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The acid-catalysed reaction of α-pinene over molybdophosphoric acid immobilised in dense polymeric membranes

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Abstract

The α-pinene hydration to α-terpineol was studied using as catalysts polymeric catalytic membranes consisting of HPMo entrapped in polyvinyl alcohol (PVA) cross-linked with 10, 20 and 30% of succinic acid, and HPMo encaged in USY zeolites dispersed in a polydimethylsiloxane (PDMS) matrix.

In the case of HPMo/PVA membranes it was observed that membrane activity increases with the polymer cross-linking, due to the increase in membrane hydrophobicity, up to the limit of the increasingly restrictions to the molecules mobility. The HPMo-USY/PDMS membrane shows a significantly higher activity for pinene hydration, which is even higher than that observed with USY encaged HPMo alone. However, selectivity to α-terpineol (65% at 80% conversion) is slightly lower than that obtained for the HPMo/PVA cross-linked with 20 or 30% of succinic acid (70–75% at 90% conversion).

For both catalytic membranes, HPMo/PVA or HPMo-USY/PDMS, the stability is reasonable good and catalyst activity increases in the subsequent uses of the same membrane, probably due to the interaction between retained α-terpineol and the polymer matrix.

Keywords: Catalytic polymeric membranes; PDMS; PVA; Heteropolyacid; Y-type zeolite; Encapsulation

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1. Introduction

The main product of the acid-catalysed hydration of α- or β-pinenes, renewable raw materials obtained from pine gum, is α-terpineol, which has many applications in the pharmaceutics and perfume industries. The use of solid acid catalysts in the hydration/isomerisation reaction of α-pinene has been widely studied in recent years [1–5]. However, the quest for high selectivities with reasonable good activities has revealed to be difficult, since pinenes easily isomerise to a large number of products and α-terpineol itself is also easily dehydrated and isomerised [6].

In previous works it was shown that α-pinene hydration can be carried out successfully over composite polymeric catalytic membranes filled with zeolites or sulphonated activated carbon, with good selectivities (55–60% at 90% conversion) [7,8]. However, the catalytic activity of these membranes is low, being required of long reaction times.

Heteropolyacids (HPAs) are very active acid catalysts for the dehydration of alcohols to olefins as well as for the hydration of olefins to alcohols, being commercially applied in the hydration of propene to isopropanol [1]. HPAs immobilised in a variety of supports from activated carbon and silica-gel to polymeric membranes, have been used as catalysts for organic reactions [9–13]. However, in a general way, these catalysts have the drawback of leaching to the aqueous phase. This leakage can be strongly reduced

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by encapsulation in the supercages of zeolite Y, like a "ship-in-a-bottle", in such a way that HPA once formed inside the supercage is not able to diffuse to the liquid phase [14–16].

In a recent work [17] the hydration reaction of α-pinene catalysed by dodecamolybdophosphoric acid (HPMo) encapsulated in the supercages of USY zeolite, was investigated. This catalyst showed high activity for α-pinene hydration, being 1000 times more active than HUSY [18] and 200 times more active than H-beta [19]. The selectivity to α-terpineol was also very high (75% at 95% conversion), indicating the high potential of this catalyst as an alternative solid acid catalyst to conventional homogeneous catalysts. However, the experiments performed re-using the same catalyst revealed that it lacks in stability and that the problem of the HPA leaching to the aqueous phases was not completely solved.

In this work HPMo was immobilised in polymeric matrixes of polyvinyl alcohol (PVA) and polydimethylsiloxane (PDMS) and the catalytic membranes so obtained were investigated in the hydration of α-pinene.

2. Experimental

2.1. HPMo/PVA membranes

PVA membranes were prepared by dissolving PVA (MERCK; average molecular weight: 72000), a suitable amount of succinic acid and HPMo in dimethylsulphoxide (DMS). The code HPMox/PVAy (Table 1) means a membrane prepared by adding a HPMo amount which is x% of the PVA amount, and y% cross-linked. The amount of succinic acid is given by

$$n_{\text{suc}} = \frac{1}{100}y\left(\frac{1}{2}n_{\text{OH}}\right),$$

where n_{suc} is the mole number of succinic acid, y the cross-linking degree and n_{OH} the mole number of hydroxyl groups in PVA.

The HPMo-USY/PVA membrane was prepared by suspending the zeolite encaged HPMo in the DMS solution of PVA and succinic acid. This suspension was sonicated for 1 h, before casting.

After casting over a Teflon plate, the solvent was evaporated at 60 °C, under moderate vacuum (∼300 mbar) during 24 h. Cross-linking was accomplished by heating the membrane to 120 °C for an additional period of 24 h. After curing the membrane for 24 h at 150 °C and ∼0 mbar, it was extracted with water, in a soxhlet apparatus, also during 24 h.

Table 1
Membrane characteristics[a]

Membrane	Thickness (mm)	HPA load (g/g_{membrane})	USY load (g/g_{membrane})
HPMo10/PVA10	0.1074	0.0757	–
HPMo20/PVA10	0.1506	0.0529	–
HPMo10/PVA20	0.1255	0.0479	–
HPMo10/PVA30	0.2203	0.0546	–
HPMo-USY/PVA20	0.2651	0.0226	0.4691
HPMo-USY/PDMS	0.2630	0.0365	0.7564

[a] The code HPMox/PVAy means a membrane prepared by adding x% (w/w) of HPA relatively to the PVA amount, with y% of –OH groups esterified in each PVA chain. HPA loads as evaluated by ICP analysis.

2.2. HPMo-USY/PDMS membrane

PDMS was delivered by General Electric as a pre-polymer (RTV-615A, linear PDMS chains with terminal vinyl groups) and a cross-linker (RTV-615B, linear PDMS chains carrying several hydride groups). The membrane was prepared according to Vankelecom et al. [20].

2.3. Zeolite encaged HPMo

USY zeolite was prepared by hydrothermal treatments from a parent Y sample (Aldrich). Dealumination was performed in three consecutive hydrothermal treatments at 630, 660 and 715 °C, respectively, for 3 h each one, under 100% steam. Before and after each treatment the zeolite sample was exchanged with 2 M aqueous NH_4NO_3 at 80 °C, washed with distilled water and dried at 120 °C. The extra framework aluminium species were leached out by washing the zeolite sample with 2 M HCl at 80 °C, for 4 h. The zeolite sample was exchanged once more with NH_4NO_3, calcined at 550 °C for 3 h, exchanged to the sodium form, by three consecutive treatments with 2 M NaCl at 80 °C, washed with distilled water and finally dried at 120 °C.

The encapsulation of PMo12 in the supercages of the USY sample was performed according to the method reported by Mukai et al. [15]. The obtained HPMo-USY catalyst was thoroughly washed with hot water.

2.4. Membrane characterisation

The success of PVA cross-linking and HPA immobilisation as well as HPA zeolite encapsulation, was evaluated by FT-IR spectroscopy. Membrane hydrophobicity was evaluated through the measurement of the contact angle of water droplets. The amount of HPMo immobilised in the membranes was measured by ICP analysis. Pinene diffusivities in the membranes were evaluated by using a two-chamber glass apparatus separated by the membrane, the two chambers being both filled with solvent and magnetically stirred. In one chamber α-pinene was added, being followed the increase of α-pinene concentration in the other chamber. For the calculations second Fick's law was used.

FT-IR spectra were recorded in a Bio-Rad FTS 155 instrument. ICP analysis was carried out in a Jobin-Yvon ULTIMA instrument. Contact angles were measured with a Goniometer Ramé-Hart, NRL C.A., model 100-00-230. Table 1 summarises the membrane characteristics.

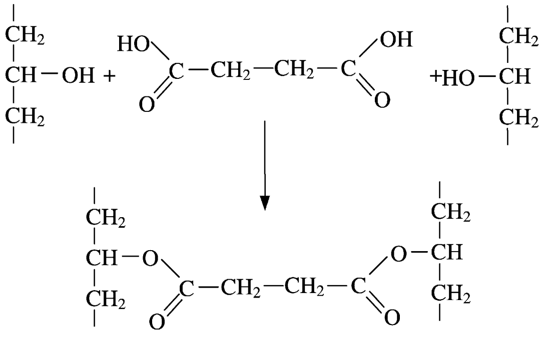
2.5. Reaction

Catalytic experiments were carried out in a jacketed batch reactor equipped with a stirrer, at 50 °C. In a typical experiment, the reactor was loaded with 114 ml aqueous acetone (1:1, v/v) and 1.1 g membrane cut in small pieces. Reactions were started by adding 7.62 mmol of α-pinene. Stirring speed was kept at 800 min^{-1}. Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column.

3. Results and discussion

3.1. Description of HPMo/PVA membranes

The HPMo/PVA membranes were prepared by entrapping dodecamolybdophosphoric acid in a cross-linked PVA matrix. The polymer cross-linking is accomplished by heating PVA with a dicarboxylic acid, succinic acid, in order to obtain the corresponding ester, according to Scheme 1. Fig. 1 shows the FT-IR spectra for pure PVA (A), PVA cross-linked with succinic acid (B), pure succinic acid (D) and HPMo/cross-linked PVA (C). The intense band at 1730 cm^{-1} in spectrum B, which does not overlap with the band present in the spectrum of succinic acid (D), characteristic of the free carboxylic group (1700 cm^{-1}), suggests that the cross-linking with succinic acid was succeeded. Also the small band present in spectrum C at 800 cm^{-1} and not appearing in spectra A and B, the band at 980 cm^{-1}, the tiny shoulder at 975 cm^{-1} and the strong band in the range of 1000–1170 cm^{-1} (its increased intensity is likely to be due to the overlapping between a matrix



Scheme 1.

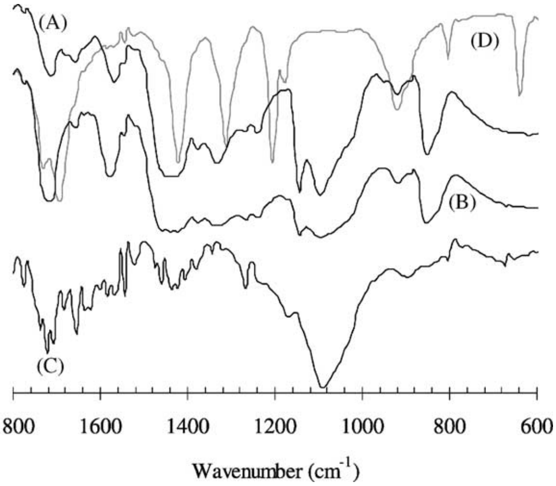


Fig. 1. FT-IR spectra of PVA membranes (KBr): (A) pure PVA; (B) PVA cross-linked with succinic acid (PVA10); (C) HPMo20/PVA10; (D) pure succinic acid.

band and the HPA band at 1075 cm^{-1}, assigned to the P–O bond), are indications that the HPA in the HPMo/cross-linked PVA membrane still retains its Keggin structure [11,21].

3.2. Description of HPMo/PDMS membranes

The preparation of HPMo/PDMS membranes by directly entrapping the HPA in the polymer matrix, was not possible, probably because the HPA inhibits the polymer cross-linking. However, in a previous work, a catalyst consisting of HPMo encaged in the supercages of USY zeolite, has been prepared and used in α-pinene hydration, successfully [17]. In this case, the HPA is directly synthesised inside the zeolite supercages, like a “ship-in-a-bottle”. As these cages are only slightly larger than the HPA anions, they are not able to diffuse out of the cages. Therefore, the alternative to the HPA direct entrapping was the dispersion of the HPMo/USY catalyst in the PDMS matrix.

3.3. Membrane activity

Similarly to what was observed with PDMS membranes filled with H-USY, H-beta or sulphonated activated carbon [7], the main product of α-pinene hydration over HPMo/PVA or HPMo-USY/PDMS membranes is α-terpineol, being also obtained minor amounts of limonene, terpinolene, β-fenchol, isoborneol and, at high α-pinene conversion, 1,8-terpine.

Fig. 2 compares the α-pinene concentration profiles for the hydration experiments carried out over the HPMo/PVA membranes. The activity values, calculated as the maximum reaction rate referred to the amount of HPA, are shown near each curve.

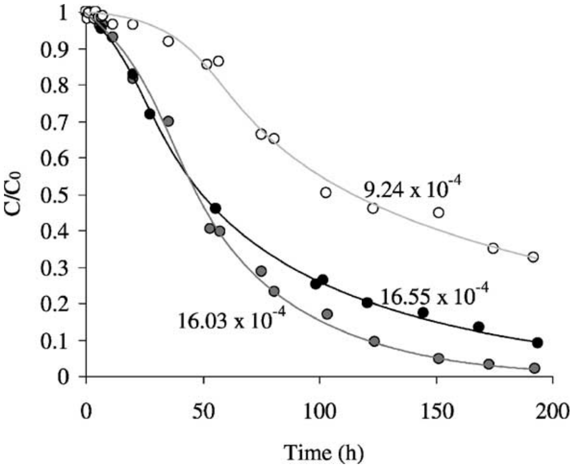


Fig. 2. α-Pinene hydration over HPMo/PVA membranes. Effect of cross-linking degree on α-pinene concentration profiles. Near each curve is indicated the value of activity (mol h^{-1} g^{-1}) taken as the maximum reaction rate referred to the HPA amount. (○) HPMo20/PVA10; (◉) HPMo10/PVA20; (●) HPMo10/PVA30.

Table 2
α-Pinene diffusivity in the PVA membranes calculated using second Fick’s law (dependence on cross-linking)

Membrane	De (m^2/h)
HPMo20/PVA10	1.14×10^{-10}
HPMo10/PVA20	3.00×10^{-10}
HPMo10/PVA30	3.63×10^{-10}

Membrane activity increases when the amount of succinic acid used in the polymer cross-linking is increased from 10 to 20%, and remains more or less constant when the amount of succinic acid is increased form 20 to 30%. This increase in activity can be explained by the increase on pinene diffusivity (Table 2), due to an increase on membrane hydrophobicity. In fact, as shown by the values obtained for the water contact angle (Table 3), the membrane hydrophobicity increases with the cross-linking degree (or the amount of succinic acid added). When the cross-linking degree increases more and more –OH groups of the polymer chains become inactive for hydrogen bonding, as a consequence of esterification by succinic acid. Therefore, the polymer matrix becomes more and more hydrophobic. Pinene diffusivity through the increasingly lipophilic membrane increases when the amount of succinic acid added is increased from 10 to 20%, but is limited for further additions by the growing cross-linking which restricts the pinene molecules mobility in the polymer matrix. Activity is increased due to the higher concentration

Table 3
Contact angles of water droplets on the PVA membranes surface (effect of cross-linking on the membrane hydrophobicity)

Membrane	Contact angle (°)
PVA	9.9
HPMo20/PVA10	17.5
HPMo10/PVA20	56.5
HPMo10/PVA30	77.5

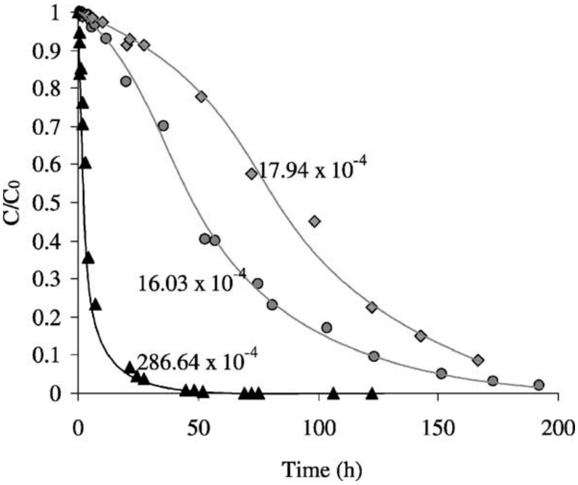


Fig. 3. α-Pinene hydration over HPMo-USY/polymer membranes compared to the HPMo10/PVA20 membrane. Effect of matrix nature on α-pinene concentration profiles. Near each curve is indicated the value of activity (mol h^{-1} g^{-1}) taken as the maximum reaction rate referred to the HPA amount. (▲) HPMo-USY/PDMS; (◆) HPMo-USY/PVA; (●) HPMo10/PVA20.

of α-pinene near the active HPMo molecules but this growth in activity is opposed by the increasing diffusional limitations due to the increasing cross-linking. The induction period observed in the concentration profiles of Figs. 2 and 3, which is more pronounced for the membrane HPMo20/PVA10 and is minimal for the membrane HPMo10/PVA30, is also a strong indication that α-pinene conversion is diffusion controlled. In fact, in a previous work it was shown that pinene molar flux through a USY/PDMS membrane increases when the amount of α-terpineol increases, leading to an autocatalytic effect on the pinene hydration reaction [8]. This autocatalytic effect, consisting of an initial induction period followed by a strong increase in the reaction rate, can also explain the induction period observed for the HPMo/PVA membranes (Figs. 2 and 3), suggesting that α-terpineol also interacts with the PVA matrix. This interaction could be even higher in this last case, due to the possible strong hydrogen bonding between the PVA–OH groups and the α-terpineol molecules.

Another indication that pinene conversion is diffusion controlled is the decrease in the turnover number (moles of pinene reacted per mole of HPA) after 150 h reaction, with the increase in HPA loading: from 209.3 observed for the HPMo10/PVA20 membrane, to 112.2 observed for the HPMo20/PVA10 membrane.

When HPMo-USY/PDMS is used as catalyst for α-pinene hydration, a spectacular increase in activity is observed (Fig. 3), which is even higher than that observed with HPMo-USY alone [17]. This enhanced activity is also explained by the higher hydrophobicity of the PDMS matrix, by comparison with the PVA matrix. This high hydrophobic character leads to a high concentration of pinene in the active sites neighbouring and, therefore, to high catalytic activity. The role of PDMS, tuning the concentration of pinene in the close neighbouring of the USY encaged HPMo molecules explains also the improved activity observed for the HPMo-USY/PDMS in relation to the HPMo-USY alone.

In the HPMo-USY/PVA membrane there is no change in the polymer matrix when compared to the HPMo/PVA membrane and, therefore, any significant change is not observed in the catalyst activity (Fig. 3).

3.4. *Membrane selectivity to α-terpineol*

Better selectivities to α-terpineol are obtained with the membranes HPMo10/PVA20 and HPMo10/PVA30 (70–75% at 90% conversion, Fig. 4). With the membrane HPMo-USY/PDMS selectivity decreases to 60% at 90% conversion (maximum: 65% at 80%

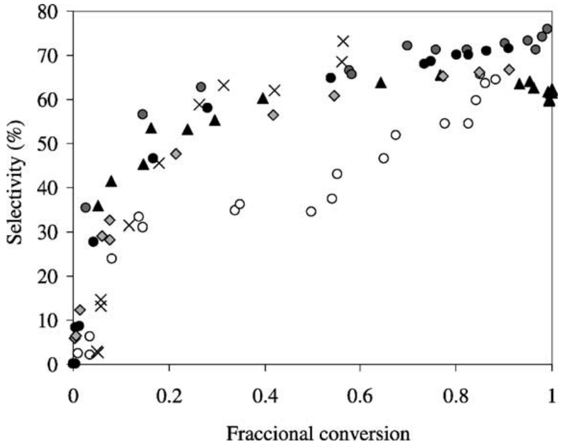


Fig. 4. α-Pinene hydration over HPMo-USY/polymer membranes. Selectivity to α-terpineol. (×) HPMo10/PVA10; (○) HPMo20/PVA10; (●) HPMo10/PVA20; (●) HPMo10/PVA30; (▲) HPMo-USY/PDMS; (◆) HPMo-USY/PVA.

Table 4
Stability studies on the HPMo10/PVA20 and HPMo-USY/PDMS membranes[a]

Experiment	HPMo10/PVA20	HPMo-USY/PDMS
First use	0.0479	0.0365
Second use	0.0214	0.0324
Third use	0.0182	0.0302
Fourth use	0.0179	0.0279

[a] HPA amounts present in each use of the same membrane ($g/g_{membrane}$) as evaluated by ICP analysis.

conversion), suggesting that a better compromise between activity and selectivity could be obtained through a better tuning of lipophilic/hydrophilic balance.

3.5. Stability studies

Aiming at the study of membrane stability, experiments were carried out in which the same membrane was reused (HPMo10/PVA20 and HPMo-USY/PDMS). After the first experiment, the membrane lost almost one-half of its HPA content, but in the following re-use experiments it seems to keep the remaining HPA (Table 4). However, the value of catalytic activity referred to the membrane weight decreases only slightly, while the value of the same catalytic activity referred to the HPA amount has a strong increase from the first to the second use and increases slightly in the following uses (Fig. 5). In what concerns the HPMo-USY/PDMS membrane the loss in HPA is much less pronounced than in the case of the PVA membrane. While in the case of the PVA membrane the maximum loss in HPA, after three uses, is 64% of the its original amount, for the PDMS membrane that loss is only 24% (Table 4). For this PDMS membrane, the value of activity referred to the membrane weight, decreases from the first to the second use but increases in the subsequent uses, while the value of the same activity, but referred to the HPA amount remains constant in the two first uses, increasing for the subsequent uses (Fig. 6).

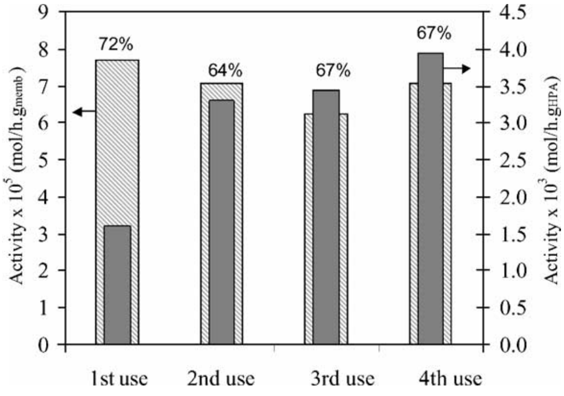


Fig. 5. Stability studies on the HPMo10/PVA20 membrane. Activity ($mol\,h^{-1}\,g^{-1}$) taken as the maximum reaction rate, referred to the HPA amount or to the membrane weight.

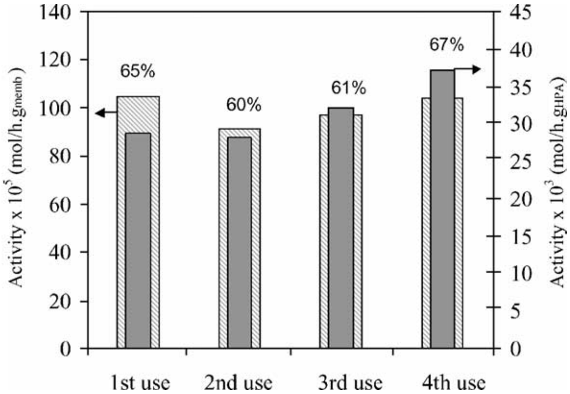


Fig. 6. Stability studies on the HPMo-USY/PDMS membrane. Activity ($mol\,h^{-1}\,g^{-1}$) taken as the maximum reaction rate, referred to the HPA amount or to the membrane weight.

Although the diffusion control of pinene conversion can explain this behaviour of activity in these reusing experiments, another possible explanation lays in the interaction between α-terpineol irreversibly absorbed in the membrane and the polymeric matrix. As mentioned above, it was shown in a previous work that pinene transport through a USY/PDMS membrane is improved by adding α-terpineol [8] and the same is likely to happen with the PVA membranes.

4. Conclusions

Polymeric catalytic membranes consisting of HPMo entrapped in PVA cross-linked with succinic acid are active for the α-pinene hydration reaction.

Membrane activity increases with the polymer cross-linking due to the increase in membrane hydrophobicity. However this growth in activity is limited by the increasingly restrictions to the molecules mobility.

It was not possible to prepare polymeric catalytic membranes consisting of HPMo directly entrapped in a PDMS matrix, probably due to interference of HPA with the polymer cross-linking. Alternatively, the preparation of a composite membrane consisting of USY encaged HPMo dispersed in a PDMS matrix was succeeded, since HPA is mostly retained inside the zeolite supercages. This membrane shows a surprisingly higher activity for pinene hydration, which is even higher than that observed with USY encaged HPMo alone. However, selectivity to α-terpineol is slightly lower than that obtained for the HPMo/PVA cross-linked with 20 or 30% of succinic acid.

Membrane stability seems to be reasonably good. For the HPMo/PVA membranes an initial loss in HPA is observed, but in the subsequent runs the amount of HPA present in the membrane seems to be stabilised. For the HPMo-USY/PDMS membrane the observed losses in HPA are much lower than those observed for the HPMo/PVA membranes, showing that the HPA zeolite encapsulation is effective in the catalyst stabilisation.

In both cases, HPMo/PVA or HPMo-USY/PDMS, catalyst activity increases in the subsequent uses of the same membrane, probably due to the interaction between retained α-terpineol and the polymer matrix, promoting a better diffusion of pinene molecules to the catalyst active sites.

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