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Selective hydrogenation reactions: A comparative study of monolith CDC, stirred tank and trickle bed reactors

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Abstract

Monolith reactors offer several advantages over traditional random fixed beds or slurry reactors, such as better mass transfer characteristics, higher volumetric productivity for a smaller amount of catalyst, elimination of filtration step and lower pressure drop. However, achieving an even gas–liquid distribution across the monolith is difficult. The cocurrent downflow contactor (CDC) reactor presents an elegant solution to this problem by establishing a stable two-phase dispersion. When comparing the CDC reactor with traditional stirred tank and trickle bed reactors for the hydrogenation of 2-butyne-1,4-diol, greater selectivity towards the alkene intermediate is observed in the CDC for a range of solvents. This is partly due to a high dispersion (67%) of Pd on the washcoat support of the monolith and also to the optimisation of the surface species concentrations as a result of greater mass transfer of hydrogen to the catalyst surface compared with alternative reactor designs. Furthermore, when considering the effect of scale-out on the monolith by comparing a single capillary with 1256 and 5026 channel monoliths, initial reaction rates and selectivity were maintained. This supports the use of the CDC as a suitable method for dispersing gas–liquid mixtures through a monolith.

Keywords: Monolith; Stirred tank; Bubble column; Selectivity; Hydrogenation; Mass transfer

1. Introduction

Catalytic, multiphase hydrogenation has been carried out commercially for over a century. A huge variety of reactions are accomplished via this process, using predominantly heterogeneous catalysts. In addition, product values and volumes vary enormously: by several orders of magnitude. Given this diversity it is therefore perhaps somewhat surprising that these reactions are carried out for the most part in just one reactor type: the stirred tank reactor. Furthermore, this type of reactor has been at the core of industry for over a century [1]. There are a number of other well-established alternatives used in the large-scale chemical industries [2] including the trickle bed reactor, which is used almost exclusively in refinery hydroprocessing and extensively for hydrogenation in petrochemical plants. However, these reactor designs prove difficult to scale-up as key length-scales do not scale in a similar fashion. Whilst at the catalyst scale diffusional path lengths remain unchanged, during scale-up the geometry of the reactor may change through an order of magnitude or more. This leads to complication in scale-up although the reasons differ from one reactor to another. For instance, in the case of the stirred reactor, as the flow area increases with increasing diameter the fluid velocity decreases. Therefore whilst energy dissipation at the impeller may be maintained, momentum and fluid velocities in the wall region are inevitably lower at the larger scale. In the case of the trickle bed reactor scaling issues arise because of changes in superficial velocities required to achieve the same residence time between a lab, pilot and production scale reactor. It is worth noting however in this context that an alternative approach to laboratory scale testing of trickle beds has been proposed that circumvents this problem [3,4]. Consequently, liquid hold up, real liquid residence time, liquid film thickness and/or wetting efficiency of the catalyst are affected.

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An alternative approach is to make the mixing and diffusional distances smaller [5]. The residence time in a large reactor can be considered as being taken up primarily by getting the reactive species around the vessel and to the active catalyst sites. If macro-mixing lengths are minimised the process will be faster as the mixing times are reduced towards those for molecular transport over short distances. Thinking is therefore moving towards the use of many small parallel reactor paths rather than the large one. In this case simple "scale-out" can, in theory, be achieved by increasing one channel to many channels [6].

The honeycomb monolith has been very successful in gas phase reactors, most notably as the structured support for the conversion of pollutants in vehicle exhausts. The potential of monoliths to act as a catalytic support for multiphase reactions has been recognised for over 20 years [7] and much recent work has been done to extend the application of monoliths to liquid and gas–liquid systems [8,9]. Monoliths offer the benefits of an absence of a need for filtering catalyst from the product, low pressure drop, high geometrical surface area, safer operation and, perhaps most significantly, potentially easy scale-up. However, the latter is crucially dependent upon being able to achieve an even gas–liquid distribution across the channels. Furthermore, maldistribution can lead to a wide residence time distribution across the radial section of monolith with consequently lower selectivities, ineffective catalyst usage and hot spots in the reactor [9,10]. Achieving optimal gas–liquid dispersion at the entrance to the monolith is a clear technical challenge and has been investigated by several workers [9,11,12] via a variety of contacting methods (e.g. injection via a nozzle, showerhead or foam). All of these studies highlight the importance of gas and liquid velocities and the liquid distributor design on attaining a uniform flow distribution. Roy and Al-Dahhan [9], using hydrodynamic data obtained γ-ray computed tomography (CT), indicate that even for the must successful injector (nozzle) with a 5 cm monolith there is a relatively narrow operating window of gas and liquid velocities where a reasonably homogeneous flow distribution can be obtained. The cocurrent downflow contactor (CDC) reactor [13] presents an elegant solution to this problem by establishing a stable two-phase dispersion consisting of bubbles of around 1–2 mm in diameter, depending on the solvent properties and operating pressure.

A comparison between the monolithic CDC reactor with traditional stirred tank and trickle bed reactors is presented for a model reaction in both terms of activity and selectivity. In addition, the scale-out of a single channel to larger monoliths of 1256 and 5026 channels is analysed, demonstrating the potential for rate and selectivity enhancements whilst allowing ease of scale-out.

The selective hydrogenation of 2-butyne-1,4-diol was studied as the model reaction. This is a consecutive reaction widely applied in the production of butane-1,4-diol, a raw material used in the polymers industry and in the manufacture of tetrahydrofuran [14]. More challenging though, is the incomplete hydrogenation to the alkene intermediate which is important in the synthesis of pharmaceuticals such as vitamins A and B_6 and several insecticides (as endosulfan). Several side reactions are possible, as illustrated in Fig. 1, for example the 4-hydroxybutyraldehyde and its cyclic hemiacetal, 2-hydroxytetrahydrofuran, as a consequence of double-bond isomerisation and hydrogenolysis reactions [15].

2. Materials and methods

Five reactors were used in total, and in the case of the monolith CDC reactors two operating modes were employed. Each of the reactors and the catalyst used are described below and in Fig. 2. All of the reactors were operated at a pressure of 200 kPa and a temperature of 55 °C with the exception of the single-capillary reactor which was operated at 100 kPa. Solutions of 2-butyne-1,4-diol (supplied by Sigma–Aldrich Ltd.) were prepared in distilled water, 2-propanol (supplied by Fisher Scientific UK Ltd.) and mixtures of the two. Dispersion of metal upon the catalyst was determined by CO pulse chemisorption using a Micromeritics 2920 Chemisorption analyser.

2.1. The stirred tank reactor

A stainless steel reactor of diameter, T = 150 mm, fitted with four baffles of width T/10 and agitated with an up-pumping pitch-blade turbine (u-PBT) of diameter, D = T/3 at an agitation

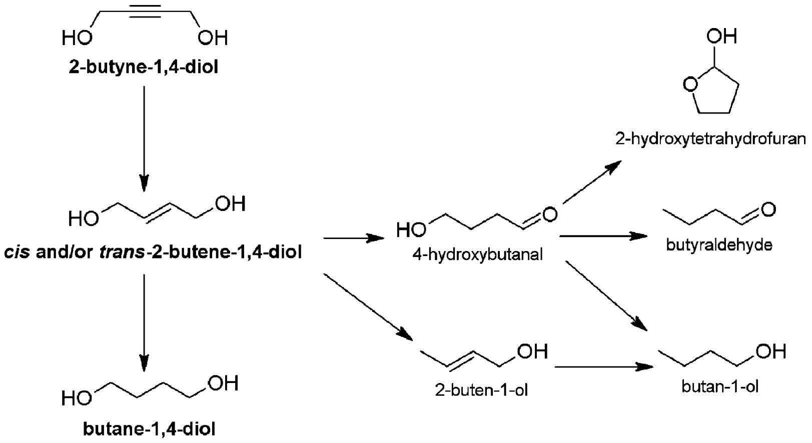

Fig. 1. Reaction scheme for hydrogenation of 2-butyne-1,4-diol.

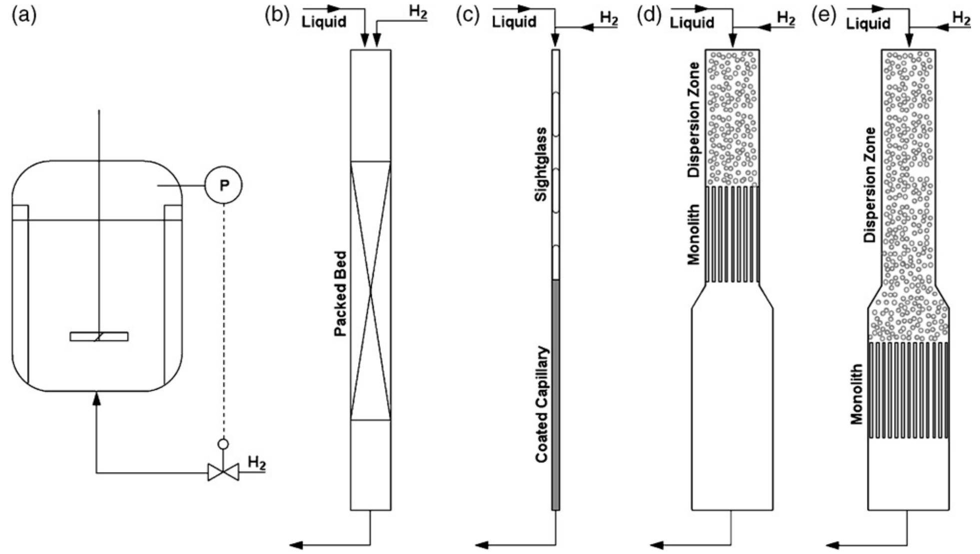

Fig. 2. Reactor layouts: (a) stirred tank reactor; (b) trickle bed reactor; (c) single-capillary reactor; monolith CDC fitted with (d) 5 cm monolith and (e) 10 cm monolith.

speed, $N = 25\ s^{-1}$ (Re_I = 15,000–65,000, dependent on the solvent properties). The reactor was operated "dead-end", i.e., hydrogen was added at a constant pressure as it was consumed by the reaction. Gas was dispersed via a sparge pipe located centrally below the impeller. A liquid height equal to the vessel diameter was used giving a total liquid volume of 2.65 dm^3 and leaving a 12% (v/v) headspace (prior to sparging). Ten grams per decimeter of a 1% Pd/γ-Al_2O_3 egg-shell type catalyst (supplied by Johnson Matthey Catalysts) with a mean particle diameter of approximately 100 μm was used. This resulted in a total palladium content of 0.265 g in the reactor. Catalysts selected for use in each reactor were typical of the catalyst types used in industry for that type of reactor. During selected reactions, bubble sizes were monitored using a video–microscope–computer system [16] via an observation window in the vessel.

2.2. The trickle bed reactor

The trickle bed reactor consisted of a glass column measuring 35 cm in length and 5 cm in diameter with the liquid recirculated in a closed loop. The catalyst bed was comprised of 6 mm spherical catalyst particles of egg-shell impregnated 0.5% Pd/Al_2O_3. This resulted in a total palladium content of 2.4 g in the reactor. The bed was also packed with sufficient fines to just fill the voids. Inert silica carbide particles of 0.2 mm diameter were used as diluents in the bed in order to improve the flow distribution and increase the interstitial fluid velocities. The fines and catalyst were added to the bed in small aquilots and tapped to consolidate the particles after each stage, according to the procedure recommended by Al-Dahhan et al. [17]. The liquid flow rate was $8.3 \times 10^{-6}\ m^3\ s^{-1}$ and gas flow rate $6.6 \times 10^{-6}\ m^3\ s^{-1}$.

2.3. Single-capillary reactor

The single-capillary reactor consisted of a 34 cm long, and 2 mm internal diameter capillary channel wash-coated with α-Al_2O_3 and impregnated with palladium by a proprietary method by Johnson Matthey Catalysts and resulting in a total palladium content of 3.7 μg in the reactor. Twenty cubic centimeters of reacting solution were contained in a glass flask and recirculated through the system by means of a piston pump. Hydrogen was combined with the liquid stream at a T-junction and supplied to the reactor capillary via a 30 cm glass capillary. Liquid flow rate was 0.5 $cm^3\ s^{-1}$ and hydrogen was supplied at a suitable rate to obtain Taylor flow as determined by visual observation of the glass capillary section. This also allowed the determination of the liquid slug and gas bubble length by photographic means.

2.4. Monolith CDC reactor

In the monolith CDC, the glass column is fully filled with reacting solution, which is continuously recirculated from the bottom to the top of the column. Hydrogen is mixed with the liquid stream at a T-junction on top of the column. The two-phase mixture is passed through an orifice plate which produces a bubble dispersion consisting of 0.3–1.0 mm bubbles in the upper section of the column, where a large degree of turbulence can be observed. These bubbles become larger as they coalesce in the column where the degree of shear and turbulence is not large enough to keep them apart, although the degree of coalescence is highly dependent on the solvent composition. The bubble dispersion height, H_D, can be controlled at different levels in the column by manipulating the gas/liquid velocity ratio. Two operating modes were employed. In Mode I the gas–liquid dispersion was set at a level just above the monolith, such that a single-phase liquid flow pre-saturated with hydrogen entered the monolith channels. In Mode II the gas–liquid dispersion extended just through the monolith, such that the channels contained a two-phase mixture. Two monoliths were used: a 5 cm monolith (with 1256 capillary channels) and a 10 cm monolith (consisting of 5026 capillary channels) placed as shown in Fig. 2. A more detailed description of the operation of the CDC can be found in Winterbottom et al. [18]. The monoliths were wash-coated with α-Al_2O_3 and impregnated with Pd as described for the single-capillary reactor. This gave a palladium content of 0.4 and 1.73 g in the 5 and 10 cm monoliths, respectively.

3. Results and discussion

Initial reaction rates and selectivity, S (defined as the mole fraction of the intermediate, 2-butene-1,4-diol, in the total number of moles of product), are given in Table 1 for a range of solvent compositions. Initial reaction rate was calculated for the first 10% conversion of 2-butyne-1,4-diol over which period the reaction rate is zero order with respect to butyne-diol concentration. Fig. 3 displays the hydrogen uptake as a function of time, clearly illustrating two distinct rate periods. The first step of the reaction displays a flat profile, and corresponds to the hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol. During this period negligible hydrogenation to 2-butane-1,4-diol occurs, because the alkyne strongly adsorbs on the catalyst, compared with the alkene. Therefore the surface is saturated with alkyne, and alkene can only adsorb and react after most of the alkyne is consumed. This explains why the rate changes sharply at 35 min, when most of the alkyne is consumed, and the reaction of alkene to alkane commences. The second hydrogenation step is faster than the first, thus explaining the acceleration of rate that occurs in the second period. Eventually the second rate reaches a maximum, and thereafter decreases, corresponding to depletion of the alkene reagent from the solution. The kinetics of the reaction in the monolith were modelled in detail by Natividad et al. [14].

From Table 1, it can be seen that selectivity towards 2-butene-1,4-diol is generally very high, however, it is apparent that the structured reactors outperform both the stirred tank and trickle bed reactors regardless of the assayed solvent. Indeed, with the use of the mixed water/2-propanol solvent complete selectivity towards the alkene is achieved without the necessity of doping catalysts [19] or having to poison the catalyst with additives such as bases [20,21]. Table 2 shows the composition of the liquid for the different reactor types at 90% and 100% conversion of 2-butyne-1,4-diol. At 90% conversion, the concentration of side products was higher in the stirred tank reactor than either of the monoliths, although side product concentration was not measured for the trickle bed reactor. GC–MS analysis confirmed that the side products present were 2-hydroxytetrahydrofuran, butyrolactone and large condensation products. 2-Hydroxytetrahydrofuran (the cyclic hemiacetal of 4-hydroxybutanal) was also observed by Chickos et al. [22]. This double-bond isomerisation reaction consumes no hydrogen and may therefore be expected to occur preferentially to the hydrogenation of the alkene if the hydrogen population at the catalyst surface is poor. However, it must also be noted that this reaction does not occur in the complete absence of hydrogen [22]. At 90% conversion of 2-butyne-1,4-diol the concentration of butane-diol in the trickle bed was much higher than for the other reactor types. At 100% conversion of 2-butyne-1,4-diol, the concentration of side products was higher in the STR than the monoliths, and the concentration of 2-butane-1,4-diol was highest in the trickle bed, followed by the STR, 10 and 5 cm monoliths.

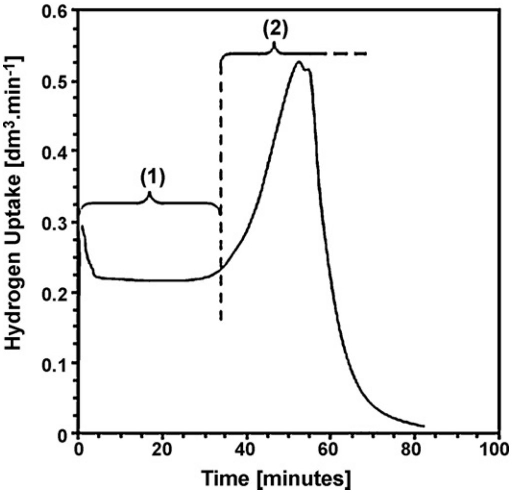

Fig. 3. Hydrogen uptake in the stirred tank reactor with 2-propanol solvent. Two rates are observed corresponding to (1) the initial alkyne hydrogenation and (2) alkene hydrogenation and side product formation.

Table 3 shows the catalyst characterisation results for the three types of catalyst used. It is observed that the metal dispersion increases from the TBR to STR to monolith catalysts. The dispersions for the TBR and STR catalysts are quite similar, and the value for the monolith is quite high. In order to calculate the amount of washcoat on the monolith, the

Table 1
Initial reaction rates and selectivity towards *cis*-2-butene-1,4-diol for CDC monolith, stirred tank and trickle bed reactors

Solvent	Reactor	Initial rate ($\times10^{-3}$ mol s^{-1} g_{Pd}^{-1})	S (90% conversion)	S (100% conversion)
Water	5 cm monolith	0.186	1.00	1.00
	10 cm monolith	0.186	1.00	0.96
	STR	0.264	0.99	0.93
	TBR	0.033	0.87	0.86
30% (v/v) 2-propanol in water (M)	5 cm monolith	0.206	1.00	1.00
	10 cm monolith	0.206	1.00	1.00
	STR	0.319	1.00	0.95
	TBR	0.330	0.93	0.90
2-Propanol	5 cm monolith	0.268	0.99	0.90
	STR	0.522	0.97	0.87

Table 2
Product distributions for different reactor types at 90% and 100% conversion of 2-butyne-1,4-diol in water and water/2-propanol mixtures

	Compositions (%) at 90% conversion of 2-butyne-1,4-diol				Compositions (%) at 100% conversion of 2-butyne-1,4-diol			
	5 cm monolith	10 cm monolith	STR	TBR	5 cm monolith	10 cm monolith	STR	TBR
Solvent: water								
Butyne-diol	10.0	10.0	10.0	10.0	0.0	0.0	0.0	0.0
Butene-diol	89.8	89.6	89.1	78.1	99.6	96.3	93.0	86.1
Butane-diol	0.00	0.1	0.1	11.9	0.1	2.4	5.1	13.9
Side products	0.2	0.3	0.8	–	0.3	1.3	1.9	–
Solvent: 30% propanol–70% water								
Butyne-diol	10.0	10.0	10.0	9.9	0.0	0.0	0.0	0.0
Butene-diol	89.9	89.8	89.7	84.6	99.7	99.6	95.2	90.8
Butane-diol	0.0	0.0	0.0	5.5	0.1	0.1	3.4	9.2
Side products	0.1	0.2	0.3	–	0.2	0.3	1.4	–

Table 3
Chemisorption characterisation of the three catalyst samples

	Powder used in STR	Pellet used in TBR	Monolith
Dispersion (%)	22.99	16.54	67.76
Metallic surface area ($m^2\ g^{-1}_{sample}$)	0.512	0.736	3.019
Metallic surface area ($m^2\ g^{-1}_{metal}$)	102.46	73.66	301.86
Active particle diameter (nm)	4.87	6.77	1.65

weight of an uncoated monolith was subtracted from the weight of the coated monolith. The washcoat weight on the sample of 3 g used in chemisorption then scaled according to the sample weight relative to that of a complete monolith. For the monolith catalyst the chemisorption results are subject to greater uncertainty than the powder or pellet, owing to the difficulty of cutting a representative sample from the monolith structure. The outside surface of the monolith is covered with a thicker coating of washcoat compared with the internal channels, such that it can be difficult to estimate the amount of washcoat in the sample. Similar to the dispersion reported for the monolith in this work, very high dispersions of Pd have been reported for fresh automotive monolith catalysts of up to 89.9% [23]. The increasing selectivities reported in Table 1 follow the same order as the dispersions of the catalysts in those reactors, such that the monolith has the highest selectivity towards 2-butyne-1,4-diol. However, the selectivity observed in the monolith also depends on whether it is operated single-phase or two-phase flow, suggesting that mass transfer also plays a role in influencing the selectivity in these reactors.

Examining the trickle bed reactor, the presence of stagnant zones could be expected to lead to a broader residence time distribution compared with the structured catalysts and therefore poorer selectivity. Under the same operating conditions, however, it has been shown that the disparity between residence time distributions for both reactors is not substantial [24]. All three reactors can thus be considered to operate under plug flow. In addition to the effect of catalyst dispersion in the three reactors, mass transfer rates of hydrogen to the catalyst surface may vary. This would result in varying hydrogen population at the surface of catalyst in each reactor, therefore making the side reaction more favourable. In order to assess the role of mass transfer in each reactor, the mass transfer coefficients must be compared. General empirical correlations for predicting mass transfer parameters are not well established however they are sufficient for an approximate comparison of the reactors. The values obtained in the binary solvent for each reactor are reported in Table 4. Clearly, both solid–liquid and gas–liquid volumetric mass transfer rates are higher in the structured catalysts than in both the stirred tank and trickle bed reactors by around an order of magnitude. The stirred tank reactor displays slightly higher volumetric rates than the trickle bed reactor although this is chiefly due to the large interfacial areas that are observed due to the use of small catalyst particles and high energy dissipation to disperse the gas bubbles. Therefore the order of increased selectivity follows the pattern of increased mass transfer rates.

Comparing the three solvent compositions (Table 1) it is found that the highest selectivity is observed in the binary solvent. It has been suggested that the presence of relatively low concentrations of alcohol in water dramatically reduces coalescence due to surface polarization effects [16,30,31] and in this system the 2-butyne-1,4-diol itself can act as the surface-active molecule. It was noted that in the bubble imaging studies

Table 4
Mass transfer parameters in 30% (v/v) 2-propanol in water

Reactor	$k_L a_i$ (s^{-1})	$k_S a_s$ (s^{-1})
Single capillary	0.262 [25]	0.192 [25]
5 cm monolith	0.914 [25]	0.722 [25]
10 cm monolith[a]	0.834 [25]	0.742 [25]
10 cm monolith[b]	–	0.619 [25]
STR	0.086 [26]	0.060 [27]
TBR	0.016 [28]	0.036 [29]

[a] Mode II: bubble flow introduced into monolith channels.

[b] Mode I: saturated solution introduced into monolith channels.

of Hu et al. [16], catalyst particles could be distinguished from bubbles, and were not found to adhere to bubble surfaces. Of the three solvents studied here, the smallest bubbles observed by video–microscope–computer system occur in the 30% (v/v) 2-propanol in water mixture [16] and therefore a higher gas–liquid interfacial area is observed. Hence, volumetric gas–liquid mass transfer is improved by solvent selection and consequently may explain the improvement in selectivity.

If, indeed, superior hydrogen transfer is responsible for improved selectivity it must also be pointed out that in the CDC reactor, unlike the trickle bed reactor, the hydrogen–liquid mixture is contacted before entering the reactor channels. Therefore, the solution could be considered to be pre-equilibrated with hydrogen. Again, this would be expected to result in higher hydrogen population at the catalyst surface.

Finally, it should be noted that in the monolith reactor, gas–liquid–solid mass transfer also occurs via the thin film of liquid between the bubble and channel walls. This third transfer rate again promotes the hydrogen population on the catalyst. To some extent a similar process may occur in the trickle bed when portions of the bed momentarily dry out due to fluctuating flow patterns, however, in this study the bed appears to be fully wetted with all solvents. At any rate, as this behaviour is a function of the packing this would result in constrained areas of the bed with improved hydrogen population and not, therefore, a global pattern of improved hydrogen transfer throughout the reactor. In the stirred tank reactor no interaction between the gas bubbles and the catalyst particles is observed and therefore gas–solid mass transfer can be considered negligible.

Whilst the monolith CDC reactor shows promise for achieving high selectivity in this class of reaction, there is still the question of scale-out of the reactor. Therefore, the initial reaction rate and selectivity towards 2-butene-1,4-diol were studied in a single-capillary reactor, a 5 cm monolith consisting of 1256 channels and a 10 cm monolith of 5026 channels using the binary solvent of 30% (v/v) 2-propanol. The operating pressure for experiments in the monolith CDC reactor was 200 kPa whereas the single-capillary reactor was open to the atmosphere. Under initial reaction conditions the reaction was found to be first order with respect to hydrogen concentration and therefore the pressure difference may be accounted for. In addition, further reactions were performed in the 5 and 10 cm monolith CDC reactors using water as the solvent. An initial 2-butyne-1,4-diol concentration of 0.055 kmol m^{-3} was used in both the 5 cm monolith CDC reactor and the single-capillary reactor whereas in the 10 cm monolith the starting concentration was 0.1162 kmol m^{-3}. The results are shown in Table 5. Examining the results obtained in the binary solvent it can be seen that despite the change in pressure, selectivity is not affected when increasing the number of channels from one to over 5000 channels when similar hydrodynamic conditions are employed (Mode II with bubbles in the channels). Furthermore initial reaction rates were maintained (not reported for the single-capillary reactor due to the pressure difference). However, the hydrodynamic operating mode is important, and reaction rates are considerably diminished when a single-phase solution pre-saturated with hydrogen is passed through the 10 cm monolith (Mode I operation) rather than a two-phase mixture in Taylor flow (Mode II operation). When operating with the single-phase liquid flow in Mode I, 10 l of solution containing 0.1162 kmol m^{-3} 2-butyne-1,4-diol reacts to 100% conversion within 200 min, at a flow rate of 7 l min^{-1}. Under these conditions, there are approximately 138 passes through the reactor, and the average change of concentration of alkyne per pass is 8.2×10^{-4} kmol m^{-3}. The saturated concentration of hydrogen in the solution at the entrance to the monolith is 1.69×10^{-3} kmol m^{-3} [14]. Over the length of the monolith, 49% of the saturated hydrogen reacts, depleting the concentration to approximately 8.5×10^{-4} kmol m^{-3} at the bottom of the monolith channels. Consequently a considerable concentration gradient develops over the length of the monolith when operating in single-phase Mode I. This problem is avoided in two-phase Mode II, whereby the dissolved hydrogen concentration in the liquid is replenished by dissolution of hydrogen from the gas bubbles. Indeed the initial rate of reaction reported in Table 5 for the monolith operating in single-phase mode is much lower than the initial rate for two-phase mode, reflecting the lower concentration of hydrogen in solution for the single phase. However, even then the decrease in selectivity between these two cases is small, especially when compared to the performance of the stirred tank and trickle bed reactors. This suggests that even if poor distribution of the gas–liquid distribution occurs selectivity can be maintained.

In the case of water a drop in selectivity was observed when increasing the monolith size although this drop is still relatively small. This may be due to the monolith not operating under Taylor flow since bubble sizes considerably smaller than the channels are generated (Sauter mean bubble diameter of around 300 μm compared [16] with 2 mm channels). Bubbles smaller

Table 5
Effect of scaling out and solvent on activity and selectivity towards *cis*-2-butene-1,4-diol

Solvent	Reactor	Initial rate ($\times 10^{-3}$ mol s^{-1} g_{Pd}^{-1})	S (90% conversion)	S (100% conversion)
Water	5 cm monolith	0.186[a]	1.00	1.00
	10 cm monolith	0.186[a]	1.00	0.96
30% (v/v) 2-propanol in water (M)	Single capillary	–	1.00	1.00
	5 cm monolith	0.206[a]	1.00	1.00
	10 cm monolith	0.206[a]	1.00	1.00
		0.062[b]	0.98	0.97

[a] Mode II: bubble flow introduced into monolith channels.

[b] Mode I: saturated solution introduced into monolith channels.

than the monolith channels were seen to be exiting the monolith by visual observation of the glass column. Clearly, this problem could therefore be solved by using a smaller channel size with the added benefit of even smaller mixing and diffusional distances and higher catalyst specific surface area with the possibility of consequentially higher volumetric activity. Alternatively, it may be as a result of the greater solubility of hydrogen in the mixed solvent and consequentially higher hydrogen population at the catalyst surface. It has been reported previously that liquid residence time distributions across the radial section of a monolith CDC increases slightly towards the column wall [32]. However, the effect on selectivity is negligible, particularly in comparison with the other reactor configurations.

4. Conclusions

The cocurrent downflow contactor (CDC) monolith reactor achieved the highest selectivity towards the alkene intermediate in the hydrogenation of 2-butyne-1,4-diol when compared to stirred tank and trickle bed reactors. Loss of selectivity is for the most part due to the formation of non-hydrogenation side products. The high selectivity observed in the monolith can be partly attributed to the high dispersion of palladium and small palladium particle size on the washcoat support. However, differences in product distribution between single- and two-phase modes of operation suggest that mass transfer of hydrogen to the catalyst surface also influences the selectivity. The reactor design and operating mode can therefore be optimised to achieve maximum selectivity. Additionally, a comparison of a single capillary with 5 and 10 cm monoliths (1256 and 5026 channels, respectively) indicates that initial reaction rates and selectivity are maintained. The CDC therefore presents an effective means of dispersing gas–liquid mixtures across the face of a monolith. Moreover, this class of reaction may be studied in a single-capillary reactor with a good degree of certainty that scaling-out to a monolith CDC reactor will not considerably affect selectivity and activity.

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