Zachodniopomorski
Uniwersytet Technologiczny
w Szczecinie

Wydział
Technologii i Inżynierii
Chemicznej

mgr inż. Jadwiga Grzeszczak

Dziedzina nauk inżynieryjno-technicznych
Dyscyplina inżynieria chemiczna

Utlenianie alfa-pinenu na katalizatorach heterogenicznych
Oxidation of alpha-pinene over heterogeneous catalysts

rozprawa doktorska

napisana pod kierunkiem
prof. dr hab. inż. Agnieszki Wróblewskiej

Katedra Inżynierii Materiałów Katalitycznych i Sorpcyjnych

Szczecin, 2024

Niniejszą pracę doktorską dedukuję moim cudownym Rodzicom
w podziękowaniu za trud wychowania oraz nieustanne wsparcie w każdej chwili
mojego życia. Dziękuję za Waszą miłość i wiarę w moje możliwości.

Składam serdeczne podziękowania
Pani prof. dr hab. inż. Agnieszce Wróblewskiej
za okazywaną życzliwość, poświęcony czas i wszelką pomoc w realizacji
niniejszej pracy.

Z całego serca dziękuję mojej rodzinie, a w szczególności
Mężowi Piotrowi i Bratu Pawłowi za ogromne wsparcie, cierpliwość oraz
pomoc w realizacji marzeń.

Spis treści

Streszczenie

Związki organiczne pochodzenia naturalnego, w tym terpeny, cieszą się obecnie zainteresowaniem wielu badaczy na całym świecie. Związki te charakteryzują się wysoką dostępnością, a możliwość ich wykorzystania jako naturalnego surowca do syntezy cennych dla przemysłu kosmetycznego i dla medycyny związków jest bardzo korzystna z ekologicznego oraz ekonomicznego punktu widzenia i stanowi nowe podejście do ich zagospodarowania. Jednym z odnawialnych i łatwo dostępnych surowców pochodzenia naturalnego jest alfa-pinen (α-pinen) – nasycony, bicykliczny węglowodór terpenowy. Cennym źródłem tego węglowodoru jest terpentyna, która stanowi odpad z przemysłu papierniczego. Naturalnym i odnawialnym źródłem alfa-pinenu są też olejki eteryczne pozyskiwane z różnych roślin, takich jak na przykład: sosna, rozmaryn, rumianek, czy pomarańcza. W celu otrzymania produktów o wysokiej wartości dodanej, terpeny poddaje się różnym przemianom chemicznym, w tym reakcji utleniania, która przebiega w obecności odpowiednio dobranego katalizatora heterogenicznego. Główne pochodne tlenowe alfa-pinenu, takie jak: tlenek alfa-pinenu, werbenol oraz werbenon, są szeroko wykorzystywane w przemyśle spożywczym, kosmetycznym oraz perfumeryjnym – związki te są głównie stosowane jako składniki o właściwościach smakowych i zapachowych, które są dodawane do żywności, napojów, kosmetyków oraz perfum. Pochodne tlenowe alfa-pinenu znalazły również cenne zastosowania w medycynie.

W niniejszej pracy doktorskiej przedstawiono badania nad utlenianiem alfa-pinenu na wybranych katalizatorach heterogenicznych. W ramach pracy doktorskiej jako katalizatory do utleniania alfa-pinenu zastosowano następujące materiały porowate: syntetyczne katalizatory zeolitowe TS-1 o różnej zawartości tytanu, syntetyczne katalizatory ZSM-5 o różnej zawartości glinu, katalizatory węglowe otrzymane z szyszek sosny oraz naturalne klinoptylolity o różnej wielkości cząstek. Reakcję utleniania alfa-pinenu na katalizatorach heterogenicznych prowadzono bez rozpuszczalnika, a jako utleniacz zastosowano tlen cząsteczkowy. W pracy opisano właściwości fizykochemiczne wyżej wymienionych katalizatorów heterogenicznych za pomocą odpowiednio dobranych metod instrumentalnych, zbadano ich aktywność katalityczną w procesie utleniania alfa-pinenu oraz wyznaczono najkorzystniejsze parametry prowadzenia tego procesu, takie jak: temperatura, ilość katalizatora oraz czas reakcji. W ostatnim etapie pracy doktorskiej przeprowadzono badania nad aktywnością przeciwutleniającą ekstraktów etanolowych otrzymanych z roślin zawierających alfa-pinen metodami DPPH i ABTS oraz przygotowano emulsje kosmetyczne z tymi ekstraktami. Wykazano, że emulsje te są stabilnymi produktami kosmetycznymi o wysokim potencjale przeciwutleniającym.

1. Wykaz opublikowanych i powiązanych tematycznie artykułów naukowych stanowiących rozprawę doktorską, o którym mowa w art. 187, pkt. 3 ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. z 2023 r. poz. 742, 1088, 1234, 1672, 1872, 2005, z 2024 r. poz. 124, 227)

Rozprawa doktorska w oparciu o cykl publikacji
Utlenianie alfa-pinenu na katalizatorach heterogenicznych

Cykl publikacji pt. *Utlenianie alfa-pinenu na katalizatorach heterogenicznych* stanowi zbiór pięciu powiązanych tematycznie artykułów naukowych w recenzowanych czasopismach naukowych, znajdujących się w wykazie czasopism określonym przez ministra właściwego do spraw nauki. Artykuły przedstawiono w odpowiedniej kolejności, biorąc pod uwagę ich daty opublikowania. W czterech artykułach jestem pierwszym autorem i również w czterech artykułach mój wkład w powstanie prac jest przeważający.

1.1. Agnieszka Wróblewska*, **Jadwiga Grzeszczak**, Piotr Miądlicki, Karolina Kiełbasa, Marcin Kujbida, Adrianna Kamińska, Beata Michalkiewicz, The studies on α-pinene oxidation over the TS-1. The influence of the temperature, reaction time, titanium and catalyst content, *Materials*, 14(24), 2021, 7799. DOI: 10.3390/ma14247799.

- *Impact Factor* : **3,748**
- *5-letni Impact Factor*: **3,8**
- *punkty MNiSW*: **140**
- liczba cytowań (*Scopus*): **6**

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* autor korespondencyjny

** dla wszystkich prac naukowych *Impact Factor*, *5-letni Impact Factor* i punkty *MNiSW* podano zgodnie z rokiem opublikowania pracy

*** dla wszystkich prac naukowych *Impact Factor* i *5-letni Impact Factor* podano według listy *Journal Citation Reports* (*JCR*)

Mój udział w przygotowaniu artykułu polegał na współtworzeniu koncepcji badań katalitycznych, zbadaniu wpływu: zawartości tytanu w katalizatorze TS-1, temperatury, czasu reakcji i ilości katalizatora w mieszaninie reakcyjnej na konwersję alfa-pinenu i selektywności odpowiednich produktów, na wykonaniu analiz jakościowych i ilościowych mieszanin poreakcyjnych metodą chromatografii gazowej wraz z ich interpretacją oraz na współtworzeniu pierwszej wersji publikacji, edycji i wizualizacji pracy.

Mój udział procentowy szacuję na 33%.

Udział procentowy pozostałych autorów: Agnieszka Wróblewska – 35%, Piotr Miądlicki – 5%, Karolina Kiełbasa – 5%, Marcin Kujbida – 2%, Adrianna Kamińska – 2%, Beata Michalkiewicz – 18%.

1.2. Jadwiga Grzeszczak, Agnieszka Wróblewska*, Monika Bosacka, Zvi C. Koren, Beata Michalkiewicz*, Studies on the catalytic activities of ZSM-5 zeolites with different aluminum contents in the green oxidation of α-pinene to high value-added products, *Chemical Engineering Research and Design*, 192, 2023, 338-349. DOI: 10.1016/j.cherd.2023.02.031.

- *Impact Factor*: **3,9**
- *5-letni Impact Factor*: **3,7**
- *punkty MNiSW*: **140**
- liczba cytowań (*Scopus*): **7**

Mój udział w przygotowaniu artykułu polegał na współtworzeniu koncepcji badań katalitycznych i ich metodologii, na wykonaniu i interpretacji analiz instrumentalnych badanych katalizatorów, takich jak: UV-Vis i FTIR, na przeprowadzeniu serii badań aktywności katalitycznej zeolitów ZSM-5 mających na celu wyznaczenie najkorzystniejszych warunków utleniania alfa-pinenu, takich jak: temperatura, ilość katalizatora i czas reakcji, na przeprowadzeniu analiz jakościowych i ilościowych mieszanin poreakcyjnych za pomocą chromatografii gazowej wraz z ich interpretacją, a także na współtworzeniu pierwszej wersji publikacji, edycji i wizualizacji pracy oraz na przygotowaniu wykresów.

Mój udział procentowy szacuję na 51%.

Udział procentowy pozostałych autorów: Agnieszka Wróblewska – 30%, Monika Bosacka – 5%, Zvi C. Koren – 2%, Beata Michalkiewicz – 12%.

1.3. Jadwiga Grzeszczak, Agnieszka Wróblewska*, Adrianna Kamińska, Piotr Miądlicki, Joanna Sreńscek-Nazzal, Rafał Wróbel, Zvi C. Koren, Beata Michalkiewicz*, Carbon catalysts from pine cones – Synthesis and testing of their activities, *Catalysis Today*, 423, 2023, 113882. DOI: 10.1016/j.cattod.2022.08.024.

- *Impact Factor*: **5,3**
- *5-letni Impact Factor*: **5,4**
- *punkty MNiSW*: **140**
- liczba cytowań (*Scopus*): **3**

Mój udział w przygotowaniu artykułu polegał na współtworzeniu koncepcji badań, na otrzymaniu serii katalizatorów węglowych z szyszek sosny, przeprowadzeniu serii badań katalitycznych otrzymanych materiałów węglowych mających na celu zbadanie wpływu temperatury, ilości katalizatora i czasu reakcji na konwersję alfa-pinenu i selektywności odpowiednich produktów, opracowaniu najkorzystniejszych warunków utleniania alfa-pinenu, przeprowadzeniu analiz jakościowych i ilościowych mieszanin poreakcyjnych metodą chromatografii gazowej wraz z ich interpretacją, na współtworzenie pierwszej wersji publikacji, edycji i wizualizacji pracy oraz na przygotowaniu wykresów.

Mój udział procentowy szacuję na 50%.

Udział procentowy pozostałych autorów: Agnieszka Wróblewska – 25%, Adrianna Kamińska – 5%, Piotr Miądlicki – 5%, Joanna Sreńscek-Nazzal – 2%, Rafał Wróbel – 5%, Zvi C. Koren – 2%, Beata Michalkiewicz – 6%.

1.4. Jadwiga Grzeszczak, Agnieszka Wróblewska*, Karolina Kiełbasa, Zvi C. Koren, Beata Michalkiewicz*, The application of clinoptilolite as the green catalyst in the solvent-free oxidation of α-pinene with oxygen, *Sustainability*, 15(13), 2023, 10381. DOI: 10.3390/su151310381.

- *Impact Factor*: **3,9**
- *5-letni Impact Factor*: **4,0**
- *punkty MNiSW*: **100**
- liczba cytowań (*Scopus*): **4**

Mój udział w przygotowaniu artykułu polegał na współtworzeniu koncepcji badań, na wykonaniu analiz instrumentalnych badanych katalizatorów, takich jak: UV-Vis i FTIR wraz z ich interpretacją, na przeprowadzeniu badań wpływu temperatury, ilości katalizatora i czasu reakcji na konwersję alfa-pinenu i selektywności odpowiednich produktów, mających na celu opracowaniu najkorzystniejszych warunków utleniania alfa-pinenu, na współtworzeniu pierwszej wersji pracy, edycji i wizualizacji pracy oraz na przygotowaniu wykresów.

Mój udział procentowy szacuję na 50%.

Udział procentowy pozostałych autorów: Agnieszka Wróblewska – 30%, Karolina Kiełbasa – 5%, Zvi C. Koren – 5%, Beata Michalkiewicz – 10%.

1.5. Jadwiga Grzeszczak, Agnieszka Wróblewska*, Adam Klimowicz*, Sylwia Gajewska, Łukasz Kucharski, Zvi C. Koren, Katarzyna Janda-Milczarek, Antioxidant activities of ethanolic extracts obtained from α-pinene-containing plants and their use in cosmetic emulsions, *Antioxidants*, 13(7), 2024, 811. DOI: 10.3390/antiox13070811.

- *Impact Factor* : **6,0**
- *5-letni Impact Factor*: **6,7**
- *punkty MNiSW*: **100**
- liczba cytowań (*Scopus*): **0**

Mój udział w przygotowaniu artykułu polegał na współtworzeniu koncepcji badań aktywności przeciwutleniających i ich metodologii, na przygotowaniu ekstraktów etanolowych z roślin zawierających alfa-pinen, na wykonaniu analiz jakościowych i ilościowych otrzymanych ekstraktów metodą GC-MS wraz z ich interpretacją, na współwykonaniu badań aktywności przeciwutleniającej ekstraktów etanolowych metodami DPPH i ABTS oraz na ich opisie, na przygotowaniu emulsji kosmetycznych oraz zbadaniu ich stabilności i właściwości przeciwdrobnoustrojowych, a także na współtworzeniu pierwszej wersji publikacji, edycji i wizualizacji pracy oraz na przygotowaniu wykresów.

Mój udział procentowy szacuję na 51%.

Udział procentowy pozostałych autorów: Agnieszka Wróblewska – 15%, Adam Klimowicz – 10%, Sylwia Gajewska – 8%, Łukasz Kucharski – 3%, Zvi C. Koren – 5%, Katarzyna Janda-Milczarek – 8%.

- Sumaryczny ***Impact Factor*** dla cyklu publikacji: **22,848**
- Sumaryczny ***5-letni Impact Factor*** dla cyklu publikacji: **23,6**
- Sumaryczna ***liczba punktów MNiSW*** dla cyklu publikacji: **620**
- Sumaryczna ***liczba cytowań*** (*Scopus*) dla cyklu publikacji: **20**

2.Wykaz pozostałego dorobku naukowego

2.1. Wykaz opublikowanych artykułów, niewchodzących w skład cyklu publikacji

1. Agnieszka Wróblewska*, Piotr Miądlicki*, **Jadwiga Tołpa**, Joanna Sreńscek-Nazzal, Zvi C. Koren, Beata Michalkiewicz, Influence of the titanium content in the Ti-MCM-41 catalyst on the course of the α-pinene isomerization process, *Catalysts*, 9(5), 2019, 396. DOI: 10.3390/catal9050396.

- *Impact Factor*: **3,520**
- *5-letni Impact Factor*: **3,708**
- *punkty MNiSW*: **100**
- liczba cytowań (*Scopus*): **24**

Mój udział w przygotowaniu artykułu polegał na uczestniczeniu w obliczeniach głównych funkcji opisujących badany proces na podstawie analiz wykonanych metodą chromatografii gazowej oraz interpretacji danych.

Mój udział procentowy szacuję na 2%.

2. Anna Fajdek-Bieda, Agnieszka Wróblewska*, Piotr Miądlicki, **Jadwiga Tołpa**, Beata Michalkiewicz, Clinoptilolite as a natural, active zeolite catalyst for the chemical transformations of geraniol, *Reaction Kinetics, Mechanisms and Catalysis*, 133, 2021, 997–1011. DOI: 10.1007/s11144-021-02027-3.

- *Impact Factor*: **1,843**
- *5-letni Impact Factor*: **1,589**
- *punkty MNiSW*: **40**
- liczba cytowań (*Scopus*): **12**

Mój udział w przygotowaniu artykułu polegał na uczestniczeniu w obliczeniach głównych funkcji opisujących badany proces na podstawie analiz wykonanych metodą chromatografii gazowej oraz interpretacji danych.

Mój udział procentowy szacuję na 2%.

3. Agnieszka Wróblewska*, **Jadwiga Tołpa**, Dominika Kłosin, Piotr Miądlicki, Zvi C. Koren, Beata Michalkiewicz, The application of TS-1 materials with different titanium contents as catalysts for the autoxidation of α-pinene, *Microporous and Mesoporous Materials*, 305, 2020, 110384. DOI: 10.1016/j.micromeso.2020.110384.

- *Impact Factor*: **5,455**
- *5-letni Impact Factor*: **4,862**
- *punkty MNiSW*: **100**
- liczba cytowań (*Scopus*): **15**

Mój udział polegał na współtworzeniu pierwszej wersji pracy.

Mój udział procentowy szacuję na 5%.

4. Adrianna Kamińska*, Joanna Sreńscek-Nazzal, Karolina Kiełbasa*, **Jadwiga Grzeszczak**, Jarosław Serafin, Agnieszka Wróblewska, Carbon-supported nickel catalysts—comparison in alpha-pinene oxidation activity, *Sustainability*, 15(6), 2023, 5317. DOI: 10.3390/su15065317.

- *Impact Factor*: **3,9**
- *5-letni Impact Factor*: **4,0**
- *punkty MNiSW*: **100**
- liczba cytowań (*Scopus*): **1**

Mój udział polegał na współtworzeniu pierwszej wersji pracy.

Mój udział procentowy szacuję na 5%.

- Sumaryczny ***Impact Factor*** dla artykułów niewchodzących w cykl publikacji: **14,718**
- Sumaryczny ***5-letni Impact Factor*** dla artykułów niewchodzących w cykl publikacji: **14,159**
- Sumaryczna ***liczba punktów MNiSW*** dla artykułów niewchodzących w cykl publikacji: **340**
- Sumaryczna ***liczba cytowań*** (*Scopus*) dla artykułów niewchodzących w cykl publikacji: **52**

2.2. Wykaz recenzowanych monografii naukowych

1. Anna Fajdek-Bieda, **Jadwiga Tołpa**, Marcin Kujbida, Agnieszka Wróblewska, *Biomasa i jej zastosowania*, Akademia im. Jakuba z Paradyża w Gorzowie Wielkopolskim, 2020, ISBN 978-83-66703-19-3, **punkty MNiSW – 80.**

Mój udział w przygotowaniu monografii polegał na współtworzeniu pierwszej wersji pracy, przygotowaniu rysunków i schematów.

Mój udział procentowy szacuję na 25%.

2. Anna Fajdek-Bieda, **Jadwiga Grzeszczak**, Piotr Miądlicki, Agnieszka Wróblewska, *Charakterystyka wybranych katalizatorów tytanowo-silikalitowych*, Akademia im. Jakuba z Paradyża w Gorzowie Wielkopolskim, 2022, ISBN 978-83-66703-93-3, **punkty MNiSW – 80.**

Mój udział w przygotowaniu monografii polegał na współtworzeniu pierwszej wersji pracy, przygotowaniu rysunków i schematów.

Mój udział procentowy szacuję na 25%.

2.3. Udzielone patenty oraz zgłoszenia patentowe międzynarodowe i krajowe

Patenty

1. Agnieszka Wróblewska, **Jadwiga Tołpa**, Miądlicki Piotr, *Sposób utleniania alfa-pinenu na katalizatorze TS-1*, Pat.238459, 23.08.2021.

Mój udział procentowy wynosi: 33%.

2. Agnieszka Wróblewska, **Jadwiga Tołpa**, Miądlicki Piotr, *Sposób utleniania alfa-pinenu na katalizatorze TS-1*, Pat.238460, 23.08.2021.

Mój udział procentowy wynosi: 33%.

3. Agnieszka Wróblewska, Piotr Miądlicki, Anna Fajdek-Bieda, Aleksandra Radomska-Zalas, Andrzej Perec, **Jadwiga Tołpa**, Marcin Kujbida, *Sposób izomeryzacji geraniolu w obecności katalizatora*, Pat.241532, 17.10.2022.

Mój udział procentowy wynosi: 5%.

4. Agnieszka Wróblewska, Piotr Miądlicki, Anna Fajdek-Bieda, Aleksandra Radomska-Zalas, **Jadwiga Tołpa**, *Sposób izomeryzacji geraniolu w obecności haloizytu jako katalizatora*, Pat.242205, 30.01.2023.

Mój udział procentowy wynosi: 11%.

5. Agnieszka Wróblewska, **Jadwiga Tołpa**, Piotr Miądlicki, Beata Michalkiewicz, *Sposób utleniania alfa-pinenu w obecności katalizatora ZSM-5*, Pat.242206, 30.01.2023.

Mój udział procentowy wynosi: 30%.

6. Agnieszka Wróblewska, Piotr Miądlicki, Anna Fajdek-Bieda, Aleksandra Radomska-Zalas, **Jadwiga Tołpa**, *Sposób izomeryzacji geraniolu*, Pat.242666, 03.04.2023.

Mój udział procentowy wynosi: 11%.

7. Agnieszka Wróblewska, **Jadwiga Tołpa**, Piotr Miądlicki, *Sposób otrzymywania katalizatora tytanowo-silikatowego i jego zastosowanie*, Pat.243065, 12.06.2023.

Mój udział procentowy wynosi: 42%.

8. Joanna Sreńscek-Nazzal, Agnieszka Wróblewska, Adrianna Kamińska, **Jadwiga Tołpa**, Piotr Miądlicki, *Sposób wytwarzania katalizatora węglowego zawierającego żelazo i jego zastosowanie do utleniania α-pinenu*, Pat.243077, 19.06.2023.

Mój udział procentowy wynosi: 20%.

9. Agnieszka Wróblewska, **Jadwiga Tołpa**, Piotr Miądlicki, *Sposób otrzymywania katalizatora tytanowo-silikatowego i jego zastosowanie*, Pat.243584, 11.09.2023.

Mój udział procentowy wynosi: 38%.

10. Agnieszka Wróblewska, Piotr Miądlicki, Anna Fajdek-Bieda, Aleksandra Radomska-Zalas, **Jadwiga Tołpa**, *Sposób izomeryzacji geraniolu w obecności katalizatora*, Pat.243585, 11.09.2023.

Mój udział procentowy wynosi: 11%.

11. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, Marcin Kujbida, *Sposób utleniana alfa-pinenu w obecności katalizatora tytanowo-silikatowego*, Pat.244073, 27.11.2023.

Mój udział procentowy wynosi: 40%.

12. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, *Sposób utleniania alfa-pinenu w obecności katalizatora węglowego*, Pat.244677, 19.02.2024.

Mój udział procentowy wynosi: 50%.

Zgłoszenia patentowe

1. Joanna Sreńscek-Nazzal, Agnieszka Wróblewska, Adrianna Kamińska, **Jadwiga Grzeszczak**, Piotr Miądlicki, *Sposób izomeryzacji alfa-pinenu w obecności katalizatora węglowego*, P.439341, 28.10.2021.

Mój udział procentowy wynosi: 20%.

2. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, Marcin Kujbida, *Sposób otrzymywania katalizatora tytanowo-silikatowego otrzymanego z wykorzystaniem templatów*, P.441469, 14.06.2022.

Mój udział procentowy wynosi: 45%.

3. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, Marcin Kujbida, *Sposób utleniania α-pinenu w obecności katalizatora tytanowo-silikatowego otrzymanego z wykorzystaniem templatów*, P.441470, 14.06.2022.

Mój udział procentowy wynosi: 45%.

4. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, *Sposób utleniania alfa-pinenu w obecności katalizatora węglowego*, P.441864, 28.07.2022.

Mój udział procentowy wynosi: 50%.

5. Joanna Sreńscek-Nazzal, Agnieszka Wróblewska, Adrianna Kamińska, **Jadwiga Grzeszczak**, *Sposób wytwarzania katalizatora węglowego zawierającego nikiel*, P.442754, 08.11.2022.

Mój udział procentowy wynosi: 25%.

6. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, *Sposób utleniania alfa-pinenu*, P.443497, 16.01.2023.

Mój udział procentowy wynosi: 50%.

7. Agnieszka Wróblewska, Joanna Sreńscek-Nazzal, Adrianna Kamińska, **Jadwiga Grzeszczak**, *Sposób wytwarzania katalizatora węglowego z wykorzystaniem biomasy i roztworu wodnego H_3PO_4 i zastosowanie katalizatora węglowego do izomeryzacji alfa-pinenu*, P.443841, 21.02.2023.

Mój udział procentowy wynosi: 25%.

8. Agnieszka Wróblewska, Sylwia Gajewska, **Jadwiga Grzeszczak**, *Sposób utleniania geraniolu w obecności katalizatora*, P.446094, 14.09.2023.

Mój udział procentowy wynosi: 20%.

9. Agnieszka Wróblewska, Sylwia Gajewska, **Jadwiga Grzeszczak**, *Sposób utleniania geraniolu w obecności katalizatora*, P.446095, 14.09.2023.

Mój udział procentowy wynosi: 20%.

10. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, *Sposób otrzymywania katalizatora tytanowo-silikatowego otrzymanego z wykorzystaniem templatów*, P.442825, 16.11.2023.

Mój udział procentowy wynosi: 50%.

11. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, Sylwia Gajewska, *Sposób utleniania geraniolu*, P.448010, 14.03.2024.

Mój udział procentowy wynosi: 47,5%.

Wskaźniki charakteryzujące dorobek naukowy

- Sumaryczny ***Impact Factor*** według listy *Journal Citation Reports* (*JCR*): **37,566**
- Sumaryczny ***5-letni Impact Factor*** według listy *Journal Citation Reports* (*JCR*): **37,759**
- Sumaryczna ***liczba punktów MNiSW***: **960**
- Sumaryczna ***liczba cytowań*** według bazy *Scopus*: **72**

2.4. Aktywny udział w międzynarodowych i krajowych konferencjach naukowych

1. **Jadwiga Tołpa**, Agnieszka Wróblewska, Piotr Miądlicki, *Pozyskiwanie alfa-pinenu i otrzymywanie jego tlenowych pochodnych*, Ogólnopolska Konferencja Młodych Naukowców, Nowe Wyzwania dla Polskiej Nauki – IV Edycja, 01.12.2018, Poznań – **poster (wyróżnienie).**

2. **Jadwiga Tołpa**, Piotr Miądlicki, Agnieszka Wróblewska, *Właściwości i zastosowanie alfa-pinenu oraz jego tlenowych pochodnych*, IV Szczecińskie Sympozjum Młodych Chemików, 14.05.2019, Szczecin – **poster**.

3. **Jadwiga Tołpa**, Piotr Miądlicki, Agnieszka Wróblewska, *Oxidation of α-pinene on TS-1 catalyst – temperature effect*, XI Konferencja Technologie Bezodpadowe i Zagospodarowanie Odpadów w Przemyśle i Rolnictwie, 13.06.2019, Międzyzdroje – **poster**.

4. Piotr Miądlicki, **Jadwiga Tołpa**, Agnieszka Wróblewska, *Isomerization of alpha-pinene over natual minerals – comparsion of activity*, XI Konferencja Technologie Bezodpadowe i Zagospodarowanie Odpadów w Przemyśle i Rolnictwie, 13.06.2019, Międzyzdroje – **poster**.

5. **Jadwiga Tołpa**, Agnieszka Wróblewska, *Extraction of essential oils from the plants of the Pinaceae Family*, XI Ogólnokrajowa Konferencja Naukowa, Młodzi Naukowcy w Polsce – Badania i Rozwój, 30.03.2020, Poznań – **poster**.

6. Jadwiga Tołpa, Agnieszka Wróblewska, *Rosemary as a source of valuable organic compounds*, XII Ogólnokrajowa Konferencja Naukowa, Młodzi Naukowcy w Polsce – Badania i Rozwój, 16.11.2020, Poznań – **poster**.

7. **Jadwiga Tołpa**, Agnieszka Wróblewska, *Preparation, characteristics and properties of silica materials*, Międzynarodowa Konferencja Naukowa, Przemysł 4.0. Algorytmizacja problemów oraz digitalizacja procesów i urządzeń, 20.11.2020, Gorzów Wielkopolski, konferencja odbywała się on-line – **poster**.

8. Jadwiga Tołpa, Agnieszka Wróblewska, *Electricity generation from biomass using a microbial fuel cells*, Międzynarodowa Konferencja Naukowa, Przemysł 4.0. Algorytmizacja problemów oraz digitalizacja procesów i urządzeń, 20.11.2020, Gorzów Wielkopolski, konferencja odbywała się on-line – **poster**.

9. Jadwiga Tołpa, Agnieszka Wróblewska, *Wood biomass as a source of electric energy*, Międzynarodowa Konferencja Naukowa, Przemysł 4.0. Algorytmizacja problemów oraz digitalizacja procesów i urządzeń, 20.11.2020, Gorzów Wielkopolski, konferencja odbywała się on-line – **poster**.

10. Jadwiga Tołpa, Marcin Kujbida, Piotr Miądlicki, Agnieszka Wróblewska, *Extraction of biologically active compounds from the Aegopodium Podagraria using the Soxhlet apparatus*, XII Ogólnokrajowa Konferencja Naukowa, Młodzi Naukowcy w Polsce – Badania i Rozwój 22.03.2021, konferencja odbywała się on-line – **poster**.

11. Jadwiga Tołpa, Marcin Kujbida, Agnieszka Wróblewska, *Studies on the catalytic activity of materials obtained from waste in the form of coffee grounds in oxidation and isomerization reactions*, RETASTE: Rethink Food Waste, 6-8.05.2021, Ateny, konferencja odbywała się on-line – **referat**.

12. Jadwiga Tołpa, Agnieszka Wróblewska, *Composition, distribution, characteristics and applications of activated carbons*, National Scientific Conference, Science and Young Researchers – V Edition, 05.06.2021, Łódź – **poster**.

13. Jadwiga Tołpa, Agnieszka Wróblewska, *Biomass and its applications*, IX Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Wyzwania dla Polskiej Nauki, 2-5.09.2021, Gdańsk – **referat**.

14. Jadwiga Tołpa, Agnieszka Wróblewska, *Examples of activating agents and precursors used for the production of activated carbon*, IX Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Wyzwania dla Polskiej Nauki, 2-5.09.2021, Gdańsk – **referat**.

15. **Jadwiga Tołpa**, Agnieszka Wróblewska, *Process for obtaining activated carbon*, IX Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Wyzwania dla Polskiej Nauki, 2-5.09.2021, Gdańsk – **referat** **(wyróżnienie)** .

16. **Jadwiga Tołpa**, Agnieszka Wróblewska, *Carbon catalysts from pine cones - preparation and testing of their activity*, 5th EuChemS Conference on Green and Sustainable Chemistry (5thEuGSC), 26-29.09.2021, konferencja odbywała się on-line – **referat** **(zaproszenie do przesłania pełnego manuskryptu wygłoszonej prezentacji)**.

17. **Jadwiga Grzeszczak,** Agnieszka Wróblewska, *Methanol extraction of needles and cones of Scots pine using Soxhlet apparatus*, 52nd International Symposium on Essential Oils (ISEO 2022), 4-7.09.2022, Wrocław – **poster**.

18. Agnieszka Wróblewska, **Jadwiga Grzeszczak**, Marcin Kujbida, *The use of the Soxhlet apparatus for obtaining geranium extracts*, 52nd International Symposium on Essential Oils (ISEO 2022), 4-7.09.2022, Wrocław – **poster**.

19. **Jadwiga Grzeszczak**, *The oxidation of limonene with oxygen over the TS-1 catalyst*, Rethink Food Waste, 20-21.10.2022, Heraklion, konferencja odbywała się on-line – **referat**.

20. **Jadwiga Grzeszczak**, *Process for obtaining activated carbon*, V Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Analiza Zagadnienia, Analiza Wyników – Wystąpienie Młodego Naukowca, 28-29.01.2023, Kraków – **referat**.

21. **Jadwiga Grzeszczak**, *The obtaining of Matricaria chamomilla ethanol extracts using the Sohlet apparatus*, V Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Analiza Zagadnienia, Analiza Wyników – Wystąpienie Młodego Naukowca, 28-29.01.2023, Kraków – **referat**.

22. **Jadwiga Grzeszczak**, *Ethanol extraction of Artemisia absinthium L. using Soxhlet apparatus*, V Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Analiza Zagadnienia, Analiza Wyników – Wystąpienie Młodego Naukowca, 28-29.01.2023, Kraków – **referat**.

23. **Jadwiga Grzeszczak**, *The use of the Soxhlet apparatus for obtaining Piper nigrum L. ethanol extracts*, V Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Analiza Zagadnienia, Analiza Wyników – Wystąpienie Młodego Naukowca, 28-29.01.2023, Kraków – **referat**.

24. **Jadwiga Grzeszczak**, Agnieszka Wróblewska, *Oxidation of alpha-pinene over natural minerals – comparison of activity*, 24th Polish Conference of Chemical and Process Engineering, 13-16.06.2023, Szczecin – **poster**.

25. **Jadwiga Grzeszczak**, *Alpha-pinene – terpene abundant in nature*, VII Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Trendy w Badaniach Naukowych –

Wystąpienie Młodego Naukowca, 20-22.10.2023, Kraków – **referat** **(wyróżnienie za aktywność podczas konferencji)**.

26. Jadwiga Grzeszczak, *Therapeutic properties of alpha-pinene*, VII Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Trendy w Badaniach Naukowych – Wystąpienie Młodego Naukowca, 20-22.10.2023, Kraków – **referat** **(wyróżnienie za aktywność podczas konferencji)**.

27. Jadwiga Grzeszczak, *Applications of alpha-pinene*, VII Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Trendy w Badaniach Naukowych – Wystąpienie Młodego Naukowca, 20-22.10.2023, Kraków – **referat** **(wyróżnienie za aktywność podczas konferencji)**.

28. Jadwiga Grzeszczak, *Oxygenated derivatives of alpha-pinene*, VII Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Trendy w Badaniach Naukowych – Wystąpienie Młodego Naukowca, 20-22.10.2023, Kraków – **referat** **(wyróżnienie za aktywność podczas konferencji)**.

29. Jadwiga Grzeszczak, *Alpha-pinene - terpene abundant in nature*, VI Edycja Ogólnopolskiej Konferencji Młodych Naukowców, Nowe Trendy w Badaniach Naukowych – Wystąpienie Młodego Naukowca,15-17.03.2024, Kraków – **referat**.

30. Jadwiga Grzeszczak, *Utlenianie alfa-pinenu, najczęściej występującego w przyrodzie terpenu na mironekutonie*, VII Ogólnopolska Konferencja Naukowa, Rośliny w naukach medycznych i przyrodniczych, 23.05.2024, Lublin – **poster**.

2.5. Osiągnięciach dydaktyczne oraz popularyzacja nauki

1. Działania popularyzujące naukę – udział w przygotowaniu i przeprowadzeniu warsztatów chemicznych *„Pachnące warsztaty”* dla uczniów Technikum Chemicznego Zespołu Szkół im. Ignacego Łukasiewicza w Policach, 09.02.2017.

2. Działania popularyzujące naukę – udział w przygotowaniu i przeprowadzeniu warsztatów chemicznych *„Świat Szalonego Chemika”* w ramach wydarzenia *„Moc Naukowców”*, 31.03-01.04.2017.

3. Działania popularyzujące naukę – udział w przygotowaniu i przeprowadzeniu ćwiczeń laboratoryjnych *„Ekstrakcja i destylacja jako metody wyodrębniania substancji aktywnych z materiału roślinnego”* z uczniami Zespołu Szkół im. Ignacego Łukasiewicza w Policach 2 klasy Technikum Technologii Chemicznej, 14.12.2018.

4. Działania popularyzujące naukę – udział w przygotowaniu i przeprowadzeniu warsztatów chemicznych w ramach wydarzenia *„Festiwal Nauki”* dla uczniów z Liceum

Ogólnokształcącego w Szczecińskiej Szkole Florystycznej oraz z I Liceum Ogólnokształcącego im. Marii Skłodowskiej – Curie w Szczecinie, 21 i 24.09.2021.

5. Działania popularyzujące naukę – udział w przygotowaniu i przeprowadzeniu warsztatów dla uczniów z klas 7 i 8 ze Szkół Podstawowych w Wolinie i Jarszewie, 19.04.2023.

6. Uczestnictwo w prowadzeniu zajęć dydaktycznych: surowce przemysłu syntezy chemicznej, laboratorium przeddyplomowe w roku akademickim 2019/2020.

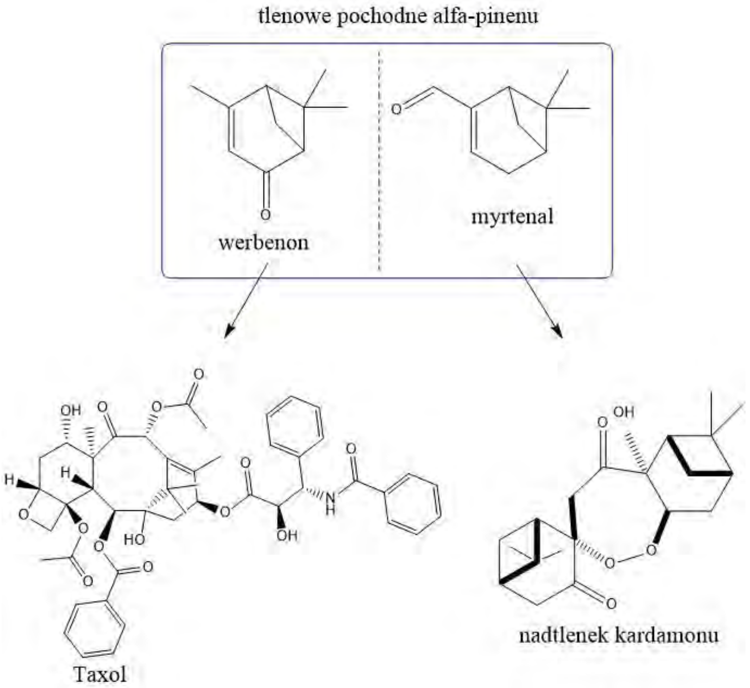
7. Uczestnictwo w prowadzeniu zajęć dydaktycznych: leki pochodzenia naturalnego, operacje jednostkowe w technologii chemicznej w roku akademickim 2020/2021.

8. Uczestnictwo w prowadzeniu zajęć dydaktycznych: zjawiska powierzchniowe i przemysłowe procesy katalityczne, laboratorium przeddyplomowe w roku akademickim 2021/2022.

3. Autoreferat stanowiący rozprawę doktorską

3.1. Wstęp

Terpeny to biologicznie aktywne związki chemiczne, które od dziesięcioleci wykorzystywane są jako surowce do syntezy cennych dla przemysłu kosmetycznego i dla medycyny złożonych związków chemicznych. Jednym z przykładów takiego procesu jest synteza Taxolu, leku o działaniu przeciwnowotworowym, w którym jako surowiec wykorzystano naturalnie występującą w przyrodzie tlenową pochodną alfa-pinenu – werbenon (Rysunek 1). Kolejny przykład stanowi synteza nadtlenku kardamonu, leku przeciwmalarycznego. W tym procesie jako surowiec wykorzystano myrtenal, który również stanowi produkt utleniania alfa-pinenu (Rysunek 1) [1]. Myrtenal naturalnie występuje w przyrodzie, a jego głównym źródłem są owoce i zioła, takie jak: mandarynka, malina, jeżyna, truskawka, imbir, chmiel, czarna herbata, mięta pieprzowa, pieprz oraz cząber [2].

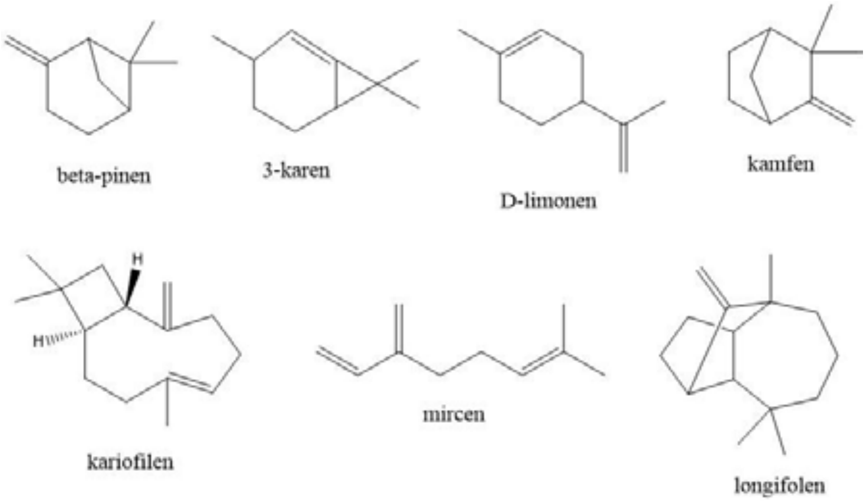


Rysunek 1. Uproszczony schemat otrzymywania Taxolu i nadtlenku kardamonu z pochodnych tlenowych alfa-pinenu (opracowanie własne na podstawie źródła literaturowego [1])

Alfa-pinen jest głównym składnikiem terpentyny otrzymywanej z żywicy drzew iglastych, głównie sosny (Rysunek 2).

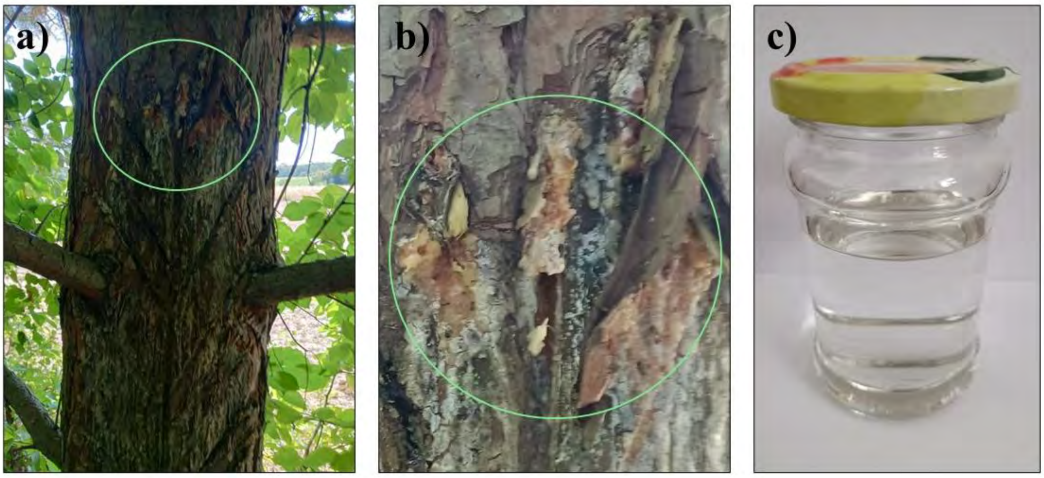
Rysunek 2. Główne źródło alfa-pinenu (opracowanie własne)

Zawartość alfa-pinenu w terpentynie sosnowej zależy od gatunku sosny oraz od obszaru geograficznego, na którym ona rośnie. Zawartość alfa-pinenu w terpentynie sosnowej mieści się zwykle w zakresie 20–95% [3]. Poza alfa-pinenem składnikami terpentyny są następujące związki: beta-pinen, 3-karen, D-limonen, kamfen oraz inne terpeny (Rysunek 3) [4,5].



Rysunek 3. Główne składniki terpentyny (opracowanie własne na podstawie źródeł literaturowych [4,5])

Jedną z metod pozyskiwania terpentyny z żywicy sosnowej (Rysunek 4) jest destylacja próżniowa. Poza terpentyną składnikiem żywicy sosnowej jest kalafonia [4], która stanowi 80% oleożywicy [5]. Otrzymana terpentyna zawiera około 67% alfa-pinenu oraz około 22% beta-pinenu [4].



Rysunek 4. Żywica sosnowa – rysunki a) i b) oraz produkt destylacji żywicy sosnowej – terpentyna – rysunek c) (opracowanie własne)

Terpentynę sosnową otrzymuje się jako produkt uboczny procesu Krafta, stosowanego w produkcji masy celulozowej, z której powstaje papier. Szacuje się, że światowa produkcja terpentyny, zarówno odpadowej (70%), jak i terpentyny pozyskanej w wyniku destylacji (30%), w ostatniej dekadzie wynosiła 330 tysięcy ton/rok. Pozwoliło to na obniżenie cen terpentyny, która w przyszłości może stać się cennym źródłem biopaliw [5]. Głównymi producentami terpentyny są obecnie Chiny (około 50% światowej produkcji) i Brazylia [4].

Na skalę przemysłową alfa-pinen jest otrzymywany z odpadowej terpentyny metodą rektyfikacji próżniowej, która składa się z kilku etapów. Pierwszy etap tej metody polega na usunięciu z odpadowej terpentyny lotnych związków siarki, takich jak: merkaptan metylu, siarczek dimetylu i disiarczek dimetylu za pomocą destylacji z parą wodną. Następnie terpentynę, która zawiera śladowe ilości siarki (poniżej 500 ppm), poddaje się destylacji pod zmniejszonym ciśnieniem. W wyniku przeprowadzenia procesu destylacji otrzymuje się terpentynę siarczanową, która zawiera około 60–70% alfa-pinenu i około 20–25% beta-pinenu [3]. W Polsce prace nad pozyskaniem alfa-pinenu z odpadowej, pochodzącej z przemysłu celulozowo-papierniczego terpentyny, były realizowane w skali przemysłowej w Śląskich Zakładach Rafineryjnych w Czechowicach-Dziedzicach. W Zakładach tych uzyskano alfa-pinen o czystości 95%, który zawierał 40–90 ppm siarki [6].

Innym naturalnym i odnawialnym źródłem alfa-pinenu są zioła (lawenda [7], rozmaryn [8], szałwia [7], rumianek [9], werbena cytrynowa [10], pietruszka, bazylia, koper, chmiel, kminek, konopia, krwawnik pospolity, mięta [7]), owoce (mandarynka, pomarańcza, cytryna [11]) oraz drzewa iglaste (świerk [12], jodła [13,14], jałowiec [14]).

Alfa-pinen występuje w olejkach eterycznych znajdujących się w różnych częściach roślin. Zawartość alfa-pinenu w olejkach eterycznych zależy od gatunku roślin oraz od obszaru geograficznego, na którym ta roślina rośnie. Alfa-pinen jest pozyskiwany z roślin metodą destylacji z parą wodną (hydrodestylacji). Zawartość alfa-pinenu w olejkach pozyskiwanych z drzew iglastych z rodziny sosnowatych mieści się w zakresie 12-66% [15,16].

Alfa-pinen jest stosowany jako surowiec w syntezie kamfory, która stanowi składnik farmaceutyków stosowanych w chorobach skóry. Monoterpen ten jest także wykorzystywany jako środek owadobójczy. Alfa-pinen znalazł również zastosowanie jako zielony rozpuszczalnik, który może być stosowany zamiast toluenu w destylacji wykorzystywanej do oznaczania zawartości wody w produktach spożywczych [17–19]. Monoterpen ten jest również stosowany w medycynie. Alfa-pinen jest między innymi składnikiem takich leków, jak: Rowatinex i Rowachol. Pierwszy z nich działa moczopędnie, natomiast drugi wykazuje działanie żółciopędne [20].

Alfa-pinen stanowi surowiec odnawialny pozyskiwany z biomasy, którą stanowi odpadowa terpentyna i jest chętnie wykorzystywany jako surowiec w syntezie związków zapachowych w różnych procesach chemicznych. Jednym z ważniejszych procesów, w którym alfa-pinen jest przekształcany do cennych dla przemysłu perfumeryjno-kosmetycznego i dla medycyny związków jest reakcja utleniania.

Dotychczas w literaturze opisano badania nad utlenianiem alfa-pinenu w obecności mezoporowatych katalizatorów silikatowych, takich jak: Ti-MCM-41 [21,22], Ti-HMM [23], Ti-HMS [24], Ti-MCM-48 [25] oraz Cr-SBA-15 [26]. Jako katalizatory utleniania alfa-pinenu stosowano również zeolity ZSM-5 i Y, które były modyfikowane kobaltem [27–29]. Badania nad utlenianiem alfa-pinenu prowadzono także na katalizatorach węglowych, modyfikowanych różnymi metalami, na przykład niklem [30]. W procesie utleniania alfa-pinenu stosowano również z powodzeniem nanocząstki metali, takich jak: miedź [31], ruten [32] oraz wanad [33]. Proces utleniania alfa-pinenu prowadzono w obecności różnych utleniaczy i rozpuszczalników.

Reakcję utleniania alfa-pinenu na katalizatorze Ti-MCM-41 prowadzono w temperaturze 70°C przez 7 godzin. Jako utleniacz zastosowano nadtlenek wodoru. Proces prowadzono w acetonitrylu, który użyto w roli rozpuszczalnika. W badanych warunkach uzyskano następujące wartości selektywności głównych produktów: werbenon od 36 do 54% mol, werbenol od 13 do 46% mol, a aldehyd kamfoleinowy od 0 do 27% mol. Konwersja alfa-pinenu mieściła się w zakresie 1-37% mol [21,22].

Katalizator Ti-MCM-41 o różnym stosunku molowym tytanu do krzemu został zastosowany przez Mai i współpracowników w reakcji utleniania alfa-pinenu nadtlenkiem wodoru. Jako rozpuszczalnik podczas utleniania zastosowano acetonitryl. Proces prowadzono w temperaturze 60°C przez 1 godzinę. W badanych warunkach uzyskano następujące wartości selektywności głównych produktów: werbenol od 47 do 68%, werbenon od 0 do 21%, tlenek alfa-pinenu od 9 do 19%, trans-karweol od 0 do 12% oraz aldehyd kamfoleinowy od 7 do 9%. Konwersja alfa-pinenu mieściła się w zakresie 6-7% [22].

Robles-Dutenhefner ze współpracownikami do utleniania alfa-pinenu wykorzystał katalizator Cr-MCM-41, a jako utleniacz w tym procesie został zastosowany tlen. Utlenianie prowadzono w temperaturze 60°C przez 3,5-6 godzin. Selektywności przemiany do odpowiednich produktów były następujące: werbenol 25-33%, werbenon 26%, tlenek alfa-pinenu 5-8%, aldehyd kamfoleinowy 3-4%, a konwersja alfa-pinenu wyniosła 38-40% [34].

Kolejnym mezoporowatym katalizatorem stosowanym do utleniania alfa-pinenu był katalizator Ti-HMM. Proces utleniania alfa-pinenu na Ti-HMM prowadzono w temperaturze 55°C przez 6 godzin. Jako utleniacz w tym procesie zastosowano nadtlenek wodoru. Podczas badań selektywność przemiany do tlenku alfa-pinenu wyniosła 99%, konwersja alfa-pinenu osiągnęła wartość 23% mol, a konwersja nadtlenku wodoru wyniosła 50% mol [23].

Katalizator Ti-HMS zastosowano do utlenienia alfa-pinenu wodoronadtlenkiem tert-butylu. Jako rozpuszczalnik zastosowano acetonitryl. Reakcję prowadzono w temperaturze 77°C przez 24 godziny. W badanych warunkach uzyskano następujące wartości selektywności głównych produktów: tlenek alfa-pinenu do 5%, aldehyd kamfoleinowy do 82%, werbenol do 6%, werbenon do 51% i 1,2-pinanodiol do 5% [24].

Kapoor i Raj przedstawili metodę utleniania alfa-pinenu na katalizatorze tytanowo-silikatowym Ti-MCM-48, przy użyciu nadtlenku wodoru jako utleniacza. Katalizator Ti-MCM-48 został użyty w ilości 2% wag. Reakcję prowadzono w temperaturze 55°C przez 5 godzin. Produktem utleniania był tlenek alfa-pinenu (selektywność 100% mol), a konwersja alfa-pinenu wyniosła 8% mol [25].

Selvaraj ze współpracownikami opisał utlenianie alfa-pinenu na mezoporowatych katalizatorach chromowo-silikatowych takich jak: Cr–SBA-15, za pomocą wodoronadtlenku tert-butylu jako utleniacza. Reakcję prowadzono w chlorobenzenie, w temperaturze 85°C, a czas reakcji wynosił 24 godziny. Uzyskana selektywność przemiany do werbenonu mieściła się w zakresie 19-88%, natomiast uzyskana selektywność przemiany do werbenolu wynosiła 4-20%, do tlenku alfa-pinenu 6-13%, a konwersja alfa-pinenu osiągała wartości w zakresie 25-92%. Podczas badań wykazano, że następowało znaczące wymywanie chromu ze struktury katalizatora Cr–SBA-15 [26].

Qi ze współpracownikami opisał metodę utleniania alfa-pinenu, w której katalizatorem był materiał porowaty Co-ZSM-5, do którego wprowadzono ligandy typu zasady Schiff'a. Jako czynniki utleniające zastosowano: tlen z powietrza, wodoronadtlenek tert-butylu, podchloryn sodu, nadjodan sodu oraz nadtlenek wodoru. Utlenianie prowadzono w dimetyloformamidzie, dimetyloacetamidzie, dioksanie, cykloheksanolu i toluenie (rozpuszczalniki). Temperatura prowadzenia reakcji wynosiła 90°C, a czas prowadzenia reakcji utleniania wynosił 5 godzin. W badanych warunkach uzyskano następujące wartości selektywności przemiany do głównych produktów: tlenek alfa-pinenu od 28 do 88%, werbenol od 0 do 18%, werbenon od 7 do 60%. Konwersja alfa-pinenu mieściła się w zakresie 1-95%. Najwyższą konwersję alfa-pinenu oraz najwyższą selektywność przemiany do związku epoksydowego uzyskano, gdy proces prowadzono w dimetyloformamidzie oraz w obecności wodorotlenku tert-butylu, który zastosowano jako inicjator reakcji oraz przy użyciu tlenu z powietrza, które doprowadzono do środowiska reakcji przez bełkotkę [27] .

Tang i współpracownicy zastosowali zeolity Co-ZSM-5 jako katalizatory utleniania alfa-pinenu. Proces prowadzono w obecności dimetyloformamidu jako rozpuszczalniku i wodorotlenek tert-butylu jako inicjatora reakcji. Utleniaczem w procesie był tlen z powietrza, doprowadzany do środowiska reakcji przez bełkotkę. Reakcją prowadzono w temperaturze 90°C przez 5 godzin. W badanych warunkach uzyskano następujące wartości selektywności przemiany do głównych produktów: tlenek alfa-pinenu 86%, werbenol 4%, a werbenon 8%. Konwersja alfa-pinenu wyniosła 93% [28].

Do utleniania alfa-pinenu tlenem cząsteczkowym zastosowano również katalizatory na bazie zeolitu Y. Reakcję prowadzono w dimetyloformamidzie, który stosowano jako rozpuszczalnik. Utlenianie prowadzono w temperaturze 100°C przez 4 godziny. W badanych warunkach selektywność przemiany do tlenku alfa-pinenu mieściła się w zakresie 60-71%, natomiast selektywności przemiany do pozostałych związków wynosiły odpowiednio: do werbenolu 10-12%, do werbenonu 16-20%, a do trans-karweolu 1-10%. Konwersja alfa-pinenu wynosiła natomiast 31-48% [29].

W badaniach nad utlenianiem alfa-pinenu prowadzonych przez zespół Pani prof. Agnieszki Wróblewskiej zastosowano katalizatory węglowe modyfikowane niklem. Proces prowadzono bez udziału rozpuszczalnika, a jako utleniacz zastosowano tlen podawany do środowiska reakcji przez bełkotkę. W najkorzystniejszych warunkach, takich jak: temperatura 100°C, ilość katalizatora 0,5% wag. i czas reakcji 150 minut, selektywność przemiany do tlenku alfa-pinenu wyniosła 34% mol, a konwersja alfa-pinenu osiągnęła wartość 34% mol [30].

Nanocząstki rutenu okazały się aktywne jako katalizatory do utleniania alfa-pinenu wodoronadtlenkiem tert-butylu. Proces prowadzono w temperaturze 20°C przez 3 godziny. Jako główny produkt otrzymano werbenon z wydajnością od 29 do 39%. Konwersja alfa-pinenu wynosiła od 75 do 100% [32].

Resul ze współpracownikami do utlenienia alfa-pinenu w roli katalizatora zastosował polioksometalan na bazie wolframu o wzorze $(\{PO_4[WO(O_2)_2]_4{}^{3-})$. Utlenianie alfa-pinenu prowadzono w temperaturze 50°C przez 20 minut. W procesie tym nie zastosowano rozpuszczalnika, a jako utleniacz wykorzystano nadtlenek wodoru. Produktem utleniania był tlenek alfa-pinenu (selektywność 100%), a konwersja nadtlenku wodoru wyniosła 93% [35].

W literaturze naukowej opublikowanej w ostatnich pięciu latach istnieją doniesienia na temat utleniania alfa-pinenu na katalizatorach innych niż tytanowo-silikatowe katalizatory heterogeniczne. W artykule opublikowanym w 2023 roku opisano proces utleniania alfa-pinenu tlenem, w którym jako katalizator zastosowano SeO_2, a jako rozpuszczalnik użyto etanol. Proces ten prowadzono od 5 do 13 godzin w temperaturze 78°C. Jako główne produkty otrzymano myrtenol (selektywność od 44% do 72%) i myrtenal (selektywność od 28% do 56%). Konwersja alfa-pinenu mieściła się w zakresie 18-50%. W procesie tym nie otrzymano tlenku alfa-pinenu [36].

W tym samym roku opublikowano artykuł, w którym Zheng ze współpracownikami zastosował materiał węglowy immobilizowany fosfowolframianem amonu, jako katalizator do utleniania alfa-pinenu nadtlenkiem wodoru. Proces utleniania prowadzono w acetonitrylu jako rozpuszczalniku, w temperaturze 40°C i w czasie reakcji wynoszącym 3 godziny. W procesie tym otrzymano takie związki jak: 1,4-acetylo-1-metylo-1-cykloheksen (selektywność 2,6%), tlenek alfa-pinenu (selektywność 0,8%), aldehyd kamfoleinowy (selektywność 7,5%), werbenol (selektywność 8,6%), werbenon (selektywność 8,3%), karweol (selektywność 5,6%), sobrerol (selektywność 40,5%), 1,2-pinanediol (selektywność 6,6%), 5-(2-hydroksypropan-2-yl)-2-metylocykloheks-2-en-1,4-diol (selektywność 3,4%), a konwersja alfa-pinenu wyniosła 90,6% [37].

Mdletshe ze współpracownikami wykorzystał w roli katalizatorów do utlenienia alfa-pinenu nanostrukturalne spinele $CuFe_2O_4$ oraz CuO, a jako utleniacz zastosował wodorotlenek tert-butylu. Reakcję prowadzono w temperaturze 80°C przez 20 godzin w acetonitrylu, który pełnił rolę rozpuszczalnika. Selektywności przemiany do głównych produktów mieściły się w zakresie: tlenek alfa-pinenu 10-60%, werbenol 12-37% oraz werbenon 8-39%. Konwersja alfa-pinenu wynosiła natomiast 10-47% [38].

Do fotoutleniania alfa-pinenu zastosowano nanokatalizatory CeO_2 z tlenkami takich metali jak: Cu, Co, Ni, Mn i Fe. Reakcję prowadzono w temperaturze 25°C przez 5 godzin w acetonitrylu. Selektywności przemiany do głównych produktów wynosiły odpowiednio: tlenek alfa-pinenu 39-58%, werbenol 3-14%, a werbenon 3-11%, natomiast konwersja alfa-pinenu mieściła się w zakresie 28-71% [39].

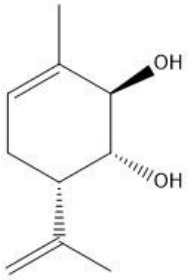
Inną grupę katalizatorów stosowanych do utleniania alfa-pinenu stanowią metaloporfiryny (FeClDPDME). Reakcję utleniania alfa-pinenu na metaloporfirynach prowadzono w temperaturze 105°C przez 7 godzin i bez udziału rozpuszczalnika. Jako czynnik utleniający stosowano w tym procesie tlen. Selektywności przemiany do głównych produktów wynosiły odpowiednio: werbenol 32%, werbenon 29%, tlenek alfa-pinenu 2%, a konwersja alfa-pinenu osiągnęła wartość 42% [40].

Główne pochodne tlenowe alfa-pinenu, takie jak: tlenek alfa-pinenu, werbenol i werbenon są szeroko wykorzystywane w przemyśle chemicznym, spożywczym, kosmetycznym, perfumeryjnym oraz w medycynie. Związki te są stosowane między innymi jako dodatki smakowe i zapachowe do żywności, napojów, kosmetyków oraz jako składniki kompozycji zapachowych do perfum. Tlenowe pochodne alfa-pinenu są stosowane do otrzymywania związków biologicznie czynnych, które są cenne dla medycyny, ale także same są wykorzystywane w nowoczesnych terapiach w medycynie, na przykład jako związki o działaniu antynowotworowym, czy antybakteryjnym.

Tlenek alfa-pinenu jest stosowany jako surowiec w syntezie związków zapachowych, takich jak: aldehyd kamfoleinowy i trans-karweol [41].

Werbenol znalazł szerokie zastosowanie w przemyśle spożywczym i perfumeryjnym, jako dodatek smakowy i zapachowy dodawany do deserów, napojów, perfum i kosmetyków. Werbenol jest także stosowany w rolnictwie do zwalczania szkodliwych owadów. Związek ten znalazł również zastosowanie jako surowiec do produkcji cennych dla przemysłu perfumeryjnego i dla medycyny związków chemicznych, jako przykład należy podać cytral i witaminę A [42,43]. Naturalnym i odnawialnym źródłem werbenolu jest imbir lekarski. Werbenol występuje w olejku imbirowym w ilości około 52% [44]. Ze względu na swoje właściwości przeciwutleniające i przeciwzapalne, werbenol można uznać za substancję aktywną biologicznie o szerokim spektrum działania [45].

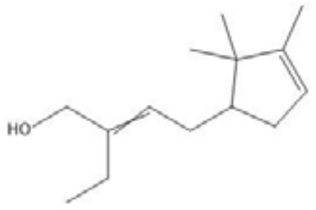
Werbenon jest wykorzystywany do syntezy (1R,2R,6S)-3-metylo-6-(prop-1-en-2-ylo)cykloheks-3-en-1,2-diolu (Rysunek 5), który wykazuje aktywność terapeutyczną w leczeniu choroby Parkinsona [46].



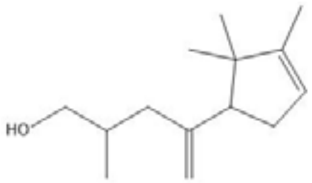
Rysunek 5. Wzór (1R,2R,6S)-3-metylo-6-(prop-1-en-2-ylo)cykloheks-3-en-1,2-diolu (opracowanie własne na postawie źródła literaturowego [46])

Ponadto werbenon stosuje się do produkcji Taxolu, leku o działaniu przeciwnowotworowym [1,47]. Taxol znalazł między innymi zastosowanie w leczeniu nowotworów: jajnika, piersi i płuc. Związek ten jest również stosowany w leczeniu takich chorób, jak: łuszczyca, Alzheimer i Parkinson [48].

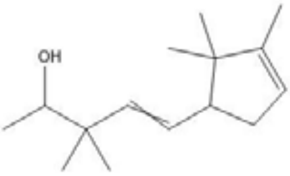
Aldehyd kamfoleinowy jest stosowany jako surowiec w syntezie substancji zapachowych, które są składnikiem olejku eterycznego pozyskiwanego z drzewa sandałowego. Na rysunku 6 przedstawiono wzory i nazwy tych związków. Związki te produkowane są przez szwajcarskie firmy, takie jak: Firmenich i Givaudan, niemiecką firmę Symrise i japońską firmę Kao [49,50] – są to najwięksi producenci substancji zapachowych na świecie.



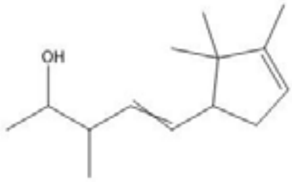
Dartanol
2-buten-1-ol, 2-etylo-4-(2,2,3-trimetylo-3-cyklopenten-1-yl)



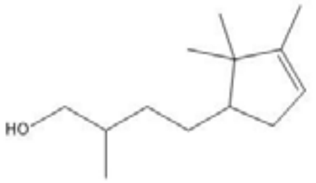
Firzantol
4-penten-1-ol, 2-metylo-4-(2,2,3-trimetylo-3-cyklopenten-1-yl)



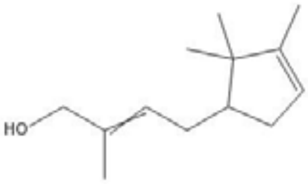
Polysantol
4-penten-2-ol, 3,3-dimetylo-5-(2,2,3-trimetylo-3-cyklopenten-1-yl)



Ebanol
3-metylo-5-(2,2,3-trimetylo-3-cyklopenten-1-yl)-4-penten-2-ol



Brahmanol
2,2,3-tetrametylocyklopent-3-ene-1-butanol



Sandalmysore Core
2-metylo-4-(2,2,3-trimetylo-3-cyklopneten-1-yl)-2-buten-1-ol

Rysunek 6. Substancje zapachowe otrzymywane na bazie aldehydu kamfoleinowego (opracowanie własne na podstawie źródła literaturowego [49])

Możliwość otrzymania z alfa-pinenu, który stanowi naturalny, odnawialny i łatwo dostępny surowiec, jego cennych tlenowych pochodnych, takich jak: tlenek alfa-pinenu, werbenol oraz werbenon o licznych zastosowaniach w przemyśle spożywczym, kosmetycznym, perfumeryjnym, farmaceutycznym oraz w medycynie, skłoniła mnie do podjęcia badań nad utlenianiem tego terpenu. Należy podkreślić, że w literaturze naukowej istnieje niewiele doniesień na temat utleniania tego związku na katalizatorach tytanowo-silikatowych. Nie ma również wielu informacji na temat prowadzeniu tego procesu na katalizatorach pochodzenia naturalnego, tzn. na minerałach i katalizatorach węglowych otrzymanych z odpadowej biomasy.

3.2. Cel pracy

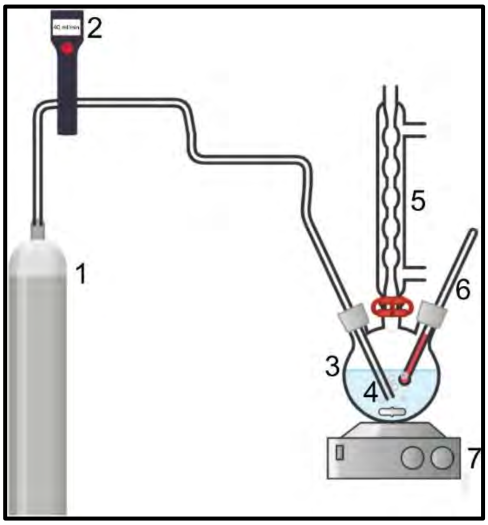
Celem rozprawy doktorskiej było zbadanie aktywności katalitycznej materiałów porowatych w bezrozpuszczalnikowym procesie utleniania alfa-pinenu tlenem cząsteczkowym. Badania przedstawione w niniejszej pracy polegały na jakościowym i ilościowym oznaczeniu produktów utleniania alfa-pinenu, z wykorzystaniem chromatografii gazowej (GC) i chromatografii gazowej sprzężonej ze spektrometrią mas (GC-MS), oraz na wyznaczeniu najkorzystniejszych parametrów prowadzenia tego procesu, takich jak: temperatura, ilość katalizatora oraz czas reakcji, pozwalających otrzymać tlenek alfa-pinenu, werbenol oraz werbenon jako główne produkty utleniania alfa-pinenu. W celu przeprowadzenia szeregu badań nad utlenianiem alfa-pinenu na katalizatorach heterogenicznych zaprojektowano specjalną aparaturę, którą przedstawiono na rysunku 7.

W ramach niniejszej pracy doktorskiej, jako katalizatory do badań procesu utleniania alfa-pinenu, zastosowano następujące materiały porowate: syntetyczne zeolity TS-1 o różnej zawartości tytanu, syntetyczne zeolity ZSM-5 o różnej zawartości glinu, katalizatory węglowe otrzymane z szyszek sosny zwyczajnej oraz klinoptylolity (zeolity pochodzenia naturalnego) o różnej wielkości cząstek. Katalizatory heterogeniczne zostały scharakteryzowane za pomocą następujących metod instrumentalnych: UV-Vis, FTIR, EDXRF, XRD, SEM, DTA-TG oraz XPS. Parametry teksturalne otrzymanych materiałów określono na podstawie pomiarów sorpcji azotu w temperaturze -196°C. Dla katalizatora TS-1 przeprowadzono również badania kinetyki utleniania alfa-pinenu.

W ostatnim etapie pracy przeprowadzono badania nad aktywnością przeciwutleniającą ekstraktów etanolowych uzyskanych z roślin zawierających alfa-pinen – badania te prowadzono metodami DPPH i ABTS, oraz przygotowano emulsje kosmetyczne z tymi ekstraktami. Badania te miały na celu pokazanie innych, możliwych zastosowań alfa-pinenu, nie tylko w roli substratu w syntezach organicznych, ale również jako związku mogącego znaleźć zastosowania w medycynie i w kosmetyce do przygotowania preparatów o działaniu leczniczym i kosmetycznym na skórę.

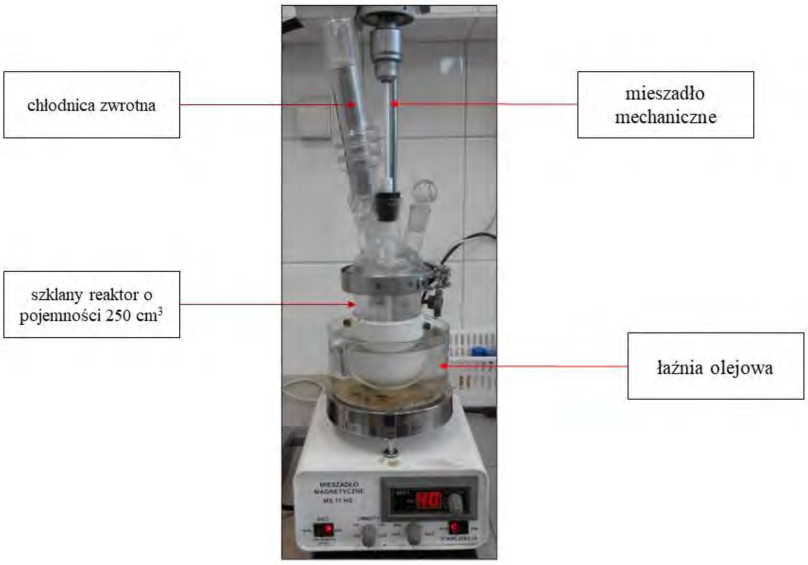
3.3. Omówienie wyników badań

Syntetyczne zeolity TS-1 o różnej zawartości tytanu miały posłużyć do badań izomeryzacji alfa-pinenu przeprowadzanych przez zespół Pani prof. Agnieszki Wróblewskiej. Podczas badań wstępnych nieoczekiwanie okazało się, że otrzymane katalizatory są nieaktywne w procesie izomeryzacji alfa-pinenu, a ich zastosowanie powoduje zachodzenie procesów autoutleniania alfa-pinenu tlenem z powietrza. Ze względu na aktywność otrzymanych katalizatorów TS-1 w procesie autoutleniania alfa-pinenu tlenem z powietrza, postanowiono zbadać aktywność katalityczną TS-1 w bezrozpuszczalnikowym procesie utleniania alfa-pinenu tlenem cząsteczkowym (99.99%, Messer, Szczecin, Poland), doprowadzanym do środowiska reakcji przez bełkotkę. W tym celu skonstruowano specjalną aparaturę przedstawioną na rysunku 7, która posłużyła do badań nad utlenianiem alfa-pinenu na katalizatorach heterogenicznych.



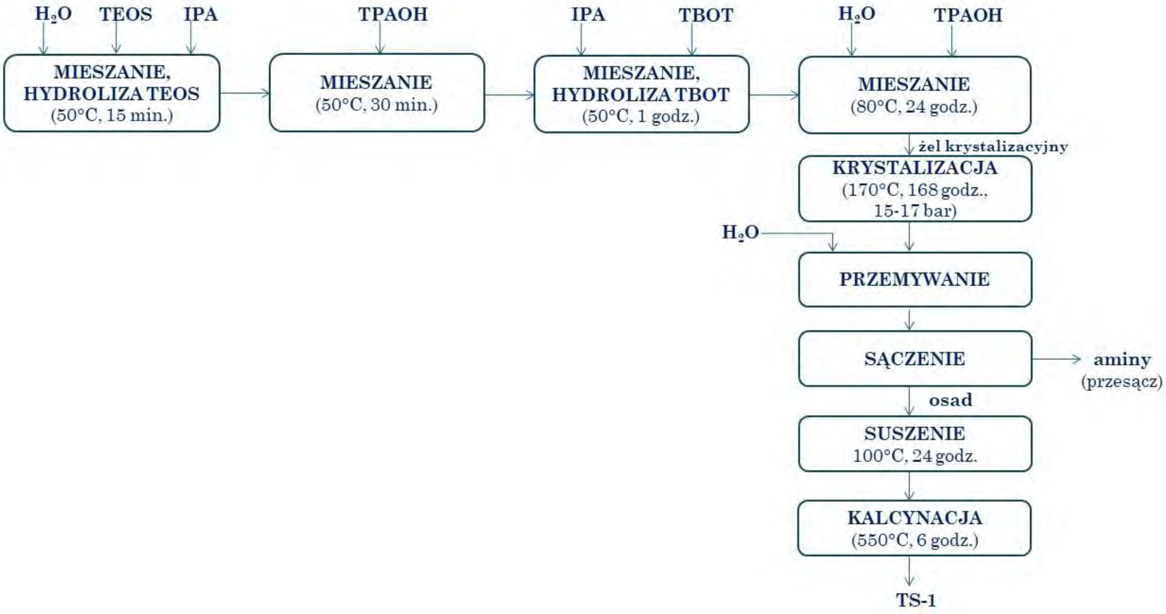
Rysunek 7. Schemat aparatury wykorzystanej w procesie utleniania alfa-pinenu na katalizatorach heterogenicznych (opracowanie własne): 1 – butla z tlenem, 2 – regulator przepływu tlenu, 3 – reaktor szklany o pojemności 25 cm^3, 4 – bełkotka szklana do podawania tlenu, 5 – chłodnica zwrotna, 6 – termometr, 7 – mieszadło magnetyczne posiadające funkcję grzania

Serię katalizatorów TS-1 o różnej zawartości tytanu otrzymano w oparciu o metodę opisaną przez Taramasso i współpracowników [51]. Syntezę katalizatora TS-1 prowadzono w szklanym reaktorze o pojemności 250 cm^3, wyposażonym w chłodnicę zwrotną, mieszadło magnetyczne oraz łaźnię olejową. Aparaturę stosowaną do syntezy TS-1 przedstawiono na rysunku 8.



Rysunek 8. Aparatura do syntezy żelu syntezowego katalizatora TS-1 (opracowanie własne)

Katalizatory TS-1 otrzymano metodą hydrotermalną z wykorzystaniem ortokrzemianu tetraetylu (TEOS) jako źródła krzemu, wodorotlenku tetrapropyloamoniowego jako templantu (TPAOH) oraz ortotytanianu tetrabutylu (TBOT) jako źródła tytanu. Schemat blokowy otrzymywania katalizatora TS-1 metodą hydrotermalną przedstawiono na rysunku 9.



Rysunek 9. Schemat blokowy otrzymywania katalizatora TS-1 metodą hydrotermalną (opracowanie własne na podstawie źródła literaturowego [51])

Podczas syntezy mikroporowatych materiałów TS-1 zmieniano stosunek molowy krzemu do tytanu od 10:1 do 40:1. Otrzymane katalizatory oznaczono jako: TS-1_1 (zawartość tytanu 9,92% wag.), TS-1_2 (zawartość tytanu 5,42% wag.), TS-1_3 (zawartość tytanu 3,39% wag.) i TS-1_4 (zawartość tytanu 3,08% wag).

Otrzymane katalizatory TS-1 poddano następującym badaniom instrumentalnym: XRF, XRD oraz SEM. Parametry teksturalne otrzymanych materiałów określono na podstawie pomiarów sorpcji azotu w temperaturze -196°C. Dla badanego procesu wyznaczono również energię aktywacji. Zawartość tytanu w materiałach TS-1 określono metodą EDXRF. Strukturę MFI oraz symetrię ortorombową katalizatorów TS-1 potwierdzono wykorzystując metodę XRD.

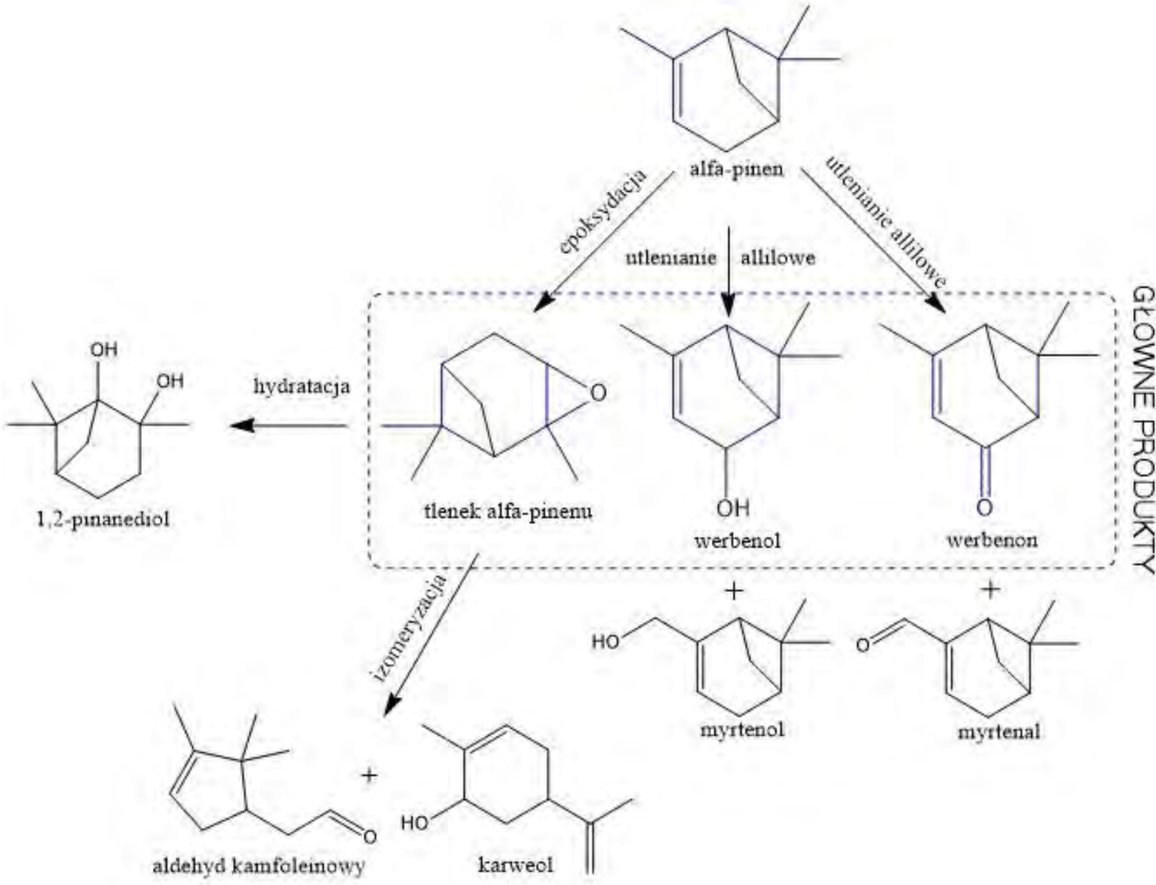
W pierwszym etapie badań aktywności katalitycznej otrzymanych materiałów, określono wpływ zawartości tytanu w katalizatorze TS-1 na konwersję alfa-pinenu oraz selektywności odpowiednich produktów. Spośród testowanych katalizatorów najbardziej aktywnym okazał się katalizator TS-1_2 o zawartości tytanu wynoszącej 5,42% wag., dla którego uzyskano najwyższą konwersję alfa-pinenu wynoszącą 31% mol. Podczas badań wykazano, że ilość tytanu wbudowanego w strukturę TS-1 wpływa na aktywność katalityczną TS-1 w procesie utleniania alfa-pinenu. Jednak zbyt duża ilość tytanu, wynosząca 9,92% wag., zmniejsza aktywność katalityczną TS-1. Spowodowane jest to powstawaniem anatazu (TiO_2), który osadza się w porach katalizatora TS-1. Tytan występuje w centrach aktywnych katalizatora TS-1 i bierze udział w reakcji utleniania alfa-pinenu, dlatego zbyt mała ilość tytanu włączonego do struktury katalizatora (poniżej 5,42% wag.) może zmniejszać aktywność katalityczną zeolitu TS-1.

Katalizator TS-1_2 zastosowano w kolejnych etapach badań, które polegały na zbadaniu wpływu temperatury w zakresie 75-100°C, czasu reakcji od 1 do 48 godzin oraz ilości katalizatora od 0,1 do 5% wag. w mieszaninie reakcyjnej na konwersję alfa-pinenu i selektywności głównych produktów. Analizę jakościową i ilościową produktów utleniania alfa-pinenu przeprowadzono za pomocą metod: GC i GC-MS. Dla każdej z przeprowadzonych syntez obliczano bilans masowy. Na podstawie tych bilansów wyznaczano takie funkcje opisujące proces utleniania alfa-pinenu jak: konwersja alfa-pinenu i selektywności odpowiednich produktów, które obliczono według następujących wzorów:

- Konwersja alfa-pinenu = (liczba moli przereagowanego alfa-pinenu / liczba moli wprowadzonego do reaktora alfa-pinenu) * 100% [% mol],

- Selektywność produktu = (liczba moli produktu / liczba moli przereagowanego alfa-pinenu) * 100% [% mol].

Analizy jakościowe przeprowadzone metodami GC i GC-MS wykazały, że głównymi produktami przemian alfa-pinenu na katalizatorach TS-1 są: tlenek alfa-pinenu, werbenon i werbenol. W mniejszych ilościach w procesie utleniania alfa-pinenu powstawały następujące związki: aldehyd kamfoleinowy, pinokarweol, myrtenal, myrtenol, karweol, karwon oraz pinanediol. Tlenowe pochodne alfa-pinenu oraz drogi powstawania tych związków przedstawiono na rysunku 10.



Rysunek 10. Drogi powstawania odpowiednich produktów w procesie utleniania alfa-pinenu (opracowanie własne)

Badania wykazały, że mikroporowate materiały porowate TS-1 o różnej zawartości tytanu są aktywnymi katalizatorami w bezrozpuszczalnikowym procesie utleniania alfa-pinenu tlenem cząsteczkowym. Stwierdzono, że najkorzystniej jest prowadzić proces utleniania alfa-pinenu w obecności katalizatora TS-1 o zawartości tytanu wynoszącej 5,42% wag. (TS-1_2), w temperaturze 85°C, przez 6 godzin i przy zawartości katalizatora TS-1_2 w mieszaninie reakcyjnej wynoszącej 1% wag. W tych warunkach konwersja alfa-pinenu wyniosła 34% mol, a selektywności głównych produktów procesu utleniania alfa-pinenu były następujące: tlenek alfa-pinenu 29% mol, werbenol 15% mol i werbenon 12% mol. Pełne wyniki badań przedstawiono w pracy **[1.1.]** opublikowanej w czasopiśmie *Materials*.

Następne katalizatory, które zastosowano do bezrozpuszczalnikowego utleniania alfa-pinenu tlenem cząsteczkowym to prekursory TS-1. W artykule **[1.2.]** opublikowanym w czasopiśmie *Chemical Engineering Research and Design* opisano badania aktywności katalitycznej komercyjnych zeolitów ZSM-5 o różnej zawartości glinu. Trzy badane zeolity ZSM-5 zostały oznaczone w następujący sposób (zgodnie z ich procentową zawartością glinu): ZSM5_1 (2,5% wag.), ZSM-5_2 (0,59% wag.) i ZSM-5_3 (0,38% wag).

Charakterystykę fizykochemiczną katalizatorów ZSM-5 przeprowadzono za pomocą następujących metod instrumentalnych: UV-Vis, FTIR, EDXRF, XRD, SEM oraz DTA-TG. Parametry teksturalne zeolitów ZSM-5 określono na podstawie pomiarów sorpcji azotu w temperaturze -196°C.

Analizując widma UV-Vis zeolitów ZSM-5 potwierdzono obecność atomów glinu w strukturze tych materiałów. Obecność struktury krzemianowej, charakterystycznej dla zeolitów oraz obecność grup hydroksylowych pochodzących od cząsteczek wody zaabsorbowanych na powierzchni ZSM-5, potwierdzono wykorzystując analizę metodą FTIR. Zawartość glinu w zeolitach ZSM-5 określono za pomocą metody EDXRF. Strukturę MFI oraz symetrię ortorombową katalizatorów ZSM-5 potwierdzono wykorzystując metodę XRD. Morfologię powierzchni katalizatorów ZSM-5 oceniano za pomocą skaningowego mikroskopu elektronowego. Stabilność termiczną zeolitów ZSM-5 zbadano metodą DTA-TG. Na podstawie pomiarów sorpcji azotu w temperaturze -196°C potwierdzono, że zeolity ZSM-5 to głównie materiały mikroporowate.

Testy katalityczne porowatych materiałów ZSM-5 polegały na zbadaniu wpływu temperatury w zakresie 75-110°C, ilości katalizatora od 0,025 do 5% wag. w mieszaninie reakcyjnej oraz czasu reakcji od 1 do 48 godzin, na konwersję alfa-pinenu i selektywności głównych produktów. Badania aktywności katalitycznej zeolitów ZSM-5 o różnej zawartości glinu wykazały, że te porowate materiały są aktywnymi katalizatorami utleniania alfa-pinenu tlenem, gdy utlenianie jest prowadzone bez udziału rozpuszczalnika. Stwierdzono, że najkorzystniej jest prowadzić proces utleniania alfa-pinenu w obecności katalizatora ZSM-5 o zawartości glinu wynoszącej 0,59% wag. (ZSM-5_2), w temperaturze 95°C, przez 6 godzin i przy ilości katalizatora ZSM-5_2 w mieszaninie reakcyjnej wynoszącej 0,05% wag. (podczas badań instrumentalnych katalizatorów ZSM-5 to właśnie ten katalizator ZSM-5 charakteryzował się największą powierzchnię właściwą). W tych warunkach konwersja alfa-pinenu wyniosła 49% mol, a selektywności głównych produktów procesu utleniania alfa-pinenu były następujące: tlenek alfa-pinenu 28% mol, werbenol 16% mol i werbenon 18% mol.

Kolejną grupę materiałów porowatych badanych w tej dysertacji w bezrozpuszczalnikowym procesie utleniania alfa-pinenu tlenem były węgle aktywne otrzymane z szyszek sosny zwyczajnej. Przygotowanie katalizatorów węglowych polegało na aktywacji chemicznej wodnym roztworem wodorotlenku potasu i karbonizacji otrzymanego prekursora. Karbonizację szyszek sosnowych prowadzono przez 1 godzinę w zakresie temperatur od 700 do 1000°C i w atmosferze gazu obojętnego (N_2). Na rysunku 11 przedstawiono schemat blokowy otrzymywania katalizatorów węglowych z szyszek sosnowych.

Rysunek 11. Schemat blokowy otrzymywania katalizatorów węglowych z szyszek sosnowych (opracowanie własne)

Otrzymane katalizatory oznaczono następująco: PC_700, PC_750, PC_800, PC_850, PC_900, PC_950 i PC_1000, gdzie liczby oznaczają temperaturę procesu karbonizacji tych materiałów.

Charakterystykę otrzymanych węgli aktywnych przeprowadzono za pomocą następujących analiz instrumentalnych: XRD, SEM i XPS. Parametry teksturalne katalizatorów węglowych określono na podstawie pomiarów sorpcji azotu w temperaturze -196°C. Strukturę grafitową i czystość materiałów węglowych zbadano techniką XRD. Materiały węglowe charakteryzowały się dobrze rozwiniętą strukturą porowatą, którą potwierdzono wykonując zdjęcia elektronowym mikroskopem skaningowym. Zawartość pierwiastków i grup funkcyjnych na powierzchni katalizatorów węglowych zbadano metodą XPS. Powierzchnię właściwą, całkowitą objętość porów, objętość mikroporów oraz procent objętości mikroporów określono na podstawie pomiarów sorpcji azotu w temperaturze -196°C. Węgle aktywne wytworzone w niższych temperaturach były mikroporowate (zawartość procentowa mikroporów mieściła się w zakresie 78–88%). Materiały otrzymane w temperaturach 950 i 1000°C były mikro-mezoporowate (materiały te zawierały około 50% mikroporów).

W pierwszym etapie badań aktywności katalitycznej otrzymanych węgli aktywnych przeprowadzono testy wpływu temperatury na konwersję alfa-pinenu i selektywności odpowiednich produktów, a temperaturę zmieniano od 80 do 140°C. Następnie przeprowadzono testy wpływu ilośći katalizatora w zakresie 0,1-1,5% wag. i czasów reakcji od 1 do 24 godzin na konwersję alfa-pinenu i selektywności odpowiednich produktów. Spośród siedmiu testowanych katalizatorów węglowych najbardziej aktywny okazał się katalizator PC_850, który zawierał najwięcej grup keto-enolowych oraz dużą liczbę grup C=O i COOH. Obecność tych grup na powierzchni węgli aktywnych ma wpływ na aktywność katalityczną materiałów węglowych, ponieważ grupy te stanowią centra kwasowe i biorą udział w reakcji utleniania alfa-pinenu. Katalizator PC_850 ma najmniejszy rozmiar porów w porównaniu z innymi badanymi katalizatorami węglowymi (mikropory o średnicach 1,00-1,25 nm). Wielkość cząsteczki alfa-pinenu wynosi około 0,7 nm, dlatego najprawdopodobniej najmniejsze mikropory obecne w materiale PC_850 są najbardziej istotne dla procesu utleniania tego związku.

Wykazano, że najkorzystniej jest prowadzić proces utleniania alfa-pinenu w temperaturze 100°C przez 1 godzinę z użyciem katalizatora PC_850, którego ilość w mieszaninie reakcyjnej wynosi 0,5% wag. W tych warunkach konwersja alfa-pinenu wyniosła 41% mol, a selektywności głównych produktów procesu utleniania alfa-pinenu były następujące: tlenek alfa-pinenu 28% mol, werbenol 16% mol i werbenon 13% mol. Pełne wyniki badań przedstawiono w pracy **[1.3.]** opublikowanej w czasopiśmie *Catalysis Today*.

Ostatnią grupą materiałów, które zastosowano jako katalizatory do utleniania alfa-pinenu, były materiały porowate pochodzenia naturalnego. Badania nad zastosowaniem naturalnych glinokrzemianów w procesie utleniania alfa-pinenu zostały przeprowadzone z wykorzystaniem klinoptylolitów (zeolity pochodzenia naturalnego) o różnej wielkości cząstek, które zostały oznaczone (zgodnie z ich wielkością cząstek), jako: clin_1 (20 µm), clin_2 (50 µm), clin_3 (200 µm) i clin_4 (500-1000 µm). Materiały te scharakteryzowano następującymi metodami instrumentalnymi: EDXRF, XRD, SEM, UV-Vis oraz FTIR. Parametry teksturalne klinoptylolitów określono na podstawie pomiarów sorpcji azotu w temperaturze -196°C. Zawartość glinu oraz krzemu określono metodą EDXRF. Wyniki analizy były podobne do wyników opisanych w literaturze [52,53]. Morfologię powierzchni klinoptylolitów oceniano za pomocą skaningowego mikroskopu elektronowego. Analizując widma UV-Vis klinoptylolitów potwierdzono obecność atomów glinu w strukturze tych materiałów. Obecność struktury krzemianowej charakterystycznej dla zeolitów oraz obecność grup hydroksylowych pochodzących od cząsteczek wody zaabsorbowanych na powierzchni katalizatorów określono wykorzystując analizę FTIR.

Pierwszy etap badań polegał na sprawdzeniu aktywności katalitycznej czterech klinoptylolitów o różnej wielkości cząstek w bezrozpuszczalnikowym utlenianiu alfa-pinenu tlenem. Warunki wstępne prowadzenia procesu były następujące: temperatura 100°C, ilość katalizatora 0,1% wag. oraz czas reakcji 3 godziny. Na podstawie testów katalitycznych stwierdzono, że wszystkie badane klinoptylolity były aktywne w utlenianiu alfa-pinenu i mogą być stosowane jako katalizatory w tym procesie. Spośród czterech testowanych klinoptylolitów najbardziej aktywny okazał się zeolit clin_4 o średniej wielkości cząstek 500-1000 µm, dla którego zaobserwowano najwyższą konwersję alfa-pinenu (36% mol) i najwyższą selektywność przemiany do tlenku alfa-pinenu (24% mol). Najwyższą aktywność clin_4 potwierdziły badania FTIR, EDXRF oraz rozkład wielkości porów. Obecność grup ≡Si-OH i ≡Al-OH ma wpływ na aktywność katalityczną klinoptylolitów, ponieważ grupy te stanowią centra aktywne katalizatora i biorą udział w reakcji utleniania alfa-pinenu. Podczas badań stwierdzono, że ilość wapnia i potasu wpływa na aktywność klinoptylolitów w procesie utleniania alfa-pinenu. Zbyt duża ilość tych pierwiastków zmniejsza aktywność katalityczną materiałów klinoptylolitowych, ponieważ pierwiastki te blokują centra aktywne katalizatorów. Clin_4 zawiera najmniejszą ilość wapnia i potasu w porównaniu z innymi badanymi klinoptylolitami, najprawdopodobniej dlatego katalizator ten był najbardziej aktywny w procesie utleniania alfa-pinenu. Clin_4 zawiera jednocześnie największą ilość mezoporów, co może wskazywać na to, że to właśnie pory o tej wielkości są odpowiedzialne za większą aktywność katalityczną clin_4 i, że proces utleniania zachodzi głównie w nich.

W celu ustalenia najkorzystniejszych warunków prowadzenia procesu utleniania alfa-pinenu dla najbardziej aktywnego katalizatora wybranego w pierwszym etapie badań (clin_4) zbadano wpływ temperatury, ilości katalizatora oraz czasu reakcji na konwersję alfa-pinenu i selektywności odpowiednich produktów. Parametry wpływające na przebieg procesu utleniania zmieniano w następujących zakresach: temperatura 80-110°C, ilość katalizatora 0,05-1,5% wag. i czas reakcji 0,25-6 godzin. Stwierdzono, że najkorzystniej jest prowadzić proces utleniania alfa-pinenu w obecności klinoptylolitu o średniej wielkości cząstek 500-1000 µm (clin_4), w temperaturze 100°C, przez 3,5 godzin i przy ilości katalizatora clin_4 w mieszaninie reakcyjnej wynoszącej 0,05% wag. W tych warunkach konwersja alfa-pinenu wyniosła 35% mol, a selektywności głównych produktów procesu utleniania alfa-pinenu były następujące: tlenek alfa-pinenu 29% mol, werbenol 17% mol i werbenon 13% mol. Pełne wyniki badań przedstawiono w pracy **[1.4.]** opublikowanej w czasopiśmie *Sustainability*.

W ostatnim etapie pracy przeprowadzono badania nad aktywnością przeciwutleniającą ekstraktów etanolowych pozyskanych z roślin zawierających alfa-pinen. Surowce do badań stanowiły świeże części *Pinus sylvestris* L., takie jak: szyszki, igły i gałęzie, a także suszone niezmielone i suszone zmielone szyszki; suszone i świeże liście *Rosmarinus officinalis*; suszone liście *Levisticum officinale* oraz suszone liście *Salvia officinalis* L. Materiały roślinne ekstrahowano 40% (v/v), 70% (v/v) i 96% (v/v) etanolem przy użyciu ekstrakcji wspomaganej ultradźwiękami przez 15, 30 lub 60 minut. Dla wybranych materiałów roślinnych przeprowadzono również ekstrakcję przy użyciu aparatu Soxhleta 96% (v/v) etanolem. Aktywność przeciwutleniającą ekstraktów oceniano metodami: DPPH i ABTS. Obecność alfa-pinenu w ekstraktach etanolowych została potwierdzona za pomocą metody GC-MS. Ekstrakty z trzech materiałów roślinnych o najwyższej aktywności przeciwutleniającej (suszone liście *Rosmarinus officinalis*, suszone liście *Salvia officinalis* L. oraz suszone i zmielone szyszki *Pinus sylvestris* L.) dodano do emulsji kosmetycznych zawierających monostearynian glicerolu i Olivem 1000 (emulgatory). Ekstrakty dodawano w następujących ilościach: 7,5%; 10%; 12,5%; 15%; 17,5%; 20%; 22,5%. 25%, 27,5%, 30%, 40% i 50%. W pierwszym etapie oceniano stabilność i aktywność przeciwutleniającą otrzymanych emulsji. W drugim etapie badano właściwości przeciwdrobnoustrojowe tych emulsji przy użyciu testów mikrobiologicznych. Wykazano, że emulsje bez dodatku ekstraktów oraz z dodatkiem ekstraktów w ilościach: 7,5%; 10%; 12,5%; 15%; 17,5%; 20%; i 22,5% były stabilne. Emulsja z dodatkiem suszonego ekstraktu z liści *Rosmarinus officinalis* w ilości 25% była stabilna, podczas gdy emulsje z dodatkiem pozostałych dwóch ekstraktów w tej samej ilości (25%) były niestabilne. Emulsje z ilością ekstraktów powyżej 25%, tj. 27,5%, 30%, 40% i 50%, były niestabilne niezależnie od użytego surowca. Na podstawie testów mikrobiologicznych można stwierdzić, że wszystkie emulsje z dodatkiem ekstraktów etanolowych uzyskanych z roślin zawierających alfa-pinen wykazują doskonałą stabilność przeciwdrobnoustrojową. Pełne wyniki badań przedstawiono w pracy **[1.5.]** opublikowanej w czasopiśmie *Antioxidants*.

3.4. Wnioski

Przeprowadzone w ramach rozprawy doktorskiej badania wykazały, że materiały porowate, takie jak: TS-1, ZSM-5, węgle aktywne otrzymane z szyszek sosny oraz klinoptylolity są aktywnymi katalizatorami w przyjaznym środowisku naturalnemu i „zielonym procesie” utleniania alfa-pinenu tlenem, który był prowadzony bez udziału rozpuszczalnika. Najważniejsze wnioski wynikające z przeprowadzonych badań są następujące:

1. Wszystkie badane parametry procesu, takie jak: temperatura, ilość katalizatora i czas reakcji mają wpływ na konwersję alfa-pinenu i selektywności otrzymanych produktów. Im dłuższy czas reakcji utleniania, tym większa konwersja alfa-pinenu.
2. Zawartość tytanu w katalizatorze TS-1 ma wpływ na aktywność tego katalizatora w procesie utleniania alfa-pinenu. W trakcie syntezy TS-1 zaobserwowano powstawanie TiO_2 (anatazu), który osadza się w porach. Im większa ilość tytanu wbudowanego w strukturę TS-1, tym większa również zawartość anatazu w otrzymywanym materiale porowatym. Zawartość tytanu w TS-1 ma wpływ na właściwości teksturalne tego katalizatora. Im wyższa zawartość tytanu, tym niższe wartości powierzchni właściwej, całkowitej objętości porów i objętości mikroporów TS-1. Ponadto im większa ilość tytanu wbudowanego w strukturę TS-1, tym większa średnica porów TS-1.
3. Nieoczekiwanie w badaniach nad utlenianiem alfa-pinenu na katalizatorach TS-1 okazało się, że przy dłuższych czasach reakcji (24 godziny i 48 godzin), możliwe jest uzyskanie wysokich selektywności przemiany do werbenonu (38% mol i 43% mol), przy bardzo wysokiej konwersji alfa-pinenu (sięgającej 90% mol i 100% mol). Im więc dłuższy czas reakcji, tym wyższa selektywność przemiany do werbenonu. Może to być najprawdopodobniej związane z utlenianiem werbenolu do werbenonu podczas prowadzenia procesu (atmosfera utleniająca). Podczas badań wykazano jednocześnie, że zwiększenie temperatury i wydłużenie czasu reakcji zmniejsza selektywność przemiany do tlenku alfa-pinenu, który rozkłada się, ponieważ jego struktura nie jest stabilna lub ulega on izomeryzacji do karweolu i aldehydu komfoleinowego.
4. Energia aktywacji dla reakcji utleniania alfa-pinenu tlenem cząsteczkowym wynosi 80,6 kJ/mol. Reakcja ta zachodzi zgodnie z kinetyką reakcji pierwszego rzędu.
5. Katalizator ZSM-5 o zawartości glinu wynoszącej 0,59% wag. (ZSM-5_2) wykazał wyższą aktywność w procesie utleniania alfa-pinenu niż katalizator TS-1 o zawartości tytanu wynoszącej 5,42% wag. (TS-1_2). Zastosowanie ZSM-5_2 znacznie zmniejszyło ilość wymaganego w reakcji katalizatora, od 1% wag. dla TS-1_2 do 0,05% wag. dla ZSM-5_2. Zastosowanie katalizatora ZSM-5_2 pozwoliło na uzyskanie wyższej o 15%

mol konwersji alfa-pinenu w porównaniu z katalizatorem TS-1_2 zastosowanym do utleniania alfa-pinenu.

6. Zastosowanie katalizatorów węglowych pozwala na skrócenie czasu prowadzenia reakcji utleniania alfa-pinenu z 6 godzin dla katalizatorów TS-1 i ZSM-5 do 1 godziny dla katalizatorów węglowych.
7. Biomasa odpadowa w postaci szyszek sosnowych stanowi doskonały surowiec do syntezy węgli aktywnych z wykorzystaniem wodorotlenku potasu jako czynnika aktywującego.
8. Temperatura karbonizacji wpływa na właściwości teksturalne otrzymanych katalizatorów węglowych. Im wyższa temperatura karbonizacji, tym wyższe wartości powierzchni właściwej, całkowitej objętości porów i objętości mikroporów katalizatorów węglowych, z wyjątkiem objętości mikroporów PC_1000. Temperatura karbonizacji wpływa również na wielkość porów otrzymanych katalizatorów węglowych. Węgle aktywne otrzymane w wyniku karbonizacji w temperaturze 700–900°C były mikroporowate, a węgle aktywne otrzymane w wyniku karbonizacji w temperaturze 750–1000°C były mikro-mezoporowate. Spośród testowanych katalizatorów węglowych najbardziej aktywnym okazał się katalizator PC_850 o najmniejszym rozmiarze porów, które najprawdopodobniej są najbardziej istotne dla tego procesu, ponieważ wielkość cząsteczki alfa-pinenu wynosi około 0,7 nm.
9. Temperatura karbonizacji wpływa na zawartość tlenu na powierzchni katalizatorów węglowych otrzymanych z szyszek sosnowych. Im wyższa temperatura karbonizacji, tym niższa zawartość tlenu na powierzchni katalizatorów węglowych. Prawdopodobnie jest to związane z rozkładem grup węglowo-tlenowych na produkty gazowe zachodzącym w wyższych temperaturach karbonizacji (850–1000°C). Na aktywność katalizatorów węglowych wpływa zawartość grup keto-enolowych, które stanowią centra kwasowe katalizatora. Spośród testowanych katalizatorów węglowych najbardziej aktywnym katalizatorem okazał się katalizator PC_850 o najwyższej zawartości grup keto-enolowych.
10. Klinoptylolity o różnej wielkości cząstek to materiały makroporowate zawierające pewną ilość mezoporów (udział makroporów wynosi około 30-40% całkowitej objętości porów). Dla najbardziej aktywnego klinoptylolitu (clin_4) zaobserwowano największą objętość mezoporów mniejszych niż 100 nm. Wielkość cząstek klinoptylolitu wpływa na objętość mezoporów. Im większy rozmiar cząstek, tym większa objętość mezoporów. W przypadku clin_4 najlepsze warunki dla procesu

utleniania były następujące: temperatura 100°C, ilość katalizatora 0,05% wag. i czas reakcji 3,5 godziny. W warunkach tych selektywności głównych produktów były następujące: tlenek alfa-pinenu 29% mol, werbenol 17% mol, werbenon 13% mol, a konwersja alfa-pinenu wyniosła 35% mol. Badania aktywności katalitycznej dla katalizatora clin_4 wykazały bardzo podobne wyniki, jak w przypadku katalizatora TS-1_2. Dla obu katalizatorów, dla najlepszych warunków, wartości najważniejszych funkcji opisujących proces były zbliżone (selektywność przemiany do tlenku alfa-pinenu była taka sama i wynosiła 29% mol, natomiast selektywność przemiany do werbenolu wynosiła 15-17% mol, selektywność przemiany do werbenonu 12-13% mol, a konwersja alfa-pinenu osiągnęła wartość w zakresie 34-35% mol). Zastosowanie klinoptylolitu clin_4 pozwala na skrócenie czasu prowadzenia reakcji utleniania alfa-pinenu z 6 godzin dla katalizatorów TS-1 i ZSM-5 do 3,5 godziny dla clin_4. Dla najlepszych warunków, wartości najważniejszych funkcji opisujących proces utleniania na clin_4 były zbliżone do uzyskiwanych na katalizatorach ZSM-5_2 i PC_850, a wartość konwersji alfa-pinenu dla clin_4 była niższa o 14% mol w porównaniu z katalizatorem ZSM-5_2 i o 6% mol niższa w porównaniu z katalizatorem PC_850.

11. Naturalne glinokrzemiany oraz katalizatory węglowe są ekologiczną alternatywą dla syntetycznych katalizatorów tytanowo-silikatowych, dlatego, że są tanie i łatwo dostępne, spełniają warunki zrównoważonego rozwoju, nie zawierają szkodliwych substancji oraz są łatwe do usunięcia z mieszaniny poreakcyjnej. Uzyskiwane na naturalnych glinokrzemianach wyniki są bardzo podobne, jak w przypadku katalizatora TS-1_2 (Tabela 1). Zastosowanie naturalnych glinokrzemianów oraz katalizatorów węglowych pozwala na skrócenie czasu prowadzenia reakcji utleniania alfa-pinenu z 6 godzin dla katalizatorów TS-1 i ZSM-5 do 1 godziny dla katalizatorów węglowych oraz do 3,5 godziny dla naturalnych glinokrzemianów.

Tabela 1. Wartości selektywności tlenku alfa-pinenu, werbenolu, werbenonu i konwersji alfa-pinenu dla najkorzystniejszych warunków utleniania na najbardziej aktywnych z danej grupy materiałach porowatych

Katalizator	Najkorzystniejsze warunki	Selektywność głównych produktów (% mol)			Konwersja alfa-pinenu (% mol)
		tlenek alfa-pinenu	werbenol	werbenon	
TS-1_2	85°C, 1% wag., 6 h	29	15	12	34
ZSM-5_2	95°C, 0,05% wag., 6 h	28	16	18	49
PC_850	100°C, 0,5% wag., 1 h	28	16	13	41
clin_4	100°C, 0,05% wag., 3,5 h	29	17	13	35

12. Spośród wszystkich badanych w ramach rozprawy doktorskiej katalizatorów wykazano, że najbardziej aktywnym katalizatorem stosowanym do utleniania alfa-pinenu jest katalizator ZSM-5 o zawartości glinu wynoszącej 0,59% wag. (ZSM-5_2), dla którego uzyskano najwyższą konwersję alfa-pinenu wynoszącą 49% mol.
13. Najkorzystniejsze temperatury prowadzenia procesu utleniania alfa-pinenu mieszczą się w zakresie 85–100°C. Stosunkowo niskie temperatury prowadzenia utleniania powodowały, że proces mógł być przeprowadzony w łagodnych warunkach. Najkorzystniejsza ilość katalizatora była stosunkowo niska i mieściła się w zakresie 0,05– 1% wag, a najkorzystniejszy czas prowadzenia reakcji mieścił się w zakresie 1 – 6 godzin.
14. Główną zaletą przedstawionego procesu utleniania alfa-pinenu tlenem jest brak rozpuszczalnika w medium reakcyjnym. Zaproponowana metoda przekształcania alfa-pinenu w kierunku otrzymywania wartościowych związków jest przykładem procesu przyjaznego środowisku z możliwością wykorzystania odpadu w postaci terpentyny (odnawialnego i roślinnego źródła alfa-pinenu). Warto również podkreślić, że produkty utleniania alfa-pinenu są produktami o bardzo dużym potencjale aplikacyjnym w medycynie, a także w przemyśle kosmetycznym, perfumeryjnym i spożywczym.
15. Cechą charakterystyczną proponowanej metody utleniania alfa-pinenu na katalizatorach heterogenicznych jest to, że oddzielenie mieszaniny poreakcyjnej po procesie utleniania jest stosunkowo proste, ponieważ mieszanina poreakcyjna nie zawiera rozpuszczalnika, a jedynie nieprzereagowany substrat organiczny i produkty utleniania, co obniża koszty rozdziału mieszaniny poreakcyjnej na czyste składniki oraz eliminuje koszty odzysku i regeneracji rozpuszczalnika. Ze względu na fakt, że czynnikiem utleniającym nie jest wodny roztwór nadtlenku wodoru, ale tlen cząsteczkowy, nie obserwuje się tworzenia drugiej fazy w mieszaninie poreakcyjnej w postaci warstwy wodnej, co niekorzystnie wpływa na proces oznaczania i wyodrębniania produktów.
16. Ekstrakcja wspomagana ultradźwiękami może być stosowana jako efektywna metoda do otrzymywania ekstraktów zawierających alfa-pinen, charakteryzujących się wysoką aktywnością przeciwutleniającą. Badania nad przygotowaniem emulsji z tymi ekstraktami wykazały, że zastosowanie Olivem 1000 jako emulgatora umożliwiło stworzenie stabilnych emulsji kosmetycznych wykazujących wysoką aktywność przeciwutleniającą. Testy mikrobiologiczne tych emulsji wykazały akceptowalną ilość mikroorganizmów w otrzymanych preparatach. Ekstrakty te mogą więc zmniejszyć

stopień zanieczyszczenia mikrobiologicznego w preparatach kosmetycznych. Natomiast potwierdzona badaniami wysoka aktywność antyoksydacyjna tych ekstraktów, wskazuje na możliwość wykorzystania ekstraktów zawierających alfa-pinen jako potencjalnych składników kosmetyków zapobiegających starzeniu się skóry.

3.5. Literatura

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materials

Article

The Studies on α-Pinene Oxidation over the TS-1. The Influence of the Temperature, Reaction Time, Titanium and Catalyst Content

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Abstract: The work presents the results of studies on α-pinene oxidation over the TS-1 catalysts with different Ti content (in wt%): TS-1_1 (9.92), TS-1_2 (5.42), TS-1_3 (3.39) and TS-1_4 (3.08). No solvent was used in the oxidation studies, and molecular oxygen was used as the oxidizing agent. The effect of titanium content in the TS-1 catalyst, temperature, reaction time and amount of the catalyst in the reaction mixture on the conversion of α-pinene and the selectivities of appropriate products was investigated. It was found that it is most advantageous to carry out the process of α-pinene oxidation in the presence of the TS-1 catalyst with the titanium content of 5.42 wt% (TS-1_2), at the temperature of 85 °C, for 6 h and with the catalyst TS-1 content in the reaction mixture of 1 wt%. Under these conditions the conversion of α-pinene amounted to 34 mol%, and the selectivities of main products of α-pinene oxidation process were: α-pinene oxide (29 mol%), verbenol (15 mol%) and verbenone (12 mol%). In smaller quantities also campholenic aldehyde, trans-pinocarveol, myrtenal, myrtenol, L-carveol, carvone and 1,2-pinanediol were also formed. These products are of great practical importance in food, cosmetics, perfumery and medicine industries. Kinetic studies were also performed for the studied process.

Keywords: TS-1 catalyst; oxidation; α-pinene; α-pinene oxide; verbenol; verbenone

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1. Introduction

Titanium-silicate catalysts, both microporous (TS-1, TS-2, Ti-BETA, Ti-MWW) and mesoporous (Ti-MCM-41, Ti-MCM-48, Ti-SBA-15, Ti-SBA-16), enjoy the constant interest of researchers. The first group of catalysts mentioned above is used mainly in reactions involving small size organic molecules, while the second group has found applications in reactions involving large and branched organic molecules—it is mainly related to the pore diameter of these catalysts. The advantage of these catalysts is that they can be easily separated from the post-reaction mixture and can be used multiple times in the process. These catalysts also have disadvantages (especially those of the older generation, e.g., Ti-MCM-41 or TS-1). These disadvantages mainly relate to the stability of their structure under hydrothermal conditions, as well as leaching from their structure of titanium, which is the active center of these catalysts.

Currently, research is being carried out on new methods of synthesis these catalysts, for example by introducing an additional step of crystallization during the synthesis of these materials, with the previously obtained porous structure dissolving earlier—an example may be the hollow TS-1 catalyst (HTS-1) [1]. Two methods for the synthesis of HTS-1 have been described: acid-base treatment and base treatment. In the first method, in order to dissolve the originally obtained TS-1 porous structure, organic and inorganic acids are used (e.g., hydrochloric acid) and their salts (e.g., ammonium chloride). The acid-treated TS-1 is then added to an organic base (e.g., amine or quaternary ammonium salt). The acid treatment is omitted in the second method. Larger spaces in the HTS-1 crystal lattice are obtained using the acid-base treatment [2]. In comparison to the standard TS-1, HTS-1 has unique voids in the crystal lattice and is characterized by a high content of titanium [3]. New titanium-silicate porous materials having of micro- and mesoporous structure are also obtained based on the structure of the TS-1 catalyst and using hexadecyltrimethylammonium bromide [4]. The catalysts obtained in this way were more active in the epoxidation of cyclohexene than TS-1 catalyst [4,5]. Another and very important way of modifying of titanium-silicate catalysts and increasing their activity can be also modification of TS-1 catalyst by the increasing the amount of titanium incorporated into the structure of titanium-silicate catalysts [6].

For the first time, the TS-1 catalyst was obtained by the hydrothermal method in the early 1980s at the Enichem group research center in Italy, and it was one of the greatest achievements in catalysis [7–9]. This porous material is characterized by a three-dimensional system of channels with a diameter of about 0.5 nm (linear-zigzag pattern, MFI-type structure) [7]. Currently, the TS-1 catalyst is one of the most frequently used titanium-silicate catalysts in catalytic processes (it is also used in industrial processes). It is especially used in oxidation processes with the use of hydrogen peroxide as an oxidant (e.g., epoxidation of allyl alcohol [10,11], allyl chloride [12–14], limonene [15], diallyl ether [16,17], cyclohexene [18], or phenol hydroxylation [19,20]. Based on the previous applications of the TS-1 catalyst we decided to select this catalyst for research on the oxidation of α-pinene.

Organic raw materials of natural origin, including terpenes, are currently very popular among research laboratories and industry. This is mainly due to the fact that they are renewable resources, which are characterized by high availability and a relatively low price [21–23]. α-Pinene is a terpene hydrocarbon that can be obtained from various raw materials of natural origin (biomass). The advantage of these raw materials is that they are relatively easily available and renewable resources. One of the valuable sources of this compound is turpentine, which is obtained from the resin of conifers (e.g., pine) by steam distillation or gasoline extraction of pine stump. The content of α-pinene in turpentine is 60–70%. Apart from α-pinene, the main ingredients of turpentine are: β-pinene and 3-caren [24]. α-Pinene is also the main ingredient of pine oil, which can be obtained by the steam distillation of young pine shoots and needles. The amount of α-pinene in pine oil is 14–65%. In addition to α-pinene, this essential oil includes: 3-carene (0–61%), β-pinene (1–40%), limonene (0–34%), camphene (0–8%) and β-phellandrene (0–29%) [25]. α-Pinene is a very valuable compound that can be used to obtain fragrances and biologically active compounds that are used in medicine and cosmetics (camphene, limonene, isobornyl acetate, isoborneol, camphor, terpenocyclohexanols, α-terpineol, terpinyl acetate or *p*-menthol) [26]. The antibacterial [27], antifungal [28], anti-inflammatory [29] properties of α-pinene and its anticancer activity are also of great interest [27].

In the oxidation of α-pinene, valuable oxygen derivatives of this compound can be obtained, such as: α-pinene oxide, verbenol and verbenone. The oxidation process also allows for the production of: campholenic aldehyde, trans-pinocarveol, myrtenal, myrtenol, L-carveol, carvone and pinanediol [30]. It should be emphasized that α-pinene oxidation products are very valuable compounds, widely used in medicine and in perfumery, food, and cosmetics industries. Among many compounds of natural origin, monoterpenes play the important role of both anti-cancer agents and substances used in anti-cancer therapy. For example, carvone and carveol have been shown to have anti-tumor activity in breast cancer studies [31]. Moreover, verbenone is a compound that is a substrate for the synthesis of taxol [32], a drug used in the treatment of cancer. Monoterpenes also have flavor and aroma properties that can be used in perfumery as perfume ingredients. In the perfume industry, monoterpenes obtained directly from essential oils, for example carvone and myrtenol, are of key importance [33]. Carvone is characterized by a refreshing

perfume ingredients. In the perfume industry, monoterpenes obtained directly from essential oils, for example carvone and myrtenol, are of key importance [33]. Carvone is characterized by a refreshing mint aroma, and its properties make it not only used in the perfume industry, but also in the food industry and in agriculture [34–35]. Verbenone, together with verbenol, has a smell that resembles camphor and mint. These compounds are obtained from pine and eucalyptus [36]. First from these products—verbenone is used as a fragrance component in compositions with the scent of strawberry, raspberry, dill, rosemary and green mint. Moreover, the use of verbenol, verbenone and pinocarvone as components of pheromones creates new opportunities to fight bark beetles and other coniferous pests [37]. A number of other monoterpenes have been used to improve or create new, previously unknown fragrances. Attempts are being made to produce new analogues of compounds with aromatic properties, for example an analogue of santanol was obtained from (R) (−)-carvone—(Z)-normethyl-carvo-beta-santalol, with a "slightly forest smell with a hint of cedrol" [35]. Some of the monoterpenes with unique aromatic properties are formed in natural conditions by the transformation of appropriate precursors. As an example, mention should be made of (R) (+)-limonene, which is oxidized in plants of the genus Mentha, e.g., to (R) (−)-carvone (M. spicata) and (−)-menthol (M. piperita), while (S) (+)-carvone is formed by oxidation of (S) (−)-limonene in caraway fruit (Carumcarvi) [38]. All applications of products of oxidation of α-pinene are presented in Figure 1.

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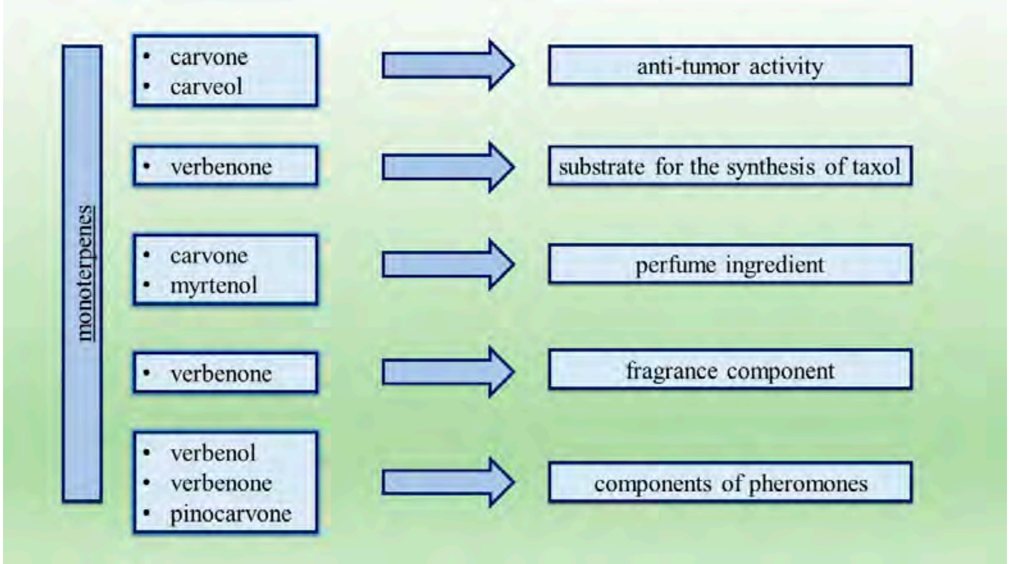

Figure 1. Monoterpenes obtained during oxidation of α-pinene and their applications.

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So far, research has been conducted with the use of heterogeneous titanium-silicalite catalysts on the oxidation of α-pinene with the participation of various oxidants, e.g., hydrogen peroxide and tert-butyl hydroperoxide. An article published in 2008 by Casuscelli et al. described the oxidation of α-pinene using the mesoporous Ti-MCM-41 catalyst. The oxidation reaction was carried out at the temperature of 70 °C for 7 h. Hydrogen peroxide was used as an oxidant for the studies. The process was carried out in acetonitrile which served as the solvent. Under the tested conditions, the following selectivity values of the main products were obtained: campholenic aldehyde up to 27 mol%, verbenol up to 18 mol% and verbenone up to 39 mol%. When using Ti-MCM-41, the highest α-pinene conversion was achieved, equal to 37 mol% [39].

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Kapoor and Raj presented the method for oxidizing α-pinene over the Ti-MCM-48 catalyst using hydrogen peroxide as the oxidant. The Ti-MCM-48 catalyst was used in an amount of 2 wt%. The reaction was carried out at 55 °C for 5 h. The product of oxidation was α-pinene oxide (selectivity 100 mol%), and the conversion of α-pinene was 8 mol% [40].

Suh et al. described the oxidation of α-pinene with a Ti-HMS catalyst [41,42]. The process was carried out in the presence of acetonitrile as the solvent. The oxidant was tert-butyl hydroperoxide. The reaction was carried out at the temperature of 77 °C for 24 h.

Under the tested conditions, the following selectivity values of the main products were obtained: α-pinene oxide up to 5 mol%, campholenic aldehyde up to 82 mol%, verbenol up to 6 mol%, verbenone up to 51 mol%, and 1,2-pinanediol up to 5 mol% [42].

Wróblewska et al. [6] described the autoxidation of α-pinene on TS-1 catalysts with different titanium content. Originally, the α-pinene isomerization reaction was investigated. However, it turned out that instead of the isomerization reaction, the autoxidation of α-pinene takes place. Among the main products of autooxidation was determined: α-pinene oxide, verbenol, verbenone, and campholenic aldehyde. In addition, there were present also such compounds as: myrtenal, myrtenol, carveol, and 1,2-pinanediol. At the most beneficial conditions (for the catalyst TS-1 20:1): temperature 80 °C, content of the catalyst in reaction mixture 1 wt%, and reaction time 24 h, α-pinene oxide was formed with the selectivity of 30.25 mol% and at the conversion of α-pinene amounted to 41.81 mol%.

Based on our results presented in the above-mentioned reference [6], we decided to check how the process of α-pinene oxidation would be affected by introducing the oxidant in the form of oxygen from the cylinder to the reaction environment—such studies on the oxidation of α-pinene have not been described in literature so far. Will it allow to increase the selectivity of the transformation to selected products and increase the conversion of α-pinene, which would be beneficial considering the separation of the post-reaction mixture into pure components (separation of products and their purification is very expensive with a large number of by-products)? It would also be advantageous to increase the conversion of α-pinene, then less of this organic material would have to be recycled back to the process. The aim of this work was therefore to investigate the activity of TS-1 catalyst samples with different titanium content in the oxidation of α-pinene with oxygen, but without the participation of a solvent (which would be beneficial from an ecological point of view). The research presented in this work consisted in determining the qualitative and quantitative products of α-pinene oxidation and determining the most favorable parameters of this process (temperature, reaction time and catalyst content). The aim was also kinetic studies of the tested process of α-pinene oxidation. In order to carry out research on the oxidation of α-pinene, a special installation was built to conduct these studies.

2. Results and Discussion

2.1. Characteristics of the TS-1 Materials

The titanium content in the TS-1 materials was determined by the XRF method. The results were showed in Table 1.

Table 1. The Ti content and textural parameters of the TS-1 materials.

TS-1 Material	Ti (wt%)	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)
TS-1_1	9.92	438	0.355	0.168
TS-1_2	5.42	463	0.397	0.180
TS-1_3	3.39	488	0.423	0.191
TS-1_4	3.08	484	0.430	0.189

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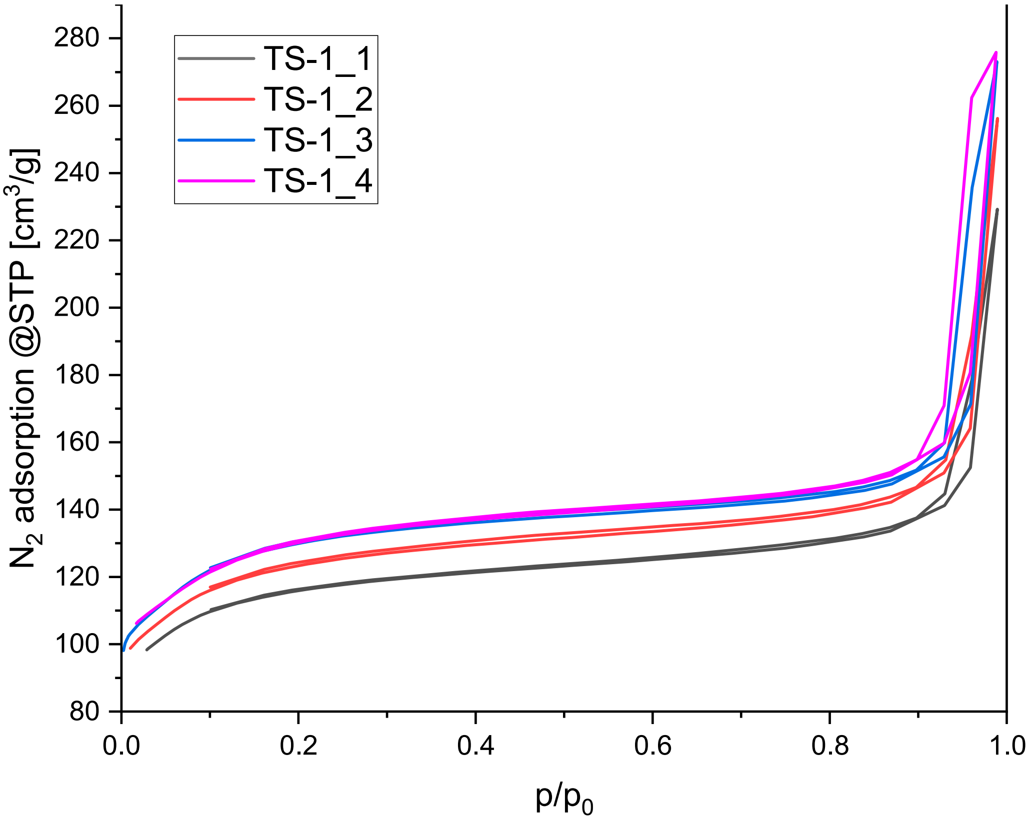

Figure 2. N_2 sorption isotherms at temperature of 77 K.

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All the isotherms were type II with H3 hysteresis representing unrestricted monolayer-multilayer adsorption. According to [43] H3 hysteresis is typical for the II isotherm and the lower limit of the desorption branch is located at the cavitation-induced p/p0. The beginning of hysteresis was located at 0.9 is usually attributed to the condensation within the voids formed between the zeolitic particles [44].

The textural properties listed in Table 1 were similar for all the TS-1 samples and typical for the TS-1 zeolite [45]. However, the influence of Ti content on the textural parameters values was clearly seen. The specific surface area, total pore volume and micropore volume decreased with titanium content. This is probably due to the existence of extra framework titanium.

The X-ray diffraction patterns of the TS-1 are shown in Figure 3. All of the TS-1 materials had characteristic diffraction peaks of the MFI topology, that were sited at 2θ values of 7.9, 8.8, 23.0, 23.9, and 24.4° [46] proving that the addition of Ti up to about 10 wt% did not change the topology.

On the basis of single reflections around 2θ equal to 24.4° and 29.3° was stated that symmetry of the TS-l materials was orthorhombic. The orthorhombic symmetry proved the location of Ti in the zeolite framework [8]. The symmetry of pure silicate framework is monoclinic and presents double reflections at the 2θ equal to 24.4° and 29.3° [47]. The low intense peaks at 2θ = 25.4 and 48.1° characteristic of crystalline anatase (TiO_2) were also identified [48]. These observations indicates the presence of extra-lattice Ti in TS-1 samples. The higher the concentration of titanium, the higher the intensity of these peaks and they were more visible. In order to show this phenomenon clearly, these peaks were also shown separately in the insets in the Figure 3.

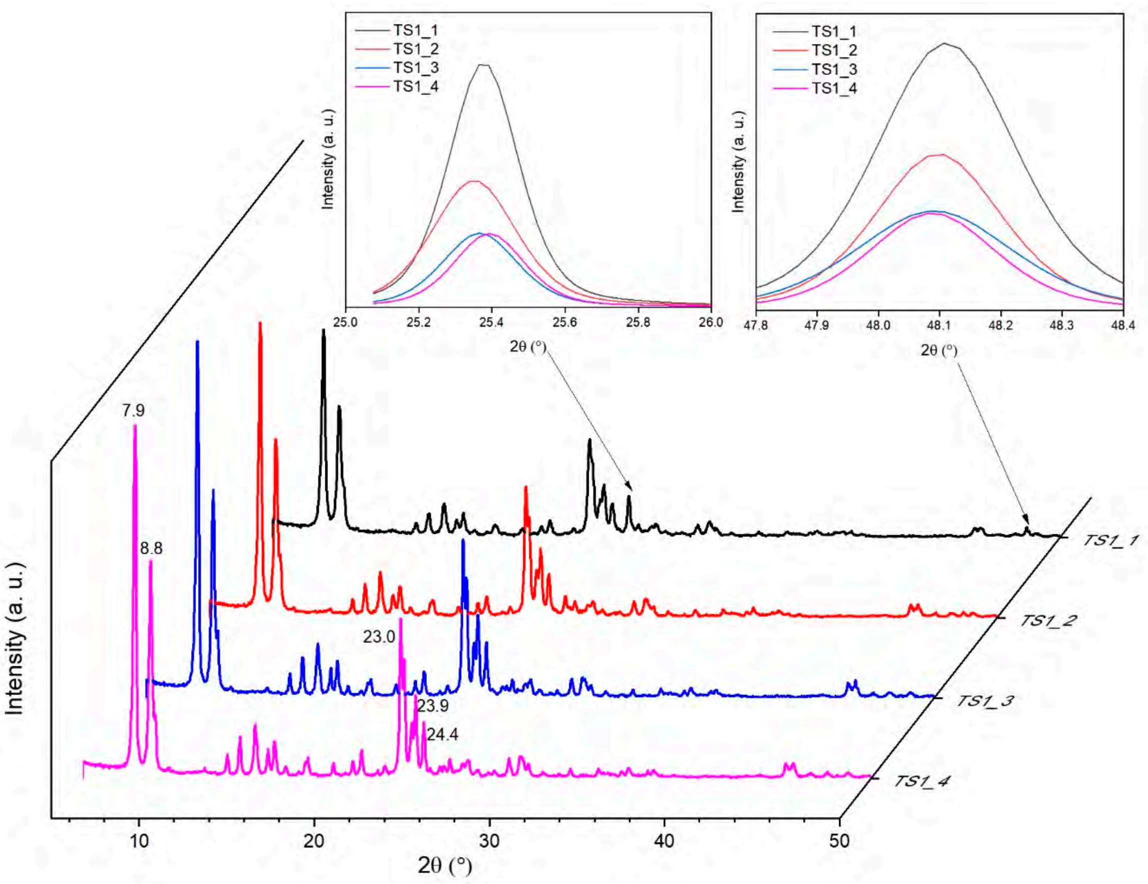

Figure 3. XRD patterns of the TS-1 materials.

Representative SEM images of TS-1 materials were shown in Figure 4.

The SEM technique confirmed the absence of any amorphous material in all the TS-1 samples. The micrographs clearly showed that the TS-1 materials were very homogeneous, consisting of well-defined crystallites with similar hexagonal shapes. Only TS-1_1 was quite different. The hexagonal shape of it was built from the smallest crystals. The other authors found that the TS-1 crystals shapes were similar [49–51].

On the basis on SEM measurements the particle-size distribution was calculated and presented at the histogram (Figure 5). The sizes of a hundred particles were estimated for every material. The histograms showed that the sizes of particles of TS-1 materials were quite similar, and the range of the diameters was narrow. However, it is also evident that the average diameter of the TS-1_1 particles was the highest. The average diameters of the materials were in the following order: TS-1_1 > TS-1_2 > TS-1_3 > TS-1_4. It is noteworthy that the distribution profile of the diameters (blue curve) followed the Weibull function well. The average size of the particles and other statistic parameters are presented in Table 2.

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Materials 7 of 18

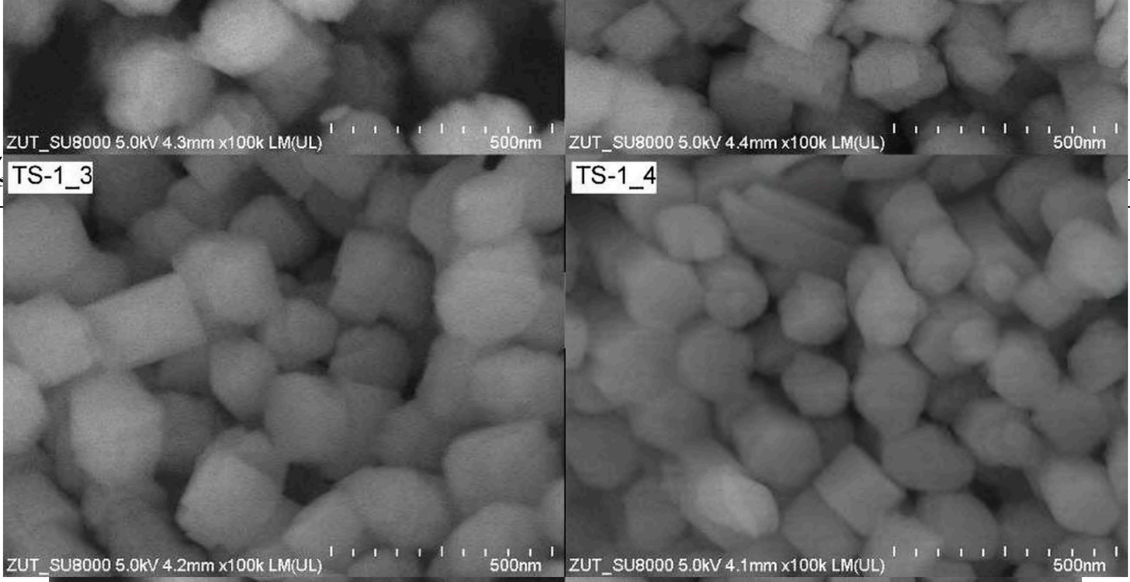
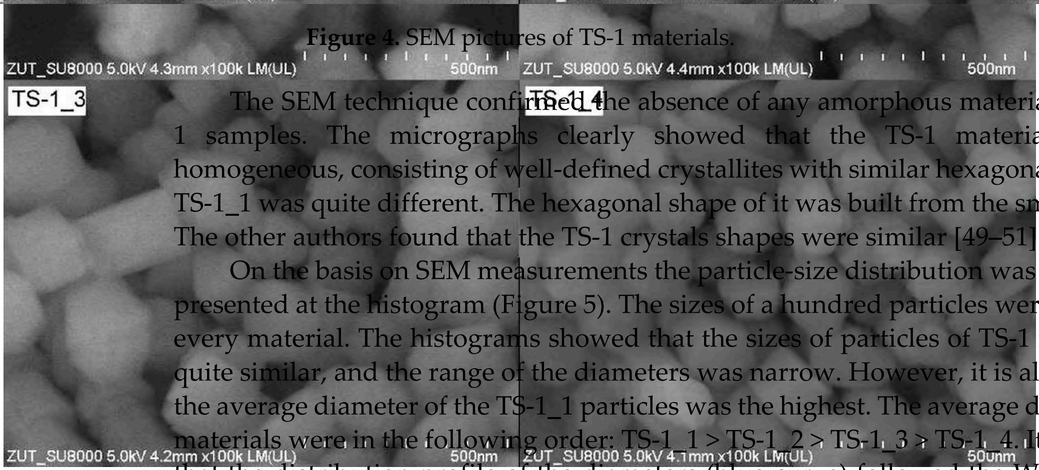


Figure 4. SEM pictures of TS-1 materials.



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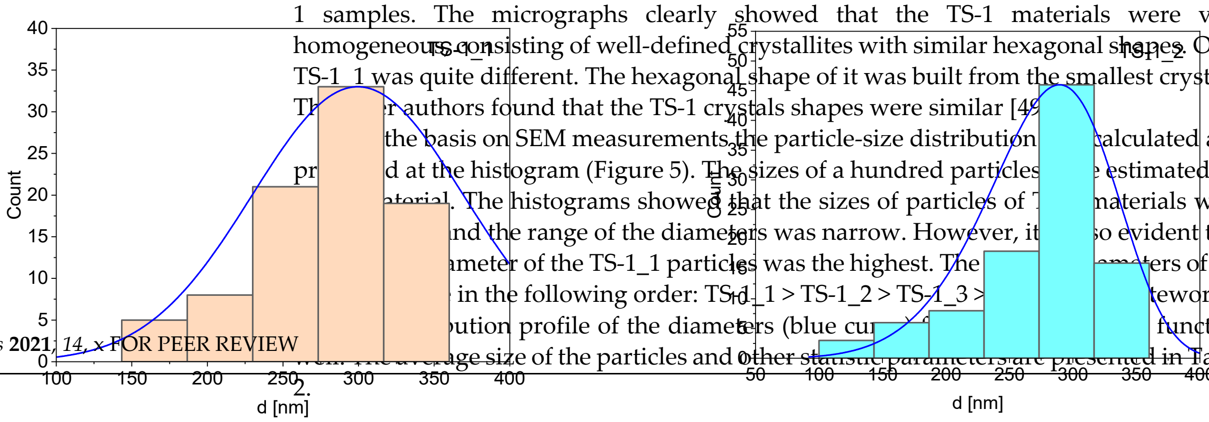

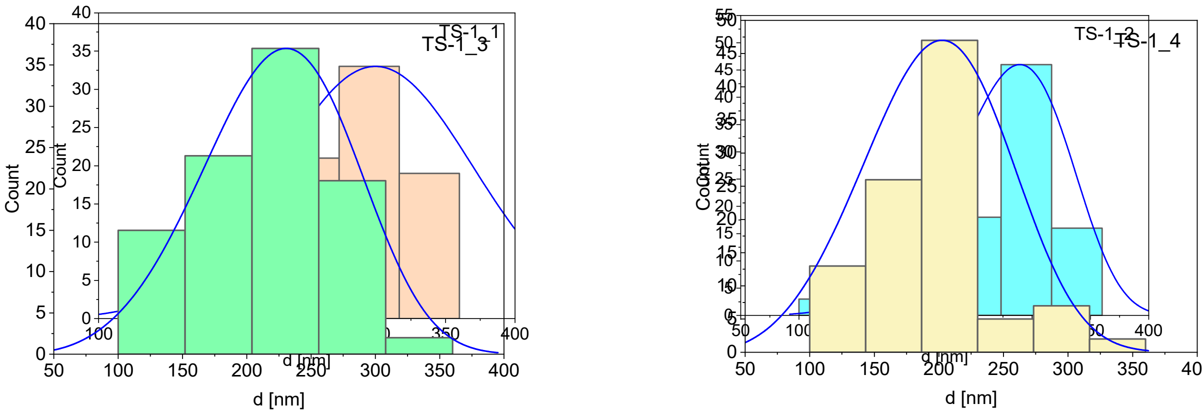

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Table 2. The statistical data concerning the particle size distribution.

Sample	Mean (nm)	Standard Deviation	Minimum (nm)	Maximum (nm)
TS-1_1	299	69.8	150	450
TS-1_2	277	52.1	130	380

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TS-1_3	223	58.5	110	360
TS-1_4	198	50.3	120	350

2.2. Studies on the Catalytic Activity of TS-1 Catalysts in the α-Pinene Oxidation Process

The qualitative determinations of post-reaction mixtures made with the GC and GC-MS methods showed that the main products of α-pinene oxidation over TS-1 catalysts in the presence of oxygen as the oxidant were: α-pinene oxide, verbenol, verbenone and campholenic aldehyde (Figure 6). The following products were formed in smaller amounts: pinocarveol, myrtenal, myrtenol, carveol, 1,2-pinanediol and carvone (Figure 6).

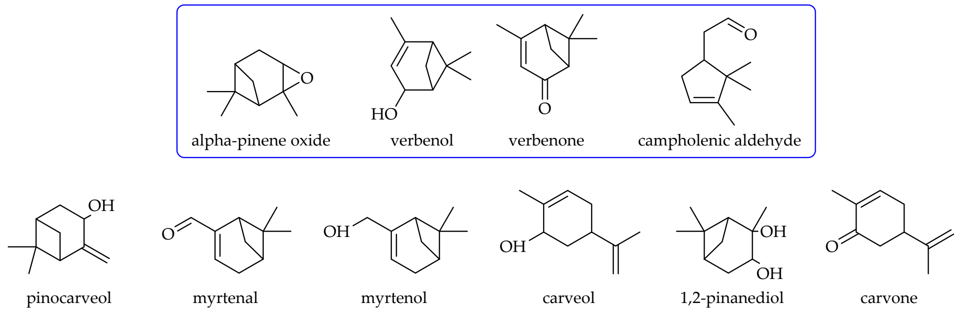

Figure 6. α-Pinene oxidation products.

In the first stage of the research, the influence of titanium content in the TS-1 catalyst on the conversion of α-pinene and the selectivities of the appropriate products was determined. Four catalysts with the following titanium content were used for the tests: TS-1_1 with the titanium content of 9.92 wt%, TS-1_2 with the titanium content of 5.42 wt%, TS-1_3 with the titanium content of 3.39 wt% and TS-1_4 with the titanium content of 3.08 wt%. The oxidation was carried out at the temperature of 85 °C for 6 h. The catalyst content in the reaction mixture was 2.5 wt%. The results of these studies are shown in Figure 7.

Figure 7 shows that the major oxidation product of α-pinene is α-pinene oxide. The selectivity of the transformation to α-pinene oxide remained at a similar level for the 4 tested catalyst samples and amounted to about 26–29 mol%. Similarly, the selectivities of transformation to verbenol and verbenone practically did not change during the research at this stage and amounted to approximately 15% and 11–13 mol%, respectively. Among the tested catalysts, the most active catalyst turned out to be the TS-1_2 catalyst with a titanium content of 5.42 wt%, for which the highest conversion of α-pinene, amounting to 31 mol%, was obtained. On this catalyst with the highest selectivities among the formed products, we obtained: α-pinene oxide (26.0 mol%), verbenol (14.6 mol%), verbenone (11.8 mol%) and carvone (9.5 mol%). In the case of the remaining catalysts, the α-pinene conversion was slightly lower and amounted to about 26–28 mol%. The TS-1_2 catalyst was selected as the most active for the next stage of research (temperature impact studies). Comparing the results obtained in our research with the results presented in the literature for such catalysts as carbon-supported Pt catalysts [52], it can be said that the use of TS-1 catalysts in the oxidation of α-pinene allows to obtain a lower summary selectivity of transformation to verbenol and verbenone (allylic oxidation products) than that obtained on carbon-supported Pt catalysts (respectively, about 28 mol% for all tested TS-1 catalysts and 47–59 mol% for carbon-supported Pt catalysts). In our study, the summary selectivity of the transformation to products of allylic oxidation is similar to the selectivity of the transformation to the compound formed as the result of the epoxidation (α-pinene oxide).

On the other hand, the increase in selectivity of transformation to epoxy product in relation to the sum of selectivity of verbenol and verbenone was observed in studies with carbon nanotubes and activated carbons [53]. In these studies, the selectivity of the transformation to α-pinene oxide was usually about three times higher than the summary selectivity of the transformation to allylic oxidation products. Differences in the oxidation of α-pinene on our TS-1 catalysts and carbon-supported Pt catalysts, carbon nanotubes and activated carbons described in the literature may result from different structures (including the presence of pores of the appropriate volume and shape) of these catalysts and different types of active sites as well as their location in the structure of these catalysts.

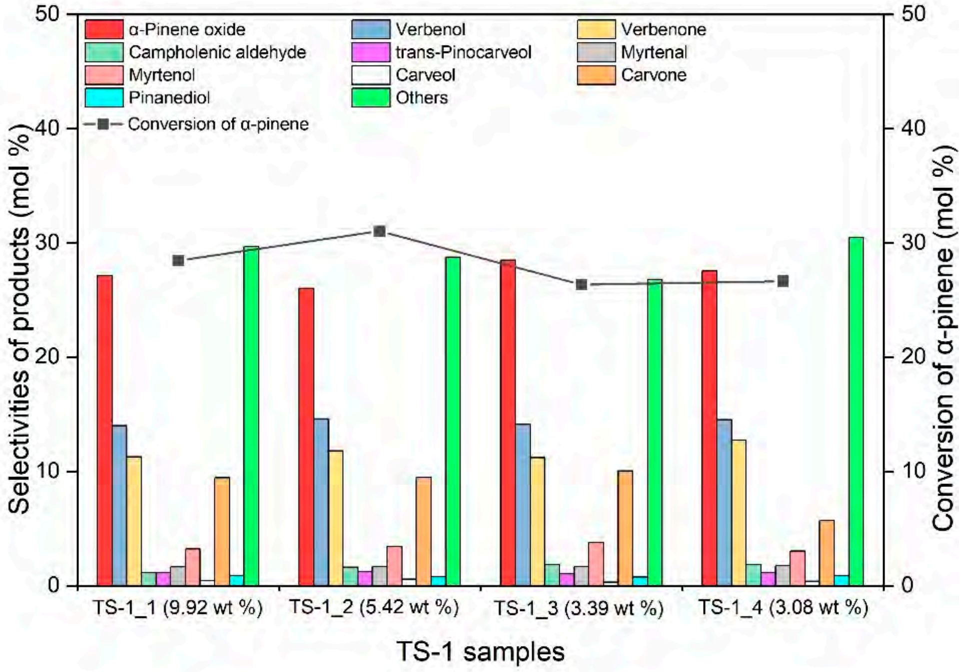

Figure 7. Values of conversion of α-pinene and selectivities of appropriate products in the oxidation of α-pinene over TS-1_1, TS-1_2, TS-1_3 and TS-1_4 catalysts (temperature 85 °C, catalyst content 2.5 wt% and reaction time 6 h). The figure shows the sum of the remaining by-products, which were formed with low selectivities.

In the second stage of the catalytic activity tests, the influence of temperature on the conversion of α-pinene and the selectivities of the appropriate products during the oxidation of α-pinene was investigated. The temperature of the oxidation process was changed in the range from 75 to 100 °C, the content of the TS-1_2 catalyst was 2.5 wt%, and the reaction time was 6 h. Changes in the conversion of α-pinene and the selectivities of the appropriate products are shown in Figure 8.

Figure 8 shows that as the temperature of the oxidation process increases, the conversion of α-pinene increases, reaching the maximum value of 49 mol% at 100 °C. With increasing temperature, the selectivity of transformation to α-pinene oxide increases from 23 mol% (temperature 75 °C) to 26 mol% (temperature 85 °C), and then decreases to 1 mol% (temperature 100 °C). Low values of the selectivity of transformation to α-pinene oxide at temperatures in the range of 95–100 °C may indicate that it has been isomerized to campholenic aldehyde or hydrated to 1,2-pinanediol. In studies conducted at this stage, verbenol was produced with similar selectivity in the entire temperature range studied (14–18 mol%). However, with increasing temperature, the selectivity of the transformation to verbenone first decreased from 19 mol% (temperature 75 °C) to 12 mol% (temperature 85 °C), and then increased to 20 mol% (temperature 100 °C). In the studies of the influence of temperature, a very large increase in the summary selectivity of the transformation to the products of allylic oxidation in comparison to the selectivity of the transformation to

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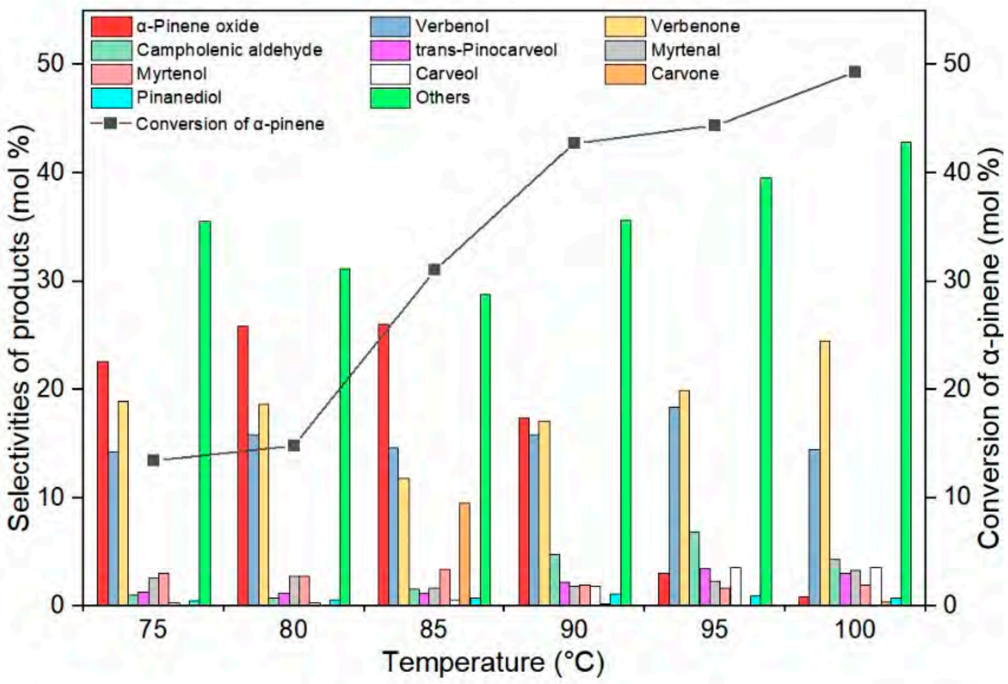

Figure 8. Influence of temperature on the conversion of α-pinene and selectivities of appropriate products in the oxidation of α-pinene over the TS-1_2 catalyst (catalyst content 2.5 wt%, reaction time 6 h), the figure shows the sum of the selectivities of the remaining by-products, which were formed with low selectivities.

In order to investigate the influence of the reaction time on the conversion of α-pinene and the selectivity of the transformation to the corresponding products, a series of tests was carried out at the temperature of 85 °C, which was selected as the most favorable in the previous stage of the research. The tested range of reaction times ranged from 1 to 48 h, and the amount of TS-1_2 catalyst was 2.5 wt%. These studies showed that the longer the reaction time, the higher the α-pinene conversion, as shown in Figure 9.

Figure 9 shows that the selectivity of the transformation to α-pinene oxide increases from 20 mol% (reaction time 1 h) to 28 mol% (reaction time 5 h) and then it decreases to 1 mol% (reaction time 48 h). The selectivity of the transformation to verbenol is maintained at the level of 13–18 mol% in the range of reaction times 1–11 h, and then it decreased to 3 mol% (reaction time 48 h). With longer reaction times (24 h and 48 h) it is possible to obtain high selectivities of the transformation to verbenone (corresponding: 38 mol% and 43 mol%), while at the same time high α-pinene conversion (respectively 90 mol% and 100 mol%). In the tested range of reaction times, the conversion of α-pinene increases from 8 mol% (reaction time 1 h) to 100 mol% (reaction time 48 h). Time influence studies showed a very large increase in the summary selectivity of the transformation to the allylic compounds, especially to verbenone (for the longest reaction times). The significant

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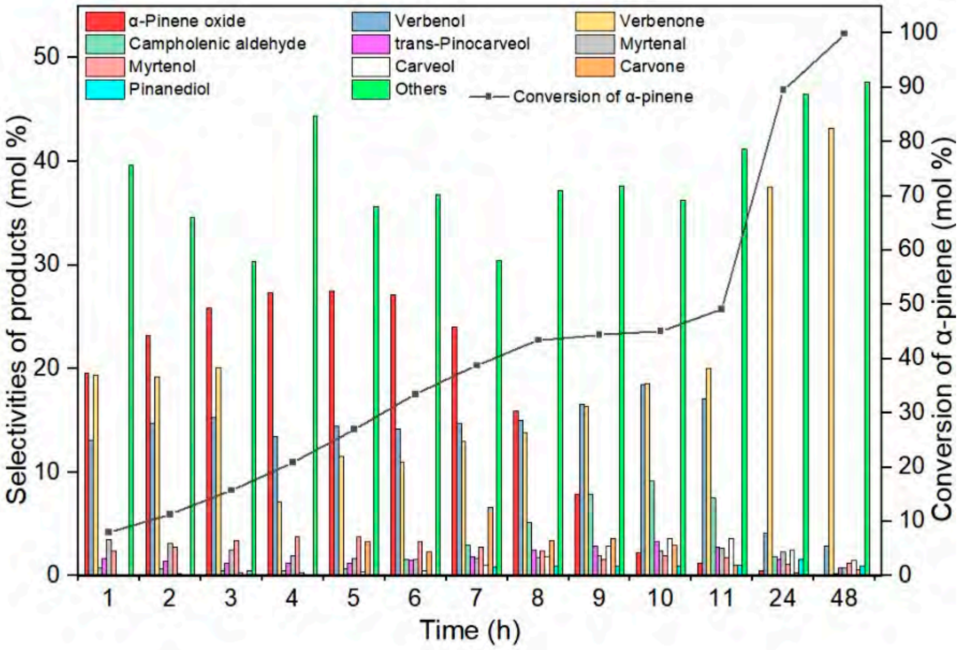
increase in the amount of verbenone is probably related to the conversion of verbenol to verbenone under the reaction conditions (oxidizing atmosphere). On the other hand, the reduction of the selectivity of transformation to the epoxy compound is related to the instability of this compound at elevated temperature and its isomerization to carveol and campholenic aldehyde. Research on the influence of the reaction time on the course of oxidation of *α*-pinene shows that the optimal results were obtained for the reaction time of 6 h (taking into account the selectivity of the transformation to *α*-pinene oxide), therefore this time was chosen as the most favorable for the next stage of the research.



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The influence of the catalyst content on the conversion of *α*-pinene and the selectivities of the respective products was tested at the temperature of 85 °C and for the reaction time of 6 h, these parameters were considered the most favorable in the previous stages of the research. At this stage of studies, the tested range of catalyst content was from 0.1 to 5 wt%. The results of these studies are shown in Figure 10.

Studies on the influence of the TS-1_2 catalyst content in the reaction mixture have shown that the selectivity of *α*-pinene oxide reaches the value of about 27 mol%, the selectivity of verbenone about 13 mol%, and the selectivity of verbenol about 15 mol%, in the entire range of the tested catalyst contents. There was also no significant influence of changes in the amount of catalyst in the reaction mixture on the selectivity of the other main products (trans-pinocarveol, myrtenal, and myrtenol). During the research at this stage, the conversion of *α*-pinene varied in the range of 26–34 mol%. In this case, the ratio of the selectivity of transformation to the epoxy compound and the summary selectivity of the transformation to allylic compounds was close to 1 and did not change with the increase in the amount of catalyst in the reaction mixture. The analysis of the obtained results showed that the most advantageous amount of the TS-1_2 catalyst in the reaction mixture was 1 wt% (the selection was made on the basis of the values of conversion of *α*-pinene and the selectivity of *α*-pinene oxide).

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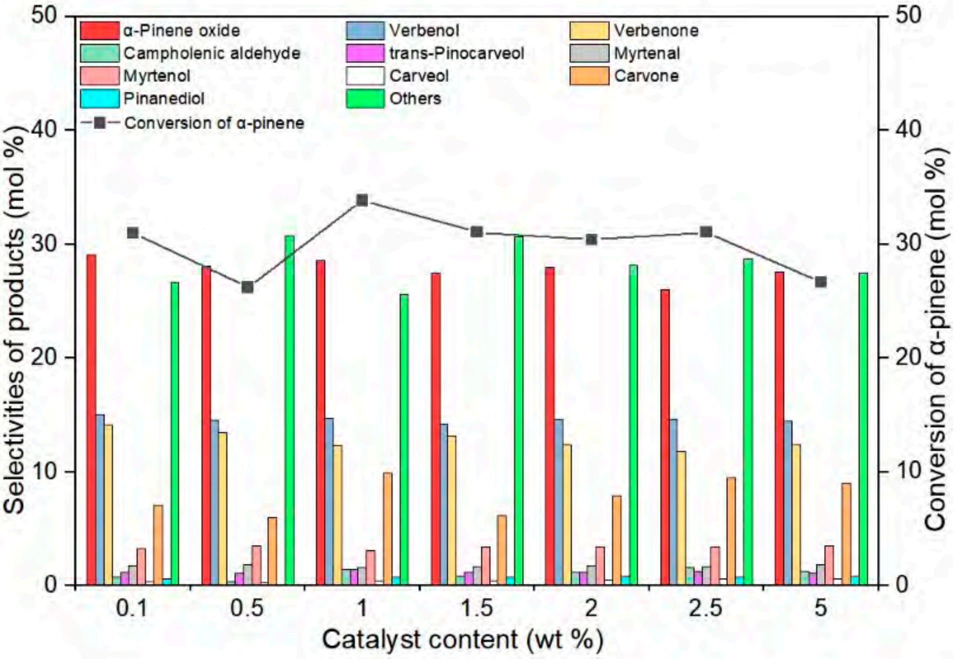

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The overall kinetic studies of the α-pinene oxidation over TS-1 catalyst were also performed. The kinetic studies were modeling considering a constant oxygen uptake (expressed in mol/dm^3) based on a series of experiments in which the effect of the different factors on the reaction rate were checked, e.g., temperature, reaction time, and amount of the catalyst. For each experiment (75, 80, 85, 90, 95 and 100 °C; P_{O2} = 1 bar) the reaction mixture composition was determined at the varied points of oxygen uptake/α-pinene ratio (defined in mol$_{O2}$. mol$_{\alpha\text{-pinene}}$). The α-pinene oxidation rates were calculated by kinetic curves differentiation. The turbulence created around the catalyst particles by a dynamic stirring of the reaction mixture helps to eliminate the external diffusion resistance between the bulk liquid and surface of the catalyst. Internal diffusion resistance was also negligible because of the small size of catalyst particles (0.24 μm ≤ dp ≤ 0.27 μm) used in the runs. It was observed that product content slightly depends on oxygen uptake/α-pinene ratio. Moreover, the α-pinene oxidation rate increases along with increase of the oxidation temperature. Activation energy estimated from Arrhenius dependence was 80.6 ± 4.7 kJ/mol and the effective kinetic constant was $k_{eff} = 1.6 \times 10^{10}$ mol$^{0.5}$·dm$^{-1.5}$·min^{-1} (the regression coefficient equals 0.9502). Consequently, under the reaction conditions the reaction rate of α-pinene oxidation by molecular oxygen can be expressed as follows:

$$R_O = k_{eff}\ f(\text{concentration})^{0.5} \cdot P^0{}_{O2} \cdot \exp(-E_a/RT)\ [\text{mol} \cdot \text{dm}^{-3} \cdot \text{min}^{-1}]. \quad (1)$$

Calculated activation energy matches results achieved for typical values of activation energy for α-pinene oxidation by molecular oxygen (81.3 kJ/mol) [54] as well as cis-pinene oxidation (79.5 kJ/mol) [55] or dibenzyl ester oxidation initiated by azoisobutyronitrile (93.66 kJ/mol) [56].

3. Materials and Methods

3.1. Raw Materials

In the tested process, the following reagents were used for oxidation carried out with the use of titanium-silicate TS-1 catalysts: α-pinene I (98%, Sigma Aldrich, Poznań, Poland).

Studies on the influence of the TS-1_2 catalyst content in the reaction mixture
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stage, the conversion of α-pinene varied in the range of 26–34 mol%. In this case, the
of the selectivity of transformation to the epoxy compound and the summary selec
of the transformation to allylic compounds was close to 1 and did not change wi
increase in the amount of catalyst in the reaction mixture. The analysis of the obt
results showed that the most advantageous amount of the TS-1_2 catalyst in the rea
mixture was 1 wt% (the selection was made on the basis of the values of conversion
pinene and the selectivity of α-pinene oxide).

The overall kinetic studies of the α-pinene oxidation over TS-1 catalyst were
performed. The kinetic studies were modeling considering a constant oxygen u
(expressed in mol/dm^3) based on a series of experiments in which the effect of the dif
factors on the reaction rate were checked, e.g., temperature, reaction time, and amou
the catalyst. For each experiment (75, 80, 85, 90, 95 and 100 °C, P_{O2} = 1 bar) the rea
mixture composition was determined at the varied points of oxygen uptake/α-p
ratio (defined in mol$_{O2}$. mol$_{\alpha\text{-pinene}}$). The α-pinene oxidation rates were calculated by k
curves differentiation. The turbulence created around the catalyst particles by a dyr
stirring of the reaction mixture helps to eliminate the external diffusion resistance bet
the bulk liquid and surface of the catalyst. Internal diffusion resistance was also negl
because of the small size of catalyst particles (0.24 μm ≤ dp ≤ 0.27 μm) used in the ru
was observed that product content slightly depends on oxygen uptake/α-pinene
Moreover, the α-pinene oxidation rate increases along with increase of the oxid

and oxygen (99.99%, Messer, Szczecin, Poland). Moreover, the following compounds were used as standards for chromatographic analyzes: α-pinene oxide (97%, Sigma Aldrich, Poznań, Poland), verbenol (95%, Sigma Aldrich, Poznań, Poland), verbenone (≥93%, Sigma Aldrich, Poznań, Poland), *trans*-pinocarveol (≥96%, Sigma Aldrich, Poznań, Poland), myrtenal (98%, Sigma Aldrich, Poznań, Poland), myrtenol (95%, Sigma Aldrich, Poznań, Poland), carveol (≥95%, Sigma Aldrich, Poznań, Poland), carvone (98%, Sigma Aldrich, Poznań, Poland), pinanediol (99%, Sigma Aldrich, Poznań, Poland). Campholenic aldehyde was identified by GC-MS method.

3.2. Synthesis of TS-1 Catalysts

The TS-1 catalysts were obtained by the hydrothermal method, with different molar ratios of silicon to titanium in the crystallization gel, according to the method described in the literature [6]. The obtained catalysts were marked as: TS-1_1 (titanium content 9.92 wt%), TS-1_2 (titanium content 5.42 wt%), TS-1_3 (titanium content 3.39 wt%), TS-1_4 (titanium content 3.08 wt%).

3.3. Characteristics of the TS-1 Catalysts

Characterization of the obtained four TS-1 catalysts was performed based on the following instrumental methods: XRF, N_2 sorption measurements at 77K, XRD and SEM.

The titanium content in TS-1 materials was estimated using an energy dispersive X-ray fluorescence (EDXRF) spectrometer with the Epsilon 3 PANalytical B.V. instrument (manufacturer, city, state, country).

The surface area, total pore volume, micropore volume and pore size distribution of the TS-1 materials were determined on an automatic N_2 sorption instrument Quadrasorb evo™ Gas Sorption analyzer (Anton Paar, St Albans, UK; previously Quantachrome Instruments, USA, 2014) at 77 K. The specific surface areas (SBET) of the samples were calculated by the Brunauer–Emmett–Teller method. The total pore volume (Vtot) was calculated utilizing the volume of N_2 adsorption at $p/p_0 = 0.99$. The t-Plot method was utilized to determine the micropore volume. The weight of the samples was in the range: 0.2708–0.3201 g. Before the measurement, the samples were dried at 250 °C for 20 h.

The XRD analysis was performed at ambient temperature using a X'Pert–PRO, Panalytical, Almelo, The Netherlands, 2012) with Cu-Kα (λ = 1.54056Å) radiation. The data were taken for the 2θ range of 5° to 50° with a step of 0.026°. The XRD patterns were compared with the JCPDS (Joint Committee on Powder Diffraction Standard) to identify the phases.

The SEM pictures were obtained using ultra-high resolution field emission scanning electron microscope (UHR FE-SEM) via the Hitachi SU8020 (Ultra-High Resolution Field Emission Scanning Electron Microscope; Hitachi Ltd, Tokyo, Japan, 2012). TS-1 materials were spread on the carbon tape and placed over the surface of SEM stub.

3.4. Oxidation of α-Pinene

The oxidation of α-pinene over TS-1 catalysts with the use of molecular oxygen as the oxidant was carried out in a 50 cm^3 glass reactor equipped with a reflux condenser, a magnetic stirrer with heating function and a glass bubbler for oxygen supply from the cylinder. α-Pinene was introduced into the reactor first, followed by the addition of the appropriate amount of TS-1 catalyst and the supply of oxygen from a bottle at a rate of 40 mL/min. The flask was placed in the paw, immersed in the oil bath and agitated at 500 rpm. The oxidation was carried out at the temperatures of 75–100 °C, during 1–48 h and with the catalyst content of 0.1–5 wt%. After the reaction, the post-reaction solution was separated from the catalyst using a centrifuge. Figure 11 shows the apparatus used in the oxidation of α-pinene with oxygen.

appropriate amount of TS-1 catalyst and the supply of oxygen from a bottle a
mL/min. The flask was placed in the paw, immersed in the oil bath and ag
rpm. The oxidation was carried out at the temperatures of 75–100 °C, durin
with the catalyst content of 0.1–5 wt%. After the reaction, the post-reaction s
separated from the catalyst using a centrifuge. Figure 11 shows the apparatu
oxidation of α-pinene with oxygen.

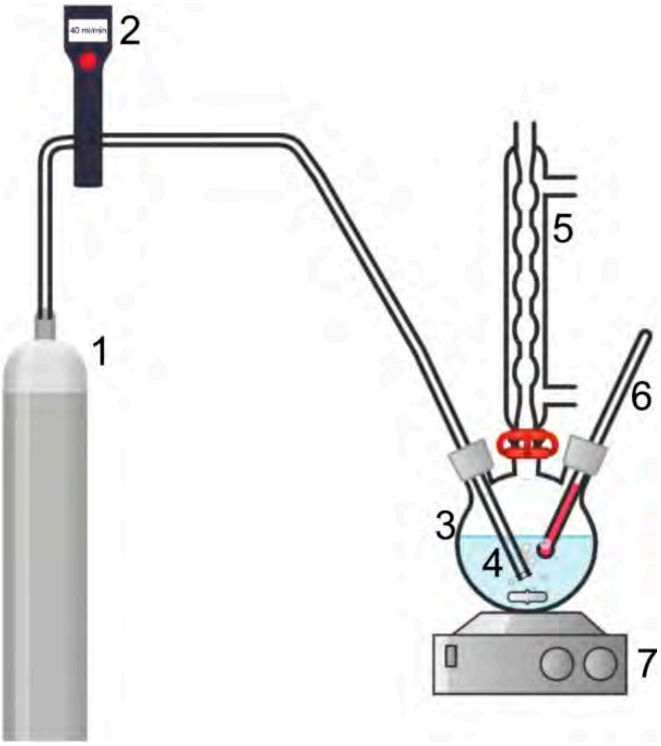

Figure 11. Apparatus used in the oxidation of α-pinene with oxygen: 1—oxygen cylinder, 2—oxygen flow regulator, 3—glass reactor with the capacity of 50 cm^3, 4—glass bubbler for oxygen supply, 5—reflux condenser, 6—thermometer, 7—magnetic stirrer with heating function.

3.5. Identification of the Products of Oxidation by the Gas Chromatography Method

Qualitative and quantitative analyzes of post-reaction mixtures were carried out by means of gas chromatography using a Thermo FOCUS apparatus (Thermo Fisher Scientific, Waltham, MA, USA, 2009) with an RTX-1701 column equipped with a flame ionization detector. The analysis conditions were as follows: isothermally at 50 °C for 2 min, temperature increase at 6 °C/min to 120 °C, isothermally at 120 °C for 4 min, then temperature increase at 15 °C/min up to 240 °C, the temperature of the dispenser 200 °C, and the flow of the carrier gas 1.2 mL/min. The quantitative analysis was carried out using the method of internal normalization (the error related to chromatographic analyses was 1%). For each of the performed syntheses, a mass balance was prepared, taking into account such functions of the process as: conversion of α-pinene and selectivities of the respective products.

Qualitative analyzes of the products present in the post-reaction mixtures were also carried out by GC-MS using a ThermoQuest apparatus equipped with a Voyager detector and a DB-5 column (filled with phenyl-methylsiloxanes with dimensions 30 m × 0.25 mm × 0.5 µm). The conditions in which the analyses were carried out were as follows: helium flow 1 mL/min, sample chamber temperature 200 °C, detector temperature 250 °C, oven temperature isothermally for 2.5 min at 50 °C, followed by an increase at a rate of 10 °C/min up to the temperature of 300 °C.

Before performing the analyzes by GC-MS and GC methods, the post-reaction solution was separated from the catalyst by centrifugation in a laboratory centrifuge. The solution thus separated was then diluted with acetone (0.750 mL of acetone was added to 0.250 mL of the solution).

4. Conclusions

The influence of titanium content on the textural properties was proved. The higher Ti content the lower values of the textural properties was observed. At the same time, along with the increase in titanium content, the catalytic activity of the obtained TS-1 catalysts should increase, because titanium is the active center of the catalyst in which the reaction we are studying takes place. Based on the catalytic tests of four titanium-silicate catalysts, it was confirmed that TS-1 catalysts are active in the oxidation of α-pinene with oxygen. During the tests it was shown that the most active catalyst in this process was the TS-1_2 catalyst, which contained 5.42 wt% of Ti. All the tested process parameters (temperature, reaction time and amount of the catalyst) influenced on the conversion of α-pinene and the selectivity of the obtained products. Increasing the temperature and extending the reaction time increased the conversion of α-pinene. It has been found that the most advantageous oxidation of α-pinene is carried out at the temperature of 85 °C for 6 h using 1 wt% of the TS-1_2 catalyst in the reaction mixture. Comparing the results presented in our earlier publication [6] with those described in this paper, it was observed that increasing the temperature from 80 to 85 °C and the use of the TS-1_2 catalyst in the amount of 2.5 wt% in the reaction mixture allows to increase the conversion of α-pinene almost doubled (up to 31 mol% from 17 mol%) compared to the studies described in our earlier work. However, this did not affect the value of the selectivity of the transformation to α-pinene oxide, as in both studies it remained at a similar level and amounted to approximately 30 mol%. Unexpectedly, in the research presented in this study, it turned out that with longer reaction times (24 and 48 h) it is possible to obtain high selectivities of verbenone (38 mol% and 43 mol%) with a very high conversion of α-pinene (90 and 100 mol%). In general, the presented studies have shown that increasing the temperature and lengthening the reaction time reduces the selectivity of peroxide compound formation, which either decomposes because its structure is not stable or isomerizes to carveol and campholenic aldehyde. The increase in the content of verbenone along with the extension of the reaction time may, however, be related to the oxidation of verbenol to verbenone under the reaction conditions (oxidizing atmosphere).

The comparison the results obtained in our research with the results described in the literature for carbon-supported Pt catalysts [52] showed that the use of TS-1 catalysts in the oxidation of α-pinene allows to obtain a lower summary selectivity of transformation to verbenol and verbenone (allylic oxidation products) than on carbon-supported Pt catalysts and in our study (in first stage of our studies). It was changed during raising temperature and prolonging of the reaction time over chosen TS-1 catalyst (at this stage of studies the summary selectivity of transformation to verbenol and verbenone raises). The increase in selectivity of transformation to epoxy product in relation to the sum of selectivity of verbenol and verbenone was observed in studies with carbon nanotubes and activated carbons [53]. In these studies, the selectivity of the transformation to α-pinene oxide was usually about three times higher than the summary selectivity of the transformation to allylic oxidation products. In the case of our research, such significantly higher values of epoxide selectivity were not achieved, the maximum ratio of epoxy selectivity to the sum of selectivity of compounds formed as a result of oxidation at the allylic position was about 1. Differences in the oxidation of α-pinene on our TS-1 catalysts and carbon-supported Pt catalysts, carbon nanotubes and activated carbons described in the literature may result from different structures (including the presence of pores of the appropriate volume and shape) of these catalysts and different types of active sites as well as their location in the structure of these catalysts.

The main advantage of the presented process of oxidation of α-pinene with oxygen is the lack of a solvent in the reaction medium. The proposed method of transforming α-pinene in the direction of obtaining valuable compounds is an example of an environmentally friendly process with the possibility of using waste in the form of turpentine (a renewable and vegetable source of α-pinene). It is also worth emphasizing that the products of α-pinene oxidation are products with a very high application potential in medicine, as well as in the cosmetics, perfumery and food industries.

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Studies on the catalytic activities of ZSM-5 zeolites with different aluminum contents in the green oxidation of α-pinene to high value-added products

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ABSTRACT

α-Pinene is the terpene abundant in nature. It is present in the oils of coniferous trees, mainly pine. We demonstrate that from this renewable stock, high value-added products such as verbenone, verbenol, α-pinene oxide, can be obtained as the main products, and smaller quantities of pinanediol carvone myrtenol pinocarveol campholenic aldehyde, myrtenal, and carveol are also produced. All the products have numerous applications in medicine, cosmetics, and foods. Heterogeneous ZSM-5 zeolite catalysts with different aluminum contents – designated as (in wt% of Al) ZSM-5_1 (2.5), ZSM-5_2 (0.59), and ZSM-5_3 (0.38) – were applied in the green α-pinene oxidation with oxygen and without solvent. To date, the use of the ZSM-5 catalyst in the α-pinene oxidation process has not been described. The catalysts were characterized by UV-Vis, FTIR, EDXRF, XRD, SEM, DTA techniques, and by the nitrogen sorption method at 77 K. The effects of catalyst amount and properties, temperature and reaction time, on product selectivity and α-pinene conversion, were determined.

1. Introduction

The importance of raw materials of natural origin obtained from plant biomass, including waste, is increasing. Such raw materials are used both in the organic industry and in the production of polymers. Additionally, these compounds and their transformation products have very important applications in medicine, cosmetics and in the food industry. The advantages of raw materials of natural origin are their renewable nature and relatively low price. Producing organic compounds from biomass allows for its management, as is the case of, for example, limonene obtained from waste orange peels remaining from the production of orange juice. Among the compounds of natural origin, particular attention is given to terpenes. Examples of such terpene compounds that are subjected to, e.g., oxidation or isomerization

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processes to produce even more valuable compounds for medicine, cosmetics or organic syntheses, are α-pinene, limonene, and geraniol. Heterogeneous catalysts, including natural and synthetic zeolites, are currently of great importance in the transformation of terpenes. One such catalyst is the synthetically obtained ZSM-5 zeolite with the MFI structure. Although it has already found numerous applications in industrial processes (e.g., in the cracking of hydrocarbons, or in the MTO and MTG processes), it is still popular with many research groups and new methods of synthesizing this catalyst are being developed in order to increase its activity. Further, new applications in catalysis are still being sought for this material (Weissenberger et al., 2020; Jia et al., 2020; Reis Bernardes et al., 2019; Sun et al., 2017; Chen et al., 2021; Jerzak et al., 2022; Miskolczi et al., 2019; Liang et al., 2016; Sanhoob et al., 2022). It should be emphasized that so far, the use of pure ZSM-5 catalyst in the oxidation of α-pinene has not been described, and only its counterparts modified with appropriate metal (cobalt) have been discussed.

α-Pinene is the terpene compound that is most abundant in nature. It arouses the interest of research teams from various fields of science around the world. Studies on the transformations of this inexpensive and renewable compound into more useful products with the use of heterogeneous catalysts are of particular importance. Natural sources of α-pinene are coniferous trees, citrus fruits, and herbs (Aydin et al., 2013; Gobato et al., 2015; Mushtaq Ahmad et al., 2006). In significant amounts, this monoterpene is found in turpentine, which is extracted as a by-product of the processing of resinous wood into cellulose (Singh et al., 2022). α-Pinene exhibits medicinal effects as this compound fights bacteria, relieves inflammation, and improves memory (Joshee et al., 2019). The natural origin and chemical structure of α-pinene (an unsaturated and bicyclic hydrocarbon) allows for extensive use of this terpene as a renewable resource for the production of valuable compounds (Liu et al., 2021; Corma Canos et al., 2007). α-Pinene can be converted to more valuable products by oxidation and also by the isomerization reaction. The first method (oxidation) is described in this article, along with a discussion of the applications of the main products of α-pinene oxidation, namely α-pinene oxide, verbenone, verbenol (Casuscelli et al., 2008; Maksimchuk et al., 2005; Eze et al., 2022; Mukhtar Gunam Resul et al., 2021) (Fig. 1).

The second way of transforming α-pinene into more valuable products is the isomerization of this compound. Among the products of α-pinene isomerization, camphene and limonene are particularly important. Camphene can be applied as the raw material in the synthesis of camphor. This compound shows medical and anticancer properties. Moreover, camphene is used as a fragrant and flavor additive and in the production of cleaning agents (Miądlicki et al., 2021). Limonene is also widely used. This compound can be converted to (−)-carvone, which is used as a peppermint flavor. Limonene has also found applications as a fumigant and repellent, and can be used as the solvent in extraction methods. The application of limonene as an additive for plastics was also described. Moreover, limonene finds numerous applications in medicine and cosmetics due to its beautiful smell and its anti-bacterial and anti-cancer properties (Miądlicki et al., 2021; Wróblewska, 2014).

The process of oxidation of α-pinene, is one of the most important ways of managing turpentine (Eze et al., 2022). The products of this process have applications in perfume, cosmetic, and food industries, and in medicine. In recent years, the oxidation of α-pinene on heterogeneous catalysts has been intensively studied. For example, this process has been performed using such porous materials as Ti-MCM-41 (Mai et al., 2011; Cánepa et al., 2011), Ti-MMM-2 (Maksimchuk et al., 2005), and TS-1 (Wróblewska et al., 2021) as the catalysts. However, there are some reports on the use of the modified ZSM-5 zeolite materials in this process.

B. Qi et al. presented a method for the oxidation of α-pinene using Co-ZSM-5 material, which consisted of ZSM-5 after ion exchange of sodium for cobalt. The process was performed mainly in dimethylformamide, but the following solvents were also used in this process: dimethylacetamide, dioxane, cyclohexanol, and toluene. As the initiator of the reaction, tert-butyl hydroxide was utilized. The oxidant was oxygen from the air, which was supplied by the barbotage method. The reaction was accomplished at the temperature range of 50–100 °C for 5 h, and the authors obtained an α-pinene conversion of 68.3%. The main oxidation product was α-pinene oxide (maximum selectivity of 71.4%), and verbenol and verbenone were also obtained. The studies showed that the introduction of Schiff base-type ligands into Co-ZSM-5 increased not only the conversion of α-pinene to 95.3% but also the selectivity of transformation to α-pinene oxide to 88.4% (Qi et al., 2011).

B. Tang et al. described studies on the cobalt form of zeolites, Co-ZSM-5, 3 A, 4 A, and Y, as catalysts for α-pinene oxidation. Application of Co-ZSM-5 allowed for the attainment of the highest conversion of α-pinene – equal to 92.8%. The selectivity to α-pinene oxide was 86.1%, and the other products were verbenol and verbenone. The process was performed in the presence of dimethylformamide and tert-butyl hydroperoxide. The oxidant was atmospheric oxygen

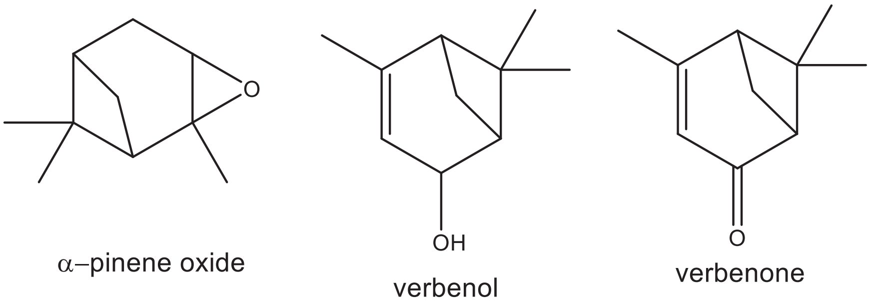

Fig. 1 – The main oxidation products of α-pinene.

supplied to the reaction medium by the barbotage method, and the reaction was performed for 5 h at 90 °C (Tang et al., 2012).

The current work aims to perform the sustainable and green technology of α-pinene oxidation to high value-added products. α-Pinene is the terpene abundant in nature in, e.g., the oils of coniferous trees, mainly pine. We showed that from this renewable stock, high value-added products such as verbenone, verbenol, α-pinene oxide can be obtained as the main products, and also carvone, carveol, pinanediol, myrtenol, myrtenal, pinocarveol, campholenic aldehyde are produced. All the products have numerous applications mainly in medicine, cosmetics, and foods. The oxidation was performed without any solvents, and the oxidant was oxygen, which was supplied to the reaction mixture by the barbotage method. The ZSM-5 zeolites with different alumina contents were applied as catalysts. They were characterized by UV-Vis, FTIR, EDXRF, XRD, SEM, DTA, and nitrogen sorption at 77 K. The study on the activity of ZSM-5 as catalys was based on the development of the most beneficial conditions for the oxidation of α-pinene, such as temperature, amount of catalyst, and reaction time. Successful results of these catalytic tests would allow finding new applications for the ZSM-5 catalyst, which is commercially available and relatively inexpensive. At the same time, it would show that it is not necessary to modify this material by introducing other metals into its structure or impregnating it on its surface, which would significantly reduce the cost of catalyst synthesis for the oxidation of α-pinene, as well as for the oxidation of other natural olefins. It should also be emphasized that this catalyst is easy to regenerate and can be used multiple times in the oxidation process, which also significantly reduces the cost of performing this oxidation process.

2. Experimental

2.1. Raw materials

The ZSM-5 porous material (zeolite) samples kindly donated by the German company, Tricat Zeolites GmbH, were tested as the catalysts. The three ZSM-5 zeolites were marked in the following way (according to their wt% of aluminum): ZSM-5_1 (with 2.5 wt% Al), ZSM-5_2 (0.59 wt%), and ZSM-5_3 (0.38 wt%). In tests of the catalytic activities of the ZSM-5 zeolites, α-pinene (purity 98%, Sigma-Aldrich) was used as an organic raw material, as well as oxygen (purity 99.99%, Messer) as an oxidant. Table 1 summarizes the substances used as standards for the quantitative and qualitative analyses of the mixtures obtained after syntheses. Campholenic aldehyde, a secondary oxidation product of α-pinene, was identified by the GC-MS method (gas chromatography which is coupled to mass spectrometry method).

Table 1 – Standards (from Sigma-Aldrich) that were taken for the chromatographic analyses of the reaction mixtures.

Standard	Purity
α-pinene oxide	97%
verbenol	95%
verbenone	≥ 93%
trans-pinocarveol	≥ 96%
myrtenal	98%
myrtenol	95%
carveol	≥ 95%
carvone	98%
pinanediol	99%

2.2. Characteristics of the ZSM-5 catalysts

The ZSM-5 catalyst were characterized using: UV-Vis, FTIR, EDXRF, XRD, SEM, and DTA methods. The textural parameters of ZSM-5 zeolites were also determined from nitrogen sorption measurements at 77 K.

UV-Vis spectra were prepared by Jasco 650 spectrometer for a wavelength range of 200–600 nm. The barium sulfate spectrum was used as a background. FTIR spectra were measured using a Thermo Electron Nicolet 380 spectrometer. The range of wavenumber was 400–4000 cm^{-1}, and the spectrum of KBr was used as the background. The Al content in catalysts was determined by an EDXRF (Energy Dispersive X-ray Fluorescence) () spectrometer (Epsilon 3, PANalytical, Almelo). The XRD analysis was performed using an Empyrean PANalytical X-ray diffractometer with the use of Cu-Kα radiation. The identification of the phases was accomplished by comparison of the XRD spectra with JCPDS cards. The SEM images were prepared using the ultra-high resolution SU8020 Hitachi field emission scanning electron microscope. The DTA measurements were performed using an instrument of the SDT 650 DISCOVERY series (TA Instruments, USA) and in air atmosphere. Samples (of ~20 mg each) were heated in corundum crucibles from 20 °C up to ~1000 °C and at a heating rate amounting to 10 °C/min.

The textural parameters were determined on the basis of nitrogen sorption at a temperature of 77 K. The Gas Sorption Surface Area and Pore Size Analyzer ASAP 2460 Micromeritics was utilized. The specific surface area (S_{BET}) was calculated on the basis of the Brunauer–Emmett–Teller equation. The DFT method was used to calculate the pore size distribution and the micropore volume. The total pore volume (V_{tot}) was calculated on the basis of the nitrogen volume adsorption at $p/p_0 \approx 1$. Prior to the measurements, the zeolites were dried at 250 °C for 20 h.

2.3. Oxidation of α-pinene over ZSM-5 zeolites

To investigate the catalytic activities of ZSM-5 zeolites in the oxidation of terpene compound - α-pinene, about 10 g of α-pinene was introduced into a three-necked 50-cm^3 spherical flask having a magnetic stirrer for studying the effect of temperature and amount of catalyst. For the study of the effect of reaction time, we used more α-pinene, amounting to 25 g. Subsequently, an appropriate amount of ZSM-5 was introduced. Oxygen from a cylinder was supplied to the reaction medium by the barbotage method at a rate of 40 mL/min, and the rate was regulated with a flow meter. The flask was then placed in an oil bath heated to the set temperature, and stirring was initiated at a speed of 500 rpm. In order to separate the reaction mixture from the catalyst, after the reaction was completed, about 1 cm^3 of this mixture was introduced into a plastic Eppendorf tube and placed in a laboratory centrifuge.

2.4. *Identification of oxygenated α-pinene derivatives by the GC method*

Quantitative and qualitativeanalyses of the mixtures after syntheses were performed using a Thermo Electron FOCUS apparatus. This apparatus was equipped with a DB-5 column and also with a flame ionization detector. The analysis conditions were as follows: carrier gas flow of 1.2 mL/min, dispenser temperature of 200 °C, oven temperature – isothermal at the temperature of 50 °C for 2 min, temperature rise at 6 °C/min to the temperature of 120 °C, isothermal at the temperature of 120 °C for 4 min, then a temperature rise at 15 °C/min to the temperature of 240 °C. The internal normalization method was used for the quantitative analysis of the mixtures after syntheses.

A ThermoQuest apparatus was used for qualitative analyses of post-reaction mixtures. This instrumentation was equipped with a DB-5 column and a Voyager detector. The conditions at which the analyses were performed were as follows: helium flow rate of 1 mL/min, the temperature of sample chamber 200 °C, the temperature of detector 250 °C, the temperature of oven – isothermal for 2.5 min at the temperature of 50 °C, followed by an increase at a rate of 10 °C/min to the temperature of 300 °C.

3. Results and discussion

3.1. *Characteristics of the ZSM-5 zeolites*

The UV-Vis spectra of the zeolites are shown in Fig. 2. The band located at 240 nm is assigned to the Al-O charge-transfer transition for four-coordinated framework aluminum, which is characteristic of these types of zeolites (Saux et al., 2016). The intensity of this band increases with increasing aluminum content.

The FTIR spectra are shown in Fig. 3. The band at 2359 cm^{-1} is attributed to hydroxyl groups originating from H_2O molecules adsorbed on the ZSM-5 surface. The ZSM-5_1 zeolite, which has the highest aluminum content, is characterized by the most intense band. The 1627 cm^{-1} band seen in the figure is attributed to deformation vibrations of H_2O molecules, and the most intense band occurs for ZSM-5_1. The figure shows bands at 1213 cm^{-1} and 1058 cm^{-1}, which are associated with asymmetric stretching vibrations characteristic of Si-O-Si groups. The most intense 1213 cm^{-1} band is observed, as before, for the highest Al content zeolite, ZSM-5_1. The ZSM-5 materials do not differ much in the 1058 cm^{-1} band intensity. The most intense band of 794 cm^{-1}, which is attributed to symmetric stretching vibrations of Si-O-Si groups, is observed for ZSM-5_1. The 543 cm^{-1} band indicates the Si-O-Al bonds presence (Caldeira et al., 2016; Khatamian and Irani, 2009; Zhang et al., 2017; Wang et al., 2013).

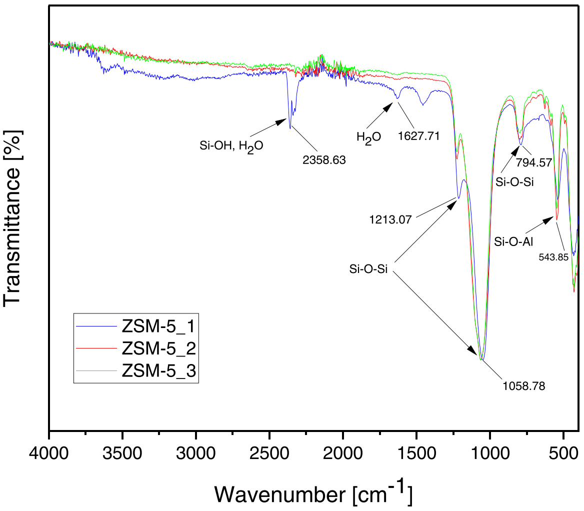

Fig. 3 – FTIR spectra of the ZSM-5 with various aluminum contents.

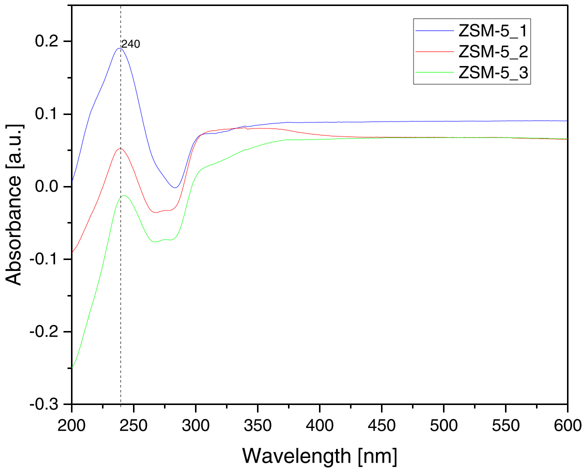

Fig. 2 – UV–VIS spectra for the ZSM-5 catalysts with various aluminum contents.

The N_2 sorption isotherms are showed in Fig. 4. All the isotherms represent type I with a high adsorption at low relative pressures, lower than 0.01. Such isotherm curves, almost coincide with the y-axis, and are indicative of the presence of micropores. All the isotherms also exhibited the features of IV type hysteresis loops H4, which demonstrates the presence of mesopores. The first hysteresis loops located in the p/p_0 range from 0.1 to 0.35 were attributed to the presence of internal structural defects (Huang et al., 2020) and were caused by the fluid-to-crystalline phase transformation of adsorbed nitrogen (Zhang et al., 2018). This phenomenon was described for ZSM-5 with high silicon content

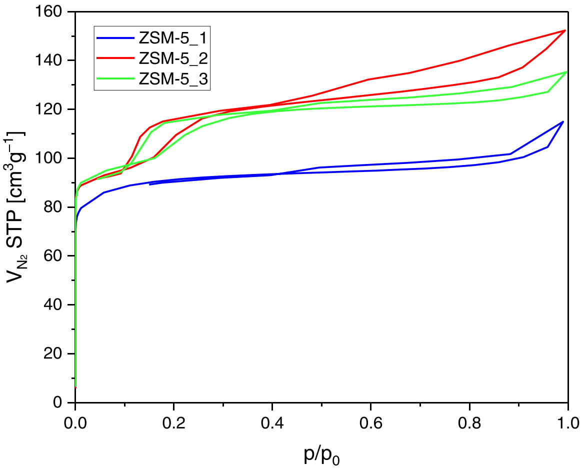

Fig. 4 – N_2 sorption isotherms for the ZSM-5 with various aluminum contents.

(Zieliński et al., 2021). The first hysteresis loops in Fig. 4 were observed only for ZSM-5_2 and ZSM-5_3 materials with low aluminum content. The second hysteresis loops located in the p/p$_0$ range between 0.4 and 1 are typical for mesoporous materials. In summary, on the basis of the shapes of isotherms presented in Fig. 4, it can be concluded that ZSM-5 materials contained micropores and mesopores.

The pore size distribution showed in Fig. 5 and the values of textural parameters (Table 2) confirm the conclusions drawn based on of nitrogen sorption isotherms (Fig. 4). It is clearly seen from Fig. 5 that the micropores were the dominant pores and for the ZSM-5_1, the micropore volume was the highest.

The XRD results are presented in Fig. 6. Well-resolved diffraction peaks corresponding to the typical MFI structure were observed, according to the JCPDS-44–0003 card. For ZSM-5_2 and ZSM-5_3 at the 2θ range of 24.3 – 24.5°, double reflections were observed, whereas for ZSM-5_1 only one signal was present. The transformation of the characteristic “doublet” in the 24.3 – 24.5° range into a single reflection was due to a change of symmetry from monoclinic to orthorhombic (Fyfe et al., 1984). The ZSM-5 material with the highest aluminum content had orthorhombic symmetry whereas ZSM-5 with low Al content had monoclinic symmetry. The peaks observed for ZSM-5 with the highest aluminum content (ZSM-5_1) were considerably lower than those observed for ZSM-5_2 and ZSM-5_3, as the crystallinity of ZSM-5_1 was the lowest.

Fig. 7 presents the SEM images for the ZSM-5 catalysts with different aluminum contents. ZSM-5_2 and ZSM-5_3 showed the typical morphology, i.e., hexagonal prisms. The sizes of the ZSM-5_3 particles were more uniform than the sizes of ZSM-5_2 particles. The morphology of ZSM_5_1 containing the most aluminum is completely different, and the SEM micrographs showed small rectangular particles.

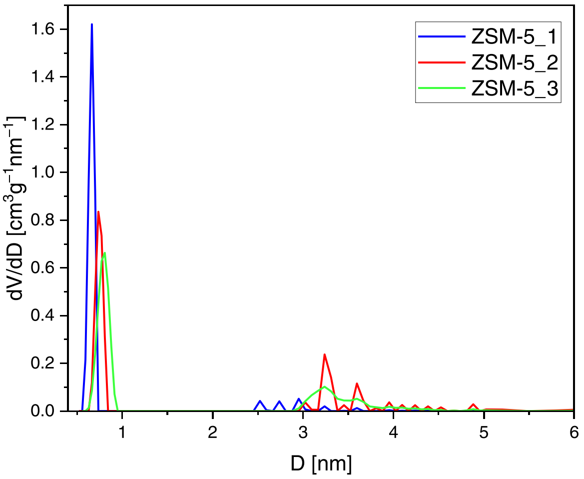

Fig. 5 – Pore-size distribution for the ZSM-5 catalysts with various aluminum contents.

Table 2 – The Al content and textural parameters of the ZSM-5 zeolites.

ZSM-5	Al [wt%]	S$_{BET}$ [m^2/g]	V$_{tot}$ [cm^3/g]	V$_{mic}$ [cm^3/g]	%V$_{mic}$ [%]	Max size [nm]
ZSM-5_1	2.50	346	0.178	0.138	77	194
ZSM-5_2	0.59	376	0.235	0.123	52	318
ZSM-5_3	0.38	367	0.209	0.126	60	594

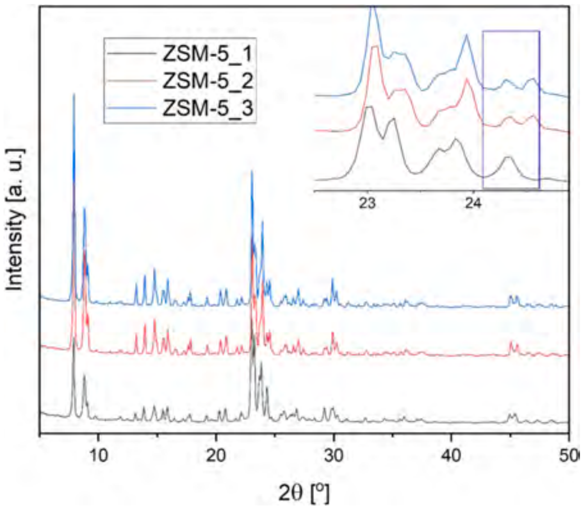

Fig. 6 – XRD patterns of the ZSM-5 catalysts with various aluminum contents.

To determine the thermal stability of the ZSM-5_1 and ZSM-5_3 zeolites, both samples were studied by the DTA-TG method at the temperature 25–1000 °C (Fig. 8). Both DTA curves of these zeolites are similar to each other. One endothermic effect was recorded with the onset temperature of 66 °C. The weight loss below 200 °C recorded on the TG curves, related to the first endothermic effects on the DTA curves, were mainly ascribed to the moisture (de et al., 2016). The weight loss of zeolites ZSM-5_1 and ZSM-5_3 at this stage was 8.14 and 3.09 wt%, respectively. However, clearly marked two steps can be seen in the TG curve of zeolite ZSM-5_3, which is related to the two types of water binding sites. In the case of this material, above 300 °C the weight loss is gradual with increasing temperature and does not greatly change up to 1000 °C, and the total weight loss was 3.36 wt%.

From the TG curves of zeolite ZSM-5_1 in Fig. 8, we could observe that the weight was decreasing with a slow gradient in the temperature range 25–500 °C. The total weight loss up to 500 °C was 10.75 wt%. Above this temperature, there is a slight change in weight, and the total weight loss recorded on the TG curve of zeolite ZSM-5_1 was 11.85 wt%.

The DTA measurements showed that ZSM-5_3 is more stable at the highest temperature, as this catalyst contained the most silicon. Usually zeolites containing more silicon are more resistant to high temperatures than those with less silicon (Cruciani, 2006).

3.2. *Tests of catalytic activity of ZSM-5 zeolite materials in the process of oxidation of terpene compound - α-pinene with oxygen*

The main products that were formed during the oxidation of α-pinene with oxygen on the tested ZSM-5 catalysts are shown in Fig. 9.

Oxidation of α-pinene on the ZSM-5_1 catalyst (with 2.5 wt % Al) was carried out at 75–100 °C for 6 h. The results of the influence of temperature on product selectivities and α-pinene conversion are shown in Fig. 10. As the temperature increases, it is visible that the conversion of α-pinene grows

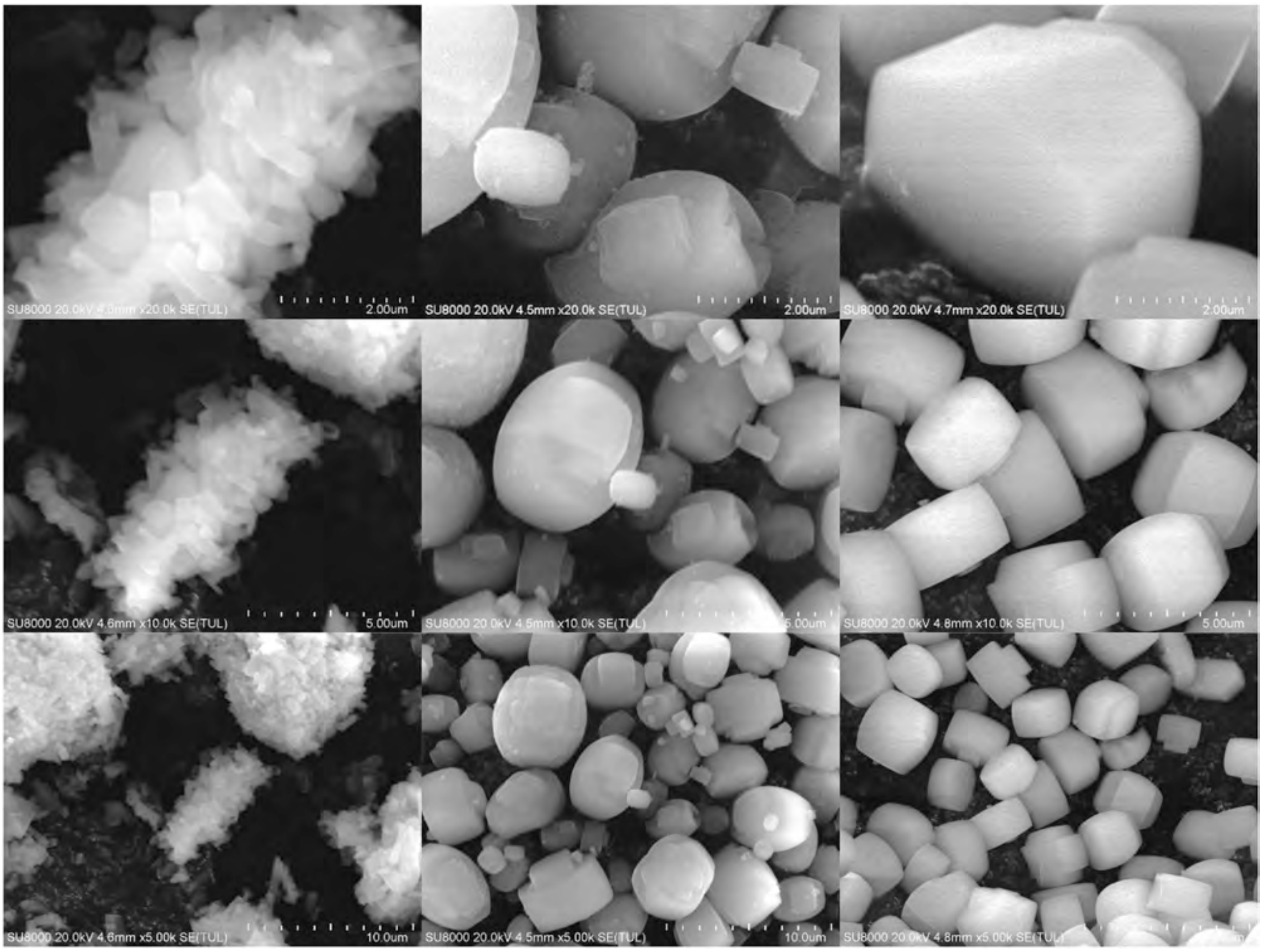

Fig. 7 – SEM images for the ZSM-5 catalysts with various aluminum contents: ZSM-5_1 (1st column), ZSM-5_2 (2nd column), and ZSM-5_3 (3rd column).

and reaches a maximum value (about 47 mol%) at the temperature amounting to 100 °C. The selectivity of α-pinene oxide remains at the level of 25–30 mol% in the range of 75–90 °C, and then falls to 15 mol% at 100 °C. The selectivity of verbenol is all the time at the level of 16–18 mol% over the range of tested temperatures. The selectivity of verbenone amounts to 20–21 mol%. Only for two temperatures, 90 and 95 °C, a slight reduction in the value of this function to 14–16 mol% is observed; this difference, however, lies within the error of the determination method. The highest selectivity of α-pinene oxide (30 mol%) was recorded for 90 °C, which was chosen as the most favorable temperature.

Studies on the effect of the contents of the ZSM-5_1 materials in the mixture on product selectivities and α-pinene conversion were conducted at 90 °C for 6 h and in the range of 0.1–5 wt% of catalyst. The received results are shown in Fig. 11. It is observed that the conversion of α-pinene decreases slightly, as catalyst content increases, from 44 mol% (content of the catalyst 0.1 wt%) to 31–39 mol% (content of the catalyst 2.5 and 5 wt%). This is probably connected with the formation of small amounts of oligomeric or polymeric products that are not detected by the GC method. The selectivity of α-pinene oxide is kept at the level of 25–30 mol% in the whole range of the catalyst contents. Additionally, the selectivity of verbenol is kept at the level of 15–17 mol%, and the selectivity of verbenone is maintained at 13–14 mol%. The most favorable amount of catalyst was found to be 0.5 wt%; the selectivity of α-pinene oxide for this catalyst content amounts to 30 mol%.

The results of the effect of reaction time on product selectivities and α-pinene conversion for ZSM-5_1 are shown in Fig. 12. The oxidation was performed at 90 °C, the catalyst amount was 0.5 wt%, and the reaction time was changed from 1 to 48 h. As the reaction time is prolonged, the conversion of α-pinene is growing, taking the maximum value (100 mol%) for the reaction time of 48 h. The selectivity of α-pinene oxide is kept at the level of 23–30 mol% from 1 to 8 h. After a time of 8 h, the selectivity of epoxide compound decreases to 0.3 mol% (reaction time of 48 h). The selectivity of verbenol remains at the level of 18–20 mol% for the reaction time from 1 to 12 h, and then it lowers to 2 mol% (reaction time 48 h). The selectivity of verbenone is kept at the level of 16–24 mol% in the range of 1–12 h, then this function increases to 46 mol% (reaction time 48 h). Based on the selectivity to α-pinene oxide values the reaction time of 7 h can be taken as the most beneficial; the selectivity of epoxide compound (α-pinene oxide) amounts for this reaction time to 29 mol%, selectivity of verbenol 18 mol%, selectivity of verbenone 16 mol%, and α-pinene conversion is 45 mol%.

Another zeolite tested in terms of its activity in the oxidation of α-pinene was the ZSM-5_2 material. The oxidation reaction of α-pinene on ZSM-5_2 was performed at 75–105 °C

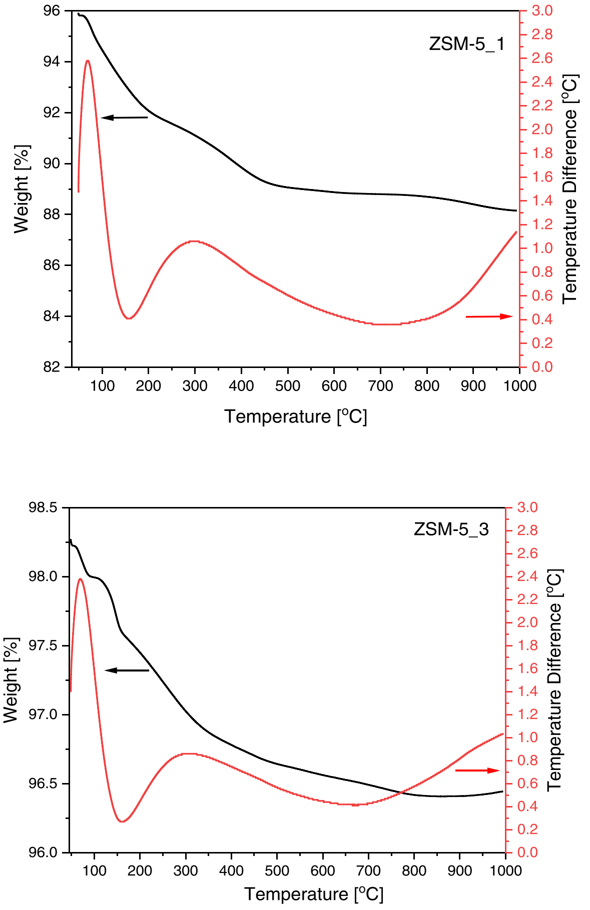

Fig. 8 – DTA and TG curves of ZSM-5_1 and ZSM-5_3.

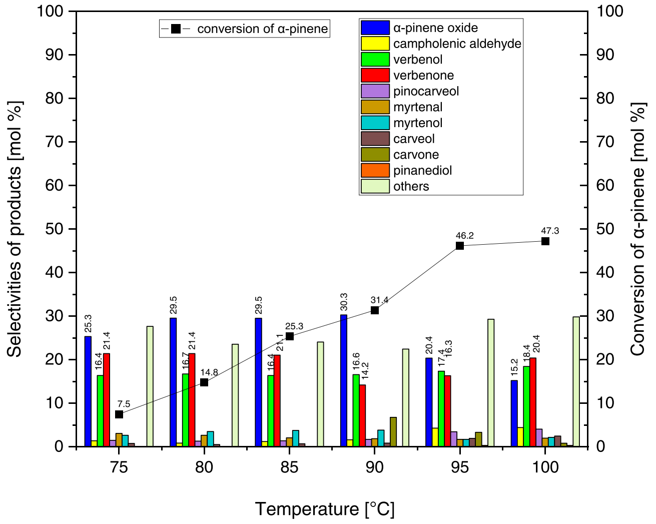

Fig. 10 – Effect of temperature on product selectivities and α-pinene conversion for ZSM-5_1 catalyst (Al content in catalyst 2.5 wt%, reaction time 6 h, and catalyst content in reaction mixture 2.5 wt%).

for 6 h, and the catalyst amount was 0.5 wt%. The results of the effect of temperature on product selectivities and conversion of α-pinene are shown in Fig. 13.

The analysis shows that the temperature of 75 °C is too low for the oxidation of α-pinene, since the selectivities of the main products amount to 0 mol%, and the conversion of α-pinene is only 1 mol%. With increasing in temperature, the

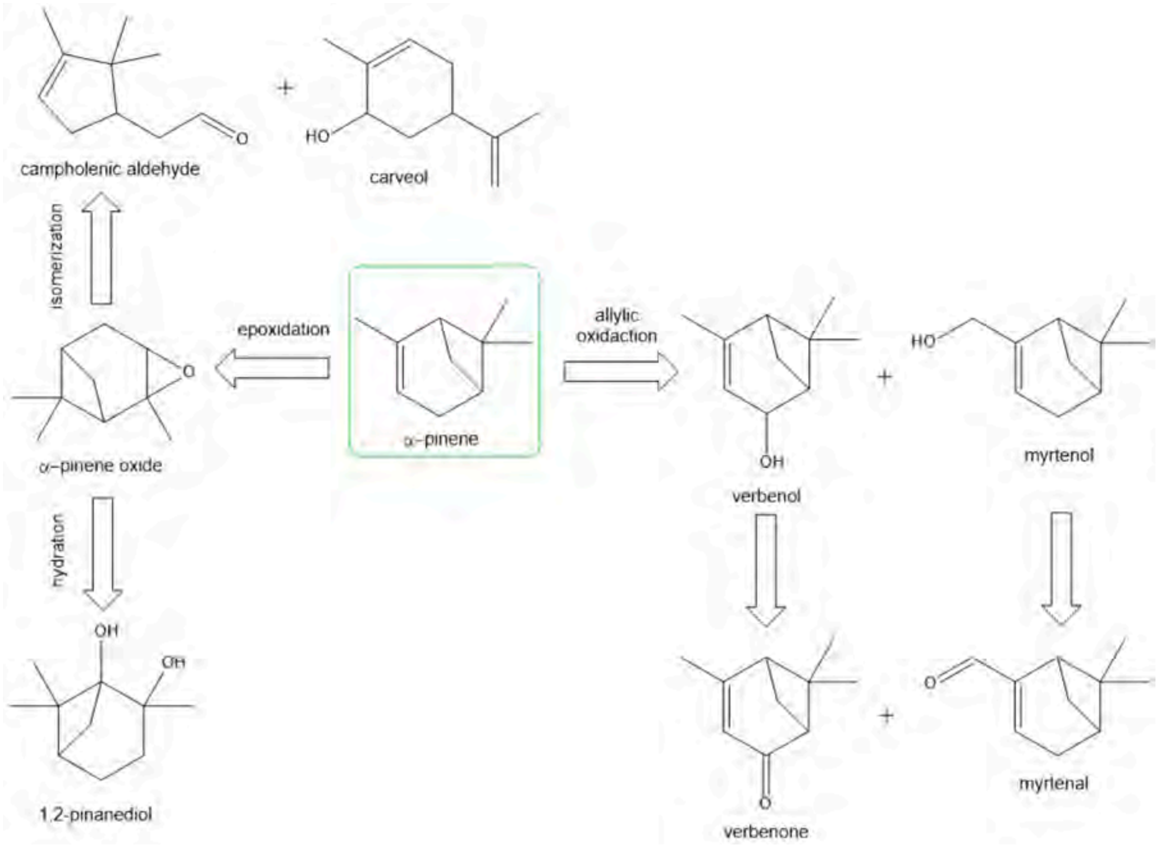

Fig. 9 – The main products that were formed during the oxidation of α-pinene with oxygen on the tested ZSM-5 catalysts.

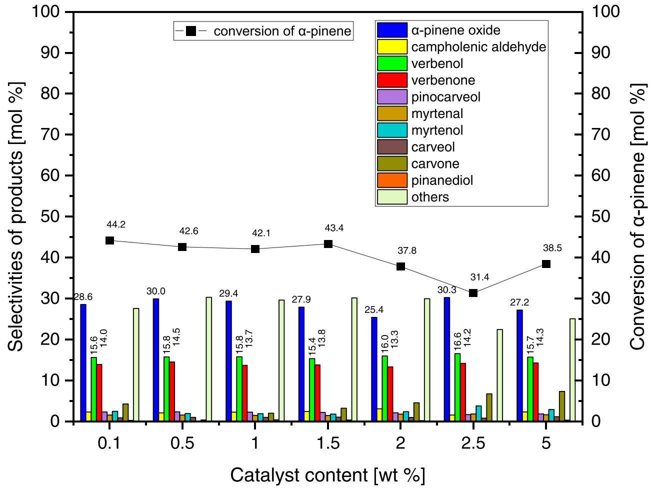

Fig. 11 – Effect of ZSM-5_1 catalyst content on product selectivities and α-pinene conversion (Al content in catalyst 2.5 wt%, temperature 90 °C, and reaction time 6 h).

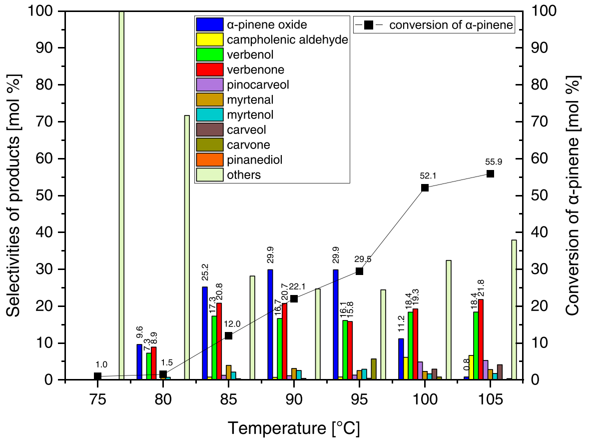

Fig. 13 – Effect of temperature on product selectivities and α-pinene conversion for ZSM-5_2 (Al content in catalyst 0.59 wt%, reaction time 6 h, and catalyst amount in reaction mixture 0.5 wt%).

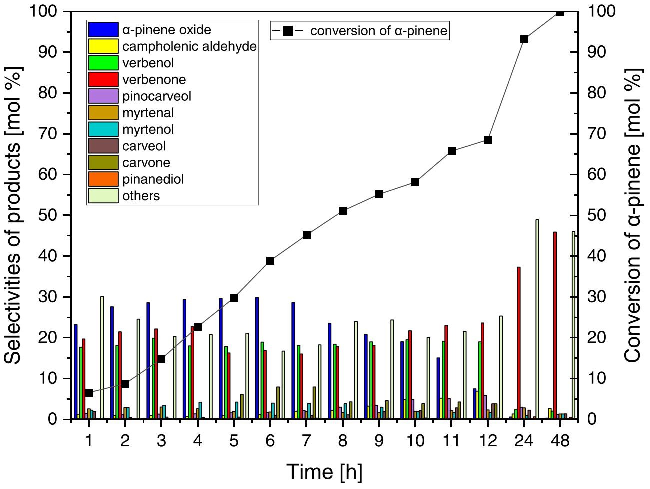

Fig. 12 – Effect of reaction time on product selectivities and α-pinene conversion for ZSM-5_1 (Al content in catalyst 2.5 wt%, temperature 90 °C, and catalyst amount 0.5 wt%).

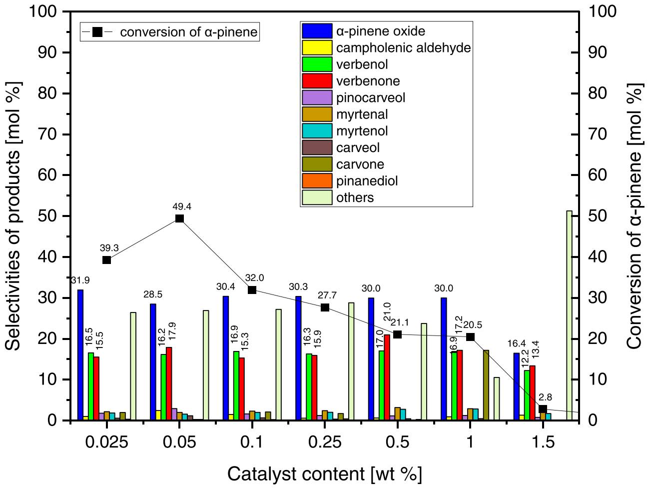

Fig. 14 – Effect of ZSM-5_2 catalyst content on product selectivities and α-pinene conversion (Al content in catalyst 0.59 wt%, temperature 95 °C, and reaction time 6 h).

conversion of α-pinene increases to 56 mol% (temperature 105 °C). This value of conversion obtained during the tests on the influence of temperature is about 5 mol% higher than the value for the ZSM_1 catalyst. The selectivity of epoxide compound increases from 0 mol% (temperature 75 °C) to 30 mol% (temperature 95 °C), and then lowers to 0.8 mol% (temperature 105 °C). This reduction in the selectivity of α-pinene oxide at higher temperatures is much more noticeable for the ZSM-5_2 catalyst than for ZSM-5_1. In the range of temperatures of 75–80 °C, the selectivity of verbenol is low, and ranges from 0 to 7 mol%. For the ZSM-5_1 catalyst at these two temperatures, the selectivity of this compound amounted to about 16 mol%. It shows that this catalyst was more active at lower temperatures in formation of verbenol. In the temperatures of 85–105 °C, the value of selectivity of transformation is about 16–18 mol%; this value is similar to that obtained on the ZSM-5_1 catalyst. The selectivity of verbenone, as it was for verbenol, is low in the temperatures of 75–80 °C (0–9 mol%), and in the range of 85–105 °C the values of selectivity of verbenol is higher (16–22 mol%). Based on the conversion of organic raw material (α-pinene) and the selectivity of epoxide compound, it was found that the reaction is most favorably performed at the temperature of 95 °C.

The results of the tests on the effect of the content of the ZSM-5_2 catalyst on the conversion of α-pinene and the selectivities of the appropriate products are shown in Fig. 14. The tested range of the amount of ZSM-5_2 catalyst was 0.025–1.5 wt%. We extended the tested catalyst contents in the lower range to see if this would not allow for higher α-pinene conversions. The reaction was conducted at 95 °C for 6 h.

A twofold increase in catalyst content from 0.025 to 0.05 wt% increases the conversion of α-pinene by 10 mol% (from 39 to 49 mol%). However, increasing in the catalyst amount in the range of 0.1–1.5 wt% decreases α-pinene conversion from 32 to 3 mol%. The selectivity of epoxide compound remains at the level of 29–32 mol% for catalyst contents of 0.025–1 wt%. The lowest value of the selectivity of α-pinene oxide (16 mol%) was recorded for the catalyst content of 1.5 wt%. The value of this selectivity was about 10 mol % lower than for the ZSM_5_1 catalyst. The selectivity of

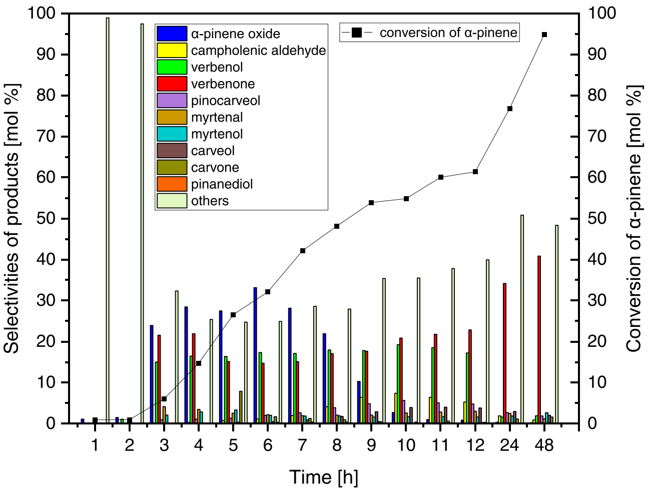

Fig. 15 – Effect of reaction time on product selectivities and α-pinene conversion for ZSM-5_2 (Al content in catalyst 0.59 wt%, temperature 95 °C, and catalyst content in reaction mixture 0.05 wt%).

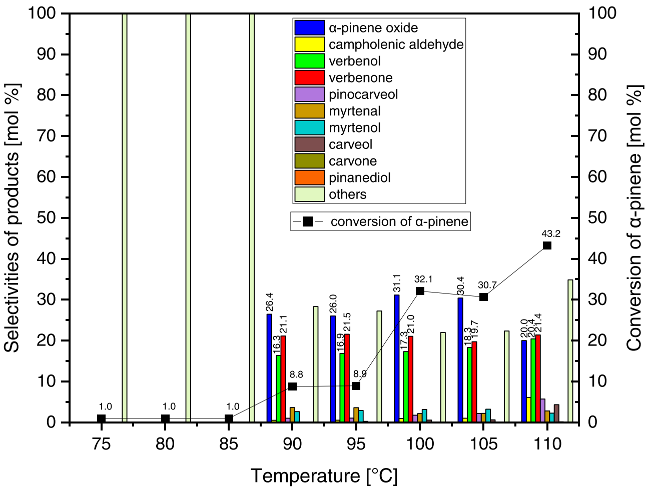

Fig. 16 – Effect of temperature on product selectivities and α-pinene conversion for ZSM-5_3 (Al content in catalyst 0.38 wt%, catalyst amount 2.5 wt%, and reaction time 6 h).

verbenol remains at the level of 12–17 mol% in the catalyst content range of 0.025–1 wt%; these values were very similar to ZSM-5_1. The selectivity of verbenone changes similarly to the function presented above and amounts to 13–21 mol% at the studied catalyst content. The most favorable amount of catalyst was considered to be 0.05 wt% -taking into account the conversion of α-pinene and the selectivity of t epoxide compound.

The next stage of catalytic testing of the ZSM-5_2 zeolite was to study the effect of reaction time on the conversion of organic raw material (α-pinene) and the selectivities of the appropriate products. These studies were conducted at 95 °C for a catalyst content of 0.05 wt%. The results of the study are shown in Fig. 15.

The analysis of the results for ZSM-5_2 material showed that the time of 1–2 h is too short to carry out the α-pinene oxidation process. It was not observed for the ZSM-5_1 catalyst, but the research on the influence of catalyst content was carried out for higher amounts of this catalyst (0.5 wt%). Generally, it is noticeable that the conversion of α-pinene is growing with increasing the reaction time. The maximum value of α-pinene conversion obtained for the time of the reaction of 48 h is about 5 mol% lower in comparison to the ZSM-5_1 catalyst. It can also be observed that when extending the time, the selectivity of epoxide compound increases and reaches the maximum value of 29 mol% after 6 h. After this reaction time, this function decreases to 0.2 mol% (48 h). For shorter reaction times (1 and 2 h), low selectivities of verbenol (0–1 mol%) were obtained. In the range of 3–12 h, the selectivity of verbenol is maintained at the level of 15–19 mol%. For 24 and 48 h, the selectivity of verbenol is 2 mol%. For shorter reaction times (1 and 2 h), the selectivity of verbenone is 0 mol%. Similarly, as for the ZSM-5_1 catalyst, in the range of 3–12 h reaction time, the selectivity of verbenone remains at the level of 15–23 mol%, and then increases to 41 mol% (reaction time of 48 h). On the basis the values of the selectivity of α-pinene oxide the reaction time of 6 h can be taken as the most beneficial; for this time, the selectivity of epoxide compound (α-pinene oxide) amounts to 29 mol%, verbenol 17 mol%, verbenone 15 mol%, and conversion of α-pinene is 32 mol%.

The last tested zeolite catalyst was ZSM-5_3 with the lowest aluminum content (0.38 wt%). The oxidation reaction of α-pinene on ZSM-5_3 was performed at 75–110 °C for 6 h, and the catalyst amount was 2.5 wt%. The results of the effect of temperature on product selectivity and α-pinene conversion for ZSM-5_3 catalyst are shown in Fig. 16.

The analysis of the results on the studies of the influence of temperature for the ZSM-5_3 catalyst shows that temperatures of 75–85 °C are too low to conduct the oxidation of α-pinene, as the conversion of this monoterpene is only 1 mol%. The selectivity of α-pinene oxide is kept at the level of 26–31 mol% in the temperature range of 90–105 °C, and falls to 20 mol% at 110 °C. In the case of this catalyst, therefore, a longer maintenance of the high selectivity of the epoxide compound is evident during the temperature increase, even up to 105 °C, as compared with the two previous catalysts tested. The selectivity of verbenol is kept at the level of 16–20 mol% in the temperature range of 90–110 °C. Very similar changes were observed for the selectivity of verbenone. Based on the conversion of α-pinene and the selectivity of transformation to the epoxide compound, it was shown that the studied reaction is most favorably carried out at the temperature of 100 °C; for this temperature, the selectivity of epoxide compound (α-pinene oxide) amounts to 31 mol%, and for verbenol it achieved 17 mol%, for verbenone 21 mol%, and conversion of α-pinene is 32 mol%.

Studies on the effect of the amount of ZSM-5_3 catalyst on the selectivities of the main products and the conversion of organic raw material (α-pinene) were conducted in the range of 0.1–5 wt% catalyst content, at 100 °C and for 6 h. The achieved results are shown in Fig. 17.

It is observed that the tenfold increase in the catalyst amount from 0.1 to 1 wt% increases the conversion of α-pinene by 10 mol% (from 42 to 53 mol%), and simultaneously does not lead to significant changes in the selectivities of the main products. Increasing the catalyst content by 1 wt%, from 1.5 to 2.5 wt% has the following effects: (a) reduces the conversion of α-pinene by about 10 mol% (from 42 to 32 mol %); (b) increases the selectivity of epoxide compound by 11 mol% (from 20 to 31 mol%); (c) reduces the selectivity of verbenol by 2 mol% (from 19 to 17 mol%); and (d) increases the selectivity of verbenone by 4 mol% (from 17 to 21 mol%). A twofold increase in catalyst amount from 2.5 wt% to 5 wt%

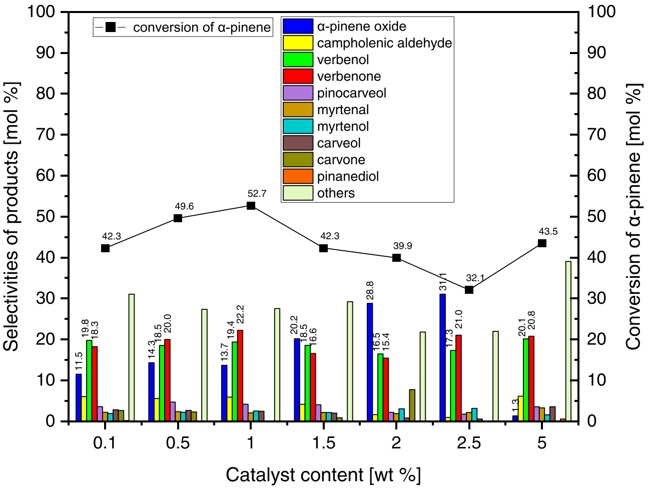

Fig. 17 – Effect of ZSM-5_3 catalyst content on product selectivity and α-pinene conversion (Al content in catalyst 0.38 wt%, temperature 100 °C, and reaction time 6 h).

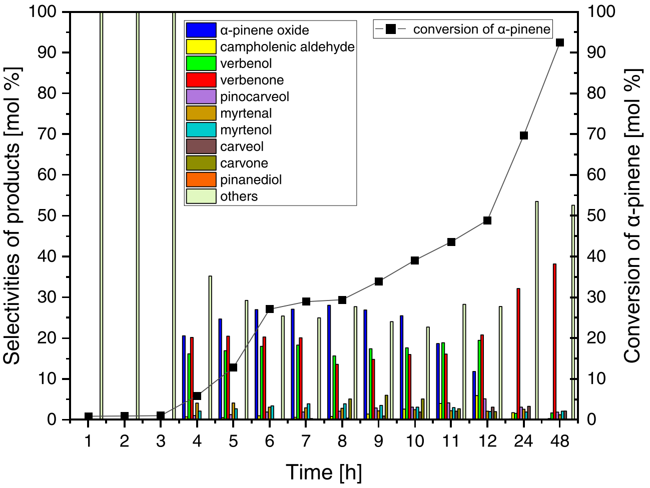

Fig. 18 – Effect of reaction time on product selectivities and α-pinene conversion for ZSM-5_3 (Al content in catalyst 0.38 wt%, temperature 100 °C, and catalyst content 2 wt%).

has these effects: (a) increases the conversion of α-pinene by 10 mol% (from 32 to 42 mol%), while (b) significantly reducing the selectivity of epoxide compound by 30 mol% (from 31 to 1 mol%); (c) increases the selectivity of verbenol by 3 mol% (from 17 to 20 wt% mol); and (d) causes no change in the selectivity of verbenone. On the basis of the results obtained, the most favorable catalyst amount was considered to be 2 wt%; for this catalyst amount, the selectivity of α-pinene oxide (epoxide compound) amounts to 29 mol%, verbenol 16 mol%, verbenone 1 mol%, and conversion of α-pinene is 40 mol%.

Fig. 18 shows the results of the research on the effect of reaction time on product selectivities and α-pinene conversion for ZSM-5_3. The studies were conducted at 100 °C, in the range of 1–48 h, and for the catalyst amount of 2 wt%.

It is noticeable that the longer the time of reaction, the higher the conversion of α-pinene. The maximum value of conversion of α-pinene (92 mol%) is slightly lower than the maximum value of conversion for all previous studied ZSM-5 catalysts. Based on the study of the effect of time, it was shown that a time of 1–3 h is too short to carry out the oxidation of α-pinene, since the conversion of α-pinene is only 1 mol%. The selectivity of epoxide in the time of 4–8 h increases from 21 to 28 mol%, and then falls to 0 mol% (reaction time of 48 h). The selectivity of verbenol remains at the level of 16–19 mol% for the reaction time of 4–12 h, and then falls to 2 mol% (reaction time 48 h). For reaction time from 4 to 12 h the selectivity of verbenone changes from 14 to 20 mol%, and for longer reaction times (24 and 48 h), the selectivity of verbenone is much higher, ranging from 32 to 38 mol%. It is observed that this value is lower than that obtained for all previous studied ZSM-5 catalysts (the difference amounts to about 8 mol%). The most favorable time established for the zeolite ZSM-5_3 is 8 h; the selectivity of epoxide compound (α-pinene oxide) amounts to 28 mol%, verbenol 16 mol%, verbenone 14 mol%, and conversion of α-pinene is 29 mol%.

Table 3 summarizes the values of selectivities of α-pinene oxide, verbenol, verbenone and the conversion of α-pinene for the most favorable conditions obtained for the three tested ZSM-5 catalysts.

Zeolite ZSM-5_2 with the aluminum content of 0.59 wt% proved to be the most active in the process of oxidation of α-pinene. It is used in the amount 0.05 wt% in the reaction mixture. This amount is 10 times lower than that of the ZSM-5_1 catalyst and 40 times lower than that of the ZSM-5_3 catalyst. Moreover, despite such a small amount of the ZSM-5_2 material used, the time required to achieve α-pinene conversion of 32 mol% is shorter by 2 h than the most favorable time determined for the ZSM-5_3 catalyst, and by 1 h from the time determined for ZSM-5_1. With the ZSM-5_1 catalyst, after 7 h, conversion of α-pinene amounted to 45 mol%.

The tests presented in Table 2 on the textural properties of the three tested ZSM-5 catalysts confirm the results of catalytic tests, because it is the ZSM-5_2 catalyst that has the largest specific surface.

4. Conclusions

The studies on the catalytic activities of three ZSM-5 zeolites with different aluminum contents show that these porous materials are active catalysts in the green oxidation of

Table 3 – Values of selectivities of α-pinene oxide, verbenol, verbenone, and conversion of α-pinene for the most favorable conditions of conducting the oxidation of α-pinene on ZSM-5 catalysts.

ZSM-5	Al [wt%]	The most favorable conditions	Selectivities of the main products [mol%]			Conversion of α-pinene [mol%]
			α-pinene oxide	verbenol	verbenone	
ZSM-5_1	2.50	90 °C, 0.5 wt%, 7 h	29	18	16	45
ZSM-5_2	**0.59**	**(95 °C, 0,05 wt%, 6 h)**	**28**	**16**	**18**	**49**
ZSM-5_3	0.38	(100 °C, 2 wt%, 8 h)	28	16	14	29

terpene compound (α-pinene) with oxygen without any solvent. The most active was the ZSM-5_2 catalyst with 0.59 wt % of Al in the structure. This catalyst has the largest specific surface area of all the studied catalysts. The most favorable temperatures and reaction times were determined for the catalysts. The most favorable temperatures varied from 90 °C for ZSM-5_1 to 100 °C for ZSM-5_3. These relatively low temperatures ensure that the oxidation process was carried out under mild conditions. For the tested catalysts, the most favorable reaction times changed from 6 h for the ZSM-5_2 catalyst to 8 h for the ZSM-5_3. On the other hand, the ZSM-5_2 showed the greatest activity, considering its required amount to be used in the process, which was only 0.05 wt%.

It can therefore be surmised that the use of ZSM-5 catalysts allows for effective transformation of α-pinene, a natural raw material, into high value-added products, α-pinene oxide, verbenol or verbenone. However, considerably longer reaction times are required for the latter compound. The oxidation of α-pinene on the ZSM-5 catalysts using oxygen as the oxidant is one of environmentally friendly process, which may be used in the future to oxidize turpentine, the main component of which is α-pinene. Compared to the previously used methods of turpentine oxidation, e.g. with the use of an aqueous solution of hydrogen peroxide (Fomenko et al., 2021), which required the additional use of a solvent (e.g. acetonitrile), the technology we propose is simple and allows the oxidation of α-pinene and other main components of turpentine (α-pinene, 3-carene) without separating them. In addition, the separation of the post-reaction mixture after the oxidation process is much simpler, because the post-reaction mixture does not contain the solvent, but only unreacted substrates and oxidation products. Due to the fact that the oxidizing agent is not the aqueous solution of hydrogen peroxide, but oxygen, we also do not have a second phase in the mixture in the form of a water layer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Carbon catalysts from pine cones – Synthesis and testing of their activities

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Verbenone

ABSTRACT

The work presents research on the synthesis of carbon catalysts from pine cones and their application in the oxidation of α-pinene. The preparation of carbon catalysts involved chemical activation with an aqueous potassium hydroxide solution and carbonization of the obtained precursor. The pine cones carbonization was performed for 1 h at the temperatures range from 700° to 1000°C in an inert gas atmosphere (N_2). Characterizations of the activated carbons were performed with the following instrumental analyses: XRD, SEM, and XPS. No solvent was used in the oxidation studies, and molecular oxygen was the oxidizing agent. The effects of three parameters – temperature, amount of the carbon catalyst, and reaction time – on the values of conversion of α-pinene, as well as the product selectivities, were investigated. It was shown that it is most advantageous to perform the oxidation of α-pinene at 100 °C for 1 h with the PC_850 catalyst (so-named for the temperature of its carbonization process, 850 °C), whose content in the reaction mixture is 0.5 wt%. Under these conditions, the conversion of α-pinene amounted to 41 mol%. Moreover, the selectivities of the three main products were: α-pinene oxide (28 mol%), verbenol (16 mol%), and verbenone (13 mol%). In addition to these products, other valuable compounds, such as campholenic aldehyde, pinocarveol, myrtenal, myrtenol, carveol, carvone, and pinanediol were also produced.

1. Introduction

Intensive studies are being conducted worldwide into the conversion of biomass to useful products, such as activated carbons. Biomass is very often a waste from agriculture and the food industry and must be disposed of in various ways. In this study, pine cones were used as a natural source for the synthesis of activated carbons. Pine cones are easily available and quite common in many countries, but have not been widely used so far. The possibility of using pine cones in the production of activated carbons is very advantageous from an ecological and economic point of view, and represents a new approach of utilizing them.

Until now, research has been performed with the preparation of activated carbons from pine cones with different activation agents, e.g., $ZnCl_2$ [1–3], H_3PO_4 [4–7], KOH [8,9], and NaOH [10,11]. An article published in 2013 by Jamalzadeh et al. [1] describes the method of preparation of activated carbon from pine cones using $ZnCl_2$ as the activator. The process of obtaining the activated carbon from pine cones consisted of two steps: chemical activation with a $ZnCl_2$ solution and carbonization of the precursor. Prior to the activation step, the pine cones were cut into small pieces, washed and air-dried for the duration of a day. After drying, the pine cones were mixed with a $ZnCl_2$ solution and heated to obtain a pulp consistency. Then, the mixture was dried at 100 °C for 6 h. The pine cones carbonization was performed for 1 h at 500 °C in an inert gas atmosphere (N_2). Next, the activated carbon was washed with an aqueous H_3PO_4 solution (10 wt%) at 60 °C for 1 h. Subsequently, the obtained carbon was washed with distilled water and then dried at 110 °C for 6 h. The synthesized carbon material was characterized by a specific surface area of 2242 m^2/g. This activated carbon combined with zeolite was used as catalyst support in a Pd/carbon-zeolite nanocatalyst for the total oxidation of xylene at low temperatures.

Momčilović et al. [5] presented the method of preparation of activated carbon from pine cones using H_3PO_4 as the activator. Ground pine cones were mixed with 85 wt% aqueous H_3PO_4 in the weight ratio of 1:3. Afterwards, the material was placed in a muffle furnace and heated in two stages in the inert gas atmosphere (N_2). In the first step, the

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mixture was heated at the rate of 6 °C/min up to 170 °C, and maintained at this temperature for 60 min. In the next stage, the mixture was heated at the rate of 8 °C/min up to 500 °C, and then maintained at this temperature for an additional 60 min. Afterwards, the sample was cooled to room temperature and then washed with hot distilled water. The final stage of the production of the carbon catalyst was drying the material in the oven at 110 °C for 24 h. The activated carbon was obtained with the yield of 55.7%, and its specific surface area was 1094 m^2/g. The catalytic material was mesoporous and had a significant amount of oxygen functional groups on the surface. Activated carbon obtained from pine cones was used as an adsorbent for the removal of lead(II) ions from aqueous solutions, as this material has good sorptive capacity towards these ions.

Gomez-Delgado et al. [8] described the method for obtaining activated carbon from *Pinus canariensis* cones (Buenos Aires, Argentina) using KOH as the activator. These pine cones were washed with water, sun-dried, ground and screen-sieved. They were then carbonized for 1 h at 500 °C in a nitrogen atmosphere. Afterwards, the carbonized product was cooled to room temperature in the inert atmosphere followed by impregnation with KOH. The mass ratios of KOH/carbonized precursor were, respectively, 1, 2, and 3. The material was dried in the oven at 80 °C for 24 h, and then the activated carbon was thermally treated. This process was performed in the nitrogen atmosphere and consisted of two steps. Firstly, the temperature was increased from room temperature to 300 °C (at 10 °C/min) and maintained for 1 h. Then, each sample was heated to different final temperatures: 600, 700, and 800 °C, and the final temperature was kept for 2 h. Finally, the samples were cooled to room temperature in the nitrogen atmosphere. The activated carbon was washed with a 0.1 M aqueous solution of HCl and then with distilled water. Finally, the material was dried in the oven at 110 °C. The yields of the activated carbons were between 15% and 22%, and their specific surface areas ranged from 395 to 2202 m^2/g. The activated carbons obtained from pine cones were used in the CO_2 adsorption process.

The various applications of the activated carbons produced from pine cones have been described. These materials were mostly applied as adsorbents for the following cations, anions, and dyes from the liquid phase: Pb [5], Cr [3], Zn [12], Cu [11], F [13], nitrate [14], acid black and acid blue [15], methylene blue [7], and also pharmaceuticals [16]. Some applications as gas sorbents were also described – CO_2 adsorption [9,17], CH_4 [6] – and also as the electrode material for supercapacitors [18–20].

The oxidation of α-pinene using various catalysts is of interest to many researchers. α-Pinene is a very valuable compound of natural origin (biologically active, organic compound). The main, valuable source of this compound is turpentine, which is obtained by the steam distillation of resin collected from cut pine trees (balsamic turpentine) and extraction with gasoline of pine stump (extraction turpentine). α-Pinene is therefore a renewable compound with high availability [21]. Other natural sources of α-pinene are essential oils extracted from various plants [22]. Due to its bicyclic structure and the presence of a double bond (Fig. 1), α-pinene is readily used in a number of different chemical reactions, especially oxidation.

Currently, the oxidation of α-pinene is performed in the presence of various catalysts, including titanium-silicate catalysts, such as TS-1 [21, 23], Ti-MCM-41 [24–27], and modified carbon catalysts obtained from biomass, for example from orange peels [28]. The main products that are formed during α-pinene oxidation are typically α-pinene oxide, and also verbenol, and verbenone. Moreover, the oxidation process enables formation of campholenic aldehyde and trans-pinocarveol, and also myrtenal, myrtenol, L-carveol, carvone, and 1,2-pinanediol. The main oxygen derivatives of pinene are value-added compounds used in food, cosmetics, perfume, and medicine. They are mainly used as flavor and fragrance additives in food, beverages, perfumes, and cosmetics [21].

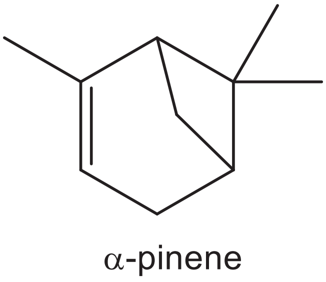

Fig. 1. α-Pinene.

The main aim of this work was to synthesize activated carbons from pine cones, characterize these materials using the selected instrumental methods, and test the catalytic activities of these activated carbons in the process of α-pinene oxidation with oxygen, and without using a solvent. The preparation of carbon catalysts involved chemical activation with an aqueous potassium hydroxide solution and carbonization of the raw material at the temperature range from 700° to 1000°C for 1 h in the inert gas atmosphere (N_2).

Characterizations of the seven synthesized carbon catalysts were performed by the following methods: N_2 sorption measurements at 77 K, XRD, SEM, and XPS. The studies testing the catalytic activities of the catalysts relied on qualitative and quantitative determinations of the transformation products of α-pinene during its oxidation process and establishing the most advantageous parameters of this process. The conditions studies were temperature, catalyst content, and reaction time. Considering the numerous applications of activated carbons from pine cones it was found that these materials have never been applied as catalysts. According to our knowledge, the use of pine cones as a starting material for the catalyst production without any other promoters was not described up to now.

2. Materials and methods

2.1. Raw materials

The raw materials used for the preparation of activated carbons were pine cones (Tanowo, Poland). A saturated solution of KOH (Sigma-Aldrich, Burlington, MA, USA) was applied for the chemical activation of this biomass (raw material). Potassium hydroxide was removed by washing of the sample with deionized water and a 1 M aqueous solution of HCl (Sigma-Aldrich, Burlington, MA, USA).

The oxidation of α-pinene (98%, Sigma Aldrich) was performed with the synthesized carbon catalysts and oxygen as the oxidizing agent (99.99%, Messer). The following compounds were used as standards for identifying the products in the gas chromatography method: α-pinene oxide (97%, Sigma Aldrich), trans-pinocarveol (≥96%, Sigma Aldrich), verbenol (95%, Sigma Aldrich), verbenone (≥93%, Sigma Aldrich), carveol (≥95%, Sigma Aldrich), carvone (98%, Sigma Aldrich), myrtenal (98%, Sigma Aldrich), myrtenol (95%, Sigma Aldrich), and pinanediol (99%, Sigma Aldrich). One of the products, campholenic aldehyde, was identified with help of the GC-MS method.

2.2. Preparation of the carbon catalysts from pine cones

The first step in the method of synthesis of activated carbons from pine cones was drying the raw material at 60 °C for 192 h and then cutting it into small pieces and grinding them. The method of catalyst synthesis relied on mixing ground cones with the saturated solution of KOH until a homogeneous mass was obtained and leaving the mixture for 3 h at room temperature (the weight ratio of biomass to activator was 1:1). The next step in this method was drying this mixture in the oven at 200 °C for 19 h, followed by placing the dried material in the quartz boat and in the oven. The pine cones carbonization was performed in horizontal, tubular oven of diameter equal to 116 mm for 1 h at the temperature range from 700° to 1000°C in the inert gas atmosphere. Nitrogen flow was equal to 18 dm^3/h. After the carbonization, the carbon samples were cooled to room temperature in the nitrogen atmosphere. The activated carbons containing the products of KOH decomposition were washed with distilled water until the pH was neutral. After evaporation of the excess solution, the materials were treated with a 1 mol/dm^3 aqueous solution of HCl and left for 19 h at room temperature. In order to completely eliminate the chloride ions, the carbon catalysts were washed with distilled water until they were neutral.

The final stage of the preparation of the catalysts was drying the materials in the oven at 200 °C for 19 h. In this way, seven activated carbons were obtained and named as follows: PC_700, PC_750, PC_800, PC_850, PC_900, PC_950, and PC_1000, where the numbers in the label indicate the carbonization temperature. The resulting carbon materials were used in the catalytic studies on the oxidation of α-pinene with oxygen. Fig. 2 shows the simplified block diagram for obtaining carbon catalysts from pine cones.

2.3. Characteristics of the carbon catalysts from pine cones

The textural parameters of the carbon catalysts were determined using the nitrogen sorption instrument, QUADRASORB evo Gas Sorption Surface Area and Pore Size Analyzer. The specific surface areas (S_{BET}) were calculated on the basis of the Brunauer–Emmett–Teller equation. The total pore volume (V_{tot}) was found on the basis of nitrogen adsorbed at $p/p_0 \approx 1$. The DFT method was applied to find the pore size distribution and the volume of micropores. Before the N_2 adsorption measurements, the activated carbons were dried at 250 °C for 20 h.

The Empyrean PANalytical X-ray diffractometer equipped with a copper lamp (Cu-Kα, $\lambda = 1.54056$ Å) was applied at ambient temperature for XRD analysis. The data were taken for the 2θ range of 10–70° with a step of 0.026°. The phases were identified on the basis of JCPDS cards.

The SEM pictures were taken utilizing Hitachi SU8020 ultra-high resolution field emission scanning electron microscope (UHR FE-SEM). Carbon catalysts from pine cones were placed on the carbon tape and placed over the surface of the SEM stub.

The XPS (X-ray Photoelectron Spectroscopy) characterization was performed with the ultra-high vacuum system (PREVAC, Rogów, Poland, 2007). The base pressure prior to the measurements was in the low 10^{-10} mbar range. The kinetic energy of the photoelectrons was measured with hemispherical energy analyzer (SES-2002, Scienta Scientific AB, Uppsala, Sweden, 2002). The Ag 3d5/2 transition was used for spectrometer calibration. Pulverized samples were degassed for several hours prior to measurement in order to achieve low 10^{-9} mbar range vacuum during the XPS measurements. The Mg Kα ($h\nu = 1253.7$ eV) nonmonochromatic radiation was used. The charge corrections were corrected with the use of the C 1 s signal at 284.6 eV. The spectra were evaluated with the use of CasaXPS software (V2.3.15 CASA Software Ltd., UK).

2.4. Oxidation of α-Pinene

The catalytic tests were performed with the use of a glass reactor (capacity of 25 cm^3) with an installed reflux condenser. During the oxidation process we also used a magnetic stirrer, and a glass sparger for supplying oxygen. In tests involving the influence of temperature and catalyst content 10 g of α-pinene was used, and 20 g in tests involving the influence of time. These quantities and the appropriate amounts of the catalyst (0.1–1.5 wt%) were placed in the reactor. The reaction was performed at temperatures from 80° to 140°C, for times from 1 to 24 h. During studies on the influence of the reaction time 1 cm^3 samples of the reaction mixture were removed after reaction times of 1, 2, 3, 4, 5, 6, and 24 h, respectively, with an oxygen flow rate of 40 mL/min and at a stirring speed of 500 rpm. The post-reaction solution was separated from the carbon catalyst with a centrifuge. For each of the syntheses, a mass balance was calculated. On the basis of these balances, such functions as conversion of α-pinene and selectivities of products were established. The conversion of α-pinene and selectivities of the appropriate products were calculated according to the following formulas:

- **Conversion of α-pinene** = (number of moles of reacted α-pinene / number of moles of α-pinene introduced into the reactor) * 100%

- **Appropriate product selectivity** = (number of moles of product / number of moles of reacted α-pinene) * 100%

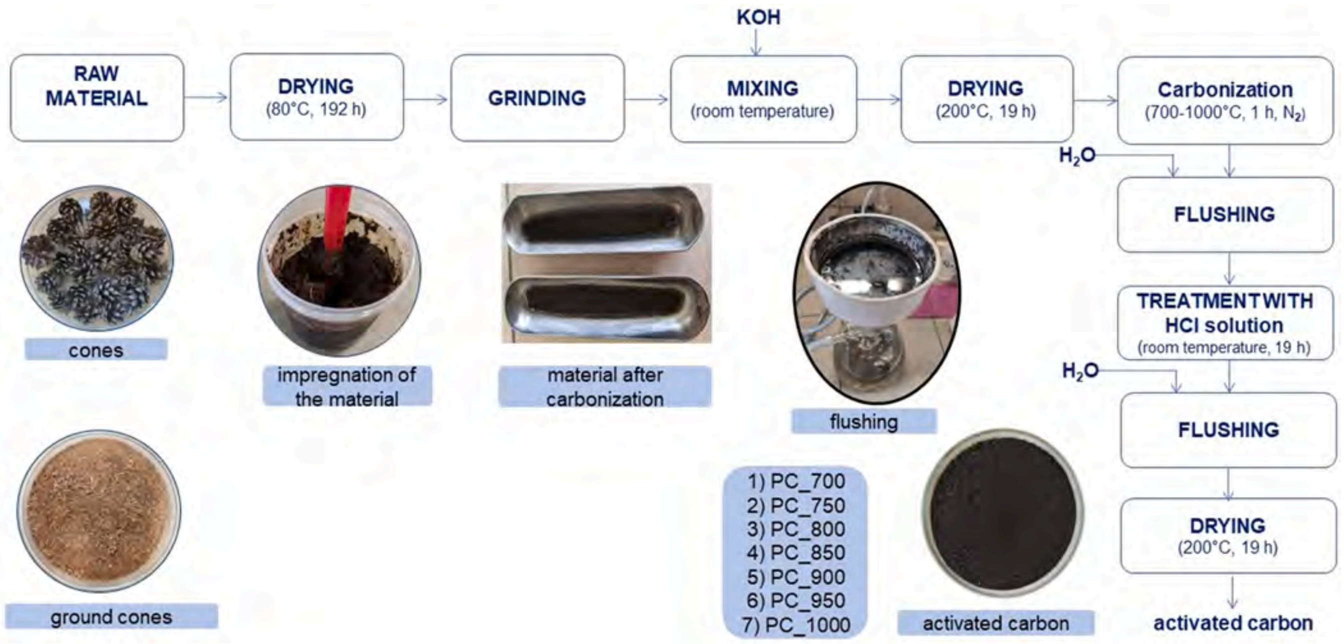

Fig. 2. Simplified block diagram for preparing carbon catalysts from pine cones.

2.5. *Identification of the products of oxidation by the gas chromatography method*

Qualitative and quantitative analyses of the post-reaction solutions were conducted by means of gas chromatography using a Thermo Electron FOCUS apparatus with a ZB-1701 column (dimensions: 30 m × 0.53 mm × 1 µm, column filling: 14% cyanopropylphenyl, and 86% dimethylpolysiloxane; supplier: Anchem, Warszawa, Poland, 2009) equipped with a flame ionization detector (FID). The temperature program for sample analyses consisted of the following steps: first stage: isothermally at 50 °C for 2 min, temperature increase at 6 °C/min to 120 °C; second stage: isothermally at 120 °C for 4 min, then a temperature increase of 15 °C/min up to 240 °C. Values for the other main parameters were: the temperature of the dispenser 200 °C, and the carrier gas flow rate 1.2 mL/min. The method of the internal normalization (the error of 1%) was used for the quantitative analyses of the post-reaction solutions.

Qualitative analyses were conducted by the GC-MS method using ThermoQuest apparatus. This apparatus was equipped with a Voyager detector and a DB-5 column (column filling: phenyl-methylsiloxanes, dimensions: 30 m x 0.25 mm×0.5 µm). Parameters of analyses: helium flow rate 1 mL/min, detector temperature 250 °C, and sample chamber temperature 200 °C. The temperature program for sample analyses was: isothermally for 2.5 min at 50 °C, followed by an increase at a rate of 10 °C/min up to the temperature of 300 °C.

Before the chromatographic analyses, the post-reaction solutions were separated from the catalyst using centrifugation and next diluted in acetone (0.750 mL of acetone was added to 0.250 mL of the solution).

3. Results and discussion

3.1. *The yield of the carbon production from pine cones*

Table 1 presents the yield of the carbon production from pine cones. The increase of the carbonization temperature reduced the carbon yield. At the lowest temperatures, the yield decreased from about 36–27%, and at the highest the yield decreased to13.93%. The reason for the decrease in the mass listed in Table 1 was not only the carbonization process but also some loss of carbon during washing the material in order to remove sodium compounds. It should be assumed that the losses during washing were similar for each material, and were independent of the temperature of carbonization.

3.2. *Characteristics of the carbon catalysts from pine cones*

The N_2 sorption isotherms are presented in Fig. 3.

The isotherms of the activated carbons obtained from pine cones represented a type I isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification [29]. A steep uptake at very low p/p_0 is characteristic for microporous materials with mainly narrow micropores and is a result of enhanced adsorbent-adsorbate interactions. The sorption isotherms of activated carbons produced at temperatures 950 and 1000 °C displayed a mixture of types I and IV isotherms. For PC_950 a narrow hysteresis loop type H4 was observed from 0.4 p/p_0. For PC_1000 the hysteresis loop type H4 was considerably wider; the hysteresis indicated the presence of mesopores.

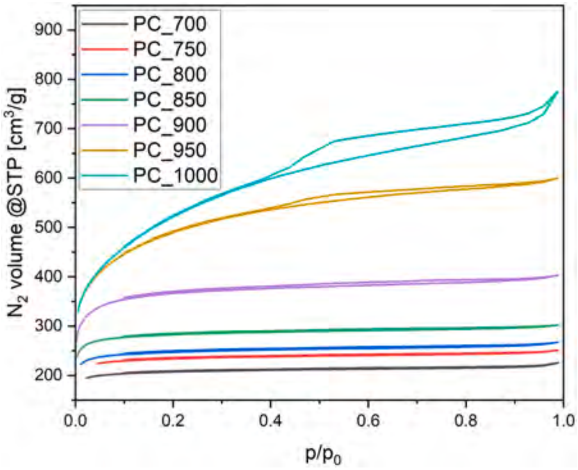

Fig. 3. N_2 sorption isotherms at 77 K.

The specific surface area (S_{BET}), total pore volume (V_{tot}), micropore volume (V_{mic}) and percentage of microporous volume (%V_{mic}) are listed in Table 2. All the textural parameters increased with increasing temperature of the synthesis except the micropore volume of PC_1000. The values from Table 2 confirmed the conclusions drawn on the basis of Fig. 3. The activated carbons produced at lower temperatures were microporous (78 – 88% micropores). The materials obtained at temperatures of 950 and 1000 °C were micro-mesoporous (about 50% micropores). Detailed pore size distribution is presented in Fig. 4 (the red bars represent the micropores and the blue bars represent the mesopores).

The graphitic structure and the purity of carbon materials were investigated by the XRD technique (Fig. 5). The sodium compounds residues were not found in all materials. Two wide peaks located at about 16–29° and 39–48° 2θ were found. These peaks correspond to the (002) plane and (100/101) of the graphitic structure. The wide peaks showed a disordered structure of carbon materials. It was stated that the carbons produced at the lower (700 and 750 °C) and the higher (1000 °C) temperatures showed the peaks with relatively narrower intensities. Similar results were described by Serafin et al. [30]. This could be ascribed to the higher crystallinity of these materials.

The SEM pictures of the carbon catalysts obtained from pine cones are shown in Fig. 6. The SEM images show the morphology of the carbon materials, which featured a well-developed porous structure. Structures with quite regular shapes and multiple macropores with a developed inner surface area were observed.

The XPS method relies on electrons originating from a depth of about 1 nm. Therefore, this method is extremely surface sensitive and vital for heterogeneous catalysis applications. The method enables elemental content measurements, but due to the chemical shift, the oxidation state and the type of chemical bonding can also be determined. All the samples were characterized with the XPS method by making the survey scan and detailed scan for the C1s signal. The survey scan enabled elemental content measurements. Only carbon and oxygen were detected while the

Table 1
The yield of the carbon production from pine cones.

Temperature [°C]	Carbon yield [%]
700	35.61
750	37.26
800	33.68
850	34.92
900	27.00
950	19.91
1000	13.93

Table 2
Textural properties of carbon materials obtained from pine cones.

Carbon catalysts	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	%V_{mic} (%)
PC_700	665	0.350	0.300	86
PC_750	801	0.389	0.341	88
PC_800	831	0.415	0.358	86
PC_850	937	0.469	0.410	87
PC_900	1225	0.625	0.488	78
PC_950	1665	0.930	0.513	55
PC_1000	1761	1.023	0.452	44

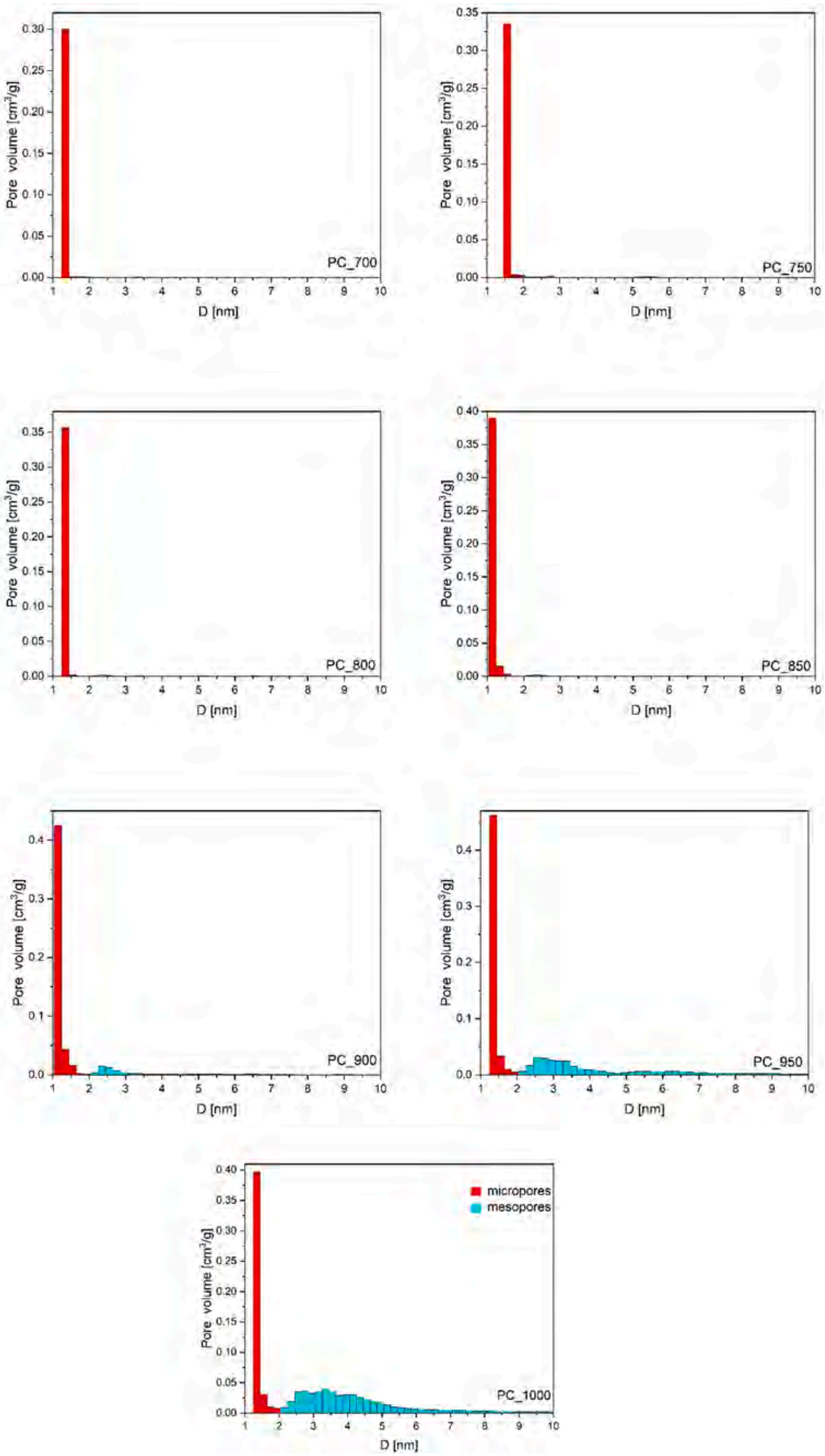

Fig. 4. Pore distribution histograms.

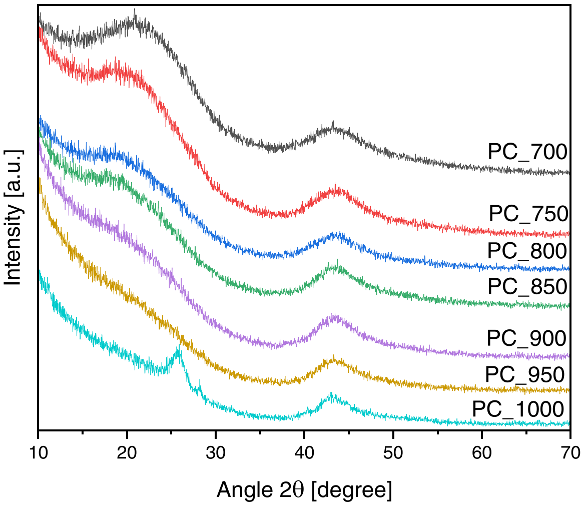

Fig. 5. XRD patterns of the carbon catalysts from pine cones.

other elements signals were below the detection limit. An example of a survey scan is presented in Fig. 7(a). Except for the XPS signals (O1s, C1s) there are visible Auger electron transitions (C KLL, O KLL).

The analysis of survey spectra enabled surface elemental content measurements presented in Table 3. The content of oxygen decreases with the increase in temperature. However, a significant decrease is observed above 850 °C. Obviously one can expect that at higher temperatures decomposition of carbon-oxygen groups to gaseous products can occur.

The detailed analysis of the C1s signal (cf. Fig. 7b) enables analysis of carbon-oxygen functional groups. The carbon-oxygen bonding causes a shift of the carbon electrons towards the more electronegative oxygen, which results in the remaining C1s electrons exhibiting higher binding energy. The most pronounced effect can be observed for the COOH group where two oxygen atoms attract electrons from the carbon atom. The deconvolution method of the C1s signal is described elsewhere [31].

The concentrations of different oxygen groups over the sample surfaces are presented in Table 4. In general, the concentration of different oxygen groups decreases with temperature, as was observed in Table 3. However, the amount of C-O groups is the lowest for the PC_850 catalyst. On the other hand, the amount of keto-enolic groups is the highest for the same sample. For C═O and COOH groups one can observe the gradual decrease of quantity with increasing temperature. The satellite

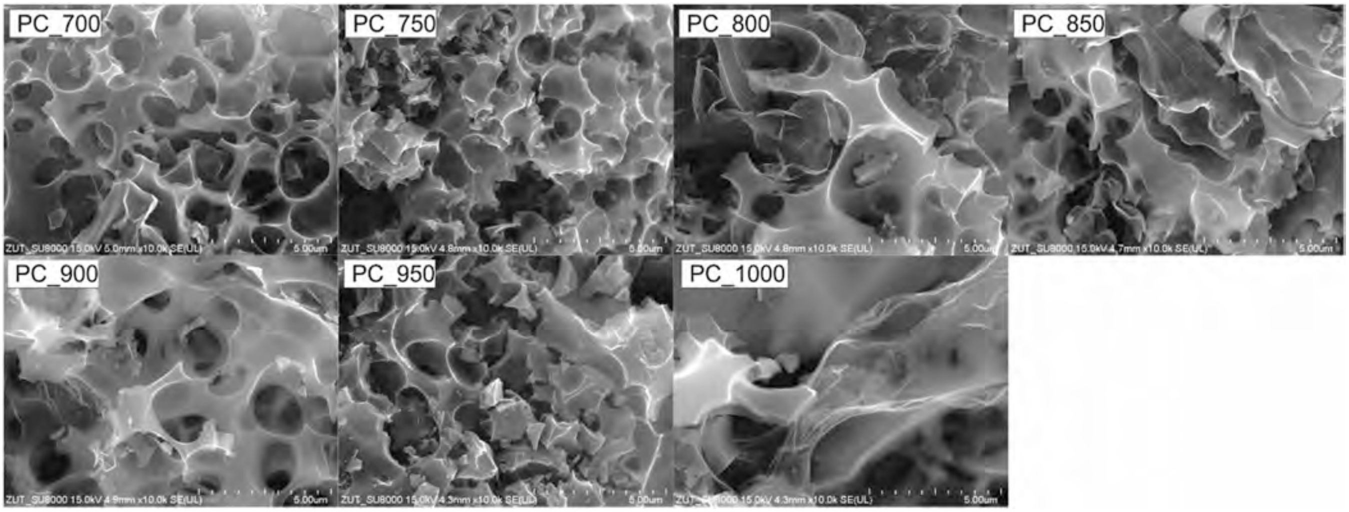

Fig. 6. SEM images of the carbon catalysts obtained from pine cones.

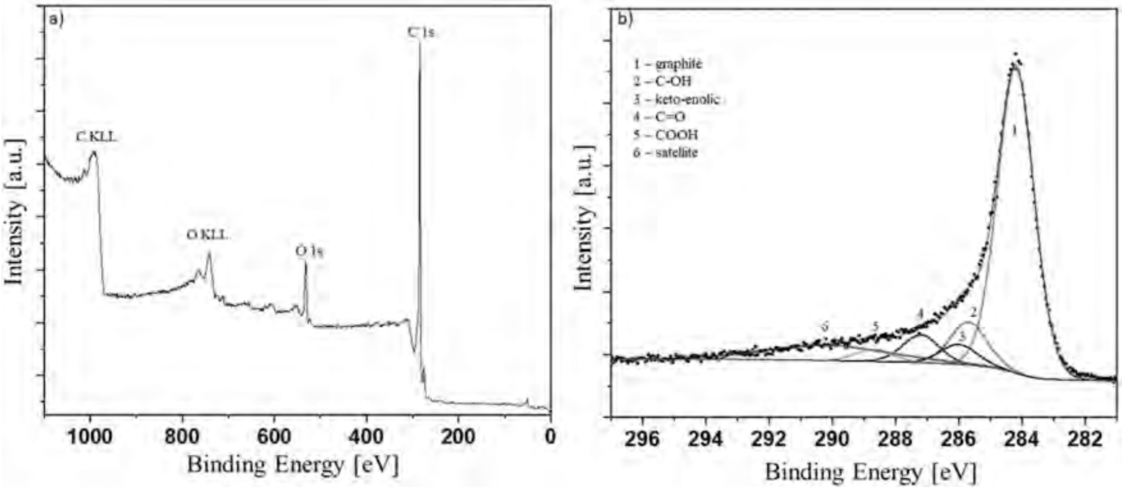

Fig. 7. X-ray photoelectron spectra for the PC_850 carbon catalyst: a) survey spectrum; b) deconvoluted C1s signal with attributed carbon-oxygen groups.

Table 3
The elemental content determined by the XPS method.

	PC_700	PC_750	PC_800	PC_850	PC_900	PC_950	PC_1000
C [at%]	91.4	92.7	92.8	92.7	95.5	94.8	96.4
O [at%]	8.6	7.3	7.2	7.3	4.5	5.2	3.6

Table 4
The content of oxygen components in the carbon signal.

	PC_700	PC_750	PC_800	PC_850	PC_900	PC_950	PC_1000
C	66.3	64.91	63.02	66.5	62.62	62.4	62.21
C–O	12.0	10.3	10.8	9.4	12.3	12.3	12.0
Keto-enolic	2.2	3.8	3.0	4.4	1.1	1.3	0.6
C=O	6.4	6.5	5.9	6.0	5.2	5.2	4.0
COOH	3.0	2.7	2.9	2.5	1.4	1.8	0.7
Satellite	10.1	11.9	14.4	11.2	17.4	17.0	20.5

signal is typical for delocalized electrons occupying graphitic rings. The observed increase of the satellite signal is associated with the decrease of oxygen content. The oxygen-carbon groups inhibit the delocalization of the electrons and thus the observed phenomenon is clear.

3.3. *Studies on the catalytic activities of the carbon catalysts from pine cones in the α-pinene oxidation process*

The catalytic activities of the seven activated carbons were investigated in the oxidation with oxygen of α-pinene, a terpene compound. First, temperature influence tests on the conversion of α-pinene and the selectivities of the correct products were performed (the temperature was changed from 80° to 140°C). Next, the catalyst content influence tests (in the range 0.1–1.5 wt%) and reaction times (from 1 to 24 h) were conducted.

The qualitative analyses performed with the GC and GC-MS methods showed that the main products of α-pinene transformations over the carbon catalysts prepared from pine cones (oxidation with oxygen as the oxidant) were: α-pinene oxide, verbenone and verbenol (Fig. 8). The by-products which were formed in smaller amounts were: campholenic aldehyde and pinocarveol, and also myrtenal, myrtenol, carveol, carvone, and 1,2-pinandiol (Fig. 8).

The catalytic activity of PC_700 was first investigated. The temperature of the oxidation process was changed in the range from 80° to 140°C, the content of the PC_700 catalyst was 0.5 wt%, and the reaction time was 1 h. The results showing the changes in values of the conversion of α-pinene and the selectivities of the correct products are presented in Fig. 9(a)-(c).

Fig. 9(a) shows that as the temperature of the oxidation process increases, the conversion of α-pinene increases from 3 mol% (temperature 80 °C) to 22 mol% (at 120 °C), and then slightly decreases to 16–17 mol% (at 130–140 °C). With increasing in values of temperature, the selectivity of the first main product, α-pinene oxide, increases from 16 mol% (temperature 80 °C) to 32 mol% (120 °C), and then slightly decreases to 28 mol% at 140 °C. The selectivity of the second main product, verbenol, increases with increasing temperatures, reaching the maximum value of 18 mol% at 140 °C. With the increase in temperature, the selectivity of the transformation of the third main product, verbenone, first grew to 20 mol% (temperature 90 °C), and then decreased to 9 mol% (temperature 140 °C). The results obtained at this stage of the studies for the PC_700 catalyst showed that it is most advantageous to carry out the process of α-pinene oxidation at the

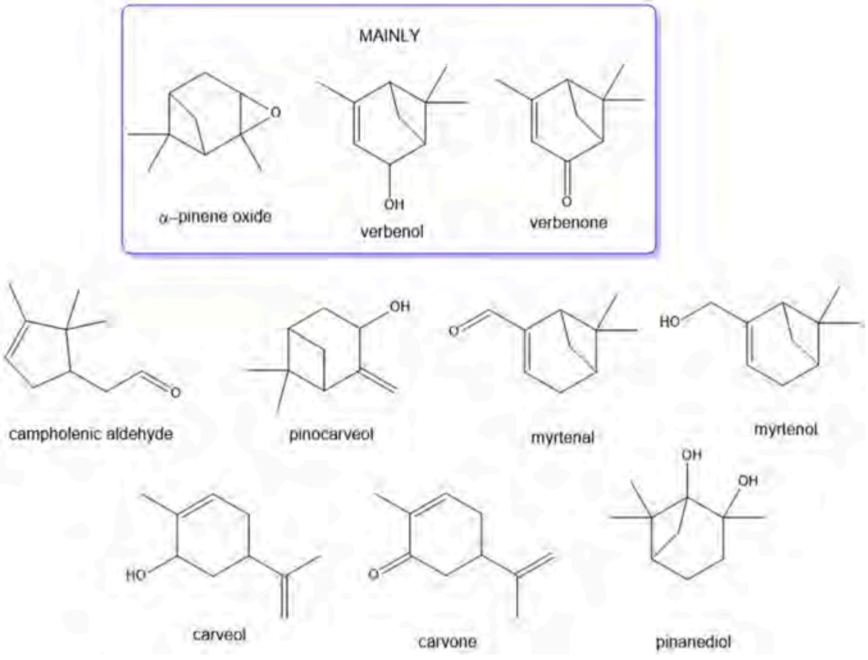

Fig. 8. The main and secondary α-pinene oxidation products.

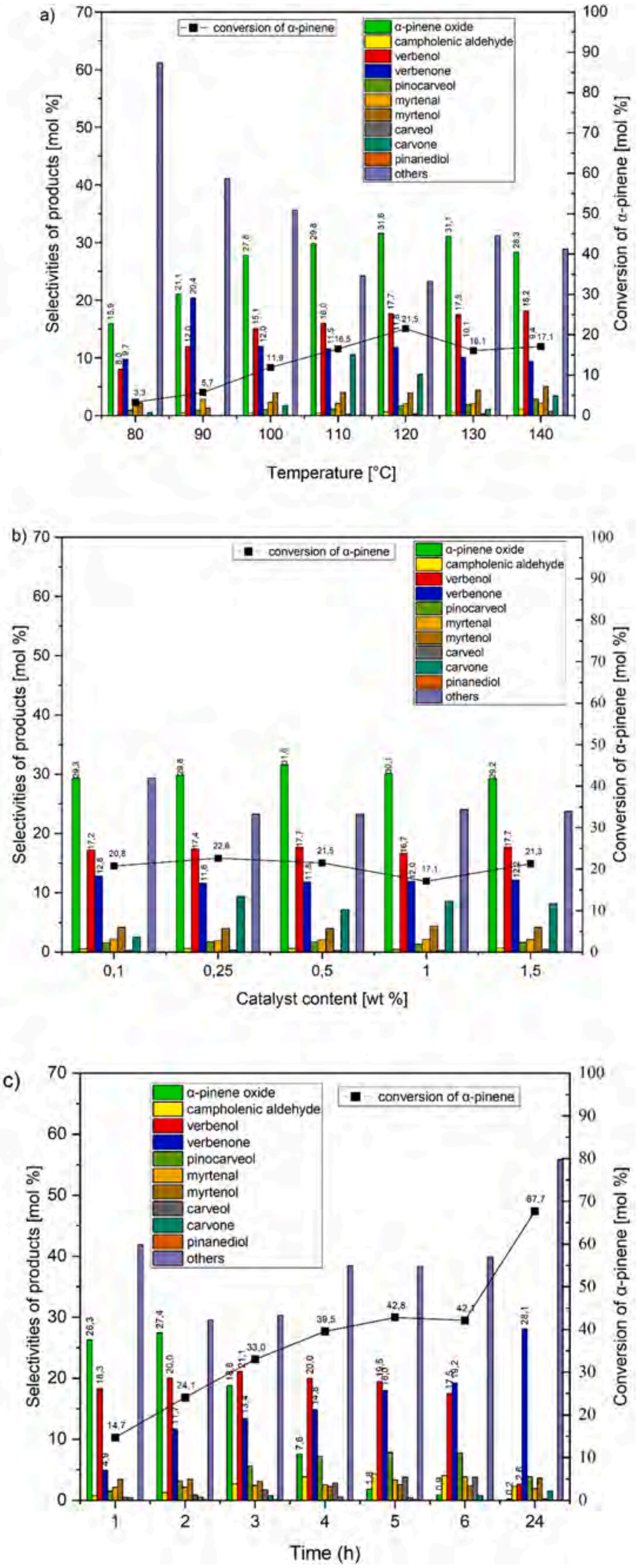

Fig. 9. Influence of temperature (a), catalyst content (b), and reaction time (c) on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over the PC_700 catalyst ("others" means the sum of the selectivities of by-products formed in smaller amounts).

temperature of 120 °C, the temperature at which the highest selectivity of the transformation to α-pinene oxide is achieved. At this temperature, the following selectivities of the main products were achieved: α-pinene oxide 32 mol%, verbenol 18 mol%, verbenone 12 mol%, and the conversion of α-pinene was 22 mol%.

The influence of the PC_700 catalyst content on the conversion of α-pinene and the selectivities of the products were examined at 120 °C and for the reaction time of 1 h. At this stage of tests, the catalyst content varied from 0.1 wt to 1.5 wt%. The results of these studies are shown in Fig. 9(b). These studies show that the selectivity of α-pinene oxide reaches about 30 mol%, for verbenone about 12 mol%, and verbenol about 17 mol%, in the studied range of catalyst amounts. The conversion of α-pinene varied in the range of 17–23 mol%. The most advantageous amount of the PC_700 catalyst in the reaction mixture was taken to be 0.5 wt% (on the basis of the values of conversion of α-pinene and the selectivity of α-pinene oxide).

In order to investigate the influence of the reaction time on the conversion of α-pinene and the selectivities of the transformation to the products, a series of tests were performed at 120 °C, which was selected as the best in the previous stage. The amount of PC_700 catalyst was 0.5 wt%. The reaction times were changed from 1 to 24 h. These tests indicated that the longer the reaction time, the greater the α-pinene conversion, as shown in Fig. 9(c). Fig. 9(c) shows that the selectivity to α-pinene oxide increases from 26 mol% (reaction time 1 h) to 27 mol% (reaction time 2 h) and then it decreases to 0.2 mol% (reaction time 24 h). The selectivity of verbenol is maintained at the level of 17–21 mol % in the range of 1–6 h reaction times, and then it decreases to 3 mol% (reaction time 24 h). Fig. 9(c) also shows that the selectivity of verbenone increases from 5 mol% (reaction time 1 h) to 28 mol% (reaction time 24 h). In the tested range of times, the conversion of α-pinene increases from 15 mol% (reaction time 1 h) to 68 mol% (reaction time 24 h). Studies on the influence of the reaction time on the oxidation of α-pinene shows that the best reaction time is 2 h (taking into account the selectivity of the first main product, α-pinene oxide).

The studies on the catalytic activities of activated carbons PC_750 and PC_800 showed very similar results as for the PC_700 activated carbon. For the PC_750 catalyst, the best conditions for the oxidation process were as follows: temperature of 130 °C, catalyst content 0.5 wt %, and reaction time 2 h. Practically the same conditions were found to be the best for the PC_800 catalyst (except for the temperature, where in this case the most preferred was 120 °C, the same as for the PC_700 catalyst). For both catalysts, for the best conditions, the values of the most important functions describing the process were close to those obtained for the PC_700 catalyst (selectivity of α-pinene 28–30 mol%, selectivity of verbenol 19–20 mol%, selectivity of verbenone 11–12 mol %, and conversion of α-pinene 22–24 mol%).

Fig. 10(a)-(c) shows the results of the studies on the catalytic activity of PC_850. As for the previously mentioned catalysts, the temperature of the oxidation process was changed in the range 80–140 °C, the content of the catalyst was 0.5 wt%, and the reaction time was 1 h.

Fig. 10(a) shows that as the temperature of the oxidation process increases, the conversion of α-pinene increases from 5 mol% (temperature 80 °C) to 35 mol% (temperature 140 °C). With increasing temperature, the selectivity of transformation to α-pinene oxide also increases from 18 mol% (temperature 80 °C) to 41 mol% (at 100 °C), and then decreases to 23 mol% (at 140 °C). The value of 41 mol% was the highest value of the selectivity of the transformation to α-pinene oxide observed so far in our research. With increasing temperature, the selectivity of transformation to verbenol increases from 13 mol% (temperature 80 °C) to 21 mol% (at 140 °C) and the selectivity of transformation to verbenone decreases from 25 mol% (at 80 °C) to about 17 mol% (temperature 130–140 °C). In the case of verbenone, however, one can notice a few percentage points increase in its selectivity at the two lowest tested temperatures (by about 5–9 mol%) compared to the catalysts previously tested. Considering mainly the α-pinene oxide selectivity values, the temperature equal to 100 °C was taken as the most favorable temperature. The most preferred temperature selected for this catalyst was 20–30 °C lower than the most advantageous temperature selected for the catalysts tested earlier.

Fig. 10(b) shows the influence of the catalyst content on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over the PC_850 catalyst. The reaction was performed at 100 °C for 1 h. With increasing catalyst content, the selectivity of transformation to α-pinene oxide increases from 27 mol% (catalyst content 0.1 wt%) to 41 mol% (0.5 wt%), and then decreases to 30 mol% (1.5 wt%). The selectivity of the transformation to verbenol is maintained at the level of 16–18 mol% in the entire range of the tested catalyst contents. With increasing catalyst content, the selectivity of transformation to verbenone decreases from 24 mol% (catalyst content 0.1 wt%) to 14 mol% (0.5 wt%), and then increases to about 23 mol% (1–1.5 wt%). The tests showed that the best amount of the PC_850 catalyst in the reaction mixture was 0.5 wt% (taking into account the values of conversion of α-pinene and the selectivity of α-pinene oxide).

Fig. 10(c) shows the influence of the reaction time on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over the PC_850 catalyst. The reaction was performed at 100 °C and the amount of catalyst was 0.5 wt%. Fig. 10(c) shows that the selectivity of the transformation to α-pinene oxide increases from 27 mol% (reaction time 1 h) to 30 mol% (reaction time 3 h), and then decreases to 0.2 mol % (reaction time 24 h). Compared to the previously tested catalysts, it was possible to maintain a high value of selectivity of the transformation to α-pinene oxide (over 21 mol%) with the PC_850 catalyst for a longer period (up to 5 h). The selectivity of the transformation to verbenol is maintained at the level of 16–18 mol% in the range of reaction times 1–6 h, and then it decreases to 3 mol% (reaction time 24 h). Fig. 10(c) shows that the selectivity of the transformation to verbenone decreases from 22 mol% (reaction time 1 h) to 13 mol% (reaction time 4 h), and then increases to 43 mol% (reaction time 24 h). After comparing the results obtained so far, it can be seen that in the case of verbenone, for the shortest and the longest reaction times, it was possible to obtain the highest selectivity of the transformation of α-pinene to this compound, as compared to the catalysts tested so far. In the range of reaction times, the conversion of α-pinene increases from 12 mol% (reaction time 1 h) to 98 mol% (reaction time 24 h). The influence of time on the conversion of α-pinene shows that in the case of the PC_850 catalyst for reaction times of 5, 6, and 24 h, higher values of this process function are obtained (these differences range from 10% to 20% mol) as compared to catalysts PC_700, PC_750, and PC_800.

These studies concerning the impact of the reaction time on the oxidation of α-pinene show that the best results were obtained for the time of 4 h; this value was taken on the basis of the selectivity of the transformation to α-pinene oxide. The comparison shows that the most favorable time determined for this catalyst sample (4 h) was twice as long as the most favorable time determined for all earlier catalyst samples (2 h).

Fig. 11(a)-(c) shows the results of the studies on the catalytic activity of the PC_900 carbon catalyst. The temperature during oxidation process was changed in the range 80–140 °C, the catalyst content was 0.5 wt%, and the reaction time was 1 h.

The tests conducted for the PC_900 catalyst showed that this catalyst (similar to sample PC_850) was also very active in the oxidation of α-pinene. During the studies on the influence of temperature, Fig. 11(a), the application of the PC_900 catalyst produced 10 mol% lower values of the selectivity of the transformation to α-pinene oxide (about 30 mol % at 120 °C) than for the PC_850 catalyst (about 40 mol% at 100 °C). During the study of the temperature effect, the selectivity of the transformation to verbenol was similar for both catalysts, while the selectivity of the transformation to verbenone was usually 1–6 mol% higher for the PC_850 catalyst. The conversions of α-pinene during the research on the influence of temperature were similar for both catalysts; only a large difference was noted for the highest temperature, at which the conversion obtained with the PC-850 catalyst (about 35 mol%) was

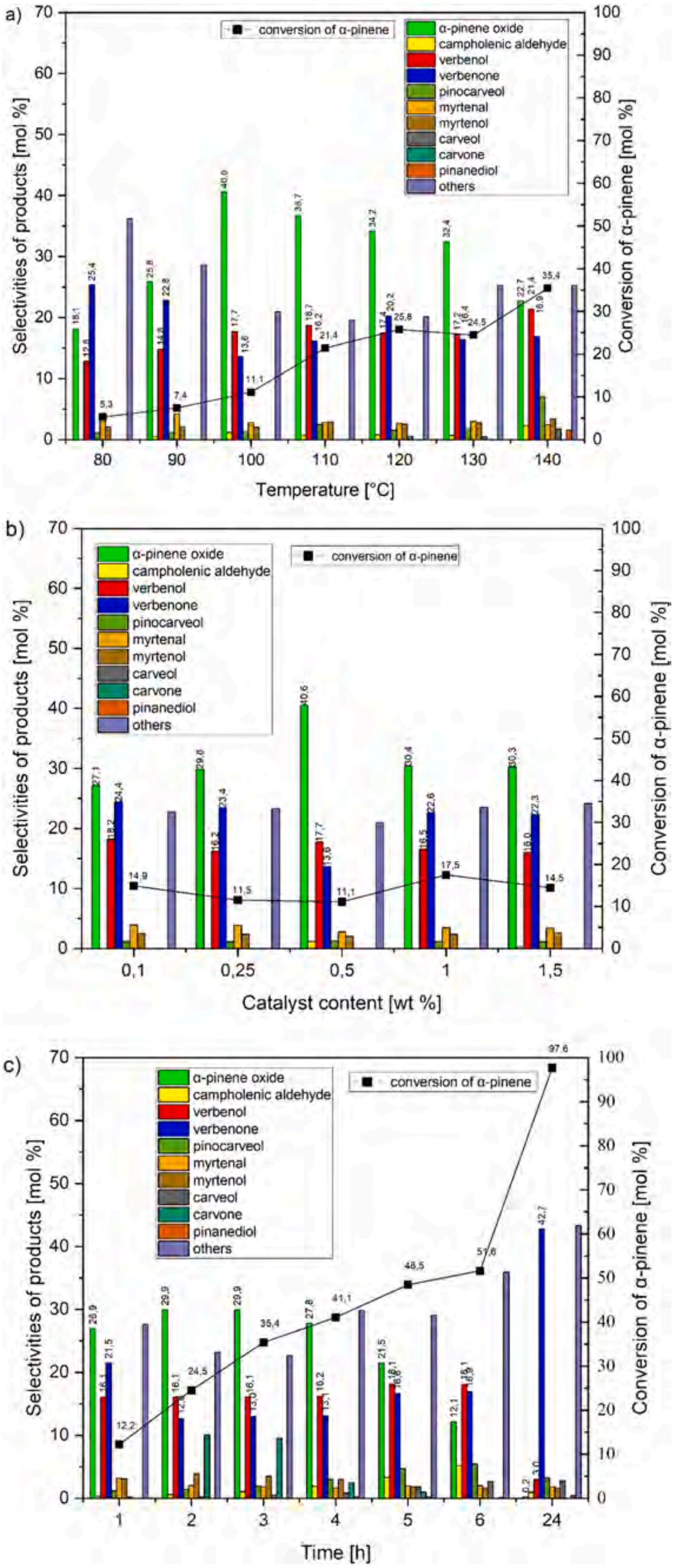

Fig. 10. Influence of temperature (a), catalyst content (b), and time (c) on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over the PC_850 catalyst ("others" means the sum of the selectivities of by-products formed in smaller amounts).

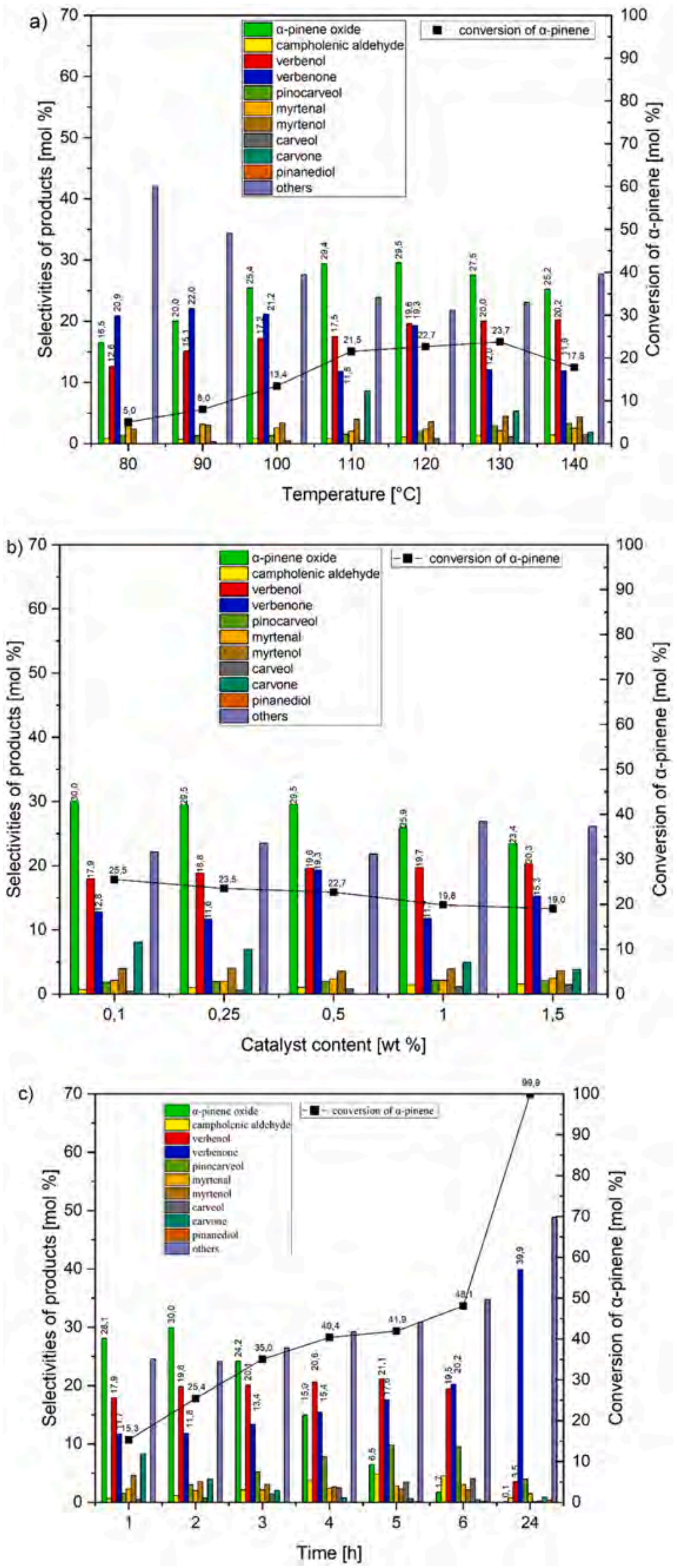

Fig. 11. Influence of temperature (a), catalyst content (b) and time (c) on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over the PC_900 catalyst ("others" means the sum of the selectivities of by-products formed in smaller amounts).

twice greater than that obtained for the PC_900 catalyst (about 18 mol %). For the PC_900 catalyst, the temperature of 120 °C was chosen as the most preferred. This temperature is 20 °C higher than the most preferred temperature selected for the PC-850 catalyst. At this temperature, the approximate selectivities of the main products were: α-pinene oxide 30 mol%, verbenol 20 mol%, and verbenone 19 mol%. The conversion of α-pinene was about 23 mol%.

The comparison of the results of the research on the influence of the amount of PC_850 and PC_900 catalysts, Figs. 10(b) and 11(b), on the course of α-pinene oxidation, shows that in the case of the selectivity of the transformation to α-pinene oxide performed with the PC_850 catalyst, values of this function were usually obtained by several percent higher than with PC_900 catalyst. At the same time, the selectivities of the transformation to verbenol obtained with the PC_900 catalyst were slightly lower, and for verbenone 5–13 mol% higher. The conversions of α-pinene obtained in the presence of PC_900 catalyst were 5–10 mol% higher than in the presence of PC_850 catalyst. The most advantageous amount of catalyst determined for the PC_900 sample was 0.25 wt% and this catalyst content was lower by half than for the PC_850 catalyst.

Fig. 11(c) shows that the selectivity of the transformation to α-pinene oxide decreased in the studied range of reaction times, similar to the PC_850 catalyst, but for the PC_850 catalyst, significantly higher values of this selectivity were observed in the range of reaction times of 3–6 h (by 6–15 mol%). The selectivity of the transformation to verbenol was slightly higher in the tests with the PC_900 catalyst than in the tests with the PC_850 catalyst (by 3–4 mol%). The selectivity of the transformation to verbenone was similar for both tested catalysts. Similar to the tests conducted for the PC_850 catalyst, in the tests performed for the PC_900 catalyst, after 24 h, a high selectivity of the transformation to verbenone was also obtained – about 40 mol%. In the case of the PC_900 catalyst, the time of 2 h was found to be the best reaction time. This time is twice as short as was considered the best for the PC_850 catalyst.

Tests conducted with the use of PC_950 and PC_1000 catalysts showed that these two catalyst samples were less active in the tested process than samples of PC_850 and PC_900 catalysts. Considering, for example, the study of the influence of time, there is a reduction in the selectivity of the transformation to α-pinene oxide (even up to 15–18 mol% compared to the PC_850 catalyst sample) and for verbenone (even by 15–21 mol%) compared to the PC_850 catalyst sample). On the other hand, the selectivities of the transformation to verbenol for these catalysts were by 3–4 mol% higher than for PC_850 catalyst. The results obtained for the PC_1000 sample are presented in Fig. 12(a)-(c).

Comparing the results achieved for the catalysts produced by carbonization at temperatures of 700 and 1000 °C (Figs. 9 and 12), it can be observed that for these catalysts very similar selectivity values of the main products and conversion of α-pinene were obtained.

The most favorable results, considering the selectivities of the three main products (α-pinene oxide, verbenol, and verbenone) and the α-pinene conversion, were obtained in the presence of the PC_850 catalyst. Very similar values of the selectivities of the main products and conversion of the organic substrate were also obtained for the PC_900 catalyst. On the basis of the results presented in Fig. 4 (pore distribution histogram), it can be assumed that this difference in the activity of these two catalyst samples in relation to the others may be related to the presence of micropores with a diameter of 1.00–1.25 nm, which was not observed in the case of other catalysts. However, the difference in the activity of the PC_850 and PC_900 catalysts may be due to the fact that the PC_900 sample also contains mesopores ranging from 2 to 3 nm, the presence of which was not found in the PC_850 sample. Moreover, considering the results presented in Table 4, it can be noticed that the PC_850 catalyst contains the most keto-enolic groups among the tested catalysts, as well as a large number of C═O and COOH groups. The PC_900 catalyst differs from the PC_850 catalyst by a 4-fold lower amount of keto-enolic groups. On its surface there is also a smaller number of C═O and COOH groups. This difference in the groups present on the surface of both catalysts may also be the reason for differences in their activity.

If we assume that in the case of keto-enol groups the ketone form is the dominant form, then the PC_850 catalyst sample has 1.7 times more carbonyl groups than the PC_900 sample. At the same time, it is known that the oxidation process of α-pinene in the presence of carbon catalysts follows the radical mechanism [32]. Therefore, it can be assumed that carbonyl groups can support the formation of radicals with the participation of α-pinene molecules; according to the literature data, carbon catalysts do not catalyze the conversion of α -pinene oxide, verbenol and verbenone. The carbonyl groups may also affect the way and strength of binding these radicals to activated carbon surface, as well as their durability. This also has a significant impact on the course of the oxidation process and the type of products formed (epoxy compound) and allylic oxidation products (verbenol and verbenone). A thorough analysis of the catalytic test results for the PC_850 and PC_900 catalyst samples shows that one more parameter has a significant impact on the direction of α-pinene transformations, namely the reaction time. For both catalyst samples for reaction times above 6 h (PC_850 catalyst) or 4 h (PC_900 catalyst), products formed as a result of allylic oxidation – verbenol, and for the longest reaction time (24 h), verbenone – begin to dominate. According to the mechanism of α-pinene oxidation proposed by Cao et al. [32] it may indicate that for longer reaction time pathway III, in which a radical with the general structure R-O-R* is formed (where R comes from the α-pinene molecule), is inhibited. This pathway of α-pinene transformation, as was described by Cao et al. [32], increases the selectivity of transformation to epoxide. For longer reaction time, the main pathways of α-pinene oxidation are pathways I and II, in which the following radicals are formed: R* , ROO* , ROOR* , and RO* . The formation of the latter radical in particular is required for the formation of verbenol and verbenone. The increased selectivity of the transformation to these two products for longer reaction times indicates that there has been an increase in the stability of this radical. A detailed explanation of the mechanism of the ongoing process requires, however, further detailed research.

4. Conclusions

The studies presented in this work show that the waste biomass in the form of pine cones is an excellent source for the synthesis of activated carbons using potassium hydroxide as the activating agent. These materials are active catalysts in the oxidation of α-pinene with oxygen. It was shown that the most active catalyst in the oxidation process was the activated carbon named PC_850 catalyst, which has the smallest pore size compared to the other catalysts tested. Also, the presence of functional groups on the activated carbon surface, such as a carbonyl group, and the reaction time can affect the direction of oxidation in the α-pinene molecule. It was found that this process is most preferably conducted at 100 °C for 4 h using 0.5 wt% of the PC_850 catalyst in the reaction mixture. Under these conditions, the conversion of α-pinene was 41 mol%, and the selectivities of the main three products of α-pinene oxidation were: α-pinene oxide (28 mol%), verbenol (16 mol %) and verbenone (13 mol%). Moreover, it was also shown that after 24 h it is possible to obtain the high selectivity of verbenone (43 mol%), with a very high conversion of α-pinene (98 mol%).

The proposed method of α-pinene oxidation not only allows for the disposal of waste pine cones, but also enables the transformation of natural α-pinene into more useful added value compounds. The characteristic feature of the proposed oxidation method is that it does not require the use of a solvent, which reduces the costs of dividing the post-reaction mixture into pure components as well as the costs of solvent recovery and regeneration.

In the future, we would like to obtain activated carbons from other parts of the pine tree, such as needles or branches. These items can also be a valuable raw material for obtaining activated carbons, and their activities may differ from those obtained from pine cones. We would also like to increase the selectivity of selected main products by

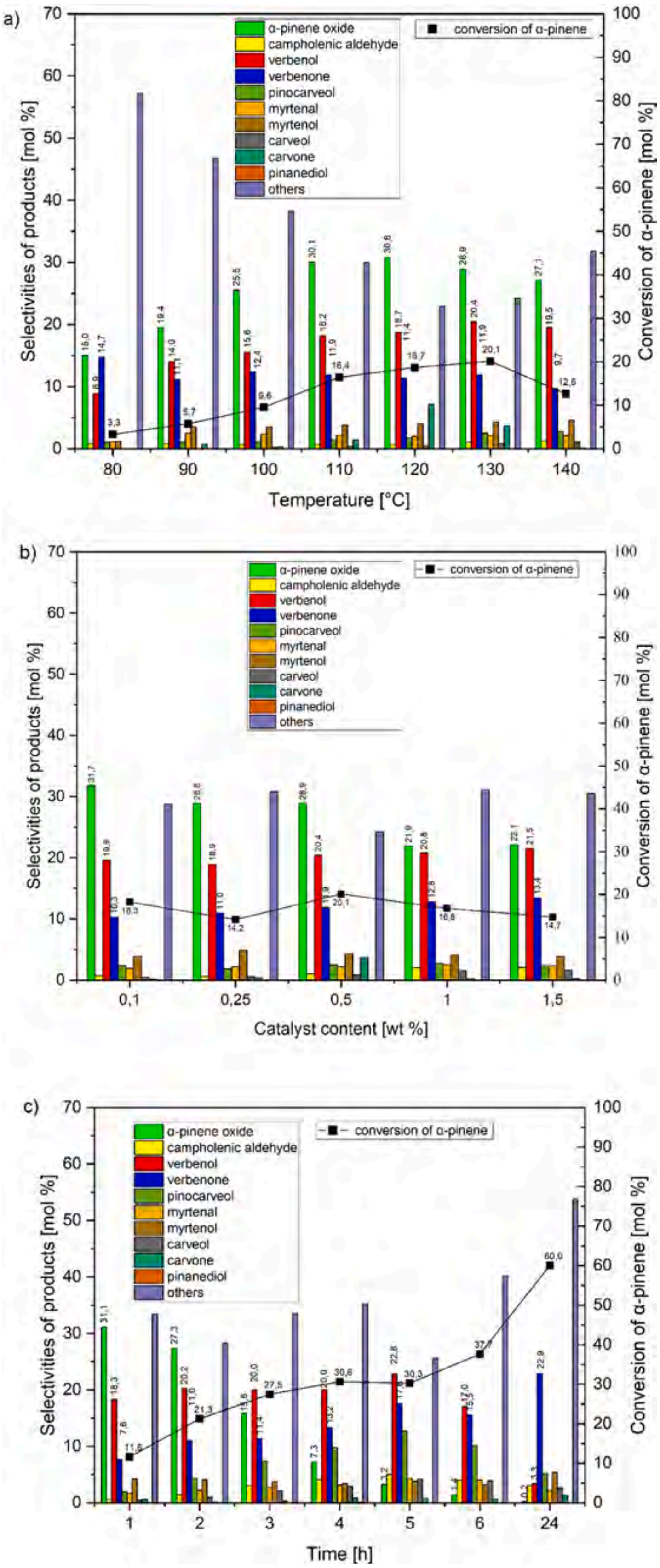

Fig. 12. Influence of temperature (a), catalyst content (b) and time (c) on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over the PC_1000 catalyst ("others" means the sum of the selectivities of by-products formed in smaller amounts).

modifying the surface of active carbons with appropriately selected metals, e.g. Ti or Fe. Another route may be to use a different oxidant in the process, e.g. t-butyl hydroperoxide.

CRediT authorship contribution statement

J. Grzeszczak: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft. **A. Wróblewska**: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **A. Kamińska**: Investigation. **P. Miądlicki**: Investigation. **J. Sreńscek-Nazzal**: Investigation. **R.J. Wróbel**: Investigation. **Zvi C. Koren**: Writing – original draft, Writing – review & editing. **B. Michalkiewicz**: Investigation, Methodology, Validation, Writing - original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Article

The Application of Clinoptilolite as the Green Catalyst in the Solvent-Free Oxidation of α-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 α-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 α-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 α-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: α-pinene oxide (selectivity 29 mol%), verbenol (selectivity 17 mol%), and verbenone (selectivity 13 mol%). The conversion of α-pinene under these conditions amounted to 35 mol%. Additionally, the kinetic modeling of α-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 α-pinene. The catalytic application of clinoptilolite in the oxidation of α-pinene has not yet been reported in the literature.

Keywords: clinoptilolite; zeolite catalysts; α-pinene; oxidation

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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.

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 α-pinene on H_2SO_4-modified clinoptilolite. Performing the isomerization at 70 °C and for 4 min allowed for the complete conversion of α-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 α-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 α-pinene (content about 75–85%), turpentine contains the following compounds: limonene (5–15%), β-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 α-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]. α-Pinene is extracted from the waste turpentine by vacuum rectification (content of α-pinene amounts to about 70%) [34,35].

α-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]. α-Pinene derivatives include such compounds as α-pinene oxide, campholenic aldehyde, L-carveol, verbenol, verbenone, trans-pinocarveol, myrtenal, myrtenol, carvone, and 1,2-pinanediol [41,42]. α-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 α-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, $CuCl_2$, $PdCl_2$, and $PdBr_2$ [56]. Carbonaceous materials obtained from pine cones were also described as catalysts for the oxidation of α-pinene [41]. The oxidation process of α-pinene was performed using various solvents (acetonitrile, acetone, and methylene chloride). As the oxidants in this process, H_2O_2, 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 α-pinene.

This paper describes the application of clinoptilolite as the catalyst in the solvent-free oxidation of α-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, multi-stage 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 µm average particle size), clin_2 (50 µm average particle size), clin_3 (200 µm average particle size), and clin_4 (500–1000 µm 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_2 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 2θ from 5 to 80° (Cu Kα

= 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^{-1} wavenumber range, were measured using a Thermo Electron Nicolet 380 spectrometer.

2.3. Oxidation of α-Pinene over Clinoptilolite Materials

The following conditions were used for the oxidation of α-pinene: 25 cm^3 round-bottom glass flask, reflux condenser, magnetic stirrer, oxygen flow regulator, and glass bubbler supply. Amounts of 10–20 g of α-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 α-Pinene by the Gas Chromatography Method

The products of α-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 α-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.

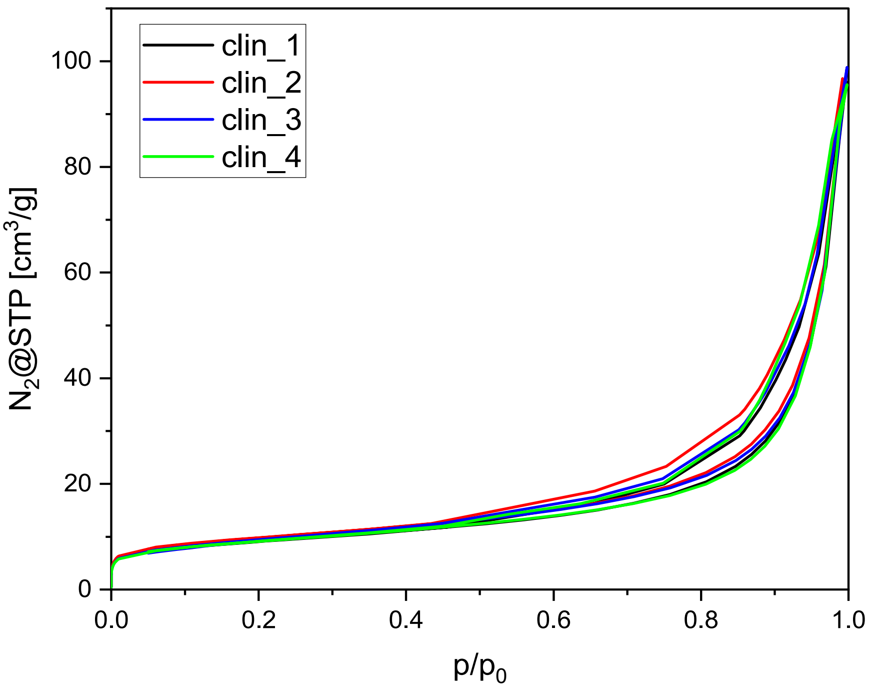

Figure 2. N_2 adsorption–desorption isotherms of clinoptilolite samples.

The textural properties of clinoptilolites are presented in Table 1.

Table 1. Textural properties of the samples.

	S_{BET} [m²/g]	V_{tot} [cm³/g]	V_{meso} [cm³/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

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.

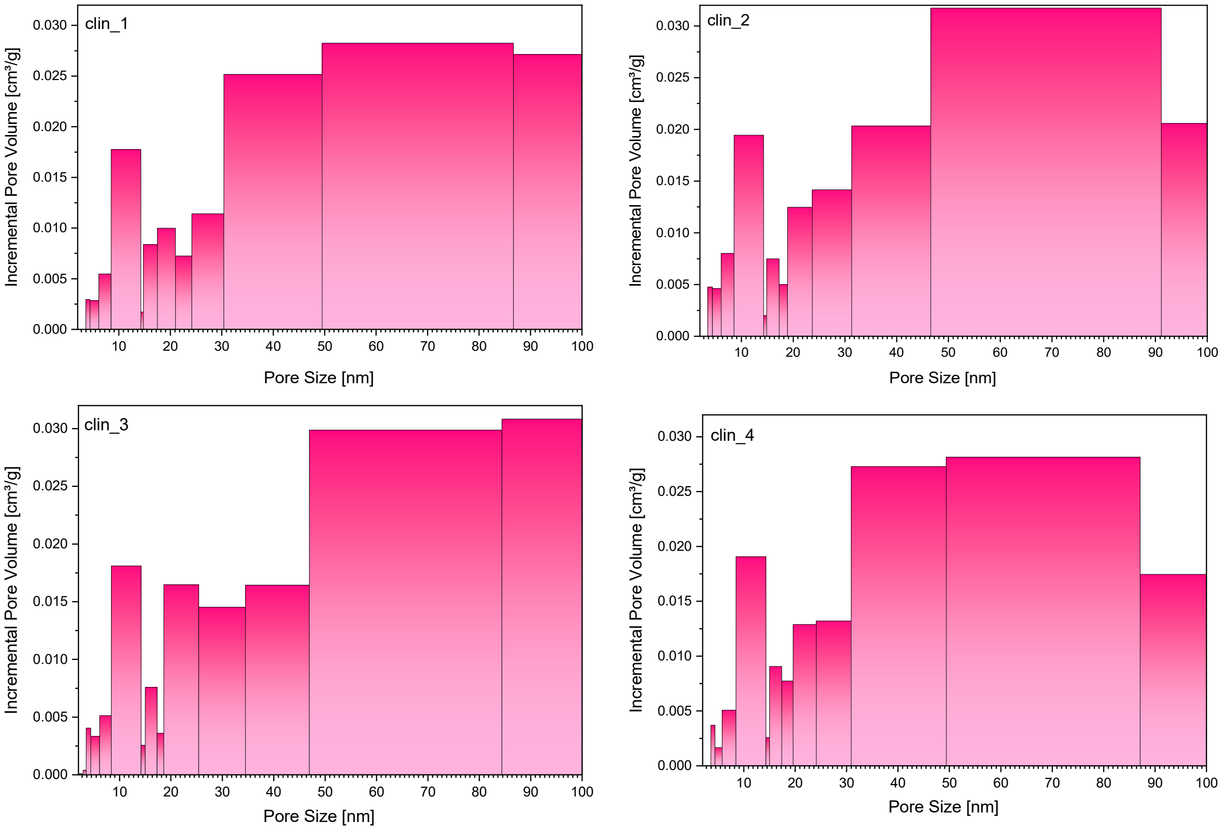

Figure 3. Pore size distributions calculated by the BJH method for clinoptilolite samples.

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	K
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 (2θ = 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.

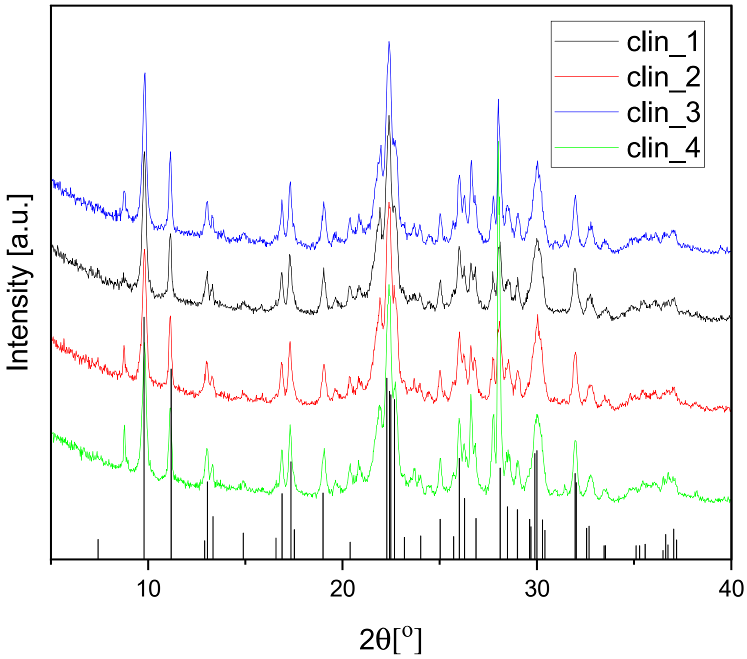

Figure 4. XRD patterns of clinoptilolite samples. The black bars represent clinoptilolite according to JCPDS No. 70-1859.

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.

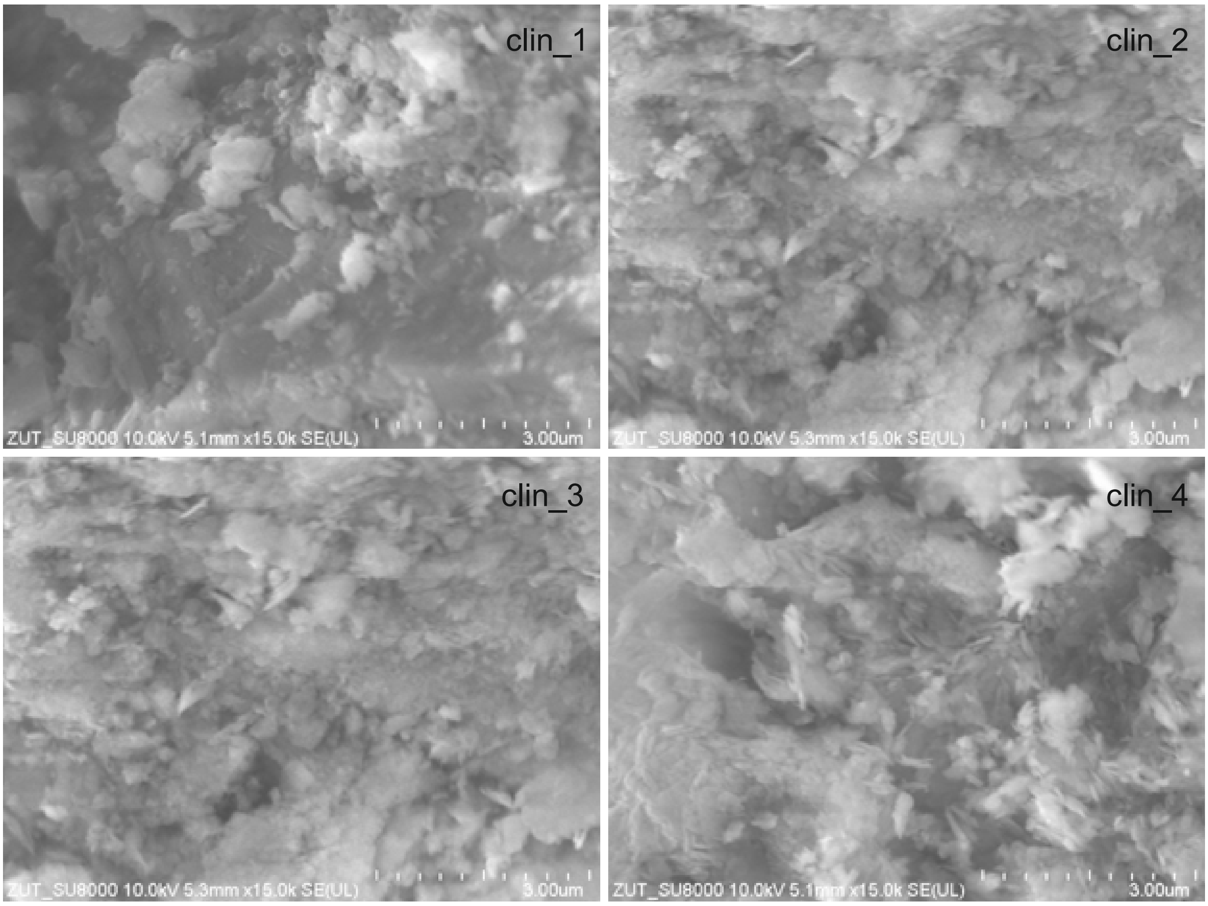

Figure 5. SEM images of the samples.

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^{3+} 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_2O_3 on the zeolite surface or of oxygen-to-metal charge transfer transitions that involve octahedral Fe^{3+} species [61].

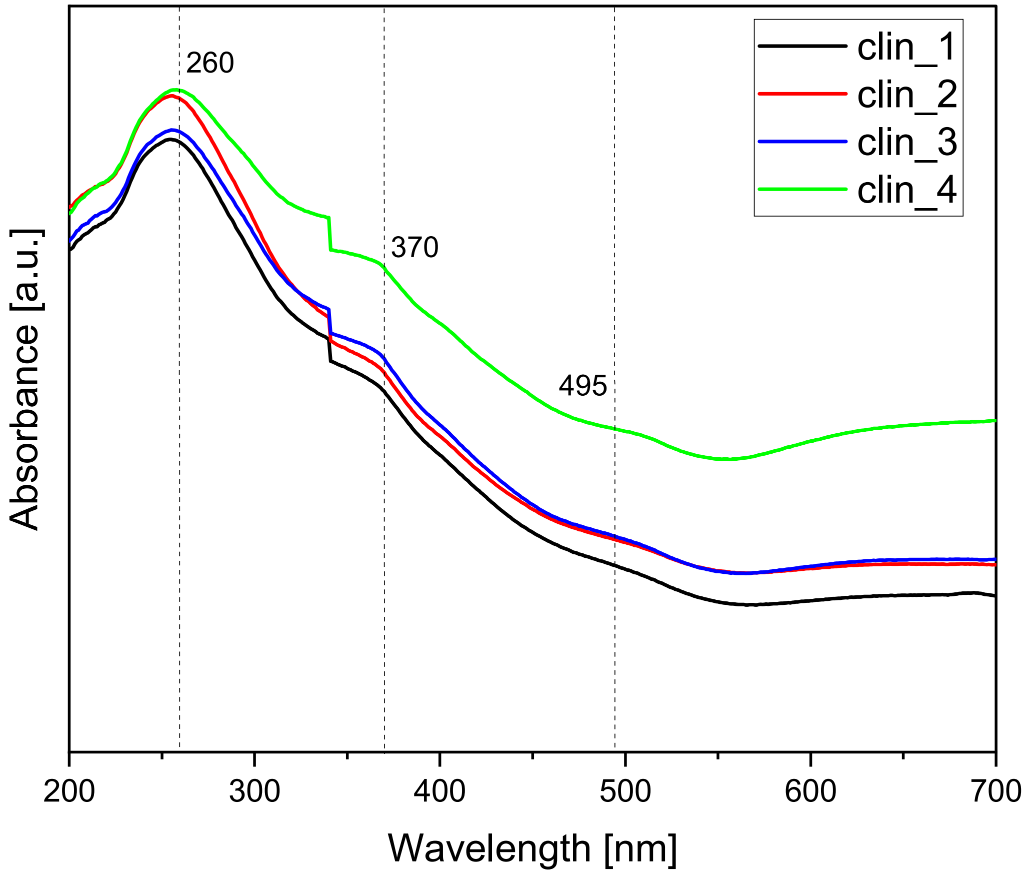

Figure 6. UV-VIS spectra for the clinoptilolite materials with different particle sizes.

The FTIR bands in the range of 3700–1600 cm^{-1}, seen in Figure 6, can be attributed to adsorbed water molecules [62,63]. The 1628, 3410, and 3622 cm^{-1} 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^{-1} 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^{-1} band is attributed to the hydrogen bonding of the water molecule to surface oxygen, and the 1637 cm^{-1} band is attributed to the bending vibrations of the water molecules [62]. The 3622 cm^{-1} band is assigned to the bridging OH groups' vibrations in ≡Al-OH-Si≡ 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^{-1} (Figure 7). This band is attributed to the asymmetric stretching vibrations of T-O bonds in tetrahedral TO_4, 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^{-1}. The 796 and 465 cm^{-1} 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^{-1} is characteristic of the pore opening. The 727, 671, and 600 cm^{-1} bands, seen in Figure 6, are assigned to extra-framework cations in the clinoptilolite matrix [63].

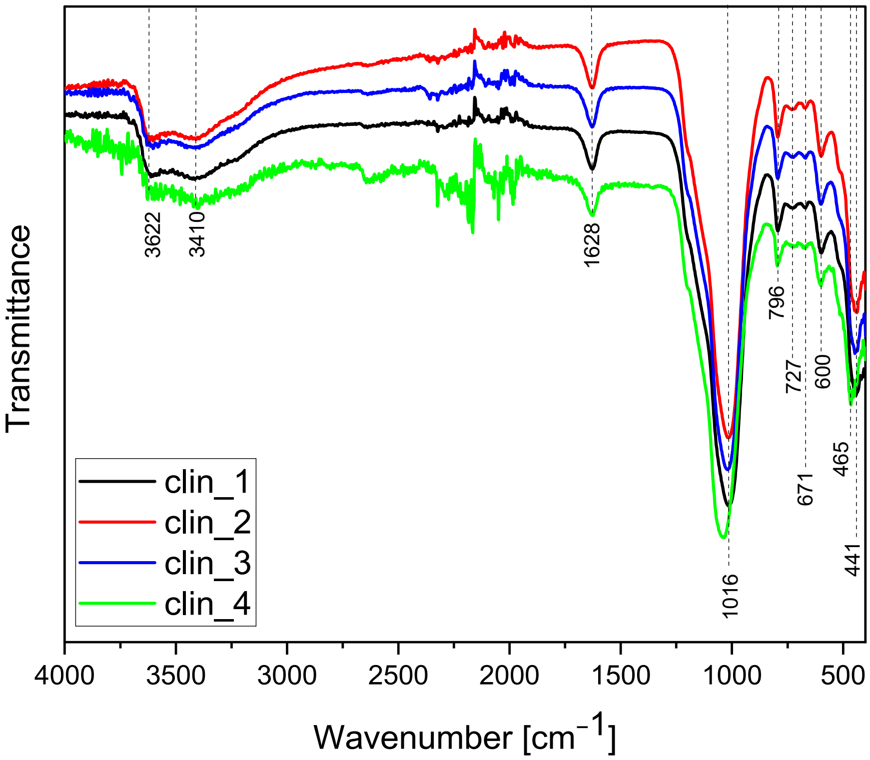

Figure 7. FTIR spectra for the clinoptilolite materials with different particle sizes.

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

The first stage of the studies consisted of checking the activity of four clinoptilolite materials in the oxidation of α-pinene. The process conditions were as follows: temperature of 100 °C, catalyst content 0.1 wt% in relation to the mass of α-pinene introduced into the reactor (the mass of α-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 α-pinene (Figure 8), and can be used as catalysts in this process.

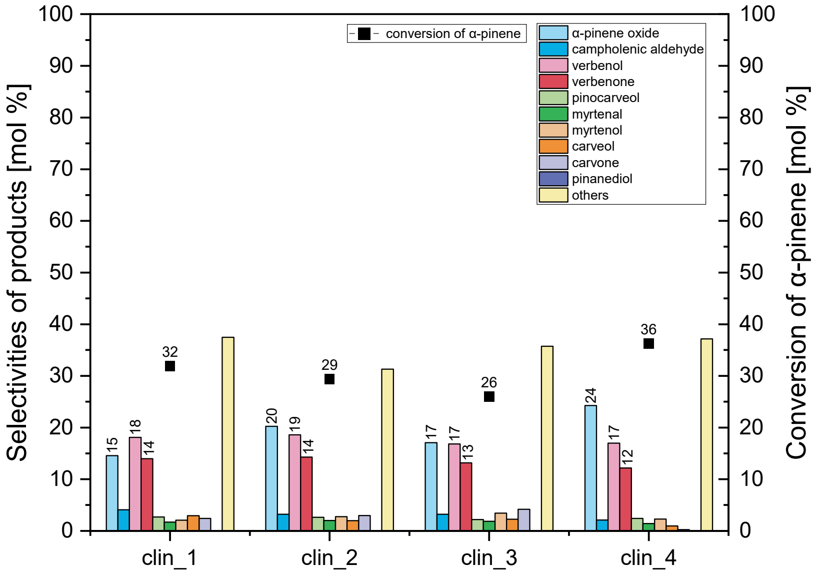

Figure 8. Catalytic activities of clinoptilolite materials in α-pinene oxidation (temperature 100 °C, catalyst content 0.1 wt%, and reaction time 3 h).

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

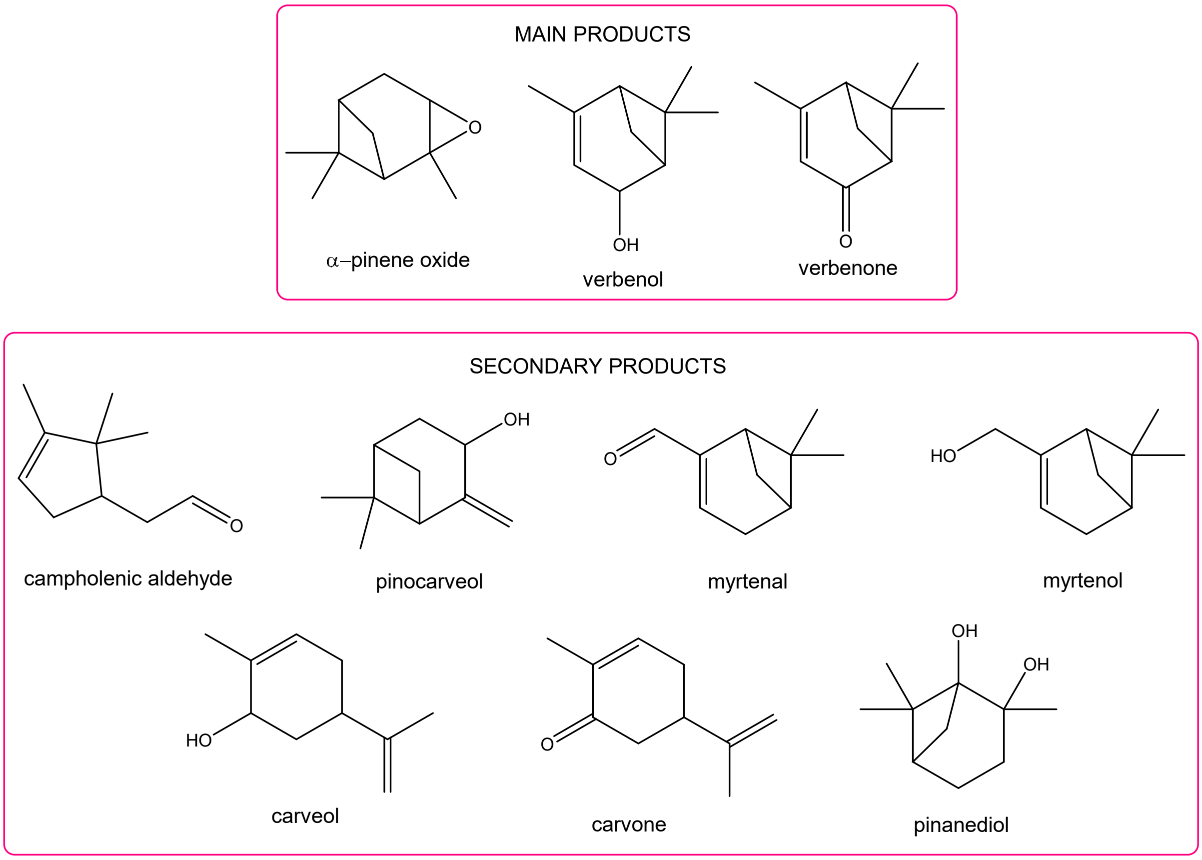

Figure 9. The main and secondary α-pinene oxidation products.

From the four clinoptilolites that were tested, the most active was the clin_4 zeolite with an average particle size of 500–1000 μm, for which the highest conversion of α-pinene

(36 mol%) and the highest selectivity of α-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 α-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 ≡Si-OH and ≡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 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 α-pinene. The lower activity of the other clinoptilolites may be related to the effect on the -OH groups present in ≡Al-OH-Si≡ 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).

The activity of clinoptilolites in the α-pinene oxidation reaction may also be related to the intensity of the 796 cm^{-1} band (Figure 7). Clin_4 has the most intense band at 796 cm^{-1}, 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^{-1} band shift toward a higher wave number (1043 cm^{-1}) 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 clin_4 material is lower compared to the amount of Al and Si in the other 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 ≡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_2O_3 molecules and mononuclear Fe species, which may play an important role (active phase) in the α-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 α-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 α-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 α-pinene was 10 g, and for the studies on the effect of reaction time, the amount of α-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 α-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 α-pinene and a reaction time of 3 h.

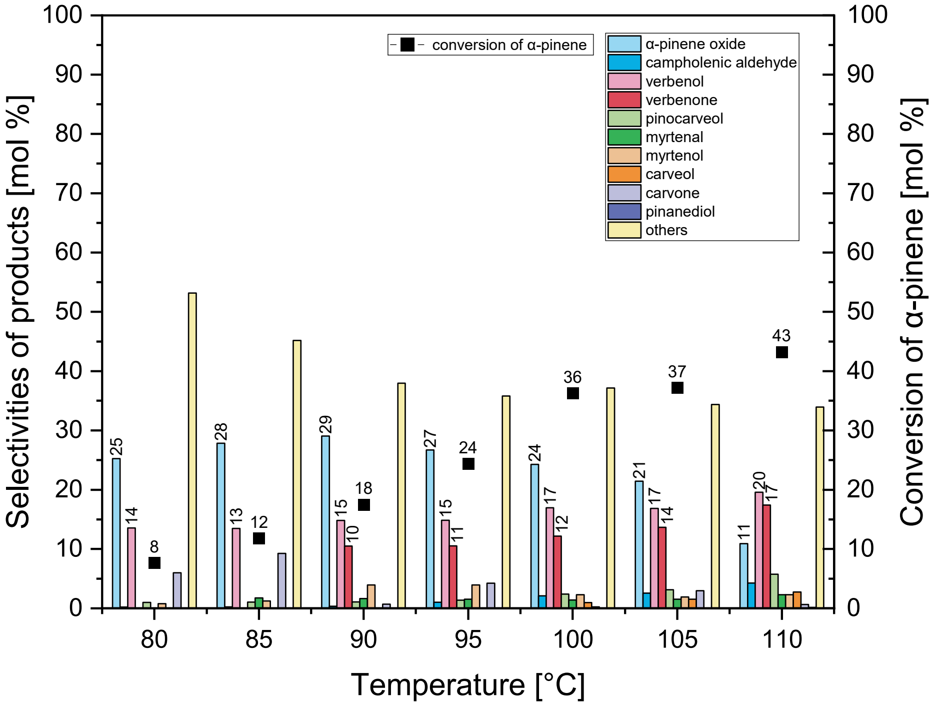

Figure 10. Influence of temperature on the conversion of α-pinene and selectivities of products in the oxidation of α-pinene over clin_4 clinoptilolite.

It is noticeable that the conversion of α-pinene increases with increasing temperature and reaches the maximum value (43 mol%) at 110 °C. The selectivity of α-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 α-pinene oxide amounts to 24 mol%, verbenol 17 mol%, verbenone 12 mol%, and conversion of α-pinene is 36 mol%.

Studies on the effect of the amount of catalyst were conducted at 100 °C for 3 h. The results obtained during these studies are shown in Figure 11.

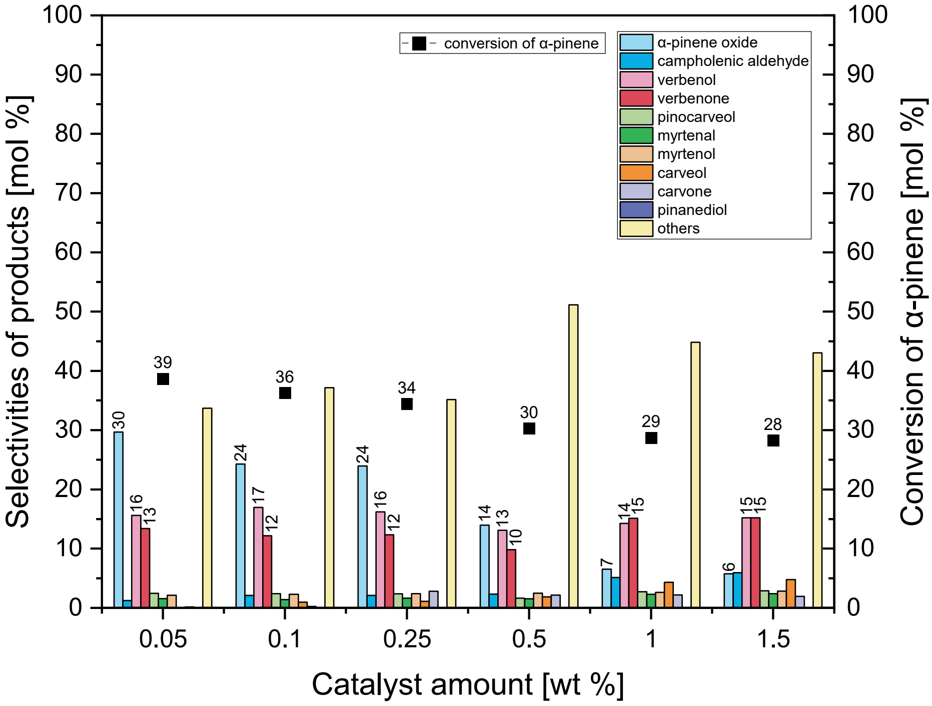

Figure 11. Influence of catalyst content on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over clin_4 clinoptilolite.

Figure 11 shows that increasing the catalyst amount from 0.05 to 1.5 wt% causes a decrease in the conversion of α-pinene from 39 to 28 mol%. This increase in the clin_4 material content also causes a decrease in the selectivity of α-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 α-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 α-pinene oxide was obtained (30 mol%) at the conversion of α-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 α-pinene molecules to the active centers, and this, in turn, may lead to a decrease in the conversion of α-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 α-pinene, are observed.

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

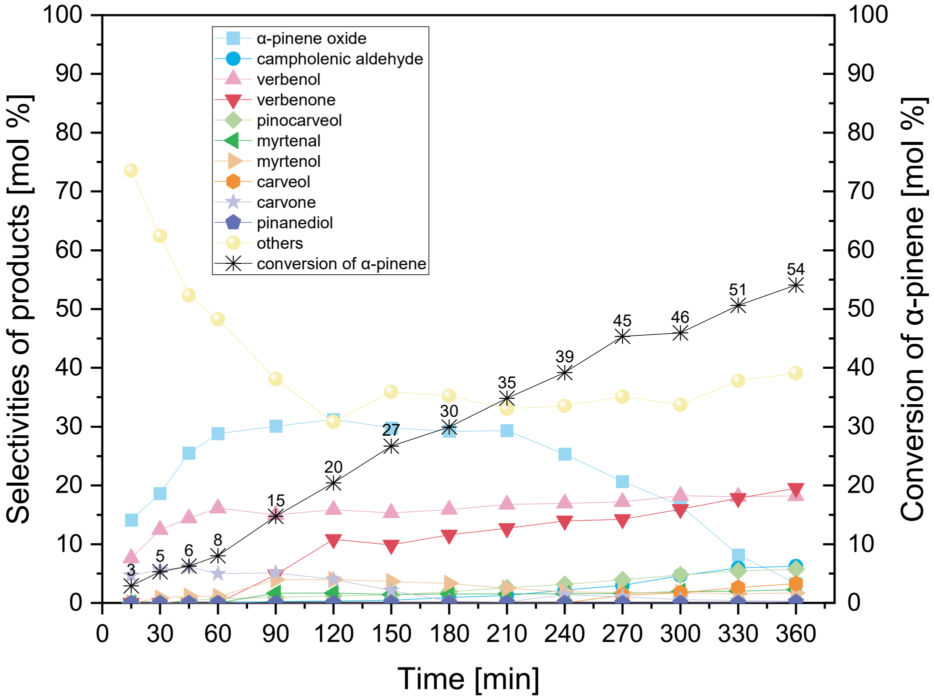

Figure 12. Influence of reaction time on the conversion of α-pinene and selectivities of the products in the oxidation of α-pinene over clin_4 clinoptilolite at 100 °C (catalyst amount 0.05 wt%).

It can be seen that, as the reaction time increases from 15 to 120 min, the selectivity of α-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 selectivities of these derivatives amount to 0 mol%). After the reaction time of 60 min, 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 α-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, resulting 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 α-pinene oxide, verbenol, verbenone, and the conversion of α-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 α-pinene oxide amounts to 29 mol%, verbenol 17 mol%, verbenone 13 mol%, and the conversion of α-pinene is 35 mol%.

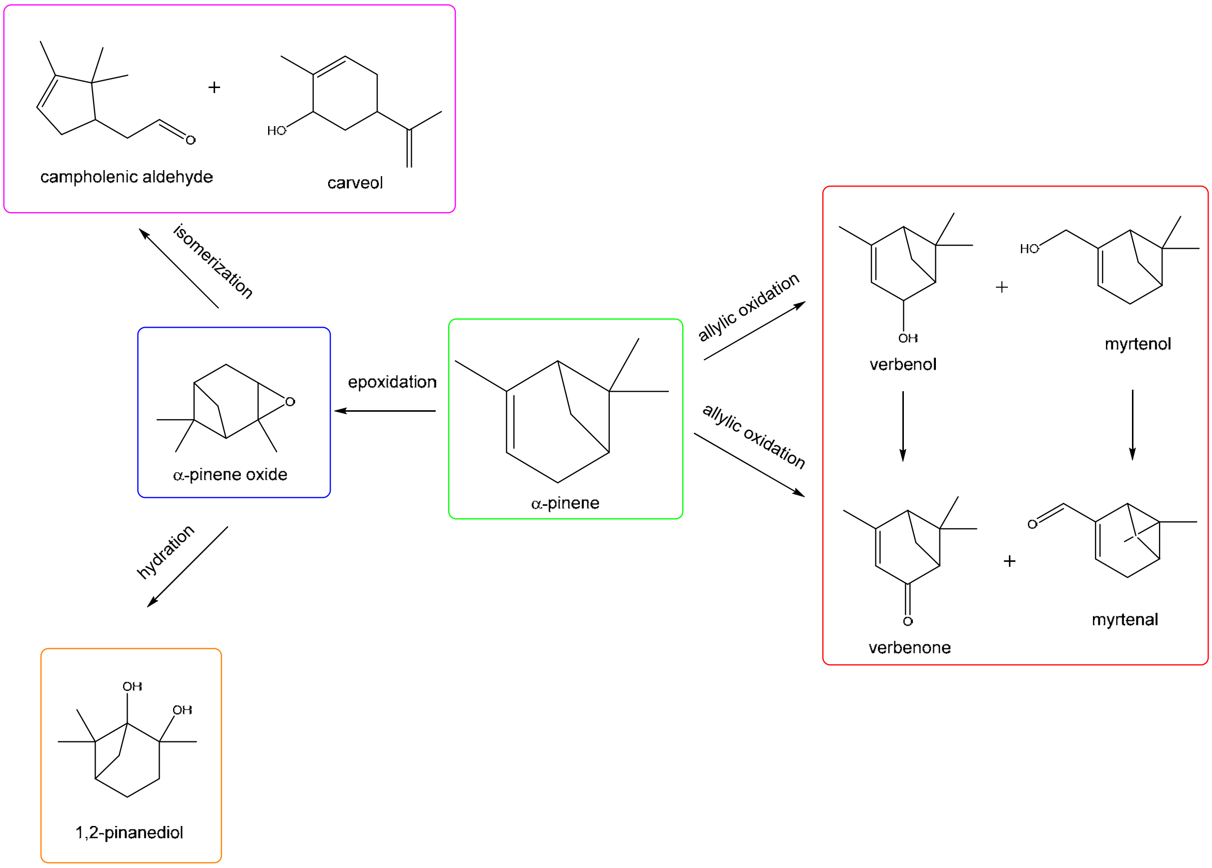

Figure 13. Transformation pathways of α-pinene and α-pinene oxide.

It is also interesting to note the changes in the selectivity of the transformation of α-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 α-pinene molecules to the active sites. As a result, we can observe the low conversion of α-pinene (3–8 mol%). In our earlier publication [42] concerning the oxidation of α-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 α-pinene of about 4 mol% was achieved. For the reaction time of 360 min, the conversion of α-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 °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 α-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 α-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 α-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 α-pinene oxide is reduced to 15 mol%. This proves the greater stability of the α-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 α-pinene oxide in the pores.

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 α-pinene 100 °C, and the amount of catalyst 0.5 wt%). For the reaction time of 1 h, a low α-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 α-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 α-pinene to α-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 α-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 α-pinene oxide. At the same time, this would confirm the conclusion that catalysts containing micropores can be used to obtain α-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 α-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 α-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: α-pinene oxide 29 mol%, verbenol 17 mol%, verbenone 13 mol%, and α-pinene conversion was 35 mol%. Our method for the oxidation of α-pinene on clinoptilolite is cost-effective and energy-efficient, 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 α-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 α-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 α-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 α-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 α-pinene oxide, and for which it is possible to obtain the higher conversion of α-pinene (even above 40 mol% for the catalyst obtained from pine cones). Therefore, in order to obtain α-pinene oxide with the selectivity of about 30 mol%, and, at the same time, the high conversion of α-pinene, it is better to use microporous catalysts. Further research on the use of clinoptilolite in the oxidation of α-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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Antioxidant Activities of Ethanolic Extracts Obtained from α-Pinene-Containing Plants and Their Use in Cosmetic Emulsions

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Abstract: α-Pinene is the bicyclic, unsaturated terpene hydrocarbon present in many plants. Due to its beneficial chemical properties, this compound is of great interest and has found numerous applications as a raw material in many chemical industries as well as in medicine and cosmetics. The aim of this study was to evaluate the antioxidant activities of ethanolic extracts obtained from plants containing α-pinene and to test the properties of cosmetic emulsions prepared with these extracts. The raw plant materials consisted of fresh parts of *Pinus sylvestris* L., such as cones, needles, and branches, as well as dried unground and ground pinecones; dried and fresh *Rosmarinus officinalis* leaves; dried *Levisticum officinale* leaves; and dried *Salvia officinalis* L. leaves. The plant materials were individually extracted with 40% (*v*/*v*), 70% (*v*/*v*), and 96% (*v*/*v*) ethanol using ultrasound-assisted extraction (UAE) for 15, 30, or 60 min. This method is a green extraction technique, frequently applied to isolate active substances from plants. For the selected plant materials, Soxhlet extraction with 96% (*v*/*v*) ethanol was also performed. The qualitative and quantitative analyses of the components in the selected extracts were performed with gas chromatography coupled with mass spectrometry (GC-MS). The antioxidant activities of the extracts were evaluated with the DPPH and ABTS methods. The extracts of three plant materials with the highest antioxidant activities—dried *Rosmarinus officinalis* leaves, dried *Salvia officinalis* L. leaves, and dried and ground *Pinus sylvestris* L. cones—were selected to be incorporated in cosmetic emulsions containing glyceryl monostearate and Olivem 1000 as emulsifiers. The stabilities and antioxidant activities of the emulsions were evaluated. Moreover, the antimicrobial properties of the emulsions using microbiological tests were also determined. The findings suggest that the prepared emulsions are stable cosmetic products with a high antioxidant potential.

Keywords: α-pinene; *Pinus sylvestris* L. cone; *Rosmarinus officinalis* leaves; *Salvia officinalis* L. leaves; antioxidant activity; DPPH; ABTS; emulsion

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1. Introduction

α-Pinene is a bicyclic, unsaturated terpene hydrocarbon widely found in nature. Natural sources of α-pinene include coniferous trees, such as juniper [1], spruce [2], fir [3], and pine [4], and herbs and fruits. This monoterpene compound can be obtained from various parts of the pine tree, such as needles [5], branches [6], and cones [7], as well as from many herbs, such as sage [8], lovage [9], thyme [10], chamomile [11], and black pepper [12]. α-Pinene is the main component of rosemary oil with anticancer, anti-inflammatory, and antioxidant activity [13]. This monoterpene can be found in citrus fruits, such as tangerines [14], grapefruits [15], lemons [16], and oranges [17], as well as in other fruits such as watermelons [12] and walnuts [18]. This compound has a specific, fresh, pine-like scent [12,19]. Due to its valuable chemical properties, it is frequently used in the chemical and perfumery industries as well as in medicine [20].

α-Pinene exhibits a number of therapeutic properties. This compound has been shown to be active against Gram-positive and Gram-negative bacteria [21]. It was observed that it is effective in inhibiting ovarian and liver cancer [12]. Moreover, α-pinene has anti-inflammatory [22], antifungal [23], and antinociceptive properties [24] and exhibits anti-osteoarthritis, anti-ulcerogenic, and gastroprotective effects [5].

The antioxidant activities of ethanolic extracts or essential oils obtained from pinene-containing plants were described in several scientific reports. However, different methods of producing the extracts were used in these studies. Therefore, it is very difficult to compare the results obtained in these studies. An example of different processing methods is the research on rosemary. Christopolou et al. [25] studied the antioxidant activity of the essential oil obtained from fresh rosemary leaves. In that study, an ethanolic extract was prepared from 8-day old dried leaves, which were then subjected to maceration for 25 days in 40 mL of solvent containing 38% (*v*/*v*) ethanol at 20–25 °C. Both the essential oil and the extract exhibited good antioxidant activity, but rosemary essential oil was far more effective than the ethanolic extract [25]. A different processing method for the preparation of rosemary extracts is the work of Kamli et al. [26]. In these studies, the plant material was first dried in the shade at 30 ± 2 °C, then crushed in a blender, followed by filtering the powdered material using a sieve of about a 0.3 mm aperture size. This material was then individually extracted with each of these three organic solvents, ethyl acetate, ethanol, and water, for 48 h using a Soxhlet extractor. The extracted material was concentrated and was stored at −80 °C for future use. These studies showed that the antioxidant potential of the three extracts tested was in the following order: ethyl acetate > ethanol > aqueous [26].

The unique structure of α-pinene allows for this monoterpene compound to be used as a raw material in the synthesis of valuable organic compounds, which can be applied in the perfume, food, agricultural, and pharmaceutical industries. As an example, verbenone, one of the main products of α-pinene oxidation, is used as a cough suppressant and as an insect repellent. Camphor, derived indirectly from α-pinene, is applied as a flavoring, pharmaceutical, and cosmetic agent and as a plasticizer. Other α-pinene derivatives such as sabinene, thujone, thujene, and umbellulate are used as food flavorings, perfume ingredients, and antimicrobial agents [20].

An interest in emulsions and their applications has increased over the years, as they can be beneficial in many applications [27,28]. Emulsions contain aqueous and oil phases, and in order to obtain a stable emulsion, emulsifiers are added. Recently, substances of natural origin were used as emulsifiers. One such emulsifier is Olivem 1000, which consists of cetearyl olivate and sorbitan olivate [29], and emulsions containing natural active substances with this emulsifier were produced [28].

The use of ethanolic extracts obtained from α-pinene-containing plants to prepare emulsions using Olivem 1000 as the emulsifier has not been described in the scientific literature so far. Similarly, the antioxidant activities of emulsions obtained in this way was not tested. These are two directions of research that are new in our work compared to the current state of knowledge.

The purpose of the first stage of our research was to examine the possibility of using the ultrasound-assisted extraction (UAE) method to obtain ethanolic extracts from α-pinene-containing plants, such as *Pinus sylvestris* L., *Rosmarinus officinalis*, *Levisticum officinale*, and *Salvia officinalis*. These extracts were performed with 40% (*v*/*v*), 70% (*v*/*v*), and 96% (*v*/*v*) ethanol. The antioxidant activities of these extracts were evaluated with the

DPPH and ABTS methods. To verify whether the selected plants contain α-pinene, the ethanol extracts were subjected to an analysis with the GC-MS method.

In the second stage, for selected plant materials, Soxhlet extraction with 96% (*v*/*v*) ethanol was also performed. Both ultrasound-assisted extraction and Soxhlet extraction are known as methods that lead to good recovery of the active compounds from the plant material. Additionally, UAE is a green technique with low solvent consumption, and the aim of our research was to assess the possibility of using this method compared to the more classic ones.

In the next phase of our study, emulsions containing ethanolic extracts with the highest antioxidant activities were prepared using glycerol monostearate and Olivem 1000 as emulsifiers, and their stabilities were evaluated. The aim of this investigation was to determine whether it would be possible to produce stable emulsions with Olivem 1000 as well as to compare the emulsifying abilities of Olivem 1000 and glycerol monostearate. The optimal amount of α-pinene extract that is to be added to obtain the stable emulsion was also evaluated. The antioxidant activities of the emulsions were studied, and microbiological tests were performed to determine their antimicrobial properties. The aim of this latter investigation was to investigate how ethanolic extracts containing α-pinene affect the presence of bacteria and fungi in these emulsions.

Our research is intended to constitute a scientific basis for emphasizing the importance of extracts containing α-pinene as ingredients with antioxidant properties and may constitute a starting point for the development of cosmetic preparations with high antioxidant activity.

2. Materials and Methods

2.1. Raw Materials

For the ultrasound-assisted extractions, the plant materials were individually extracted with 40% (*v*/*v*), 70% (*v*/*v*), and 96% (*v*/*v*) ethanol. The 40% (*v*/*v*) and 70% (*v*/*v*) ethanol solutions were prepared from 96% (*v*/*v*) ethanol (Stanlab, Lublin, Poland) via dilution with water. The following plant materials were used for the preparation of ethanolic extracts: fresh parts of *Pinus sylvestris* L., such as cones, needles, and branches, as well as dried unground and ground pinecones (Tanowo, Poland); dried and fresh *Rosmarinus officinalis* leaves (Rolpol Agra, Tarkowo Górne, Poland); dried *Levisticum officinale* leaves (Rolpol Agra, Tarkowo Górne, Poland); and dried *Salvia officinalis* L. leaves (Rolpol Agra, Tarkowo Górne, Poland).

Raw materials for the extraction of α-pinene using the Soxhlet apparatus consisted of the following (shown in Figure 1): dried *Rosmarinus officinalis* leaves (Rolpol Agra, Tarkowo Górne, Poland); dried *Salvia officinalis* L. leaves (Rolpol Agra, Tarkowo Górne, Poland); and dried and ground *Pinus sylvestris* L. cones (Tanowo, Poland). A concentration of 96% (*v*/*v*) ethanol (Stanlab, Lublin, Poland) was used to extract α-pinene from these raw materials.

Figure 1. Raw plant materials selected for the studies: 1—dried *Rosmarinus officinalis* leaves, 2—dried *Salvia officinalis* L. leaves, 3—dried ground *Pinus sylvestris* L. cones.

The following components were used to prepare the emulsions: cetyl alcohol, lanolin, almond oil (all from Zrób sobie krem, Prochowice, Poland), and glycerin (Sigma Aldrich, Poznań, Poland). Glyceryl stearate (Zrób sobie krem, Prochowice, Poland) and Olivem 1000 (EcoSpa, Józefosław, Poland) were used as emulsifiers.

2.2. Ultrasound-Assisted Extraction of Plant Materials

The method of performing the ultrasonic-assisted extraction process was adopted based on the results of the research conducted and described in our previous works [30–32].

To prepare the extracts into glass tubes fitted with glass stoppers, 0.5 g of the appropriate plant material was placed, and then, 9.5 mL of solvent—40% (*v*/*v*), 70% (*v*/*v*), or 96% (*v*/*v*) ethanol—was added. Each set of 9 stoppered tubes containing one type of raw material and one of the solvents described above was subjected to ultrasound-assisted extraction (Polsonic, Poland working at a frequency of 40 kHz) for 15, 30, or 60 min, respectively. No heating was used during the extraction.

After the extraction, the contents of the tubes were filtered using filter strainers to separate the plant residues from the extract. The extracts were stored in tightly sealed glass vials in the dark at room temperature in the same solvent in which they were extracted until the antioxidant activity was determined.

Ultrasound-assisted extraction is a green extraction technique due to, among other factors, low solvent consumption, reduction of extraction time and energy consumption, safety, and environmental friendliness [33].

2.3. Extraction of Plant Materials Using Soxhlet Apparatus

A 100 mL Soxhlet apparatus, consisting of a 500 mL round-bottom flask, a reflux condenser, and a heating mantle, was used to prepare extracts from the following selected plant materials: dried *Rosmarinus officinalis* leaves, dried *Salvia officinalis* L. leaves, and dried and ground *Pinus sylvestris* L. cones. In this method, 10 g of the appropriate plant material was put into a thimble in the Soxhlet apparatus, then 200 mL of 96% (*v*/*v*) ethanol was added into the round-bottom flask, and the extraction was performed for 1 h. Extracts obtained using the Soxhlet method were subjected to further processing (i.e., filtration using filter papers) that was similar to those obtained using the ultrasound-assisted extraction method. We attempted to remove the solvent from the obtained extracts using an evaporator, but the yield of the process was very low; hence, we added dissolved extracts, not dry ones, to the emulsion.

2.4. Analysis of Ethanol Extracts by GC-MS

The ethanol extracts were subjected to qualitative and qualitative analysis with the gas chromatography coupled with mass spectrometry (GC-MS) method in order to identify the various components in the extracts [34].

The apparatus for this analysis consisted of a Trace 2000 gas chromatograph (ThermoQuest/CE Instruments, Milan, Italy) with a Voyager quadrupole mass spectrometer (ThermoQuest/Finnigan, MassLab Group, Manchester, UK) operated in electron impact ionization (EI+) mode. An Agilent J&W DB-5MS column with a length of 30 m, an inner diameter of 0.25 mm, and a layer thickness of 0.5 μm was used. Helium, grade 6 (Air Liquid, Szczecin, Poland), was used as the carrier gas at a constant flow rate of 1 mL/min. The temperature of the split/splitless injector was 200 °C. Sample volumes of 0.1 μL were injected manually into the injection port of the gas chromatograph by means of a 1-microliter syringe. The oven was maintained at 50 °C for 2.5 min, and then, the temperature was increased by 10 °C/min to 300 °C and maintained for 4 min. The temperature of the transfer line was 200 °C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. Mass spectra were obtained in full-scan mode in the mass range *m*/*z* 35–500.

Identification of the individual compounds present in the extracts was performed by comparing their mass spectra with those of the standards from REPLIB. In all experiments, the spectra were examined manually in Qual Browser. Quantitative GC-MS analysis was performed using the surface normalization method. The relative content [%] of individual compounds in the extracts was determined using Xcalibur software version 1.2 as the percentage of the area of their peaks relative to the total peak area of all compounds in the chromatogram.

2.5. Antioxidant Characterizations of Ethanolic Plant Extracts via Spectrophotometric Methods

The antioxidant activities of ethanolic extracts obtained from plants containing α-pinene were evaluated with the spectrophotometric method based on DPPH and ABTS radical reduction, as previously described [35,36]. The absorbances at 517 nm (DPPH) and 734 nm (ABTS) wavelengths were measured using a Hitachi U-5100 Spectrophotometer. Activity was expressed as Trolox equivalent antioxidant capacity (TEAC) [mg Trolox/g].

The antioxidant activities of emulsions were evaluated via the spectrophotometric method based on DPPH radical reduction by measuring the absorbance at 517 nm. Activity was expressed as radical scavenging activity [%RSA] as follows:

$$\%RSA = \left(1 - \frac{A_t}{A_0}\right) \times 100\%,$$

where A_t is the absorbance of the tested sample and A_0 is the absorbance of the control sample.

DPPH and ABTS calibration curves were prepared based on the relationship of %RSA versus Trolox concentration and the relationship of absorbance versus Trolox concentration. The Supplementary Equations (S1) and (S2) present the calibration curves.

Evaluation of the Antioxidant Activities of Ethanol Extracts Obtained from Plants Containing α-Pinene

- DPPH method

An aliquot of 2500 µL of working ethanolic DPPH radical solution (absorbance 1.00 ± 0.02 at 517 nm) was introduced into a spectrophotometric cuvette, and then, 132 µL of extract was added, and the contents were mixed. The incubation time was 10 min at room temperature, and after this time, absorbance measurements were taken at 517 nm. All the analyses were performed in 3 replicates, and the results were expressed as Trolox equivalent antioxidant capacity (TEAC) in mg/g [35,36].

- ABTS method

An aliquot of 2500 µL of 7 mM ABTS solution was introduced into a spectrophotometric cuvette, and then, 25 µL of extract was added. The contents of each cuvette were mixed by shaking and then incubated at room temperature for 6 min. After this time, the absorbance was measured at 734 nm. All the analyses were performed in 3 replicates, and the results were expressed as Trolox equivalent antioxidant capacity (TEAC) in mg/g [35,36].

2.6. Preparation of Emulsions with Ethanolic Plant Extracts

In the first step, a standard emulsion was prepared without extract. For this purpose, 6.00 g glyceryl stearate or 6.00 g Olivem 1000, 0.500 g cetyl alcohol, 1.00 g lanolin, and 2.00 g almond oil were introduced into the tube. The whole mixture was heated in a water bath at 80 °C until the ingredients dissolved. Next, 36.50 g of water and 1.50 g of glycerin were introduced into a 50 mL glass beaker, and here too, the whole mixture was heated in a water bath at 80 °C until the ingredients dissolved. Then, the oil phase was added to the water phase, and the mixture was mixed with a recipe mixer from Eprus at 1960 rpm for 5.45 min.

In the second stage, emulsions were prepared with the addition of extracts from three plant materials with the highest antioxidant activity, i.e., dried *Rosmarinus officinalis* leaf extract, dried *Salvia officinalis* L. leaf extract, and dried and ground *Pinus sylvestris* L. cone extract (Figure 2).

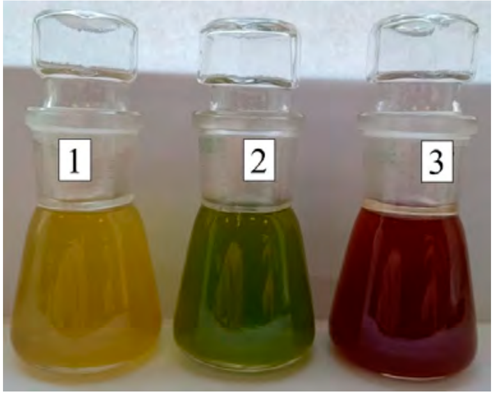


Figure 2. Ethanolic extracts: 1—dried *Rosmarinus officinalis* leaf extract, 2—dried *Salvia officinalis* L. leaf extract, 3—dried and ground *Pinus sylvestris* L. cone extract.

For this purpose, 6.00 g of glyceryl stearate emulsifier or 6.00 g of Olivem, 0.50 g of cetyl alcohol, 1.00 g of lanolin, and 2.00 g of almond oil were introduced into the tube. The whole mixture was heated in the water bath at 80 °C until the ingredients dissolved. Next, 12.75 g to 32.94 g water and 1.50 g glycerin were introduced into a 50 mL glass beaker. The beaker was heated in a water bath at 80 °C until the ingredients dissolved. The oil phase was added to the water phase, and the emulsion was cooled to 40 °C. Then the extracts were added in the following amounts: 7.5%; 10.0%; 12.5%; 15.0%; 17.5%; 20.0%; 22.5%; 25.0%; 27.5%; 30.0%; 40.0%; 50.0% to the total. The whole mixture was mixed using Eprus mixer at 1960 rpm for 5.45 min.

Evaluation of the Stabilities and pH of the Emulsions

To test the stabilities of the resulting emulsions, 5.0 g of emulsion was collected in the glass tube and centrifuged at a speed of 3500 rpm (1776× *g*).

The pH of each resulting emulsion was tested using a pH meter.

2.7. Testing the Antioxidant Activities of Emulsions

To test the antioxidant potential of the prepared emulsions, 1.0 g of emulsion was placed in the glass flask, then 9.0 g of acetone was added. The whole mixture was stirred at 500 rpm for 30 min. After this time, 2500 µL of working DPPH solution was added into the glass cuvette, then 132 µL of the mixture (emulsion or acetone) was added, and the content of each cuvette was mixed by shaking. Three samples were made for each mixture. The incubation time was 10 min at room temperature, and after this time, absorbance measurements were taken at 517 nm.

2.8. Testing the Antimicrobial Stabilities of Emulsions

The antimicrobial stabilities of selected emulsions with the highest antioxidant activities (the highest activity of the evaluated plant material) were determined using microbiological tests. These emulsions contained extracts of dried *Rosmarinus officinalis* leaves (amount of extract 22.5% and 25.0%), dried *Salvia officinalis* L. leaves (amount of extract 22.5%), dried ground *Pinus sylvestris* L. cones (amount of extract 22.5%), and the reference emulsion.

For microbiological tests, sterile plates with the medium applied on both sides were used. Two types of medium (*Mikrocount DUO*) were applied: the medium on the pink background was Rose Bengal Agar medium for yeast and mold determinations, and the yellow medium was *TTC* agar for incubation of bacteria.

In order to examine the antifouling stabilities of the selected emulsions, a very thin layer of emulsion was gently spread over the entire surface on both sides of the plate. The plate with the applied emulsion was then placed in a vial and the cap was tightly screwed on. The plates were then placed in an incubator heated to 30 °C for 4 days.

2.9. Statistical Analysis

Statistical analysis was performed using StatSoft Statistica 13.0 (STATISTICA 13.0; StatSoft Inc., Palo Alto, CA, USA) and Microsoft Excel 2021. Distributions of values for individual parameters were analyzed using the Shapiro–Wilk test. Since the distribution of continuous variables differs from normal, the Kruskal–Wallis test was used to evaluate the differences between the studied parameters. Results were expressed as mean ± standard deviation (SD), and the statistical significance of the differences was determined based on median, upper quartile, and lower quartile. Spearman's correlation test was used to determine the correlations between the parameters studied. Differences were considered significant at $p \leq 0.05$.

3. Results and Discussion

3.1. Ultrasound-Assisted Extraction of Plant Materials

Ultrasound-assisted extraction was applied to obtain 81 ethanol extracts. The extracts varied in color depending on the plant material used, the concentration of the solvent, and the extraction time.

3.2. Extraction of Plant Materials Using Soxhlet Apparatus

As a result of extraction with a Soxhlet apparatus, as expected, three differently colored extracts were obtained depending on the plant material used.

3.3. Analysis of Ethanol Extracts by GC-MS

The presence of α-pinene in the ethanolic extracts was confirmed by the GC-MS analysis. In addition to α-pinene, compounds such as acetic acid, androstane-11, camphor, eucalyptol, verbenone, and others were determined in higher amounts. The detailed results of the GC-MS analyses are summarized in Supplementary Tables S1 and S2.

The main compound whose content in the extracts we were most interested in was α-pinene. The highest concentration of α-pinene in extracts obtained with ultrasound-assisted extraction was found for ethanolic extracts of dried *Rosmarinus officinalis* and *Levisticum officinale* leaves (14.5% and 9.6%, respectively). However, a comparison of extracts obtained with the two methods tested in this work (for dried *Rosmarinus officinalis* leaves, dried *Salvia officinalis* L. leaves, and dried and ground *Pinus sylvestris* L. cones) shows a significant reduction in the α-pinene content in extracts obtained in the Soxhlet apparatus. For the extract from dried *Rosmarinus officinalis* leaves, the α-pinene content decreased from 14.54% to 2.21% (almost a 7-fold reduction); for the extract from dried Salvia *officinalis* L. leaves, the content decreased from 4.83% to 2.85% (nearly a 2-fold reduction); and for the extract from dried and ground *Pinus sylvestris* L. cones, it decreased from 4.70 to 1.01% (almost a 5-fold reduction). The results presented in Supplementary Tables S1 and S2 indicate that the use of the Soxhlet extraction method was less effective. The reasons for this may be various: too short of an extraction time in the Soxhlet apparatus or a too-high temperature of the extraction medium in the Soxhlet apparatus, leading to the thermal decomposition of the extract components, mainly α-pinene (the boiling point of α-pinene is 155 °C [37]). Ultrasonic-assisted extraction was performed at an ambient temperature (approximately 25 °C, and no significant heating of the contents of the test tubes was observed during extraction). On the other hand, extraction in the Soxhlet apparatus was carried out at a temperature that was slightly lower than the boiling point of ethanol (the boiling point of ethanol is 78 °C [38]), as it was condensed in the cooler, which resulted in lowering its temperature.

To determine whether the extraction temperature in the Soxhlet apparatus may reduce the amount of α-pinene obtained (by causing the decomposition of this compound), we performed additional studies. In these studies, we extracted fresh pine needles in the Soxhlet apparatus using the two-stage extraction method. The α-pinene content in the extract obtained in this way was 20.39%. This method involved weighing about 10.0 g of plant material and placing it in the Soxhlet apparatus, and then, about 200 mL of 96% (*v*/*v*) ethanol was poured into the flask. After 6 h, the pine needles used in the extraction process were removed, another portion of fresh pine needles was weighed, and the extract obtained from the first stage of extraction served as the extraction agent in the second stage. In the second stage, extraction was also performed for 6 h. The results may therefore indicate that the extraction time using the Soxhlet apparatus in our comparative studies was most likely too short and that in future studies, this extraction time should be extended or even a multi-stage extraction should be used.

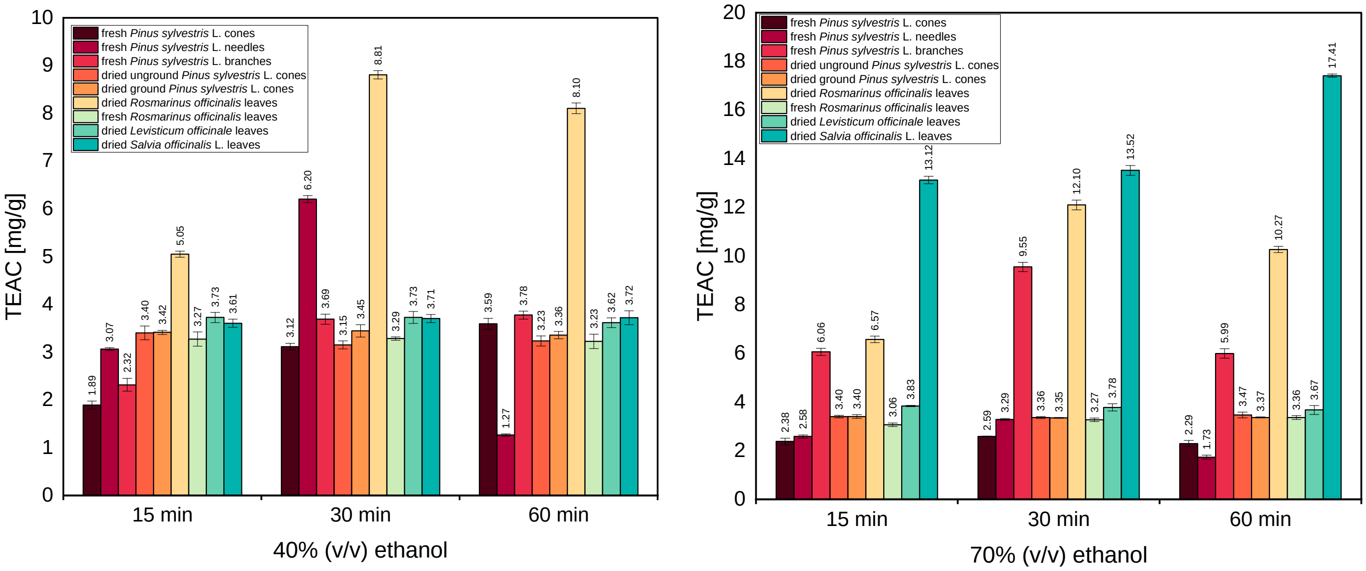
3.4. Evaluation of the Antioxidant Activities of Ethanolic Extracts Obtained from Plants Containing α-Pinene

3.4.1. Extracts Prepared with Ultrasound-Assisted Extraction

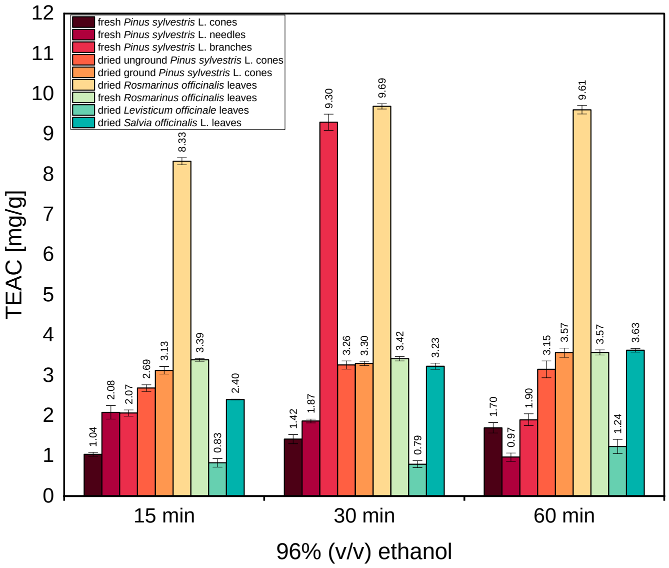
- DPPH method

Figure 3a–c show the antioxidant activities of ethanolic extracts in 40% (*v*/*v*), 70% (*v*/*v*), and 96% (*v*/*v*) ethanol, respectively, evaluated with the DPPH method.

Figure 3a shows that among the tested ethanolic extracts in 40% (*v*/*v*) ethanol, the highest antioxidant activities (5.05, 8.81, and 8.10 mg/g, for extraction times of 15 min, 30 min, and 60 min, respectively) were shown by the ethanolic extracts obtained from dried *Rosmarinus officinalis* leaves. Also noteworthy is the high TEAC value observed for fresh *Pinus sylvestris* L. needles—6.20 mg/g—after a 30 min extraction time. The TEAC values for extracts obtained from other raw plant materials were much lower and ranged from 1.89 to 3.78 mg/g.



(**a**) (**b**)



(**c**)

Figure 3. The antioxidant activities of ethanolic extracts in (**a**) 40% (*v*/*v*) ethanol, (**b**) 70% (*v*/*v*) ethanol, (**c**) 96% (*v*/*v*) ethanol, evaluated with the DPPH method. Vertical lines represent the standard deviation (SD).

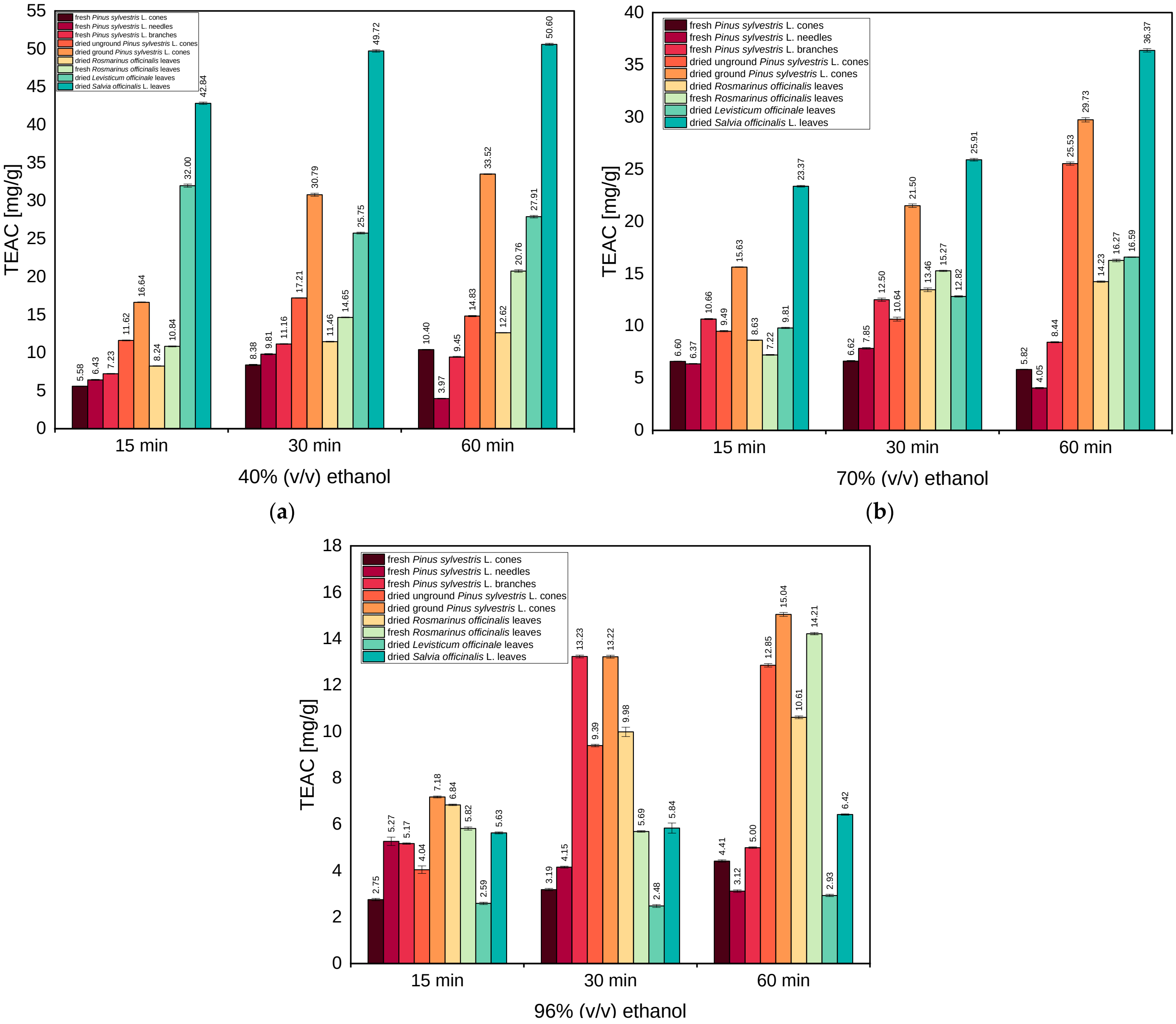
Figure 3b shows that with 70% (*v*/*v*) ethanol, the highest TEAC values were observed for extracts obtained from dried *Salvia officinalis* L. leaves. For these extracts, the TEAC value increases with increasing extraction time from 13.12 mg/g (15 min) to 17.41 mg/g (60 min). It can also be seen from the figure that high values were obtained for extracts prepared with the dried *Rosmarinus officinalis* leaves; the TEAC value increased with increasing extraction time from 6.57 mg/g (15 min) to 12.10 mg/g (30 min), though there was a small decrease to 10.27 mg/g after 60 min, as was also the case with 40% (*v*/*v*) ethanolic extraction (Figure 3a). Thus, for this *Rosmarinus* dried plant material, a comparison of the antioxidant activity results obtained for extracts prepared with 40% (*v*/*v*) and 70% (*v*/*v*) ethanol shows that it is beneficial to perform the extraction for a maximum of 30 min. Additionally, it can be seen that for this plant material, increasing the concentration of ethanol used for extraction from 40% to 70% causes an increase of approximately 50% in the TEAC value for the extraction time of 30 min. Also noteworthy are the high TEAC values obtained for the extract from fresh *Pinus sylvestris* L. branches from 6.06 mg/g (15 min) to 9.55 mg/g (30 min).

Figure 3c shows that the extracts in 96% (*v*/*v*) ethanol obtained from dried *Rosmarinus officinalis* leaves have the highest antioxidant capacity, as was the case with the 40% ethanol extract. It can be observed that the TEAC value of the extract from this plant material remains at the level of 8.33–9.69 mg/g throughout the time range tested. For this plant material, using 96% ethanol yields nearly identical results for a 30 or 60 min extraction time. However, for 30 min extraction, this value is significantly lower than for extracts for this plant material obtained using 70% (*v*/*v*) ethanol. As in the case of extracts obtained from 70% (*v*/*v*) ethanol for 30 min extraction time, a high TEAC value (9.30 mg/g) was observed for the 96% ethanolic extract obtained from fresh *Pinus sylvestris* L. branches.

In summary, in almost all tests performed at this stage of our study, the highest TEAC values were generally found for extracts obtained from dried *Rosmarinus officinalis* leaves that were prepared for 30 min. Increasing the concentration of ethanol from 40% to 70%, used for the extraction of dried *Rosmarinus officinalis* leaves, increases the TEAC value to 12.10 mg/g for the extraction time of 30 min. The same ethanol concentration (70%) and the same extraction time (30 min) were also beneficial for the extraction of fresh *Pinus sylvestris* L. branches because the prolongation of the extraction time did not cause an increase in the TEAC values for this plant material. The use of ethanol at the concentration of 70% (*v*/*v*) was also beneficial to obtain the high values of TEAC for extracts from dried *Salvia officinalis* L. leaves. These were the highest TEAC values, 13.12 mg/g (15 min) to 17.41 mg/g (60 min), among those obtained for all extracts tested. For ethanol with other concentrations, such high TEAC values for this plant raw material were not observed.

- ABTS method

Figure 4a–c show the antioxidant activity of extracts in 40% (*v*/*v*), 70% (*v*/*v*), and 96% (*v*/*v*) ethanol, respectively, evaluated with the ABTS method.



(**a**) (**b**)

(**c**)

Figure 4. The antioxidant activities of ethanolic extracts in (**a**) 40% (*v*/*v*) ethanol, (**b**) 70% (*v*/*v*) ethanol, and (**c**) 96% (*v*/*v*) ethanol, evaluated with the ABTS method. Vertical lines represent the standard deviation (SD).

From Figure 4a, it can be seen that among the ethanolic extracts tested, the one obtained from dried *Salvia officinalis* L. leaves after the extraction time of 60 min shows the highest antioxidant activity (50.60 mg/g). High values of TEAC were also observed for shorter extraction times for this plant material (42.84 mg/g for 15 min and 49.72 mg/g for 30 min). Additionally, high TEAC values were obtained for extracts from dried *Levisticum* *officinale* leaves (for 15 min—32.00 mg/g, for 30 min—25.75 mg/g, and for 60 min—27.91 mg/g). Similar TEAC values (excluding the extraction time of 15 min) were also obtained for dried ground *Pinus sylvestris* L. cones, 16.64 mg/g (15 min), 30.79 mg/g (30 min), and 33.52 mg/g (60 min).

Figure 4b shows that for extracts obtained with 70% (*v*/*v*) ethanol, the highest TEAC value (36.37 mg/g) was also obtained for dried *Salvia officinalis* L. leaves after the extraction time of 60 min. However, TEAC values obtained for this plant material were slightly lower than for studies with 40% (*v*/*v*) ethanol. The observed TEAC values for dried ground *Pinus sylvestris* L. cones were also very similar to values obtained for extraction with 40% (*v*/*v*) ethanol, 15.63 mg/g (15 min), 21.50 mg/g (30 min), and 29.73 mg/g (60 min). For the extraction time of 60 min, a high TEAC value was observed for another plant material—dried unground *Pinus sylvestris* L. cones (25.53 mg/g).

Figure 4c shows that the highest TEAC values were obtained for dried ground *Pinus sylvestris* L. cones. The TEAC values for this plant material increased from 7.18 mg/g (15 min) to 15.04 mg/g (60 min). Additionally, high values of TEAC were obtained for fresh *Rosmarinus officinalis* leaves and dried unground *Pinus sylvestris* L. cones (14.21 mg/g and 12.85 mg/g, respectively). Also noteworthy is the high TEAC value for fresh *Pinus sylvestris* L. branches obtained after the 30 min extraction (13.22 mg/g). In general, however, the TEAC values obtained during extraction with 96% (*v*/*v*) ethanol are lower than those obtained using 40% (*v*/*v*) or 70% (*v*/*v*) ethanol.

In summary, in almost all tests, the highest values of TEAC were observed for dried *Salvia officinalis* L. leaves and dried ground *Pinus sylvestris* L. cones. It was also observed that extraction with ethanol with the highest concentration caused the decrease in the values of TEAC for all studied plant materials.

3.4.2. Soxhlet Extraction

During the studies on the antioxidant activities of the extracts obtained using the ultrasound-assisted extraction assessed with both the DPPH and ABTS methods, the ethanolic extracts obtained from dried *Rosmarinus officinalis* leaves showed the highest antioxidant activity. Moreover, it was observed that the antioxidant activities of the obtained ethanolic extracts increased in the following order: dried ground *Pinus sylvestris* L. cones < dried *Salvia officinalis* L. leaves < dried *Rosmarinus officinalis* leaves.

Since Soxhlet extraction is a standard technique used to obtain extracts, it was decided to compare the antioxidant activities of extracts obtained with this method with the extracts obtained using ultrasound-assisted extraction. Studies with a Soxhlet apparatus were performed for the three selected plant materials that were mentioned above. In the Soxhlet extraction, 96% (*v*/*v*) ethanol was applied.

Figure 5 shows the antioxidant activities of extracts in 96% (*v*/*v*) ethanol obtained with the Soxhlet apparatus and evaluated with the DPPH and ABTS methods.

Figure 5 shows that for extracts obtained in the Soxhlet apparatus, higher TEAC values were obtained for the DPPH method than for the ABTS method. This is a different result from that obtained using ultrasound-assisted extraction. For example, in the case of dried *Rosmarinus officinalis* leaves, these values for the DPPH method are more than three times higher. At the same time, it can be observed that the highest TEAC value was obtained for extracts obtained for dried *Rosmarinus officinalis* leaves, and this conclusion is similar to that from studies performed with ultrasound-assisted extraction, described earlier. A comparison of the results obtained at this stage of the studies with the results shown in Tables S1 and S2 shows that in the case of dried *Rosmarinus officinalis* leaves, there was a significant reduction in the α-pinene content from 14.5% (ultrasound-assisted extraction) to 2.21% (extraction in the Soxhlet apparatus); however, the extract still showed very good antioxidant properties—significantly higher in the DPPH method than the extract obtained using ultrasonic-assisted extraction. This means that other compounds present in this extract also influence its antioxidant effect. These compounds can be camphor and eucalyptol, whose antioxidant effects were also described in the scientific literature [39,40]. A comparison of the content of these compounds in extracts from dried *Rosmarinus officinalis* leaves shows that the concentration of these two compounds also decreased significantly in the extract obtained using the Soxhlet apparatus. However, new compounds, such as verbenol, were also determined in this extract. The antioxidant properties of verbenol have been described in the scientific literature [41]. However, determining which components of the extract have such a strong antioxidant effect requires further research.

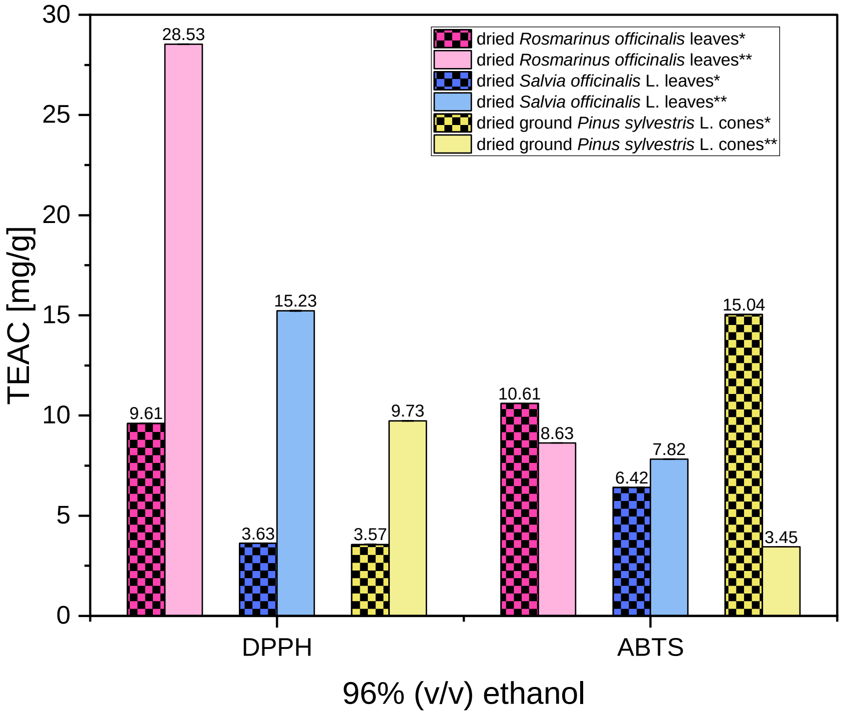


Figure 5. The antioxidant activities of ethanolic extracts in 96% (*v*/*v*) ethanol (60 min extraction time) obtained with the ultrasound-assisted extraction and the Soxhlet apparatus and evaluated with the DPPH and ABTS methods. Vertical lines represent the standard deviation (SD). * ultrasound-assisted extraction; ** the Soxhlet apparatus.

In summary, it can be concluded that ethanolic extracts obtained from plants containing α-pinene show different antioxidant activities, which depend mainly on the type of plant material, solvent concentration (ethanol), extraction time, method of extraction and method applied to evaluate the antioxidant activity of the extract (a summary table is given as Supplementary Table S3). Taking into account the above-mentioned parameters, the extract of dried *Salvia officinalis* L. leaves obtained with 40% (*v*/*v*) ethanol for 60 min using ultrasound-assisted extraction and evaluated with the ABTS method shows the highest antioxidant activity among the tested extracts. The next important conclusion that can be drawn from the research presented above is that ultrasound-assisted extraction as the method of obtaining extracts with high antioxidant capacity is a very effective method. It allows for obtaining such extracts in a short time and at a relatively low temperature, which allows for the reduction of the costs associated with, for example, conducting the continuous extraction process using the Soxhlet method at the boiling point of the extraction medium. In our future research, it would be necessary to determine which of the compounds present in the extracts, apart from α-pinene, can significantly influence the antioxidant activity of the extracts. Compounds such as camphor, eucalyptol, and verbenol should be taken into account.

3.5. Comparison with Other Studies

Several studies were performed to evaluate the antioxidant activities of the extracts obtained from plants containing α-pinene. However, the methods of obtaining extracts and establishing the antioxidant activity presented in these studies were different from the methods applied in our study. Therefore, it is very difficult to compare our results with those previously described in the scientific literature. Below, we present the most important literature reports regarding the determination of the antioxidant activities of extracts obtained from plant materials containing α-pinene and the description of the methods applied to obtain extracts.

In the work of Christopoulou et al. [25], the ethanolic extract from rosemary was obtained from leaves dried for 8 days, which then were subjected to maceration for 25 days in 40 mL of solvent containing 38% (*v*/*v*) ethanol at 20–25 °C. In comparison with the ultrasound-assisted extraction method used in our study, this method required a very long extraction time, as much as 25 days. On the other hand, the preparation of our extracts took a relatively short time, maximum 60 min. The antioxidant activities of the ethanolic rosemary extracts were tested with DPPH, ABTS, and FRAP assays. Using the first method, the free radical scavenging activity, expressed in mg BHT/mL, was in the range of 1.04 ± 0.06 mg/mL. The ferric-reducing power evaluated with the FRAP method expressed in mg $FeSO_4$/mL was 0.52 ± 0.05 mg/mL. The antioxidant activity determined with the ABTS method was in the range of 0.25 ± 0.02 mg Trolox/mL [25].

Kamli et al. [26] also studied the antioxidant activities of rosemary extracts, which they prepared as described in the Introduction above. The powdered plant material was extracted with three organic solvents, ethyl acetate, ethanol, and water, for 48 h using a Soxhlet extractor. The extracted material was concentrated and was stored at −80 °C for future use. The method of obtaining extracts used in their work is therefore very time-consuming, and such long extraction times at elevated temperatures may lead to changes in the structure of biologically active compounds as a result of thermal decomposition, isomerization, oxidation, or oligomerization. The antioxidant potential of the three extracts tested was found to be in the order of ethyl acetate > ethanol > aqueous, with IC50 values (the required concentration of extract sample for scavenging of 50% DPPH free radicals) of 272 μg/mL, 387 μg/mL, and 534 μg/mL, respectively. Moreover, the total phenolic content of various rosemary extracts was estimated with the Folin–Ciocalteu method and was represented as gallic acid equivalents (GAE/g extract). A significant amount of the phenolic content of 804 GAE /g extracts was found in ethyl acetate extract, followed by ethanolic (473 GAE/g) and aqueous (273 GAE/g).

Saini et al. studied the antioxidant activity of the ethanolic extract of rosemary leaves with the DPPH and ABTS methods. The higher antioxidant activity of 70 ± 4.67 μg/mL was obtained when the second method was used. In contrast, the antioxidant activity evaluated with the DPPH method was in the range of 40.76 ± 2.81 μg/mL. In their work, the extract for antioxidant tests was prepared in the following way: rosemary leaves were dried at 50 °C for 12 h followed by grinding and sieving. Powdered leaves were extracted with 70% ethanol for 24 h at 40 °C. The extract was collected and concentrated under reduced pressure, and the semisolid mass was dried overnight at 50 °C to obtain the dried extract. The extracts were reconstituted with the same solvent as used for the extraction to obtain 5% solutions and stored at 4 °C [42]. The method of preparing the extract for antioxidant tests presented in their work is very complicated and time-consuming compared with ultrasound-assisted extraction. Their extraction process lasted 24 h, followed by drying the extract and then diluting it for antioxidant tests.

Mokhtari et al. evaluated the antioxidant potential of the methanolic sage extract with the DPPH and FRAP methods. The antioxidant activity of this extract measured with the DPPH method (EC50—extract concentration reducing the absorbance of DPPH by 50%) was 77.21 ± 2.61 $\mu g\text{-}mL^{-1}$, whereas the ferric reduction potential measured with FRAP was 69.21 ± 2.61 mM Fe(II) mg^{-1} extract. In this work, the air-dried sage was ground, and next, its extract was obtained using the ultrasound-assisted extraction procedure [19], where

100 g of each ground sample was mixed with 500 mL of methanol (70%) and the mixture was sonicated in the ultrasonic bath. The solvent excess was evaporated, and the concentrated extracts were stored and freeze-dried at −18 °C [43]. In their research, the authors used ultrasound-assisted extraction, as was performed in our study, but they used methanol, which is an unfit extractant for subsequent cosmetic applications of extracts. Additionally, a significantly larger amount of plant material and solvent were used: 200 times more plant material and about 50 times more solvent. For this reason, this method of obtaining extracts seems to be less beneficial compared with our technique.

Abdelkader et al. used the DPPH method to evaluate the antioxidant activity of the methanolic extract from *Salvia officinalis* leaves. The antioxidant activity of the extract was 130.56 ± 0.87 µg/mL [44]. Their method for obtaining extracts for antioxidant studies was complicated. The leaves of *Salvia officinalis* L. were dried immediately after harvesting in a shady place over a two-week period. Next, they were packed in paper bags and kept in the dark, and after that, the leaves were crushed using the house blender. The fresh aerial part of *Salvia officinalis* L. material was subjected to hydrodistillation for approximately 4 h in a Clevenger-type apparatus. The distilled essential oils were dried over anhydrous sodium sulfate and stored in tightly closed dark vials at 4–6 °C before analysis. The diluted working solutions of the test extracts were prepared in methanol.

In the work of Farhat et al. [37], the antioxidant activities of methanolic extracts of *Salvia officinalis* were evaluated with the DPPH, ABTS, and FRAP methods. The following antioxidant activity results were obtained: 16.91 ± 0.44 µg/mL (DPPH method), 318.62 ± 14.40 µM TE/mg (ABTS method), and 180.56 ± 19.30 mM Fe(II)/mg (FRAP method) [45]. Also in this case, the method used for obtaining extracts for antioxidant studies was complicated. In their work, the plant material was dried at room temperature until it reached a constant weight. Aerial parts of each sample were subjected to hydrodistillation for 3 h using the Clevenger-type apparatus. The oil obtained was separated from water, dried over anhydrous sodium sulfate, and kept in amber vials at 4 °C. The distilled plant material was dried at 35 °C until it reached a constant weight and then finely ground to pass a 2 mm sieve. For the extraction, dried samples of 0.5 g were first homogenized with 30 mL of petroleum ether under magnetic stirring for 5 min and dried at room temperature. Second, the samples were extracted using 150 mL of methanol in a Soxhlet extractor for 2 h under a nitrogen atmosphere.

Venkatesan et al. [38] studied the antioxidant activities of ethanol extracts obtained from pine needles. The dried needles were ground in the laboratory blender into fine powder. About 10 g of needle powder was extracted with different ratios of ethanol to distilled water at 60 °C for 15 h. The ethanolic extract obtained from *Pinus densiflora* needles with 20% (*v*/*v*) ethanol showed the antioxidant activity measured with the ABTS method of 9.02 ± 0.55 µg/mL and with the DPPH method of 83.70 ± 6.22 µg/mL. These studies showed that the concentration of ethanol used for the extraction greatly affects the extract's antioxidant activity [46]. The conclusion presented in the above work agrees with that of our research reported in this article. However, in our studies, the most favorable ethanol concentration was 40% (*v*/*v*) or 70% (*v*/*v*), depending on the method used to measure antioxidant capacity.

Four methods, namely ABTS, DPPH, FRAP, and CUPRAC (CUPric Reducing Antioxidant Capacity), were used to test the antioxidant activity of the ethanolic extract obtained from *Scots pine*. The extract was obtained with a very time-consuming method in which the fresh green cones were cut into small pieces and the plant material was extracted using 5 times the volume of 90% ethanol under continuous mixing (250 rpm, 25 °C). Extraction was performed at 25 °C in the dark for 10 days. The following antioxidant activity results were obtained: 8.56 ± 0.43 mg/mL (ABTS method), 13.82 ± 0.69 mg/mL (DPPH method), 11.27 ± 0.56 mg/mL (FRAP method), and 10.90 ± 0.55 mg/mL (CUPRAC method) [47].

Šarac et al. examined the antioxidant activity of the methanolic extract of essential oil obtained from *P. nigra ssp. nigra* using the DPPH and ABTS methods. Using the first method, the antioxidant activity was 25.60 mg/mL, and for ABTS, the activity was 0.58 ± 0.005 mg/mL [48]. The essential oil was obtained with the hydrodistillation method. As in the case of the works cited above, this method is much more complicated compared with the ultrasound-assisted extraction method that we propose in this work in order to obtain extracts with high antioxidant capacity.

3.6. Statistical Analysis

Our intention was to demonstrate that in this type of work, tests indicating the significance of differences between data are commonly used for statistical inference. First, it is necessary to check whether the results obtained during the study have a distribution that follows a normal distribution. For this purpose, a test such as the Shapiro–Wilk test is used. The null hypothesis for this test assumes that our research sample comes from a population with a normal distribution. If the Shapiro–Wilk test reaches statistical significance ($p < 0.05$), this indicates a distribution that deviates from the Gaussian curve.

Depending on the Shapiro–Wilk test-checked distribution of the data, parametric tests, e.g., the Student's *t*-test; one-way analysis of variance (ANOVA) (when the results obtained do not deviate from a normal distribution); or non-parametric tests, e.g., Wilcoxon test, Mann–Whitney test (when the results obtained deviate from a normal distribution), are used.

In our study, the distribution of results deviated from the normal distribution ($p < 0.05$), so non-parametric tests were used. The Kruskal–Wallis test [41,42], which is the equivalent of the ANOVA test in parametric testing, was used to assess the statistical significance of differences between data.

Descriptive statistics of antioxidant potentials measured with the DPPH and the ABTS methods are presented in the Supplementary Materials as Supplementary Tables S4 and S5, respectively.

Table 1 shows statistically significant differences between the antioxidant potentials evaluated with the DPPH method of the extracts shown in Figures 3–5.

Table 1. Statistically significant differences between the antioxidant potentials of the extracts measured with the DPPH method (at $p \leq 0.05$).

Ethanol Concentration [% (*v*/*v*)]	**Extraction Time (min)**		
	15	**30**	**60**
40	- dried *Rosmarinus leaves* vs. fresh *Pinus* cones	- dried *Rosmarinus leaves* - vs. fresh *Pinus* cones - dried *Rosmarinus leaves* - vs. dried unground *Pinus* cones	- dried *Rosmarinus* leaves vs. fresh *Pinus* needles
70	- dried *Salvia* leaves vs. fresh *Pinus* cones - dried *Salvia* leaves vs. fresh *Pinus* needles	- fresh *Pinus* cones - vs. dried *Rosmarinus leaves* - fresh *Pinus* cones vs. dried *Salvia* leaves	- dried *Rosmarinus leaves* vs. fresh *Pinus* needles - dried *Salvia* leaves vs. fresh *Pinus* cones - dried *Salvia* leaves vs. fresh *Pinus* needles
96	- dried *Rosmarinus leaves* vs. fresh *Pinus* cones - dried *Levisticum* leaves vs. dried and fresh *Rosmarinus leaves*	- dried *Levisticum* leaves vs. fresh *Pinus* branches - dried *Levisticum* leaves vs. dried *Rosmarinus leaves*	- dried *Rosmarinus leaves* vs. fresh *Pinus* needles - dried *Rosmarinus leaves* vs. dried *Levisticum* leaves

Table 2 shows statistically significant differences between the antioxidant potential values of the extracts shown in Figures 6–8.

Table 2. Statistically significant differences between the antioxidant potential values of the extracts measured with the ABTS method (at $p \leq 0.05$).

Ethanol Concentration [% (*v*/*v*)]	**Extraction Time (min)**		
	15	**30**	**60**
40	- dried *Salvia* leaves vs. fresh *Pinus* cones - dried *Salvia* leaves vs. fresh *Pinus* needles	- dried *Salvia* leaves vs. fresh *Pinus* cones - dried *Salvia* leaves vs. fresh *Pinus* needles - fresh *Pinus* cones. vs. dried unground *Pinus* cones	- dried *Salvia* leaves vs. fresh *Pinus* needles - dried unground *Pinus* cones vs. fresh *Pinus* needles
70	- dried *Salvia* leaves vs. fresh *Pinus sylvestris* cones - dried *Salvia* leaves vs. fresh *Pinus* needles	- dried unground *Pinus* cones vs fresh *Pinus* cones - fresh *Pinus* cones vs. dried *Salvia* leaves - - dried *Salvia* leaves vs. fresh *Pinus* needle	- dried *Salvia* leaves vs. fresh *Pinus* cones - dried *Salvia* leaves vs. fresh *Pinus* needles
96	- dried *Levisticum* leaves vs. dried unground *Pinus* cones	- dried *Levisticum* leaves vs. fresh *Pinus* branches - dried *Levisticum* leaves vs. dried unground *Pinus* cones	- dried unground *Pinus* cones vs. fresh *Pinus* needle - dried unground *Pinus* cones vs. dried *Levisticum* leaves

The statistical analysis showed positive correlations between the antioxidant potentials measured with the DPPH and ABTS methods. In addition, the higher the ethanol concentration, the stronger the correlation was found (for 40% r = 0.53, for 70% r = 0.69, for 96% r = 0.87). There was also a statistically significant, strong, positive correlation (r = 0.880) between the concentration of the extract in the emulsion and the emulsion's pH value. This means that as the concentration of the plant extract in the emulsion increased, its pH value increased.

3.7. Preparation of Emulsions with Ethanolic Extracts from Plants Containing α-Pinene

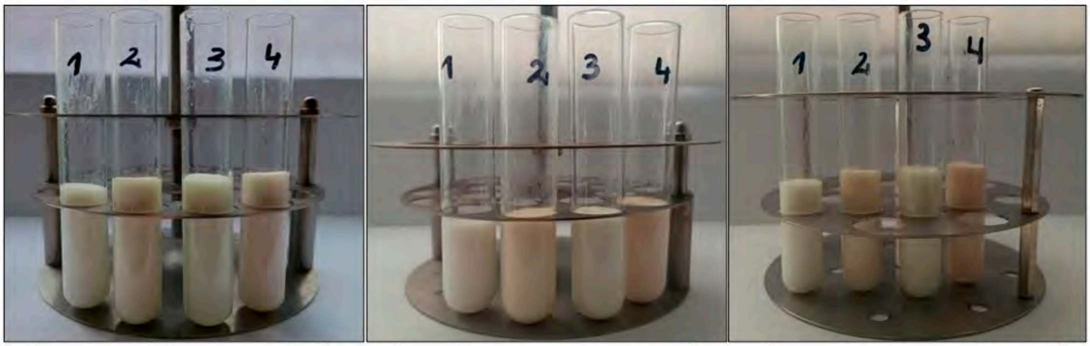
For the preparation of emulsion extracts, the plant materials with the highest antioxidant activity were selected for further study. The following materials were included: dried *Rosmarinus officinalis* leaves, dried *Salvia officinalis* L. leaves, and dried and ground *Pinus sylvestris* L. cones.

The Stability and pH of the Emulsions

Emulsions containing glycerol monostearate as an emulsifier were unstable. Supplementary Figure S2 shows these emulsions.

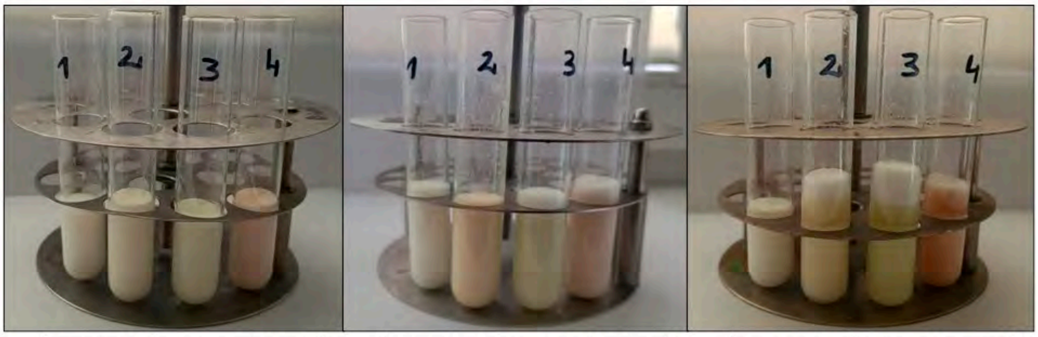
Emulsions containing Olivem 1000 as an emulsifier were prepared without an extract and with the addition of the following varying amounts of ethanolic extracts: 7.5%; 10%; 12.5%; 15%; 17.5%; 20%; and 22.5%. All these emulsions, without and with the extracts, were stable (Figures 6 and 7).

amount of extract 7.5% amount of extract 10% amount of extract 12.5%



amount of extract 15% amount of extract 17.5% amount of extract 20%

Figure 6. Emulsions containing Olivem 1000 as emulsifier: 1—base emulsion (without extract). With 7.5%, 10%, 12.5%, 15%, 17.5%, and 20% ethanolic extracts of the following plant materials: 2—dried *Rosmarinus officinalis* leaves, 3—dried *Salvia officinalis* L. leaves, 4—dried ground *Pinus sylvestris* L. cones.



amount of extract 22.5% amount of extract 25% amount of extract 27.5%

amount of extract 30% amount of extract 40% amount of extract 50%

Figure 7. Emulsions containing Olivem 1000 as emulsifier: 1—base emulsion (without extract). With 22.5%, 25%, 27.5%, 30%, 40%, and 50% ethanolic extracts of the following plant materials: 2—dried *Rosmarinus officinalis* leaves, 3—dried *Salvia officinalis* L. leaves, 4—dried ground *Pinus sylvestris* L. cones.

Figure 8 shows that the emulsion with the addition of dried *Rosmarinus officinalis* leaf extract in the amount of 25% was stable, while emulsions with the addition of the other two extracts in the same amount (25%) were unstable. Emulsions with the amount of extract above 25%, i.e., 27.5%, 30%, 40%, and 50%, were unstable regardless of the raw material used.

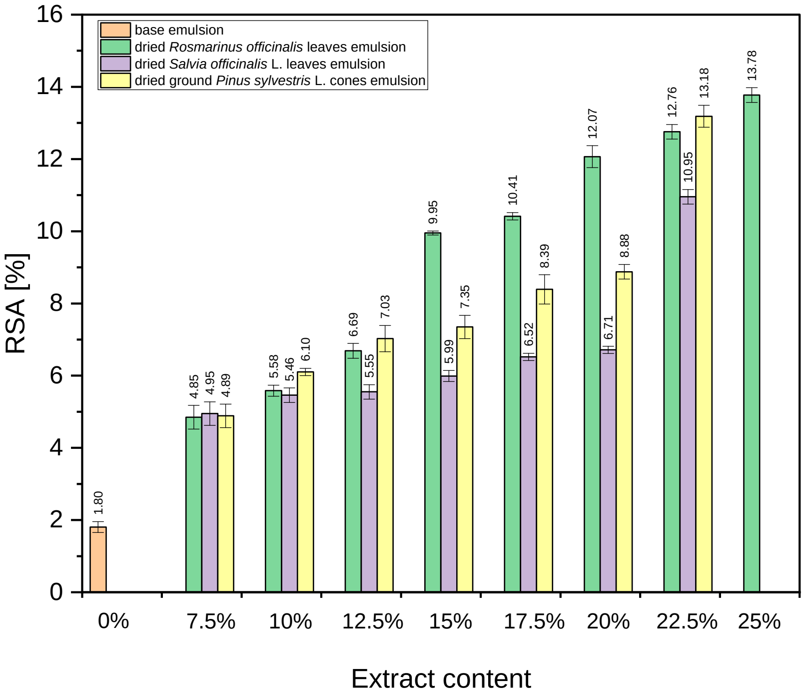


Figure 8. The antioxidant activities of the emulsions evaluated with the DPPH method and expressed as radical scavenging activity (%RSA). Vertical lines represent the standard deviation (SD).

Supplementary Figure S1 shows in detail emulsions containing Olivem 1000 as the emulsifier and different amounts of extracts prepared for our studies.

Supplementary Table S6 shows the pH values of the prepared emulsions. The results presented in this table show that the pH values of the emulsions were between 4.63 and 5.51. It can be observed that as the amount of added extract increases, the pH of the emulsions also increases (a strong correlation was found: r = 0.880).

3.8. Testing the Antioxidant Activities of Emulsions

Figure 8 shows the antioxidant activities of the obtained emulsions.

It can be observed from Figure 8 that increasing the amount of the added extract of dried *Rosmarinus officinalis* leaves increases the RSA of the emulsion from 4.85% (amount of extract 7%) to 13.78% (amount of extract 25%). With the increase in the amount of added extract from dried *Salvia officinalis* L. leaves, the RSA of the emulsion increases from 4.95% (amount of extract 7%) to 10.95% (amount of extract 22.5%). Similarly, increasing the amount of added extract from dried ground *Pinus sylvestris* L. cones increases the RSA of the emulsion from 4.89% (7% extract amount) to 13.18% (22.5% extract amount). The RSA of the base emulsion (without the addition of the extract) is 1.8%. Among the emulsions tested, the one with the addition of dried *Rosmarinus officinalis* leaf extract at 25% has the highest antioxidant activity (13.78%), while the base emulsion without the addition of an extract has the lowest antioxidant activity (1.80%).

In the case of concentrations of 7.5% and 10%, there were no statistically significant differences in the antioxidant potentials of the emulsions from different plant materials that were used to obtain the extract. In other cases (concentrations from 12.5% to 22.5%), it was found that there were statistically significant differences between the lowest and highest values of antioxidant potential ($p \leq 0.05$). These results indicate that extracts from dried *Rosmarinus* leaves and dried unground *Pinus* cones at these concentrations were equally valuable.

3.9. Antimicrobial Stabilities of the Emulsions

The antimicrobial stabilities of the selected emulsions with the highest antioxidant activity of a given plant material were determined with microbiological tests. These emulsions consisted of extracts of dried *Rosmarinus officinalis* leaves (amount of extract 22.5% and 25%), dried *Salvia officinalis* L. leaves (amount of extract 22.5%), dried ground *Pinus sylvestris* L. cones (amount of extract 22.5%), and the base emulsion. The results of the microbiological tests are shown in Figures 9 and 10.

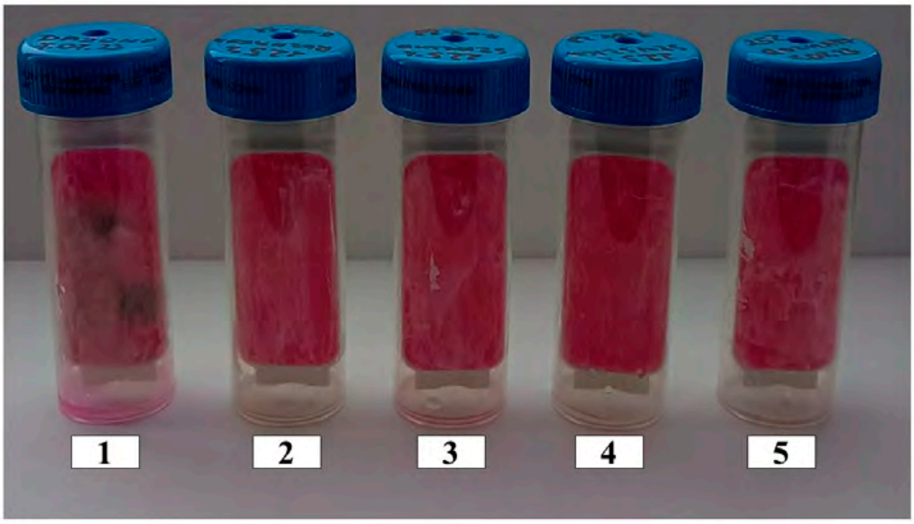


Figure 9. Microbiological plates with a medium for the determination of yeast and mold coated with emulsions: 1—base emulsion (without extract). Emulsions with a 22.5% ethanolic extract of the following plant materials: 2—dried *Rosmarinus officinalis* leaves, 3—dried *Salvia officinalis* leaves, 4—dried and ground *Pinus sylvestris* L. cones. 5—Emulsion with a 25% ethanolic extract of dried *Rosmarinus officinalis* leaves.

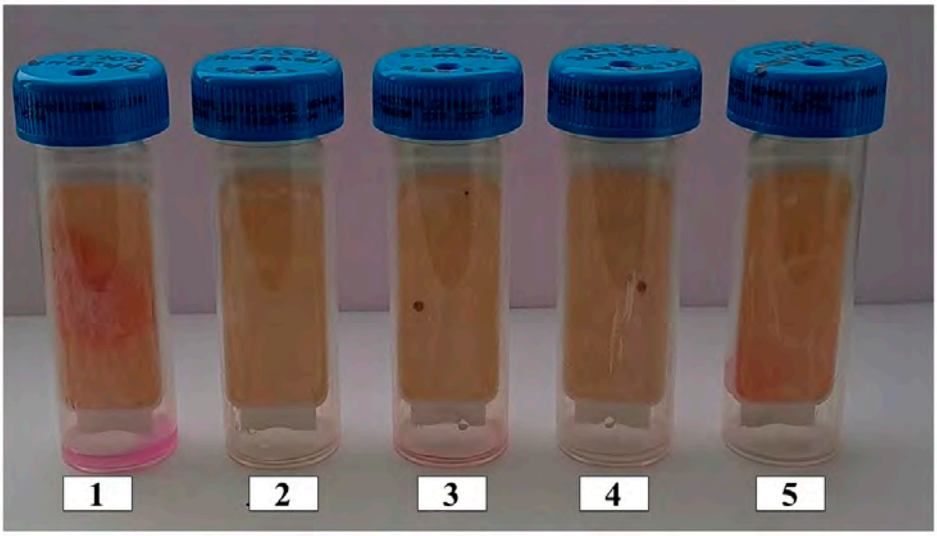


Figure 10. Microbiological plates with a substrate for the determination of bacteria coated with emulsions: 1—base emulsion (without extract). Emulsions with a 22.5% ethanolic extract of the following plant materials: 2—dried *Rosmarinus officinalis* leaves, 3—dried *Salvia officinalis* leaves, 4—

dried and ground *Pinus sylvestris* L. cones. 5—Emulsion with a 25% ethanolic extract of dried *Rosmarinus officinalis* leaves.

Fungi appeared only on the plate coated with the base emulsion without the addition of the extract. No yeast or mold was observed on the other plates, which were coated with emulsions with added extracts.

A few bacteria, in the form of a pinkish-red colony, appeared on the plate coated with the emulsion with the 22.5% extract from dried *Salvia officinalis* leaves and on the plate coated with the emulsion with the 22.5% extract from dried and ground *Pinus sylvestris* L. cones. The amount of bacteria observed on the plates is less than 1.000 C.F.U/mL (1.000 bacteria per milliliter) and is acceptable for the emulsions obtained. The part of the plate coated with the base emulsion has a uniform red color and shows numerous pink-red colonies forming a cluster of bacteria.

Based on the microbiological tests, it can be concluded that all emulsions with the addition of ethanolic extracts obtained from plants containing α-pinene show excellent antimicrobial stability.

4. Conclusions

Our research conducted with plant extracts containing α-pinene can be the scientific basis for future applications of these extracts in the cosmetics industry and in medicine. Our work fits perfectly into the new trends in modern cosmetic preparations related to the use of biologically active compounds, including preservatives and antioxidants, from natural sources instead of synthetic compounds. With the use of these bioactive components extracted from plant materials, modern cosmetic products meet such requirements in the use of renewable raw materials and the application of sustainable cosmetic-production technologies. We have shown that it is very important to select the appropriate method for the extraction of the biologically active substances from plant material as well as the selection of the appropriate plant source of these substances.

This study demonstrates that the ultrasound-assisted extraction method can be used as a tool to obtain extracts containing α-pinene with a high antioxidant activity. Furthermore, our studies on the preparation of emulsions with these extracts showed that the application of Olivem 1000 as the emulsifier made it possible to create stable cosmetic emulsions exhibiting high antioxidant activity. Microbiological tests of these emulsions yielded the acceptable limited amount of microorganisms in the resulting preparations and that these extracts can reduce the degree of microbiological contamination in cosmetic preparations. It may suggest the possibility of using extracts containing α-pinene as the potential ingredients of anti-aging cosmetics. However, refining the optimal composition of the cosmetic product requires further research.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/antiox13070811/s1, Table S1: GC-MS determinations of ethanolic extracts (with ultrasound-assisted extraction); Table S2: GC-MS determinations of ethanolic extracts (with the Soxhlet apparatus); Table S3: The comparison of the antioxidant activities of ethanolic extracts evaluated with the DPPH and ABTS methods; Table S4: The descriptive statistics of the antioxidant potentials of extracts measured with the DPPH method as TEAC values (mg/g); Table S5. The descriptive statistics of the antioxidant potentials of extracts measured with the ABTS method as TEAC values (mg/g); Table S6: The pH values of the obtained emulsions; Figure S1: Emulsions containing Olivem 1000 with different amounts of extracts: 1—base emulsion (without extract). With ethanolic extracts of the following plant materials: 2—dried *Rosmarinus officinalis* leaves, 3—dried *Salvia officinalis* L. leaves, 4—dried ground *Pinus sylvestris* L. cones; Figure S2: Emulsions containing glycerol monostearate as emulsifier: 1—base emulsion (without extract), 2—emulsion with extract of dried *Rosmarinus officinalis* leaves, 3—emulsion with extract of dried *Salvia officinalis* L. leaves, 4—emulsion with extract of dried ground *Pinus sylvestris* L. cones; Supplementary Equation (S1): %RSA versus Trolox concentration; Supplementary Equation (S2): Absorbance versus Trolox concentration.

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