Mass transport on composite dense PDMS membranes with palladium nanoclusters

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Received 3 July 2006; received in revised form 25 October 2006; accepted 28 October 2006
Available online 15 November 2006

Abstract

Sorption, diffusion and permeability coefficients of argon, hydrogen, propane, propylene and propyne were determined for unfilled poly(dimethylsiloxane) (PDMS) membranes at 308 K and for PDMS membrane filled with palladium nanoclusters (5 wt.%). Time-lag and sorption methods were used to obtain kinetic and equilibrium relevant parameters for characterizing the mass transport.

Mass transport in a PDMS composite membrane differs from the corresponding unfilled membrane mainly during the transient regime, when a concentration profile is being settling down across the membrane thickness. The presence of the palladium nanoclusters modifies the mass transport during the transient regime not only because the nanoclusters can act as adsorption wells (mainly in the case of hydrogen), but also because they lead to a tortuosity increase. At steady-state condition the relevant parameters that characterize the transport are the sorption and diffusion coefficients in the polymeric matrix, the filler volume content and the tortuosity. All experiments were successfully modelled using parameters obtained from independent experiments.

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Keywords: Mass transport; Filled membrane; Time-lag; PDMS; Hydrocarbons; Palladium

1. Introduction

Catalytic membrane processes using polymeric membranes can advantageously be used for reactions performed at temperatures below 200 °C [1]. Besides, dense polymeric catalytic membranes can actively interfere in the reaction by regulating sorption and diffusion of reagents and products [2]. For such applications, membranes with ultra fine clusters (nanosized) and uniformly distributed throughout the membrane can be generated, departing from homogeneously distributed precursors totally solved by the polymer membrane [3].

Testing and modelling a polymeric catalytic membrane reactor (pCMR), containing palladium nanoclusters in the polymeric matrix, is the aim of a future work, which will consider alkyn and alkene hydrogenations at nearly room temperature. However, to have access to the parameters governing the mass transport and the chemical reaction kinetics, independent experiments have to be performed. Kinetic parameters for propylene and propyne hydrogenations were reported for a batch reactor at 308 K (35 °C) using Pd nanoclusters stabilized with a surfactant [4,5]. This paper discusses the mass transfer across a polydimethylsiloxane (PDMS) membrane filled with palladium nanoclusters that is critical for subsequent modelling of a pCMR.

PDMS is undoubtedly the most studied polymer system for catalytic reactions, as referred by Vankelecom and Jacobs [2]. First, this highly permeable elastomer is prepared easily and combines a fairly high thermal stability (up to 250 °C) along with mechanical and chemical resistances, the later being of utmost importance under reactive conditions [2]. On the other hand, a polymer with high diffusivity is strongly favoured on a pCMR because reagents and products must be able to diffuse to and from the catalyst’s active sites with an acceptable rate [6].

The mass transport mechanism of a sorbate crossing a dense membrane is normally represented using the so-called sorption–diffusion model [7]. Sorption characterises the interactions between polymer and sorbate and is described by the thermodynamics. Molecular diffusion characterises the transport of molecules through the polymer matrix [8].

Usually three methods can be employed to characterize the mass transport in membranes: the so-called sorption, differential
and integral methods [9]. All these methods are based on the dynamic response obtained from a sudden change at the membrane boundaries of the partial or total concentration.

In the sorption method, when the polymer contacts a fluid phase, the sorbate present in both phases is exchanged until the chemical potentials become equal [10]. Sorption of a single gaseous species can be determined by exposing a pre-weighed polymeric sample to a controlled pressure and weighing it after equilibrium [11]. Each experiment provides a single sorption equilibrium isotherm datum. Repeating the process under different pressures completes the sorption equilibrium isotherm. By performing sorption experiments on polymeric films under well-controlled experimental conditions, it is possible to obtain both sorption isotherms and the diffusion coefficients by measuring sorption rates during the transient state of the process—uptake experiments [10].

In the differential method a constant partial pressure difference (driving force) is applied to both sides of the membrane and the permeate flowrate is measured. This can be done directly, using a very sensitive flowmeter, or indirectly, allowing the permeate flowrate to mix with a carrier gas and analysing the flowrate and composition of the stream leaving the cell. In the differential method both sides of the membrane are at equal total pressure.

In the integral method a quasi-constant pressure difference is applied to both sides of the membrane and the accumulation of gas on the permeate side is measured. This method, usually known as time-lag method, is implemented using an accurate pressure sensor and was first suggested by Daynes [12]. In the time-lag method the membrane test cell is placed between two tanks, the feed and the permeate tanks. Initially, both chambers of the membrane module should be filled with a gas at the same pressure. At this point, the sorbed gas in the membrane is in equilibrium with the gas phase in both chambers, meaning that the initial concentration of the sorbed gas in the membrane is uniform and hence constant in time. At a given instant \( t = 0 \), the valve between the feed tank and the membrane cell is opened, originating a positive pressure step perturbation at the membrane feed side. At the same time, the pressure at the permeate tank, which is connected with the permeate chamber of the membrane cell, is recorded. The permeation system must be at constant temperature.

In all three methods, the diffusivity and sorption coefficients, which characterize the mass transfer of a gas in the polymeric matrix, are calculated by fitting the sorption–diffusion model to the experimental data. In this work, sorption and time-lag methods are used to characterize mass transport of different gases through PDMS membranes, loaded or not with palladium nanoclusters.

2. Experimental

2.1. Chemicals

Palladium(II) acetate (Chempur) was used as catalyst precursor. All solvents were purchased from Merck as analytical grade. The cross-linkable PDMS Dehesive® 942, from Wacker Silicones Corporation, was used to prepare both noble metal containing polymer films and unfilled polymer films.

2.2. Membrane preparation

About 10 g of solvent-free PDMS Dehesive® 942 was dissolved in THF to form a 10 wt.% solution. The required amount (1 wt.% of polymer) of cross-linker/catalyst was added, followed by mixing with a ca. 10 wt.% solution of palladium(II) acetate in THF to form a final concentration of 10 wt.% palladium(II) acetate in PDMS. Directly after mixing, the solution was poured in a casting ring supported by Teflon®-coated glass plate heated at 50°C and left overnight. During this period of time the solvent evaporation occurred along with cross-linking. About 0.025 m² of composite membrane was obtained, with ca. 300 μm in thickness. The membrane was reduced by 1% NaBH₄ in ethanol/water (1/1 volume) and then dried in a vacuum oven at 100°C overnight. A Pd content of 5 wt.% was calculated. The average size of the palladium clusters was estimated by XRD to be 8.8 nm in diameter and the membrane thickness 280.5 μm, determined by SEM.

The unfilled membrane was prepared as describe above, but in this case there was no addition of the palladium(II) acetate solution to the polymer one. Membrane thickness of 278.7 μm was determined with a precision digital micrometer.

2.3. Gases

Pure sorption and diffusion coefficients of hydrogen, argon, propyne, propylene and propane in the prepared membranes were determined. All gases were supplied by Praxair (propane 99.5%; propylene 99.5%; propyne 97%; hydrogen 99.999%; argon 99.999%) and were used as received.

2.4. Determination of sorption and diffusivity parameters

The previously referred sorption method (uptake curves) was implemented using a magnetic suspension balance from Rubotherm (0.01 mg weighing resolution, 0.02 mg reproducibility), which uses a pressure sensor (Druck, ref. 4010, 0.7 bara, ±0.04% FS) and a thermocouple (type K) to control, respectively, the pressure and the temperature in the basket container of the balance. An auxiliary jacketed stainless steel tank was used to supply each gas species to the balance. The temperature was kept at 308 K with the help of a water bath (Hubber, Polystat K6-1, ±0.1 K).

A turbo-molecular connected to a rotary vacuum pump system was used to evacuate the tanks and to degas the membrane samples. The evacuation system can attain pressures well below 0.1 mbar. The magnetic suspension balance used corrects automatically the buoyancy effect and allows the acquisition of weighing data as a function of time. The complete system is described elsewhere [13,14].

The lab set-up that implements the time-lag method is shown schematically in Fig. 1. It considers two stainless steel...
tanks of 5 dm$^3$ (feed) and 28.7 cm$^3$ (permeate, calibrated volume). These tanks are connected to a permeation cell with 10.2 cm$^2$ effective area. The permeation cell comprises a sintered disk, used to support the membrane, and a viton O-ring, used to seal the cell. Two pressure sensors are used to control the pressure; one is placed at the feed tank and is used to control the feed pressure (Lucas Schaevitz, ref. 914, 10 bara, ±0.04%FS, P1). At the permeate tank, a high precision differential pressure sensor was used (Druck, ref. 4110, 20 mbar, ±0.04% FS, P3). A reference tank under high vacuum (below 0.01 mbar, P2) is used with the differential pressure sensor. In this set-up, the high vacuum system made of a turbo-molecular pump in series with a rotary vacuum pump was also employed.

The time-lag unit is placed inside a thermostatic cabinet at 308 K. This unit is operated with the help of three low power electric valves. These valves are commanded, and the pressures are read using an acquisition system based on a personal computer. To control the unit, a software application in LabView 5.0 (National Instruments) was developed.

3. Model

The model used to describe the permeation for the synthesised membranes is the sorption-diffusion model [7]. Fick’s law is used for describing the diffusion transport through the membrane and it is assumed that the permeating species is in sorption equilibrium at both membrane surfaces. It is also assumed that the sorption equilibrium is described by the Henry’s law and that there is no concentration polarization. This appears to be the case in almost all membrane processes, but may fail, for example, in transport processes involving facilitated transport or in diffusion of gases through metals, where interfacial adsorption/desorption can be slow [7].

3.1. PDMS membrane

Fick’s first law is the starting point for the mathematical description of permeation through polymeric dense membranes:

$$ J = -D \frac{\partial C}{\partial x} \quad (1) $$

where $J$ is the flux through the membrane, $C$ the concentration of the species inside the membrane, $D$ the diffusion coefficient and $x$ is the membrane spatial coordinate.

Using the Fick’s second law, under the assumption of a constant diffusion coefficient, the gas transport through the membrane is described by

$$ \frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} = 0 \quad (2) $$

This equation is subject to different initial and boundary conditions, depending if the time-lag method or the sorption method holds, as follows:

- **Sorption method:**
  $$ t = 0, \quad \forall x, \quad C = C_0 \quad (3a) $$
  $$ t \geq 0, \quad x = 0, \quad \frac{\partial C}{\partial x} = 0 \quad (3b) $$
  $$ t \geq 0, \quad x = \frac{l}{2}, \quad C = S P^F \quad (3c) $$

  where $l$ is the thickness of the membrane, $C_0$ the initial concentration of the permeating species inside the membrane, $S$ the sorption equilibrium coefficient between the gas phase and the membrane (Henry’s law), usually called sorption coefficient, and $P^F$ is the pressure at the feed side. In the sorption method, the membrane is submitted to a concentration perturbation at both faces. Assuming that the membrane is homogeneous, the mass transport through it is symmetric. The spatial coordinate should then be defined as $x=0$ at the membrane centre and $x=l/2$ at either surfaces in order to simplify the solution of the mass balance.

- **Time-lag method:**
  $$ t = 0, \quad \forall x, \quad C = 0 \quad (4a) $$
  $$ t \geq 0, \quad x = 0, \quad C = S P^F \quad (4b) $$
  $$ t \geq 0, \quad x = l, \quad \frac{D}{\eta} \frac{\partial C}{\partial x} + l \frac{\partial C}{\partial t} = 0 \quad (4c) $$

and $\eta$ is defined as the capacitance parameter [15]:

$$ \eta = \frac{SAI R T}{V^P} \quad (5) $$

where $A$ is the membrane effective area, $R$ the gas constant, $T$ the absolute temperature and $V^P$ is the permeate volume, which comprises the volume of the permeate chamber of the membrane module plus the permeate tank—Fig. 1. In the time-lag method, the concentration perturbation is only performed at the feed membrane surface. In this case the origin of the spatial coordinate should be defined at the feed surface and $x=l$ at the feed membrane surface.
permeate surface of the membrane. Eq. (4c) takes into account the pressure build up inside the permeate volume.

The time-lag model (Eqs. (2) and (4a)–(4c)) was solved using a fast Fourier transform algorithm [15]. The transient response enables to easily compute a characteristic time from the experimental data, the time-lag parameter, \( \eta \). This parameter can be obtained graphically from the interception of the abscissa coordinate placed at the initial permeate pressure with the linear extrapolation of the permeate pressure history at pseudo steady-state [16]. The time-lag parameter relates with the effective diffusion coefficient:

\[
\eta = \frac{L^2}{6D} 
\]

Both \( \eta \) and \( \eta \) were obtained by fitting the model to the experimental permeation data using the least squares method [15].

3.2. Pd/PDMS membrane

For modelling the mass transport through the PDMS composite membrane, three situations can be considered: (i) the nanoclusters act like inert particles for the permeating species; (ii) adsorption occurs at the surface of the palladium nanoclusters and (iii) the sorption occurs in all the palladium nanoclusters volume, such as when hydrogen is the permeating species [17].

For a non-sorbing gas species, like argon, palladium nanoclusters will just augment the diffusion pathway of this molecule through the polymeric phase [16]. The diffusion equation taking into account the change in the diffusion pathway is

\[
J = \frac{D}{\tau} \frac{\partial C}{\partial x} = -D' \frac{\partial C}{\partial x} 
\]

where \( \tau \) is a tortuosity factor that takes into account the influence of the solid barrier created by the nanoclusters into the diffusivity and \( D' = D/\tau \). The mass balance equation becomes then:

\[
\frac{\partial C}{\partial t} + \frac{D'}{\tau} \frac{\partial^2 C}{\partial x^2} = 0 
\]

The boundary and initial conditions represented by Eqs. (3a)–(3c) and (4a)–(4c) are still valid, but the boundary condition Eq. (4c) becomes

\[
(1 - \phi) \frac{D}{\tau} \frac{\partial C}{\partial x} |_{x=\ell} + \frac{I}{\eta} \frac{\partial C}{\partial t} = 0 
\]

as the flux inside the permeate chamber occurs only through the polymeric phase. In this equation \( \phi \) is the volume fraction of catalyst.

If Eq. (9) is divided by \( (1 - \phi) \), the capacitance parameter becomes:

\[
\eta' = \frac{SA(1 - \phi)RT}{V^P} = \frac{S'AIRT}{V^P} 
\]

where \( S' = S(1 - \phi) \) and the time-lag equation for this case is

\[
\eta' = \frac{L^2}{6D} 
\]

For a species that adsorbs at the palladium’s surface, the mass balance has to take into account the uptake at the nanoclusters surface. The mass balance of a species that adsorbs on palladium’s surface following a generic adsorption equilibrium isotherm is [16]:

\[
(1 - \phi) \frac{\partial C}{\partial t} + \frac{\partial C'}{\partial t} = (1 - \phi) \frac{D}{\tau} \frac{\partial^2 C}{\partial x^2} = 0 
\]

where \( f(C) = d(f(C)/dC \) and \( f(C) \) is the adsorption equilibrium isotherm at palladium’s surface. If the adsorption equilibrium isotherm of the permeating species at the palladium’s surface is linear, \( \mu = kC \), Eq. (12) becomes:

\[
\frac{\partial C}{\partial t} - \frac{D}{\tau} \frac{\partial^2 C}{\partial x^2} = 0 
\]

where \( \mu \) is the adsorbed concentration of the permeating species at the palladium’s surface. It is assumed that the permeating species is in equilibrium at the polymer/metal interface. With this assumption, Eq. (13) reduces to a similar form of Eq. (2):

\[
\frac{\partial C}{\partial t} - \frac{D}{\tau} \frac{\partial^2 C}{\partial x^2} = 0 
\]

The capacitance parameter is given by Eq. (10), as the boundary condition given by Eq. (9) still holds for a gas adsorbing in the nanoclusters.

When hydrogen diffuses through a Pd/PDMS membrane, after adsorbing at palladium’s surface it diffuses into the nanoparticles volume. In this way, the palladium nanoclusters act as a sink for hydrogen.

The mass balance equations for this system are [16]:

\[
(1 - \phi) \frac{\partial C}{\partial t} + \frac{\partial C'}{\partial t} = (1 - \phi) \frac{D}{\tau} \frac{\partial^2 C}{\partial x^2} = 0 
\]

\[
\frac{\partial C}{\partial t} - \frac{D}{\tau} \frac{\partial^2 C}{\partial x^2} = 0 
\]

\[
\frac{\partial C}{\partial t} = \frac{3}{R^\mu} \int_0^{R^\mu} r^2 C_{\mu} dr 
\]

where \( C_{\mu} \) refers to the hydrogen concentration in the palladium nanoparticles, \( R^\mu \) the cluster radius and \( D^\mu \) is the hydrogen diffusion coefficient inside the cluster, which is assumed to be constant. These equations are subject to the initial and boundary conditions given by Eqs. (3a)–(3c) or (4a), (4b) and (9), together with \( \partial C_{\mu}/\partial r = 0 \) for \( r = 0 \), \( C_{\mu} = f(C) \) for \( r = R^\mu \) and \( C_{\mu} = 0 \) for \( t = 0 \), where \( f \) is the sorption equilibrium isotherm.
4. Results and discussion

4.1. PDMS membrane

The diffusion coefficients determined by the time-lag method are shown in Fig. 2. The values for the diffusion coefficient of hydrogen, argon, propane, propylene and propyne were obtained using Eqs. (2), (4a)–(4c) and (6), at different feed pressures and at 308 K, for a 278.7 µm thick PDMS membrane. The membrane module was initially evacuated at a pressure not higher than 0.1 mbar. Fig. 2 shows that the diffusivity of all gases in the PDMS membrane is essentially independent of the feed pressure. This is expectable for permanent gases, which exhibit a linear sorption isotherm in PDMS and for organic vapours at low concentrations, where the linear sorption equilibrium also holds [18].

Fig. 3 plots the sorption coefficients obtained by the time-lag method for different feed pressures. Sorption coefficients of argon, propane, propylene and propyne in PDMS at 308 K were obtained according to Eqs. (2), (4a)–(4c) and (5). Fig. 3 shows that the sorption coefficients are also essentially constant for all gases. Thus, a linear sorption isotherm in PDMS is expected for these sorbates at 308 K and up to the highest pressures studied.

For confirming the time-lag results, uptake experiments for some of the gases considered above were performed. Fig. 4 shows the sorption equilibrium data at 308 K for propane, propylene and propyne in PDMS. These sorption equilibrium isotherms are linear in the range of pressures studied. Solid lines were drawn from the average linear sorption coefficients obtained using the time-lag method. The adsorption isotherm of argon was also included in Fig. 4. This figure indicates that propane, propylene and propyne adsorb far more in PDMS than argon. Sorption coefficients from both methods agree very well for the gases studied.

Table 1 presents the diffusion, sorption and permeability coefficient values obtained experimentally using the time-lag method for the unfilled PDMS membrane, and the corresponding values found in literature. Although experimental conditions are, in some cases, slightly different, it is usually seen a reasonable agreement between our results and the ones found in literature.

Of practical interest to separation processes applications are the permeability coefficients, which are related to the mass transfer at steady-state conditions. Permeability coefficients for species $j$, $L_j$, are obtained from the relation:

$$L_j = D_j S_j$$  \hspace{1cm} (19)

Eq. (19) results from integrating the Fick’s law (Eq. (1)) from 0 to $l$ (membrane thickness) assuming steady-state:

$$J_s = -\frac{D}{l} \frac{\Delta C_s}{l}$$  \hspace{1cm} (20)

where $\Delta C$ is the concentration difference between the sorbed species at the two membrane surfaces. When the relation between the gas pressure and the sorbed concentration at the interface is described by a linear sorption equilibrium isotherm, Eq. (20) becomes:

$$J_s = -\frac{L}{l} \frac{\Delta P}{l}$$  \hspace{1cm} (21)

where $L$ is the permeability of the membrane given by Eq. (19) [7].
Table 1
Experimental sorption, diffusion and permeability coefficients for different gases in PDMS, obtained through the time-lag method at 308 K, and comparison with literature values

<table>
<thead>
<tr>
<th>Component</th>
<th>Experimental values$^a$</th>
<th>Literature values$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S$ (mol m$^{-3}$ bar$^{-1}$)</td>
<td>$D$ ($\times 10^{10}$ m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>H$_2$</td>
<td>3.4 ± 0.6</td>
<td>74 ± 8</td>
</tr>
<tr>
<td>C$_3$H$_4$</td>
<td>400 ± 21</td>
<td>7.7 ± 0.3</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>280 ± 10</td>
<td>6.3 ± 0.2</td>
</tr>
<tr>
<td>Ar</td>
<td>14.1 ± 0.9</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

$^a$ At 308 K, vacuum pressure in the permeate chamber and 1 bar difference across the membrane. The errors were obtained for a 95% confidence level ($t$-distribution).

$^b$ Literature references are given between square brackets.

$^c$ Computed from results at 323 K for a pressure difference of 2 bar and vacuum condition in the permeate stream.

$^d$ Value at 313 K, for a pressure difference of 2 bar across the membrane and atmospheric pressure in the permeate side.

$^e$ Value at 303 K.

$^f$ Value at 293 K.

$^g$ Obtained from a model, in our conditions.

Fig. 5 shows the permeability coefficients, obtained using Eq. (19), and considering the time-lag method for all the gases/vapours studied, in PDMS and at 308 K. It is clear that the most permeable species is propyne and the less permeable are argon and hydrogen.

Direct comparison of the sorption and diffusion coefficients for propylene in PDMS with the literature ones was not possible. However, a qualitative comparison can be performed. It should be assumed that the heat of sorption and the diffusion activation energy of propane and propylene in PDMS are similar, which is very reasonable owing to their very similar condensabilities and molecular sizes. Tanaka et al. [22] reported sorption and diffusion selectivities of propylene and propane at 323 K in PDMS. They reported a diffusion selectivity for propylene:propane of 1.3 and a sorption selectivity for propylene:propane of 0.9. Comparing with our experimental results, a diffusion selectivity of 1.29 and a sorption selectivity of 0.93 were obtained, that are in agreement with the literature values.

Permeation data for propyne in PDMS were not found in the open literature. Based on condensability parameters, it is expected that the sorption coefficient for propyne is higher than the corresponding one for propane or propylene. Propyne has a smaller molecular diameter than propylene and propane, indicating a higher diffusivity in PDMS. One can thus expect higher values of permeability coefficients due to the higher sorption and diffusion coefficients when compared either with propylene or propane. Indeed, a value of ca. 9100 barrer was obtained, indicating a permeation selectivity of 2.1 compared with propane and 1.7 compared with propylene (Fig. 5 and Table 1).

4.2. Pd/PDMS membrane

Up to now all the mass transport parameters obtained were for unfilled PDMS membranes. These parameters are used as a comparison basis for the study of the mass transport parameters through PDMS membranes filled with palladium nanoclusters.

Time-lag and uptake experiments were performed with a PDMS membrane filled with 5 wt.% palladium nanoclusters. The first gas considered with this membrane was argon. A comparison between the diffusion coefficient of argon in PDMS and the diffusion coefficient in PDMS filled with palladium nanoclusters allows for computing the tortuosity factor. Fig. 6 shows the $D/D'$ ratio for the different feed pressures applied. We can see that these ratios are approximately constant (within the experimental error) and equal to 1.5. This means that...
Fig. 7. Adsorption equilibrium isotherms of the different gases in surfactant-stabilized palladium nanoclusters at 308 K (♦, propane; ■, propylene; ▲, propyne), and fitting with data shown in Table 2.

Fig. 6 also shows the plot of $S/S'$. The sorption ratio is approximately equal to 1. This was expectable because the volume fraction of palladium in the membrane is very small ($\phi = 0.004$). One can thus conclude that the mass transport of a non-adsorbing gas species in the composite membrane can be characterized by the sorption and diffusion coefficients of the same species obtained for an unfilled membrane, the tortuosity factor and the filler content in the membrane.

Propane adsorbs on palladium nanoclusters, over the pressure range studied and at 308 K, with a nearly linear isotherm. Fig. 7 shows the adsorption equilibrium isotherm on palladium nanoclusters stabilized using the surfactant tetracatdecylammonium bromide, $n$-(C$_{18}$H$_{37}$)$_4$N$^+$Br$^-$, where the amount sorbed on the surfactant shell showed to be negligible. This way, the adsorption equilibrium isotherms determined for the stabilized palladium clusters relates only with the adsorption equilibrium on the palladium clusters. Complete characterization and preparation of these surfactant-stabilized nanostructured palladium clusters are reported elsewhere, [4] and [27], respectively. The adsorption constants obtained for propane on palladium nanoclusters are shown in Table 2. The corresponding constants referred to the propane concentration in the polymeric phase are also included, which are easily computed using the sorption coefficient for each species presented in Table 1.

Fig. 8 shows $D/D_{\text{mod}}$ and $\eta/\eta'$ values for propane. The $D/D_{\text{mod}}$ ratio is ca. 1.5, which should be mainly due to the tortuosity factor. The ratio $\eta/\eta'$ for propane is the same as for argon and then equal to 1, within the experimental uncertainty.

The uptake experiments performed with the Pd/PDMS composite membrane and propane allowed drawing the complementary of the dimensionless mass fraction uptake (1 − $F$) plot [16], as shown in Fig. 9. The mass balance, Eq. (13), subject to the boundary conditions, Eqs. (3a)–(3c), and using the diffusivity coefficient obtained for propane in the unfilled PDMS, the tortuosity factor and the palladium Henry’s constant, $K$, fits very well the experimental mass fraction uptake obtained from the gravimetric experiments. One can conclude that the diffusivity coefficient determined by the time-lag method for propane fits with the value obtained from the gravimetric uptake experiments.

For propyne and propylene, the same procedure was followed, regarding time-lag and uptake experiments. First, adsorption equilibrium isotherms for both gases were determined using stabilized palladium clusters in a surfactant. The corresponding plots are shown in Fig. 7. Both gases present a Langmuir-type adsorption isotherm at 308 K for the concentration range considered. It is clear that propylene and propyne adsorb more in palladium than propane, indicating that some adsorption selectivity of palladium for species with multiple bonds occurs. It is still observed an about 10-times propyne over propylene adsorption capacity. The Langmuir adsorption equilibrium isotherm parameters for propylene and propyne in palladium nanoclusters are given in Table 2, which provided the fittings shown in Fig. 7.

For the time-lag experiments with propylene and propyne, Eq. (12) was solved numerically with the initial and bound-
ary conditions given by Eqs. (4a), (4b) and (9). Fig. 10 shows the dimensionless pressure build up at the permeate chamber for time-lag experiments with propylene and propyne in the Pd/PDMS composite membrane during the pseudo steady-state conditions. It should be emphasized that there are no fitting parameters in Eq. (12); all parameters were previously determined in independent experiments. Fig. 10 shows that the model fits very well the time-lag results for the pseudo steady-state conditions. The mass transport at the pseudo steady-state depends only on the sorption and diffusion coefficients of the species on the polymer. For a steady-state experiment, only these parameters, together with the tortuosity factor and the filler content, are relevant. Cussler and co-workers drawn the same general conclusions as us, the added fillers do not affect the steady-state transport across the film, but they do increase the time before permeability begins [28].

Considering the gravimetric experiments, Fig. 9 shows the complementary of the dimensionless mass uptake history (1 − F) for propylene and propyne in the PDMS membrane filled with palladium nanoclusters, together with the model line obtained using Eq. (12) and subject to the initial and boundary conditions, Eqs. (3a)–(3c) [16]. Again, the model fits well the transient behaviour of the sorption experiments for propylene and propyne.

Finally, the hydrogen sorption and diffusion coefficients in the Pd/PDMS composite membrane are discussed below.

The transient mass transport of hydrogen diffusing through a Pd/PDMS composite membrane is influenced by the large hydrogen uptake in the palladium nanoclusters [29]. After sorbing at palladium’s surface, the hydrogen atoms diffuse to the interior of the clusters, which act as a sink for hydrogen.

Fig. 11 shows the adsorption equilibrium isotherm of hydrogen on palladium nanoclusters inside the PDMS membrane and on nanoclusters stabilized in the above-mentioned surfactant, the last one showing a lower sorption capacity. A cluster diameter of 7.3 nm was obtained for the surfactant-stabilized ones [4], while in the membrane the size of the clusters was estimated to be 8.8 nm (by XRD). According to Sachs et al. [29], the difference between the adsorption on both palladium nanoparticles is related to the size of the clusters, independently of the stabilization agent used. These issues were corroborated by other authors. Actually, chemisorption studies have indicated that H2 adsorption should be similar on surfactant-stabilized palladium clusters and on a commercial palladium catalyst with the same particle size [30]. Regarding the particle size influence, the effect noticed by us was also observed in particles sizes of 4 and 5 nm, and an even higher difference in the sorption capacity was observed if compared with bulk palladium [31].

The sorption isotherm of hydrogen in palladium can be divided into three parts: the α-phase, at low hydrogen pressures, an intermediate phase, where α and β coexist, and the β phase, where palladium hydride is present [17]. The transition from the α phase towards the α/β phase starts nearly at 20 mbar and ends at around 30 mbar, at 308 K. Uptake experiments at these pressures showed to be necessary to wait about $2 \times 10^3$ s to reach the equilibrium, when using surfactant-stabilized clusters, while the waiting time for PDMS-stabilized clusters was higher (ca. 6–7 $\times 10^3$ s) due to the PDMS mass transfer resistance. At lower

![Fig. 10. Dimensionless permeate pressure build up in the permeate chamber obtained by the time-lag method for the 5 wt. % Pd/PDMS membrane, at pseudo steady-state (○, propylene, $P_F = 50$ mbar; △, propyne, $P_F = 25$ mbar). The solid line corresponds to the model fitting.](image)

![Fig. 11. Sorption equilibrium isotherms for hydrogen in palladium nanoclusters at 308 K (○, 5 wt. % Pd/PDMS membrane; ●, surfactant-stabilized palladium clusters).](image)
pressures the equilibrium was reached almost instantaneously, thus indicating a concentration-dependent diffusion coefficient.

The sorption equilibrium isotherm of hydrogen in palladium is related with different kinds of interactions between hydrogen and palladium and hydrogen–hydrogen [17] and a fitting function to the experimental data is not straightforward. A concentration-dependent diffusion coefficient during the uptake for the different parts of the sorption isotherm has been reported for nanocrystalline palladium [32], what makes the hydrogen sorption pattern in palladium more difficult to be modelled.

To simplify, only the adsorption equilibrium in the α-phase was studied using the time-lag method. A nearly constant hydrogen diffusion coefficient for the α-phase of the H/Pd system was reported by Mutschele and Kircheim [32], at 293 K and in the range of our experimental conditions. This diffusion coefficient, with a value of ca. $1.5 \times 10^{-10} \text{m}^2 \text{s}^{-1}$, was used in our simulations. A relationship between the diffusion time constant in the polymer phase and inside the clusters was adapted from dual-mode diffusion in zeolites [16]. A comparison between the two time constants indicates that the one in the polymeric phase (with a value of ca. 10 s) is several orders of magnitude higher than the time scale for diffusion inside the clusters (in the range of $10^{-7}$ s), owing to the very small size of the clusters. This means that the diffusion is controlled by the polymer phase and that the adsorption inside palladium is comparably fast. In this way, Eqs. (16)–(18), which describe the mass transport of hydrogen inside a slab membrane, reduce to Eq. (12).

Despite the diffusion inside palladium being fast, the flux inside the cluster does not contribute to the overall flux because the desorption step from palladium surface is very limited at 308 K [33], and palladium nanoclusters act like a sink.

A simple linear sorption isotherm was used to describe the hydrogen sorption in palladium, $C_P = KC$. The parameter obtained for the hydrogen sorption in the α-phase of palladium is shown in Table 2. For linear adsorption isotherms, as for hydrogen in α-phase-palladium, Eq. (12) can reduce to Eq. (13). Fig. 12 shows the relative pressure history obtained from a time-lag experiment for hydrogen considering only α-phase palladium, and just for comparison it is included a time-lag experiment performed with hydrogen permeating the unfilled PDMS membrane. It is apparent the hydrogen high adsorption capacity in palladium nanoclusters. Eq. (13) was solved numerically subjected to boundary conditions Eqs. (4a), (4b) and (9). It can be seen that the model describes quite well the mass transport through the palladium-filled PDMS membrane.

Again, the steady-state mass transport through the membrane does not depend on the hydrogen adsorption isotherm in the palladium clusters.

5. Conclusions

Time-lag method and gravimetric experiments were employed to determine the mass transport parameters of argon, hydrogen, propane, propylene and propyne in PDMS at 308 K. The sorption–diffusion model was used to fit the experimental results. The parameters obtained from independent time-lag and gravimetric experiments agree. All the experiments were successfully modelled and the pertinent parameters determined independently. The results were compared with reported ones, whenever possible.

It was also concluded that:

- The mass transport of gas species in PDMS membrane filled with palladium nanoclusters differs from that in the unfilled PDMS membrane mainly for the transient part of the time-lag experiment. The presence of solid clusters in the membrane work as wells that may retain significant amounts of the penetrant species and increase the pathway for diffusion, making then the pseudo steady-state of permeation to be delayed.
- The sorption in the palladium nanoclusters leads to the increase of the time-lag, in time-lag experiments.
- At the pseudo steady-state conditions, the relevant parameters for the mass transport are sorption and diffusion coefficients in the polymeric phase, the filler content and the tortuosity factor.

Acknowledgements

Authors would like to acknowledge Eng. Pedro Taveira for his kindly help with the time-lag experimental set-up. Lúcia Brandão is grateful to the Portuguese Foundation for Science and Technology (FCT) for her PhD grant (reference SFRH/BD/3383/2000). Financial support by FCT through the project POCTI/32452/EQU/2000 is also acknowledged.

### Nomenclature

- $a$: Langmuir isotherm parameter ($\text{mol} \text{m}^{-3} \text{Pd} \text{mol}^{-1} \text{PDMS}$)
- $A$: membrane area (m$^2$)
- $b$: Langmuir isotherm parameter ($\text{mol}^{-1} \text{m}^3 \text{PDMS}$)
- $C$: sorbed concentration in the polymer phase ($\text{mol} \text{m}^{-3} \text{PDMS}$)
References


