Propylene Hydrogenation in a Continuous Polymeric Catalytic Membrane Reactor

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A continuous polymeric catalytic membrane reactor (pCMR), using a poly-(dimethylsiloxane) (PDMS) composite membrane that contained palladium nanoclusters, was studied and modeled for the propylene hydrogenation. The PDMS catalytic membrane has an average thickness of 4.4 μm, and was loaded with 5 wt % of nanosized palladium clusters ~9 nm in diameter. The reaction was performed at 308 K, and several feed compositions and flow rates were tested. The pCMR model proposed represents the experimental data (i.e., the flow rates and mixture compositions in the permeate and retentate chambers, and, therefore, the overall advancement) fairly well. In the hydrogenation rate equation, the propylene adsorption parameter and the kinetic constant were obtained by fitting the model to the experimental data. On the other hand, the hydrogen kinetic parameter and the mass-transport parameters were obtained from independent experiments.

1. Introduction

Catalytic membrane reactors are being used to conduct high-temperature reactions (400–1173 K). Therefore, it is not surprising that organic polymers are hardly ever used as materials for catalytic membranes (except for bioreactors that use enzymes as a catalyst), because they lack thermal stability under these harsh conditions. However, under milder conditions, such as those at which hydrogenations occur, organic polymers are applied successfully.† On the other hand, some of the main challenges for inorganic, porous membranes in membrane reactors are the control of the thickness, the large-scale preparation, and the crack-free synthesis; however, all these factors are much less problematic with polymer-based catalytic membranes.

Among other reactions in which polymeric catalytic membranes might be advantageous, it is worth noting the selective hydrogenation of propadiene and propyne impurities in propylene streams, which is an important reaction in the petrochemical industry. As a monomer for the production of polypropylene, propylene should contain <10 ppm of propadiene and <5 ppm of propyne.‡ In this purification process, the overhydrogenation of propylene to propane should be avoided. Usually, the hydrogenation process is accomplished in a fixed-bed catalytic reactor.³ However, the use of polymeric membrane reactors is also possible.

For this and other gas-phase hydrogenations, catalytically active membranes based on poly-(dimethylsiloxane) (PDMS) have been developed and used. This highly permeable elastomer is prepared easily and combines a fairly high thermal (up to 250 °C) and mechanical stability with chemical resistance, the latter being of the utmost importance under reactive conditions.⁴ Moreover, a polymer with high diffusivity is strongly recom-

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Figure 1. Schematic diagram of the polymeric catalytic membrane reactor (pCMR).
as follows: (1) steady-state operation; (2) negligible pressure drop in the retentate and permeate chambers; (3) ideal gas behavior; (4) Fickian transport across the membrane; (5) sorption equilibrium between the bulk gas phase and the membrane surface, as described by the Henry’s law; (6) no concentration polarization; (7) constant diffusion coefficients; (8) isothermal operation; (9) perfectly mixed flow pattern in both chambers; and (10) the reaction occurs only on the surface of catalyst nanoparticles, which are distributed uniformly across the membrane.

Mass Balance in the Membrane and Boundary Conditions:

\[\begin{align*}
(1 - \phi) \frac{D_i}{\tau} \frac{dC_i}{dx} + \phi \rho_{\text{f}} v_F &= 0 \quad \text{(for } i = \text{H}_2, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8) \quad (1) \\
\phi &= 0, \quad C_i = H_2 \gamma^R P^R \quad \text{(for } i = \text{H}_2, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8) \quad (2) \\
\phi &= \delta, \quad C_i = H_2 \gamma^P P^P \quad \text{(for } i = \text{H}_2, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8) \quad (3)
\end{align*}\]

Partial and Total Mass Balances in the Retentate Chamber:

\[\begin{align*}
P_f^F - P_R^F + (1 - \phi) A \frac{D_i}{\tau} \frac{dC_i}{dx} |_{x=0} &= 0 \quad \text{(for } i = \text{H}_2, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8) \quad (4)
\end{align*}\]

Partial and Total Mass Balances in the Permeate Chamber:

\[\begin{align*}
P_f^P + (1 - \phi) A \frac{D_i}{\tau} \frac{dC_i}{dx} |_{x=0} &= 0 \quad \text{(for } i = \text{H}_2, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8) \quad (5)
\end{align*}\]

\[\begin{align*}
P_f^P + (1 - \phi) A \sum_i \frac{D_i}{\tau} \frac{dC_i}{dx} |_{x=0} &= 0 \quad \text{(for } i = \text{H}_2, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8) \quad (7)
\end{align*}\]

The subscript \(i\) refers to the \(i\)th component and the superscripts \(F, R,\) and \(P\) refer to the feed, retentate, and permeate conditions, respectively; \(x\) refers to the spatial coordinate of the membrane, with thickness \(\delta\), whereas \(v_i\) is the stoichiometric coefficient of species \(i\). \(P\) is the total pressure, \(D\) is the diffusion coefficient, \(H\) is the Henry’s constant, \(F\) is the total molar flow rate and \(y\) is the molar fraction. \(\phi\) is the volume fraction of catalyst (0.004), which was obtained from the mass fraction (5 wt %) and density of the clusters \(\rho_{\text{pd}} = 12 \text{ g/cm}^3\) and from the density of the polymer \(\rho_{\text{PDMS}} = 1 \text{ g/cm}^3\). The remaining symbols have the usual meaning and are described in the nomenclature section.

To facilitate convergence, and using an approach similar to that described by Sousa et al., the set of equations in dimensionless form was solved by adding a time derivative term to the right-hand side of eqs 1, 4, and 6, while eqs 5 and 7 were solved explicitly for the molar flow rate. Equation 1 was further transformed to a set of ordinary differential equations (ODEs) using finite differences and the resulting time-dependent equations were solved using LSODA. The steady-state solution was obtained when a step time increase did not make any further change in the dependent variables, within a pre-defined error.

2. Experimental Section

2.1. Chemicals. Palladium acetate (Chempur) was used as a catalyst precursor. All solvents were analytical grade and purchased from Merck. The cross-linkable PDMS Dehesive 942 (from Wacker) was used to prepare the noble-metal-containing polymer films. Porous poly-(acrylonitrile) (PAN) membranes (GKSS Research Centre) with a nonwoven backing (pore size of ~14 nm; N\(_2\) flux of 200 m\(^3\)/m\(^2\) N m\(^{-1}\) h\(^{-1}\) bar\(^{-1}\)) were used as thin-film supports.

2.2. Membrane Preparation and Characterization. The PDMS solution was obtained by dissolving Dehesive in tetrahydrofuran (THF) to form a 10 wt % solution. The required amount of crosslinker (1% of polymer) and catalyst was then added. A ca. 10 wt % solution of palladium(II) acetate in THF was finally added to the previous solution to form a final concentration of 10 wt % palladium(II) acetate in PDMS. After mixing, this solution was supplied to a coating machine and the composite membrane prepared on the porous PAN support via dip-coating. Subsequent crosslinking of the obtained membrane was performed by contacting it with a stream of hot air at 100 °C. The palladium was then reduced using a solution of 1% NaBH\(_4\) in ethanol/water (1/1 volume), and an isotropical distribution of the catalyst throughout the polymer matrix was obtained. A metal content of 5 wt % was calculated, corresponding to a volume fraction loading (\(\phi\)) of ca. 0.004. The quality of the films was finally checked by gas-selectivity measurement. A selectivity of \(\alpha (\text{O}_2/\text{N}_2) > 2.1\) indicates that the membrane is defect-free.

The thickness of the thin catalytic Pd/PDMS membrane was obtained via scanning electron microscopy (SEM). Figure 2 shows a micrograph of the supported catalytic PDMS membrane, in which the thickness of the catalytically active layer is not constant; therefore, an averaged thickness of 4.4 ± 0.5 μm was computed from several micrographs. Because it was not possible to obtain a direct read of the palladium clusters via X-ray diffraction (XRD) using the thin membranes, a 300-μm nonsupported membrane was prepared using exactly the same procedure and the average size of the corresponding palladium clusters obtained via XRD. The value obtained, 8.8 nm in diameter, was considered to be equal to the average size of the palladium clusters in the thin catalytic PDMS membrane and is consistent with the literature.
membrane was also used to compute the tortuosity factor ($\tau = 1.70 \pm 0.05$) from permeability experiments, using argon and propane as probing gases.

2.3. Membrane Reactor. A scheme of the pCMR experimental setup is shown in Figure 3A. The feed gas system considers three mass flow controllers (Bronkhorst Hi-Tec, model F201, with flow rates of 0–1, 0–0.1, and 0–0.3 L/min, ±1% FS) connected, respectively, to hydrogen, propylene, and propane gas cylinders. The gas mixture is promoted using an expanding-reduction fitting in the gas line. All gases were supplied by Praxair (purities: hydrogen, 99.999%; propylene, 99.5%; propane, 99.5%).

The membrane reactor has an effective area of 13.9 cm$^2$ (membrane diameter of 42 mm) and was placed inside a thermostatic oven. Figure 3B shows a sketch of the membrane cell used. The flow pattern in the retentate chamber is difficult to model, because of the geometry used. However, if high feed flow rates or not-too-permeable mixtures are used, the input concentration becomes very similar to the outlet concentration and the retentate flow pattern can hence be approximately described by the perfectly mixed model. In this work, high feed flow rates and hydrogen-rich feed compositions (hydrogen is the less-permeable component) were used.

A thermocouple (1/16 in. in diameter, type K) was inserted into the membrane reactor to read the temperature directly over the membrane surface, at the retentate side. Different feed gas streams at different flow rates (ranging from 216 ± 7 mL/min to 323 ± 14 mL/min) and different compositions ($H_2/C_3H_6$ ratios of 2–9) were used, at a pressure of 1.2 bar (Druck, ref. 4010, 7 bar, ±0.04% FS) and 308 K. The permeate pressure was set to 100 mbar (Druck, ref. 4010, 2 bar, ±0.04% FS) with the help of a diaphragm vacuum pump (Thomas, No. 7011-0069). All the experiments were repeated at least twice. Feed, permeate, and retentate streams were fed sequentially, in triplicate, to an on-line gas chromatograph (Dani GC 1000 with FID and TCD (Valco Inc.) in-series detectors), using an automatic injection valve (Valco, Inc.). The gas chromatograph has a 30-m capillary plot fused silica column (GS-GasPro, J&W) operated with argon as the carrier gas, which allowed the simultaneous quantification of hydrogen, propylene, and propane. A temperature program starting at 50 °C and ending at 110 °C, with a rate of 10 °C/min, was used.

3. Results and Discussion

3.1. Mass-Transport Characterization. Mass transfer in dense polymeric membranes is governed by the solution–diffusion model. Thus, the sorption and diffusion coefficients of hydrogen, propane, and propylene in PDMS at 308 K were determined using the time-lag method. The mass transport of gas species in the PDMS membrane filled with palladium nanoclusters differs from that in the unfilled PDMS membrane, mainly for the transient regime. Actually, solid clusters that are present in the membrane function as wells that may retain significant amounts of the penetrant species (particularly hydrogen) and increase the pathway for diffusion, making the steady state of permeation become delayed. Under steady-state
The propylene hydrogenation was determined previously in order to obtain the metal surface area of surfactant-stabilized palladium nanoclusters.13 The average Pd-clusters size was calculated based on XRD measurements, while a value of 27 m²/gpd was obtained by CO chemisorption. These results indicate that only ca. 40% of the metal sites are accessible to the CO molecules because the surfactant is blocking some sites, to stabilize the clusters.

Table 1 gives the sorption, diffusion, and permeability coefficients of hydrogen, propane, and propylene, determined at 308 K for a nonporous ca. 300-μm-thick PDMS membrane.

3.2. Determination of the Kinetic Equation. The kinetics of the propylene hydrogenation was determined previously in a batch reactor using palladium nanoclusters stabilized by a surfactant (n-(C₁₈H₃₇)₄N⁺Br⁻) shell that prevents cluster agglomeration and showed no mass-transfer resistance.12

\[
r_{C₃H₆} = \frac{kK_{H₂}^{i}K_{H₂}^{C₃H₆}C_{H₂}^{C₃H₆}}{(1 + K_{H₂}^{i}C_{H₂}^{i} + K_{H₂}^{C₃H₆}C_{H₂}^{C₃H₆})³} \tag{8}
\]

where \( r_{C₃H₆} \) is the rate constant, \( C_{i} \) the gas-phase concentration of species \( i \), and \( K_{i} \) its adsorption equilibrium constant on the catalyst surface. The parameters of eq 8 are given in Table 2.

Table 2. Kinetic Parameters of Propylene Hydrogenation over Palladium Nanoclusters Stabilized on Different Matrices (T = 308 K)

<table>
<thead>
<tr>
<th>parameter</th>
<th>surfactant</th>
<th>PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k (\text{mol g}_{pd}^{-1} \text{s}^{-1}) )</td>
<td>5.659</td>
<td>18.3</td>
</tr>
<tr>
<td>( K_{H₂}^{i} (\text{m}³ \text{mol}^{-1}) )</td>
<td>2.55 × 10⁻²</td>
<td>1.31 × 10⁻¹</td>
</tr>
<tr>
<td>( K_{H₂}^{C₃H₆} (\text{m}³ \text{mol}^{-1}) )</td>
<td>9.7 × 10⁻⁴</td>
<td>9.7 × 10⁻⁴</td>
</tr>
<tr>
<td>average Pd-clusters size (nm)</td>
<td>7.3</td>
<td>8.8</td>
</tr>
</tbody>
</table>

where \( k \) is the rate constant, \( C_{i} \) the gas-phase concentration of species \( i \), and \( K_{i} \) its adsorption equilibrium constant on the catalyst surface. The parameters of eq 8 are given in Table 2.

Different kinetic parameters may be observed when the catalyst is deposited on different supports.13,14 Indeed, the aforementioned kinetic parameters, determined over palladium nanoclusters stabilized with a surfactant, did not accurately describe the propylene hydrogenation experiments in the pCMR, where the palladium nanoclusters are dispersed inside the PDMS membrane. Different factors may account for this discrepancy. First, it has been reported that the active surface area of palladium nanoclusters stabilized with a surfactant and determined by CO chemisorption is much smaller than the active metal surface.15,16 In the present case, the palladium nanoclusters were stabilized using an octadecyl chain surfactant called tetraoctadecylammonium bromide.12 This surfactant has a large alkyl chain that should interfere strongly with the adsorption of reactant species, especially the larger species such as propylene. It was also reported that, in the case of surfactant-stabilized catalysts, the hydrogenation activity was still relatively high, despite the smaller active metal surface, because hydrogen penetrates through the protecting shell, because of its very small size.16

XRD measurements and CO chemisorption were then used to obtain the metal surface area of surfactant-stabilized palladium clusters.12 A surface area of 68 m²/gpd (assuming spherical palladium nanoparticles) was calculated based on XRD measurements, while a value of 27 m²/gpd was obtained by CO chemisorption. These results indicate that only ca. 40% of the metal sites are accessible to the CO molecules because the surfactant is blocking some sites, to stabilize the clusters.

Because of the issues mentioned, the Langmuir–Hinshelwood (L–H) parameters of the propylene hydrogenation kinetics, catalyzed by palladium nanoclusters stabilized with a surfactant, should be comparatively different from those of palladium nanoclusters supported in a PDMS membrane, except for the hydrogen adsorption constant (\( K_{H₂} \)). The reaction mechanism is assumed to be the same in both cases. This way, runs using the palladium-doped PDMS membrane were performed in an open reactor and the propylene adsorption constant (\( K_{C₃H₆} \)) and kinetic constant (\( k \)) obtained. These parameters were obtained by fitting the developed pCMR model and the kinetic rate equation (eq 8) to the experimental values by minimizing the sum of the square residues. A surface response analysis was applied to perform the optimization, based on commercially available software (JMP).

The hydrogenation of propylene occurs inside the PDMS membrane. Assuming that the reaction mechanism proposed for the reactants in the gas phase12 is valid for the reactants in the membrane phase, the following relationship between the adsorption constants can be obtained:

\[
K_{i} = \frac{K_{i}^{g}}{H_{i}RT} \tag{9}
\]

where \( H_{i} \) is the Henry’s constant that relates the gas-phase concentration with the sorbed concentration of species \( i \) in the membrane.

The values of the kinetic parameters are reported in Table 2 for surfactant-stabilized palladium and PDMS-supported palladium, the later being obtained by the fitting process already described and using the experimental data shown below. A five-times increase on the propylene adsorption constant was obtained for the Pd/PDMS system, suggesting that some surface sites at the surfactant-stabilized palladium are hindered, which is compatible with the observed CO chemisorption data. It is also noticeable an increase in the kinetic constant \( k \) by a factor of about 3, indicating that the palladium nanoclusters are more active when incorporated into the PDMS membrane than when stabilized with the surfactant.

3.3. Hydrogenation Experiments in the pCMR. The performance of the polymeric catalytic membrane reactor (pCMR) was studied for the propylene hydrogenation at 308 K, and the results were compared with the proposed model. Figure 4 shows the experimental values of the permeate flow rate leaving the reactor as a function of the hydrogen/propylene molar ratio fed to the membrane reactor, and for the two feed flow rates tested. The membrane permeability toward propylene is higher than toward hydrogen (see Table 1). Consequently, as the feed molar fraction of propylene increases (decreasing \( \frac{f_{H₂}}{f_{C₃H₆}} \)), the permeated flow also increases. The model fits reasonably the permeate flow for the different feed hydrogen/
propylene ratios and predicts that trend. The nonuniform thickness of the membrane, as well as the uncertainty related to the transport parameters of the different gases in the membrane, should explain some differences between the model and the experimental results, despite the experimental values showing large error bars. These errors are mainly related with the equipment used to determine the mass flow rates. Indeed, the mass flow meters used to read the permeate flow rate (the hot-wire principal) show large uncertainties when the stream is a mixture of gases with very different correction factors.¹⁷ Flow rate relative errors in the range of ±15% are then expectable.

Figure 5 shows the hydrogen concentrations (molar fractions, in percentage values) at the retentate and permeate outlet streams for different feed hydrogen/propylene molar ratios, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (Δ) feed flow rate = 323 mL/s/min and (- - -) the respective model fitting; (O) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Figure 4. Permeate flow rate as a function of the feed hydrogen/propylene molar ratio, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (Δ) feed flow rate = 323 mL/s/min and (- - -) the respective model fitting; (O) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Figure 6. Propylene composition in the retentate and permeate chambers as a function of the feed hydrogen/propylene molar ratios, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (Δ, Δ) feed flow rate = 323 mL/s/min and (- - -) the respective model fitting and (●, ●) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Figure 5. Hydrogen composition in the retentate and permeate chambers as a function of the feed hydrogen/propylene molar ratios, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (●, ●) feed flow rate = 323 mL/s/min and (---) the respective model fitting; (○, ○) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Figure 6. Propylene composition in the retentate and permeate chambers as a function of the feed hydrogen/propylene molar ratios, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (●, ●) feed flow rate = 323 mL/s/min and (---) the respective model fitting; (○, ○) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Figure 7. Propane composition in the retentate and permeate chambers as a function of the feed hydrogen/propylene molar ratios, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (●, ●) feed flow rate = 323 mL/s/min and (---) the respective model fitting and (○, ○) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Figure 7. Propane composition in the retentate and permeate chambers as a function of the feed hydrogen/propylene molar ratios, obtained during the steady-state operation of the pCMR at 308 K. Symbol legend: (●, ●) feed flow rate = 323 mL/s/min and (---) the respective model fitting and (○, ○) feed flow rate = 216 mL/s/min and (- - -) the respective model fitting. Retentate pressure, 1.2 bar; permeate pressure, 0.1 bar.

Concentrations in the retentate stream are much higher than those on the permeate side, because of the low hydrogen permeability.

Figure 6 shows the propylene compositions (molar fractions, in percentage values) at the retentate and permeate chambers, as a function of the feed hydrogen/propylene molar ratios and for both feed flow rates. In this case, higher propylene concentrations are observed in the permeate chamber when compared with the retentate composition, because of the high PDMS permeability toward propylene (see Table 1). Figure 6 also shows the fitting of the model to the experimental data; a reasonable agreement can be observed again. One can also notice that, as the feed flow rate increases, the retentate composition approaches the feed composition. This leads to a slight increase of the permeate flow rate (Figure 4), which is essentially attributed to an increase of the permeated propylene, the most permeable species. Consequently, its concentration increases in both chambers (see Figure 6). This way, the assumption of completely mixed flow pattern at the retentate side is only approximately hold. Anyway, the proposed model is able to capture the composition and permeate flow rate trends observed for the tested feed flow rates.

Propane molar fractions in both chambers are presented in Figure 7. Experimental propane molar concentration in the permeate chamber reaches 40% at feed hydrogen/propylene
molar ratios of 5–6 and for the lowest feed flow rate. Higher concentrations of propane are expected when gas mixtures that ensure a high hydrogen/propylene molar ratio at the catalyst surface are fed to the reactor. However, to define the feed H₂/C₃H₆ molar ratio that originates the highest propane concentration in the permeate chamber is not straightforward. First, the maximum reaction rate is obtained for high hydrogen/propylene molar ratios, ca. 9, as can be deduced from the reaction kinetic equation. On the other hand, H₂ diffusivity in PDMS is much higher than that of C₃H₆ (see Table 1); therefore, shifting the maximum propane concentration toward smaller H₂/C₃H₆ molar ratios. This is consistent with the findings of Theis et al.18 where the reference pressure (PREF) is 1 bar and the reference flow rate (FREF) is the feed flow rate. The contact time also affects the permeate flow rate by 10%. The reactants permeabilities (Lᵢ) affect mainly the corresponding permeate composition and flow rate. The propane molar fraction at the permeate side (yₚ) is mainly affected by the kinetic constant (7%), as expected; however, it is also affected by the hydrogen adsorption constant at the catalyst surface (Kₐ) (6%). From this analysis, we may conclude that the permeabilities do not affect the advancement as much as they affect the permeate flow rate or composition. On the other hand, the retentate flow rate and its composition are essentially insensitive to these parameters (data not shown).

Simulations for different permeate and retentate pressures, while keeping constant the kinetic and transport parameters, the feed flow rate and the feed reagents ratio, were performed to gain insight into those operating variables. Figure 9 shows the influence of the permeate and retentate pressure, in terms of advancement (Figure 9A) and molar fraction of propane produced and present in the permeate stream–product recovery at the permeate side (see Figure 9B). The recovery is defined as follows:

$$\varphi_{C_3H_8}^P = \frac{F_{C_3H_8}^{P,r} + F_{C_3H_8}^{P,a}}{F_{C_3H_8}^{P,r} + F_{C_3H_8}^{P,a}}$$

Figure 9A shows that, when increasing the retentate pressure, the advancement increases, which is mainly attributed to the reaction rate increase, although the driving force for permeation is also a concern. The advancement also increases with the permeate pressure. Similarly, Theis et al.1 reported experimen-
Figure 9. Advancement of reaction (A) and product recovery (B), as a function of the retentate pressure for different permeate pressures. Feed flow rate = 323 mL$_N$ min$^{-1}$, $\gamma_{P}^F / \gamma_{C, H_6}^F = 5.67$.

Table 3. Relative Change of the Advancement, and the Flow Rate and Composition of the Permeate, Obtained by Changing Each Parameter by 10%.*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\Delta X$ (%)</th>
<th>$\Delta Q^P$ (mL$_N$/min)</th>
<th>$\Delta Y_{H_2}^P$ (%)</th>
<th>$\Delta Y_{C, H_6}^P$ (%)</th>
<th>$\Delta Y_{C, H_6}^P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>7</td>
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<td>-4</td>
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<td>-5</td>
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<tr>
<td>$K_{H_2}$ (m$^3$/mol)</td>
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<td>-3</td>
<td>6</td>
<td>-5</td>
</tr>
<tr>
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<td>10</td>
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<td>8</td>
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<td>-2</td>
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<td>$\Gamma$</td>
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<td>1</td>
<td>1</td>
<td>2</td>
<td>-4</td>
</tr>
</tbody>
</table>

*Reference conditions: feed flow rate = 323 mL$_N$/min, $\gamma_{P}^F / \gamma_{C, H_6}^F = 5.67$, retentate pressure = 1.2 bar and permeate pressure = 0.1 bar.

tally an increase in the catalytic performance with permeate pressure for propylene hydrogenation over PDMS membranes that contain palladium clusters at 303 K. Finally, Figure 9B shows that $q_{C, H_6}^P$ increases with the retentate pressure but decreases significantly with the permeate pressure. This happens because as the permeate pressure increases, the higher propane partial pressure on the permeate side promotes an increase in the propane molar flux to the retentate side of the membrane, negatively affecting its recovery.

4. Conclusions

The performance of a continuous polymeric catalytic membrane reactor (pCMR), which contained palladium nanoclusters in the polymeric matrix of a PDMS composite membrane, was studied for propylene hydrogenation at 308 K, both experimentally and theoretically.

The model developed for the pCMR includes the mass balances to the retentate and permeate chambers as well as the mass balance to the catalytic membrane, which comprises the transport and the propylene hydrogenation kinetics. The mass transport parameters were obtained from an independent study, by the time-lag method. The model predicts the experimental data (i.e., the flow rates and mixture compositions at both chambers) fairly well, with some kinetic parameters (propylene adsorption constant and kinetic constant) being obtained by fitting the model to experimental data, while the hydrogen kinetic parameter was obtained from independent experiments.

The pCMR performance was mainly studied as a function of the feed hydrogen/propylene ratio. It was observed that high concentrations of propane were obtained in the permeate chamber when the feed hydrogen/propylene molar ratio was in the range of 5–6. The proposed model allowed us to understand this behavior, which is mainly related to the reaction kinetics and to the diffusion selectivity. The model predicts also the reaction advancement for the various operating conditions considered quite well, showing that it is able to capture the main phenomena present in the studied pCMR.

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Nomenclature

$A =$ membrane area (m$^2$)
$C_i =$ concentration of component $i$ inside the membrane (mol/ m$^3$)
$C_i^g =$ concentration of component $i$ in the gas phase (mol/m$^3$)
$D_i =$ diffusion coefficient of component $i$ (m$^2$/s)
$F =$ molar flow rate (mol/s)
$H_i =$ Henry’s sorption coefficient of component $i$ (mol m$^{-3}$ bar$^{-1}$)
$k =$ kinetic constant (mol g$_{Pd}^{-1}$ s$^{-1}$)
$K_i =$ adsorption equilibrium constant of component $i$ in the catalyst surface based on membrane concentration (mol/mol)
$K_i^g =$ adsorption equilibrium constant of component $i$ in the catalyst surface based on gas phase concentration (mol/mol)
$L_i =$ permeability coefficient of component $i$ (mol m$^{-2}$ bar$^{-1}$ s$^{-1}$)
$p_i =$ partial pressure of component $i$ (bar)
$P =$ total pressure (bar)
$Q =$ volumetric flow rate (mL$_N$/min)
$r =$ local reaction rate (mol g$_{Pd}^{-1}$ s$^{-1}$)
$R =$ gas constant (bar m$^3$ mol$^{-1}$ K$^{-1}$)
$T =$ temperature (K)
$x =$ spatial coordinate of the membrane (m)
$X =$ Advancement of reaction
$y =$ Molar fraction

Greek Symbols

$\delta =$ membrane thickness (m)
$\nu_i =$ stoichiometric coefficient of component $i$
\( \rho \) = catalyst or polymer density \( (g/m^3) \)

\( \phi \) = catalyst volume fraction

\( \psi_{C_3H_8}^P \) = recovery

\( \tau \) = tortuosity factor

\( \Gamma \) = contact time

**Subscripts/Superscripts**

\( i \) = component \( i \)

\( \text{F} \) = feed

\( \text{P} \) = permeate

\( \text{R} \) = retentate

\( g \) = gas phase

**Literature Cited**


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