“BABEŞ-BOLYAI” UNIVERSITY
Faculty of Chemistry and Chemical Engineering

THE STUDY OF α-PINENE ISOMERIZATION IN ACIDIC HETEROGENEOUS CATALYSIS

PhD Thesis Abstract
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Content

Keywords: monoterpenes, isomerization, heterogeneous catalysis, zeolites, heteropolyacids.

Summary

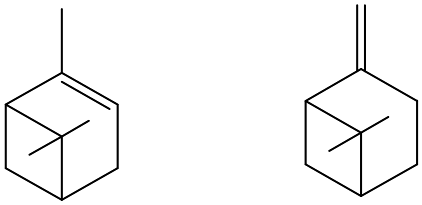
The monoterpenes are essential ingredients in fine chemical industry and flavor and perfume industry. The most important constituents of monoterpenes are α- and β-pinene, the main components of terebenthine oil. World flavor and perfume industry uses about 30.000 tones of α-, β- pinene per year, which highlights their importance for these industrial branches, being also starting materials for numerous important technologies, such as those for the synthesis of myrcene, camphene, limonene, α-terpineol, camphor, carvone and paracymene. An important number of researchers are involved in the study of this domain with particular practical and theoretical importance. Most of the industrial processes applied until now are based on the homogenous catalysis method, leading to substantial amounts of dangerous acidic waste. The heterogeneous catalysis, less studied in this domain, could offer solutions for the isomerization of α-pinene, positive opportunities related to improving the yields and selectivity of these processes.

Considering the facts presented above, the research on the isomerization reaction of α-pinene in heterogeneous catalysis constitutes a vast field, very attractive for the fine chemical industry, unexplored until now.

1. Introduction

1.1 α-Pinene

The monoterpenes are essential ingredients in fine chemical industry and flavor and perfume industry. The most important constituents of monoterpenes are α- and β- pinene (Figure 1) which are the main components of terebenthine oil.



(1)
α-pinen

(2)
β-pinen

Figure 1. α- şi β- pinene.

α- şi β- Pinene, with relatively high abundance in nature, obtained from renewable sources, have a defining role in the terpenes production. The world production of terebenthine was about 330.000 tones in 1995.[1] The terebenthine can be classified – according to Gscheidmeier and Flewig – function of the used starting material (different tree species) and production method.[2] In conclusion, 5 types of terebenthine could be highlighted: terebenthine balm (terebenthine oil), terebenthine oil from wood, terebenthine-sulphate oil, terebenthine-sulphite oil and terebenthine oil DDW.

Terebenthine oils are mobile liquids, usually non-colored or slightly colored, with characteristic pleasant odor. The boiling point of the oils varies between 154-170°C, and melting point between -60 and 50°C. The density varies between 0.854-0.868 g/mL. The oils are not soluble in water, but are soluble in alcohols, ethers, carbon bisulfite and in other oils.[3] Highly pure α- and β- pinene can be obtained by fractional distillation of terebenthine oil. World flavor and perfume industry uses about 30000 tones of pinenes.[1]

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[1] Swift, K.A.D. *Topics in Catalysis,* **2004**, *27*, 143-155;

[2] Gscheidmeier, P.; Flewig, W. *Ullmann's Encyclopedia of Industrial Chemistry*, **1996;**

[3] Budavari, S. *The Merck Index, 12th ed. Merck & Co., Inc.,* **1996;**

The world production of limonene is also 30000 tones, which highlights that terebenthine oil and pinenes are essential renewable ingredients in fine chemical industry. About 55% from the world production of terebenthine oil is used by the varnish and paint industry, the rest being used as starting material in flavor and perfume industry. The main products obtained from terebenthine oil are: myrcene, camphene, limonene, α-terpineol, camphor, menhol, linalool, geraniol, citronellol, carvone and paracymene, etc.[6] Part of these can function as precursors or solvents (Figure 2).

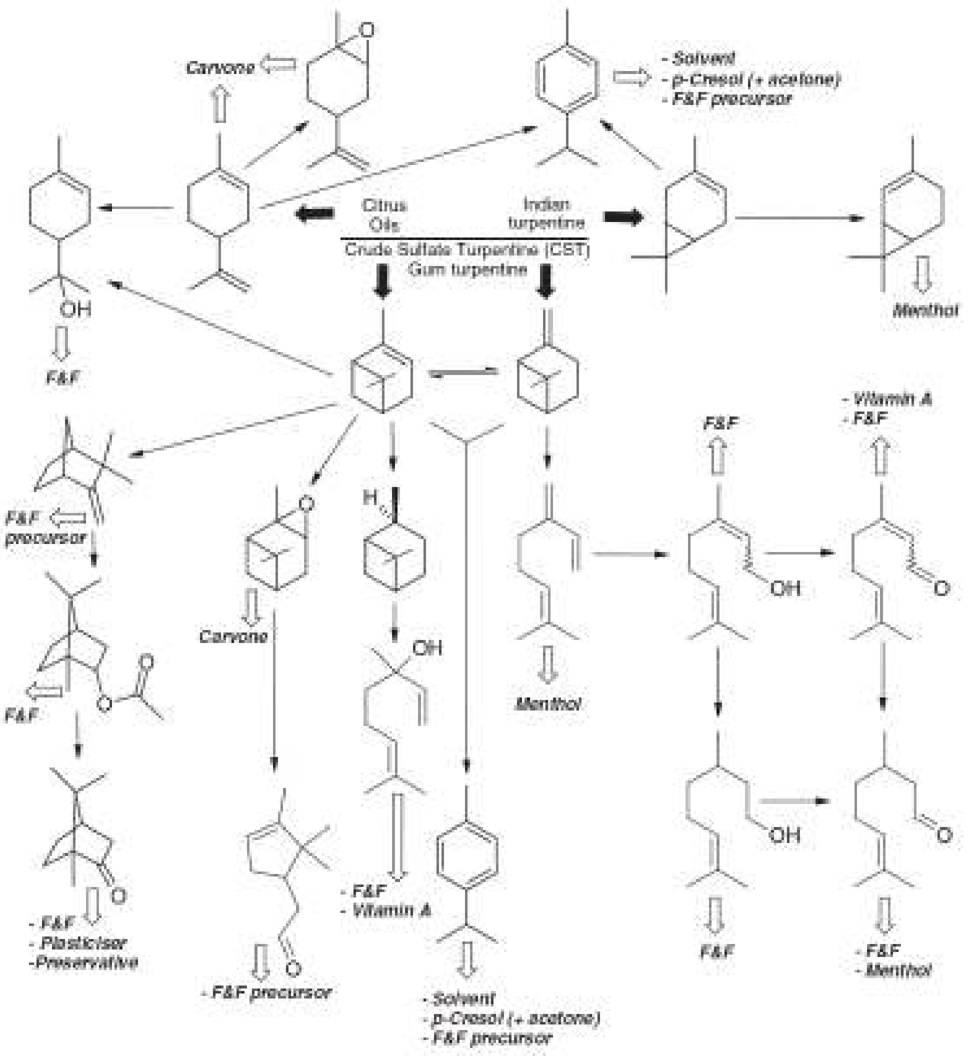

Figure 2. Industrial branches based on terebenthine oil.[1]

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[6] Radoias, G.; Bosilcov, A.; Bâtiu, I. *Odorante naturale în parfumeria modernă*, Casa Cărții de Ştiință, Cluj-Napoca, **2005**, 578;

1.2 Isomerization of α-pinene in acidic catalysis

The structure of α-pinene (1) having a sufficient tense and tight skeleton of bicyclo[3.3.1]heptene, easily participates in cycle opening reactions and molecular rearrangement reactions, leading to different mono- and bicyclic products. α-Pinene is involved in a cycle opening reaction in acidic catalysis to obtain major products with p-menthanic and p-menthadiene skeleton. Using solid acids, different bicyclic structures, such as camphene, are obtained from α-pinene by molecular rearrangement reactions.[8] In order to describe the mechanism of the isomerization of α-pinene in acidic catalysis, we must specify where the electrophilic attack will take place and which will be the intermediate carbocation. According to N. Flores-Holguín et all., calculations (Gaussian 03 and Materials Studio 4.1),[9] the electrophilic attack of the proton will take place at C5 from double bond, (Figure 3).

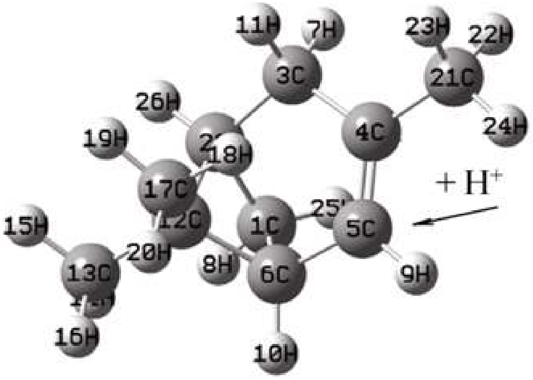

Figure 3. The electrophilic attack on α-pinene.

The carbocation (**3**) will be obtained by the electrophilic attack, which is more stable than (**3'**) with 13-20 kcal/mol. Due to the fact that 1,2 hydrogen transfer is not favored in the case of the carbocation pinanyl, the next step consists in a Wagner-Meerwein rearrangement, with the formation of isobornyl carbocation (**4**) by the cycle opening. F.

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[8] Erman, M.B.; Kane, B.J., *Chemistry & Biodiversity*, **2008**, 5, 910-918;

[9] Flores-Holguín, N.; Aguilar-Elguézabal, A.; Rodríguez-Valdez, L.M.; Glossman-Mitinik, D. *Jurnal of Molecular Structure: Theochem*, **2008**, 854, 81-88;

Ebmeyer calculations confirm the obtaining of the isobornyl carbocation, which is with 8,8 kcal/mol more stable than pinanyl carbocation.[10] The *p*-menthenyl carbocation (**5**) is also formed in the same time with the formation of isobornyl carbocation (Figure 4). The ration between these two carbocations is function of different factors, such as acidic catalyst characteristic and temperature. Isobornyl carbocation leads to camphyl (**11**) by a 1,2 sigmatropic rearrangement, which will be further deprotonated to obtain the main isomerization product, the camphene (**12**).

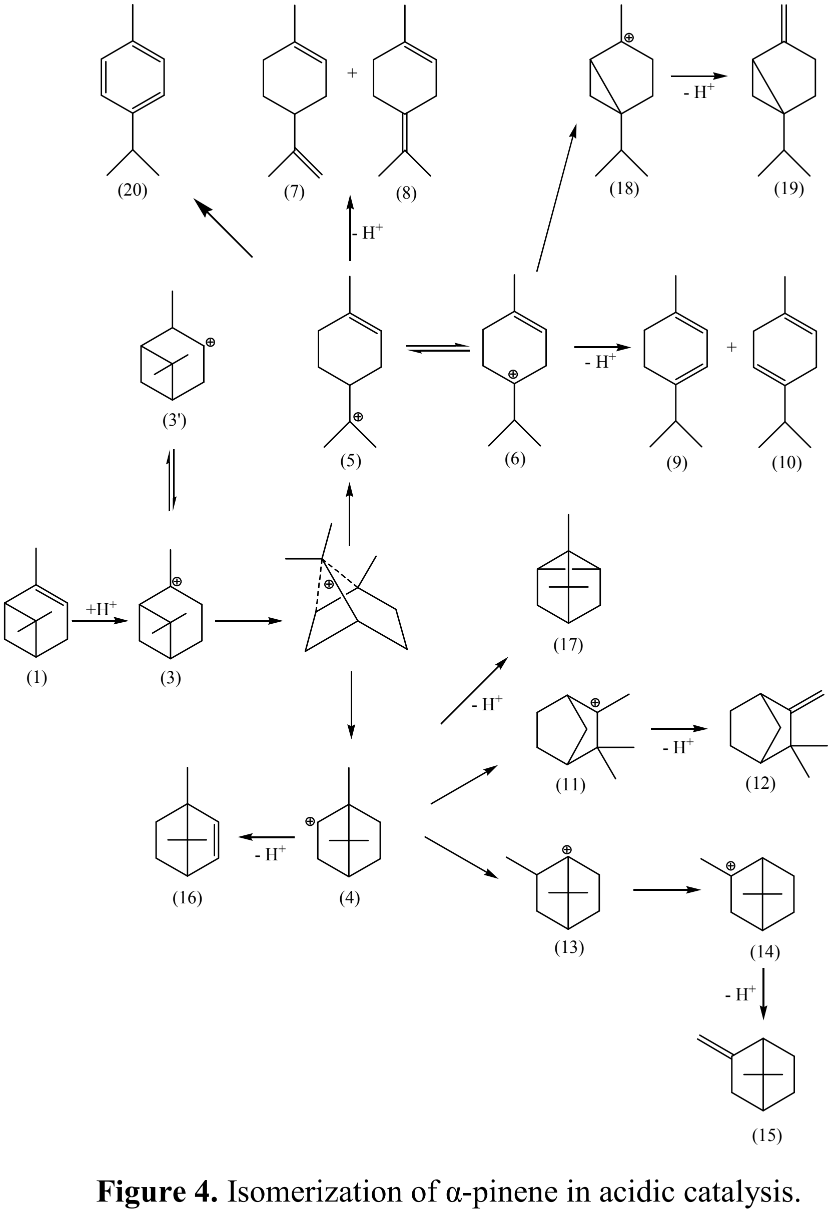

Figure 4. Isomerization of α-pinene in acidic catalysis.

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[10] Ebmeyer, F. *Jurnal of Molecular Structure*, **2001**, 582, 251-255;

Isobornyl will not lead only to the obtaining of camphene, secondary products are also defined. A simple deprotonation of isobornyl conducts to bornylene (**16**), and tricyclene (**17**) with the formation of cyclopentadiene moiety. α-Fenchene (**15**) can be also observed in the reaction mass. The first step consists in formation of the intermediate carbocation (**13**) with 1,2 transfer of methylic group, followed by 1,2 transfer of the proton, obtaining fenchyl carbocation (**14**). Deprotonation of **14** made possible the formation of α-fenchene.

p-Menthenyl is the key intermediate for the reaction described above. This carbocation appears in equilibrium with carbocation (**6**), which, deprotonated leads to the following compounds: limonene (**7**), terpinolene (**8**), α-terpinene (**9**) and γ-terpinene (**10**). According to F. Ebmeyer, the carbocation (**6**) is more stable than *p*-menthyl, so, using this methodology, α-terpinene is the major product.[10] Due to the fact that the stability of this product is much lower than of the others, sabinene can be also obtained, which was observed in traces. During the isomerization process, in special conditions, from p-menthyl, p-cymene (**20**) could be obtained as a secondary product.

The chirality of the products obtained in acidic catalysis depends on several factors: characteristic and strength of the acid catalyst, temperature. Generally, by the isomerization of an optically pure α-pinene catalyzed by strong acids in aqueous solutions, a partial or complete mixture was obtained. Using solid acids, the rearrangement of α-pinene without racemization was observed.[11]

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[1]1 Stefanis, A.; Perez, G.; Tomilinson, A.A.G.; Ursini, O.; Lilla, E. *React. Kinet.Catal.Lett.*, **2003**, 78,267-273;

2. Isomerization of α-pinene – Original Contributions

In this chapter the original contributions to isomerization of α-pinene will be presented. The target of this research was the elaboration and improvement of methods for the preparation of the catalysts and the study of α-pinene isomerization, respectively, the elaboration of some more efficient and selective methods in order to obtain some utile products, such as camphene and limonene.

During the researches, some steps were followed:

1) The elaboration of some new catalytically methods for the isomerization of α-pinene

2) The optimization of catalytically methods for:
   - preparation of catalysts
   - pretreatment of catalysts
   - catalytic process

3) Study of the factors that influence the catalytic process.

In order to study the chemical processes of isomerization reaction, the gas chromatography was used as an analytical method. For this purpose, a gas chromatograph Hewlett Packard 5890 series II with automatic injector and FID detector was used.

The qualitative identification of the components from reaction mass was realized by comparing the retention time of the non-identified peak with the retention times for some standard series, using the method of standards adding and GC-MS.

2.1 Isomerization of α-pinene in acetic acid

In this chapter the results obtained by isomerization in acetic acid, using catalysts: $B(OAc)_3$, H_3BO_3, B_2O_3, paratoluenesulfonic acid (APTS) and zeolite 13X, will be presented.

2.1.1 Reactions of α-pinene in acetic acid

Two series of products were obtained from the reaction of α-pinene with acetic acid (Figure 20): esters [fenchyl acetate (**25**), bornyl acetate (**27**) and terpenyl acetate (**28**)] and isomerization products (camphene (**12**), limonene (**7**), terpinolene (**8**)).[78]

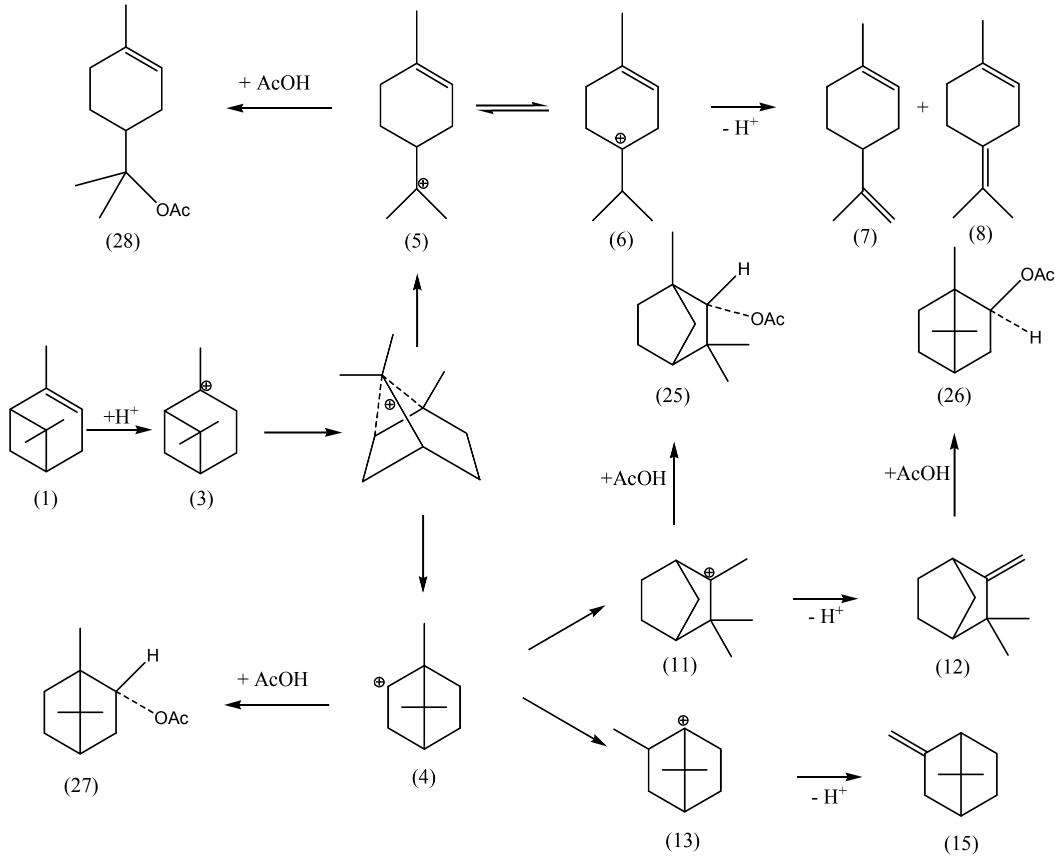

Figure 5. Isomerization processes and the obtaining of the esters in presence of acetic acid.

2.1.2 Reactions of α-pinene in acetic acid catalyzed by $B(OAc)_3$, H_3BO_3, B_2O_3, paratoluenesulfonic acid (APTS) and zeolite 13X

Isomerization processes in acetic acid, using solid catalysts, were studied. The results obtained are presented in Table 23.

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[78] Valkansas, G.N., *J.Org.Chem.,* **1976**, 41, 1179-1183;

Table 23. Conversion and selectivity function of the used catalyst (molar ratio α-pinene/acetic acid 1:3, 150 ºC).

Nr	Catalyst	Time (h)	C (%)	Selectivity (%)									
				Isomerization products						Esters			
				Bicyclic terpenes		Monocyclic terpenes							
				Fen[a]	Cf[b]	α-T[c]	Lim[d]	γ-T[e]	T[f]	Fac[g]	Bac[h]	iso-Bac[i]	Tac[j]
1	without catalyst	8	97	**3.1**	**8.7**	**1.7**	**39.2**	**1.3**	**14.4**	**10.3**	**17.3**	**1.5**	**1.7**
2	$B(OAc)_3$	3	100	0.6	8.2	12.5	7.7	8.5	21.4	8.1	17.7	7.2	0.5
3	H_3BO_3	5	100	1.1	8.3	9.4	12.2	6.6	21.9	8.1	17.8	7.5	0.7
4	B_2O_3	6	100	0.7	8	12	8.3	8.3	22	8.1	17.8	7.3	0.5
5	APTS	6	100	1.6	9.3	9.9	18	6.6	17.9	3.3	21.7	2.8	1
6	13X	8	95	3.5	9	1.1	40.2	1.6	13.8	9.7	16.7	1.2	1.1

[a] Fenchen; [b] Camphen; [c] α-Terpinene; [d] Limonene; [e] γ-Terpinene; [f] Terpinolene; [g] Fenchyl acetate; [h] Bornyl acetate; [i] Isobornyl acetate; [j] Terpenyl acetate.

Comparing the results presented in Table 23, we can conclude that using solid catalysts the isomerization process changed, one exception being catalyst 13X, when the composition of the mixture is not modified. It can be clearly seen that in presence of catalysts (exception 13X), the selectivity of fenchene goes down and the selectivity of camphene remains almost constant. The influence of the catalysts is more evident in the ratio of the obtained monocyclic terpenes: using catalysts, the selectivity for α-terpinene rises from 1.7% to 9.4-12.5% and for γ-terpinene from 1.3% to 6.6-8.5%. The selectivity of limonene decreases from 39.2% to 7.7-18%, and that of terpinolene increases from 4.4% to 17.9-22%. These differences can be explained by the fact that in presence of solid catalysts the catalytic medium is stronger and the isomerization of the obtained limonene take also place – described in chapter 1.3.1.1 – producing larger amounts of α-, γ- terpinene and terpinolene.

The use of the catalysts influences also the reaction time for the conversion over 95%. The effect of the catalysts on the reaction time is illustrated in Figure 24.

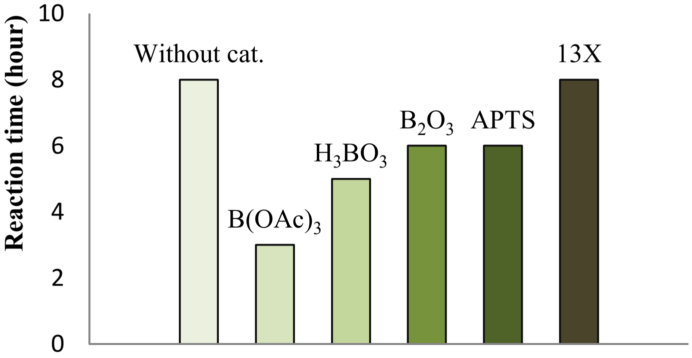

Figure 24. Time needed for obtaining conversion ≥ 95%.

2.1.3 Reactions of α-pinene in acetic acid catalyzed by $B(OAc)_3$, H_3BO_3, B_2O_3, paratoluenesulfonic acid (APTS) and zeolite 13X under microwave conditions

Taking into account the favorable effects induced by microwave irradiation over chemical reactions,[79] this technique was extended on the isomerization reaction of α-pinene in acetic acid catalyzed by solid catalysts. The obtained results are presented in Table 25.

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[79] Loupy, A., *Microwaves in Organic Synthesis*, **2006**, Ed., vol 1, 2nd Ed. Wiley-VCH Verlag GmbH and Co.KgA, Weiham;

Table 25. Conversion and selectivity function of the used catalyst (molar ratio α-pinene/acetic acid *1:3*; 150 ºC; 100W; reaction time 0.5h).

Nr	Catalyst	C (%)	Selectivity (%)									
			Isomerization products						Esters			
			Bicyclic terpenes		Monocyclic terpenes							
			Fen	Cf	α-T	Lim	γ-T	T	Fac	Bac	iso-Bac	Tac
1	without catalyst	70	4.2	11	1.6	39.7	1.4	11.4	9.3	15.4	1	2
2	$B(OAc)_3$	53	4.3	14.7	1.9	32.9	1.9	12.8	6.6	12	1.2	7.4
3	H_3BO_3	45	4.1	13.5	0.9	32.4	1.6	11.6	6.6	11.6	0.7	9.1
4	B_2O_3	91	4.3	14.5	4.4	32.5	3.3	17.7	4.8	10.1	2.2	2
5	APTS	98	1.1	10.2	0.1	17.9	5.3	9.9	3.2	4.6	14.3	2.1
6	13X	30	4	13.1	1.7	31.9	1.7	10.1	8.1	13.1	0.7	10.4

Comparing the obtained results in microwave conditions with those obtained in classical conditions without catalyst, we could conclude that the composition of the obtained mixture not differ substantially. Differences can be observed for the synthesis of bicyclic terpenes, where the selectivity increases from 11.9% to 15.2%, while the selectivity of monocyclic terpenes remains almost constant. Some minor modifications are observed in the selectivity of the reaction towards acetates. In microwave conditions the selectivity for every product decreases with 1-2%, expetion for terpenyl acetate, where is constant. Significant differences could be evidenced only when refer to reaction time.

For an obvious comparison, the obtained results using $B(OAc)_3$ are presented in Figure 26.

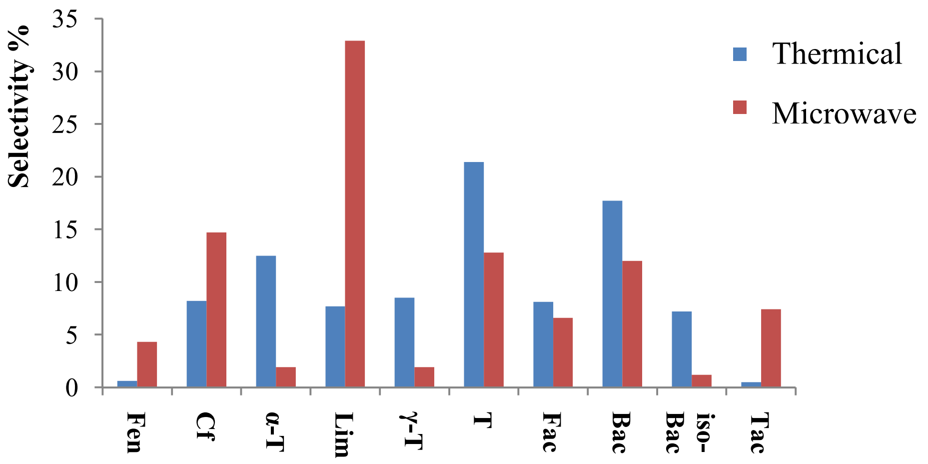

Figure 26. Selectivity of the thermical reactions and under microwave irradiation using $B(OAc)_3$ as a catalyst.

The graphic presented in Figure 7 clearly illustrates the major differences between the two methods. First, the selectivity of limonene is four times better when microwave conditions are used. A significant difference could also be observed in the case of terpenyl acetate, whose selectivity is 15 times higher than in classical conditions. Comparatively, when compared the two methods, the classical one seems to be better for the obtaining of terpinolene.

The results obtained in presence of APTS are illustrated in Figure 27.

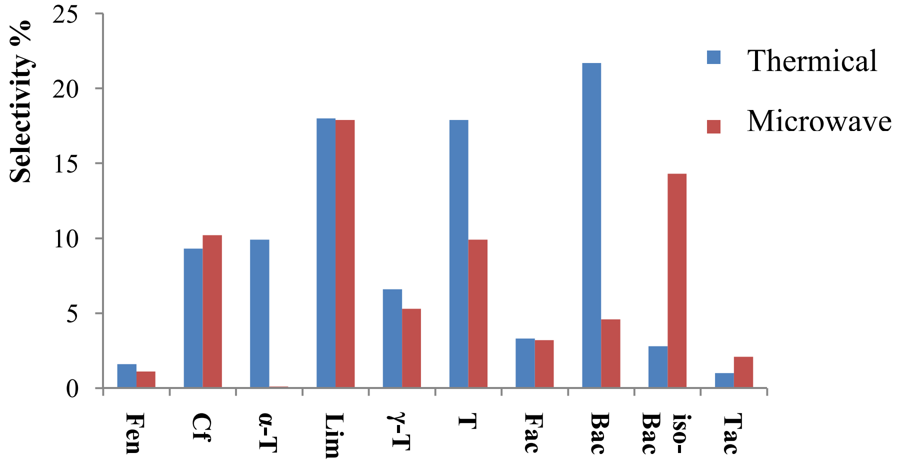

Figure 27. Selectivity of thermical reactions and under microwave irradiation when APTS used.

The best results with microwave irradiation could be observed in the case of bornyl acetate, whose selectivity increases from 2.8% to 14.3%. In the other cases the selectivity is higher when classical conditions are used.

2.2 Isomerization of α-pinene catalyzed by H-ZSM-5 with reduced aluminum content with respect to initial zeolite

2.2.1 Reduction method of aluminum quantity from zeolite H-ZSM-5 and characterization of the catalysts

The ratio Si/Al in the zeolites is very important when using zeolite as a catalyst, due to the fact that concentration and strength of the Brønsted acidity are governed by the number of aluminum atoms in the structure.[80] In order to study efficiently the isomerization of α-pinene in acidic catalysis, the control of Brønsted acidity is needed. The literature suggests that the strong acidic positions and high reaction temperature favor the obtaining of monocyclic products, but the weak acidic positions and low reaction temperature favor the synthesis of bicyclic compounds.[81] Sulfuric acid solutions in different concentrations (5%, 10%, 20%, 30%, 50%) were used to reduce the aluminum content in the structure of zeolite H-ZSM-5.

Modifications in the crystalline structure of the zeolite after the reduction treatment of aluminum content were proved by X-Ray powder diffraction. The obtained results are presented in Figure 29. The results confirm that during the reduction process the structure of the zeolite is not destroyed, crystalline degree remains constant.

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[80] Breck, D.W., *Zeolit Molecular Sieves*, **1974**, Wiley, New York;

[81] Severino, A.; Esculcas, A.; Rocha, J.; Vital, J.; Lobo, L.S., *Appl. Catal. A: Gen.*, **1996**, 132, 255-261;

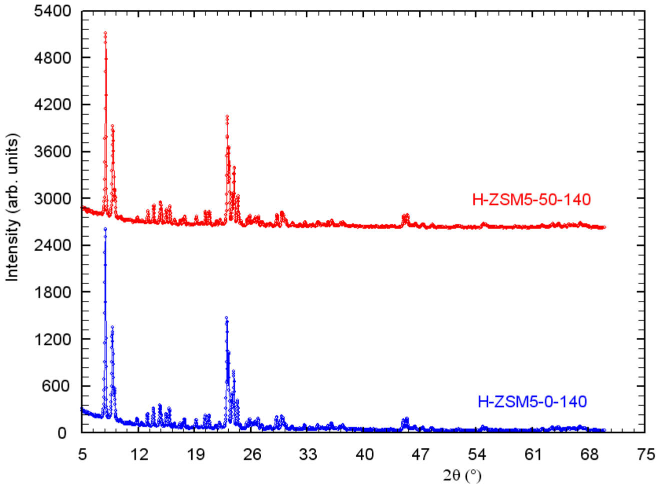

Figure 29. X-Ray powder diffraction of initial zeolite (blue) and zeolite with sulfuric acid 50% (red).

The morphology of zeolite particles was analyzed using electronic transmission microscopy (TEM); Figure 30 a and b presents TEM images of H-ZSM-5-0-140 and H-ZSM-5-5-140. It can be observed that the H-ZSM-5 crystals have the diameter smaller than 10 μm.

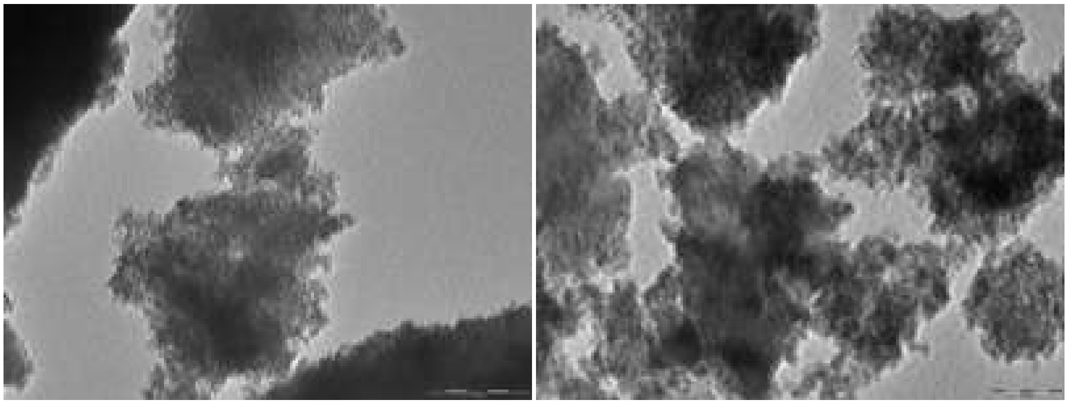

Figure 30 a. TEM images of zeolite H-ZSM-5-0-140.

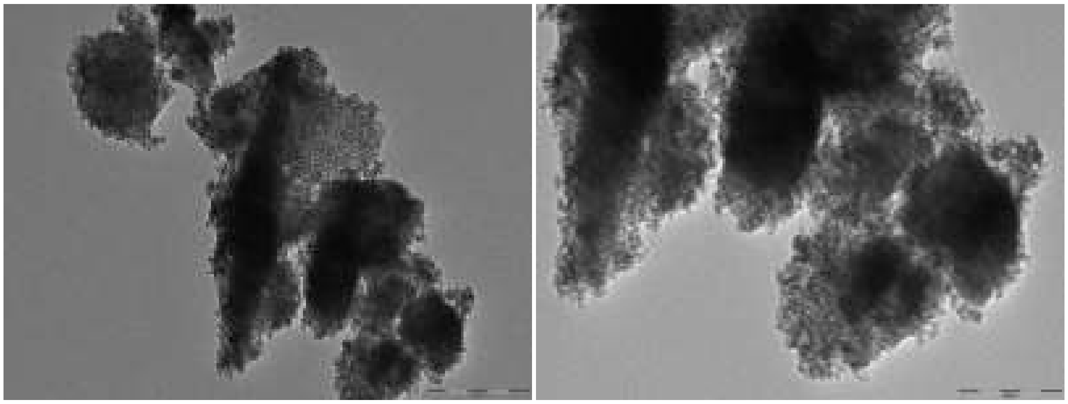

Figure 30 b. TEM images of zeolite H-ZSM-5-5-140.

2.2.2 The study of catalytic activitie of zeolite H-ZSM-5 with reduced aluminum content

The catalytic activity of zeolite with reduced aluminum content was studied by refluxing α-pinene on the catalyst (mass ratio catalyst/α-pinene was 5%). The obtained results are presented in Figure 33.

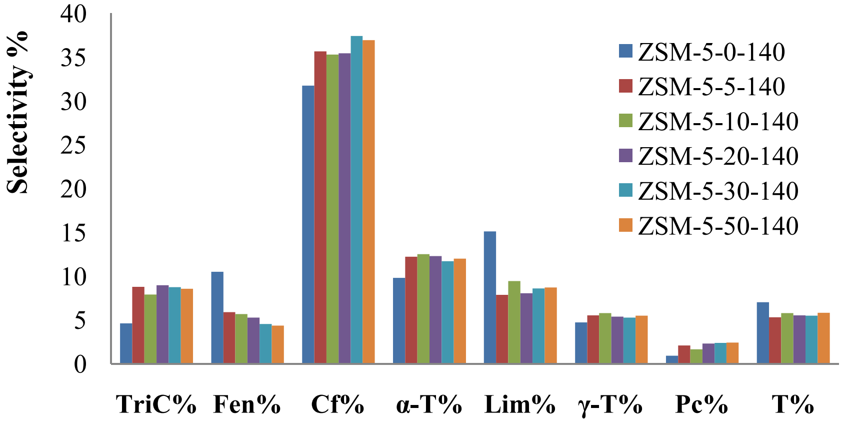

Figure 33. The selectivity of catalysts with reduced aluminum content.

In the case of initial catalyst H-ZSM-5-0-140, the time needed for the conversion 90% was 8 hours, but in the case of catalysts with reduced aluminum content, independent of the reduced degree, the time needed till desired conversion decreases to 2 hours. The selectivity of the catalysts is also influenced by the reduction of aluminum amount. No significant modifications could be observed when refer to γ-terpinene, paracymene and terpinolene, but major differences appeared in the case of tricyclene, fenchene and limonene. The ratio of volatile products was verified after each synthesis by water stream distillation of 5g oil. The ratio was calculated using the following equation:

$$\mathrm{V} = \frac{\text{m ulei antrenat}}{\text{m ulei inițial}} \times 100\%$$

Figure 12 prezents the variation of the volatile products function of H_2SO_4 concentration.

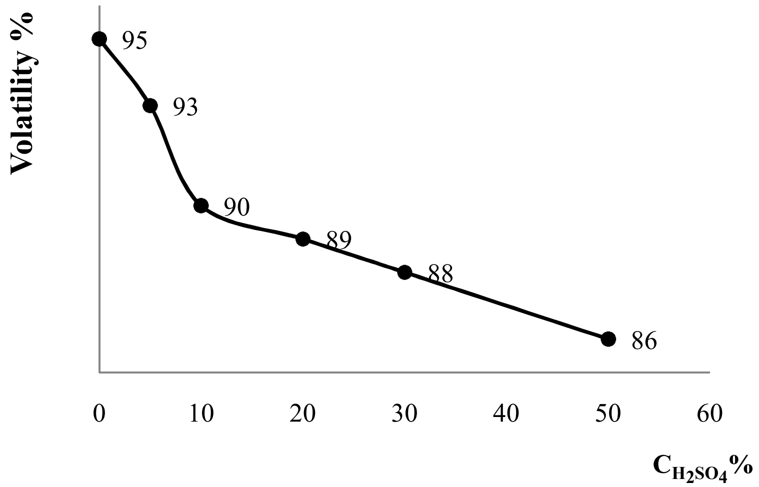

Figure 35. Volatility variation depending on the concentration of H_2SO_4.

Diagram presented above illustrates that by increasing the concentration of sulfuric acid used to reduce the aluminum content, the percent of volatile products decreases.

2.2.4 The effect of reaction temperature over the activity and selectivity of catalyst H-ZSM-5 with reduced aluminum content

The effect of reaction temperature was studied on H-ZSM-5-**5**-100, using 5% with respect to α-pinene. The reaction temperature was 160-175 (reflux), 140 and 120°C. The results are highlighted in Figure 37.

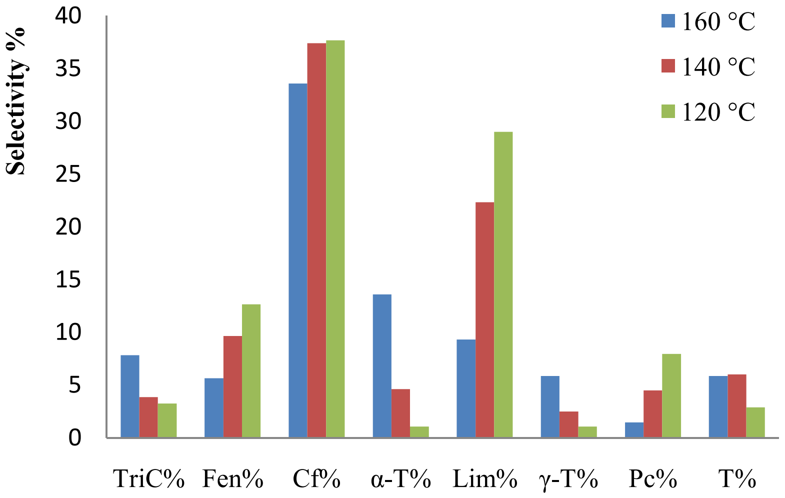

Figure 37. Selectivity function of reaction temperature.

This study reveals that reaction temperature influence significantly the activity and selectivity of catalyst H-ZSM-5-**5**-100. It can be easy seen that decreasing gradually the temperature with 20°C, the time needed to a good conversion becomes longer. The study proved that the activity of the catalyst decreases in time.

Significant differences in the selectivity of catalytic processes are observed (Figure 37). First, the selectivity decreases for the secondary product, tricyclene, but also for α- and γ-terpinene and terpinolene when the temperature decreases. Second, the selectivity of camphene, limonene and paracymene increases at lower temperature. The ratio of the volatile products remains constant no matter what temperature was used.

2.2.5 The effect of ratio catalyst/α-pinene on the activity and selectivity of zeolite H-ZSM-5 with reduced aluminum content

The effect of the amount of catalyst with respect to substrate was studied with H-ZSM-5-5-100 at the refluxing temperature. The ratio catalyst/α-pinene was 5, 2.5, 1.25 and 0.625%. First, it can be observed that the ratio catalyst/α-pinene strongly influence reaction time needed towards needed conversions. The following diagram presents this effect:

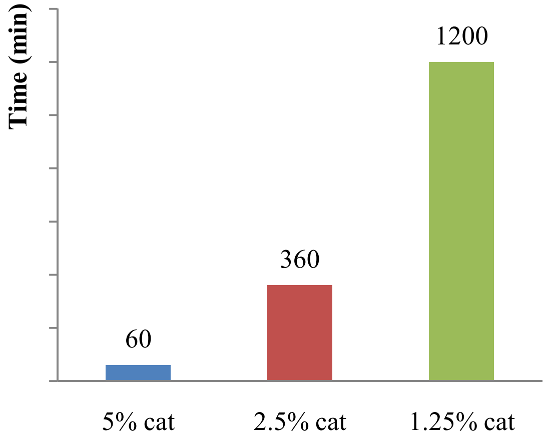

Figure 40. Time needed towards 70% conversion.

The selectivity of isomerization process is also influenced by the change of catalysts/ α-pinene ratio, as it can be observed in Figure 41.

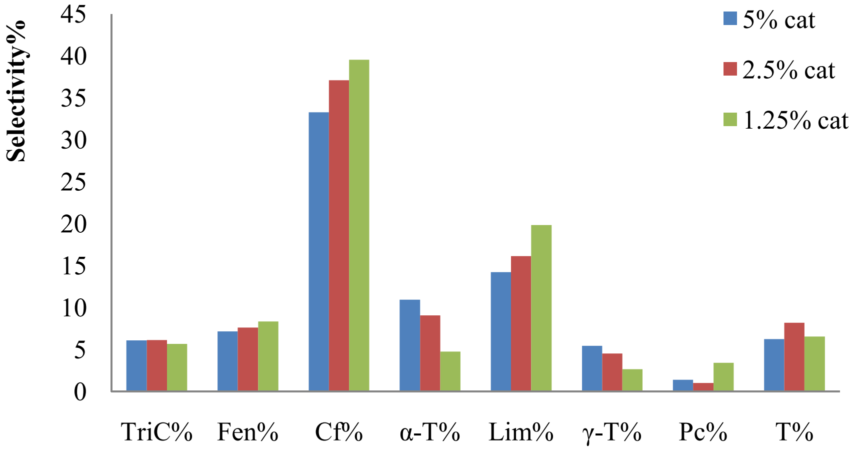

Figure 41. Selectivity of isomerization function of catalyst/α-pinene ratio.

As illustrated above, it can be observed that decreasing the ratio catalyst/α-pinene the selectivity increases; when used 1.25% catalyst the higher selectivity was for camphene.

This study on the effect of catalyst/α-pinene ratio was extended also to water stream distillation yield. Figure 43 demonstrates the variation of the yield.

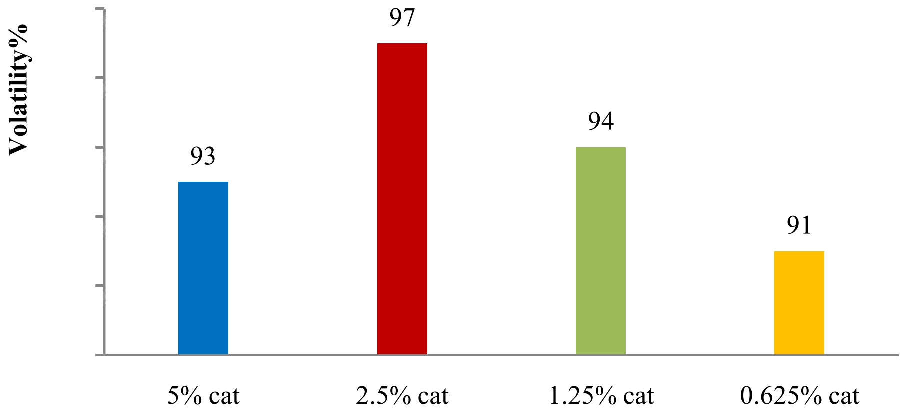

Figure 43. Volatility function of catalyst/α-pinene ratio.

2.3 Isomerization of α-pinene catalyzed by heteropolyacids deposed on oxides support and H-ZSM-5

The study of isomerization of α-pinene in heterogeneous acidic catalysis was followed by the research and optimization of processes catalyzed by molibdophosphoric acid (PMo) ($H_3PMo_{12}O_{40}{\cdot}xH_2O$) and wolframosilicic acid (SiW) ($H_4SiW_{12}O_{40}{\cdot}xH_2O$). SiO_2, Al_2O_3, TiO_2, and H-ZSM-5 were used as solid supports.

2.3.1 Preparation of the catalysts

The preparation of the catalysts was performed by impregnation method. In this way, the acid was solved in methanol, and then mixed with the solid support and agitated at room temperature for 24 hours. The solvent was removed by simple vacuum distillation. The degree of deposition was calculated using following equation.

$$G_d = \frac{m_{acid}}{m_{acid}+m_{suport}} \times 100\%,$$

where G_d is the degree of deposition, m_{acid} amount of the acid, şi m_{suport} amount of the support.

2.3.2 Characterization of the catalysts

2.3.2.1 Textural characteristics of the supports and catalysts

The textural characteristics of the supports and catalysts were determined by nitrogen adsorption at 77K, after a degassed probe at 200°C for 2 hours was obtained. The results are presented in Table 33.

Table 33. Textural characteristics of the catalysts.

Catalyst	S_{BET} (m^2/g)	V_{pors} (cm^3/g)	Classification of the porosity
SiO_2	489	0.73	mezoporous (73%)
$H_3PMo_{12}O_{40}$10%/SiO_2	421	0.63	mezoporous

$H_4SiW_{12}O_{40}$10%/SiO_2	412	0.62	mezoporous
$H_4SiW_{12}O_{40}$10%/H-ZSM-5	259	0.17	mezoporous

2.3.2.2 Morphologic characteristics of the catalysts

The morphology of the catalysts was analyzed by electronic transmission microscopy (TEM). In Figure 53 are presented TEM images: catalyst $H_3PMo_{12}O_{40}$10%/SiO_2 (Figure 53a), catalyst $H_3PMo_{12}O_{40}$10%/Al_2O_4 (Figure 53b), catalyst $H_3PMo_{12}O_{40}$10%/TiO_2 (Figure 53c) and catalyst $H_3PMo_{12}O_{40}$10%/H-ZSM-5 (Figure 53d).

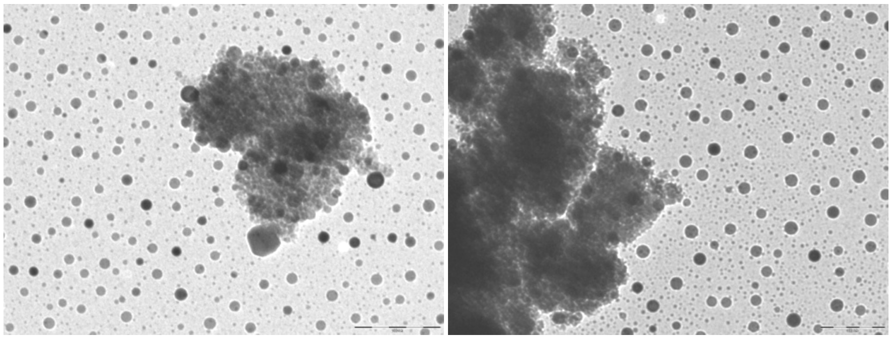

Figure 53a.

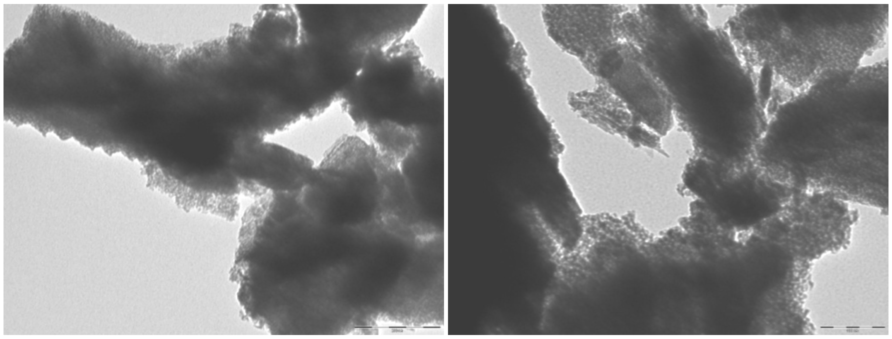

Figure 53b.

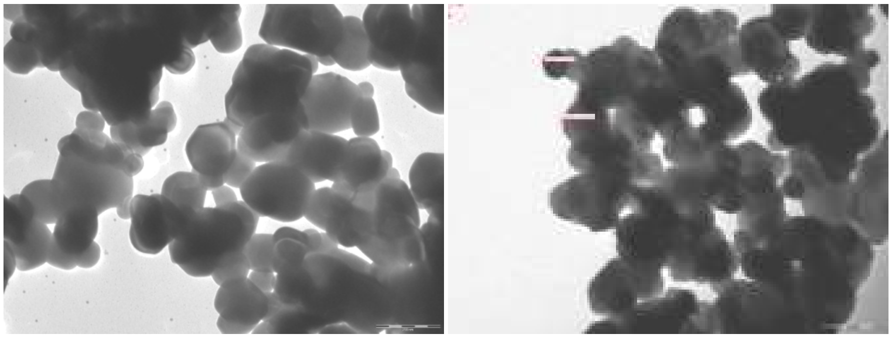

Figure 53c.

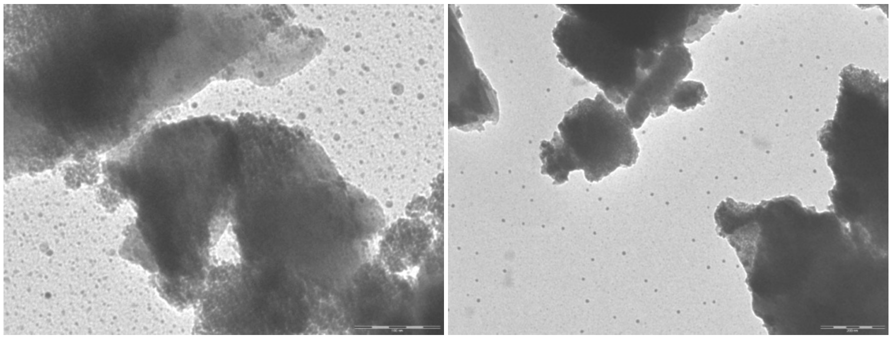

Figure 53d.

2.3.3 Isomerization of α-pinene catalyzed by molibdophosphoric acid deposed on supported

The catalytic properties of molibdophosphoric acid (PMo) were studied by deposing it on different supports, such as SiO_2, Al_2O_3, TiO_2 and H-ZSM-5. The catalysts were prepared by the method described above.

2.3.3.1 Isomerization of α-pinene catalyzed by molibdophosphoric acid deposed on SiO$_2$

2.3.3.1.1 Effect of deposition degree on the activity and selectivity of the catalyst PMo/SiO$_2$

First step of this study proposed SiO$_2$ as a support. Three types of catalysts with different deposition degrees (20%, 10% and 2%) have been prepared. The results obtained during this study are presented in Table 34.

Table 34. The selectivity of isomerization of α-pinene on PMo/SiO$_2$, at 100°C, using 1% catalyst function of G$_d$.

Nr	G$_d$ (%)	Time (h)	C (%)	Selectivity (%)								Volatile (%)	Ratio bicyclic/monocyclic
				TriC	Bicyclic terpenes		Monocyclic terpenes						
					Fen	Cf	α-T	Lim	γ-T	Pc	T		
1	20	1	74	1.1	4.2	28.3	7.1	37.8	3.9	1,1	10.7	96	0.55
		2	**86**	**1.2**	**4.2**	**29.2**	**8.0**	**37.6**	**4.2**	**1,6**	**11.5**		
2	10	1	49	1.5	4.2	31.7	5.3	38.7	3.2	1,1	9.9	96	0.67
		5	**88**	**1.2**	**4.0**	**32.2**	**4.9**	**35.5**	**3.3**	**2,4**	**10.1**		
3	2	5	5	11.4	9.1	**54.5**	4.5	**35.3**	4.5	4,5	9.1	98	1.19

First, it can be clearly seen that the deposition degree of PMo on SiO$_2$ influenced substantially the activity of the catalyst. We can affirm that the selectivity of the isomerization processes catalyzed by PMo/SiO$_2$ is high enough for monocyclic terpenes.

2.3.3.1.4 The effect of reaction temperature on the activity and selectivity of the catalyst PMo10%/SiO_2

The next step in the study and optimization of catalytic processes was represented by researches about the effect of reaction temperature on the activity and selectivity of the catalyst PMo10%/SiO_2. In order to effectuate this study, the catalytic processes at 60, 100, 130°C and refluxing temperature, using 1% catalyst, were tested. The results are presented in the following table:

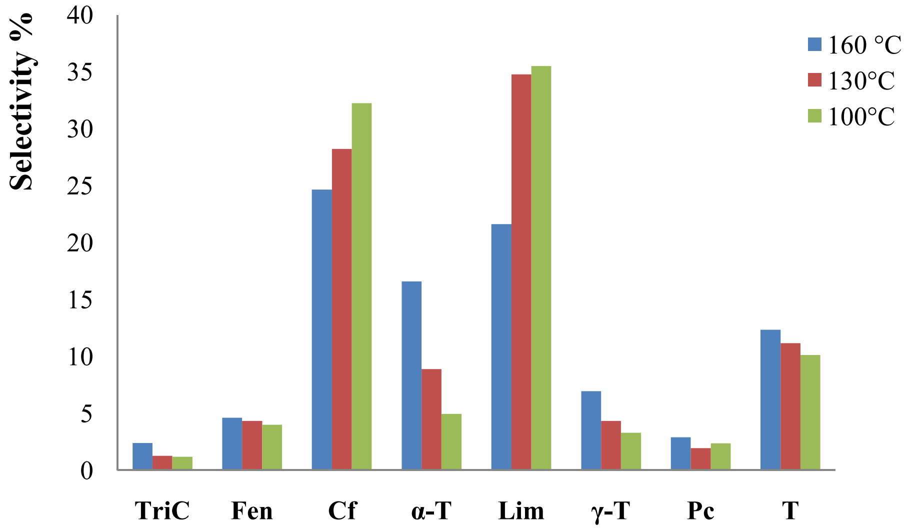

Figure 58. Selectivity of isomerization using 1% PMo10%/SiO_2 function of temperature.

The diagram presented in Figure 18 leads us to the conclusion that in the case of tricyclene, fenchene, paracymene and terpinolene the effect of reaction temperature si almost negligible, while for camphene, α-terpinene, limonene and γ-terpinene more spectacular modifications could be observed.

2.3.3.3 Isomerization of α-pinene catalyzed by molibdophosphoric acid deposed on TiO_2

The next step consisted in the preparation of the catalyst PMo/TiO_2, and testing-optimization of the catalytic processes. The catalysts were prepared according to the method described in chapter 2.3.1, having a deposition degree of 10% TiO_2.

2.3.3.3.1 The effect of reaction temperature on the activity and selectivity of the catalyst PMo10%/TiO_2 activated la 100°C

The first step in the study and optimization of catalytic processes was the research of the effect of reaction temperature on the activity and selectivity of the catalyst PMo10%/TiO_2. In order to realize these studies, the catalytic process at 100, 130°C and refluxing temperature using 1% catalyst were tested. The results are illustrated in the next figure.

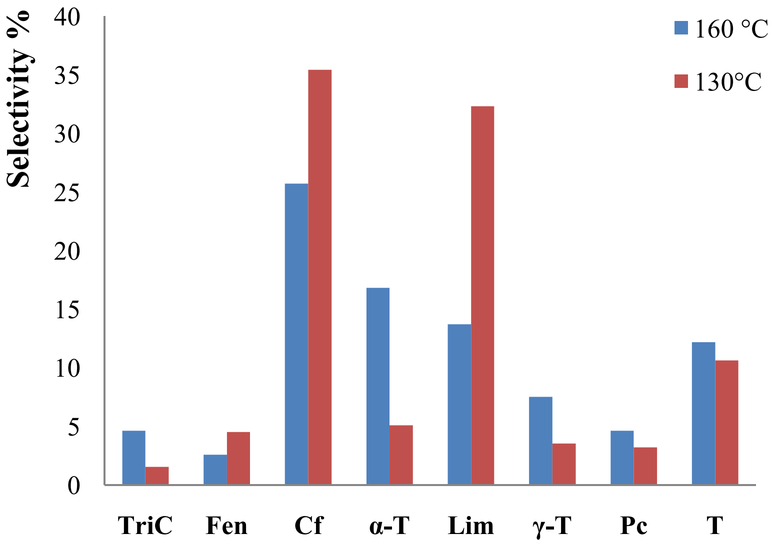

Figure 62. Selectivity of isomerization using 1% PMo10%/TiO_2, function of reaction temperature.

De diagram presented above proved the differences obtained at refluxing temperature and at 130°C. Due to the fact that the results obtained for PMo10%/TiO_2 activated at 100°C were not satisfactory, the catalyst was activated at 150°C (3 hours). In this way we tried to prepare a more active and selective catalyst in the isomerization reaction of α-pinene. With the catalyst in our hands, the catalytic test was performed in the same conditions as in the cases presented above. The results obtained with different catalysts are highlighted in Figure 63.

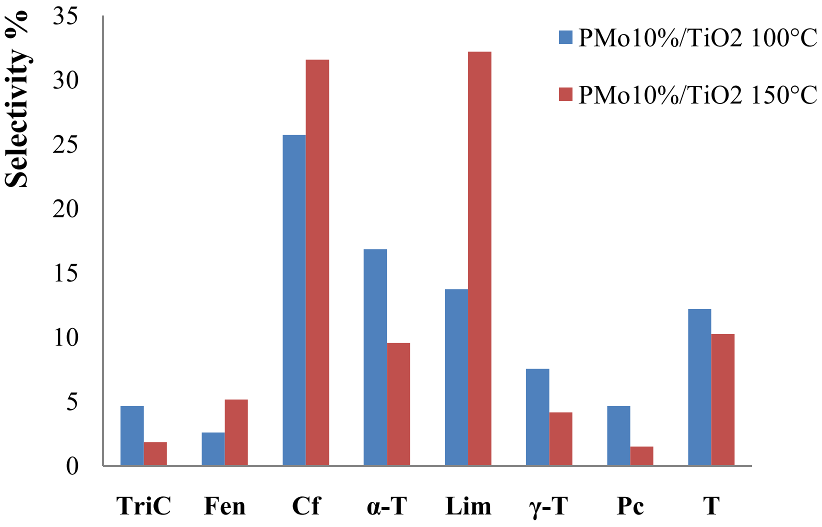

Figure 63. Selectivity of the isomerization at reflux, using 1% PMo10%/TiO_2, activated at 100°C and 150°C.

These results presented that changing the preparation process of the catalyst increases also the selectivity of the synthesis at the refluxing temperature.

2.3.4 Isomerization of α-pinene catalyzed by wolframosilicic acid deposed on support

The catalytic properties of wolframosilicic acid (SiW) were studied by deposing it on different support materials: SiO_2, TiO_2, and H-ZSM-5. The catalysts were obtained by the methodology described in chapter 2.3.1.

2.3.4.1 Isomerization of α-pinene catalyzed by wolframosilicic acid deposed on SiO_2

The first step consisted in the deposition of wolframosilicic acid on SiO_2.

2.3.4.1.1 The effect of reaction temperature on the activity and selectivity of the catalyst SiW10%/SiO_2

The study and optimization of the catalytic processes started with the effect of reaction temperature on the activity and selectivity of the catalyst SiW10%/SiO_2. For this study, the catalytic process at 60, 100, 130°C and refluxing temperature (155-175°C), using 1% catalyst was followed. The results are presented in Figure 68.

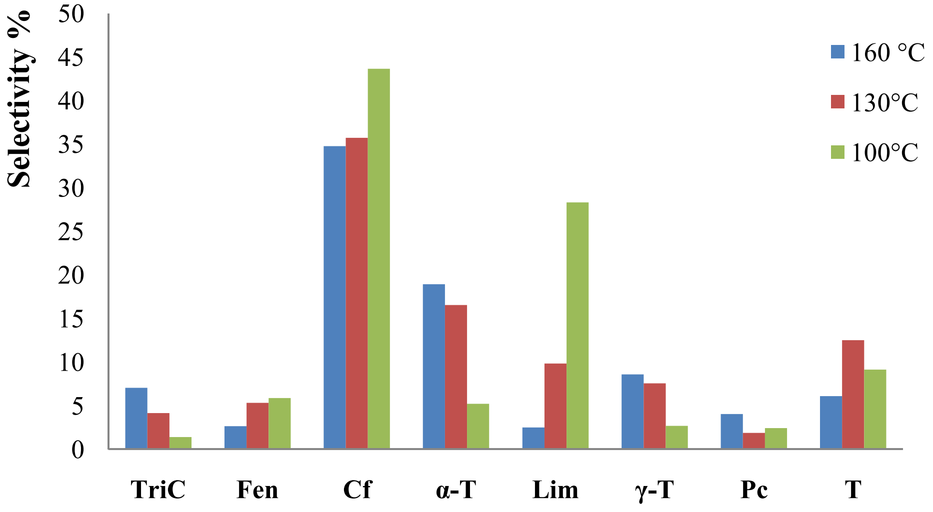

Figure 68. Selectivity of isomerization using 1% SiW10%/SiO_2, function of temperature.

Significant effects on the selectivity of the reaction could be observed when the reaction temperature was decreased. First, an improvement in the selectivity of camphene was evidenced. This phenomenon was also observed in the case of limonene, the selectivity being: 2.5%, 9.8% and respectively 28.3%.

2.3.4.1.2 The effect of the ratio catalyst/α-pinene on the activity and selectivity of the catalyst SiW10%/SiO_2

The effect of the ratio catalyst/α-pinene was also studied in the case of the catalyst prepared from SiW, with a deposition degree of 10% on SiO_2. The reactions were performed at 130°C using 1%, 0.5% and 0.25% catalyst. The ratio amount catalyst/α-pinene is the first very important factor and influence the reaction time and selectivity. There are substantial differences between the three syntheses when the selectivity of isomerization is taken into account. These differences for camphene and limonene are presented in the diagram from Figure 70.

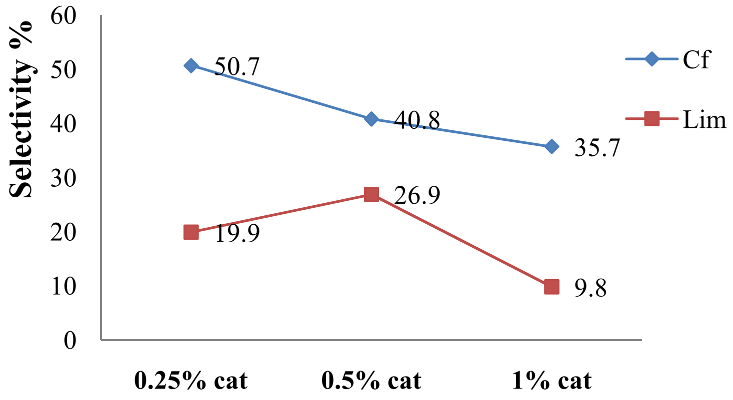

Figure 70. Selectivity for camphene and limonene function of the ratio catalyst/α-pinen.

Figure 70 illustrates that an increase of the selectivity in the case of camphene is observed when the amount of catalyst decreases. It must be highlighted that the selectivity of camphene is 50.7% (the highest until now) using 0.25% catalyst. In the case of limonene the maximum selectivity is obtained when used 0.5% catalyst. A decrease of the ratio leads to a decrease of the selectivity.

2.3.4.2 Isomerization of α-pinene catalyzed by wolframosilicic acid deposed on support based on TiO_2

The next step of the study realized on the acidic catalyst prepared from SiW deposed on solid support was the use of TiO_2 as a support.

2.3.4.2.1 The effect of reaction temperature on the activity and selectivity of the catalyst SiW10%/TiO_2

In this chapter the results obtained in the study of the effect of reaction temperature on the activity and selectivity of the catalyst SiW10%/TiO_2 will be presented. For each study, the catalytic process at 100, 130°C and refluxing temperature using 1% catalyst was tested. The results are presented in Table 46.

Table 46. Selectivity of isomerization of α-pinene on SiW10%/TiO_2 function of temperature.

Nr	Reaction temperature (°C)	**Time (h)**	**C (%)**	**Selectivity (%)**								**Volatile (%)**	**Ratio bicyclic/monocyclic**
				TriC	**Bicyclic terpenes**		**Monocyclic terpenes**						
					Fen	**Cf**	**α-T**	**Lim**	**γ-T**	**Pc**	**T**		
1	Reflux (155-175)	**30***	**100**	**9.0**	**6.4**	**34.1**	**16.5**	**1.2**	**8.0**	**6.4**	**3.4**	70	1.04
2	130	**8**	**85**	**1.9**	**6.1**	**44.1**	**3.4**	**27.4**	**1.8**	**4.8**	**7.1**	93	0.89
3	100	**36**	**83**	**1.4**	**6.3**	**46.1**	**2.5**	**28.6**	**1.6**	**4.9**	**6.4**	95	1.09

* reaction time in minutes

From the selectivity point of view we can clearly observe that the decrease of reaction temperature positively influence the obtaining of products (camphene and limonene). The analysis of the diagram in Figure 73 sustains this argument.

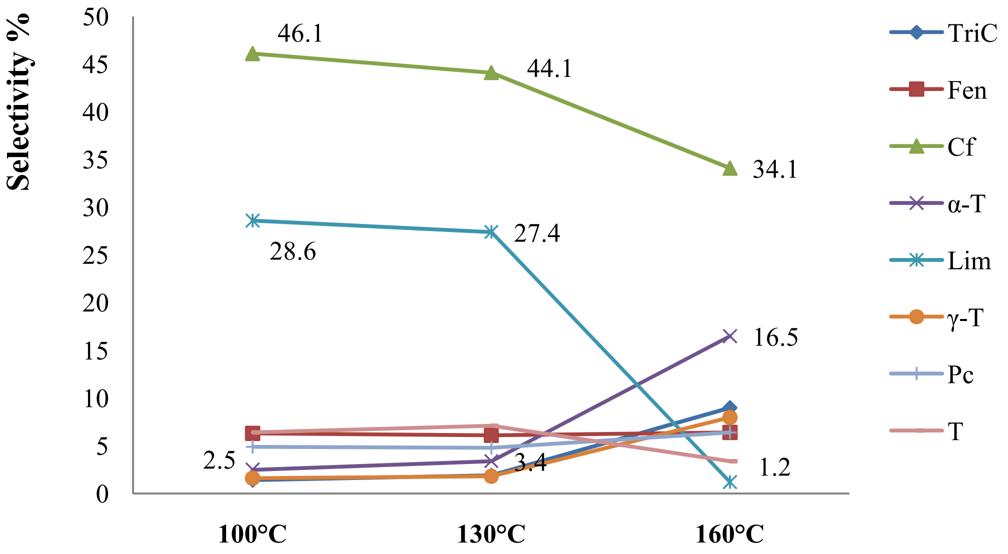

Figure 73. Selectivity of isomerization using 1% SiW10%/TiO_2, function of temperature.

The diagram reveals that in the case of camphene and limonene the improvement of the selectivity is directly proportional with the decrease of reaction temperature.

3.Conclusions

1. The reactions of α-pinene in acetic acid have been performed, using solid catalysts: $B(OAc)_3$, H_3BO_3, B_2O_3, paratoluenesulfonic acid (APTS) and zeolite 13X. New synthesis methods have been elaborated for the synthesis of bornyl acetate and –in the group of isomerization products – of terpinolene. These methods are more efficient from energetic point of view.

2. The reactions of α-pinene in acetic acid have been performed, using solid catalysts: $B(OAc)_3$, H_3BO_3, B_2O_3, paratoluenesulfonic acid (APTS) and zeolite 13X in microwave conditions. The knowledge area with regard to α-pinene reactions in acetic acid and isomerization reactions in microwave conditions was developed, new synthesis methods of isobornyl acetate and terpenyl acetate being elaborated. These methods are simpler, more rapid and more efficient energetically than those performed with microwave irradiation, but in the presence of water and supercritical conditions (270°C, 270 bars).

3. Have been prepared active and efficient catalysts for the isomerization of α-pinene, based on zeolite H-ZSM-5 by the treatment with different concentrations of sulfuric acid. Using this treatment, the aluminum content in the structure of zeolite has been reduced (improvement in its catalytic selectivity), controlling its acidic character, without any change in the structure of the zeolite. The method used for the reduction of aluminum content is simple, efficient and does not produce dangerous waste when recirculation of acidic solutions was performed. The zeolite catalysts were characterized by electronic transmission microscopy (TEM), nitrogen adsorption/desorption at 77K and powder X-Ray diffraction.

4. The isomerization process catalyzed by zeolite H-ZSM-5 with reduced aluminum content has been optimized, studying the catalytic process function of temperature and ratio catalyst/substrate. The method optimized is simple, needs very small amounts of catalyst, does not need special working conditions and permits simultaneous obtaining of limonene and camphene with high selectivity. Using these catalysts the secondary processes are negligible, the water stream distillation yields being very high. The secondary products obtained can also be further used.

5. Different catalysts based on molibdophosphoric acid and wolframosilicic acid deposed on various oxides (SiO_2, Al_2O_3, TiO_2) and zeolite H-ZSM-5 have been prepared. The preparation method is energetically efficient, does not need complex procedures or special equipments. The catalysts have been characterized by electronic transmission microscopy (TEM) and their specific surface by nitrogen adsorption/desorption at 77K. The prepared catalysts are efficient for the catalysis of isomerization reaction of α-pinene.

6. The isomerization process catalyzed by molibdophosphoric acid and wolframosilicic acid deposed on oxide support and zeolite ZSM-5 have been optimized. Simple and efficient methods have been elaborated to obtain simultaneously camphene and limonene with high selectivity. The catalysts are efficient to catalyze the isomerization of α-pinene with low deposition degree (10%), using very small amount of substrate. The secondary processes are negligible when using these catalysts, and ratio of volatile products in the reaction mass is higher than 95%. The secondary products can also be further used.

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