

Supported $H_4SiW_{12}O_{40}$ catalysts for α -pinene isomerization

Research Article

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Abstract: The heterogeneous isomerization of α -pinene was studied at 100, 130 and 160°C using 10% supported $H_4SiW_{12}O_{40}$ (SiW) on SiO_2 , TiO_2 and HZSM-5. The effect of the reaction temperature and the concentration of the catalyst over the conversion of α -pinene and the selectivity of camphene, limonene and terpinolene had been monitored. The recovery, reuse and leaching effect of the catalysts were studied. Simple, environmentally friendly and economic methods for the synthesis of camphene and limonene were developed and optimized.

Keywords: Heteropolyacids • Monoterpenes • Catalytic activity • Isomerization • Selectivity

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1. Introduction

Monoterpenes are essential ingredients of flavor and fragrance, perfumery, cosmetics, fine chemicals and pharmaceutical industries. The most important constituent of the monoterpene group is α -pinene which contains a labile bicyclo[3.1.1]heptene carbon skeleton and frequently participates in ring-opening reactions and rearrangements, producing various acyclic, mono- and bicyclic terpenes [1]. In many cases, heterogeneous acid catalysis is used for the conversion of α -pinene into valuable products such as: camphene, limonene and terpinolene.

The main products of α -pinene isomerization in the presence of the solid acidic catalysts are camphene and limonene. Camphene is an important intermediate in the synthesis of camphor; limonene can be transformed into other monocyclic terpenes such as: terpinolene, α -, γ -terpinene, heavier dimeric and polymeric products [2]. Conventionally, for the isomerization of α -pinene to

camphene, the industrial process is based on a weak acidic TiO_2 catalyst [3]. In order to reduce energy consumption and to increase selectivity toward camphene, many solid catalysts were studied: sulfated zirconia [4-6], activated clays [7-11], modified molecular sieves [12-14] and zeolites [15-18]. Each solid catalyst leads to a complex mixture of terpenes, when usually, camphene, the major product, is obtained with a selectivity of 30-50%.

The literature data suggests that the bicyclic/monocyclic terpenes ratio is dependent on several factors, such as: the reaction temperature and the acid strength. Severino *et al.* [19] studied the α -pinene isomerization using zeolites and concluded that, on the Lewis sites, camphene and bicyclic products were preferentially formed, while on the Brønsted sites, monocyclic terpenes were favored. Recently, in addition to these catalysts, a new family of acids on solid supports, the heteropolyacids family, were successfully used in α -pinene isomerization [20-22]. Heteropolyacids (HPAs), especially the Keggin series, are very attractive for researchers because of

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its numerous opportunities on many heterocatalytic systems, having a major economic impact and green benefits [23,24].

In this work, we report the isomerization of α -pinene in heterogeneous catalysis, using supported HPAC catalysts. The Keggin heteropolyacid used for these studies was $H_4SiW_{12}O_{40}$, the most commonly encountered heteropolyacid. SiO_2 , TiO_2 and HZSM-5 zeolite were used as solid supports.

2. Experimental procedure

2.1. Chemicals

All chemicals used in this study were purchased from commercial sources. α -Pinene was 97% pure and before use was distilled, the other chemicals were used without further purification.

2.2. Catalyst preparation

A series of SiW acid catalysts were prepared by impregnation with loading 10 wt% SiW/solid support. A 5 mL alcoholic solution of 0.27 g SiW was added to 2.5 g of solid support and the mixture was allowed to stir at room temperature for 24 h. After the removal of methanol by vacuum distillation, the samples were dried in an oven, under atmospheric pressure at 100°C for 2 h [29].

2.3. Catalyst characterization studies

Surface areas and pore volumes of the catalysts were obtained by nitrogen absorption isotherms, at liquid nitrogen temperature, after sample degassing, under vacuum at 220°C, for 3 h, using a Sorptomatic 1990 instrument (Thermo Electron) up to $p/p_0 \sim 0.95$. The estimated specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller method in the p/p_0 range of 0.03–0.3, set so that the correlation factors to be 0.9999.

Powder XRD patterns were measured with a Bruker D8 Advance Powder diffractometer at 40 kV and 40 mA, equipped with an incident beam Ge 111 monochromator using $CuK\alpha$ radiation ($\lambda = 1.540598\text{\AA}$).

2.4. Catalytic test

The prepared catalysts were tested in isomerization reactions of α -pinene. The reactions were carried out at normal atmospheric pressure in a three-necked flask equipped with an efficient magnetic stirrer, reflux condenser and a temperature controller. Typically, 20 g α -pinene and 0.2 g catalyst were loaded in the reactor, stirred and heated up to working temperature

(100–160°C). The reaction products were analyzed by gas chromatography (Hewlett Packard 5890/II) with flame ionization detector (FID), using a SUPELCOWAX™ 10 (60 m $\times$ 0.32 mm) capillary column. H_2 was used as the carrier gas with a flow of 0.2 mL min^{-1} and the temperature was programmed from 60 to 210°C at a rate of 4°C min^{-1} increase. The identification of reaction products was realized by comparison of retention time with standards and GC-MS. The mass spectra were recorded with a Hewlett Packard GC-MSD 5890 series II- 5972 spectrometer, with DB-5MS (30 m/0.25 mm) capillary column.

3. Results and discussion

3.1. Catalysts characterization

Nitrogen adsorption data were evaluated using the BET method. Table 1 presents the surface area and pore volume measurement of the catalyst and support. The specific surface areas and the specific pore volumes slightly decrease when the deposition of the catalysts on solid surfaces take place.

Nitrogen physisorption isotherms were measured at 77 K to verify the porosity of $H_4SiW_{12}O_{40}/SiO_2$ catalyst. The sample exhibits a type II isotherm with a H2 hysteresis loop (Fig. 1a). The pore size distribution (Fig. 1b) (Dollimore-Heal method) indicates the completion of mesopore filling (99.71% of the volume of pores). A narrow distribution of the pore diameter is observed, 92.8% of pores being between 3.7 and 8.6 nm. The specific surface area is 412 $\text{m}^2 \text{g}^{-1}$ ($p/p_0 = 0.03 - 0.3$), with 0.62 mL/g specific pore volume at $p/p_0 = 0.95$.

Fig. 2a shows the isotherm curves for nitrogen physisorption at 77K in the case of the $H_4SiW_{12}O_{40}/TiO_2$ catalyst. The specific surface area is 8 $\text{m}^2 \text{g}^{-1}$ and the specific pore volume is 0.006 mL g^{-1} . Fig. 2b confirms the mesoporosity of the sample (94.27% mesopores).

Nitrogen adsorption/desorption isotherms of $H_4SiW_{12}O_{40}/HZSM-5$ measured at 77K are presented

Table 1. Some characteristics of the catalysts and their support materials.

Support/Catalyst	$S_{\text{BET}}^a (\text{m}^2 \text{g}^{-1})$	$V_{\text{pore}}^b (\text{mL g}^{-1})$
SiO_2 (1)	489	0.73
TiO_2 (2)	9	0.006
HZSM-5 (3)	321	0.21
$H_4SiW_{12}O_{40}/SiO_2$ (4)	412	0.62
$H_4SiW_{12}O_{40}/TiO_2$ (5)	8	0.006
$H_4SiW_{12}O_{40}/HZSM-5$ (6)	259	0.17

^aspecific surface area, ^bpore specific volume

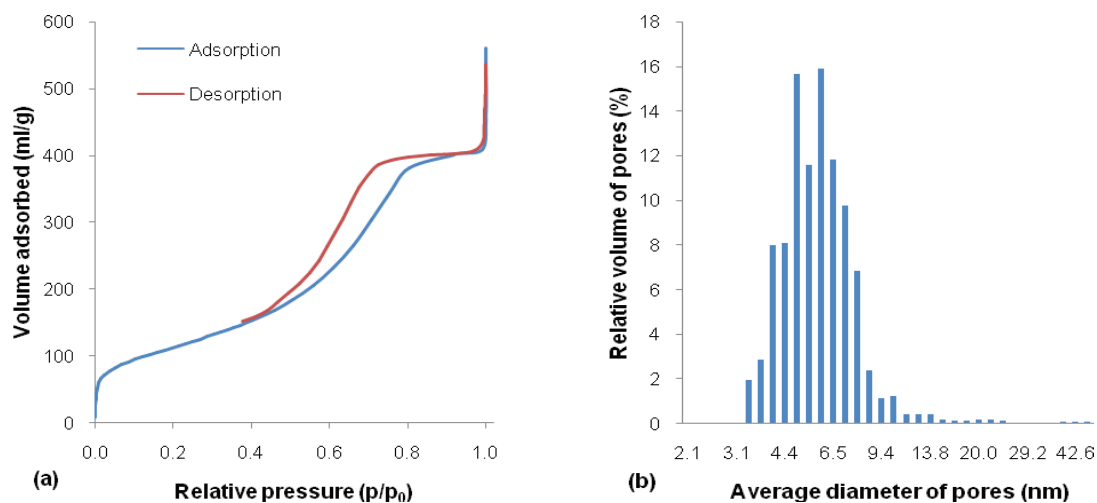


Figure 1. (a) Nitrogen adsorption/desorption isotherms at 77 K; (b) Pore size distribution of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyst.

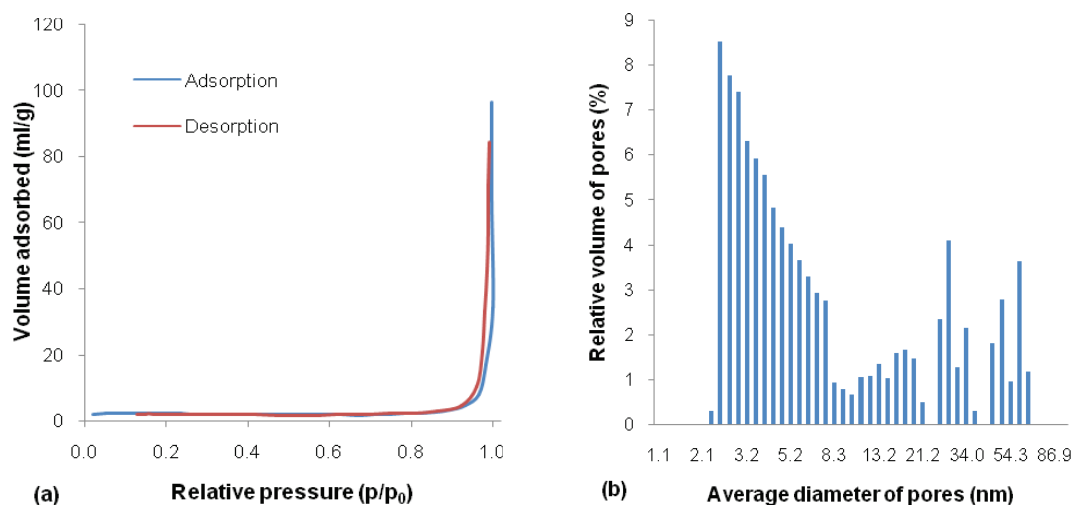


Figure 2. (a) Nitrogen adsorption/desorption isotherms at 77 K; (b) Pore size distribution of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ catalyst.

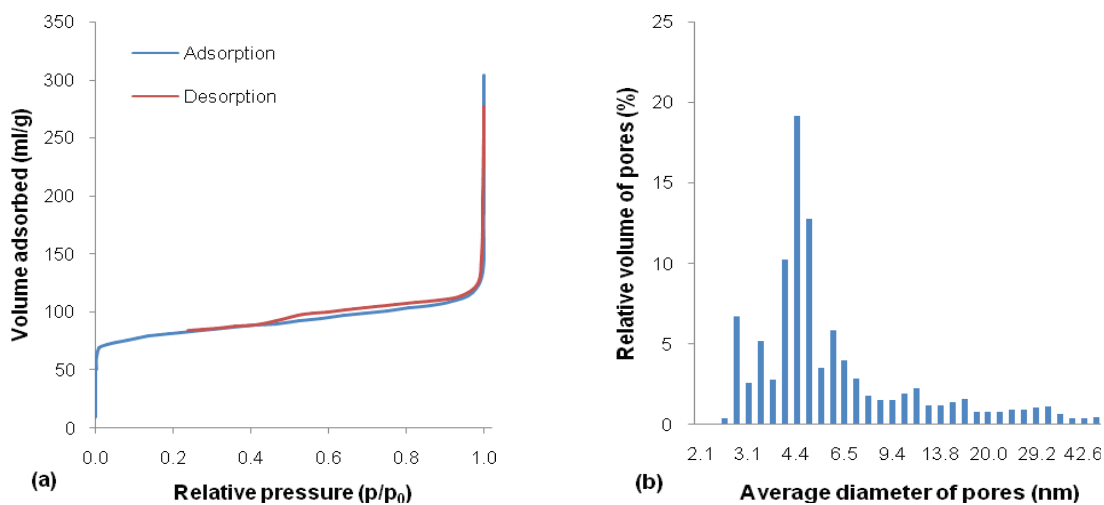


Figure 3. (a) Nitrogen adsorption/desorption isotherms at 77 K; (b) Pore size distribution of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{HZSM-5}$ catalyst.

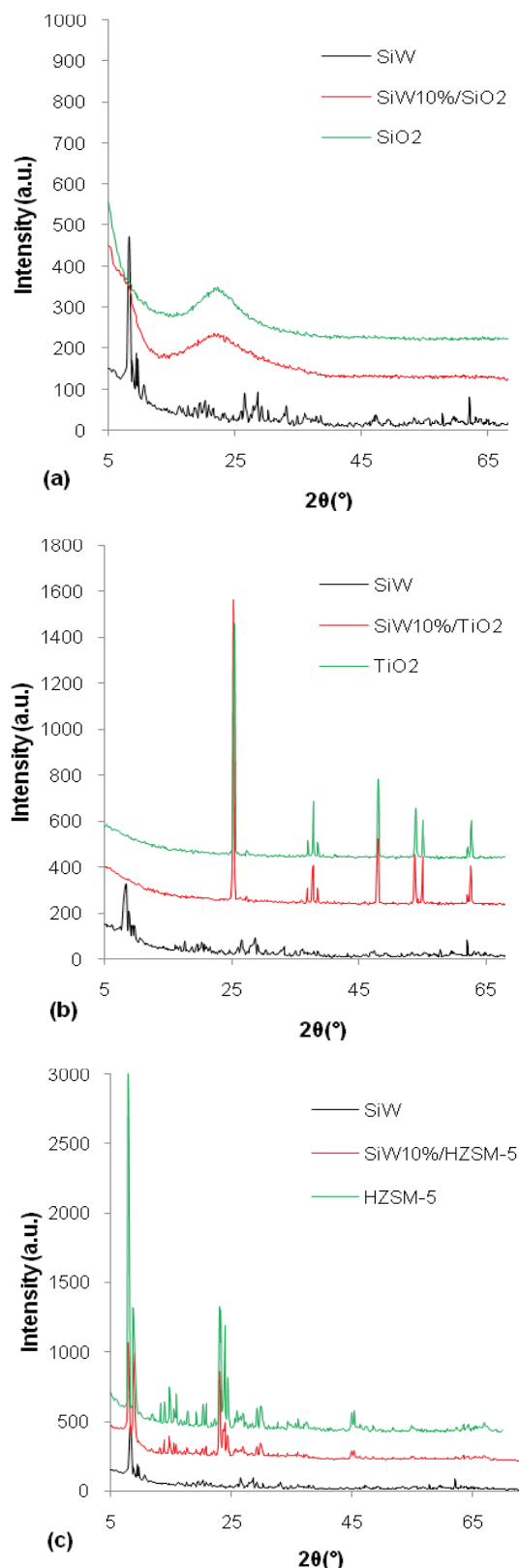


Figure 4. PXRD patterns for: (a) SiW, SiW10%/SiO₂, SiO₂; (b) SiW, SiW10%/TiO₂, TiO₂; (c) SiW, SiW10%/HZSM-5, HZSM-5.

in Fig. 3a. The sample exhibits a type II isotherm, with slight hysteresis. The pore size distribution, presented in Fig. 3b, confirms the mesoporosity of the catalyst. The physisorption data estimates that the specific surface area is 259 m² g⁻¹ ($p/p_0 = 0.03 - 0.3$) and the specific pore volume is 0.17 mL g⁻¹ at $p/p_0 = 0.95$. Adding H₄SiW₁₂O₄₀ onto the zeolite kept the isotherm type, but it may be observed a decrease of specific surface and pore volume.

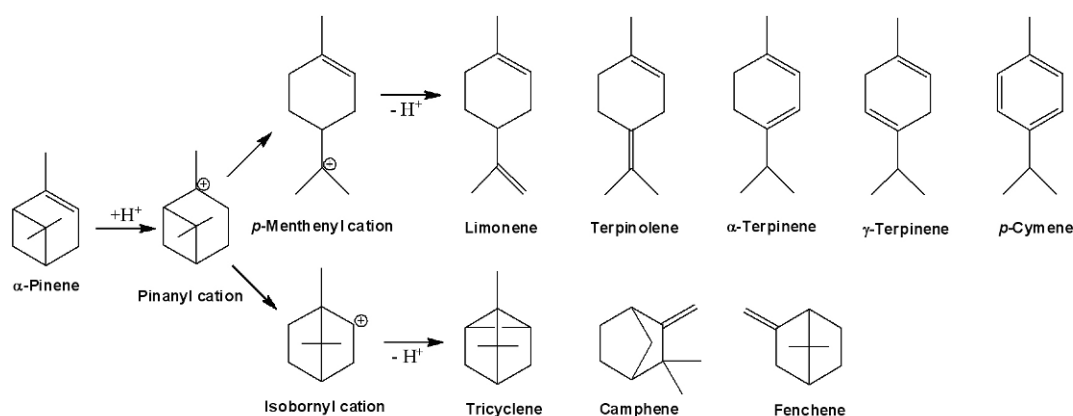
The PXRD patterns for SiO₂, TiO₂ and HZSM-5 supported H₄SiW₁₂O₄₀ (Fig. 4) display no reflections corresponding to the SiW Keggin structure. These results indicate that HPA was highly dispersed at 10% loading on the supports and are in accordance with literature data [25].

3.2. Isomerization of α -pinene

Catalytic activity and selectivity of the mentioned supported SiW catalysts for the isomerization of α -pinene were studied in liquid phase. Scheme 1 presents two parallel routes for the isomerization of α -pinene, resulting tricyclic terpenes (tricyclene), bicyclic terpenes (fenchene, camphene) and monocyclic terpenes (α -, γ - terpinene, limonene and terpinolene). The double bond in the terpene skeleton is protonated by an electrophilic attack when the pinanyl carbocation is obtained. This intermediate is further involved in a Wagner-Meerwein rearrangement, with the formation of isobornyl and p-menthenyl carbocations [26-28]. These two carbocations represent the key for the formation of the complex mixture of isomerization products.

The catalytic activity of SiO₂ (1), TiO₂ (2) and HZSM-5 (3) in the isomerization of α -pinene (1% catalyst, 160°C) was tested. In the case of SiO₂ (1) and TiO₂ (2) α -pinene remained unreacted even after a long time at this high temperature. An exception was observed in the case of HZSM-5 (3), which proved to act itself as a catalyst. Table 2 highlights the distribution of isomerization products, using the supports and the supported catalysts. Camphene and limonene proved to be the main products of isomerization reactions.

In the presence of catalyst 6, the isomerization reaction of α -pinene did not take place under the same conditions as in the case of catalysts 4 and 5 (5 hours, 100°C). When the reaction temperature was increased up to 160°C for 2 hours (Table 2), the results obtained were good. As presented in this table, when the isomerization reaction was performed using 4 and 5 as catalysts, a low conversion of α -pinene was obtained. Our purpose was to optimize these reactions in order to obtain comparable utile conversions. So, our strategy was focused on extending the reaction time, without any modifications of the temperature and the catalyst



Scheme 1. Acid-catalyzed isomerization of α -pinene.

Table 2. Distribution of the products for isomerization of α -pinene over the catalyst (20 g α -pinene, 0.2 g catalyst).

Catalyst	Composition (% mole)								
	α -Pinene	Tricyclene	Fenchene	Camphene	Terpinenes	Limonene	p-Cymene	Terpinolene	Others
4^a	26.6	0.5	3.1	31.5	6.1	22.8	1.5	7.2	0.7
5^a	74.6	0.4	1.6	10.6	1.6	7.3	0.5	2.0	1.4
6^a	95.9	0.2	0.3	1.5	0	0.8	0.3	0.2	0.8
6^b	3.9	2.6	6.2	37.3	14.4	18.7	0.5	10.8	5.6
3^b	74.1	1.4	2.0	9.0	3.2	4.4	0.2	1.6	4.1

^aReaction temperature 100°C, reaction time 5 hours

^bReaction temperature 160°C, reaction time 2 hours

Table 3. Conversion of α -pinene and selectivity to camphene, limonene and terpinolene (20 g α -pinene, 0.2 g catalyst).

Catalyst	Reaction time (h)	Conversion (%)	Selectivity (%)		
			Camphene	Limonene	Terpinolene
4^a	8	81	43.7	28.3	9.1
5^a	36	83	46.1	28.6	6.4
6^b	2	96	38.7	19.5	11.6
3^b	24	70	38.0	20.0	8.0

^aReaction temperature 100°C

^bReaction temperature 160°C

concentration. After the work-up, the conversion of α -pinene and the selectivity to camphene, limonene and terpinolene were calculated and the results were presented in Table 3. Concerning the conversion, the best results could be observed when catalyst 6 was used. In the case of catalysts 4 (reaction time 8 h) and 5 (reaction time 36 h), good results were obtained with respect to the selectivity of camphene and limonene.

Conversion of α -pinene and selectivity of products were calculated using the following equations:

$$\text{Conversion (C)} = \frac{\text{amount of } \alpha\text{-pinene isomerized}}{\text{initial amount of } \alpha\text{-pinene}} \times 100$$

$$\text{Selectivity (S)} = \frac{\text{amount of product } i}{\text{amount of } \alpha\text{-pinene isomerized}} \times 100$$

The selectivity of the main products was almost the same in the case of the catalysts based on the oxide supports (4 and 5). Significant differences could be highlighted with respect to the reaction time until a favorable conversion was reached. So, a good utile conversion was obtained 4.5 times earlier when catalyst 4 was used. This phenomenon can be attributed to the major differences between the specific surfaces of those two catalysts. Catalyst 6 represents a special case: the main products, camphene and limonene, being obtained less selective than when catalysts 4 and 5 were used. When compared the catalytic activity of 3 and 6, important differences could be also observed in the reaction time of the isomerization of α -pinene. The results presented in Table 3 concluded that the high catalytic activity of 6 was caused by the presence of the heteropolyacid

$\text{H}_4\text{SiW}_{12}\text{O}_{40}$, which did not change the behavior and the selectivity of the zeolite.

In literature, studies of supported heteropolyacids (PW) catalyzed isomerization of α -pinene were focused on the reaction in liquid or gas phase. When silica-supported PW (0.6 wt% PW20%/SiO₂) was used as a catalyst [29], best results were obtained at 100°C, in liquid phase. After 1 h, the conversion of α -pinene was 90%, selectivity of camphene 50% and of limonene 28%.

Studies concerning the TiO₂-supported PW (PW15%/TiO₂) effect on the isomerization reaction were also reported [30]. The reaction was accomplished in gas phase at 200°C, 20 mL min⁻¹ flow rate, 10 h time on nitrogen stream. In this case, the conversion of α -pinene

was 88% and the selectivity of camphene and limonene was 56%, 7% respectively. Recently, Atalay and Gündüz [22] reported some results for the isomerization reaction of α -pinene in liquid phase using a non-conventional support, a natural zeolite, clinoptilolite. The reaction was conducted in a nitrogen atmosphere and at a constant temperature of 125°C. A 2.3 wt% PW4.25%/zeolite was used and after 3 h the conversion was almost total. The selectivity for camphene proved to be 39.3% and for limonene 12.6%.

Our results are similar to those reported until now, even better with respect to limonene. We proved that can be achieved good results with minimum costs. Our supported SiW catalysts can be simply obtained in mild conditions without any additional precautions.

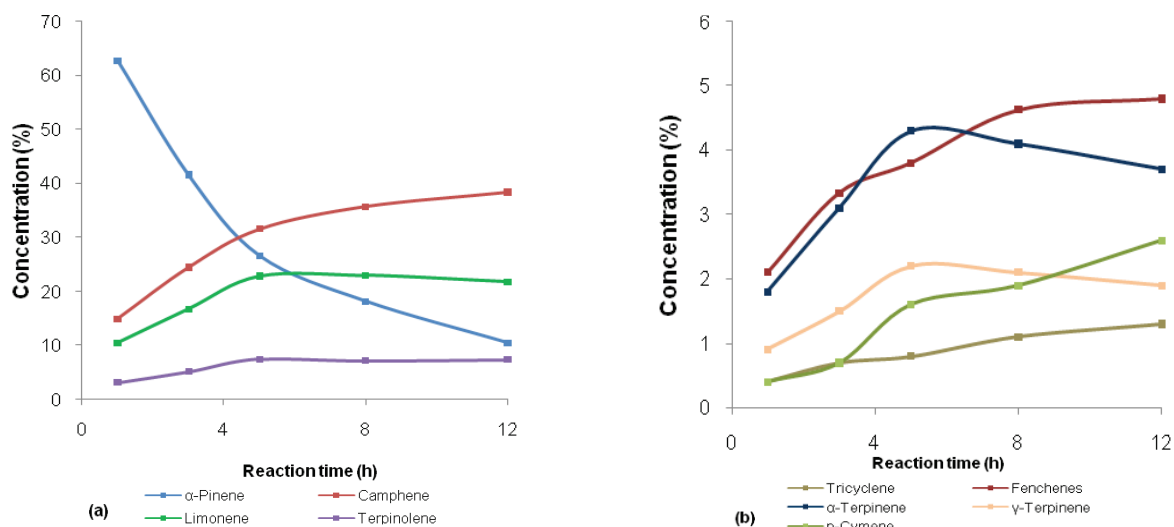


Figure 5. (a) Concentration of the major products in the reaction mixture depending on the reaction time for $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyst (α -pinene/catalyst ratio of 100/1, at 100°C); (b) Concentration of the minor products in the reaction mixture depending on the reaction time for $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyst (α -pinene/catalyst ratio of 100/1, at 100°C)

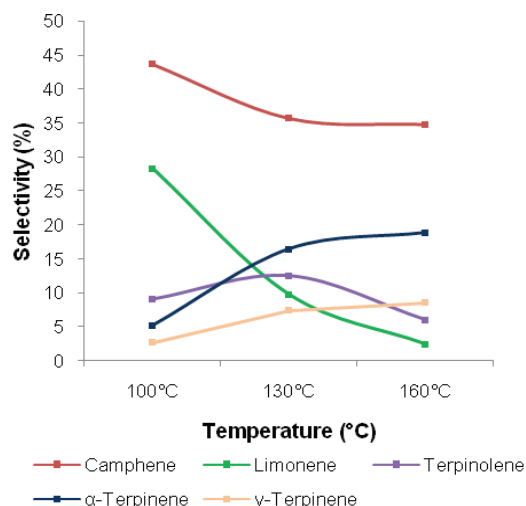


Figure 6. Effect of the reaction temperature on the selectivity of camphene, limonene and terpinolene (α -pinene/catalyst: 100/1, catalyst $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$)

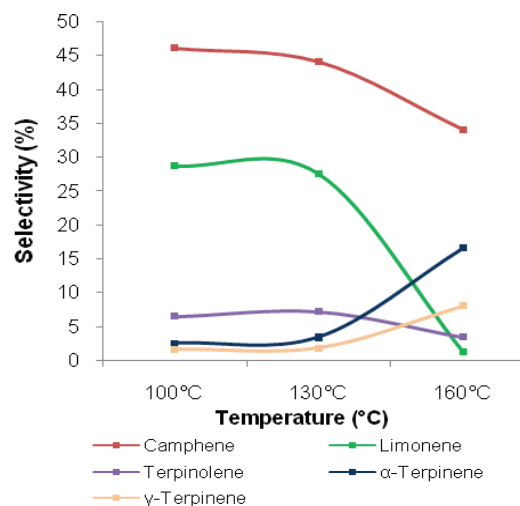


Figure 7. Effect of the reaction temperature on the selectivity of camphene, limonene and terpinolene (α -pinene/catalyst: 100/1, $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ as a catalyst).

Typical kinetic curves for $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ catalyst are presented in Fig. 5.

According to Fig. 5a, the concentration of α -pinene decreases, while the concentration of the main products (camphene and limonene) increases after 12 hours to 38.4% and 21.8%, respectively. Terpinolene reaches also a concentration of 7.4%. Other isomerization products, Fig. 5b, are obtained in traces (<4%).

3.2.1. The effect of temperature

Temperature plays an important role in the selectivity of terpene products. Fig. 6 reveals the effects of reaction temperature on the selectivity of camphene, limonene and terpinolene using $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ as a catalyst. For these studies, the α -pinene/catalyst ratio was adjusted to 100/1, and the isomerization processes were achieved at 100, 130 and 160°C.

High temperatures led to a decreased selectivity with respect to camphene, limonene and terpinolene. Best results were obtained at 100°C for camphene and limonene, and 130°C for terpinolene. It is worth mentioning that at 160°C fair selectivity could also be observed for α - and γ -terpinene, 18.9% and 8.6%, respectively. Concerning the reaction time required for conversions higher than 80% it can be stated that it significantly decreases as the temperature increases: after 8 hours at 100°C a conversion of 81% was obtained, after 30 minutes at 130°C a total conversion was obtained, and at 160°C a total conversion was already observed after 5 minutes.

Interesting results could be highlighted when using $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ as a catalyst. A graphical picture including the effect of the temperature on the selectivity is shown in Fig. 7.

When TiO_2 was used as a support, the highest selectivity of camphene was obtained at a lower temperature (see Fig. 7). The selectivity of camphene decreased when the reaction was performed at higher temperatures. Similar results are observed in the case of limonene, but more obvious variation of selectivity is defined; at 130°C the selectivity level remains almost constant, but at 160°C the selectivity drops to 1%. According to literature data, this phenomenon can be explained by the fact that during the reaction limonene reacts further obtaining other products [31]. The proof of this affirmation is the formation of α - and γ -terpinene with a selectivity of 24.5%. In case of terpinolene the highest selectivity is achieved at 130°C. As stated above, the reaction time for a total conversion decreases when higher temperatures are used, so, the best conversion is obtained after 30 minutes at 160°C.

The effect of temperature over the activity and selectivity of the catalyst was also studied for

$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{HZSM-5}$. These studies were based on a ratio of 100/1 α -pinene/catalyst. The catalytic activity was tested at 100, 130 and 160°C and significant conversions were obtained only at 160°C. At this temperature, after 2 hours, the conversion of α -pinene was 96%. The selectivity of reaction products was monitored and the results were 39% for camphene, 20% for limonene and 12% for terpinolene. Another compound, terpinene, was obtained with high selectivity (15%).

3.2.2. The effect of catalyst concentration

The effect of catalyst concentration, for supported SiW with the loading of 10% on SiO_2 (Fig. 8) was studied. The reactions were performed at 130°C, using different α -pinene/catalyst ratios, as follows: 100/1, 100/0.5 and 100/0.25.

The selectivity of camphene decreases by increasing the ratio α -pinene/catalyst (Fig. 8). In the case of terpinolene it can be noticed that the selectivity enhances with the increasing of the α -pinene/catalyst ratio. When analyzing the selectivity of the limonene, interesting results are observed. A maximum selectivity is obtained when the ratio is 100/0.5. When adding more catalyst in the synthesis (100/1), a fair selectivity is not achieved. This phenomenon can be explained by the weak stability of the limonene in these conditions and the formation of other terpenoidic derivatives, such as α - and γ -terpinene. The isomerization reaction time to obtain useful conversions was important for our studies. Four days were needed for a desired conversion when less catalyst was used but only a few minutes when more catalyst was added (100/1).

$\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{TiO}_2$ proved to be less active than the catalyst loaded on SiO_2 ; the reaction time being prolonged and the conversion of α -pinene unsatisfactory. Therefore, different concentrations of catalyst and temperatures were needed. Very good results were obtained using 2% catalyst at 130°C for only 1 hour, the conversion being 98%. This catalyst disadvantage yielded substantial changes in the composition of the obtained mixture: fenchene and tricyclene were obtained with relatively high selectivity (9.7%, 10.1% respectively), camphene was obtained with a relatively low selectivity (34.7%) and limonene appeared only in traces. The most important change was observed for p-cymene, synthesized with high selectivity (20.1%).

Another catalyst taken into account for our studies concerning the effect of the concentration of catalyst over the conversion of α -pinene and the selectivity of terpenoidic compounds was represented by $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{HZSM-5}$. The results of these studies performed at 160°C are presented in Fig. 9.

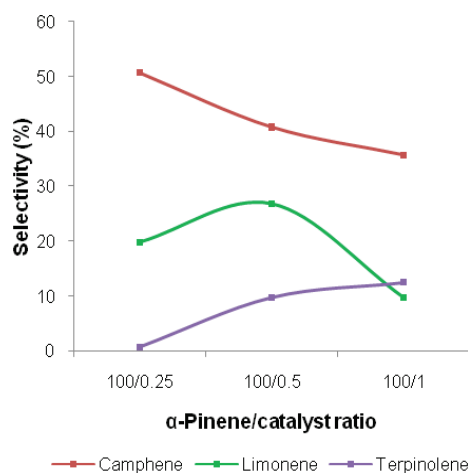


Figure 8. Effect of the catalyst concentration on the selectivity of camphene, limonene and terpinolene at 130°C, using $H_4SiW_{12}O_{40}/SiO_2$ catalyst.

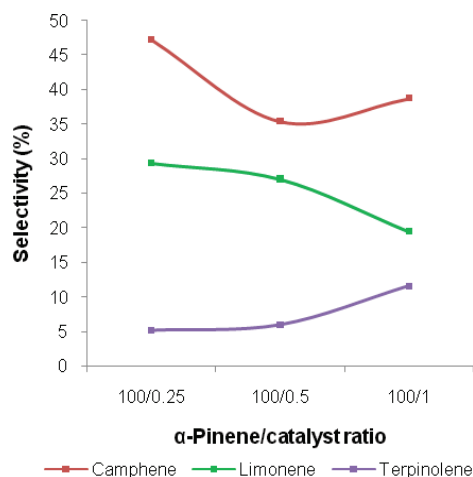


Figure 9. Effect of the catalyst concentration on the selectivity to camphene, limonene and terpinolene (160°C, $H_4SiW_{12}O_{40}/HZSM-5$).

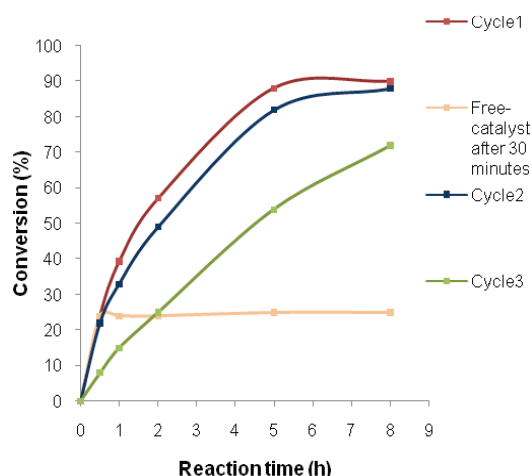


Figure 10. Kinetic curves for three recovery/reutilization cycles and the effect of the SiW leaching for $H_4SiW_{12}O_{40}/SiO_2$ catalyst (α -pinene/catalyst ratio of 100/1, at 100°C).

As shown in the figure above, using 0.25% catalyst, the highest selectivity for camphene and limonene is obtained. Almost similar results as in the case of $H_4SiW_{12}O_{40}/SiO_2$ were determined for terpinolene. An interesting effect of the concentration of catalyst can be observed for camphene. When using 0.5% $H_4SiW_{12}O_{40}/HZSM-5$, the selectivity decreases (35.4%), but at higher concentration of the catalyst (1%), the selectivity of camphene rises up to 38.7%. Concerning the reaction time, the results were in accordance with those for the catalysts presented above. α -Pinene was highly converted (96%) to camphene only after 2 hours when the ratio α -pinene/catalyst was 100/1.

3.2.3. Recovery and reuse of catalyst. Evaluating catalyst leaching

One of the most challenging issues concerning the advantage of using heterogeneous catalysis for the isomerization of α -pinene is represented by the possibility of recovery and reuse of the solid catalyst. Another problem that arises is the leaching of catalyst components that can cause its deactivation. Herein, the study of the stability of supported $H_4SiW_{12}O_{40}$ on SiO_2 , TiO_2 and HZSM-5 is presented. The recovery yields (94–98%) of solid catalyst were gravimetrically determined after filtration at reaction temperature. The results obtained after three recovery/reutilization cycles for catalysts 4 and 6 are presented in Figs. 10 and 11. As shown, the catalytic activity of supported SiW on SiO_2 and HZSM-5 decreases with the increase of reutilization cycles, but even after three cycles, a promising utile conversion is obtained (around 75%). That sustains the stability of these catalysts under reported reaction conditions. In the case of the TiO_2 based catalyst, only two reutilization cycles were performed (Fig. 12). As expected, the catalytic activity sharply decreased, due to the fact that the specific surface of catalyst 5 was smaller than in the other two cases.

The study of catalyst leaching was evaluated. When the catalyst leached into a product phase, the sample should exhibit some catalytic activity [32]. The efficient method that allowed the evaluation of leaching required the removal of the catalyst by filtration, exclusively at reaction temperature, and the reaction continued to run in its absence. The kinetic curves of the reactions catalyzed by supported SiW before and after its removal are displayed in Figs. 10, 11 and 12. As it can be observed, no catalyst leaching occurred, proving that the isomerization reactions took place in heterogeneous catalysis.

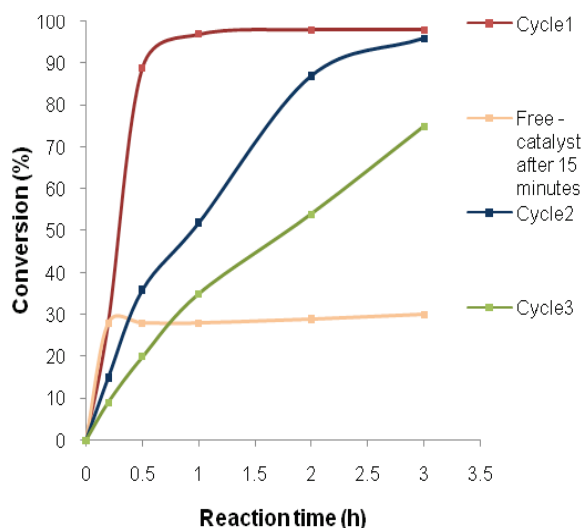


Figure 11. Kinetic curves for three recovery/reutilization cycles and the effect of the SiW leaching for $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ /HZSM-5 catalyst (α -pinene/catalyst ratio of 100/1, at 160°C).

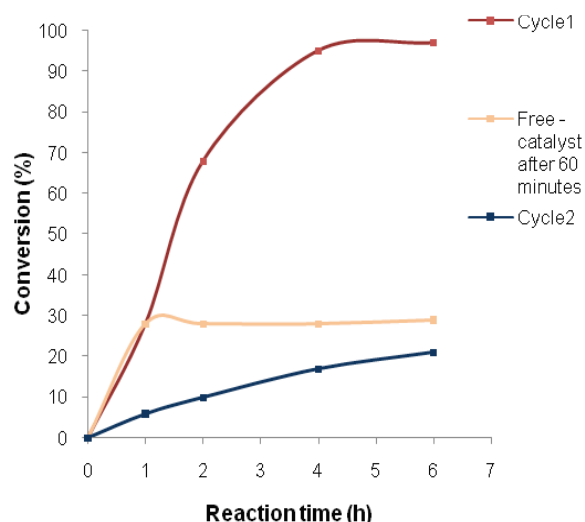


Figure 12. Kinetic curves for three recovery/reutilization cycles and the effect of the SiW leaching for $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ / TiO_2 catalyst (α -pinene/catalyst ratio of 100/1, at 130°C).

4. Conclusion

Isomerization of α -pinene in the presence of the solid acidic catalysts became an important methodology in industry since camphene and limonene, essential intermediates in organic chemistry, were obtained. A simple, clean and economic methodology for the preparation of supported catalysts was developed. The XRD studies indicated that SiW was completely dispersed on the supports. Here, the isomerization of α -pinene in heterogeneous catalysis using catalysts prepared from $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW) supported on different oxides and

HZSM-5 was studied. The effect of reaction temperature and catalyst concentration in the isomerization process was also determined. We succeeded in the optimization of an efficient synthetic route to obtain simultaneously camphene and limonene. No leaching effect could be observed with respect to all the three studied catalysts. From the recovery/reuse cycles, one may conclude that catalysts 4 and 6 are stable under used reaction conditions. The isomerization method presented here offers also advantages such as high yields and simple procedures for synthesis, recovery and reuse of catalysts.

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