

# Dimerization of $\alpha$ -pinene, Using Phosphotungstic Acid Supported on SiO<sub>2</sub> as Catalyst

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**Abstract:** The  $\alpha$ -pinene dimerization in liquid phase was studied by using phosphotungstic acid catalysts H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, (HPW) supported on commercial silica. These catalysts were characterized by XRD, FT-IR and FT-IR of pyridine adsorbed. Catalyst characterization by XRD showed the presence of HPW crystals on HPW/Si catalyst. FT-IR spectra showed only bands assigned to the pyridine adsorption on Brønsted acid sites. The catalytic activity was found to depend on the reaction temperature and the amount of catalyst loaded in the reactor, and the highest selectivity in dimers corresponded to the HPW supported. Under reaction conditions 130°C and 4% catalyst, the most active catalyst showed 100%  $\alpha$ -pinene conversion and 55% selectivity to dimers. The selectivity to dimers increases with the increase of the reaction temperature and the amount of catalyst loaded in the reactor.

**Keywords:**  $\alpha$ -pinene, Biojet, Brønsted, Dimerization, Monoterpenes, Phosphotungstic acid, Terpenes.

## INTRODUCTION

Efficient production of fuels from renewable sources is one of the key challenges of this century. Recently, a big effort has been carried out for developing biofuels for transport. However, there are limited studies focused on the production of high density fuels for air transportation.

Conversion of propene and butylene to dimers/oligomers is one of the first commercial processes in the petroleum industry [1]. In this sense, Wright *et al.* [2] obtained oligomers by using highly efficient transition metal catalysts in the presence of methylaluminoxane, giving rise to the production of hydrocarbon jet fuel.

Terpenes, having general formula C<sub>10</sub>H<sub>16</sub>, are renewable raw materials that do not compete with food, and can undergo condensation reactions producing dimers and oligomers. Monoterpenes are widely distributed in nature and they are present in nearly all-living plants. They are used in pharmaceutical, cosmetic and food industries as active components of drugs and ingredients of artificial flavors and fragrances. Under soft reaction conditions,  $\alpha$ -pinene, in the presence of an acidic catalyst, transforms into a variety of isomeric products, bicyclic compounds as camphene, tricyclene, and bornylene that are obtained through a cyclic rearrangement, and monocyclic compounds as limonene, terpinolene,  $\alpha$  and  $\gamma$  terpinene are obtained by means of the rupture of one of the rings. Under severe reaction conditions, dimers and oligomers are obtained. The isomerization of  $\alpha$ -pinene in the presence of different acid solids has been studied by several authors [3-8]. Our group studied the iso-


merization reaction of  $\alpha$ -pinene with catalysts such as clays, sulfated zirconia and phosphotungstic acid (HPW) supported on different materials [9-11], among them sulfated zirconia was found to be the most effective for the production of bicyclics such as camphene, bornylene and fenchene, with a selectivity of about 75%. When using clay and supported by HPW the selectivity to bicyclics is about 50%, and to monocyclic 50%, where limonene,  $\alpha$  and  $\gamma$  terpinene and terpinolene are the main products.

In the reaction of  $\alpha$ -pinene transformation, the nature of the acid site, the catalyst support and the experimental conditions have a remarkable influence on the reaction mechanism. In the presence of Lewis acid sites and under soft reaction conditions, the selectivity to bicyclic compounds is favored [12]. On the other hand, if the reaction conditions are more severe, dimers are obtained with the molecular formula C<sub>20</sub>H<sub>32</sub>, containing at least one double bond. Dimerization of  $\alpha$ - and  $\beta$ -pinene has been reported using Brønsted acid catalysts, such as phosphoric acid [13], Lewis acid catalyst such as BF<sub>3</sub> [14] and acidic zeolites [15].

In this work we show results that have shown the dimers terpenic obtained from the transformation of  $\alpha$ -pinene catalyzed by phosphotungstic acid supported on silica. When these dimers are hydrogenated, the compounds obtained are an alternative as biojet fuels.

## MATERIALS AND METHODS

HPW/SiO<sub>2</sub>, catalysts were prepared by impregnation of the Silica (Degusa) with adequate amount of ethanol-water solution of HPW (Fluka) to obtain nominal loadings of 50%. The ethanol-water solution was prepared with 50% water and 50% alcohol. The precursors were dried 110°C for 12 h. The catalyst was prepared calcining the precursor at 300°C for 4 h. The supported catalyst will be indicated with

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**Table 1.**  $\alpha$ -pinene Conversion and Selectivity to Monoterpene and Dimer, in Different Experimental Conditions.

Experiment	Catalyst	% Catalyst*	Temperature (°C)	Time (min)	(X%)	%S <sub>MT</sub>	%S <sub>D</sub>
F1	HPW/SiO <sub>2</sub>	1	45	180	28	99	1
F2	HPW/SiO <sub>2</sub>	1	80	120	93	80	20
F3	HPW/SiO <sub>2</sub>	1	130	20	100	50	50
F4	HPW/SiO <sub>2</sub>	2	100	60	100	62	37
F5	HPW/SiO <sub>2</sub>	4	100	60	100	56	44
F6	HPW/SiO <sub>2</sub>	4	130	60	100	46	55
F7	HPW	**	100	60	100	83	17

\* expressed as % w (g) / V (mL) (weight of catalyst in volume  $\alpha$ -pinene)

\*\* 200 mg de HPW to compare with F4

HPWSi50, indicating HPW (phosphoric acid), Si, SiO<sub>2</sub> support and 50 percent load was expressed as HPW / (SiO<sub>2</sub> + HPW).

The textural properties of the catalysts were measured by N<sub>2</sub> physisorption at liquid nitrogen temperature using a Micromeritics Accusorb 2100E analyzer and BET analysis method. Samples were outgassed for 2 h at 300°C before N<sub>2</sub> physisorption measurements.

X-Ray diffraction (XRD) measurements of the catalyst powders were recorded using a Rigaku D-Max III diffractometer equipped with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5378$  Å).

The nature of the acid centres (Brønsted and Lewis) of the supported catalysts was studied through the adsorption of pyridine coupled to FT-IR (Perkin-Elmer Spectrum RX1). Self-supported wafers 12mg/cm<sup>2</sup> were prepared from the finely divided powders. These wafers were impregnated with 2 $\mu$ L of pyridine. The discs were left in an air flow for 12 h to eliminate the physisorbed pyridine, and then the spectrum was recorded at room temperature. Brønsted and Lewis sites were identified by bands at 1536cm<sup>-1</sup> and 1440cm<sup>-1</sup>, respectively.

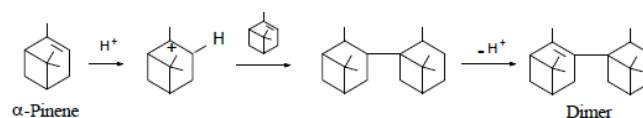
The dimerization reactions in liquid phase were carried out using a batch reactor with magnetic stirring. The reactor was heated at the desired temperature using a temperature controlled glycerine bath. In a typical reaction, 10 cm<sup>3</sup> of  $\alpha$ -pinene and 0.1 g of catalyst were set in the reactor without adding solvent. Aliquots were sampled at defined times for chromatographic analysis. The reaction products were analyzed using a Shimadzu GC-17A gas chromatograph with a capillary column DB1 of 30 m of length and an FID detector. The product identification was carried out using GC-MS.

## RESULTS AND DISCUSSION

### Reaction of $\alpha$ -Pinene Dimerization

Both of them, the isomerization and the dimerization, originate from the carbocations formation. The predominance of the isomerization at low temperatures can be due to carbocations that do not undergo many collisions and they can rearrange to form isomers. On the other hand, at high

temperatures there are more collisions and a carbocation can meet with  $\alpha$ -pinene molecule, generating a dimer. A possible reaction pathway is as follows:



Once the carbocations are generated due to the presence of the acid catalyst, they can rearrange and transform into isomers or to form dimers. Generally, the isomers and the terpene dimer are produced giving a mixture, which includes, at least, one monoterpene having molecular formula C<sub>10</sub>H<sub>16</sub> and an inorganic acid. The reaction conditions, temperature and amount of catalyst must be carefully controlled according to the desired products, isomers or dimers.

In Table 1 results of conversion and selectivity to monoterpenes (S<sub>MT</sub>) and dimers (S<sub>D</sub>) obtained for the catalyst HPWSi50 are summarized.

Data in Table 1 were obtained by changing the temperature, the amount of catalyst and the reaction time. When  $\alpha$ -pinene reacts in the presence of HPWSi50 as catalyst and under moderated experimental conditions (low temperatures and a small amount of catalyst), the isomerization reaction is prevalent and the main reaction products obtained are camphene and limonene. Under severe reaction conditions (high temperatures and high amounts of catalyst),  $\alpha$ -pinene produces dimers of formula C<sub>20</sub>H<sub>32</sub> (free of oligomeric terpenes), b) non-condensed isomers of  $\alpha$ -pinene.

The formed dimeric terpenes have at least a double bond and include C<sub>20</sub>H<sub>32</sub> isomers, which present tricyclic, bicyclics and/or monocyclic structures. The GC-MS analysis indicates that the region, where dimers are found, includes a complex mixture of peaks with a molecular weight of 272.

Experiments F1, F2 and F3 (Table 1) clearly showed that with the increase of the temperature, the dimerization reaction is favored, and the selectivity to dimers changes from 1% to 50% from 45°C to 130°C. On the other hand, when the temperature decreases, the isomerization reaction is favored and the selectivity to monoterpenes changes from 50% to 99%. A similar behavior in the case of experiments F5 and F6 is observed.

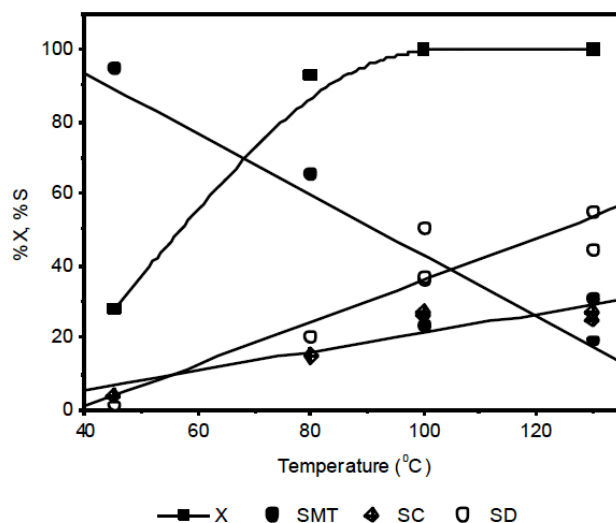


Fig. (1). Influence of the temperature on Conversion and selectivity.

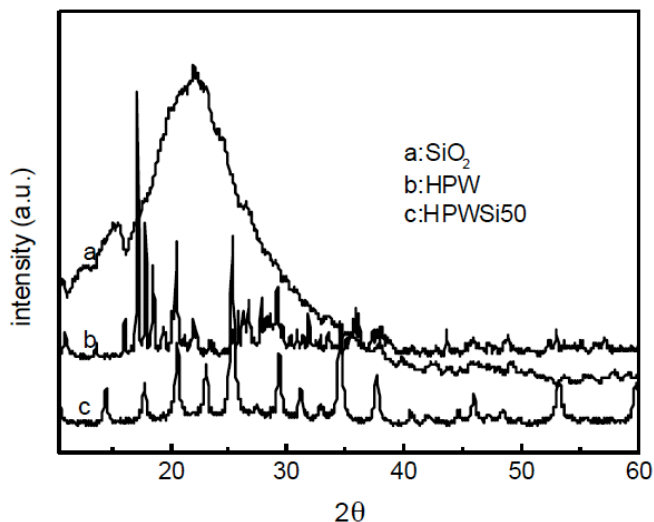


Fig. (2). X-ray results.

Fig. (1) showed all experiments in which HPWSi50 catalyst is used, and temperature and amount of catalyst are modified was observed. A remarkable correlation between the reaction temperature and selectivity to dimers. When the results of experiment F4 are compared with that of F5 and the ones of F3 with those of F6, a direct correlation between the mass of catalyst and the selectivity to dimer. However, the change of temperature stimulates a stronger effect.

The supported HPW (experiment F7) generates monoterpenes in a higher proportion than the experiments with the supported phosphotungstic acid. This seems to indicate that when HPW is supported there are spatial conditions and attractive forces which favor the dimerization. HPW is a relative by big molecule (144 Å) of transversal section) with 3 terminal hydrogens and silica possess hydroxyl groups at the surface. Some of these groups (terminal hydrogen and hydroxyl) react produce to water molecules anchoring the HPW molecule and restricting its movement. Carbocations formed on the supported catalyst have a more restricted movement due to the bigger size of the system HPW-support and can be more easily accessible to  $\alpha$ -pinene molecules,

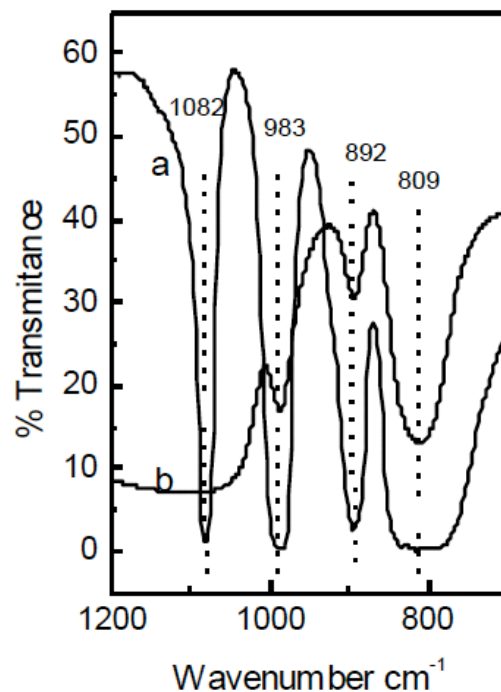


Fig. (3). FT-IR results. a: HPW; b: HPWSi50.

instigating more favorable conditions to the formation of dimers.

#### Characterization of catalysts

In order to find or ascertain the difference in selectivity to dimers between supported and unsupported catalysts specific surface area measurements were performed. One of the problems associated to the use of HPW is its low surface areas, 5-8 m<sup>2</sup>/g. For this reason, it is necessary to prepare a supported catalyst with the aim to increase its activity. The surface area of the SiO<sub>2</sub> support is 186 m<sup>2</sup>/g, when adding HPW to it, a decrease in the surface area was observed (72 m<sup>2</sup>/g). This remarkable decrease was attributed to the high loading of active phase.

From the results of the catalytic activity it was observed that specific surface area does not influence the activity of the catalyst, but selectivity of dimers is affected.

To corroborate, the HPW is supported by silica studies were performed actually X-ray diffraction, as Fig. (2) shows the results for silica, HPW and HPWSi50.

Silica is an amorphous solid, while the catalyst exhibits the characteristic reflection lines for HPW ( $2\theta = 25.3^\circ$ ;  $34.3^\circ$ ), confirming that HPW is crystallized [16].

The FT-IR spectrum of the HPWSi50 (Fig. 3) shows that the Keggin structure is maintained after impregnating the silica with HPW the signal corresponding to the value of 1082 cm<sup>-1</sup> is not observed.

FT-IR spectra after pyridine adsorption show the characteristic bands from Lewis acid sites (1610 and 1450 cm<sup>-1</sup>) and of the pyridinium ion formed by interaction with Brønsted acid sites (1640 and 1540 cm<sup>-1</sup>). Both types of adsorbed species contribute to the band at 1490 cm<sup>-1</sup>. The spectrum for HPWSi50 (Fig. 4) only shows a band at 1540 cm<sup>-1</sup>, which is

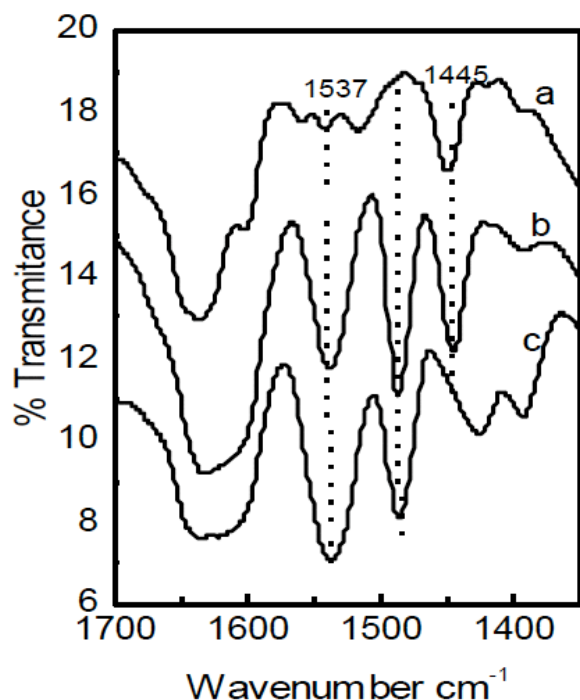


Fig. (4). FT-IR adsorbed pyridine a) SiO<sub>2</sub>, b) HPWSi50, c) HPW.

characteristic of Brønsted acid sites, and the contribution at 1490 cm<sup>-1</sup>. Damyanova *et al.* [17] assigned the corresponding signal at 1446 cm<sup>-1</sup> to the hydrogen bridge formed between silica and pyridine. Brønsted acid sites act as H<sup>+</sup> donors reacting with  $\alpha$ -pinene, giving rise to formation of a carbocation. The signal of 1445 cm<sup>-1</sup> observed in Fig. (3) corresponds to the hydrogen bridge formed between silica and pyridine and not is a Lewis sites.

The presence of Brønsted acid sites with severe operating conditions lead to an increase in the selectivity of dimers.

## CONCLUSIONS

In this work it is demonstrated that catalysts of HPW supported on silica are efficient in the formation of dimers from  $\alpha$ -pinene. Working at high reaction temperatures and high catalyst loading higher concentration dimers were obtained. The effect of the temperature on the formation of dimers can be explained by taking into account the molecular shaking (or the increase of the kinetic energy) producing more collisions between formed carbocations and  $\alpha$ -pinene and producing dimers. While at low reaction temperatures, fewer collisions allow carbocation rearrangement, leading to the formation of monoterpenes. Carbocation formation is benefitted by the presence of acidic sites Brønsted as observed by FTIR. The specific surface area does not influence the activity of the catalyst, but the selectivity of dimers is affected.

## CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

## ACKNOWLEDGMENTS

Authors want to thank CONICET, ANPCyT, and project FQM 01661 (Proyecto de Excelencia de la Junta de Andalucía, Spain), and to Dra. Esther Ponzi for her collaboration in the discussion of the results.

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