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Eprints ID: 15959

To link to this article: DOI: 10.1002/aic.15379
URL: https://dx.doi.org/10.1002/aic.15379

To cite this version:
Gu, Yingying and Bacchin, Patrice and Favier, Isabelle and Gin, Douglas L. and Lahitte, Jean-Francois and Noble, Richard D. and Gómez, Montserrat and Remigy, Jean-Christophe

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A polymeric catalytic membrane was previously prepared that showed remarkable efficiency for Suzuki-Miyaura C-C cross-coupling in a flow-through configuration. A mathematic model was developed and fitted to the experimental data to understand the significant apparent reaction rate increase exhibited by the catalytic membrane reactor compared to the catalytic system under batch reaction conditions. It appears that the high palladium nanoparticles concentration inside the membrane is mainly responsible for the high apparent reaction rate achieved. In addition, the best performance of the catalytic membrane could be achieved only in the forced flow-through configuration, that, conditions permitting to the reactants be brought to the catalytic membrane by convection. © 2016 American Institute of Chemical Engineers AIChE J, 63: 698–704, 2017

Keywords: polymeric catalytic membrane, palladium nanoparticles, forced flow-through, modeling, mechanism

Introduction

Catalytic membranes have been extensively studied in the last two decades because they represent a process intensification. More recently, catalytic polymeric membranes, which were less studied than inorganic ones, have attracted growing interest because of their relatively low cost and high efficiency.1 They were found catalytically active on a variety of reactions (e.g., alcohol and ether syntheses,2 C-C cross-couplings3-5 hydrogenations,6 chemical reductions7,8), Some polymeric catalytic membranes even gave full conversion of substrates within residence time of seconds,3,8 showing prospective potential of the catalytic polymeric membranes containing palladium nanoparticles (PdNPs). Whereas there is a lack of investigations into the reasons why those polymeric catalytic membranes are so efficient. This understanding is undoubtedly important to provide guidelines to design catalytic membrane reactors.

One major type of catalytic membrane reactors are membrane contactors. Due to their nonpermselectivity toward reactants and products, membrane contactors can offer higher throughput than extractor and distributor catalytic membranes. It is generally accepted that main function of membrane contactors consists of favoring mass transfer by intensifying the contact between reactants and catalyst.9,10 Nagy established several mathematical models to study the mass transfer accompanied by reactions in the catalytic membrane.11 Herein, we deduced using a similar model that the intensified contact between catalyst and reactants was not the only factor responsible for the high catalytic activity observed in a forced-flow membrane contactor using a catalytic membrane with immobilized PdNPs. The results obtained provide further understanding into the principles involved in catalytic membrane contactors. In this work, PdNPs were used as catalyst for their catalytic performance, especially in carbon–carbon bond formation.12

Materials and Methods

Catalytic polymeric membrane, PdNPs colloidal solution and the corresponding Pd-catalyzed Suzuki-Miyaura C-C cross-coupling reactions were previously reported3

The catalytic membrane was prepared through the functionalization of a microfiltration membrane whose nominal pore size is 0.2 μm, with a very narrow pore-size distribution.
To run the reaction using the catalytic membrane, the reaction mixture was premixed and then filtered through the membrane. The permeate flow rate was varied by using the peristaltic pump (with the flux density \( j \) fell in the range of 27–1300 L h\(^{-1}\) m\(^{-2}\)). The transmembrane pressure was in the range of 1–150 mbar. The mean flow velocity inside the membrane \( v_m \) can be calculated as \( v_m = j / \varepsilon \), with \( \varepsilon \) as membrane porosity, which is considered to be 0.8 in our case. As for the calculation of the flow velocity in the bulk solution, porosity is taken as 1.

The same reaction was carried out under batch conditions using a PdNPs colloidal solution.

**Mass-transfer model for the catalytic membrane**

The fluid followed a laminar flow pattern in the membrane pores (pore size \( \leq 0.2 \mu m \)), giving rise to a parabolic velocity profile. When the radial diffusion across the pore is much faster than convective mass transfer in the axial direction, the parabolic flow velocity profile can be reconciled with plug flow behavior (flat concentration profile).\(^{13,15}\) For our catalytic membrane, the residence time was \( 10^3 \) to \( 10^5 \) longer than the characteristic mixing time (to diffuse halfway across the pore, \( \tau_{max} = \frac{d^2}{D_p}, \) with \( d \) as pore diameter \( 0.2 \mu m \) and \( D \) as diffusion coefficient). Hence, a plug flow pattern was readily achieved inside the membrane, permitting a simplification of modeling of the catalytic membrane to one dimension (the concentration can be considered as homogeneous in a slice of the membrane parallel to the surface). The external mass-transfer resistance through the boundary layer around the catalyst was neglected (concentration on the catalyst surface equals to the bulk concentration, see section the Calculations on Mass-Transfer Resistance). Since the PdNPs are dense particles (unlike porous pellets), no internal diffusion needs to be considered. In addition, isothermal conditions (fluid and membrane temperature were constant and in complete agreement) were also achieved under the experimental conditions according to Westermann’s model.\(^{16}\) Therefore, a constant intrinsic reaction rate \( k_{mem} \) was imposed. The differential mass balance for the catalytic membrane at steady state taking into consideration the convective flow, diffusion and a first-order reaction can be then expressed by Eq. 1.

\[
\frac{D}{dz^2} \frac{dC}{dz} - v_m \frac{dC}{dz} - ak_{mem}C = 0
\] (1)

where \( D \) is the diffusion coefficient \( (4.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}) \); \( v_m \) is the convective velocity inside the membrane; \( C \) is concentration of the limiting reactant (1-iodo-4-nitrobenzene); \( a \) is the specific surface area of the catalyst (total catalyst surface area divided by the membrane volume, \( \text{m}^2 \text{ m}^{-3} \)); \( k_{mem} \) is the surface intrinsic reaction rate constant; and \( z \) is the space coordinate. The \( D \) value of the solute molecules at 60°C can be calculated by the Stokes-Einstein equation (Eq. 2)

\[
D = \frac{k_b T}{6 \pi \eta \mu r}
\] (2)

where \( k_b \) is Boltzmann’s constant; \( T \) is the absolute temperature; \( \mu \) is the dynamic viscosity of the solvent \( (5.9 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}) \) for ethanol at 60°C; and \( r \) is the solute molecule radius (on the order of 1 nm).

Equation 1 can be transformed into Eq. 3:

\[
\frac{d^2c}{dz^2} - Pe_m \frac{dc}{dz} - \varnothing^2 c = 0
\] (3)

where \( c \) (= \( C/C_e \)) and \( Z \) (= \( z/L \)) are the dimensionless concentration and coordinates, respectively, with \( C_e \) being the limiting reactant concentration on the feed side surface of the membrane and \( L \) being the membrane thickness. \( Pe_m \) is the Péctel number for mass transfer inside the membrane \( (Pe_m = \frac{v_m L}{D}) \); and \( \varnothing \) is the Thiele modulus \( \varnothing = \sqrt{\frac{D M}{v \eta j}} \). The boundary conditions for this differential equation are\(^{18}\) (Figure 1):

\[
Z = 0 : c = 1
\] (4)

\[
Z = 1 : \frac{dc}{dz} = 0
\] (5)

The solution for Eq. 3 is therefore:

\[
c = \frac{1}{1 - \frac{P_{eM} - \frac{\Delta Z}{L} \sqrt{\frac{P_{eM}}{P_{eM} + \Delta Z}} e^{-\frac{\Delta Z}{L}}} + 1 - \frac{P_{eM} + \frac{\Delta Z}{L} \sqrt{\frac{P_{eM}}{P_{eM} - \Delta Z}}}}{e^{\frac{\Delta Z}{L}}}
\] (6)

where

\[
\Delta = Pe_m^2 + 4 \varnothing^2
\] (7)

When there exists a concentration boundary layer of a thickness \( \delta_c \) over the feed side of the membrane, a concentration gradient in the boundary layer is produced, and \( C_e \) does not equal to the limiting reactant concentration in the bulk solution \( C_b \) (Figure 1). The conversion \( X \) can be then expressed as:

\[
X = 1 - \frac{C_f}{C_b} = 1 - \frac{C_e}{C_b} = 1 - \frac{C_1}{C_b} = 1 - C_1 \quad \text{at} \quad Z = 1
\] (8)

where \( C_f \) is the limiting reactant concentration at \( Z = 1 \).

The differential mass balance in the concentration boundary layer without reaction at steady state can be given by:

\[
\frac{D}{dz^2} \frac{dC}{dz} - v \frac{dC}{dz} = 0
\] (9)

with boundary conditions:

\[
C_{|z=\delta_c} = C_b
\] (10)

\[
C_{|z=0} = C_e
\] (11)

and \( v \) as the convective velocity in the bulk solution.

The mass-transfer flux \( J \) can be obtained by means of Eq. 12, taking into account both the diffusive and the convective flows as follows:

\[
J = -D \frac{dC}{dz} + vC
\] (12)
The relation between $C_e$ and $C_b$ can be thus deduced from Eqs. 9 to 12 as:

$$C_e = J_{1s} \frac{1-e^{Pe_M}}{1-e^{Pe_M}} + C_b \cdot e^{Pe_M}$$  \hspace{1cm} (13)

where $Pe_{BL}$ is the Péclet number of the concentration boundary layer: $Pe_{BL} = v_0C/D$. The concentration boundary layer thickness is a function of the momentum boundary layer thickness $\delta$ and Schmidt number \(Sh\) (Eqs. 14 and 15):20

$$\delta = \sqrt{\frac{\mu}{\rho v_0}} = 190 \ \mu m$$ \hspace{1cm} (14)

where $v_0$ is the agitation velocity (22 rad s\(^{-1}\)), and $\mu$ and $\rho$ are the dynamic viscosity and density of the solution, respectively.

$$\delta_c = Sh/\delta = 15.4 \ \mu m$$ \hspace{1cm} (15)

We denote $Sh$ as $Sh = J_{1s} \cdot Pe_M/(\nu_M \cdot C_e)$. Then from Eqs. 6 to 12, the expression of $Sh$ can be deduced as:

$$Sh = \frac{Pe_M - \sqrt{\Delta}}{1 - \frac{Pe_M - \sqrt{\Delta}}{Pe_M + \sqrt{\Delta}} e^{-\sqrt{\Delta}}} - \frac{Pe_M + \sqrt{\Delta}}{1 - \frac{Pe_M + \sqrt{\Delta}}{Pe_M - \sqrt{\Delta}} e^{\sqrt{\Delta}}}$$ \hspace{1cm} (16)

By combining Eq. 13 with Eq. 16, the ratio of $C_e/C_b$ can be given as follows:

$$C_e \div C_b = 1 - \frac{Sh}{Pe_M} \left(1 - e^{Pe_M}\right) = 1 - \left(1 - \frac{Pe_M - \sqrt{\Delta}}{2 \times Pe_M} \cdot \frac{Pe_M + \sqrt{\Delta}}{2 \times Pe_M} \cdot \left(1 - e^{Pe_M}\right)\right)$$ \hspace{1cm} (17)

where

$$A = 1 - \frac{Pe_M - \sqrt{\Delta}}{Pe_M + \sqrt{\Delta}} \cdot e^{-\sqrt{\Delta}}$$ \hspace{1cm} (18)

$$B = 1 - \frac{Pe_M + \sqrt{\Delta}}{Pe_M - \sqrt{\Delta}} \cdot e^{\sqrt{\Delta}}$$ \hspace{1cm} (19)

The concentration profile inside the concentration boundary layer can be obtained based on Eqs. 9–11 as follows:

$$C_{BL} = \frac{e^{Pe_M}Y^2}{\sinh(Pe_{BL}/2)} \left[\sinh\left(Pe_{BL} \cdot \frac{1-Y}{2}\right) \cdot C_b + e^{-Pe_{BL}/2} \cdot \sinh\left(Pe_{BL} \cdot \frac{Y}{2}\right) \cdot C_e\right]$$ \hspace{1cm} (20)

with $Y = (z + \delta)/\delta$.

### Results and Discussion

#### Reaction regime of the colloidal solution

The Stokes number of the colloidal solution was calculated to be $5 \times 10^{-12}$, indicating that the PdNPs follow the streamline so closely that the relative velocity between PdNPs and the liquid phase is nearly zero. Therefore, the convection becomes inefficient and actually negligible. The mass transfer is therefore effectuated only by diffusion. The mass-transport coefficient ($k_d^{\text{m}}$ in the batch reactor) and the diffusion coefficient ($D$) can be correlated by the Sherwood number $Sh$ (Eq. 21), which can be calculated using Eq. 22.

$$k_d^m \cdot D^m \cdot D = Sh$$ \hspace{1cm} (21)

$$Sh = 2 + \frac{D}{\sqrt{Sh \pi D}} \approx 2$$ \hspace{1cm} (22)

where $d_p$ is the diameter of PdNPs. At $t > 1 \times 10^{-3}$ s, then $d_p/\sqrt{\pi D} < 0.02$, and hence $Sh \approx 2$. $D = 1.22 \times 10^{-11}$ m\(^2\) s\(^{-1}\) for the colloidal system ($\mu \approx 2.0 \times 10^{-5}$ kg m\(^{-1}\) s\(^{-1}\) for the IL at 60°C).

The mass-transfer coefficient was calculated to be:

$$k_d^b = 5.8 \times 10^{-3} \ m \ s^{-1}$$ \hspace{1cm} (23)

The boundary layer thickness around the particle is hence $\delta_0 = D/k_d^b = 2$ nm. The specific surface area $a$ (total surface area of the PdNPs divided by the reaction mixture volume, m\(^2\) m\(^{-3}\)) of the colloidal system was estimated to be in the range of $5.3 \times 10^3 \ m^2 \ m^{-3}$ to $3.6 \times 10^5 \ m^2 \ m^{-3}$ (i.e., the PdNP mean diameter varying from 4 nm to 100 nm, taking into consideration the presence of aggregates). The mass-transfer flux ($a \cdot k_{\text{batch}}$) was thus found much higher (five to seven orders of magnitude greater) than the apparent reaction-rate constant. Therefore, the activity of the colloidal system was in reaction-limited regime. The intrinsic kinetic $a \cdot k_{\text{batch}}$ value was approximately the same as the apparent kinetics (Eq. 24).

$$a \cdot k_{\text{batch}} \approx k_{\text{app}} = 2.3 \times 10^{-14} \ s^{-1}$$ \hspace{1cm} (24)

The intrinsic reaction-rate constant on the catalyst surface for the batch reactor $k_{\text{batch}}$ was estimated to be in the range of $6.0 \times 10^{-10} \ m \ s^{-1}$ to $4.1 \times 10^{-8} \ m \ s^{-1}$ (The exact value of specific surface area cannot be determined; only a range could be given, see above). This means that the concentration on the PdNP surface could be considered to be the same as the bulk concentration ($k_{\text{batch}}/k_d^b \ll 1$).

#### Proposed mechanism of operation of the catalytic membrane

**Calculations on Mass-Transfer Resistance.** The mass-transfer coefficient around the catalyst supported on the membrane $k_d^m$ can be estimated by Eq. 25 and found to be $0.41 \ m \ s^{-1}$, which is much larger than that in batch reactor $k_d^b$ (5.8 $\times 10^{-3} \ m \ s^{-1}$). Calculations deduced from $Sh = 2$ (which is also valid for the catalytic membrane) gives the same $k_d^m$ value. The intrinsic reaction rate constant should be approximately the same for PdNPs in the batch reactor and inside the membrane (maybe lightly higher in the membrane since NPs in the membranes are smaller). The mass-transfer resistance imposed by the boundary layer around the catalyst particles is therefore also negligible in the case of the catalytic membrane.

$$k_d^m = D/\epsilon = 0.41 \ m \ s^{-1}$$ \hspace{1cm} (25)

In Eq. 25, $D$ is the limiting reactant diffusion coefficient in ethanol at 60°C, $4.1 \times 10^{-10} \ m^2 \ s^{-1}$, since obvious swelling of the poly(IL) occurs in ethanol (i.e., the diffusion coefficient is mainly determined by the solvent viscosity when the molecule size is smaller than polymer correlation length ($\xi_{\text{pol}}$) and $\epsilon$ the boundary layer thickness, considered to be half interparticle distance ($\epsilon \approx 1$ nm). Even if $D$ is 100 times smaller, the mass-transfer resistance imposed by the boundary layer around the catalyst would still not be a limiting factor.

**Reaction Kinetics.** The Suzuki-Miyaura cross-coupling reaction was tested at different flow rates at 60°C with a 1-iodo-4-nitrobenzene concentration of 0.016 mol L\(^{-1}\).
Conversion and productivity (interpreted as the product of Péclet number inside the membrane and convergence) were plotted as a function of Péclet number inside the membrane (Figure 2). When flow rate increased (reflected by the increase of the Péclet number inside the membrane), the conversion decreased while the productivity increased.

According to the model described in the Materials and Methods section (Eqs. 6–8, 17), the conversion is a function of Péclet numbers, Thiele modulus and membrane porosity: \( X = f(Pe_{M}, \varnothing, Pe_{BL}, \varepsilon) \). Hence, Thiele modulus is the only unknown parameter. By fitting the model to the experimental data, Thiele modulus, \( \varnothing = \sqrt{\frac{Pe_{BL}}{D_{TPDNP}}} \), was deduced to be 3.19. This result indicates that the reaction is still limited by diffusion along the membrane thickness. By taking the diffusion coefficient of ethanol at 60°C, the apparent reaction rate constant was deduced to be:

\[
 k_{app} = a k_{mem} = 3.4 \times 10^{-1} \text{s}^{-1}
\]  

(26)

When normalized to the PdNP mass and surface area, the apparent reaction-rate constant is then 431 s\(^{-1}\) g\(^{-1}\) and 0.53 s\(^{-1}\) m\(^{-2}\). Compared with catalytic batch reaction conditions (where \( k_{app, \text{batch}} = 0.22 \text{ s}^{-1} \text{ g}^{-1} \)), the catalytic membrane reactor exhibited an acceleration of the apparent reaction rate by three orders of magnitude.

The specific catalyst surface in the membrane was calculated as \( a = 4.66 \times 10^{6} \text{ m}^{-2} \); and hence, the intrinsic reaction rate constant on the catalyst supported on the membrane is \( k_{mem} = 7.4 \times 10^{-3} \text{ m}^{-1} \text{s}^{-1} \), which is the same order of magnitude as corresponding value \( k_{\text{batch}} \) in the batch reactor.

Concentration profiles

Once the ratio of \( C_{e} \) to \( C_{b} \) is determined from Eq. 17, concentration profiles in the boundary layer and in the membrane can be plotted as a function of flow velocity using Eq. 20 and Eqs. 6–8. Figure 2 shows the concentration profiles in the concentration boundary layer at the feed side and inside the membrane, predicted by the model with \( \varnothing = 3.19 \) at different residence times (flow rates or Péclet numbers). The concentration boundary layer significantly reduced the diffusion flux from the bulk solution to the membrane surface and became a limiting step.

At high flow rates (\( Pe_{BL} \geq 1.5 \)), the convection was largely dominant over diffusion. The reactant was effectively brought to the membrane surface by convection so that \( C_{e} \approx C_{b} \). Higher flow rates also lead to the increase of reactant concentration inside the membrane; thus increasing the productivity. However, the short residence time was insufficient to achieve full conversion. For Péclet numbers smaller than 1.5, the reaction was limited by diffusion. The concentration at the membrane feed surface \( C_{e} \) differentiated from the bulk solution concentration \( C_{b} \) (\( C_{e} < C_{b} \)), less reactants reached the inside of the membrane, exerting negative influence on the productivity.

As shown in Figure 3, the reaction productivity increased with the flux until the convection became largely dominant, where a maximum plateau was thus reached. The transition Péclet value (\( Pe_{BL} = 1.5 \)) where (\( C_{b} - C_{e} \)) became less noticeable corresponded to the flux (146 L h\(^{-1}\) m\(^{-2}\)) from which the productivity began to approach the maximum plateau. The reaction on the membrane became kinetically limited at maximum productivity.
Comparative study between the catalytic membrane reactor and PdNPs colloidal solution in the batch reactor and proposed explanation for the high efficiency of the catalytic membrane reactor

The differences between the colloidal system (with PdNPs dispersed in [MMPIM][NTf₂], 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide) in batch reactor and the catalytic membrane reactor are summarized in Table 1. The catalytic membrane reactor works with higher efficiency (entry 6) and selectivity (entry 7) than the colloidal system. The apparent reaction constants of the two systems were given (entry 11) and the intrinsic reaction rate constant \( k \) (entry 12). The influence of \( k \) on apparent kinetics (a factor of 1–3) should be much less remarkable than that exerted by the specific surface area \( a \).

The conventional understanding of a forced flow-through membrane reactor is based on intensified contact between the catalyst and reactants being responsible for the reaction rate increase as local mass-transfer resistance can be effectively eliminated. In consequence, improvements on mass transfer should not have obvious contributions to the apparent reaction rate when reactions were not diffusion-limited. However, for the Suzuki-Miyaura cross-coupling between 1-iodo-4-nitrobenzene and phenylboronic acid (kinetic-limited in the batch reactor), the kinetics was largely enhanced nonetheless in the catalytic membrane. A simple calculation can help to understand how the apparent reaction rate was accelerated in the catalytic membrane. The volume of the membrane used in the experiments was 0.14 cm³. Hence taking into account the porosity, the liquid volume retained in the membrane was around 0.1 cm³. For a concentration of 0.016 mol L⁻¹, the limiting reactant amount inside the membrane volume was 1.6 \( \times \) 10⁻⁶ mol. When the reaction solution was filtered through the membrane (where the catalyst got into contact with the reagents), the Pd/substrate molar ratio in the local environment of the membrane is (\( = 4.7 \)) 470 times higher than that in the batch reactor (\( = 0.01 \)). The real Pd/substrate molar ratio in the membrane can be even higher due to the heterogeneous catalyst distribution inside the membrane (there exist reactive zones inside the membrane where the catalyst is highly concentrated). To be more precise in describing the relative amount of reactant and catalyst, the ratio of catalyst surface to substrate amount should be compared (to reflect number of active sites) instead of Pd/substrate molar ratio (Table 1, entry 5).

It is also noteworthy that despite the high Pd/substrate ratio, the total palladium amount in the membrane is fairly low. The catalyst surface area ratio (catalytic membrane reactor/batch reactor) is 1:2. This ratio is close to the ratio of intrinsic reaction rate constant \( k \) (entry 12). The influence of \( k \) on apparent kinetics (a factor of 1–3) should be much less remarkable than that exerted by the specific surface area \( a \).

### Table 1. Comparison Between the Batch Reactor and the Catalytic Membrane Reactor: PdNPs Size and Distribution and Performance on Suzuki-Miyaura Cross-Coupling Between 1-Iodo-4-Nitrobenzene and Phenylboronic Acid

<table>
<thead>
<tr>
<th>Entry</th>
<th>Batch Reactor</th>
<th>Flow-through Membrane Reactor</th>
<th>Comparative Factora</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdNPs size (nm)</td>
<td>4 ± 2</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>2</td>
<td>Interparticle distance (nm)</td>
<td>50–100</td>
<td>ca. 2</td>
</tr>
<tr>
<td>3</td>
<td>Number of PdNPs (nm⁻³)b</td>
<td>1.7 ( \times ) 10¹² to 2.8 ( \times ) 10¹²</td>
<td>1.4 ( \times ) 10¹⁰ to 4.0 ( \times ) 10¹⁴</td>
</tr>
<tr>
<td>4</td>
<td>Estimated total catalyst surface area ( S ) (m²)</td>
<td>0.36</td>
<td>0.64</td>
</tr>
<tr>
<td>5</td>
<td>S/substrate ratio (m² mol⁻¹)</td>
<td>5–364</td>
<td>3.6 ( \times ) 10²⁶</td>
</tr>
<tr>
<td>6</td>
<td>Reaction time for full conversion</td>
<td>6h</td>
<td>&lt;10 s</td>
</tr>
<tr>
<td>7</td>
<td>Selectivity (%)</td>
<td>92</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>( k_{app} ) (s⁻¹)</td>
<td>2.3 ( \times ) 10⁻⁴</td>
<td>3.4 ( \times ) 10⁻¹</td>
</tr>
<tr>
<td>9</td>
<td>( k_{app}/Pd ) (s⁻¹ g⁻¹)</td>
<td>0.22</td>
<td>431</td>
</tr>
<tr>
<td>10</td>
<td>( k_{app}/S ) (s⁻¹ m⁻¹)</td>
<td>6.2 ( \times ) 10⁻¹ to 4.2 ( \times ) 10⁻²</td>
<td>5.3 ( \times ) 10⁻¹</td>
</tr>
<tr>
<td>11</td>
<td>( a ) (m² m⁻³)</td>
<td>5.3 ( \times ) 10⁵ to 3.6 ( \times ) 10⁴</td>
<td>4.66 ( \times ) 10⁶</td>
</tr>
<tr>
<td>12</td>
<td>( k ) (m s⁻¹)</td>
<td>6.2 ( \times ) 10⁻¹⁰ to 4.2 ( \times ) 10⁻⁸</td>
<td>7.4 ( \times ) 10⁻⁸</td>
</tr>
</tbody>
</table>

a(catalytic membrane reactor)/(batch reactor) value ratio.
bNumber of palladium particles/aggregates per unit volume.
cValues calculated taking into consideration the presence of aggregates (diameter = 4–100 nm).
dValue for reactive zones where palladium is highly concentrated (\( 4.0 \times 10¹⁴ \)) and an average value obtained by (amount of Pd)/(membrane volume) (\( 1.4 \times 10¹³ \)).
e\( 143 = 4.2 \times 10¹⁴/2.8 \times 10¹² \) (comparative factor between the reactive zone of the membrane and the Pd concentration in the batch reactor calculated with \( d = 4 \) nm). The ratio between the reactive zone of the membrane and the batch system taking into consideration the presence of aggregates in the latter should be in the range of \( 143 = 2.35 \times 10³ \).
fLocal ratio inside the membrane environment, porosity = 0.8.
gIn the membrane reactor, the reaction time is defined as the contact time of reagents with the membrane.
hSelectivity toward the cross-coupling product.
iApparent reaction rate constant normalized to palladium mass.
jSpecific surface: catalyst surface area divided by the reactor volume.
kIntrinsic reaction rate constant on the catalyst surface.
reactor) is only around 2 (entry 4). It is important to note that
the reaction time for full conversion in entry 6 refers to the
contact time of reagents with the membrane. The total filtra-
tion time (treating time) of the catalytic membrane reactor for
the same amount of substrate as that in the batch reactor is
around 30 min. Hence the treating time of the catalytic mem-
brane reactor is 12 times shorter than for the batch reactor.
Besides, the catalytic membrane also exhibits the advantage of
operating in a continuous manner. With the comparative factor
of total catalytic membrane surface area (entry 4) between the two systems
much smaller than that of total treating time and reaction time
(entry 6), it is clearly proved that the PdNPs size plays only a
minor role in the high efficiency of the catalytic membrane
reactor, which is in coherence with the small difference of the
intrinsic reaction rate constant between the two systems (entry
12).

The high local Pd/substrate ratio can only be beneficial in
forced flow-through configuration: every single volume of
reaction solution is forced into the local high catalyst concen-
tration environment. When the same membrane is submerged
in a batch reactor, the catalytic performance will be no more
outstanding.In brief, the Suzuki-Miyaura cross-coupling between 1-
iodo-4-nitrobenzene and phenylboronic acid is not mass-
transfer limited under batch conditions. The substantial reaction
rate increase by the catalytic membrane reactor in forced
flow-through configuration can be certainly attributed to the
concentrating effect of the membrane (i.e., packing a large
number of particles into a tiny volume). This is in agreement
with the observation of Seto and coworkers, who attributed
the small rate constant of their Pd-loaded continuous-flow
membrane reactor to the low concentration of Pd catalyst in
the membrane reactor. They suggested that densification of the
Pd catalyst in the membrane could lead to catalytic improve-
ments. The convective flow in our case serves to eliminate the
concentration gradient in the boundary layer at the membrane
feed side surface and inside the membrane, bringing reactants
from the bulk solution into the reactive membrane.

Conclusions

The polymeric catalytic membrane reactor that we prepared
was similar to, and thus can be considered as, a micro-reactor
for its small characteristic dimensions (ca. 0.2 μm). Theoretical
calculations showed that a plug-flow behavior was always
expected in the catalytic membrane pores. Therefore, there
will be virtually no preferential flow pathways. The membrane
reactor was also adapted for moderately exothermic reactions,
achieving isothermal conditions.

It is indispensable to adopt the flow-through configuration
when using the catalytic membrane reactor to attain a high cat-
alytic activity. The convective flow brings the reagents into
the catalyst highly concentrated membrane local environment
where the reaction takes place. It also helps to eliminate the
mass-transfer limit (in the boundary layer at the feed side as
well as inside the membrane).

When the catalytic membrane reactor was employed, the
Suzuki-Miyaura cross-coupling using 1-iodo-4-nitrobenzene
as substrate was complete within 10 s without formation of
any by-product. This reaction was in the reaction-limited
regime in the batch reactor. Mathematical modeling of the cat-
alytic membrane showed that there is a concentration bound-
ary layer on the feed side of the membrane and that the
reactant concentration gradient inside this boundary layer and
along the membrane thickness can be eliminated at high flux
(by convection). These features explain the productivity
increase with the flux increase. The much higher efficiency of
the catalytic membrane (compared to the PdNPs dispersed in
an IL under batch conditions) is principally attributed to the
high local catalyst concentration inside the small membrane
reactor volume since the intrinsic reaction rate constants of the
membrane reactor and the batch reactor are of the same order
of magnitude. PdNPs size (in the range of 1–6 nm) seems to
exert a negligible effect on the reactivity.

Acknowledgments

The authors gratefully acknowledge the French Ministry
of Education and Research, Paul Sabatier University and the
National Center for Scientific Research (CNRS) for providing
financial support through the FOAM2 project (Paul Sabatier University).

Notation

\( \alpha = \) catalyst specific surface area, m\(^2\) m\(^{-3}\)
\( C = \) limiting reactant concentration in the membrane, mol m\(^{-3}\)
\( C_{bl} = \) limiting reactant concentration in the boundary layer on the feed side of the membrane, mol m\(^{-3}\)
\( C_{f} = \) limiting reactant concentration in the permeate, mol m\(^{-3}\)
\( c = \) dimensionless concentration
\( D = \) diffusion coefficient, m\(^2\) s\(^{-1}\)
\( d = \) pore diameter, m
\( d_{e} = \) diameter of nanoparticles, m
\( e = \) interparticle distance, m
\( f = \) molar flux density, mol m\(^{-2}\) s\(^{-1}\)
\( j = \) filtration flux density, L h\(^{-1}\) m\(^{-2}\)
\( k = \) intrinsic reaction rate in either the batch reactor \( (k_{bath}) \) or the membrane \( (k_{mem}) \), m s\(^{-1}\)
\( k_{B} = \) Boltzmann constant \( (1.38 \times 10^{-23} \text{ J } \cdot \text{ K}^{-1}) \), J K\(^{-1}\)
\( k_{app} = \) apparent reaction rate, s\(^{-1}\)
\( k_{m} = \) mass-transfer coefficient in either the batch reactor \( (k_{bath}^{m}) \) or the membrane \( (k_{mem}^{m}) \), m s\(^{-1}\)
\( L = \) membrane thickness, m
\( P_{E} = \) Pelet number inside the membrane
\( P_{E,b} = \) Pelet number in the boundary layer
\( r = \) solute molecule radius, m
\( S = \) total catalyst surface area, m\(^2\)
\( Sc = \) Schmidt number
\( Sh = \) Sherwood number
\( T = \) temperature, K
\( v_{cm} = \) convective velocity in the membrane, m s\(^{-1}\)
\( v = \) convective velocity in the bulk solution, m s\(^{-1}\)
\( X = \) conversion
\( Z = \) dimensionless coordinate
\( \zeta = \) space coordinate, m
\( \Theta = \) Thiele modulus
\( \rho = \) liquid density, kg m\(^{-3}\)
\( \delta = \) momentum boundary layer thickness on the feed side of the membrane, m
\( \delta_{c} = \) concentration boundary layer thickness on the feed side of the membrane, m
\( \mu = \) dynamic viscosity, kg m\(^{-1}\) s\(^{-1}\)
\( \tau_{mem} = \) characteristic mixing time, s

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