Development of a flat membrane microchannel packed-bed reactor for scalable aerobic oxidation of benzyl alcohol in flow

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HIGHLIGHTS

- A membrane catalytic packed-bed reactor was designed for safe scalable alcohol oxidation.
- The reactor performance was affected by the oxygen supply.
- The main oxygen transfer resistance was in the bulk liquid within the bed.
- An effectiveness factor was proposed to aid membrane reactor design.

GRAPHICAL ABSTRACT

Flat Membrane Microchannel Reactor for Scalable Aerobic Oxidation of Alcohols

ABSTRACT

A flat membrane microchannel reactor was designed and demonstrated for the safe and scalable oxidation of solvent-free benzyl alcohol with molecular oxygen on Au-Pd/TiO\textsubscript{2} catalyst. The microchannel reactor employed a mesh-supported Teflon AF-2400 membrane, with gas and liquid channels on each side. Catalyst particles were packed in the liquid flow channel. Operation with 20 bar pressure difference between the gas and the liquid phases was possible at 120 °C. Pervaporation of organics through the membrane was experimentally measured to ensure that the organic vapour concentration remained below the lower flammability limit during the reaction. High oxygen pressure was shown to have a positive effect on reactor performance. A conversion of benzyl alcohol of 70% with 71% selectivity to benzaldehyde was obtained at 1150 gcat·s/galcohol, 8.4 bar oxygen pressure and 10 bar liquid pressure. The oxygen consumption rate was not significantly decreased when doubling the membrane thickness, indicating that the membrane generated only low resistance to oxygen mass transfer. When changing the catalyst particle size and the liquid flow rate, no significant effect was observed on the oxidation reaction rate. An effectiveness factor approach is proposed to assess the effect of oxygen permeation and transverse mass transfer on the catalyst packed in the membrane reactor, which suggests that the oxidation of benzyl alcohol on the highly active Au-Pd/TiO\textsubscript{2} catalyst is controlled by the oxygen transverse mass transfer in the bulk liquid within the catalyst bed. Scale-up of the flat membrane microchannel reactor was demonstrated through increasing the liquid channel width by approximately ten times, which increased the reactor productivity by a factor of eight.

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1. Introduction

Oxidation of alcohols is an important process in organic chemistry and is often performed with stoichiometric inorganic reagents [1–3]. To improve the atom efficiency and reduce the environmental costs, heterogeneous catalysts have been developed, and significant advances have been reported [4–8]. However, large-scale applications of aerobic oxidation of alcohols are still limited by potential safety issues caused by the oxidant-organic reactant mixtures [9,10].

Recently, several approaches have been proposed to ensure intrinsic process safety [11]. Stahl and co-workers [12,13] reported a continuous flow tube reactor for homogeneous Pd/Ca-catalyzed aerobic oxidation of primary alcohols to aldehydes, where a dilute oxygen source (8–9% oxygen in nitrogen) was used to avoid the oxygen/organic mixture entering the flammable regime. Zotova et al. [14] developed a safe process for aerobic oxidation of alcohols with a commercially available XCube® reactor, by pre-mixing and saturating the liquid with the gaseous reactant (oxygen or air) before reaching the catalyst bed.

Among these approaches, membrane reactors have attracted attention, since a membrane can act as a well-defined contacting interface for gas and liquid phases [15–17]. The membrane allows strict dosing control of gaseous reactants and avoids direct mixing of oxygen with organic compounds. A ceramic membrane reactor was previously developed by our group for oxidation of benzyl alcohol with pure oxygen [18]. The reactor consisted of a commercially available tubular ceramic membrane with catalyst packed in the inner tube. The liquid phase flowed through the inner tube and pure oxygen flowed in the opposite side of the membrane. Deficiency of oxygen in the catalyst bed area was suggested to occur for the relatively fast catalytic system investigated.

As a type of amorphous fluoroplastic, Teflon AF-2400 has gained popularity, since it has high permeabilities to gases and excellent chemical compatibility [19]. The Ley group first developed a Teflon AF-2400 tube-in-tube membrane reactor and applied it to various reactions such as C–C, C–N and C–O bond forming and hydrogenation reactions [20,21]. Chaudhuri et al. [22] used the tube-in-tube reactor to saturate the liquid stream with oxygen/air for heterogeneously catalytic oxidation of alcohols. An in-situ continuous supply of oxygen through the membrane to the catalyst was realized through packing the solid catalyst inside the inner tube of the tube-in-tube reactor [23]. This contributed to a significant improvement in both conversion and selectivity, as compared to a non-permeable reactor with oxygen presaturated feed. Greene et al. [24] developed a tube-in-shell membrane reactor with inexpensive PTFE tubing for homogeneous and heterogeneous oxidation of alcohols with molecular oxygen. Even though the price of common fluoropolymers, such as PTFE, is much lower than that of Teflon AF-2400, the high oxygen permeability of the Teflon AF-2400 membrane makes it attractive for oxidation of solvent-free benzyl alcohol within a catalyst bed.

Some potential drawbacks still exist for the packed tube-in-tube membrane reactor. The gas phase present in the annulus between the inner and outer tubes could possibly create heat transfer resistance for exothermic reactions, due to its relatively low thermal conductivity. The scale-up of the tube-in-tube reactor is not facile, since increasing the membrane diameter results to a proportional increase in radial mass transfer resistance under laminar flow [25]. In an attempt to address these issues, a Teflon AF-2400 flat membrane microchannel reactor is developed in this study. Oxidation of benzyl alcohol is performed on Au-Pd/TiO2 catalyst, which has high activity and good reusability [26]. The reaction is considered to comprise of two main parallel reactions, the oxidation reaction (Eq. (1), \(\Delta H = -218 \text{kJ/mol benzyl alcohol, adiabatic temperature rise } \Delta T_{\text{ad}} = 884 \text{ C, assuming no phase change} \)) and the disproportionation reaction (Eq. (2), \(\Delta H = -25.6 \text{kJ/mol benzyl alcohol, } \Delta T_{\text{ad}} = 127 \text{ C} \) [27,28]). Both the oxidation and disproportionation of benzyl alcohol can form the target product benzaldehyde, while the toluene by-product is generated from disproportionation. In our recent microkinetic study, hydrogenolysis of benzyl alcohol to toluene was found to play an important role for toluene formation, but at oxygen deficient conditions disproportionation prevails [29]. Hence, in our discussions in this work the hydrogenolysis pathways are neglected, since in the packed-bed membrane reactor (as will be shown) there is deficiency of oxygen supply. The amount of consumed oxygen during the reaction could be calculated based on the conversion of benzyl alcohol and selectivities to benzaldehyde and toluene [23].

\[
\begin{align*}
2\text{PhCH}_2\text{OH} + \text{O}_2 & \rightarrow 2\text{PhCHO} + 2\text{H}_2\text{O} \\
2\text{PhCH}_2\text{OH} & \rightarrow \text{PhCHO} + \text{PhCH}_3 + \text{H}_2\text{O}
\end{align*}
\]
HAuCl₄·3H₂O (Johnson Matthey) and PdCl₂ (Johnson Matthey) with Au-to-Pd weight ratio equivalent to 1:19 was added. The resultant slurry was spray-dried (nozzle temperature 220 °C) and then calcined in static air at 400 °C for 1 h. The metal content was analysed by ICP-AES and found to be 0.05 wt% Au and 0.85 wt% Pd, while the metal particle size as observed by TEM was 1–2 nm. The powder was pelletized, crushed, and sieved to the desired particle size range. The shape of the catalyst particles, as observed with a microscope, was irregular (shown in Fig. S1) and the particle density, as calculated from the skeletal density and the pore volume (measured by BET), was 2.19 g/cm³.

2.2. Design of the flat membrane microchannel reactor

The flat membrane microchannel reactor designed in this work consisted of several layers, which are shown in Fig. 1. From the bottom to the top, these are a liquid flow plate machined in 316 stainless steel (channel size length: 75 mm; width: 3 mm; depth: 1 mm), a Teflon AF-2400 membrane (length: 85 mm; width: 30 mm; thickness: 0.05 mm; thickness: 0.05 mm; hole size: 76 μm; open area: 23%; Industrial Net-304 stainless steel mesh (length: 85 mm; width: 30 mm; thickness: 1 mm; open area length: 75 mm; width: 3 mm; Altec) and a gas flow plate (with the same channel size and material to the liquid flow plate). The sealing of the reactor was achieved by compressing the membrane and the gasket with screws; the membrane also acted as a gasket for the liquid flow plate. An O-ring groove was machined in the liquid flow plate, which allowed also a sintered metal plate to be employed as the membrane support. Two holes were drilled in both liquid and gas channel plates (perpendicular, 1 mm away from the channel) for thermocouple insertion. A small circular piece of another nickel mesh (diameter: ~2 mm; thickness: 0.05 mm; hole size: 25 μm; Tecan) was placed between the liquid outlet and the fitting for retaining the catalyst. After assembling the reactor, 50 mg silica beads (particle size: 90–125 μm) were packed into the liquid channel followed by the Au-Pd/TiO₂ catalyst particles, with the help of a vacuum pump. For the 90–125 μm particles, the length of the 100 mg catalyst bed was 4.1 ± 0.2 cm, and the packing density was ~0.82 g/cm³, leading to a void fraction of the catalyst bed of 0.62.

The reactor was placed on a hotplate (Gallenkamp) fitted with a thermocouple which was inserted in the liquid flow plate hole beneath the catalyst bed for temperature measurement and control. To decrease heat loss, an insulation cap (insulation thickness: ~2 cm; WDS® Ultra, Morgan) was added between the reactor and the temperature difference within the reactor, measured by thermocouples inserted in liquid flow plate holes close to the flow channels, was ±2 °C at set temperature of 120 °C.

2.4. Reaction experiments

A schematic of the experimental set-up is shown in Fig. 2. Neat benzyl alcohol (99.0%, Sigma-Aldrich) was delivered to the microchannel reactor with a HPLC pump (Knauer P2.1S). An adjustable back pressure regulator (BPR) (Zaiput, BPR-01) was used at the liquid outlet to maintain the desired liquid pressure. Pure oxygen was regulated by a mass flow controller (Brooks, GF40 series) and directed to the gas inlet of the reactor. A BPR (1–11 bar, Swagelok, K series) was connected at the gas outlet to maintain the desired gas pressure. The pressures of the gas and liquid phases were monitored by pressure sensors (Zaiput, Hastelloy/PFA wetted parts) placed ~20 cm from the inlets of the reactor. The packed bed pressure drop was measured to be less than 0.2 bar. To avoid bubble formation in the liquid phase, the inlet pressure of the liquid phase was maintained at least 1 bar higher than that of the gas phase pressure.

The effluent from the liquid outlet was collected in a cold trap (ice-water bath) and quantitatively analysed by a gas chromatograph (Agilent 7820A) fitted with a DB-624 capillary column and a flame ionization detector. Benzyl alcohol conversion (X) and selectivity (Sᵢ) of each product were calculated according to the following equations:

\[
X = \frac{C_{\text{BPhOH}_{\text{in}}}}{C_{\text{BPhOH}_{\text{in}}}} \frac{C_{\text{BPhOH}_{\outpl}}}{C_{\text{BPhOH}_{\outpl}}} \\
S_i = \frac{C_i}{C_{\text{BPhOH}_{\outpl}}} \times X
\]  

where \( C_{\text{BPhOH}_{\outpl}} \) and \( C_{\text{BPhOH}_{\outpl}} \) are the concentration of benzyl alcohol at the inlet and outlet of the reactor, respectively and \( s_i \) is the number of moles of benzyl alcohol consumed for the production of 1 mol of product \( i \). In this study, \( S_2 \) and \( S_7 \) stand for selectivities to benzaldehyde and toluene, respectively.

The catalyst contact time (CCT) was used to characterise the reaction time of benzyl alcohol, and defined as:

\[ \text{CCT} = \frac{V}{Q} \]

where \( V \) is the volume of the liquid phase and \( Q \) is the volumetric flow rate of the liquid phase.
where $m_{\text{cat}}$ is the mass of catalyst, $v$ is the inlet volumetric flow rate of benzyl alcohol, $\rho$ is the density of benzyl alcohol at $20^\circ$C. For each experiment, at least three samples were collected and the results were averaged. The experimental errors for the conversion and selectivities were less than $\pm 2\%$ (absolute). For typical operating conditions (catalyst contact time, 577 gcat·s/galcohol; liquid pressure, 10 bara; 120°C) the conversion and selectivities obtained in different days could differ by up to 4% (absolute), primarily due to a slow catalyst deactivation. Oxygen consumption rates (OCR, at standard temperature and pressure, 0°C and 1 bara, STP) were calculated by

$$OCR = \frac{1}{2} \frac{FM_{\text{in},\text{in}} \cdot X}{n_{\text{metal}}} (S_g - S_T) \tilde{V}_{O_2}$$

where $FM_{\text{in},\text{in}}$ is the molar flow rate of benzyl alcohol and $\tilde{V}_{O_2}$ is the molar volume of oxygen at STP.

Average turnover frequency (TOF) was calculated to better represent the reaction rate, where $TOF_{\text{total}}$, $TOF_O$ and $TOF_D$ correspond to the overall reaction, the oxidation reaction and the disproportionation reaction, respectively.

$$TOF_{\text{total}} = \frac{FM_{\text{in},\text{in}} \cdot X}{n_{\text{metal}}}$$

$$TOF_O = \frac{FM_{\text{in},\text{in}} \cdot X \cdot (S_g - S_T)}{n_{\text{metal}}}$$

$$TOF_D = \frac{2FM_{\text{in},\text{in}} \cdot X \cdot S_T}{n_{\text{metal}}}$$

where $n_{\text{metal}}$ is the moles of the metals contained in the packed catalyst bed.

3. Results and discussion

3.1. Operation pressure and solvent pervaporation

Initially, the operating pressure range of the reactor was studied without any catalyst packed. The reactor temperature was kept at $120^\circ$C and atmospheric pressure was applied in the gas phase. The pressure in the liquid phase was gradually increased to 21 bara (20 bara pressure difference) and kept for 0.5 h. No leaking was detected. Notably, only slight change of the shape of the membrane was observed after testing at such pressure difference and temperature (shown in Fig. S4a). In contrast, obvious membrane shape change was observed when no mesh was used to support the membrane (shown in Fig. S4b). However, membrane shape change was restricted and breakage was prevented, because the membrane eventually touched the bottom of the gas channel with increasing liquid pressure. It should be noted that in our previous tube-in-tube membrane microreactor, the Teflon AF-2400 inner tube (1 mm thickness) broke when ~12 bara pressure difference was applied at $120^\circ$C. This indicates that the flat membrane microchannel reactor could expand the operating pressure range of the Teflon AF-2400 membrane at elevated temperature.

Even though direct mixing of oxygen with organic reactants is avoided by using the membrane reactor, organic vapour may appear in the gas phase because of pervaporation. To ensure that the organic vapour concentration remained outside the flammability limits, the pervaporation of the reactant and the main products (benzyl alcohol, benzaldehyde and toluene) through the membrane was experimentally measured and the details are shown in the Supporting Information. The pervaporation rate of toluene through the membrane was found to be the highest, which was 32.2 mg/h (for 14.3 mg/h/cm$^2$ membrane area). This corresponded to 0.13 mL/min toluene vapour in the gas phase channel at STP, highlighting the necessity of using continuous flow in the gas phase to dilute the pervaporating organics. To keep the organic vapour concentration lower than 1 vol% (which is the lower flammability limit for toluene in air at 6 bara and 120°C [31]), an oxygen flow rate of 15 mL/min at STP was utilized in the following experiments.

3.2. Catalyst stability

To evaluate the performance of the Au-Pd/TiO$_2$ catalyst and the reactor, a stability study was initially conducted and the results are shown in Fig. 3. The catalyst contact time was 577 gcat/s/galcohol and the conversion of benzyl alcohol was stable at around 57% over 24 h. The selectivities to benzaldehyde and toluene, the two main products, also showed stable trends (66% and 31%, respectively). The selectivities to other minor products (dibenzyl either, benzyl benzoate, etc.) were all less than 3% (not shown). These results demonstrate the high stability of the prepared Au-Pd/TiO$_2$ catalyst, as well as the excellent performance of the flat membrane microchannel reactor. The productivity of benzaldehyde was calculated to be 2.3 g/gcat/h.

3.3. Effect of oxygen pressure

To explore the effect of oxygen pressure on the oxidation of benzyl alcohol in the flat membrane microchannel reactor, oxygen pressure was changed from 0 to 8.4 bara. Other reaction conditions were kept the same. From Fig. 4, the conversion of benzyl alcohol was observed to be 4% at 0 bara oxygen pressure (nitrogen flowed through the gas channel at atmospheric pressure). Almost equimolar amounts of benzaldehyde (44%) and toluene (41%) were formed due to the disproportionation of benzyl alcohol [27,28,32]. With oxygen pressure increasing, the conversion gradually rose and reached 57% at 8.4 bara. The selectivity to benzaldehyde also increased from 44% to 66% within the investigated oxygen pressure range. Correspondingly, the selectivity to toluene drop from 41% to 31%. Similar behaviour was also observed in our previous tube-in-tube membrane microreactor [23]. When increasing the oxygen pressure from 3 to 7 bara, the conversion of benzyl alcohol increased from 22% to 42% with the selectivity to benzaldehyde from 61% to 65% at catalyst contact time 115 gcat/s/galcohol.

The oxygen consumption rate at STP under different oxygen pressures is shown in Fig. 5. Higher oxygen consumption rates were
observed at higher gas pressure. The maximum rate was 0.21 mL/min (STP, 0.56 mmol/h) at 8.4 bara. The fact that the oxygen consumption rate was close to zero at 0 bara oxygen pressure (nitrogen was used in the gas channel), indicates that the amount of oxygen consumed in the reaction at elevated oxygen pressure comes from oxygen permeating through the membrane during the reaction. On the basis that all other reaction conditions were kept the same and only the oxygen pressure was changed, increasing the oxygen pressure could therefore enhance the oxygen consumption and result in higher oxygen permeation.

To further investigate the effect of oxygen pressure on the reaction, TOFs at different oxygen pressures were calculated and shown in Fig. 6. In the absence of oxygen (0 bara oxygen pressure), TOF<sub>total</sub> was very close to TOF<sub>D</sub> and TOF<sub>O</sub> was practically zero. This indicates that disproportionation was the only reaction occurring and no oxidation reaction was taking place under these conditions [28]. With a rise in oxygen pressure, both TOF<sub>D</sub> and TOF<sub>O</sub> showed an upward monotonic trend. This contributed to an approximately linear increase in TOF<sub>total</sub> as well as the increasing selectivity to benzaldehyde as shown in Fig. 4. Since the oxygen solubility in the liquid increases at elevated oxygen pressure, this demonstrates that oxygen could promote both disproportionation and oxidation reactions. This has been observed previously and has been attributed to two different mechanisms for the disproportionation reaction, one anaerobic and the other aerobic [27,28,33]. At low oxygen pressure the anaerobic route dominates, but an increase of oxygen concentration promotes the aerobic disproportionation route, which has been associated with oxygen regenerating the active sites for the disproportionation reaction [28]. Higher TOF<sub>total</sub> and TOF<sub>O</sub> were observed in batch reactors and microtrickle bed reactors, when higher oxygen pressure was used. However, the TOF<sub>D</sub> in both batch and microtrickle bed reactors was observed to decrease with oxygen pressure higher than 0.2–1 bara [27,33], indicating the dominance of the oxidation reaction (as compared to both aerobic and anaerobic disproportionation) at high oxygen concentration. The detailed description of the proposed mechanism for the anaerobic and aerobic disproportionation can be found in [27,28]. The fact that TOF<sub>D</sub> in the membrane reactor was not observed to decrease within the range of oxygen pressures investigated, suggests that the reactor might not supply oxygen as efficiently as the batch and trickle bed reactors. The low oxygen supply in the membrane reactor is also indicated by the obtained TOFs, since the TOFs in the membrane reactor (TOF<sub>total</sub>, 400 h<sup>-1</sup> at 8.4 bara) were about two orders of magnitude lower than those reported in batch reactors using 2.5 wt% Au-2.5 wt% Pd/TiO<sub>2</sub> catalyst (TOF<sub>total</sub>, 26,400 h<sup>-1</sup>) [26]. So, in the following sections the oxygen transfer resistance in the reactor was investigated.

3.4. Effect of catalyst contact time and membrane thickness

The effect of membrane thickness was investigated through placing a single-layer (0.07 mm thickness) or a double-layer (0.14 mm thickness) membrane in the microchannel reactor. The results at different catalyst contact times are shown in Fig. 7. The same trend was observed for the conversion and selectivities at different catalyst contact times, that is, increasing the catalyst contact time enhanced both the conversion of benzyl alcohol and the selectivity to benzaldehyde, while decreasing the selectivity to toluene. This trend agrees with our previous results in the membrane reactors [18,23], but differs from those obtained in batch and trickle bed reactors [28,32], in which the selectivities were similar at different catalyst contact times. This is observed at higher gas pressure. The maximum rate was 0.21 mL/min (STP, 0.56 mmol/h) at 8.4 bara. The fact that the oxygen consumption rate was close to zero at 0 bara oxygen pressure (nitrogen was used in the gas channel), indicates that the amount of oxygen consumed in the reaction at elevated oxygen pressure comes from oxygen permeating through the membrane during the reaction. On the basis that all other reaction conditions were kept the same and only the oxygen pressure was changed, increasing the oxygen pressure could therefore enhance the oxygen consumption and result in higher oxygen permeation.

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probably caused by the low efficiency of oxygen supply in the membrane reactors as discussed in Section 3.3. Longer catalyst contact time in the membrane reactor could contribute to longer time for both oxygen permeation and reaction, and thus more oxygen supply per liquid volume [23]. This could further promote the oxidation reaction, resulting in benzaldehyde selectivity increase.

Notably, a conversion of benzyl alcohol of 70% with 71% selectivity to benzaldehyde was obtained at 1150 gcat·s/galcohol and 8.4 bara oxygen pressure with a single-layer membrane. At the same reaction conditions with double-layer membrane, the conversion and benzaldehyde selectivity were observed to be both 68%. When comparing the oxygen consumption rates at different membrane thicknesses (shown in Fig. 7c), higher rate was observed for the single-layer membrane at each catalyst contact time. The average oxygen consumption rate with the single-layer membrane (0.19 mL/min) was 27% higher than that with the double-layer (0.15 mL/min). This reveals that some oxygen transfer resistance exists in the membrane. However, the oxygen transfer resistance in the membrane does not seem to be the main transfer resistance, since only 27% increase of average oxygen consumption rate was observed when halving the membrane thickness.

3.5. Internal/external mass transfer

The internal mass transfer was studied using two ranges of catalyst particle sizes at different catalyst contact times. The conversion of benzyl alcohol and selectivities to benzaldehyde and toluene are shown in Fig. 8. Slightly higher conversion was observed when larger particles were used. This is attributed to slightly longer packed bed obtained with larger particles for the same catalyst weight (packed bed length: 4.1 ± 0.2 cm for 90–125 μm particles vs. 3.5 ± 0.2 cm for 45–53 μm particles), which led to increasing the membrane area available for oxygen transfer without increasing the oxygen demand by the catalytic bed. A similar effect has been observed when the catalyst bed was diluted with inert support [23]. The selectivities to benzaldehyde and toluene were similar, indicating independence on the catalyst particle size. Simplified calculation of the Weisz-Prater criterion (see Supporting Information) indicated small diffusional resistances, but due to the unknown (and likely transversely and axially varying) oxygen concentration within the catalyst bed, the criterion cannot be used reliably. However, the results with the two catalyst particle sizes indicate that internal mass transfer resistance is not a determining factor for the performance of the system investigated.

The external mass transfer was studied by comparing the TOFs for two different liquid flow rates at three catalyst contact times. The amount of catalyst packed in the reactor was changed accordingly. Note that these are average TOFs obtained at conversion levels 30–60%. In Table 1, no clear difference was seen in all the TOFs, when the liquid flow rate was increased from 5 μL/min to 10 μL/min at 577 gcat/s/
Based on the TOF$_\text{total}$ (26,400 h$^{-1}$) and the selectivity to benzaldehyde (∼67%) obtained with 2.5 wt% Au-2.5 wt% Pd/TiO$_2$ catalyst in a batch reactor [26], the TOF$_O$ of the Au-Pd/TiO$_2$ catalyst was calculated to be ∼8800 h$^{-1}$ at 120°C. This results to an oxygen demand of 13.6 mL/min at STP (36.5 mmol/h, calculation shown in the Supporting Information) for the amount of Au-Pd/TiO$_2$ catalyst packed in the membrane reactor (100 mg). The actual oxygen consumption rate within the membrane reactor was only 0.21 mL/min (0.56 mmol/h) at 8.4 bara oxygen pressure. This indicates a gap between oxygen demand by the highly active catalyst and oxygen supply in the membrane reactor. However, the maximum oxygen supply rate (the highest oxygen permeation rate) through the membrane area contacting the catalyst bed (∼40 mm × 3 mm) could be 0.74 mL/min (2.0 mmol/h) at 8.4 bara oxygen pressure, which is more than 3 times the oxygen consumption rate. This oxygen supply rate could contribute to a theoretical 4.0 mmol/h of benzaldehyde formed through the oxidation reaction (considering a stoichiometry according to Eq. (1) of 2/1: benzyl alcohol/oxygen), which is much larger than the actual 1.1 mmol/h. The difference between the maximum oxygen supply rate and the actual oxygen consumption rate indicates oxygen transfer resistance in the catalyst bed. Since the internal/external mass transfer resistance has been shown to have no significant effect on the oxidation reaction rate, the main oxygen transfer resistance is thus expected to exist in the bulk liquid within the catalyst bed.

### 3.6. Interaction of mass transfer processes with reaction in the packed bed membrane reactor

In order to assess the relative importance of the various mass transfer processes that affect reactor performance (membrane oxygen permeation and transverse mass transfer), a permeation-transverse mass transfer effectiveness factor ($\eta$) is proposed, based on the oxidation reaction rate (assumed as a first order in oxygen, the details are shown in the Supporting Information). By considering an analogy between our reactor and a single catalyst pellet where diffusion/reaction occurs, where the oxygen mass transfer through the membrane and transverse mass transfer in the reactor bed are analogous to external and internal mass transfer in a pellet respectively, we can use the standard effectiveness factor analysis.

To relate the reaction rate to the transverse mass transfer rate in the packed bed, a Damköhler number (Da) is defined by

$$Da = \frac{d_j k_{o2}}{D_{o2,T}}$$

(10)

where $d_j$ is the depth of the packed bed (i.e., liquid channel), $k_{o2}$ is the oxidation reaction rate constant based on the bed volume, $D_{o2,T}$ is the transverse dispersion coefficient of oxygen in the packed bed.

To provide a measure of oxygen permeation rate to oxygen transverse mass transfer rate, a Biot number (Bi) is defined by

$$Bi = \frac{d_j k_{o2}}{D_{o2,T}}$$

(11)

### Table 1

<table>
<thead>
<tr>
<th>CCT [g$<em>{\text{cat}}$/g$</em>{\text{alcohol}}$]</th>
<th>577</th>
<th>288</th>
<th>192</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight [mg]</td>
<td>50</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Liquid flow rate [μL/min]</td>
<td>5</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>TOF$_O$ [h$^{-1}$]</td>
<td>386</td>
<td>400</td>
<td>1.03</td>
</tr>
<tr>
<td>TOF$_D$ [h$^{-1}$]</td>
<td>143</td>
<td>138</td>
<td>0.96</td>
</tr>
<tr>
<td>TOF$_m$ [h$^{-1}$]</td>
<td>231</td>
<td>251</td>
<td>1.08</td>
</tr>
</tbody>
</table>

**Fig. 8.** Effect of catalyst particle size on the conversion of benzyl alcohol and selectivities to benzaldehyde, $S_m$ and toluene, $S_T$. Reaction conditions: Au-Pd/TiO$_2$ catalyst, 100 mg; oxygen pressure: 8.4 bara; liquid pressure, 10 bara; reaction temperature, 120°C.

**Table 1** Comparison of TOFs for different liquid flow rates. Reaction conditions: Au-Pd/TiO$_2$ catalyst (90–125 μm), 50 or 100 mg; catalyst contact time, 192–577 g$_{\text{cat}}$/g$_{\text{alcohol}}$; oxygen pressure: 8.4 bara; liquid pressure, 10 bara; reaction temperature, 120°C.

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where \( k_{on} \) is the oxygen mass transfer coefficient in the Teflon AF-2400 membrane, and is inversely proportional to the membrane thickness (shown in the Supporting Information) [25].

So, akin to an overall effectiveness factor in terms of internal and external mass transfer in a single pellet [34], a permeation-transverse mass transfer effectiveness factor (\( \eta \)) is described by

\[
\eta = \frac{\sinh \sqrt{Da}}{\sqrt{Da} \left( \cosh \sqrt{Da} + \frac{\Delta m}{m} \sinh \sqrt{Da} \right)}
\]

(12)

For the Au-Pd/TiO\(_2\) catalyst in the current flat membrane microchannel reactor, the Biot number is 68.6 (see Supporting Information), which indicates that the oxygen permeation rate in the membrane is much higher than the oxygen transverse mass transfer rate in the packed bed. This results to slight increase of oxygen consumption rate when halving the membrane thickness. Using an estimated first-order reaction rate constant from the batch reactor, the Damköhler number is 5207, which suggests that the oxidation reaction in the membrane reactor is transverse mass transfer-controlled. The permeation-transverse mass transfer effectiveness factor is found to be 0.7%, which agrees with the ratio (1.5%) of the observed TOFO in the membrane reactor (\( \sim 130\, \text{h}^{-1} \)) to the batch reactor (\( \sim 8800\, \text{h}^{-1} \)).

Since the oxygen transverse mass transfer rate is inversely proportional to the liquid channel depth, reduction in the liquid channel depth is expected to improve the performance of the membrane reactor for oxidation of benzyl alcohol. To confirm this, another reactor was fabricated with half the liquid channel depth (0.5mm) but the same channel width (3mm) as compared to the previous design. The amount of packed catalyst was also halved to keep the length of catalyst bed the same. At the same catalyst contact time (577 \text{ Biot} \sqrt{\text{molealcohol}}) and oxygen pressure (8.4 bara), a 75% conversion of benzyl alcohol with a 67% selectivity to benzaldehyde was obtained in the 0.5mm channel depth reactor, as compared to 57% conversion and 66% benzaldehyde selectivity in the 1.0mm channel depth reactor. This demonstrates that the main oxygen transfer resistance exists in the bulk liquid within the catalyst bed.

To predict catalyst performance in the packed bed membrane reactor and guide reactor design, the effectiveness factor is shown as a function of the observable \( \eta Da \) for various values of Biot number analogous to [34] in Fig. 9, together with the various regimes of possible controlling processes. When the reactor is in the transverse mass transfer controlling regime (as the symbols shown in Fig. 9, corresponding to the reactors with liquid flow channel depths of 1.0 mm (■) and 0.5 mm (●), indicate), decreasing the channel depth decreases the values of Da and Bi, which makes the effectiveness factor move towards the permeation or reaction controlling regime. When the reactor is in the permeation controlling regime, decreasing the membrane thickness increases the value of Bi, which makes the effectiveness factor move towards the reaction or transverse mass transfer controlling regime. Similarly, in the reaction controlling regime, the value of Da will increase if the reaction rate constant increases. This will make the effectiveness factor move towards the permeation or transverse mass transfer controlling regime.

3.7. Performance of the scaled-up membrane reactor

Scale-up of the flat membrane microchannel reactor was carried out through increasing the channel width by \( \sim 10 \) times, and the results obtained with fresh catalysts are shown in Table 2. The reactor was kept vertical and the liquid flowed from top to bottom. As compared to the previous microchannel reactor (channel width, 3mm), the scaled-up reactor showed a lower conversion of benzyl alcohol with a similar selectivity to benzaldehyde for the same catalyst contact time. The relative drop in conversion of \( \sim 17\% \) may be due to flow maldistribution in the wider liquid channel, possibly caused by nonuniform catalyst packing, as well as reduced oxygen flux across the membrane, due to the fins that were added in the gas channel for achieving equal flow distribution and acting also as membrane support. Nevertheless, the benzaldehyde throughput was demonstrated to be increased by a factor of 8 in the scaled-up microchannel reactor.

The effect of liquid flow direction on the performance of the scaled-up microchannel reactor was further investigated with the same (used) catalyst packing. The reactor was kept vertical with liquid flowing from top to bottom (Table 3a), bottom to top (Table 3b), or horizontal with liquid flowing from left to right (Table 3c). As shown in Table 3a, the conversion of benzyl alcohol was slightly lower (~5%) under the same conditions to that in Table 2, which could be caused by a slight catalyst deactivation after ~50h operation. However, for the three different flow directions, no obvious difference was observed in terms of conversion and selectivities. This indicates that the liquid flow direction has no effect on the liquid distribution within the liquid channel.

Finally, oxidation of benzyl alcohol was carried out with air in the scaled-up flat membrane microchannel reactor, since air is cheaper and easier to use as compared to pure oxygen. As shown in Fig. S6, the conversion of benzyl alcohol was 27%, with a selectivity of 63% to benzaldehyde. For the same reaction conditions with pure oxygen, the conversion and selectivity to benzaldehyde were 65% and 68%, respectively. The different performance in terms of conversion and selectivity was caused by the different partial pressures of oxygen; as discussed earlier, oxygen is beneficial for both conversion and benzaldehyde selectivity. These results highlight the efficiency of using pure oxygen, suggesting that to achieve similar performance with air, higher gas pressure would need to be utilised.

4. Conclusions

A flat Teflon AF-2400 membrane microchannel reactor was developed and applied for continuous flow aerobic oxidation of solvent-free benzyl alcohol on Au-Pd/TiO\(_2\) catalyst. As compared to a previous tube-in-tube membrane microreactor, the flat configuration provides wider operating pressure range and is more amenable to scale up. Both the small-width and the scaled-up reactors investigated in this work behaved isothermally, even though the reaction was highly exothermic. For further scale-up they can be combined with plate heat exchangers to realize the required temperature control. Higher reaction rates and desired product selectivities were observed at higher oxygen pressure, highlighting the importance of high oxygen concentration for this reaction. Study of the various oxygen transfer processes (permeation through membrane, transverse mass transfer in the catalyst bed, internal/external transfer in the catalyst particles) indicated...
that the main oxygen transfer resistance was in the catalyst bed. This agreed with a permeation-transverse mass transfer effectivness factor analysis, akin to internal-external mass transfer and reaction in a catalytic particle, which further provides guidance on catalyst choice and membrane reactor design. Scale-up of the microchannel reactor by an order of magnitude was demonstrated by increasing the width of the catalyst bed channel. The simple assembly of the flat membrane microchannel reactor suggests that other similar flat membranes could be used for scalable flow oxidation of organic compounds with molecular oxygen.

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Appendix A. Supplementary data

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References