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Hydration of α-Pinene over Heteropoly Acid $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$

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Abstract

Heteropoliacid acid was used as catalyst for the hydration of α-pinene using water as hydroxyl donor. Since the selectivity of desired products is influenced by the reaction conditions, in this paper we study the behavior of phosphotungstic acid (HPW) and phopholmolibdic acid (HPMo) catalysts in homogeneous system under different experimental conditions (inert or oxidizing atmosphere, different ratio water/α-pinene, partial neutralization of the HPW and HPMo to optimize the production of terpene alcohols. When operating in inert atmosphere without agitation, the HPMo is more active than the HPW and by increasing time increases the concentration of α-terpineol. When the catalyst used is HPW products are mainly low molecular weight, while if HPMo is used, preferably the products have high molecular weight. A decrease in the amount of water increases the conversion of α-pinene. When the reaction occurs in equimolar ratio water/α-pinene, using HPMo catalyst, 100% conversion is achieved in 24 hr. The partial neutralization of the acid sites with aluminum, reduces the conversion of α-pinene due to a decrease in Brönsted acidity and production of α-terpineol increases possibly caused by the Lewis acidity is increased.

Keywords: α-pinene; Heteropoly acids; Hydration; Terpenic alcohols

Introduction

Terpenic alcohols produced by hydration of α-pinene with acid catalysis are products of high value, which have many applications in the pharmaceutical, flavor and fragrance industry, which is essentially based on the chemistry of terpenes [1].

α-pinene reacts in acidic medium to provide terpenic hydrocarbons by expansion of its ring, forming compounds such as bornanes and fenchones (camphene, fenchene and bornylene), or by opening of the four-carbon ring, forming p-menthanes (limonene, terpinolene and α- and γ-terpinene). The presence of Brönsted acid sites favors formation of monocyclic compounds and the presence of Lewis sites favoring the formation of bicyclic compounds [2].

The hydration of α-pinene with acid catalysts leads to a complex mixture of monoterpenes (alcohols and hydrocarbons). When the hydration reaction is carried out in the presence of water with acid catalysts, in addition to the products mentioned above, alcohols such as α-terpineol, borneol and others alcohols are also obtained. This is a complex process because the isomerization reaction of α-pinene occurs simultaneously with hydration [3,4].

The hydration reaction of α-pinene in the presence of acid catalysts has been studied in the last fifteen years. Were used many homogeneous and heterogeneous catalysts to study this reaction. Several publications have reported using zeolites [5-11]. Some of these authors worked with different zeolites or joined him acids. Other group researchers used different acids, resins or ionic liquids [4,12-15]. In previous work we have used trichloroacetic acid on titanium oxides, silica and zirconium oxide [16]. Besides the addition of monochloroacetic acid to natural clays for hydration of α-pinene was studied [17]. We also use as a catalyst HPW on silica (HPW/Si) and HPMo on titanium dioxide (HPMo/Ti) to study the hydration of limonene [18]. The limonene conversion with HPW/Si is around 50% higher than the one of the HPMo/Ti catalyst. On the other hand, the concentration of hydration products is higher in the HPMo/Ti catalyst.

Besides the already mentioned catalysts, the heteropoly acids (HPAs) are attractive, because they are commercially available, easy to handle, they present low toxicity, are environmentally friendly.

In acid-catalyzed reactions by HPAs several acid sites of different force are present. They include proton sites in bulk HPAs, Lewis acid sites, proton sites generated by dissociation of coordinated water, and proton generated by partial hydrolysis of polyanions. Generally, reactions catalyzed by HPAs may be represented by the conventional mechanisms of acid Brönsted catalysis. The mechanism may include the protonation of the substrate followed by the conversion of the ionic intermediate to yield the reaction product [19-21]. Castanheiro et al. [22,23] reported the use of solid acid catalysts such as zeolites and impregnated HPMo on polymeric membranes, and HPMo immobilized in hydrophobically modified PVA membranes. Robles-Dutenhefner et al. [24] used HPW as catalyst and mixture of acetic acid and water as solvent for hydrating α-pinene. Also performed catalytic tests supporting the HPW on silica but the results were not satisfactory. Horita et al. [25] used a catalyst $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$. The selectivity to the desired products can be increased by controlling reaction variables (temperature, α-pinene/water, load of catalyst, reaction atmosphere, stirring).

The aim of this work is the study of the behavior of HPW and HPMo catalysts in homogeneous system under different experimental conditions (inert or oxidizing atmosphere, modified ratio α-pinene/water, partial neutralization of the HPW and HPMo to optimize the production of terpenic alcohols, operating at temperatures near environments.

Experimental

Catalysts and characterizations

The HPA used in this study were phosphotungstic acid ($H_3PW_{12}O_{40}$·

xH$_2$O, Merck) (HPW) and phosphomolibdic acid (H$_3$PMo$_{12}$O$_{40}$·xH$_2$O, Anhedra) HPMo. The catalyst was pretreated before use in the reaction at 80°C for 2 hr. The presence of the Keggin structure was confirmed by FT-IR (Perkin-Elmer Spectrum RX1). The water content was determined thermogravimetrically with a Shimadzu TGA-50. To study the modification of the surface acidity, the HPW and HPMo were partially neutralized with metal aluminum. The total number of acid centres, as well as the acid strength of these sites was determined by potentiometric titration with *n*-butylamine [26]. The nature of the acid centres (Brönsted and Lewis) of the catalysts was studied by adsorption of pyridine coupled to FT-IR.

Catalytic tests

Hydration reactions of α-pinene were carried out in a batch reactor at 30°C. The experiments were performed under different experimental conditions, resulting in 2 types of experiences:

a) In 50 ml capped vials under inert atmosphere without stirring.

b) In reactor with air flow (25 cc / h) with stirring for 30 min every 12 hr.

The analysis of the reaction components was performed by GLC with a capillary column Equity (Supelco) of 30 m and the temperature was increased from 60°C up to 120°C at a rate 2°C/min and then from 120°C up to 200°C at a rate 10°C/min. The identification of products was made by comparison of retention times with terpene standards and confirmed by GC–MS.

Results and Discussion

TGA studies show that HPW presents three weight loss regions which can be assigned to loss of water molecules. In the range of 35°C-145°C loses the HPW eleven molecules, corresponding to surface water and in the range 145°C-500°C loses five molecules corresponding to water of hydration or crystallization which are linked by Hydrogen Bridge. HPMo similar behavior is observed with intervals between 27°C-109°C where ten water molecules are lost and in the range 109°C-500°C five molecules are lost.

FTIR studies of heteropolyacids show the presence of vibration bands of 1079 cm^{-1}, 987 cm^{-1}, 895 cm^{-1} and 802 cm^{-1} (v$_4$ P-O, v$_3$ W=O, v$_2$ O-W-O y v$_1$ W-O-W) for phosphotungstic acid, and 1066 cm^{-1}, 969 cm^{-1}, 871 cm^{-1} and 787 cm^{-1} (v$_4$ P-O, v$_3$Mo=O, v$_2$ Mo-O-Mo-O, v$_1$ Mo-O-Mo) for phosphomolybdic acid, confirming the presence of both acids Keggin structure. The type of acid sites on the catalyst was determined by infrared spectroscopy of adsorbed pyridine. Pyridine adsorbed on solid acids has signs in 1536 cm^{-1}, 1445 cm^{-1} and 1480 cm^{-1} that assigned to Brönsted, Lewis and Brönsted-Lewis sites respectively [27,28]. FTIR spectra recorded to determine the nature of the active sites on the catalyst phosphotungstic acid-aluminium phosphotungstic acid (HPW-AlHPW) and phosphomolybdic acid- aluminium phosphomolybdic acid (HPMo-AlHPMo) shown in Figure 1.

FTIR signal corresponding to the Lewis acid sites of the HPW and AlHPW catalysts (Figure 1a) are substantially the same magnitude, while the FTIR signal corresponding to Brönsted acid sites is decreased to the partially neutralized catalyst with aluminum. A similar behavior is observed with catalysts HPMo and AlHPMo (Figure 1b) but with less decrease in Brönsted sites caused by partial neutralization with aluminum compared to AlHPW. The intensity of signal corresponding to the Lewis sites (L), the Brönsted sites (B), the ratio between L/B, strength acid sites measured in millivolts, and amount of acid sites expressed milliequivalents (meq) of n-butylamine per gram of solid are

shown in Table 1. The increase in relation Lewis Brönsted sites of HPW catalyst and partially neutralized AlHPW is markedly higher than the increase observed in the catalysts based on molybdenum.

When the aluminum salt is obtained, in both catalysts, an increase in Lewis acid sites is observed whereas Brönsted acid sites decrease. Brönsted acidity loss is greater in the formation of the salt AlHPW (44%) with respect to the formation of the AlHPMo salt (8%).

The increased Lewis acidity is greater when AlHPW (27%) salt is formed with respect to salt formation AlHPMo (12%). Strength and amount of acid sites was determined by potentiometric titration, the total acid strength is very similar in the four catalysts, while the total number of sites in the catalyst is greater HPMo. Aluminum neutralization decreases the amount of acid sites in both catalysts. Figure 2 shows that the HPW has a single plateau while the HPMo has 3 plateaus indicating that there are sites of the same nature in HPW and sites of different nature in HPMo.

The α-pinene hydration in aqueous solution produces a complex mixture of hydrocarbons and monoterpenic alcohols. The reaction starts with an attack of acid generating carbocation, which can be rearranged giving carbocations that loss of a proton generate bicyclic hydrocarbons, or added one hydroxyl giving bicyclic alcohols, Scheme 1. On the other hand the carbocation can undergo a ring opening 4 carbon atoms of α-pinene giving carbocations that loss of a proton generate monocyclic hydrocarbons, or by addition of a hydroxyl generate the corresponding alcohols.

The hydration reaction can produce bicyclic alcohols (BA) (borneol and fenchol), as well as monocyclic alcohols (MA) (α-terpineol, and terpinen-4-ol), and other oxygenated derivatives, whereas isomerization reaction only produce bicyclic hydrocarbons (BH) (camphene, fenchene) and monocyclic hydrocarbons (MH) (limonene, terpinolene, α and γ terpinene).
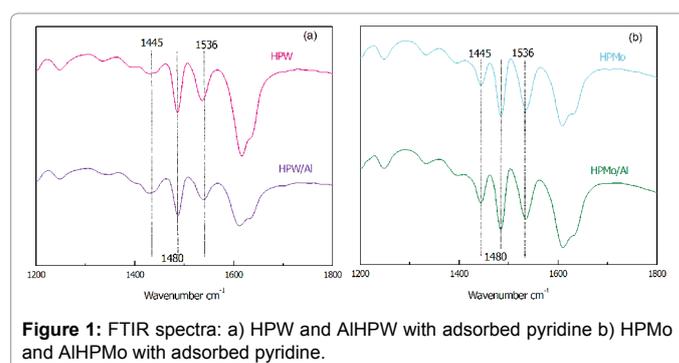

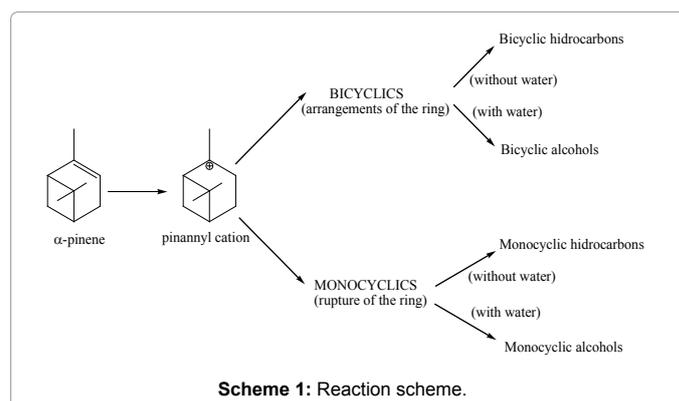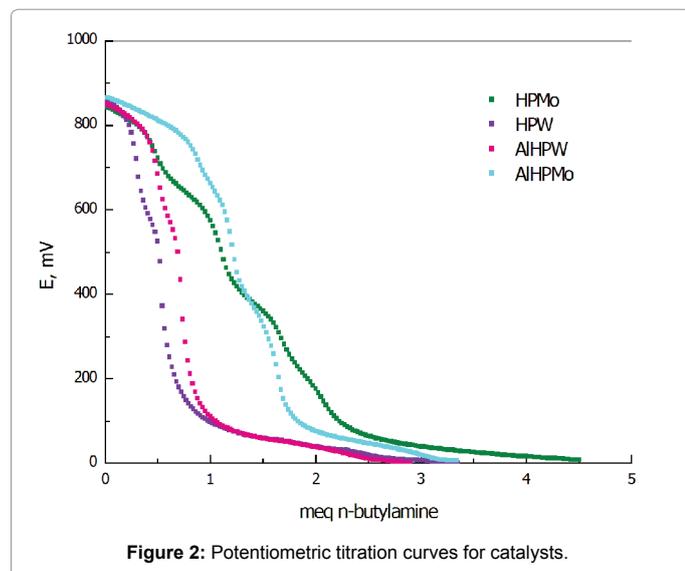**Figure 1:** FTIR spectra: a) HPW and AlHPW with adsorbed pyridine b) HPMo and AlHPMo with adsorbed pyridine.

Scheme 1: Reaction scheme.

Figure 2: Potentiometric titration curves for catalysts.

	HPW	AlHPW	WPMo	AlHPMo
L	1.1	1.5	4.6	5.2
B	4.5	2.5	8.5	7.8
L/B	0.2	0.6	0.5	0.7
Strength acid sites (mV)	850	862	843	866
Acid sites meq (n-Bta/g solid)	6	2	10	8

Table 1: Comparation between Lewis acid sites/Brönsted acid sites in the catalyst.

Solvent effect

The conversion of α-pinene was studied performing simultaneous experiences in reactors with inert atmosphere using ethanol, methanol, acetone and isopropanol as solvents. In each reactor was introduced 1 mL of α-pinene, 0.1 mL water, 22 mL of the solvent and 2.04×10^{-4} moles of HPW. The reactors were placed in a thermostatic bath at 30°C. The conversion of α-pinene to 24 hr of reaction was 10.6%, 30%, 60% and 48% for the solvents ethanol, methanol, acetone and isopropanol respectively. The conversion of α-pinene was obtained using 2.04×10^{-4} moles HPMo and solvents ethanol, methanol, acetone and isopropyl was 12.4%, 51%, 100% and 22% respectively. In view of the above results acetone as a solvent is chosen because with it the highest conversion is obtained.

Catalytic activity

Under experimental conditions to operate in a homogeneous system, was studied the catalytic performance in inert atmosphere. The results are shown in Figure 3; at the bottom of the Figure the percent conversion (% X) of α-pinene is shown.

Product distribution obtained for each of the catalysts under the same experimental conditions is different. Using HPW, hydrocarbon selectivity (camphene, limonene, γ-terpinene and terpinolene) decreases with increasing reaction time, while the selectivity of oxygenate increases (pentanal, 1,4-cineole, 1,8-cineole, cis-sabinene hydrate, trans sabinene hydrate, fenchol and α-terpineol). For 20 days of reaction the highest concentrations correspond to cis-sabinene hydrate, trans-sabinene hydrate and α-terpineol. Using HPMo, as the reaction time progresses hydrocarbon selectivity decreases and the selectivity in oxygenates (cis and trans sabinene hydrate) increased to about 7 days, then declines and the selectivity to α-terpineol increases steeply, showing the transformation of cis and trans sabinene hydrate

in α-terpineol. Can be observed that under the same experimental conditions the HPMo is more active, since in 22 days achieves a 100% conversion while the HPW only becomes 41%, this behavior is because the HPMo presents greater Brönsted acidity. Selectivity of oxygenated compounds is aproximately 95% when is used HPMo whereas it is only 70% when is used HPW. Figure 4 shows the distribution of reaction products when the amount of nucleophile (water) is modified and operate in inert atmosphere The performance of catalysts HPW and HPMo when the amount of water is changed is similar, but is more active the HPMo conversions of α-pinene of 88% for HPMo and 61% for HPW are obtained when 0.5 ml of water is used and the same reaction time. With decreasing water amount increases the reaction rate and selectivity to oxygenated terpenic compounds. Acetone, water and α-pinene competing for the active sites of the catalyst, when decrease the water concentration, also decrease the competitivity and there are more sites available for the conversion of α-pinene.

The result obtained when the reaction proceeds in an oxidizing atmosphere accompanied by agitation are shown in Figure 5, with a reaction time that would achieve 100% conversion.
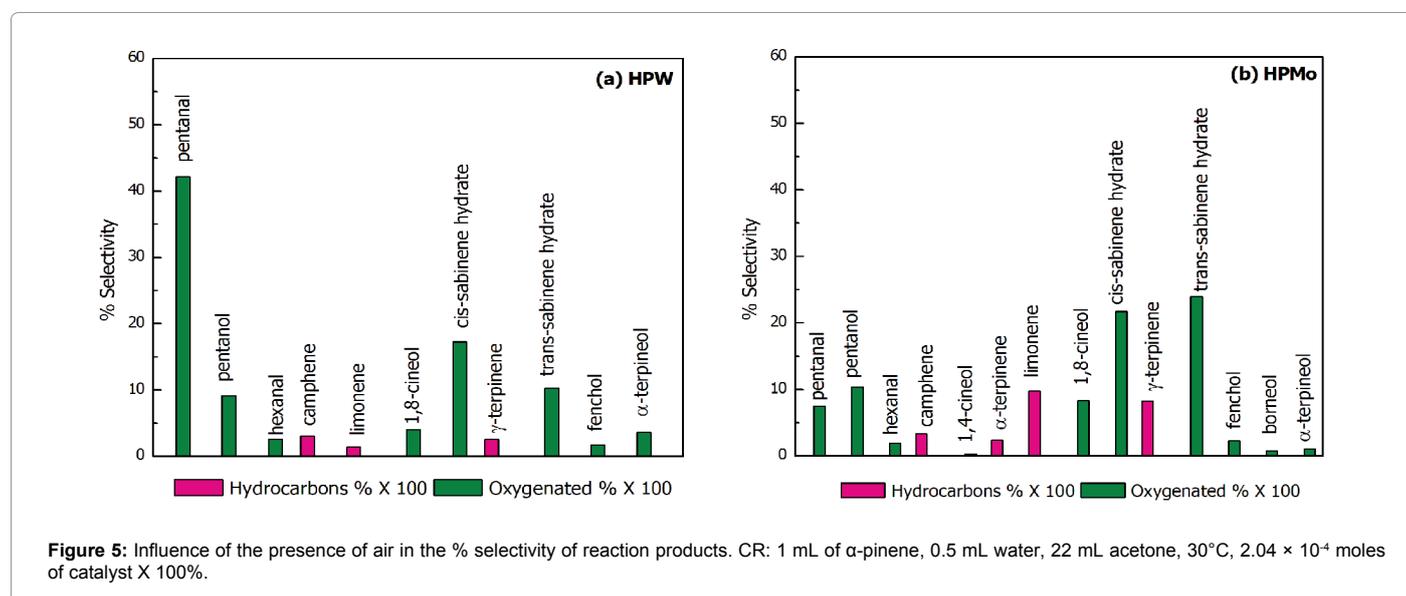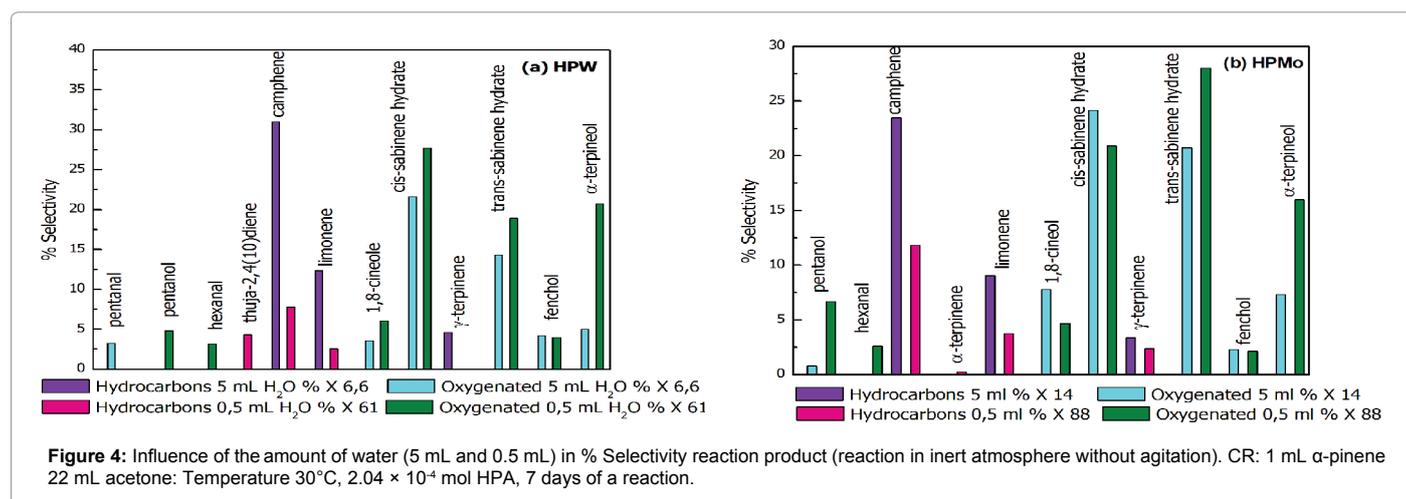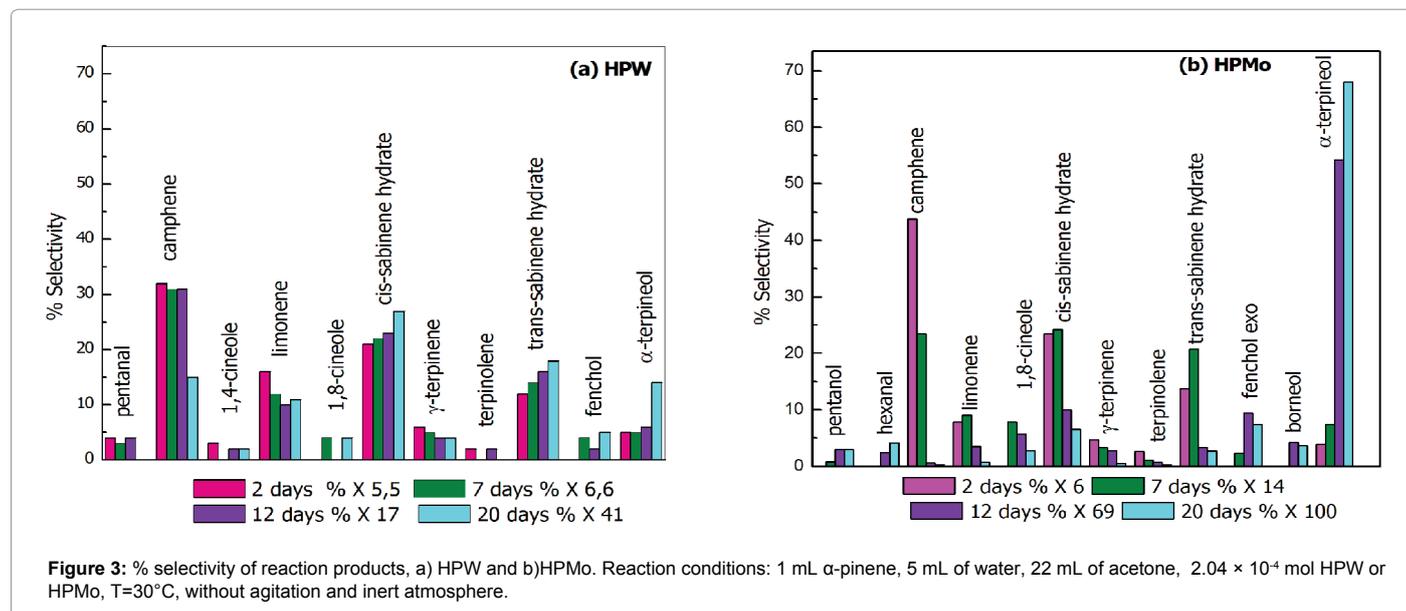
In air, the selectivity for oxygenates compounds is higher than the selectivity to hydrocarbons compounds in both catalysts. Using catalyst HPW, 92% of selectivity is obtained, with a high proportion of compounds of low molecular weight, while using the catalyst HPMo that selectivity in oxygenates compounds is only 71% but with compounds of high molecular weight. The Lewis acid sites are responsible for the formation of bicyclic hydrocarbons [2] and HPMo catalyst presents Lewis acidity high. Hydrocarbons bicyclic are converted to alcohols in the presence of water producing oxygenates high molecular weight.
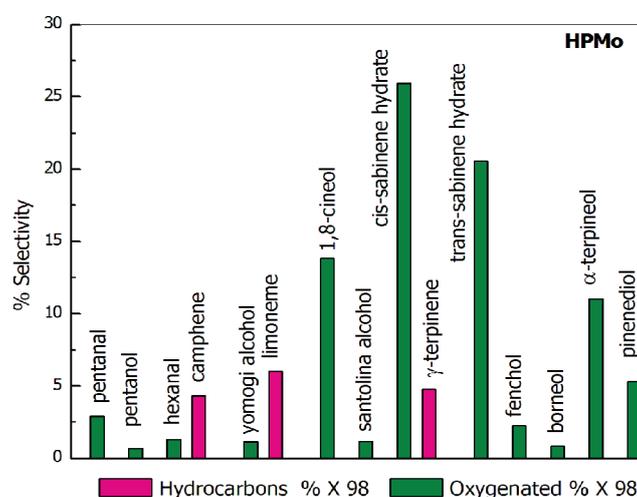
Experiences with equimolar relationship between α-pinene and water using HPMo as a catalyst, with stirring and oxidizing atmosphere are performed. The results are shown in Figure 6, α-pinene has a conversion of 98% in just 24 hr, with a total selectivity of 81% oxygenated compounds and 17% of terpene hydrocarbons, being the main oxygenated products 1-8 cineol and the cis and trans sabinene hydrate. In these operating conditions appreciable amounts of other reaction products including linear alcohols of 10 carbons (Yomogi alcohol and santolina alcohol) and pinenediol are diols generally formed from oxidation of the double bond (epoxide appear) followed by addition of a water molecule.

The HPA speed reduction is in parallel with the oxidation potential solution, E° HPMo>E° HPW. The proton can be replaced by a cation generated two type of heteropoliacid, those where the cation exchanged can be reduced (Pd, Cu, Ag) or those where the cation cannot be reduced. HPA neutralization with aluminum, can lead to a decreased activity for different reasons, by decreasing acidity due to neutralization, decreased its oxidizing power and a change in the relationship sites Bronsted / Lewis acids, compared to HPA not neutralized.

Selectivity for HPW, AlHPW, and AlHPMo, HPMo catalysts under the same experimental conditions are shown in Figure 7. The activity decreases with the addition of aluminum from 100% to 93%, for HPW and AlHPW catalysts (Figure 7a). The presence of aluminum inhibits the formation of carbon chain products C5 and C6. 75% of the compounds obtained are terpene alcohols with marked selectivity α–terpineol, which correlates with the increase in Lewis acidity, when these are partially neutralized.

The results for the catalyst HPMo (Figure 7b) show the same trends as those found when HPW is used. The presence of aluminum increases the α-terpineol selectivity. In both cases, the presence of

Figure 3: % selectivity of reaction products, a) HPW and b)HPMo. Reaction conditions: 1 mL α-pinene, 5 mL of water, 22 mL of acetone, 2.04×10^{-4} mol HPW or HPMo, T=30°C, without agitation and inert atmosphere.

Figure 4: Influence of the amount of water (5 mL and 0.5 mL) in % Selectivity reaction product (reaction in inert atmosphere without agitation). CR: 1 mL α-pinene 22 mL acetone: Temperature 30°C, 2.04×10^{-4} mol HPA, 7 days of a reaction.

Figure 5: Influence of the presence of air in the % selectivity of reaction products. CR: 1 mL of α-pinene, 0.5 mL water, 22 mL acetone, 30°C, 2.04×10^{-4} moles of catalyst X 100%.

Figure 6: Reaction in an oxidizing atmosphere and with stirring. % reaction product selectivity. C R: 1 mL of α-pinene 0.1 mL water, 22 mL of acetone, 30°C, 2.04 × 10⁻⁴ HPMo mol, 24 h.
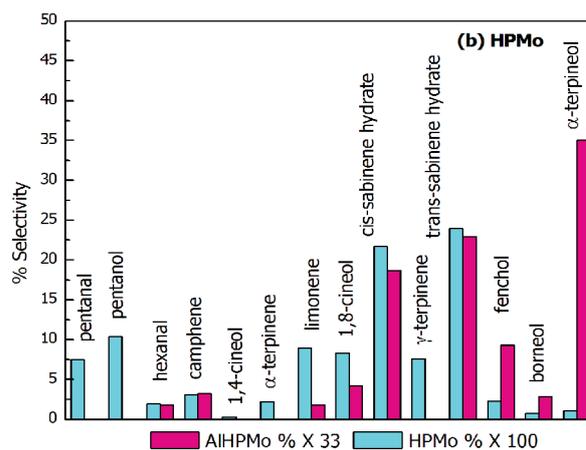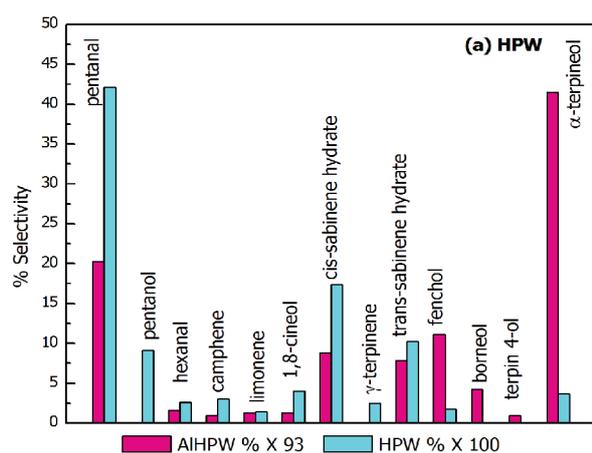
Figure 7: Selectivity (HPW- AlHPW) and (HPMo-AlHPMo). CR: 1 mL of α-pinene, 0.5 mL of water, 2.04 × 10⁻⁴ moles of catalyst, oxidizing atmosphere, with stirring, T=30°C, 7 and 6 days of reaction HPW, HPMo respectively.

aluminum decreases the conversion, which is in agreement with the decrease in Bronsted sites that are responsible for the activity of the catalyst, if transformations are performed through the formation of a carbocation.

Conclusion

The hydration reaction is greatly affected by the experimental conditions, long reaction times makes the less stable compounds are converted to other more stable, the incorporation of air produces a very different distribution of products for each catalyst, a decrease in the concentration of water, causes an increase in activity and good selectivity in α-terpineol. Complete conversion of α-pinene is obtained when operating in equimolar concentrions of the water-α-pinene and finally the partial neutralization of the catalyst increases the selectivity in α-terpineol.

In all catalysts studied, is observed Bronsted and Lewis acidity. In HPW, the Bronsted acidity decreases by the neutralization, while in the

catalyst HPMo decreases lesser extent. Activity studies carried out with different solvents, ethanol, methanol, acetone and isopropanol indicate that the best results, at low temperatures to 30°C, are achieved using acetone as solvent.

Operating in inert atmosphere without stirring, the conversions α-pinene is much higher for HPMo. The selectivity in α-terpineol is much higher, on the order of 65% with conversions of 100% at 30°C in 20 days of reaction. This increased activity in the HPMo is due to the increased presence of Bronsted sites. The decrease in water amount in both catalysts produces increased activity.

Both acetone and water compete for the active sites of the catalyst with the α-pinene, the lower the concentration of water is decreasing the competitiveness and is therefore infer that there are more places available for the transformation reaction of α-pinene.

The incorporation of air in the reaction system produces a very different distribution of oxygenates, in the case of HPW higher

proportion of low molecular weight compounds are obtained, pentanal, whereas HPMo higher molecular weight compounds are obtained such as the cis and trans sabinene hydrate.

Tests performed using an equimolar ratio of water α-pinene with HPMo catalyst indicate that a 100% conversion in only 24 hours is achieved with 85% of oxygenated compounds.

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