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Methoxylation of α -pinene over heteropolyacids immobilized in silica

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ABSTRACT

The methoxylation of α -pinene was studied using heteropolyacids immobilized on silica as catalysts, at 60 °C, being the α -terpinyl methyl ether the main product. Tungstophosphoric acid (PW), molybdophosphoric acid (PMo), tungstosilicic acid (SiW) and molybdosilicic acid (SiMo) were immobilized on silica by sol-gel method. It was observed that the catalytic activity of the silica-supported heteropolyacids decreases in the series: PW2_S > SiW_S > PMo_S > SiMo_S.

A series of PW immobilized on silica with different PW loading were prepared. It was observed that the catalytic activity increases with the amount of PW immobilized on silica. However, at high amount of PW on silica, a decrease of the catalytic activity was observed.

Good values of selectivity to α -terpinyl methyl ether (about 60% near complete conversion) were obtained with all catalysts.

Catalytic stability of the PW2_S was evaluated by performing consecutive batch runs with the same catalyst sample. After the third batch it was observed a stabilisation of the initial activity.

A kinetic model was developed assuming that the α -pinene is consumed according to the parallel reaction network. It was observed that the kinetic model fits the experimental concentration data quite well.

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1. Introduction

 α -Pinene is a renewable raw material, which constitute real building blocks for the synthesis of new important chemicals for use as fragrances, flavours and pharmaceuticals intermediates [1– 3]. The main product of the acid-catalysed methoxylation of α pinene is α -terpinyl methyl ether [4], which smells grapefruit-like and might be used as flavour and fragrance and as additive for pharmaceuticals and food industry [5]. Traditionally, sulfuric acid has been used in this reaction, as catalyst [6]. However, solid catalysts have many advantages over liquid acids, such as they do less harm to the environment, can be easily separated from liquid phase and can be reusable. The α -pinene methoxylation has been carried out over beta zeolite [7], acidic cation exchange resins [8] and sulfonic-modified mesoporous silica [9].

Recently, PVA with sulfonic acid groups were used as catalysts in the α -pinene methoxylation [10].

Heteropolyacids (HPAs) are typical strong Brönsted acids, which catalyse a wide range of reactions. The major disadvantages of HPAs as catalysts are their low thermal stability, low surface area $(1-10 \text{ m}^2/\text{g})$, separation problem from reaction mixtures and solubility [11-13]. In order to increase the specific area of the heteropolyacids, a variety of supports like, zeolite [14-17], activated carbon [18-20], silica [21-31], magnesia [32], aluminas [33] and polymers [34-37] have been used as support to immobilize HPAs.

Heteropolyacids have been used as acid catalyst in reactions where terpenes are involved, such as, hydration of α -pinene [34,35,38], limonene [38,39] and camphene [40], isomerization of α -pinene [41], acetoxylation of α -pinene [38], limonene [38,39] and camphene [40] and cyclization of pseudoionone [42].

In this work, we report the methoxylation of α -pinene over heteropolyacids immobilized on silica. The influence of various reaction parameters, such as, temperature, molar ratio of α -pinene to methanol and catalyst loading on the activity of the most active catalyst, is also studied. A simple kinetic model was developed. It was assumed that the α -pinene is consumed according to the parallel reaction network.

2. Experimental

2.1. Catalysts preparation

Tungstophosphoric acid (PW), molybdophosphoric acid (PMo), tungstosilicic acid (SiW) and molybdosilicic acid (SiMo) were immobilized on silica by sol-gel method. The catalysts samples

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(PW2_S, PMo_S, SiW_S and SiMo_S) were prepared according to Izumi et al. [24]. A mixture of water (2.0 mol), 1-butanol (0.2 mol) and heteropolyacid (5.0×10^{-4} mol) was added to tetraethyl orthosilicate (0.2 mol) and stirred at 80 °C during 3 h. The tungstophosphoric acid amount (mol) used to prepare PW1_S, PW3_S and PW4_S catalyst was 1.7×10^{-4} , 8.3×10^{-4} and 11.7×10^{-4} mol, respectively. The hydrogel obtained was dehydrated slowly at 80 °C for 1.5 h in vacuo (25 Torr). The dried gel obtained was extracted in a sohxlet apparatus with methanol during 72 h, and dried at 100 °C, overnight. The silica-included heteropolyacid was dried at 100 °C for 3 h prior to use in the catalytic reactions.

2.2. Catalysts characterization

The textural characterization of the catalysts was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

The amount of Mo and W in silica catalysts was measured by dissolving the catalyst in H_2SO_4/HF 1:1 (v/v) and analysing the obtained solution using inductively coupled plasma analysis (ICP), which was carried out in a Jobin-Yvon ULTIMA instrument. FTIR spectroscopy in KBr pellets was carried out on a Bio-Rad FTS 155 spectrometer. The spectra were taken with a resolution of 4 cm⁻¹ in the range of 400–4000 cm⁻¹, by running 1000 scans.

The X-ray diffraction (XDR) patterns of the heteropolyacid, silica and catalysts were obtained by using a Bruker powder diffractometer with built-in recorder, using Cu K α radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 5° and 70° of 2 θ at a scanning rate of 1°/min.

2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at 60 °C. In a typical experiment, the reactor was loaded with 50 cm³ of methanol and 0.2 g of catalyst. Reactions were started by adding 3 mmol of α -pinene.

A blank experiment was carried out, in the absence of catalyst, being kept all other conditions.

Stability tests of the PW2_S were carried out by running four consecutive experiments, using the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by filtration, washed with methanol and dried at 100 °C overnight.

A hot-filtration test was carried out for the catalyst sample PW2_S. The reaction was carried out as described above; after 27 h (α -pinene conversion 51%) the catalyst was removed by hot-filtration. Sampling of the liquid was continued until 140 h, since the beginning of the experiment.

Nonane was used as the internal standard. Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m \times 0.25 mm DB-1 column.

The GC mass balance was based on the substrate charge. The difference was attributed to the formation of oligomers, which were not GC determinable. The products were identified by gas chromatography mass spectrometry (GC–MS) using a FISONS MD800 (Leicestershire, UK) instrument, equipped with a 30 m \times 0.25 mm DB-1 column.

3. Results and discussion

3.1. Characterization of catalyst

The textural characterization of the catalysts was determined based on nitrogen adsorption and desorption measurements. The introduction of HPA on silica by the sol-gel method created a

Table 1

Physicochemical characterization of silica-included HPAs.

Sample	HPA load ^a (g/g _{silica})	Surface area ^b (m²/g)	Microporous volume ^c (cm ³ /g)	Total pore volume ^d (cm ³ /g)
PW1_S	0.025	489	0.23	0.24
PW2_S	0.042	458	0.24	0.25
PW3_S	0.065	254	0.11	0.12
PW4_S	0.084	141	0.07	0.07
SiW_S	0.057	332	0.16	0.16
PMo_S	0.037	478	0.25	0.26
SiMo_S	0.039	466	0.24	0.25

^a HPA load determined by ICP analysis.

^b BET.

^c *t*-Method.

^d $(p/p^{\circ}) = 0.98$.

microporous material. Similar results were also observed by Izumi et al. [24]. Table 1 shows the values of BET specific area (S_{BET}), microporous volume (V_{micro}) and the total pore volume (V_{tot}). The specific surface area was determined using the BET method, while microporous volume was determined by the *t*-method, using a standard isotherm proposed by Gregg and Sing [43]. It was observed a continuous decrease of the BET surface area, microporous volume and total pore volume with the increase of the PW loading on silica (PW1_S to PW4_S). Similar results were also observed by Izumi et al. [44]. It is known that a lower acid concentration results in a higher specific surface area due to an increase in the cross-linking level [45,46]. It was also observed that the total pore volume is similar to the micropore volume, indicating that the catalysts have low mesoporous contribution.

Fig. 1 shows the FTIR spectrum of the heteropolyacids immobilized on silica. In Keggin anion structure $[XM_{12}O_{40}]^{n-}$ there are four different kinds of oxygen atoms, according to the location they take in that unit: oxygen atoms bound to three M atoms and to the X heteroatom (O_a), bridging oxygen atoms (O_b and O_c), and terminal oxygen atoms (O_d). The symmetric and asymmetric vibrations of different M–O bonds are observed in the following regions of the vibration spectra: M–O_d bonds (1000–960 cm⁻¹); M–O_b–M bonds (890–850 cm⁻¹); and M–O_c–M bonds (800–760 cm⁻¹) [47]. However, some peaks typical of the Keggin structures of HPA are overlapped or partially overlapped with the peaks of the silica matrix framework.

The XRD diffractograms of the catalysts (not showed) do not indicate the presence of any crystalline phases related to heteropolyacid. These results suggest that the particles are too small or well dispersed to be detected by XRD. It is only observed a



Fig. 1. FT-IR spectra of catalysts: (A) silica; (B) PMo_S; (C) SiW_S; (D) SiMo_S; (E) PW2_S.

broad band centered around $2\theta = 25^{\circ}$ (amorphous silica). A similar phenomenon was also observed by Molnár et al. [31].

3.2. Catalytic experiments

The main product of α -pinene (1) methoxylation was α terpinyl methyl ether (2) being also formed γ -terpinyl methyl ether (3), β -terpinyl methyl ether (4), terpinolene (5), limonene (6), endo-bornvl methyl ether (7), β-fenchyl methyl ether (8), exobornyl methyl ether (9), bornylene (10) and camphene (11) as byproducts (Scheme 1). The alkoxylation of α -pinene proceeds via two parallel pathways, one of which resulting in by-cyclic products (route A) and the other in monocyclic products (route B). The reaction initiates by protonation of the α -pinene double bond to form the pinyl ion (A). The pinyl ion can rearrange into the bornyl ion (B) and into the terpinyl ion (C). The bornyl ion (B) can lose a proton to directly yield bornylene. Alternatively, it can be isomerized into camphene. The bornyl ion (B) can yield endobornyl methyl ether, β -fenchyl methyl ether and exo-bornyl methyl ether, after methanol addition. The pinyl ion can also rearrange into the terpinyl ion (C), which can lose a proton to directly yield terpinolene, limonene, and after methanol addition, α -terpinyl methyl ether, γ -terpinyl methyl ether and β -terpinyl methyl ether are formed (Scheme 1) [4].

Fig. 2 shows the concentration profiles obtained over the PW2_S catalysts, in the α -pinene methoxylation. In Fig. 2, H lumps all the minor products (monocycle ethers, bicycle ethers, monocycle hydrocarbons and bicycle hydrocarbons). The solid lines represent the model fitted to the data points, which assume that the α -pinene is consumed according to the parallel reaction network (Scheme 2).

The α -pinene concentration profile obtained over PW2_S, SiW_S, PMo_S and SiMo_S catalysts are shown in Fig. 3A. It was observed that the PW2_S catalyst shows the highest catalytic activity of the Keggin series. Fig. 3A shows the initial catalytic activities of silica-



Fig. 2. Methoxylation of α -pinene over PW2_S catalyst. Concentration *versus* time. (**()**) α -pinene; (**()**) α -terpinyl methyl ether; (**()**) H lumps all the minor components. The solid lines represent the model fitted to the data points. Reaction conditions: initial concentration of α -pinene = 0.061 mol dm⁻³; temperature = 60 °C; catalyst loading = 0.2 g.

included heteropolyacids (PMo_S, PW2_S, SiMo_S and SiW_S) in the α -pinene methoxylation. The light bars represent the initial activity referred to the HPA amount (mol), i.e., the maximum slope of the experimental kinetic curve of α -pinene divided by the HPA amount. On its turn, the dark bars represent the initial activity referred to the catalyst amount (HPA_silica), i.e., the maximum slope of the experimental kinetic curve divided by the catalyst (HPA plus support) amount. It was observed that the catalytic activity increases in the series: SiMo_S < PMo_S < SiW_S < PW2_S, which can be explained due to PW is the strongest acid of the Keggin series of heteropolyacids [14].

From the above results, we can conclude that the PW2_S catalyst is the most efficient catalyst for the α -pinene methoxylation. However, in order to optimise the amount of PW immobilized









Fig. 3. Methoxylation of α -pinene over heteropolyacids immobilized on silica. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the α -pinene kinetic curve. Reaction conditions: initial concentration of α -pinene = 0.061 mol dm⁻³; temperature = 60 °C; catalyst loading = 0.2 g.

on silica, catalysts with different amount of this heteropolyacid were prepared. Fig. 3B compares the initial activity of PW_S catalysts loaded with different PW amounts, on the α -pinene methoxylation. It was observed that the initial catalytic activity increases with the HPA content until a maximum, which was obtained with the PW2_S catalyst. However, with high heteropolyacid loading on silica, a decrease in the catalytic activity is observed. At a low PW loading on silica, the increase of the heteropolyacid amount leads to the increase of activity, probably, due to the kinetic effect. However, the high amount of heteropolyacid on silica leads to a decrease of the catalytic activity. This behaviour can be explained probably, due to a decrease of the accessibility to the active sites. A decrease of S_{BET} and microporous volume with the amount of PW was observed (Table 1).

When compared to other results reported in the literature, the catalytic activity $(mol/h mol_{H}^{+})$ of the different solid catalysts increases as follows: PMO-SO₃H-g (0.07 mol/h mol_{H}^{+}) [9] < ionic resin (0.43 mol/h mol_{H}^{+}) < PVA-SO_{3}H (0.66 mol/h mol_{H}^{+}) [10] < Beta (2.81 mol/h mol_{H}^{+}) [7] < PW2_S (6.86 mol/h mol_{H}^{+}).

The dependence of the selectivity to the α -terpinyl methyl ether with the α -pinene conversion, for PW1_S, PW2_S, PW3_S, PW4_S, SiW_S, PMo_S and SiMo_S catalyst is shown in Fig. 4. It was observed that all of the catalysts tested on α -pinene methoxylation exhibited good selectivity to α -terpinyl methyl ether (about 60% near complete conversion).

In order to optimise the reaction conditions, the effect of different parameters (catalyst loading, initial concentration of α -pinene and temperature) on the methoxylation of α -pinene over PW2_S catalyst was studied.

3.2.1. Effect of the catalyst loading

In order to study the effect of the PW2_S catalyst loading on the α -pinene conversion, different catalytic experiments were carried out, at 60 °C. The molar ratio of α -pinene:methanol (1:436) was kept constant. Fig. 5 shows the conversion of the α -pinene *versus*



Fig. 4. Methoxylation of α -pinene over heteropolyacids immobilized on silica. Selectivity to α -terpinyl methyl ether. (\square) PW1_S; (\square) PW2_S; (\blacktriangle) PW3_S (\square) PW4_S; (+) PM0_S; (\times) SiW_S; (-) SiM0_S.

time. It was observed that when the catalyst loading increases, the equilibrium conversion is achieved more quickly, which can be explained due to the increase of the total number of the active sites. However, when the catalyst amount increases from 0.2 to 0.3 g, only a slight increase on the α -pinene conversion was observed. It was also observed that the catalyst loading has not any effect on the equilibrium conversion (Fig. 5).

The effect of the catalyst amount on the selectivity of PW2_S to α -terpinyl methyl ether was also studied. It was observed that all the catalytic experiments over different amount of PW2_S yield good values of α -terpinyl methyl ether selectivity (about 60%, at near complete conversion of α -pinene).

3.2.2. Effect of the initial concentration of α -pinene

The initial concentration of α -pinene was varied from 0.061 to 0.305 mol dm⁻³, while the reaction temperature (T = 60 °C) and the catalyst loading (m = 0.2 g) were kept constant. The α -pinene methoxylation was carried out over PW2_S. The results are shown in Fig. 6. At a fixed contact time, it was observed that the α -pinene conversion increases when the initial concentration of α -pinene increases, under otherwise identical conditions. This behaviour can be explained due to the increase of the reaction rate with α -pinene concentration.

The effect of the initial concentration of α -pinene on the selectivity of PW2_S to α -terpinyl methyl ether was also studied. It was observed that all the initial concentration of α -pinene yield



Fig. 6. Methoxylation of α -pinene over PW2_S catalyst. Effect of the initial concentration of α -pinene. Conversion *versus* time. (**()**) $C = 0.061 \text{ mol dm}^{-3}$; (**()**) $C = 0.122 \text{ mol dm}^{-3}$; (**()**) $C = 0.305 \text{ mol dm}^{-3}$. Reaction conditions: temperature = 60 °C; catalyst loading =0.2 g.

good values of α -terpinyl methyl ether selectivity (about 60%, at near complete conversion of α -pinene).

3.2.3. Effect of the temperature

The effect of the temperature on the α -pinene methoxylation was also studied. The catalytic experiments were carried out at different temperature over PW2_S catalyst, while the molar ratio of α -pinene:methanol (1:436) and the catalysts loading (m = 0.2 g) was kept constant. Fig. 7 shows the influence of the temperature on the α -pinene methoxylation. It was observed that the α -pinene conversion increases with the temperature, at a fixed contact time under otherwise identical conditions.

The effect of the temperature on the selectivity to α -terpinyl methyl ether was also studied. At the different temperatures considered, good selectivity values (about 60%, at near complete conversion of α -pinene) were obtained.

3.2.4. Catalyst stability and reusability

In order to study the catalytic stability of the PW2_S, different batch runs with the same catalyst sample, at same conditions were carried out. It was observed similar catalytic activity for all the tests $(3.00 \times 10^{-4}, 2.89 \times 10^{-4}, 2.97 \times 10^{-4} \text{ and } 2.97 \times 10^{-4}$, in the first, second, third and fourth experiments, respectively).

In order to confirm the catalyst stability, a hot-filtration experiment was performed with the catalyst sample PW2_S. After 27 h of reaction the catalyst was separated from the reaction



Fig. 5. Methoxylation of α -pinene over PW2_S catalyst. Effect of the catalyst loading. Conversion *versus* time. (\Box) m = 0.1 g; (\bigcirc) m = 0.2 g; (\blacktriangle) m = 0.3 g. Reaction conditions: initial concentration of α -pinene = 0.061 mol dm⁻³; temperature = 60 °C.



Fig. 7. Methoxylation of α -pinene over PW2_S catalyst. Effect of the reaction temperature. Conversion *versus* time. (**(**) $T = 40 \,^{\circ}\text{C}$; (**(**) $T = 50 \,^{\circ}\text{C}$; (**(**) $T = 60 \,^{\circ}\text{C}$. Reaction conditions: initial concentration of α -pinene = 0.061 mol dm⁻³; catalyst loading = 0.2 g.



Fig. 8. α -Pinene concentration profile obtained for the blank experiment compared to that obtained with the catalyst sample PW2_S. (\blacktriangle) hot-filtration test; (\bigcirc) *normal* experiment; (\Box) with out catalyst experiment. Reaction conditions: initial concentration of α -pinene = 0.061 mol dm⁻³; temperature = 60 °C; catalyst loading = 0.2 g.

mixture, and its composition was then followed for 113 h. Fig. 8 compares the α -pinene concentration profiles obtained for the hot-filtration experiment and a *normal* catalytic experiment, both performed with the same catalyst sample. It was observed that the reaction stops when the catalyst is removed, while it continues proceeding in the *normal* experiment. When the methoxylation of α -pinene was carried out in the absence of catalyst, no α -pinene conversion was observed (Fig. 8).

3.2.5. Kinetic modelling

A simple kinetic model can be established based on the following assumptions:

- 1. Isothermal and isobaric reaction conditions.
- 2. α -Pinene is consumed according to the parallel reaction network shown in Scheme 2, where P represents α -pinene, E represents α -terpinyl methyl ether and H lumps all the other species formed.
- As in the present case α-terpinyl methyl ether seems not to be consumed, is not necessary a more complex reaction network.
- 4. The concentration profiles of the reactant and products do not exhibit any pronounced initial inductive period (Fig. 2). The external and internal diffusion of the reactants and products on the catalyst were not considered.
- 5. First order kinetics is assumed.

The reaction rate of these two pseudo elementary reaction are expressed as:

$$r_1 = k_1 C_p \tag{1}$$

$$r_2 = k_2 C_p \tag{2}$$

For batch reactor, the mole balance equations may be written as

$$\frac{\mathrm{d}C_{\mathrm{p}}}{\mathrm{d}t} = -\frac{W}{V}(r_1 + r_2) \tag{3}$$

$$\frac{\mathrm{d}C_{\mathrm{E}}}{\mathrm{d}t} = \frac{W}{V}r_{1} \tag{4}$$

$$\frac{\mathrm{d}C_{\mathrm{H}}}{\mathrm{d}t} = \frac{W}{V}r_2\tag{5}$$

The optimisation was carried out by the *SOLVER*[®] routine in a *Microsoft Excel*[®] spreadsheet.



Fig. 9. Methoxylation of α -pinene over PW immobilized on silica. Effect of the PW loading on the concentration profile of the α -pinene. (**A**) PW1_S; (**D**) PW2_S; (×) PW3_S; (**D**) PW4_S. The solid lines represent the model fitted to the data points. Reaction conditions: initial concentration of α -pinene = 0.061 mol dm⁻³; temperature = 60 °C; catalyst loading = 0.2 g.

Table 2
Model parameters obtained by fitting the model to experimental data

Catalysts	$k_1 (\mathrm{dm}^3/\mathrm{hg}_{\mathrm{cat}})$	k_2 (dm ³ /hg _{cat})
PW1_S	0.00031	0.00010
PW2_S	0.00527	0.00249
PW3_S	0.00187	0.00143
PW4_S	0.00097	0.00083
SiW_S	0.00210	0.00172
PMo_S	0.00049	0.00048
SiMo_S	0.00043	0.00040

The fitting of the model to the data points is shown in Fig. 9. It was observed that the kinetic model fits the experimental concentration data quite well. The effect of the heteropolyacid amount immobilized into silica support on the model parameters is shown in Table 2. It was observed that the apparent kinetic constants increase with the increase of the heteropolyacid amount on silica (Table 1). However, at high heteropolyacid loading on silica, a decrease on the apparent kinetic constants was observed. This behaviour can be explained due to the presence of internal limitation diffusion. Probably, a decrease of S_{BET} and total volume with the amount of PW (Table 1) were observed. It was also observed that the apparent kinetic constants decrease in the series: PW2_S > SiW_S > PM0_S > SiM0_S. This behaviour can be due to the stronger acidity of the PW catalyst [14].

4. Conclusions

Dodecatungstophosphoric acid, dodecamolybdophosphoric tungstosilicic acid and molybdosilicic acid immobilized on silica were used in the α -pinene methoxylation. The main product of α -pinene methoxylation was α -terpinyl methyl ether being also formed bornyl methyl ether, fenchyl methyl ether, limonene and terpinolene as by-products. It was observed that the catalytic activity increases in the series: SiMo < PMo_S < SiW_S < PW2_S.

Catalysts consisting in the PW immobilized on silica with different PW loading were prepared. It was observed that the catalytic activity increases with the amount of PW immobilized on silica. However, at high amount of PW on silica, a decrease of the catalytic activity was observed.

All of the catalysts tested on α -pinene methoxylation exhibited good selectivity (about 60% at near complete α -pinene conversion).

In order to optimise the reaction conditions, the effect of various parameters, such as, reaction temperature, molar ratio of $\alpha\mbox{-pinene}$ to methanol and catalyst loading of PW2_S were carried out.

Catalytic stability of the PW2_S was evaluated by performing consecutives batch runs with the same catalyst sample. It was observed similar activity for all the catalytic tests.

A simple kinetic model, which fits the experimental concentration data quite well, has been developed.

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