows for managing the biomass in the form of turpentine, which is the main source of  $\alpha$ -pinene. The catalytic application of clinoptilolite in the oxidation of  $\alpha$ -pinene has not yet been reported in the literature.

**Keywords:** clinoptilolite; zeolite catalysts;  $\alpha$ -pinene; oxidation

## 1. Introduction

Minerals that belong to the group of porous materials of natural origin are currently of interest to many research groups studying organic reactions in the presence of heterogeneous catalysts. Examples of such natural porous materials are vermiculite, sepiolite, and mordenite. An additional advantage of the catalytic applications of these materials is their easy availability and relatively low price. These materials also include clinoptilolite, which is a porous zeolite material of natural origin. Due to its unique catalytic, cation exchange, and adsorption properties, clinoptilolite is widely used in the construction, energy, paper, and cosmetics industries [1], as well as in agriculture (as an additive to animal feed) [2]. The medicinal properties of clinoptilolite are also well known. This porous material is used as an anti-diarrheal drug [3–5], included in preparations used to treat wounds on the skin [3,6,7], used in kidney dialysis [3], and it is also applied as a carrier for drugs [8–11]. The anticancer [5,12], antioxidant, immunostimulating [13], antiviral [14], and detoxification properties of clinoptilolite are also of great interest [15]. The list of uses of clinoptilolite presented above shows that it has many practical applications, but one more important application of this material is that clinoptilolite, due to its specific zeolite structure, can be one of the most valuable natural catalysts in organic syntheses.



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Clinoptilolite has found applications as the catalyst in the processes of oxidation and isomerization of monoterpenes. These processes can provide valuable compounds for medicine, as well as for the perfume, food, and cosmetic industries. An example of such a process is the isomerization of  $\alpha$ -pinene on H<sub>2</sub>SO<sub>4</sub>-modified clinoptilolite. Performing the isomerization at 70 °C and for 4 min allowed for the complete conversion of  $\alpha$ -pinene. The main products identified in this process, camphene and limonene, were formed with the selectivity of 50 and 30 mol%, respectively [16]. The first main product, camphene, is widely used in organic syntheses, in the cosmetic industry and in medicine. The medical applications of camphene are for the treatment of bacterial and fungal infections [17], treatment of skin diseases such as eczema and psoriasis [18], and lowering the level of cholesterol and triglycerides in the blood (reducing the incidence of cardiovascular diseases) [19,20]. The second main product, limonene, finds applications in agriculture, in the polymer industry, in organic syntheses and in medicine. It was confirmed that limonene exhibits antibacterial and antimicrobial activity [21] and, for example, can be used in the treatment of respiratory infections [22,23]. Moreover, limonene is applied in the treatment of mood disorders [24], diabetes, and cancer [25].

Clinoptilolite was also used as the catalyst in the isomerization of geraniol. It was shown that the process was most favorably performed at 140 °C, with the catalyst content of 12.5 wt% and for 3 h. This made it possible to obtain 6,11-dimethyl-2,6,10-dodecatrien-1-ol and thumbergol with the selectivity of 14 and 47 mol%, respectively, while, at the same time, a very high conversion of geraniol was achieved, amounting to 98 mol%. Due to its neuroprotective effects and anticancer properties, thumbergol is a valuable compound for medicine [26].

Another example of an organic process in which clinoptilolite was applied as the catalyst is S-carvone isomerization to carvacrol. It was shown that this process was most favorably performed at 210 °C, with the catalyst content of 15 wt% and for 3 h. Under these conditions, the yield of carvacrol amounted to 90 mol%. The therapeutic properties of carvacrol, such as, its analgesic, antioxidant, antibacterial, antiparasitic, and antifungal properties, make it suitable for use in medicine [27].

Other applications of clinoptilolite as the heterogeneous catalyst are the polypropylene cracking process [28], degradation of polystyrene [29], and etherification of glycerol [30]. Moreover, Gurdal et al. described the use of cobalt and manganese supported on ion-exchanged clinoptilolite catalysts in the reaction of the complete oxidation of n-hexane [31], and Khalilzadeh et al. described the use of clinoptilolite as the catalyst for carbohydrate modification [32].

The main natural source of  $\alpha$ -pinene is turpentine, which is obtained by the steam distillation of the resin of coniferous trees, mainly pine [33], but also cedar and larch. In addition to  $\alpha$ -pinene (content about 75–85%), turpentine contains the following compounds: limonene (5–15%),  $\beta$ -pinene (0–3%), and also camphene, carene, terpinolene, and myrcene [33–36]. The composition of turpentine depends on the type of pine trees and the geographic area where the pine grows [35,36]. The source of  $\alpha$ -pinene is also sulfate turpentine, which is obtained as a waste in the Kraft process during the processing of cellulose into paper [33,36,37].  $\alpha$ -Pinene is extracted from the waste turpentine by vacuum rectification (content of  $\alpha$ -pinene amounts to about 70%) [34,35].

 $\alpha$ -Pinene, as one of the most important terpene compounds, is used as the raw material for the syntheses of valuable chemical compounds, e.g., in oxidation and isomerization processes. These compounds are readily used in the cosmetic and food industries, as well as in medicine as raw materials for obtaining perfumes, flavors, pharmaceuticals, and vitamins [38–40].  $\alpha$ -Pinene derivatives include such compounds as  $\alpha$ -pinene oxide, campholenic aldehyde, L-carveol, verbenol, verbenone, trans-pinocarveol, myrtenal, myrtenol, carvone, and 1,2-pinanediol [41,42].  $\alpha$ -Pinene oxide is used in organic syntheses as the raw material for obtaining valuable compounds such as campholenic aldehyde, isopinocamphone, p-cymene, trans-sobrerol, and trans-carveol [43]. Campholenic aldehyde is a valuable compound for the cosmetic industry. This compound is used to obtain fragrances, for example, santalol. Campholenic aldehyde has found applications in the detergent industry as a replacement for the nitro musks used in laundry detergents [44,45]. Verbenone is one of the main components of the oil extracted from rosemary. Due to the antibacterial and antifungal properties of rosemary oil, it is an alternative to some antibiotics. This oil is readily used in the food industry as a food preservative. The essential oil obtained from rosemary is effectively used in the agricultural industry as a fungicide [46,47], and its main component, verbenone, is used as the anti-aggregation pheromone for bark beetles [48,49]. This monoterpene is used to produce taxol, a drug with anticancer properties [50]. Verbenone is readily used to synthesize (1R,2R,6S)-3-methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol, which shows therapeutic activity in the treatment of Parkinson's disease [51]. Verbenol is a component of citrus fruits, for example, *Citrus limon* (L.). The main components of the oil extracted from *Citrus limon* (L.) are limonene (55.40%) and neral (10.39%), and verbenol is found in this lemon in the amount of 6.43% [52]. Verbenol, like verbenone, has found widespread use in the food and agricultural industries, as well as in the syntheses of valuable chemical compounds used as flavorings, insecticides, and drugs in medicine [39].

Various catalysts were used for the oxidation of  $\alpha$ -pinene, including titanium-silicate catalysts such as Ti-MCM-41 [53,54], TS-1 [42], and Ti-MMM-2 [55], and transition metal salts such as CuI, CuCl, CuCl<sub>2</sub>, PdCl<sub>2</sub>, and PdBr<sub>2</sub> [56]. Carbonaceous materials obtained from pine cones were also described as catalysts for the oxidation of  $\alpha$ -pinene [41]. The oxidation process of  $\alpha$ -pinene was performed using various solvents (acetonitrile, acetone, and methylene chloride). As the oxidants in this process, H<sub>2</sub>O<sub>2</sub>, t-butyl hydroperoxide (TBHP), and N-hydroxyphthalamide were used [39]. So far, there are no reports in the literature on the use of clinoptilolite in the oxidation of  $\alpha$ -pinene.

This paper describes the application of clinoptilolite as the catalyst in the solvent-free oxidation of  $\alpha$ -pinene with oxygen. The purpose of the application of clinoptilolite in this reaction is to determine whether it will be a better catalyst for this oxidation reaction than, for example, the synthetic titanium-silicates (zeolite and zeolite-like materials), as well as carbon materials obtained from waste biomass (pine cones), which we studied earlier in our works. The catalysts mentioned above are obtained by complicated, multistage methods (TS-1 by the hydrothermal crystallization, and carbon materials by the carbonization method). In addition, TS-1 requires very expensive reagents for synthesis, which are neither waste nor renewable. The advantage of carbon catalysts obtained from pine cones is that they are made from waste biomass. However, these syntheses of catalysts are often burdensome for the environment and cause emissions of harmful compounds into the atmosphere (e.g., amines during the calcination of the TS-1 catalyst). It should be emphasized that, by using clinoptilolite of natural origin as the catalyst, we eliminate the process costs associated with the synthesis of this catalyst. It should also be emphasized that, due to the fact that clinoptilolite is a zeolite of natural origin, its use perfectly fits into the modern trends in organic syntheses related to green chemistry and sustainable technologies for the production of organic compounds. Another advantage of clinoptilolite is that, as a zeolite, it is characterized by a specific structure whose channels, as in the case of other zeolites, both natural and synthetic, ensure that the reaction occurs in a specific environment, facilitating the formation of only appropriate products-the shape-selective action of zeolites. In this case, it is important to compare the pore size of the zeolites used as catalysts, because this parameter may determine what products we obtain in the process.

During the tests with clinoptilolite, the most favorable conditions for conducting this process were evaluated, and these include temperature, catalyst content, particle size, and reaction time. The studied clinoptilolites were characterized using the following methods: nitrogen sorption at 77 K, EDXRF, XRD, SEM, UV-Vis, and FTIR. The aim of this study is to perform a physical and chemical characterization of clinoptilolite and to determine the main factors affecting the catalytic activity of this natural zeolite.

# 2. Materials and Methods

# 2.1. Clinoptilolite Materials Used in Catalytic Tests

The clinoptilolite materials were obtained from Rota Mining Corporation (Turkey). The clinoptilolite materials were marked as follows: clin\_1 (20  $\mu$ m average particle size), clin\_2 (50  $\mu$ m average particle size), clin\_3 (200  $\mu$ m average particle size), and clin\_4 (500–1000  $\mu$ m average particle size). Figure 1 presents photographic images of the clinoptilolite materials used in the studies.



Figure 1. Photographic images of the clinoptilolite materials used in the studies.

## 2.2. Characteristics of Clinoptilolite Materials with Instrumental Methods

The porosities and specific surface areas of the clinoptilolites were calculated based on nitrogen adsorption–desorption isotherms at the temperature of 77 K in the ASAP Sorption Surface Area and Pore Size Analyzer (Micrometrics, Novcross, GA, USA). The specific surface area was estimated using BET equations. The total pore volume was calculated on the basis of N<sub>2</sub> volume adsorbed at  $p/p_0$  value close to 1. Pore size analysis was performed utilizing the BJH method. The elemental compositions of the clinoptilolites were evaluated by means of the EDXRF (energy dispersive X-ray fluorescence) Epsilon 3 PANalytical spectrometer (Malvern, UK). The crystal structure of the clinoptilolites was examined by the powder X-ray diffraction using Empyrean diffractometer (Malvern PANalytical Ltd. Company, Almelo, The Netherlands) in the range of 20 from 5 to 80° (Cu K $\alpha$  = 0.15418 nm). The morphology of the clinoptilolite samples surface was explored by scanning electron

microscopy (SEM) at 10 kV and 15,000 magnification with the Hitachi SU8020 Ultra-High Resolution Field Emission Scanning Electron Microscope. UV-Vis spectra in the 190–900 nm wavelength range were obtained using a Jasco 650 spectrometer. Infrared spectra, for the 400–4000 cm<sup>-1</sup> wavenumber range, were measured using a Thermo Electron Nicolet 380 spectrometer.

## 2.3. Oxidation of $\alpha$ -Pinene over Clinoptilolite Materials

The following conditions were used for the oxidation of  $\alpha$ -pinene: 25 cm<sup>3</sup> roundbottom glass flask, reflux condenser, magnetic stirrer, oxygen flow regulator, and glass bubbler supply. Amounts of 10–20 g of  $\alpha$ -pinene (98%, Sigma–Aldrich, Poznań, Poland) and 0.05–1.5 wt% clinoptilolite were introduced into the flask. Then, oxygen (99.99%, Messer, Szczecin, Poland) was supplied at a rate of 40 mL/min. The contents of the flask were stirred at 500 rpm. After the process was completed, 1 mL of the post-reaction mixture was collected in an Eppendorf tube. The plastic tube was then placed in a centrifuge to separate the post-reaction solution from the solid clinoptilolite catalyst.

## 2.4. Identification of the Oxygenated Derivatives of $\alpha$ -Pinene by the Gas Chromatography Method

The products of  $\alpha$ -pinene oxidation were analyzed quantitatively by the gas chromatography (GC) method using a FOCUS apparatus with an FID detector and a ZB-1701 column. The conditions for conducting these analyses were described in detail in our earlier work [41]. The composition of the post-reaction solution was determined using the internal normalization method.

Qualitative analyses of oxygen derivatives of  $\alpha$ -pinene were performed by gas chromatography coupled to mass spectrometry (GC-MS) using ThermoQuest apparatus with Voyager detector and with a DB-5 column. The conditions for conducting these analyses were previously described [41].

Prior to the quantitative and qualitative analyses, the samples were diluted with acetone in a 1:5 weight ratio.

# 3. Results and Discussion

## 3.1. Characteristics of the Clinoptilolite Materials

According to the IUPAC classification, all the isotherms in Figure 2 exhibited Type II isotherms with H3 type hysteresis according to the IUPAC classification [57]. Type II indicates physisorption over nonporous or macroporous materials. A H3 hysteresis loop is typical for aggregated plate-like particles but also macropores not entirely filled with condensate.

The textural properties of clinoptilolites are presented in Table 1.

	S <sub>BET</sub> [m²/g]	V <sub>tot</sub> [cm <sup>3</sup> /g]	V <sub>meso</sub> [cm <sup>3</sup> /g]
clin_1	32	0.149	0.093
clin_2	34	0.150	0.098
clin_3	32	0.153	0.091
clin_4	31	0.148	0.102

Table 1. Textural properties of the samples.

According to Table 1, the contribution of macropores is about 30-40% of the total pore volume, but it should be considered that we were able to measure pores smaller than 100 nm. It can therefore be assumed that these are macroporous materials containing some amount of mesopores. The pore size distribution, calculated by the BJH method, is presented in Figure 3. The highest contribution of macropores smaller than 100 nm was observed for clin\_3, whereas, for clin\_4, the highest mesopore volume was observed. The mesopore volume, in terms of the contribution to the total pore volume, increased in the order: clin\_1 < clin\_2 < clin\_3 < clin\_4.



Figure 2. N<sub>2</sub> adsorption–desorption isotherms of clinoptilolite samples.



Figure 3. Pore size distributions calculated by the BJH method for clinoptilolite samples.

The results in Figures 2 and 3 and Table 1 were consistent and proved that all the clinoptilolites were meso-macroporous materials.

The main components of clinoptilolite were silica and aluminum. Table 2 summarizes the results of the elemental analyses. These results are similar to those reported in the literature [58,59].

Table 2. Elemental compositions (in wt%) in clinoptilolite samples as measured via EDXRF.

	Al	Si	Ca	Fe	К
clin_1	4.2	25.3	3.2	1.9	3.4
clin_2	4.6	28.1	3.3	1.8	3.4
clin_3	4.7	28.3	3.1	1.8	3.6
clin_4	3.7	22.0	2.6	1.6	2.9

The XRD diffractograms of the samples are shown in Figure 4. The characteristic peaks of a clinoptilolite ( $2\theta = 9.799$ , 11.18, 22.27, 22.48, 22.67°) were observed (according to JCPDS No. 70-1859). All the X-ray diffraction patterns were very similar, and no significant structural differences were observed.



**Figure 4.** XRD patterns of clinoptilolite samples. The black bars represent clinoptilolite according to JCPDS No. 70-1859.

Figure 5 shows the SEM images of the clinoptilolite samples. Irregular shapes were observed on the surface, with some narrow lamellar shapes. Many narrow lamellar particles, nearly needle-shaped, were observed for clin\_4.

All clinoptilolite materials show three bands at 260, 370, and 495 nm in their UV/Vis spectra (Figure 6). The band at 260 nm can be attributed to the tetrahedral framework of aluminum bonded to oxygen. The band at 370 nm is attributed to the presence of octahedral extra-framework aluminum [60]. The band at 260 nm can also be attributed to the oxygen charge transfer to Fe<sup>3+</sup> cations in the octahedral coordination and the band at 370 nm to the presence of extra-framework FeOx oligomers. The weak broad band at around 500 nm is connected with the presence of Fe<sub>2</sub>O<sub>3</sub> on the zeolite surface or of oxygen-to-metal charge transfer transitions that involve octahedral Fe<sup>3+</sup> species [61].



Figure 5. SEM images of the samples.



Figure 6. UV-VIS spectra for the clinoptilolite materials with different particle sizes.

The FTIR bands in the range of  $3700-1600 \text{ cm}^{-1}$ , seen in Figure 6, can be attributed to adsorbed water molecules [62,63]. The 1628, 3410, and 3622 cm<sup>-1</sup> bands visible in the figure can be attributed to the OH-stretching vibration mode of adsorbed water in zeolite, intermolecular hydrogen bonding, and Si-OH-Al bridges [63]. Specifically, the 3622 cm<sup>-1</sup> band is attributed to the hydroxyl group of water bound to Na and Ca in the zeolite channels and cages [62,64]. The 3414 cm<sup>-1</sup> band is attributed to the hydrogen bonding of the water molecule to surface oxygen, and the 1637 cm<sup>-1</sup> band is attributed to the bending vibrations of the water molecules [62]. The 3622 cm<sup>-1</sup> band is assigned to the bridging OH groups' vibrations in  $\equiv$ Al-OH-Si $\equiv$  and it corresponds to the location of hydrogen atoms in the vicinity of oxygen atoms in the aluminosilicate framework [61].

The most intense band in the studied range of wavenumbers is the band observed at 1016 cm<sup>-1</sup> (Figure 7). This band is attributed to the asymmetric stretching vibrations of T-O bonds in tetrahedral TO<sub>4</sub>, where T = Si and Al. This is the main zeolitic vibration related to Si–O–Si, which can be covered by the stretching vibration of Al–O–Si and Al–O. The position of this band is governed by the Al/Si ratio and is considered to be indicative of the number of Al atoms per formula unit. The highest shift was observed for clin\_4, and the band was detected at 1040 cm<sup>-1</sup>. The 796 and 465 cm<sup>-1</sup> bands observed in the figure are attributed to stretching vibrations of O-T-O groups and bending vibrations of T-O bonds [64]. The band at 441 cm<sup>-1</sup> is characteristic of the pore opening. The 727, 671, and 600 cm<sup>-1</sup> bands, seen in Figure 6, are assigned to extra-framework cations in the clinoptilolite matrix [63].



Figure 7. FTIR spectra for the clinoptilolite materials with different particle sizes.

3.2. Studies on the Catalytic Activity of the Clinoptilolite Materials in the Oxidation of  $\alpha$ -Pinene with Oxygen

The first stage of the studies consisted of checking the activity of four clinoptilolite materials in the oxidation of  $\alpha$ -pinene. The process conditions were as follows: temperature

of 100 °C, catalyst content 0.1 wt% in relation to the mass of  $\alpha$ -pinene introduced into the reactor (the mass of  $\alpha$ -pinene amounted to 10 g), and 3 h reaction time. Based on these catalytic tests, it was concluded that all clinoptilolite materials were active in the oxidation of  $\alpha$ -pinene (Figure 8), and can be used as catalysts in this process.



**Figure 8.** Catalytic activities of clinoptilolite materials in  $\alpha$ -pinene oxidation (temperature 100 °C, catalyst content 0.1 wt%, and reaction time 3 h).

The oxygenated derivatives of  $\alpha$ -pinene that were formed in this process are shown in Figure 9. The main products of this process were  $\alpha$ -pinene oxide, verbenol, and verbenone, and these were obtained with the highest selectivities.

From the four clinoptilolites that were tested, the most active was the clin\_4 zeolite with an average particle size of 500–1000  $\mu$ m, for which the highest conversion of  $\alpha$ -pinene (36 mol%) and the highest selectivity of  $\alpha$ -pinene oxide (24 mol%) were observed. Moreover, for clin\_4, the selectivity of verbenol was 17 mol%, and the selectivity of verbenone amounted to 12 mol%. For the remaining three clinoptilolites (clin\_1, clin\_2, and clin\_3), the  $\alpha$ -pinene conversion was slightly lower and amounted to 26–32 mol%. For these three clinoptilolites, the selectivity of transformation to epoxide was lower than for clinoptilolite clin\_4, and was maintained at the level of 15–20 mol%, whereas the selectivity of transformation to verbenol (17-19 mol%) and the selectivities of transformation to verbenone (about 14 mol%) were very similar to the sample of clin\_4. The increase in the activity of the clin\_4 zeolite can be related to the intensity of the bands in the FTIR spectra (Figure 7). The  $\equiv$ Si-OH and  $\equiv$ Al-OH groups constitute the active centers of clinoptilolite. Ca, K, and Mg cations can occupy the negatively charged active sites of the zeolite, while reducing its activity [61]. It can be deduced from Figure 7 that clin\_4 has the most free active sites, which are characterized by the least intense band at  $3622 \text{ cm}^{-1}$ , and are attributed to the hydroxyl group of water bound to Ca, K, and Mg atoms. This allows clin\_4 to increase its activity in the oxidation of  $\alpha$ -pinene. The lower activity of the other clinoptilolites may be related to the effect on the -OH groups present in  $\equiv$ Al-OH-Si $\equiv$  by calcium, potassium, and magnesium cations. The FTIR data are consistent with the XRF data, as the clin\_4 sample contains the least Ca, K, and Mg cations compared to the other clinoptilolites (Table 2).



**Figure 9.** The main and secondary  $\alpha$ -pinene oxidation products.

The activity of clinoptilolites in the  $\alpha$ -pinene oxidation reaction may also be related to the intensity of the 796 cm<sup>-1</sup> band (Figure 7). Clin\_4 has the most intense band at 796 cm<sup>-1</sup>, which is associated with the stretching vibrations of O-Si-O and O-Al-O, and both silicon and aluminum constitute the clinoptilolite's active center, allowing clin\_4 to increase its activity in the process. For clin\_4, a 1016 cm<sup>-1</sup> band shift toward a higher wave number (1043 cm<sup>-1</sup>) was observed. The shift was not apparent for the other materials. This shift is related to the Si/Al ratio in the clinoptilolite backbone. The results obtained by FTIR analysis are consistent with those obtained by XRF analysis, as the amount of Al and Si in the clinoptilolites (Table 2).

The increased activity of clin\_4 can also be related to the intensity of the UV-Vis bands (Figure 6). Among the studied clinoptilolites, clin\_4 has the most intense bands at 260, 370, and 495 nm. The first two bands are attributed to the presence of aluminum, which is present in the  $\equiv$ Al-OH group that constitutes the clinoptilolite's active center. The higher intensity of the band at 495 nm obtained for clin\_4, compared to the band obtained for the other materials, may be related to an increase in the number of Fe<sub>2</sub>O<sub>3</sub> molecules and mononuclear Fe species, which may play an important role (active phase) in the  $\alpha$ -pinene oxidation reaction. Similar findings were described by Kumar and co-workers [65].

Among the instrumental studies of the four clinoptilolite catalysts, the results presented in Figure 3, which show the pore size distribution calculated by the BJH method, are also noteworthy. These results indicate that the clin\_4 sample of clinoptilolite contains the largest amount of mesopores, which may indicate that it is precisely this size of pore that is responsible for the greater catalytic activity of this clinoptilolite sample, and that the oxidation process occurs mainly in them.

In order to establish the most favorable conditions for conducting the oxidation of  $\alpha$ pinene for the most active catalyst selected in the first stage of the studies (clin\_4), the effects of temperature, amount of the catalyst, and reaction time on the conversion of  $\alpha$ -pinene and selectivities of the products were studied. The parameters influencing the course of the oxidation process were changed in the following ranges: temperature 80–110 °C, catalyst amount 0.05–1.5 wt%, and reaction time 15–360 min. For the studies on the effects of temperature and amount of catalyst, the mass of  $\alpha$ -pinene was 10 g, and for the studies on the effect of reaction time, the amount of  $\alpha$ -pinene was increased to 20 g. The reaction mixture was sampled every 1 h in an amount of 1 mL.

Figure 10 shows the effect of temperature on  $\alpha$ -pinene conversion and the products' selectivities. The process was performed under the following conditions: a catalyst content of 0.1 wt% in relation to the mass of  $\alpha$ -pinene and a reaction time of 3 h.



**Figure 10.** Influence of temperature on the conversion of  $\alpha$ -pinene and selectivities of products in the oxidation of  $\alpha$ -pinene over clin\_4 clinoptilolite.

It is noticeable that the conversion of  $\alpha$ -pinene increases with increasing temperature and reaches the maximum value (43 mol%) at 110 °C. The selectivity of  $\alpha$ -pinene oxide also increases with increasing temperature and reaches the maximum value (29 mol%) at 90 °C, then it decreases to 11 mol% (at 110 °C). The selectivity of transformation to verbenol is maintained at the level of 13–20 mol% over the entire range of tested temperatures. Verbenone is formed only at temperatures in the range of 90–110 °C; the maximum value of its selectivity is achieved at 110 °C and it amounts to 17 mol%. The most favorable temperature determined for clin\_4 clinoptilolite is 100 °C. At this temperature, the selectivity of  $\alpha$ -pinene oxide amounts to 24 mol%, verbenol 17 mol%, verbenone 12 mol%, and conversion of  $\alpha$ -pinene is 36 mol%.

Studies on the effect of the amount of catalyst were conducted at 100  $^{\circ}$ C for 3 h. The results obtained during these studies are shown in Figure 11.

Figure 11 shows that increasing the catalyst amount from 0.05 to 1.5 wt% causes a decrease in the conversion of  $\alpha$ -pinene from 39 to 28 mol%. This increase in the clin\_4 material content also causes a decrease in the selectivity of  $\alpha$ -pinene oxide from 30 to 6 mol%. It should be emphasized that the value of 30 mol% was the highest selectivity of the transformation to  $\alpha$ -pinene oxide observed so far in this work. The increase in the catalyst amount did not cause an essential change in the values of the selectivities of verbenol (13–17 mol%) and verbenone (10–15 mol%). The most favorable amount of catalyst was taken as 0.05 wt%. For this amount of catalyst, the highest selectivity of  $\alpha$ -pinene oxide was obtained (30 mol%) at the conversion of  $\alpha$ -pinene of 39 mol% (the selectivity

of verbenol was 16 mol% and the selectivity of verbenone amounted to 13 mol%). The increase in the catalyst amount in the post-reaction mixture increases the content of other products in this mixture by up to 50 mol%, when taking into account their total selectivity (in Figure 11 these products are marked as "others"). Among these products, there may be oligomeric compounds with different molecular sizes, which, remaining in the pores, may block the access of  $\alpha$ -pinene molecules to the active centers, and this, in turn, may lead to a decrease in the conversion of  $\alpha$ -pinene. The solution here could be to calcinate the catalyst in order to restore its activity and, thus, it would be able to be reused in the oxidation process. Figure 11 also shows that the catalyst content of 0.25 wt% should not be exceeded in the post-reaction mixture, because, for higher catalyst amounts, the formation of other, less desirable products, and a decrease in the conversion of  $\alpha$ -pinene, are observed.

Figure 12 shows that, with prolongation of the reaction time, the conversion of  $\alpha$ -pinene increases, reaching the maximum value (54 mol%) for the reaction time of 360 min.



**Figure 11.** Influence of catalyst content on the conversion of  $\alpha$ -pinene and selectivities of the products in the oxidation of  $\alpha$ -pinene over clin\_4 clinoptilolite.

It can be seen that, as the reaction time increases from 15 to 120 min, the selectivity of  $\alpha$ -pinene oxide increases from 14 mol% (15 min) to 31 mol% (120 min). The selectivity of this epoxide compound remains at the level of 29–31 mol% over the range of reaction time of 60–210 min. After the reaction time of 210 min, the selectivity of transformation to the epoxide compound decreases to 3 mol% (reaction time of 360 min). The analysis of the studies on the influence of reaction time for the clin\_4 catalyst shows that reaction time from 15 to 60 min is too short to obtain such products as campholenic aldehyde, verbenone, and myrtenal (the selectivity of the transformation to campholenic aldehyde increases from 0.2 mol% (90 min) to 6 mol% (360 min), and the selectivity of the transformation to verbenone increases from 5 mol% (90 min) to 20 mol% (360 min). The selectivity of the transformation to verbenol remains at the level of 8–18 mol% in the range of studied reaction times from 15 to 360 min.

Taking into account the results presented in Figure 12, it can be assumed that, after a sufficiently long reaction time (210 min), part of the formed  $\alpha$ -pinene oxide undergoes two subsequent reactions (Figure 13). The first is the isomerization of the epoxide leading to campholenic aldehyde and carveol, and the second is the hydration of the epoxy ring, re-

sulting in diol formation (1,2-pinanediol); the increase in the selectivity of these compounds in Figure 12 is observable. Taking into account the selectivities of the transformation to  $\alpha$ -pinene oxide, verbenol, verbenone, and the conversion of  $\alpha$ -pinene, the reaction time of 210 min can be taken as the most beneficial for the clin\_4 catalyst sample; for this reaction time, the selectivity of  $\alpha$ -pinene oxide amounts to 29 mol%, verbenol 17 mol%, verbenone 13 mol%, and the conversion of  $\alpha$ -pinene is 35 mol%.



**Figure 12.** Influence of reaction time on the conversion of  $\alpha$ -pinene and selectivities of the products in the oxidation of  $\alpha$ -pinene over clin\_4 clinoptilolite at 100 °C (catalyst amount 0.05 wt%).

It is also interesting to note the changes in the selectivity of the transformation of  $\alpha$ -pinene to other products ("others") in the studied process. Figure 12 shows that, for very short reaction times of 15–60 min, very high values of this selectivity are observed, from about 75 mol% (reaction time 15 min) to 48 mol% (reaction time 60 min). The formation of such a large amount of other products at the beginning of the process can cause catalyst pores to be blocked, because, among these products, there are oligomeric compounds with different molecular weights that remain in the pores and can block the access of  $\alpha$ -pinene molecules to the active sites. As a result, we can observe the low conversion of  $\alpha$ -pinene (3–8 mol%). In our earlier publication [42] concerning the oxidation of  $\alpha$ -pinene on the TS-1 catalyst, for such short reaction times, the formation of such a large amount of "other products" was not observed, and their amount was about 40 mol%, but also, in this case, a low conversion of  $\alpha$ -pinene of about 4 mol% was achieved. For the reaction time of 360 min, the conversion of  $\alpha$ -pinene on the TS-1 catalyst was about 18 mol%, and the synthesis conditions were as follows: a temperature of 80 °C and a catalyst amount of 2.5 wt%. With the sample of clinoptilolite clin 4, a conversion of 54 mol% was obtained after 6 h. This value is three times higher than for the TS-1 catalyst. Taking into account the conditions in which the catalytic tests were carried out on the clin\_4 sample (temperature 100  $^{\circ}$ C, catalyst amount 0.05 wt%), the clin\_4 sample of the catalyst is much more active than our previously described TS-1 catalyst. It is particularly noteworthy that 50 times less TS-1 catalyst was used. It is also very interesting to compare the selectivity of the transformation to  $\alpha$ -pinene oxide on the clin\_4 catalyst and the TS-1 catalyst. On the clin\_4 catalyst, the selectivity of this compound for reaction times of 60–120 min remains at the level of about 30 mol%, then the selectivity of  $\alpha$ -pinene oxide gradually decreases to 25 mol% after 4 h, and 15 mol% after 5 h. In the case of the TS-1 catalyst, the high selectivities of  $\alpha$ -pinene oxide persist

longer, i.e., until the reaction time of 6 h (23–30 mol%), while, for the reaction time of 7 h, the selectivity of  $\alpha$ -pinene oxide is reduced to 15 mol%. This proves the greater stability of the  $\alpha$ -pinene oxide molecule under the reaction conditions on the TS-1 catalyst. This may be due to the shape and size of the pores of the TS-1 catalyst (0.5 nm pores, microporous material), which hinder further transformations of  $\alpha$ -pinene oxide in the pores.



**Figure 13.** Transformation pathways of  $\alpha$ -pinene and  $\alpha$ -pinene oxide.

During our research with carbon catalysts obtained from pine cones [41], other reaction products were formed for the reaction time of 60 min with the selectivity of 28 mol%, and the value of this selectivity increased with the extension of the reaction time. For the reaction time of 6 h, the selectivity was 35 mol% (catalyst sample marked as PC\_850, where 850 means the temperature at which carbonization was carried out, the temperature of the oxidation of  $\alpha$ -pinene 100 °C, and the amount of catalyst 0.5 wt%). For the reaction time of 1 h, a low  $\alpha$ -pinene conversion of about 12 mol% was observed for this sample. However, this value was slightly higher than for the clin\_4 and TS-1 catalysts. For the reaction time of 6 h, for the PC\_850 catalyst sample, the  $\alpha$ -pinene conversion was 52 mol% and it was a value close to that obtained for the clin\_4 catalyst. However, considering that the content of the PC\_850 catalyst was 10 times higher in the reaction mixture than that of the clin\_4 catalyst, the PC 850 catalyst was characterized by a lower activity than the clin 4 catalyst. For the clin\_4 catalyst, the selectivity of the transformation of  $\alpha$ -pinene to  $\alpha$ -pinene oxide was obtained at the level of about 27–30 mol% for the reaction time of 4 h; for the reaction time of 5 h, it was about 22 mol%, and, for the reaction time of 6 h, it was about 12 mol%. Thus, in the case of this catalyst, the high selectivity of the transformation to  $\alpha$ -pinene oxide could be maintained a little longer than for the clin\_4 catalyst (3.5 h), but shorter than for the TS-1 catalyst (6 h). The research presented in our publication [41] shows that the PC\_850 catalyst was characterized by a large number of micropores with diameters of 1–1.25 nm, which may be the reason for the increased stability of  $\alpha$ -pinene oxide. At the same time, this would confirm the conclusion that catalysts containing micropores

can be used to obtain  $\alpha$ -pinene oxide with higher yields compared to other products of this process.

#### 4. Conclusions

Our studies showed that clinoptilolite can be effectively used as a green catalyst in  $\alpha$ -pinene oxidation. Once the reaction is complete, clinoptilolite contains no harmful substances and is easy to dispose of. This zeolite is active at low temperatures. The trace amounts of clinoptilolite (0.05–1.5 wt%) used in the oxidation of  $\alpha$ -pinene make it possible to obtain the main products with high selectivities. For 0.05 wt% (temperature 100 °C, and reaction time 210 min), the selectivities of the main products were as follows:  $\alpha$ -pinene oxide 29 mol%, verbenol 17 mol%, verbenone 13 mol%, and  $\alpha$ -pinene conversion was 35 mol%. Our method for the oxidation of  $\alpha$ -pinene on clinoptilolite is cost-effective and energyefficient, and our results indicate that clinoptilolite can be used as a non-conventional, environmentally friendly, reusable, and promising catalyst in organic reactions. It should be noted that the described method of the oxidation of  $\alpha$ -pinene on clinoptilolite requires only a simple glass apparatus and atmospheric pressure, and the reaction itself does not require an initiator or solvent, making the method environmentally safe and requiring no separation of products from the solvent.

Taking into account the conversion of  $\alpha$ -pinene, the clinoptilolite catalyst turned out to be much more active than the TS-1 catalyst and carbon catalysts obtained from pine cones, which we studied earlier. The big advantage is that it can be used in the case of a very small amount of reaction mixture compared to the catalysts mentioned above. Taking into account the selectivity of the transformation to  $\alpha$ -pinene oxide, the use of clinoptilolite allows for the use of short reaction times (up to 210 min) with the selectivity of this compound of up to 30 mol%, while the conversion of  $\alpha$ -pinene is about 30 mol%. The other two catalysts, for reaction times up to 4–6 h, enable the maintaining of such a high selectivity of  $\alpha$ -pinene oxide, and for which it is possible to obtain the higher conversion of  $\alpha$ -pinene (even above 40 mol% for the catalyst obtained from pine cones). Therefore, in order to obtain  $\alpha$ -pinene oxide with the selectivity of about 30 mol%, and, at the same time, the high conversion of  $\alpha$ -pinene, it is better to use microporous catalysts. Further research on the use of clinoptilolite in the oxidation of  $\alpha$ -pinene should be aimed at determining the most favorable conditions for obtaining the other valuable products of this process, e.g., verbenol, verbenone, myrtenol or myrtenal.

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