Reaction and Raman spectroscopic studies of alcohol oxidation on gold–palladium catalysts in microstructured reactors

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\textbf{A B S T R A C T}

Oxidation of benzyl alcohol in the absence of solvent on 1\% (Au–Pd)/TiO\textsubscript{2} catalyst with pure oxygen was performed in silicon-glass micropacked-bed reactors (MPBRs). The overall size of the microreactor chip was 23 mm $\times$ 23 mm with a reaction channel dimension of 0.6 mm (W) $\times$ 0.3 mm (H) $\times$ 190 mm (L). A pillar structure (small rectangular posts of 60 $\mu$m (W) $\times$ 1 mm (L) 40 $\mu$m apart) was incorporated near the outlet of the reaction channel to retain the catalyst. The reaction was studied in the temperature range of 80–120 $^\circ$C and at inlet pressures up to 5 bar(a). Benzyl alcohol conversion and benzaldehyde selectivity at 80 and 120 $^\circ$C obtained in MPBRs were very close to those from conventional glass stirred reactors (GSRs) apart from the selectivity at 120 $^\circ$C. Toluene was formed in the absence of oxygen, and its production was enhanced in the presence of oxygen. Increasing pressure improved both conversion and benzaldehyde selectivity. Mass transfer resistance in MPBRs was evaluated experimentally. The external mass transfer resistance could be ignored at a volumetric flow ratio of gas (STP) to liquid above 100, at a given liquid flow rate (0.003 mL/min). The effect of catalyst particle size on the reaction was examined with two ranges of particle size: 53–63 $\mu$m and 90–125 $\mu$m. Lower conversion was obtained with particle sizes of 90–125 $\mu$m, indicating the presence of internal mass transfer resistances. In situ Raman measurements in MPBRs were performed using a specially designed microreactor stage with a different microreactor configuration. Raman spectra obtained from liquid pockets at different points along the reaction channel could be used to obtain the benzaldehyde concentration profile along the catalyst bed. Bands due to formation of highly disordered graphitic carbon were observed on the catalyst surface.

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1. Introduction

Catalytic oxidation of alcohols is of great importance for the manufacture of fragrances and many synthetic intermediates for organic synthesis [1,2]. Traditional methods for performing such a transformation involve the use of stoichiometric quantities of heavy inorganic oxidants, such as chromium(VI) or permanganate, which are toxic and pose significant environmental problems. Hence, the development of efficient and environment-friendly catalysts for alcohol oxidation using oxygen has attracted great research interest. Many researchers have reported the use of highly active metallic catalysts for the aerobic oxidation of alcohols [3].

After the pioneering work of Haruta et al. [4] who discovered that gold was the best catalyst for CO oxidation, and Hutchings [5] who showed gold to be the catalyst of choice for acetylene hydrochlorination, supported nano-gold catalysts have found a wide range of applications in selective chemical transformations [6]. With respect to alcohol oxidation, Au supported on CeO\textsubscript{2} [7], TiO\textsubscript{2} [8] and Ga\textsubscript{2}Al\textsubscript{3}O\textsubscript{9} [9] have shown effective catalytic activity. Pd supported on various supports has been found to be active for the oxidation of alcohols [10,11]. Recently, Hutchings and co-workers discovered that an alloy of Au and Pd led to a 25-fold enhancement in activity and higher selectivity by comparison to the Au or Pd mono-metallic catalysts [8]. After this discovery, supported Au–Pd catalysts have been used for the oxidation of various alcohols especially benzyl alcohol and glycerol [12–14]. Efforts have been made to improve the activity of these catalysts by modifying the synthesis procedure to get smaller particles with much narrow distribution [13]. Conventionally, reaction and kinetic studies for gas–liquid–solid systems are performed either in stirred glass vessels, autoclaves...
or in packed-bed reactors (trickle bed reactors). The continuous packed-bed reactor systems have the advantages of simplifying the process by eliminating the separation of liquid products and solid catalyst and performing the test over longer time to examine the stability of catalyst. However, flow maldistribution, incomplete wetting in packed-bed and associated external mass transfer limitations and temperature gradients could affect significantly the accuracy of kinetics under investigation [15]. In laboratory trickle bed reactors, the shortcomings can be resolved by diluting the catalyst bed with fine inert particles [16–20]. The dilution reduces axial dispersion substantially to achieve plug-flow and results to higher liquid hold-up which improves the wetting efficiency at lower velocities of gas and liquid. However, the bed dilution may also affect the residence time distribution of liquid in the bed and influence the reactant conversion due to local bypass effects [21,22].

Process miniaturization and microreaction technology have provided opportunities for improving process capability and control in chemical synthesis. In microreactors, the elevated temperature and reaction zone is confined to a small volume, which allows safer and more efficient chemical kinetics investigations. Losey et al. [23] reported the fabrication and testing of micropacked-bed reactors for gas–liquid catalytic hydrogenation of cyclohexene. Pt/Al2O3 catalyst powder with particle sizes 36–75 μm was packed into microchannel reactors without dilution. The improvement in mass transfer offered by the microreactor was demonstrated, which showed more than 100-fold increase in the value of gas–liquid mass transfer coefficient by comparing to the traditional multiphase fixed bed reactors. van Herk et al. [24] reported a multiple-parallel gas–liquid packed-bed microreactor system for performing catalyst testing. The reactors had an inner diameter of 2.2 mm and a packed-bed length of 475 mm. Reproducible and intrinsic kinetic results were obtained under conditions where the liquid flow rate, catalyst and inert dilution ratio and the sizes of catalyst and inert were optimized. The work reported here focuses on studying the catalytic oxidation of benzyl alcohol on Au–Pd/TiO2 catalyst using micropacked-bed reactors (MPBRs) and evaluating the performance of MPBRs with respect to the gas–liquid–solid mass transfer.

Spectroscopic technologies are important in the study of catalytic reactions for obtaining molecular insight and better understanding of the reaction mechanism, and can help in catalyst development and improvement. The application of spectroscopic techniques including Raman and X-ray absorption spectroscopy in microstructured reactors has been reported for homogeneous liquid systems [25–27] and for gas phase catalytic reactions [28,29]. It is an attractive approach for monitoring catalytic reactions and active species but has so far received little attention in a gas–liquid–solid reactor system. One goal of this work was to explore the feasibility of using in situ Raman spectroscopy in the study of catalytic oxidation of benzyl alcohol with molecular oxygen in MPBRs.

2. Experimental methods

2.1. Catalyst preparation

For the preparation of (Au–Pd)/TiO2 materials, aqueous solutions of PdCl2 (Sigma Aldrich) and HAuCl4 · 3H2O (Sigma Aldrich) of the desired concentrations were prepared. Polyvinylalcohol (PVA) (1 wt% aqueous solution, Aldrich, MW = 10,000, 80% hydrolyzed) and an aqueous solution of NaBH4 (0.1 M) were also prepared. To a mixed aqueous PdCl2 and HAuCl4 solution of the desired concentration, the required amount of a PVA solution (1 wt%) was added (PVA/(Au + Pd) [wt/wt] = 1:2); a freshly prepared solution of NaBH4 (0.1 M, NaBH4/[Au + Pd] (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilized by adding titania (Degussa, P25) and acidified to pH 1 by concentrated sulfuric acid under vigorous stirring. The amount of support material required was calculated so as to have a total final metal loading of 1 wt% with a metal ratio of 1:1 molar. After 2 h, the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight under static air. STEM-HAADF analysis of the prepared catalyst proved that the Au–Pd nanoparticles supported on TiO2 were homogeneous alloys with 1:1 ratio [30]. Furthermore, the filtrate solution was checked for the presence of Au and Pd. It was found that there were no metal ions in the filtrate [30], indicating that all the metals are immobilized on to the support.

2.2. Microreactor system

Catalytic oxidation of benzyl alcohol on the supported Au–Pd/TiO2 catalyst was carried out in a continuous flow microreactor which is assembled with a heating and temperature control unit (Fig. 1). The overall size of the silicon/glass microreactor chip was 23 mm × 23 mm with a reaction channel dimension of 0.6 mm (W) × 0.3 mm (H) × 190 mm (L). A pillar structure (small rectangular posts of 60 μm (W) × 1 mm (L)) was arranged at 40 μm intervals near the outlet of the reaction channel to retain the catalyst. The prepared catalyst powder was pelletized and then crushed to obtain the desired particle size fraction by sieving. The catalyst was then introduced into the reaction channel through the gas inlet with the help of vacuum at the outlet of the reaction channel. The reactor chips were prepared with different catalyst bed lengths. The weight of the catalyst loaded was determined by weighing the reactor chip before and after packing and was in the range of 2.6–14 mg.

The microreactors were fabricated by photolithography and deep reactive ion etching (DRIE) on 4” silicon wafers. The structured wafers, each containing nine microreactors, were covered with a Corning 7740 glass wafer (1 mm thick, with holes pre-drilled as inlets and outlets) and sealed by anodic bonding. Each bonded wafer was diced to obtain nine reactors. The microreactor, packed with catalyst, was mounted into a stainless steel heating block using a clamp on which flanged Teflon tubes were fitted for inlet and outlet. A ceramic packing containing thermocouples and heat cartridges was used for heating and housing the microreactor assembly.

2.3. Experimental procedures

2.3.1. Reaction in microreactors

Liquid alcohol (benzyl alcohol, 99.98%, Sigma–Aldrich) was delivered into the reactor by a liquid pump (milliGATTM). Gases were regulated by mass flow controllers (Brooks 5850TR) and directed to the gas inlet of the reactor. The effluent from the reactor passed into a small glass vial (2 mL) which was located in a cold trap (ice-water bath), where gas and liquid were separated and the liquid product was collected (Fig. 1).

Quantitative analysis was carried out using an Agilent 6890 GC with FID, a HP-INNOWax (19091-133) capillary column and an auto-liquid-sampler. Considering the amount of product from a microreactor is relatively small, an analytical protocol was employed by using mesitylene as a diluent and decane as an internal standard. 10 μl of the sample from the collected vial was taken and added to 0.5 ml mesitylene with the internal standard.

Experiments were started by setting the reactor temperature, gas flow rate and the alcohol flow rate to desired values. All the gas flow rates reported are in ml/min at Standard Temperature and Pressure (STP, 0 °C and 1.01325 bar). Once the reactor reached the set temperature, the reaction was carried out for another 20 min to stabilize the reaction system. Collection of reaction products was...
then started using a new sample vial. The first sample was taken and analyzed after 40 min and the second sample after another 20 min. Benzyl alcohol conversion ($X$) was calculated from the measured concentration of the alcohol in the outlet of the reactor:

$$X = \frac{C_{\text{alcohol,in}} - C_{\text{alcohol,out}}}{C_{\text{alcohol,in}}} \times 100\%.$$  

Selectivity to product ($S_i$) was calculated as the moles of the alcohol converted into the product divided by the total mole of the alcohol converted:

$$S_i = \frac{C_{i,\text{out}} v_i}{C_{\text{alcohol,in}} A} \times 100\%,$$

where $v_i$ is the mole number of the alcohol needed to produce 1 mole of the product. Carbon balance was obtained by comparing the sum of carbon moles in the outlet with that in the inlet of the reactor:

$$\text{Carbon Balance} = \left(1 - \sum C_{i,\text{out}} n_i \frac{v_i}{C_{\text{alcohol,in}} A}\right) \times 100\%$$

where $n_i$ is the number of carbon atoms in component $i$. Loss of benzyl alcohol, benzaldehyde and toluene in the liquid sample collection process can be ignored due to their very low vapor pressures (0.33, 7.2 and 896 Pa at 0°C for benzyl alcohol, benzaldehyde and toluene respectively). The carbon balance was within ±5%.

2.3.2. Reaction in glass stirred reactors

Benzyl alcohol oxidation was carried out in a Radleys carousel reactor using a 50 mL glass stirred reactor. In a typical reaction, the requisite amount of catalyst and substrate were charged into the reactor at room temperature which was then purged with the required gas (O$_2$ or He) 3 times before the reactor was sealed using a Teflon screw threaded cap. The reactor was always connected to the gas line to ensure the consumed O$_2$ or He would be topped up. The pressure was measured using the pressure gauge fitted in the inlet line. There was no change in the pressure during the course of the reaction. The reactor with the reaction mixture was loaded into a preheated heating block, which was maintained at the reaction temperature. The reaction started by switching on the stirring inside the reactor with a magnetic bar at 1000 rpm. After a specific time, the stirring was stopped and the reactor was cooled in an ice bath immediately. After cooling for 10 min, the reactor was opened slowly and the contents were centrifuged. An aliquot of the clear supernatant reaction mixture (0.5 mL) was diluted with mesitylene (0.5 mL) for GC analysis. It was established that no reaction occurred in the absence of the Au–Pd catalyst or in the presence of the catalyst support alone. Mass transfer was found not to be rate-limiting at a stirring speed of 500 rpm or above.
Raman measurements in gaseous atmospheres were carried out at 3.1. Oxidation of benzyl alcohol on 1% (Au–Pd)/TiO2 catalyst in packed reactor channel and at different positions along the catalyst bed under steady state reaction conditions.

Measurements under the gas–liquid flow mode, Raman spectra were taken from different spots at the same axial position of the reactor channel and at different positions along the catalyst bed. For in situ Raman measurement, a microreactor stage was used for these experiments (see inset of Fig. 2a). The overall size of the new reactor chip was 58 mm (particle size 53–63 µm) with 8 mm of glass bead bed (63–75 µm) added before the catalyst.

The whole setup (Fig. 1) was located near the Raman spectrometer; the microreactor stage was sited under the microscope, as shown in Fig. 2b. In situ Raman measurements were carried out using a Renishaw inVia Raman spectrometer coupled to a Leica microscope. Spectra were excited using the 514.5 nm line from a LaserPhysics argon ion laser. Raman scattered light was detected using a CCD. Spectra were recorded with an integration time of 20 s and averaged 2 times.

The catalyst packed in the reactor was firstly treated in Ar at 120 °C overnight and cooled to room temperature with Ar flow. Raman measurements in gaseous atmospheres were carried out at 120 °C and Raman spectra were acquired under argon, under O2 flow and in O2 flow containing benzyl alcohol. For in situ Raman measurements under the gas–liquid flow mode, Raman spectra were taken from different spots at the same axial position of the packed reactor channel and at different positions along the catalyst bed under steady state reaction conditions.

3. Results and discussion

3.1. Oxidation of benzyl alcohol on 1% (Au–Pd)/TiO2 catalyst in MPBR

3.1.1. Effect of reaction temperature

Oxidation of benzyl alcohol on 1% (Au–Pd)/TiO2 catalyst was first studied in a MPBR with a catalyst bed length of 48 mm. The reaction was carried out at 80, 100, 120 and 140 °C respectively, with an O2 flow of 0.3 mL/min and an alcohol flow of 0.003 mL/min. Conversion of alcohol and selectivities to benzoic acid and benzyl benzoate are listed in Table 1. Observed pressure drops over the range of temperatures studied were around 0.82 bar and did not vary with temperature significantly.

It can be seen from Fig. 3 that conversion of benzyl alcohol increases with reaction temperature from ~20% at 80 °C to ~84% at 140 °C. Selectivities to benzaldehyde and toluene show opposite dependence on temperature. The selectivity to benzoic acid decreases from ~81% at 80 °C to 56% at 140 °C, while to toluene increases from ~16% to 40% over the same temperature range. Selectivity to benzene, dibenzyl ether, benzoic acid and benzyl benzoate decreases slightly with temperature. Selectivity to dibenzyl ether shows an increase with temperature.

3.1.2. Effect of inlet pressure

The effect of pressure on the reaction was studied at 120 °C with an O2 flow of 0.6 mL/min and an alcohol flow of 0.003 mL/min (G/L = 200). The inlet pressure (absolute) of the reactor was varied from 2.1 bar to 5 bar. Fig. 4 shows that conversion increases from 78.5% at 2.1 bar to ca. 95% at 5 bar. Significant improvement to selectivity to benzaldehyde is observed in the whole range of pressures studied. The selectivity to benzaldehyde increases from 57.7% to 77.8%, which is correspondently accompanied with a decrease in selectivity to toluene from 38.5% to 15.8%. Selectivity to other products is listed in Table 2. Selectivity to benzene is not sensitive to pressure change, while selectivity to dibenzyl ether shows a decrease from 2.09% to 0.41%. Benzoic acid and benzyl benzoate show a pronounced increase in selectivity with pressure.

Increasing the inlet O2 pressure at a constant mass flow rate has a twofold effect on the reaction. One is the increase of the O2 solubility in reaction solution and increase in space time, which results in...
in an increase of the reaction rate. The other effect is the reduction in actual volumetric flow rate to such extent that the actual volumetric ratio of gas and liquid (G/L) is reduced, leading to a poor mass transfer in the catalyst bed and a reduction in reaction rate. The dependence of benzyl alcohol conversion on pressure, shown in Fig. 4 may reflect the combination of these effects of the inlet pressure.

### 3.1.3. Discussion

For the oxidation of benzyl alcohol on Au–Pd/TiO₂ catalyst, the high amount of toluene produced has been related to very active sol-immobilized catalysts and their higher dehydrogenation activity [12]. It can be seen that the selectivity to toluene is significantly affected by reaction temperature and pressure. The full mechanisms for the formation of benzaldehyde and toluene on Au–Pd/TiO₂ have not been fully established. It has been suggested that toluene and benzaldehyde are formed by competing parallel reactions of the initial benzyl intermediate via an adsorbed benzyli-dene species on the catalyst surface that can be either hydrogenated or oxidized [12]. In the absence of O₂, disproportionation of benzyl alcohol occurs with the formation of equal amounts of toluene and benzaldehyde [31]:

\[
2\text{PhCH}_2\text{OH} \rightarrow \text{PhCH}_3 + \text{PhCHO} + \text{H}_2\text{O}
\]

The formation of toluene increases with reaction temperature, in both the cases with and without presence of O₂ (Figs. 3 and 5). Using the data from the same reactor operated with N₂ (Fig. 5) or O₂ (Fig. 8, Section 3.3.2) at 120 °C and at a same flow conditions (O₂ = 0.3 mL/min, alcohol = 0.003 mL/min), the yield of toluene (conversion of benzyl alcohol multiplied by selectivity to toluene) can be calculated as 6.8 and 30.2%, respectively. The formation of toluene is significantly enhanced in the presence of O₂. This enhancement of toluene formation at low O₂ pressure was also observed by Meenakshisundaram et al. [32] in GSRs at 80 °C. However, with further increasing O₂ pressure, the production of toluene is reduced while the selectivity to benzaldehyde is significantly improved (Fig. 4). It seems that on (Au–Pd)/TiO₂ catalyst, O₂ has a twofold effect on the oxidation of benzyl alcohol. At low O₂ pressure, evidence has been obtained for the existence of two separate disproportionation mechanisms leading to benzaldehyde and toluene. The rate of one of these pathways is enhanced by the presence of O₂ [32]. Dimitratos et al. [12] suggested that carbonyl oxide may be formed on the catalyst surface through a surface benzylidene with the presence of O₂, which further fragments to yield free benzaldehyde and an oxo-species on the surface, capable of generating a further molecule of benzaldehyde. With increasing the O₂ pressure, the equilibrium concentration of O₂ in reaction solution increases, which increases the availability of O₂ on the catalyst surface and favors the formation of benzaldehyde.

### 3.2. Comparison of micropacked-bed reactor (MPBR) and glass stirred reactor (GSR)

The performance of MPBRs was compared with that of traditional glass stirred reactors based on the conversion and selectivity of the reaction at the same space times (STs) in both reactors. The ST is defined as follows:

For micropacked-bed reactor,

\[
ST = \frac{\text{mass of catalyst (g}_{\text{cat})}}{\text{alcohol mass flowrate (g}_{\text{alc}}/\text{s})}.
\]

And for glass stirred reactor,

\[
ST = \frac{\text{mass of catalyst (g}_{\text{cat})}}{\text{mass of alcohol (g}_{\text{alc}})} \times \text{reaction time (s)}.
\]

In MPBRs, different space times were obtained by packing the micoreactors with different catalyst bed lengths (with particle size of 53–63 μm, see Fig. 6b) while keeping gas and liquid flow rates constant. Three micropacked reactors were prepared with catalyst bed lengths of 20, 48, and 120 mm respectively. Reactions were carried out at 80 and 120 °C at atmospheric pressure with fixed alcohol flow of 0.003 mL/min and O₂ flow of 0.3 mL/min (STP), corresponding to space times of 50, 119, and 268 gcat/galc respectively. The main products observed in MPBRs were benzaldehyde and toluene. Conversion of benzyl alcohol and selectivity to benzaldehyde and toluene in the micropacked reactors at different space times are listed in Table 3. Other observed side products were benzene, benzoic acid, benzyl benzoate and dibenzyl ether with a total selectivity of 3–4%.

The oxidation of benzyl alcohol was also carried out in GSRs at the same space times at 80 and 120 °C respectively. The GSRs were loaded with 2 g of benzyl alcohol and 0.02 g of the catalyst and the reaction was carried out with 1 bar (g) of O₂ and a stirring speed of 1000 rpm. The catalyst used in experiments was crushed to small particles (<20 μm) and their size and shape did not significantly change before and after reaction, as seen from SEM micrographs (Fig. 6). The reaction products observed were mainly benzaldehyde and toluene, with traces of benzoic acid and benzyl benzoate.

### Table 2

<table>
<thead>
<tr>
<th>P, bar(a)</th>
<th>Benzene</th>
<th>Dibenzyl ether</th>
<th>Benzoic acid</th>
<th>Benzyl benzoate</th>
</tr>
</thead>
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<tr>
<td>2.1</td>
<td>0.68</td>
<td>2.09</td>
<td>0.42</td>
<td>0.63</td>
</tr>
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<td>3.1</td>
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<td>1.29</td>
<td>1.07</td>
<td>0.81</td>
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<td>4</td>
<td>0.84</td>
<td>0.62</td>
<td>4.17</td>
<td>1.52</td>
</tr>
<tr>
<td>5</td>
<td>0.92</td>
<td>0.41</td>
<td>3.26</td>
<td>1.88</td>
</tr>
</tbody>
</table>

![Fig. 5. Disproportionation of benzyl alcohol on Au–Pd/TiO₂ catalyst at different temperatures (benzyl alcohol flow 0.003 mL/min, N₂ flow 0.3 mL/min, T = 120 °C, bed = 120 mm).](image-url)
Conversion of benzyl alcohol and selectivity to benzaldehyde and toluene are listed in Table 3.

It can be seen from Table 3 that the conversions obtained in both types of reactors are very close. At 80°C, conversions in MPBRs are slightly higher than those in GSRs, with relative differences less than 9%. At 120°C, relative differences in conversion are much smaller in both types of reactors. Selectivity in both types of reactors shows the same patterns of dependences on space time and temperature. However, lower selectivity to benzaldehyde and higher selectivity to toluene is observed in MPBRs especially at 120°C. It is noted that the GSRs were operated at O2 pressure of 1 bar (g), while in MPBRs, the outlet was kept at atmospheric pressure, the inlet pressure varied from 0.2 to 1.25 bar (g). This might be one of the reasons for the lower selectivity to benzaldehyde and toluene by considering the effect of O2 pressure on the selectivity of the reaction. Another factor which might affect the performance of the two reactors could be the catalyst particle size (Fig. 6), which will need further investigation.

3.3. Study of mass transfer effects in MPBR

3.3.1. Effect of flow rate on performance of MPBRs

Since intrinsic kinetics depend only on space time and should be independent of flow velocity, external mass transfer resistances in a MPBR can be conveniently checked by variation of gas flow rate while keeping liquid flow rate constant [19]. The effect of O2 flow rate on conversion and selectivity of oxidation of benzyl alcohol was studied at 120°C at a constant alcohol flow rate of 0.003 mL/min in three MPBRs with catalyst bed length 20, 48 and 120 mm, corresponding to space times of 50, 119 and 268 s/galc respectively (using catalyst particle size of 53–63 μm). O2 flow rate was varied from 0.06 to 0.6 mL/min, corresponding to gas to liquid (G/L) values of 20–200. It can be seen from Fig. 7 that conversion of benzyl alcohol shows a pronounced increase with the ratio of gas to liquid (G/L) values up to 20–200. It can be seen from Fig. 7 that conversion of benzyl alcohol shows a pronounced increase with the ratio of gas to liquid (G/L) values up to 20–200. With further increasing O2 flow rate, conversions become independent of G/L flow ratio for MPBRs with Lbed of 20 and 48 mm. This independence is observed for the MPBR with Lbed of 120 mm at a higher G/L (=150). Selectivity to benzaldehyde and toluene is less affected by the G/L ratio, showing a slight increase to benzaldehyde and a minor decrease to toluene. Selectivities to other products are relatively low (<4% in total) and increase slightly with the G/L ratio (data not shown). Pressure drops increase with G/L almost linearly from 0.5 bar at G/L = 20 to 1.12 bar at G/L = 200 in the MPBR with Lbed = 48 mm and from 0.82 bar to 1.7 bar in MPBR with Lbed = 120 mm in the same G/L range.

In large-scale trickle bed reactors, the dominant flow patterns are trickling flow and pulsing flow. It has been shown that operating in a pulsing flow regime can improve the performance of trickle beds, but for kinetic studies, this would complicate the interpretation of mass transfer and kinetics [33] and should be avoided. The transition from trickling flow to pulsing flow in large-scale trickle beds can be estimated using the flow regime map developed by Charpentier and Favier [34]. However, in micropacked-beds, the dominant forces are viscous and interfacial forces, which lead to flow patterns completely different to those observed in large-scale trickle beds. A flow regime map presented by Losey et al.
[23] shows different pulsing transition points in micropacked beds in comparison to those in large-scale trickle beds. In the current study, the MPBRs should be operating in the trickling range based on the Losey et al. flow regime map. However, visual observation of the fluid flow in MPBRs showed a pulsing-trickling pattern, because a stable gas–liquid slug flow was formed in the microchannel before entering the catalyst bed. The size (or the length) of the pulsing region of the reactor depended on the gas flow rate. At a given liquid flow rate, high gas flow rate led to short slugs, which in turn led to short pulsing flow region.

The observed increase in benzyl alcohol conversions with increasing O₂ gas flow rate may suggest that mass transfer resistances played a role in the observed reaction data. However, at G/L > 100, the conversion shows less dependence on O₂ flow rate, indicating little influence of mass transfer. In Fig. 7, the conversions obtained in the GSR at different space times are also shown. The stabilization of conversion of the MPBRs occurs at approximately the same level of conversion as the GSR conversion. Considering that for the GSR data external mass transfer resistances were eliminated, the above indicates an absence of external mass transfer resistance in the MPBRs. It is noted that the pressure drop increased significantly with gas flow rate in MPBR with longer bed length, causing a higher inlet pressure in a longer bed MPBR than in shorter ones. The higher inlet pressure may also have contributed to the improved conversion in the longer catalyst bed of the MPBR.

3.3.2. Effect of catalyst particle size

The internal mass transfer is affected by catalyst support size. Oxidation of benzyl alcohol in two micro packed-bed reactors with a catalyst bed length of 120 mm and two catalyst particle size ranges (53–63 µm and 90–125 µm) was studied at different temperatures with an O₂ flow of 0.003 ml/min and a G/L of 100. Fig. 8 shows the conversion of alcohol and selectivities to benzaldehyde and toluene. In general, the dependences of conversion and selectivity on the reaction temperature with two catalyst particle sizes are similar, that is, the conversion of the alcohol increases with temperature while selectivity to the aldehyde decreases and to toluene increases with temperature. However, the reaction with smaller catalyst particle size produces higher conversion, especially at lower reaction temperature. It can be seen that the conversion at 80 °C is 18% with the particle size of 90–125 µm, compared to that of 47% with the particle size of 53–63 µm at the same temperature. At 140 °C, the differences in conversion for these two catalyst particle sizes are much reduced (91.7% with 90–125 µm particle and 94.4% with 53–63 µm particle). Particle size has less effect on product selectivity, showing almost the same dependence on temperature; at a given temperature, selectivities to benzaldehyde and toluene are almost same. Pressure drops over two reactors were less affected by temperature but were significantly affected by catalyst particle size: the pressure drop was 0.4–0.5 bar for the reactor with catalyst particle sizes of 90–125 µm and 1.2–1.27 bar with particle size of 53–63 µm.

Without intrinsic kinetics, it is difficult to estimate the effectiveness factor of the catalyst used in the current work. The behaviour in Fig. 8 may be due to the lower oxygen pressure and/or internal mass transfer resistance within the catalyst with a particle size of 90–125 µm. It is worth noting that at higher temperatures, con-
version approaches 100%, which could mask the presence of mass transfer resistance. Further reducing the size of catalyst particles was not considered since it would increase the pressure drop dramatically.

### 3.4. Raman measurements

Raman spectra were first acquired from the 1 wt% Au–Pd/TiO<sub>2</sub> catalyst surface at 120 °C in different gaseous atmospheres and shown in Fig. 9. The spectra are dominated by a rising background to longer wavelength (greater Raman shift) indicating electronic fluorescence from transition metal ions contained in the catalyst. These could correspond to oxidised Pd species (Pd<sup>4+</sup>) or slightly reduced TiO<sub>2</sub> (Ti<sup>3+</sup>), for example. The initial Raman spectrum obtained in argon flow shows typical peaks of the catalyst support TiO<sub>2</sub> (anatase) at Raman shifts of 143, 395, 517 and 634 cm<sup>-1</sup> respectively. The metallic Au–Pd particles have no intrinsic Raman spectrum. Strong broad features are observed at 1350 and 1585 cm<sup>-1</sup>. These are due to highly disordered graphitic carbon species derived from pyrolysis of hydrocarbon species, either initially present on the catalyst surface or perhaps introduced with the argon gas flow. By introducing O<sub>2</sub> into the MPBR, most of this band intensity was removed after 20 min indicating oxidation of the carbonaceous material thus cleaning the catalyst surface. Benzyl alcohol vapor was then introduced into the O<sub>2</sub> flow by delivering the alcohol at a flow rate which was exactly the amount of liquid required for saturating the O<sub>2</sub> flow and was evaporated on the reactor chip at 120 °C. The Raman spectrum was recorded after dosing benzyl alcohol for 20 min. No peaks could be observed that might be assigned to intermediate species linked to the catalyst surface. Such peaks could be present, but they might be obscured by the strong fluorescence signal. It can be seen from Fig. 9 that even within the same axial position relative to the reactor channel:

1. Fully wetted catalyst with liquid pocket (liquid flows in the gap of particles).
2. Fully wetted catalyst with a thin layer of liquid film.
3. Dynamically wetted catalyst surface where a very thin layer of liquid arrives and leaves from the surface, leaving the catalyst surface fluctuating between wetted and unwetted states.
4. Un-well-wetted catalyst surface, where the particle is very close to or contacts the glass wall of the micropacked-bed reactor. The surface may be not covered with liquid but may be saturated with liquid in pores.

By focusing the laser on different spots at the same axial position within the microchannel we could obtain several different types of spectra that can help calibrate our in situ observations (Fig. 10).

**Raman spectrum 1**: The laser was focused inside a liquid pocket. A typical spectrum of the reaction mixture (mainly containing benzyl alcohol, benzaldehyde and toluene) under reaction conditions was observed (compare to Fig. 11). Assignments of the strongest lines in the Raman spectrum are listed in Table 4. The spectrum was reproducible for all other liquid pockets examined at the same axial position within the reactor channel. We note that there is only minimal fluorescence that we believe to be associated with the catalyst surface and useful spectra could be recorded up to >3000 cm<sup>-1</sup> within the range of C–H vibrations. Also we see no obvious strong features associated with carbon deposition, although a weak underlying signature may possibly be present in the 1000–1700 cm<sup>-1</sup> region.

![Fig. 9. Raman spectra from catalyst surface at 120 °C at different gaseous atmospheres.](image-url)

![Fig. 10. Raman spectra obtained from different types of spots at a same axial position in the packed bed.](image-url)

![Fig. 11. Raman spectra obtained from liquid pockets at different axial positions of the packed bed (benzyl alcohol flow = 0.003 mL/min, O<sub>2</sub> = 0.3 mL/min, L<sub>bed</sub> = 58 mm, catalyst size 53–63 µm, T = 100 °C).](image-url)
Table 4

<table>
<thead>
<tr>
<th>Raman shift, cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>Symmetric ring stretch</td>
</tr>
<tr>
<td>1200–1208</td>
<td>ϕ-CHO</td>
</tr>
<tr>
<td>1384</td>
<td>C–H aldehyde bend</td>
</tr>
<tr>
<td>1393</td>
<td>Phenyl ring C–C stretch</td>
</tr>
<tr>
<td>1694–1700</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>3066</td>
<td>Ring C–H stretch</td>
</tr>
</tbody>
</table>

Raman spectrum 2: Here the laser was focused on a liquid layer of a wetted catalyst surface. The spectrum shows a slightly enhanced fluorescence background from the catalyst support and additional peaks (395, 510 and 634 cm⁻¹) of TiO₂ are present. The relative intensities of the 1597 (benzyl alcohol, benzaldehyde) and 1700 cm⁻¹ (benzaldehyde) peaks appear to be different; however, that could be affected by the presence of a broad band between 1200 and 1650 cm⁻¹ that we believe is due to production of amorphous carbon.

Raman spectrum 3: In this dynamically wetted region, liquid initially covered the measurement spot but with a very small thickness that changed during the experiment. Although sharp Raman peaks are observed due to the TiO₂ catalyst support and the benzyl alcohol/benzaldehyde molecules the spectrum is dominated by broad features covering most of the spectral range. These are most likely due to fluorescence from the catalyst surface. Although the broad features appear to have some structure, with a dip near ~1800 cm⁻¹, this could be due to the dynamic nature of the experiment that could obscure part of the signal arriving at the detector during the collection and averaging process.

Raman spectrum 4: On an un-well-wetted region, the laser produced a focusing spot similar to those on clear solid surface. Here the fluorescence signal was very strong and caused saturation of the detector for our standard recording conditions used for the other experiments. No Raman features could be observed.

In situ measurement of the evolution of the reaction product benzaldehyde was then carried out in the micropacked-bed reactor at 100 °C, benzyl alcohol flow of 0.003 mL/min and O₂ flow of 0.6 mL/min. The reaction system reached a stable state and Raman measurements were carried out at different positions along the catalyst bed. The measuring position and their corresponding catalyst bed lengths in the micropacked channel are listed in Table 5. Raman spectra obtained at these positions are presented in Fig. 11. Ex situ Raman spectra for benzyl alcohol and benzaldehyde and their mixtures were also acquired for calibration. The Raman peak at 1700 cm⁻¹ is specific to C=O stretching of benzaldehyde and this can be used for quantitative determination of the production of this compound [36]. The principal symmetric aromatic ring breathing mode at ~1000 cm⁻¹ exists for the starting benzalcohol as well as for the main products benzaldehyde and toluene, so it can likely be used as an intensity standard for studies of the mixtures once properly calibrated.

It can be seen from Fig. 11 that the formation of benzaldehyde (1700 cm⁻¹) is readily observed at Position 1 that it is located about 2.2 mm from the entrance of the catalyst bed. Benzaldehyde formation increases along the catalyst bed as indicated by the relative peak height and area. The formation of benzaldehyde is also indicated by slight shifts occurring in the peaks involved in the band between 1130 and 1220 cm⁻¹; three peaks at 1156, 1177 and 1200 cm⁻¹ for the reactant benzyl alcohol gradually become two peaks at 1163 and 1200 cm⁻¹ for pure benzaldehyde. We also noted that the underlying broad band in the 1100–1650 cm⁻¹ region becomes more apparent, and the peak at 1597 cm⁻¹ shows increased broadening. These observations indicate the formation of disordered graphitic material that may be present, suspended within the liquid.

To quantify the concentrations of benzaldehyde at different positions, a calibration was carried out by measuring the peak area ratio of the 1000 and 1700 cm⁻¹ bands in known mixtures of benzyl alcohol and benzaldehyde, with the peak at 1000 cm⁻¹ acting as an internal standard. The calculated concentrations of benzaldehyde using this method at different positions along the length of the packed bed are listed in Table 5. From Table 5 the yield of benzaldehyde is then obtained by dividing the benzaldehyde concentration (Cald) with the concentration of benzyl alcohol at inlet (Ccalc,in) which is shown in Fig. 12. At Position 11, which corresponds to a packed-bed length of 51.6 mm, a yield of benzaldehyde of 35% is observed. The yield in the MPBR with catalyst bed length of 48 mm (see Fig. 3) is 30%. These yields compare very well, considering the slightly different bed length and also that the reactor chips and the analysis methods were different (GC and Raman).

4. Conclusions

Oxidation of benzyl alcohol on 1% (Au–Pd)/TiO₂ catalyst was studied using micropacked-bed reactors (MPBRs). Conversion and selectivity at 80 and 120 °C obtained in MPBRs are very close to those from conventional glass stirred reactors (GSRs) apart from the selectivity at 120 °C. The discrepancy in selectivity may come from the operating pressure differences between the two reactor types. Main products of the reaction are benzaldehyde and toluene. The conversion of benzyl alcohol increases with reaction temperature and O₂ pressure, while the selectivity to benzaldehyde decreases with temperature and increases with O₂ pressure. Increasing O₂ pressure increases the availability of O₂ on the catalyst and favors the formation of benzaldehyde. Mass transfer resistance in MPBRs was evaluated experimentally. The external mass transfer resistance can be ignored at a volumetric ratio of

Table 5

<table>
<thead>
<tr>
<th>Position</th>
<th>Lbed, mm</th>
<th>Cald, mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.2</td>
<td>0.095</td>
</tr>
<tr>
<td>3</td>
<td>10.7</td>
<td>0.201</td>
</tr>
<tr>
<td>5</td>
<td>22.6</td>
<td>0.891</td>
</tr>
<tr>
<td>7</td>
<td>31.2</td>
<td>1.515</td>
</tr>
<tr>
<td>9</td>
<td>43.1</td>
<td>1.959</td>
</tr>
<tr>
<td>11</td>
<td>51.6</td>
<td>3.324</td>
</tr>
</tbody>
</table>

Fig. 12. Yield of benzaldehyde along the MPBR obtained from Raman measurements (benzyl alcohol flow = 0.003 mL/min, O₂ = 0.3 mL/min, Lbed = 58 mm, catalyst size 53–63 μm, T = 100 °C).
gas (STP) to liquid of 100 and above, at a given liquid flow rate (0.003 mL/min). The effect of catalyst particle size on the reaction was examined with two ranges of particle size: 53–63 μm and 90–125 μm. Lower conversion was obtained from the reactor with particle size of 90–125 μm. Although the flow pattern in MPBRs studied should be within the trickling regime based on literature, visual observation of gas–liquid flow shows a pulsing-trickling flow pattern in the MPBRs due to gas–liquid slug flow forming in the microchannel before entering the catalyst bed.

In situ Raman measurements in MPBRs were performed including characterization of the optical signals from the catalyst surface, fluorescence effects and the formation of disordered graphitic faces with thin liquid film, dynamically wetted catalyst surface with thin liquid film and un-well-wetted catalyst surface). Only from the liquid pockets, Raman spectra were less affected by fluorescence. Four types of gas–liquid–solid interaction modes in the micropacked bed reactor were observed (liquid pockets between fully wetted particles, fully wetted catalyst particle surfaces with thin liquid film, dynamically wetted catalyst surface with thin liquid film and un-well-wetted catalyst surface). Only from the liquid pockets, Raman spectra were less affected by fluorescence.

The yield of benzaldehyde calculated from Raman measurement compared very well with that obtained by gas chromatography from a MPBR operated under the same reaction conditions. Using in situ Raman spectroscopy to monitor the concentration of benzaldehyde within liquid pockets along the catalyst bed can be useful in analysis of reactor performance or reactor simulation.

Within the experimental conditions studied, the best conversion of benzyl alcohol of 95.5% with selectivity to benzaldehyde of 78% were obtained for a MPBR with catalyst sizes of 53–63 μm and a catalyst bed length of 48 mm at 120 °C and 5 bar(a).

Acknowledgements

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