ELSEVIER

Catalysis Today 67 (2001) 217–223

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The effect of α-terpineol on the hydration of α-pinene over zeolites dispersed in polymeric membranes

J. Vital*, A.M. Ramos, I.F. Silva, J.E. Castanheiro

CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825-114 Caparica, Portugal

Abstract

The hydration of α-pinene over catalytic PDMS membranes loaded with a USY zeolite is studied. The concentration profiles of reagent and products exhibited a pronounced initial induction period followed by a rapid increase of the reaction rate, suggesting an autocatalytic behaviour. The effects of the main reaction product, α-terpineol, on the membrane transport properties are investigated.

A simple diffusion-kinetic model which fits experimental concentration data quite well has been developed.

Keywords: PDMS membranes; Zeolite USY; α-Pinene hydration; Modelling

1. Introduction

The acid catalysed hydration of α-pinene yields a complex mixture of monoterpenes, alcohols and hydrocarbons [1]. The resulting terpenic alcohols are valuable products with many applications in the pharmaceutical industry. By controlling the reaction variables it is possible to make the reaction highly selective towards the desired products, namely α-terpineol [2,3].

In a previous work the hydration reaction of α-pinene catalysed by polydimethylsiloxane (PDMS) membranes filled with zeolite USY, zeolite beta or a surface modified activated carbon was reported [4]. The composite PDMS membranes showed to have complex effects on the selectivity to α-terpineol, related with the particle size of the catalysts and the solvent water content. The more interesting results were obtained for the USY zeolite, which led to an increase on the selectivity to α-terpineol.

The purpose of this work is to perform a kinetic study of the hydration of α-pinene over PDMS/USY zeolite membranes, in the reaction conditions previously tested, and to develop a model able to describe the behaviour observed.

2. Experimental

In all experiments performed the catalyst used was USY 750 zeolite, immobilised in a PDMS membrane. The procedure of the catalyst and the membrane preparation and characterisation were reported in previous works [4,5].

The characteristics of the membrane used are presented in Table 2.

The catalytic membrane reactor system was described before as well [4]. The kinetic experiments

* Corresponding author. Tel.: +351-1-2948385; fax: +351-1-2948550.
E-mail address: jmv@dq.fct.unl.pt (J. Vital).

0920-5861/01/$ – see front matter
PII: S0920-5861(01)00289-9

Table 1
Hydration of α-pinene over the catalytic membrane M2[a]

	Time (h)													
	0.1	0.6	2.4	19.2	23.9	26.2	43.3	50.5	68.4	75.1	93.0	99.2	121.6	145.1
α-Pinene	103.36	104.26	105.08	103.15	100.53	100.86	93.62	84.43	75.98	66.80	53.15	52.18	31.77	23.97
α-Fenchol	0.66	0.40	0.62	0.72	0.95	0.91	1.35	1.42	2.32	2.46	3.14	4.28	4.05	5.55
β-Terpineol	2.93	3.19	0.37	0.58	0.81	0.80	1.05	9.00	9.04	11.53	10.56	9.17	7.46	4.70
Isoborneol	0.86	0.65	0.91	0.79	1.24	1.22	1.59	1.19	1.36	2.29	2.10	2.02	3.07	3.10
Borneol	0.03	0.08	0.03	0.15	0.14	0.16	0.89	0.48	2.20	2.74	2.75	2.70	4.21	4.48
Terpineno-4-ol	0.77	0.70	0.90	1.04	1.27	1.21	1.82	2.12	2.04	3.52	4.64	4.48	7.52	7.33
4-Terpineol	0.13	0.03	0.15	1.02	1.44	1.41	3.00	3.64	5.38	7.82	11.51	12.62	17.96	20.50
α-Terpineol	3.57	2.96	3.83	4.61	5.62	5.53	8.22	9.54	11.24	13.79	20.59	21.64	30.12	31.82
1,8-Terpine	0.00	0.19	0.18	0.19	0.05	0.07	0.09	0.07	0.28	0.30	1.01	0.80	1.15	9.04
Unidentified	0.93	1.28	1.50	1.68	1.94	1.88	2.47	2.81	4.64	4.26	6.62	6.34	9.71	5.49

[a] Concentration profiles (mmol/dm^3).

were carried out at 50°C using aqueous acetone (1:1 v/v) as solvent, and a constant relationship α-pinene/catalyst 2.1 (wt). The reaction products were analysed by GC using a Konic HRGC-3000C, equipped with a 30 mm × 0.25 mm DB-1 column.

A two-chamber glass apparatus was used for the determination of the molar flux of α-pinene through the catalytic membrane. The membrane separated the two chambers, both filled with the solvent and magnetically stirred. In one chamber α-pinene was added and in the other, samples were collected and analysed periodically. The study of the effect of α-terpineol on the membrane transport properties was carried out by previously adding the same concentration of that alcohol to both chambers.

3. Results and discussion

3.1. Catalytic membrane experiments

In agreement with previous observations [4], the hydration of α-pinene carried out in the presence of a PDMS membrane loaded with a USY zeolite yields a complex mixture of monoterpenes, alcohols and hydrocarbons, dominated by α-terpineol. Table 1 and Fig. 1 show the concentration profiles obtained for the catalytic membrane M2. In Fig. 1, "*others*" lumps all the reaction products but α-terpineol.

Fig. 2 shows the effect of the catalyst (USY) loading on the concentration profile of α-pinene. A very peculiar feature of all these kinetic curves is their

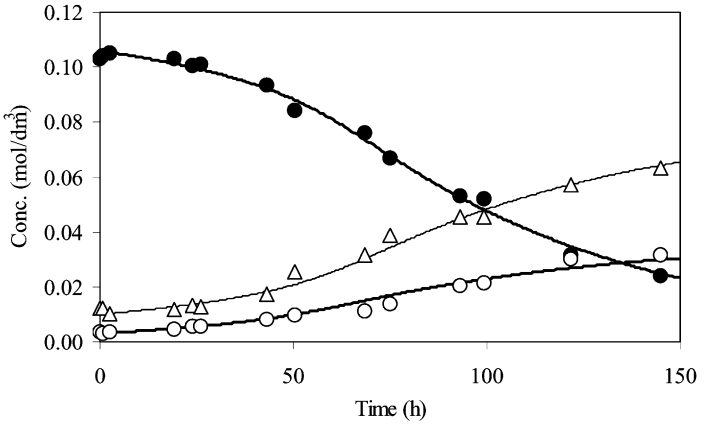


Fig. 1. Concentration profiles obtained for the catalytic membrane M2. Model fitting to data points. ●: α-pinene; ○: α-terpineol; △: others.

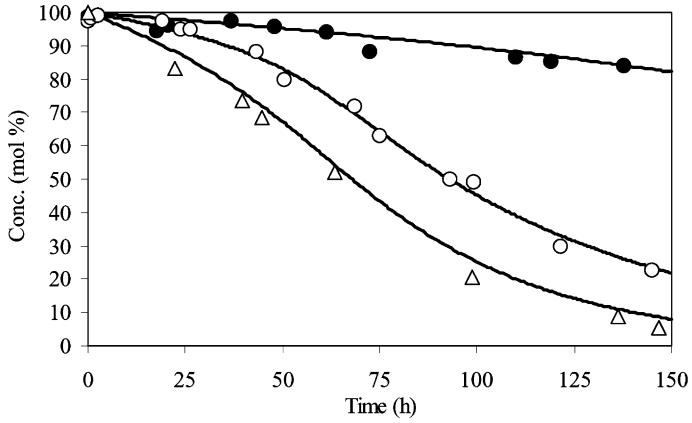


Fig. 2. Effect of the USY catalyst loading on the concentration profile of α-pinene. Model fitting to data points. ●: M1; ○: M2; △: M3.

autocatalytic behaviour, consisting in an initial inductive period followed by a rapid increasing in the reaction rate.

It is well known that organic compounds affect permeability across polymeric membranes [6–9]. Therefore, it would be expectable that a changing in the composition of the reaction mixture, namely the formation of α-terpineol, would affect drastically the membrane behaviour.

In order to investigate the effects of α-terpineol on the transport properties of PDMS membranes, the molar flux of α-pinene through the membrane M2 was measured in the absence and in the presence of increasing amounts of α-terpineol. The effects of α-terpineol concentration on the molar flux of α-pinene are shown in Fig. 3. At relatively low concentrations of α-pinene the initial molar flux seems to increase linearly with α-pinene concentration, leading to the conclusion that at low concentrations of α-pinene diffusivity is not affected by α-pinene concentration. It is notorious the increase of α-pinene permeability when the concentration of α-terpineol increases.

3.2. Membrane modelling

A kinetic diffusion-reaction model can be established based on the following assumptions:

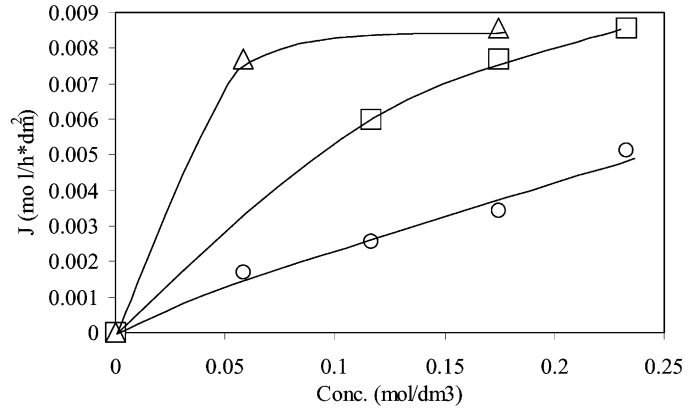


Fig. 3. Effect of α-terpineol concentration on the molar flux of α-pinene. ○: α-terpineol 0 M; □: α-terpineol 0.0058 M; △: α-terpineol 0.0116 M.

- Isothermal and isobaric reaction conditions.
- Pseudo steady-state conditions for diffusion and reaction in the membrane.
- Unidirectional diffusion.
- Membrane macrostructure is homogeneous and isotropic. Equilibrium is established between the aqueous acetone phase and membrane faces, being K_A and K_W the partition coefficients for α-pinene and water, respectively:

$$K_A = \frac{C_{Am}}{C_{Aac}}, \qquad K_W = \frac{C_{Wm}}{C_{Wac}} \tag{1}$$

where $C_{i\,m}$ and $C_{i\,ac}$ are respectively the concentrations of component i on the membrane surface and in the aqueous acetone bulk solution.

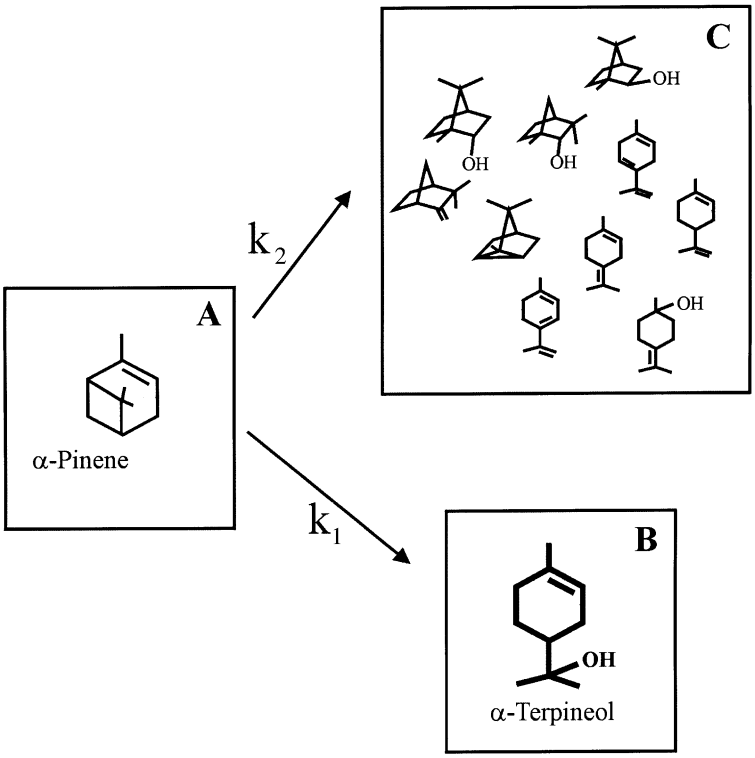
- There is zero transport resistance for α-pinene and H_2O from the aqueous acetone bulk phase to the membrane surface.
- The diffusivity of α-pinene is independent of α-pinene concentration over the range of values used. However, it depends on α-terpineol concentration, according to the generally accepted [6] empiric equation

$$D_e = D_{e0} e^{\alpha C_{Bac}} \tag{2}$$

where D_{e0} is the initial diffusivity of α-pinene and C_{Bac} is the concentration of α-terpineol in the aqueous acetone phase.

- α-Pinene is consumed according to the parallel reaction network shown in Scheme 1, where A represents α-pinene, B represents α-terpineol and C lumps all the other species formed. As in the present case α-terpineol seems not to be consumed, is not necessary a more complex reaction network.
- The internal diffusion in a zeolite particle does not affect the reaction rate.

In a previous work was shown that the hydration of α-pinene carried out in the presence of zeolite beta in aqueous acetone, under low water concentration



Scheme 1.

conditions, is a pseudo first order reaction [2]. Simultaneously, it has been shown that the water absorption capacity of PDMS membranes is low [10]. On the other hand, in the present case there is a large excess of water in relation to α-pinene, in the aqueous acetone phase. Therefore, it is reasonable to assume that the water concentration in the membrane phase is low and constant and, therefore, to assume first-order pseudo elementary reactions.

The mole balance of α-pinene over a differential membrane element of thickness dz in pseudo steady-state conditions may be written as

$$-\frac{\mathrm{d}J_\mathrm{A}}{\mathrm{d}z} + \rho r_{\mathrm{A}i} = 0 \tag{3}$$

where J_A is the molar flux of α-pinene in the direction normal to the membrane surface, ρ the density of the catalyst and $r_{\mathrm{A}i}$ the rate of the pseudo-elementary i reaction.

The molar flux of α-pinene across the membrane can be given by the Fick's first law of diffusion:

$$J_\mathrm{A} = -D_\mathrm{e}\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}z} \tag{4}$$

Since apparent first order is assumed, the reaction rate of the pseudo-elementary reaction i is

$$(-r_{\mathrm{A}i}) = k_i' C_\mathrm{A} \tag{5}$$

where $k_i' = kC_\mathrm{W}$ is the apparent kinetic constant.

Merging Eqs. (3)–(5), we get

$$\frac{\mathrm{d}^2 C_\mathrm{A}}{\mathrm{d}z^2} - \frac{k_i'\rho}{D_\mathrm{e}}C_\mathrm{A} = 0 \tag{6}$$

which can be integrated under the following boundary conditions:

$$z = 0, \qquad \frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}z} = 0$$

$$z = \pm L, \qquad C_\mathrm{A} = C_\mathrm{Am}$$

Therefore, the concentration profile in the membrane is

$$C_\mathrm{A} = C_\mathrm{Am}\frac{\cosh[\phi(z/L)]}{\phi} \tag{7}$$

where C_Am is the concentration of α-pinene on the membrane surface and

$$\phi_i = L\sqrt{\frac{k_i'\rho}{D_\mathrm{e}}} \tag{8}$$

is the Thiele modulus for the i pseudo-elementary reaction.

The effectiveness factor for the pseudo-elementary reaction i, will then be

$$\eta_i = \frac{\tanh\phi_i}{\phi_i} \tag{9}$$

The mole balance for the membrane reactor working under total recycle is given by the following set of equations:

$$\frac{\mathrm{d}C_\mathrm{Aac}}{\mathrm{d}t} = -\frac{W}{V}(\eta_1 k_1'' + \eta_2 k_2'')C_\mathrm{Aac} \tag{10}$$

$$\frac{\mathrm{d}C_\mathrm{Bac}}{\mathrm{d}t} = \frac{W}{V}\eta_1 k_1'' C_\mathrm{Aac} \tag{11}$$

$$\frac{\mathrm{d}C_{Cac}}{\mathrm{d}t} = \frac{W}{V}\eta_2 k_2'' C_\mathrm{Aac} \tag{12}$$

where $k_i'' = K_\mathrm{A}k_i'$.

The fittings of the model to data points are shown in Figs. 1 and 2. Table 2 shows the effect of the catalyst loading on the model parameters. It can be found from this table that parameter α, which reflects the pinene diffusivity increase with α-terpineol concentration, decreases when the catalyst loading increases. This effect can be explained by the decrease of the relative amount of polymer present in the membrane, since the increase of α-pinene diffusivity with α-terpineol concentration is likely to be a consequence of the interaction between this alcohol and the polymer structure.

Table 2
Effect of catalyst loading on model parameters

Membrane	Catalyst loading (wt.%)	Thickness (mm)	k_2 ($\mathrm{dm^3/h\,g_{cat}}$)	k_1 ($\mathrm{dm^3/h\,g_{cat}}$)	k_2/k_1	α ($\mathrm{dm^3/mol}$)	D_{e0} ($\mathrm{m^2/h}$)
M1	21.9	0.110	0.00307	0.00720	0.426	891.33	1.045×10^{-10}
M2	35.9	0.205	0.00095	0.00224	0.396	354.60	1.327×10^{-10}
M3	52.8	0.139	0.00470	0.00316	1.487	211.45	7.786×10^{-10}

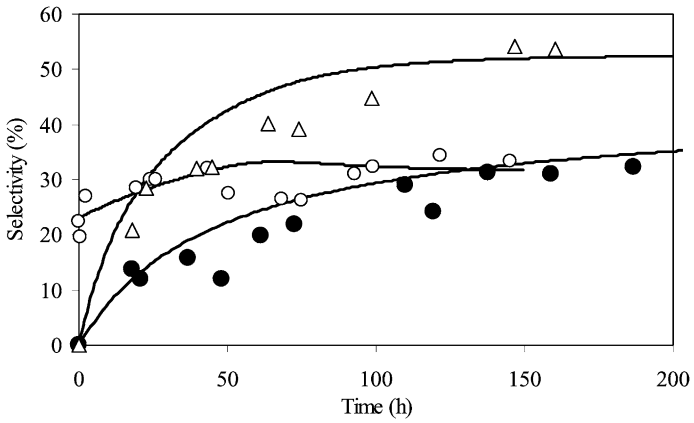


Fig. 4. Selectivity to α-terpineol. Model fitting to data points. ●: M1; ○: M2; △: M3.

Simultaneously, initial α-pinene diffusivity, D_{e0}, increases only slightly from M1 to M2, but shows a strong increase from M2 to M3, probably reflecting the increasingly membrane channeling with the catalyst loading [4,10,11].

The ratio of the apparent kinetic constants, k_1/k_2, follows the tendency of D_{e0}: it shows roughly the same value for membranes M1 and M2, but it increases strongly for membrane M3. These results are in good agreement with the ones obtained from the membrane catalytic experiments (Fig. 4) and are consistent with the channeling increase due to the catalyst loading increase. In fact, it would be expected that the increase of channeling should lead to an increase of the permeation of water through the membrane and, therefore, to an increase of the hydration product (α-terpineol).

4. Conclusions

The main reaction product of the hydration of α-pinene in the presence of a catalytic PDMS membrane loaded with a USY zeolite is α-terpineol, being simultaneously formed a number of minor products, mainly terpenic hydrocarbons.

The concentration profiles of reagent and products exhibit a pronounced initial induction period followed by a rapid increase of the reaction rate. This feature suggests an autocatalytic behavior.

α-Pinene permeation measurements across the membrane show that α-pinene molar flux depends almost linearly of pinene concentration in the range of relatively low concentrations. However, it increases strongly in the presence of increasingly amounts of α-terpineol.

A simple diffusion-kinetic model, which fits experimental concentration data quite well, has being developed. It assumes a parallel reaction network and an exponential dependence of pinene diffusivity in the membrane on α-terpineol concentration.

The value of the α-pinene initial diffusivity obtained from the model increases with the catalyst loading. Simultaneously the ratio of the model apparent kinetic constants, k_1/k_2, increases for the highest catalyst loading, reflecting an increase in selectivity to α-terpineol. This behaviour shows that the increase in the catalyst loading leads to an increase in the permeability not only of α-pinene but also of water, probably due to an increase in the membrane channeling.

Acknowledgements

The authors acknowledge financial support from Fundação para a Ciência e Tecnologia (FCT).

References

[1] R.M. Traynor, R.M. Albert, R.L Webb, In: D.F. Zinkel, J. Russels (Eds.), Naval Stores, Pulp Chemical Association, New York, 1989, Chapter 12, p. 479.

[2] J. van de Waal, H. van Bekkum, J. Vital, J. Mol. Catal. A 105 (1996) 185.0.

[3] H. Valente, J. Vital, In: H.U. Blase, A. Baiker, R. Prins (Eds.), Heterogeneous Catalysis and Fine Chemicals IV, Stud. Surf. Sci. Catal. 108 (1997) 555.
[4] J. Vital, A.M. Ramos, I.F. Silva, H. Valente, J.E. Castanheiro, Catal. Today 56 (2000) 167.
[5] A. Severino, A. Esculcas, J. Rocha, J. Vital, L.S. Lobo, Appl. Catal. 142 (1996) 255.
[6] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991.
[7] I. Vankelecom, E. Scheppers, R. Heus, J. Uytterhoeven, J. Phys. Chem. 98 (1994) 12390.
[8] I. Vankelecom, R. Parton, M. Casselman, J. Uytterhoeven, P. Jacobs, J. Catal. 163 (1996) 457.
[9] I.F.J. Vankelekom, P.A. Jacobs, Catal. Today 56 (2000) 147.
[10] S. Wu, J.E. Gallot, M. Bousmina, C. Bouchard, S. Kaliaguine, Catal. Today 56 (2000) 113.
[11] M.G. Süer, N. Baç, L. Yilmaz, J. Membr. Sci. 91 (1994) 77.