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Application of a structured multifunctional reactor for the oxidation of a liquid organic feedstock[☆]

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Abstract

Experiments are performed in a structured packed bed reactor that has been developed for the selective oxidation of organic liquids to produce pharmaceutical products. Molecular oxygen is used as the oxidant, providing a ‘‘cleaner processing route’’, than in established methods. The structured assembly consists of an integrated heat exchange system, a gas/liquid mixing zone, and provision for reactant injection. To illustrate the application, the selective oxidation of benzyl alcohol to benzaldehyde was studied. The reactor consisted of parallel reaction channels (10 cm long and square shaped) that were packed with Ru/Al_2O_3 (0.9 wt% Ru) catalyst particles. From experiments in three different sizes of channel: 2 mm × 2 mm, 3 mm × 3 mm, and 5 mm × 5 mm (at $P = 8$ bar, $T = 388$ K, with liquid and gas flows $L = 3.2\ \mathrm{kg\ m^{-2}\ s^{-1}}$, $G = 1.35 \times 10^{-2}\ \mathrm{kg\ m^{-2}\ s^{-1}}$), it was shown that in a short 10 cm length of channel, a product yield up to ca. 29% (with minimum 99.5% selectivity) could be obtained. Conversions were highest in the 3 mm × 3 mm channel. From the experiments with the reactor mounted both in horizontal and vertical planes, it was shown that gravitational influences are minor.

The choice of solvent was shown to affect the yield of benzaldehyde. The highest yield was with toluene; the application of dioxane/water mixture (70/30 by vol.) and *N*-methyl pyrrolidone (NMP) not only decreased the yield by factor 2, but NMP also caused deactivation of the catalyst.

Preliminary results are presented of work with Pt/C (Pt 3 wt%) catalyst.

Keywords: Bed reactor; Liquid organic feedstock; Oxygen

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1. Introduction

Within the pharmaceutical and fine chemicals industries, there is much interest in the viability of using molecular oxygen as the oxidant in selective oxidations of organic liquids [1]. If such a process could be developed, then it would offer a cleaner and more benign reacting environment rather than that encountered with the use of strong oxidising agents such as nitric acid. As the selective oxidation reactions are exothermic, and selectivity is often a strong function of temperature, the development of a reacting environment in which temperature can be controlled is critical. To increase the rate of the oxidation reaction(s), with gaseous oxygen, catalysts can be used, e.g. Yamaguchi and Mizuno [2].

The main motivation behind the work was to develop a reaction system using molecular oxygen as the oxidant in the reactions of selective oxidation. Reactions of selective oxidation are widely used in industry, and the need for substituting traditional stoichiometric oxidants with catalytic systems, whilst using benign oxidants, such as H_2O_2, air or molecular oxygen has been repeatedly emphasised [3]. Since selective oxidation reactions are highly exothermic, and selectivity is often a strong function of the oxygen concentration, compact multifunctional reactors may offer significant advantages through the intensified removal of

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heat and the potential for controlled addition of oxygen. Oxidation of benzyl alcohol to benzaldehyde in toluene was chosen as a test reaction, and the reaction stoichiometry can be represented by:

$$C_6H_5CH_2OH + \tfrac{1}{2}O_2 \rightarrow C_6H_5CHO + H_2O; \quad \Delta H_R^0 = -183.7\,\mathrm{kJmol^{-1}} \tag{1}$$

Ru/Al_2O_3 was selected as a catalyst, as Yamaguchi and Mizuno [2] had successfully used it.

In the literature there are many examples of applications where structured catalysts and structured reactors are used to provide an advantageous reacting environment [4,5]. In developing the reacting system described in this paper, knowledge on compact heat exchangers [6], monolithic two-phase flow reactors [7], and microreactors [8,9] was all relevant. To ensure good temperature control and hence selectivity, the creation of a reacting environment in which high rates of mass transfer and heat transfer can be achieved (even when two phase flow conditions prevail) was important. From evidence in the literature [10], these can be achieved in compact structures.

It should be emphasized that this is a relatively low flow application, where small quantities of product are produced that have a very high commercial value. Therefore, high pressures drops across the reactor were not of concern, so the selection of catalyst in the form of a powder to act as a packed bed was a viable consideration. With the catalyst in this form, high rates of reactions could be achieved per unit volume of bed, maintaining the overall dimensions of the system compact.

Unfortunately, although there is much data in the literature on three phase reactors using channels with a hydraulic diameter at the centimeter scale, and some data on multi-channel microreactors at the micrometer to 1 mm scale, experimental data on the performance of packed bed three-phase reactors at the millimeter scale is very scarce.

To advance knowledge in this field, in [11] the development of the design concept for the reactor used in this paper was described. The main advantages of this compact multifunctional reactor were seen to be in the combination of static mixers (enabling pre-mixing of gaseous and liquid reagents prior to injection in the reaction channels), small reaction channels (which are characterised by flow approaching plug-flow), and good heat exchange (which reduced the risk of unwanted side reactions, such as complete oxidation and/or catalyst coking). Results were presented of early experiments in a 10 cm long, 3 mm × 3 mm channel, packed either with Ru/Al_2O_3 (0.9 wt% of Ru) or Ru/TiO_2 (2.0 wt% Ru) catalysts. The hydrodynamic characteristics of the system were evaluated to establish pressure drop, effectiveness of gas/liquid mixing, and confirm the nature of the gas-liquid flow regime. Operating the reactor at 8 bar, 388 K, with liquid and gas flows ($L = 3.2\,\mathrm{kg\,m^{-2}\,s^{-1}}$), $G > 2.5 \times 10^{-2}\,\mathrm{kg\,m^{-2}\,s^{-1}}$, it was shown that even in a short 10 cm length of channel, a product yield up to 55% (with 99.7% selectivity) could be obtained. Although the adiabatic temperature rise at 55% yield was estimated to be ca. 180 K, the reactor was shown to operate isothermally, due to the efficient removal of heat through the integrated micro heat exchanger. Further on in [12], operating conditions were identified at which the reaction was limited significantly by chemical kinetics, and also when mass transfer limitations were more significant. Despite the achievement of high rates of reaction, the reactor was shown to operate isothermally. Staged injection of oxygen was shown to be beneficial and high activity and selectivity were observed even when working with reactant concentrations approaching industrial conditions (e.g. initial alcohol concentration = $1.0\,\mathrm{kmol\,m^{-3}}$).

This paper extends this theme, and starts with a test of the effects of channel size, and the influences of channel orientation and flow direction are also explored. In order to ensure that the overall outside dimensions of the reactor remain compact, these aspects will become very important when the flow path is designed. For example, if a vertical channel orientation was to be selected, then by using a combination of vertical up- and down-flow channels, the overall height of the reactor can be reduced. Then, it is shown that the choice of solvent is an important factor. Finally, tests are performed to assess whether or not the reaction is limited by the transfer of oxygen from the gaseous to the liquid phase. This is illustrated with the addition of *tert*-butyl hydroperoxide (a homogeneous oxidising agent) to the liquid feed, and the use of nitrogen (instead of oxygen) as the gaseous phase.

2. Experimental apparatus

The reacting system has already been described in [12] and is shown in Fig. 1. In summary, the test reactor contained five parallel packed-bed channels, each equipped with a static mixer. The length of all the reaction channels was

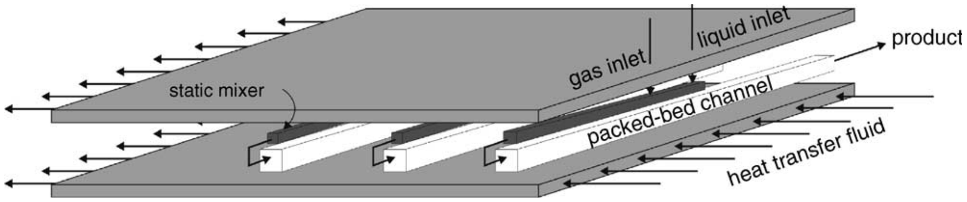

Fig. 1. Schematic diagram of the multichannel reactor.

10 cm. Channels were square shaped, with sides of 2, 3 and 5 mm. The length of static mixer was 6 cm. Glycerol was used as a heat transfer fluid and its temperature was maintained by a re-circulating bath. Three thermo-wells were placed along the length of each reaction channel. The thickness of the metal plate between the thermocouples and reaction channel was 100 μm, ensuring a quick response. The reactor was fabricated by Chart Heat Exchangers Ltd. using diffusion bonding technique. The internal structure of the reactor was prefabricated in the form of thin stainless steel plates (shims) with thickness of 100 and 250 μm, using conventional photolithography-etching technique.

The experimental procedure has been already described in detail in our earlier work [11,12]. The Ru/Al_2O_3 catalyst was prepared following the methodology described by Yamaguchi and Mizuno [2], in accordance with the procedure described in [11,12]. The Pt/C catalyst (Pt 3% by weight) was prepared by impregnating the synthetic carbon manufactured from phenolic resins (Mast Carbon Ltd., Guildford, UK) using H_2PtCl_6 as precursor as described by van Dam and van Bekkum [13].

3. Results and discussion

3.1. *Influence of channel size*

In earlier works [11,12] only 3 mm × 3 mm channels, packed with Ru/Al_2O_3 catalyst, were used to evaluate the performance of the newly designed reactor. These studies are now extended and 2 mm × 2 mm channels, and 5 mm × 5 mm channels are studied. Fig. 2 shows the influence of channel size on the average rate of oxidation (r_{Av}). The average reaction rate was calculated as follows:

$$(r_{Av}) = \frac{\dot{V}_L c_{Ald,e}}{m_{cat}}, \tag{2}$$

where $\dot{V}_L$ is the volumetric flow rate of liquid phase; $c_{Ald,e}$ the exit concentration of benzaldehyde, m_{cat} is the mass of catalyst in individual channel. All experiments were performed with fresh catalysts. The ratio of channel size to catalyst particle diameter changed as follows: 13.3 (for 2 mm × 2 mm channels), 20.0 (for 3 mm × 3 mm channels) and 33.3 (for 5 mm × 5 mm channels). From these results, the average rate of benzaldehyde formation was the highest for the 3 mm × 3 mm channel, and also for this channel size the scatter of experimental data was the smallest. In the region of low oxygen flow, the 5 mm × 5 mm channel showed high instability in some cases – there was considerable scatter in the exit concentration of benzaldehyde. These experiments were performed with the reactor mounted in a horizontal direction, and it is postulated that some gas/liquid phase separation took place inside the 5 mm × 5 mm channel, changing the flow regime inside the reactor. In all of the channels, the dispersion and mixing of oxygen/toluene were presumed to be the same (the same design of mixing channel used). Although, it is known that the ratio of the reactor to catalyst particle diameter could have an influence on cm-range catalytic reactors [14]; these type of reactors operate exclusively in either up- or down-flow modes, and not in a horizontal one.

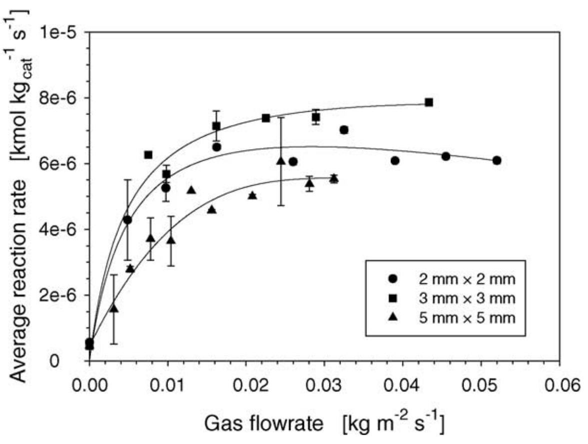

Fig. 2. The influence of the channel size on the average rate of the oxidation of benzyl alcohol to benzaldehyde. $c_{Alc,0} = 1.0$ kmol m^{-3}; $T = 388$ K; $P = 8$ bar; $L = 3.2$ kg m^{-2} s^{-1}; horizontal orientation.

3.2. *Influence of channel orientation, and direction of flow*

To clarify the influence of the orientation of the reactor, experiments were done for three extreme arrangements: (i) the vertical plane with upward flow, (ii) the vertical plane with downward flow, and (iii) the horizontal plane. The results of these experiments are summarised in Table 1. For upward flow there is a slight increase in the yield of benzaldehyde (ca. 13%); whereas for downward flow there is a decrease of the yield of oxidation (ca. 6%). There is probably a very small influence of gravity on two-phase flow patterns in the reactor, however, these differences are small. It should be noted that these experiments were performed using already deactivated catalyst (with fresh catalyst the yield of benzaldehyde formation was 22.1 ± 0.8%, compared with 9.6 ± 0.3% for the horizontally arranged reactor). Considering earlier observations [12] about the kinetics of catalyst deactivation, the change in yield due to only deactivation of the catalyst should be less than 2%.

Table 1
The changes of yield of benaldehyde formation depending on the configuration of channels

Configuration	Yield (%)
Upward flow	10.8 ± 0.6
Horizontal	9.6 ± 0.3
Downward flow	9.0 ± 0.3

Experimental conditions: $c_{Alc,0} = 1.0$ kmol m^{-3}, $T = 388$ K, $P = 8$ bar, $L = 3.2$ kg m^{-2} s^{-1}, $G = 1.3 \times 10^{-2}$ kg m^{-2} s^{-1}.

Relative small effects of channels orientation on the yield of benzaldehyde, suggest that the oxygen/liquid flow pattern in the 3 mm × 3 mm reactor channel is independent of its orientation. Also, it should be noted, that the flow direction in the mixing channel is different to that in the reactor channel (see Fig. 1).

3.3. Influence of solvent

The oxidation of benzyl alcohol to benzaldehyde was studied in a variety of solvents, including toluene (standard solvent), NMP, and dioxane/water (70%/30% by vol.) mixture. Toluene was selected as it was used successfully by Yamaguchi and Mizuno [2]. NMP was used as this was recommended by technologists from a pharmaceutical company. In studies by Crozon et al. [15], a dioxane/water mixture was used and therefore this was also included.

Experiments with NMP and dioxane/water were done with used catalyst, and therefore it was partially deactivated. Thus, in order to compare the influence of the solvent, the experiment with toluene as a solvent under standard conditions was also repeated. The results of theses studies are presented in Fig. 3. The yield of aldehyde formation in a dioxane/water mixture was much lower than that for toluene (ca. factor two), however, the catalyst was stable during the experiment. The selectivity of the oxidation reaction to form benzaldehyde in the dioxane/water mixture was slightly lower that that for toluene. The application of NMP as a reaction solvent led to fast deactivation of the catalyst, however, the selectivity was 100% (acid and ester were not detected by GC analysis). The high selectivity was probably a result of low reaction rate and hence conversion of alcohol.

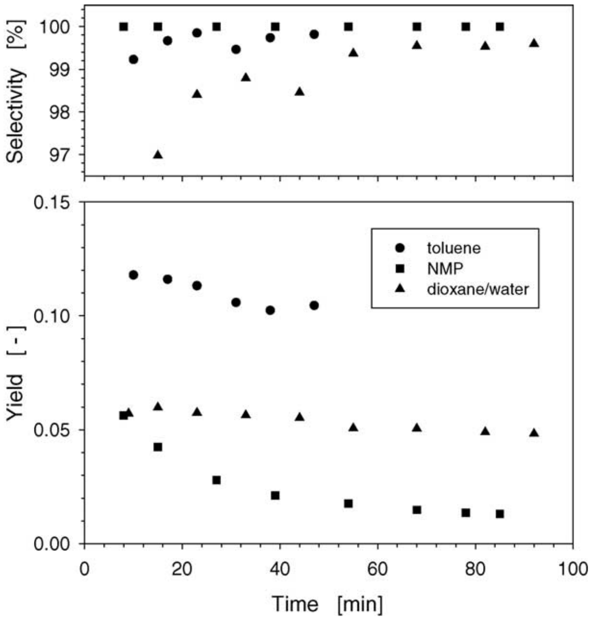

Fig. 3. The influence of the solvent on the yield of oxidation of benzyl alcohol to benzaldehyde using a Ru/Al_2O_3 catalyst. $c_{\mathrm{Alc},0} = 1.0$ kmol m^{-3}; $T = 388$ K; $P = 8$ bar; $L = 3.2$ kg m^{-2} s^{-1}; $G = 1.35 \times 10^{-2}$ kg m^{-2} s^{-1}; horizontal orientation.

3.4. Application of a homogeneous oxidising agent

The results presented in Fig. 2 indicate that above a certain flow rate the increase in the flow rate of oxygen does not influence the yield of oxidation strongly. At very low flows of oxygen, it was shown [11,12] that, the rate of oxidation was limited by the supply of oxygen. The increase of gas flow rate in the reactor either (i) decreases the external saturation of the liquid phase (i.e. the residence time of the liquid in the reactor channel) according to the equation:

$$\beta_{\mathrm{L}} = \frac{\dot{V}_{\mathrm{L}}}{\dot{V}_{\mathrm{L}} + \dot{V}_{\mathrm{G}}}, \quad (3)$$

or (ii) it could increase the slip velocity of the dispersed phase (i.e. oxygen). The latter may also influence the gas/liquid mass transfer in the catalytic bed. To endeavour to quantify the role of gas/liquid mass transfer in the packed bed (as well as the presence of gas phase in the channel), experiments were performed with a homogeneous oxidising agent (*tert*-butyl hydroperoxide [16]), and with nitrogen acting as an inert gas. As shown in Fig. 4, an increase in the flow rate of nitrogen did not have any effect on the yield. Independent of the gas phase mass flow rate, the yield of aldehyde was constant, and equal to ca. 30%. These results show that gas/liquid mass transfer was not a rate limiting factor. Similarly, the constant yield of benzaldehyde for various residence times of the liquid phase in the catalytic bed, suggest limitation of the process by the chemical reaction itself – as mass transfer of benzyl alcohol (into catalytic bed) and benzaldehyde (out of catalytic bed) between the flowing liquid and the catalyst particles was high. As the activation energy ($\Delta E_{\mathrm{A}} = 78.2$ kJ mol^{-1}) was noted previously [11,12] to be high, this also suggests that the chemical reaction itself has now become the rate limiting step. This demonstrates the viability of using structured reactors with fast mass transfer characteristics for the manufacture of pharmaceutical intermediates or speciality chemicals.

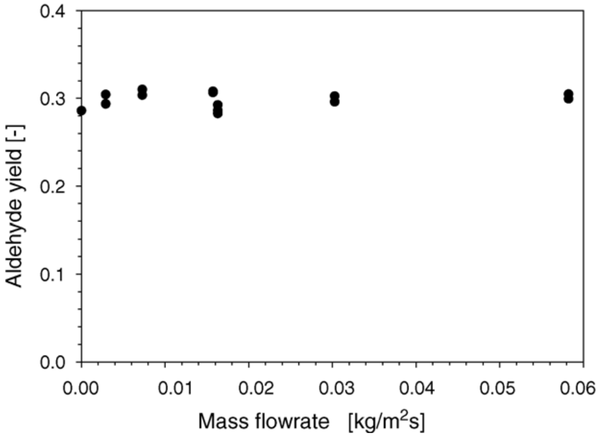

Fig. 4. The influence of nitrogen flow rate on the yield of benzaldehyde using a homogeneous oxidising agent – *tert*-butyl hydroperoxide (TBHP). $c_{\mathrm{TBHP}} = 1.2$ kmol m^{-3}; $c_{\mathrm{Alc},0} = 1.0$ kmol m^{-3}; $T = 364$ K; $p = 8$ bar; $L = 3.2$ kg m^{-2} s^{-1}; horizontal orientation.

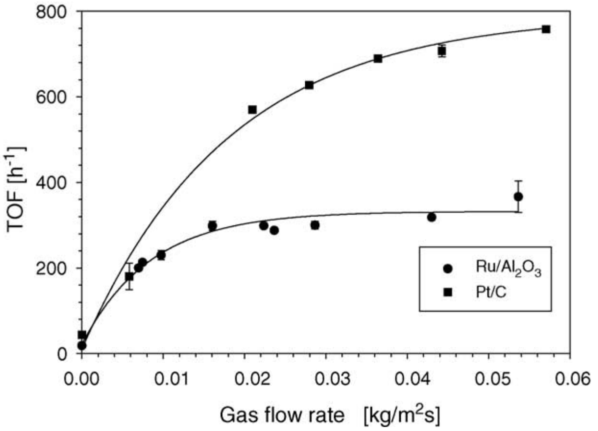

Fig. 5. The influence of the flow rate of oxygen on TOF for the oxidation of benzyl alcohol applying two catalytic systems: $c_{\mathrm{Alc},0} = 1.0$ kmol m^{-3}; $P = 8$ bar; $L = 3.2$ kg m^{-2} s^{-1}; horizontal orientation. (a) Ru/Al_2O_3, toluene (●), $T = 388$ K, (b) Pt/C, dioxane (■), $T = 368$ K.

3.5. Increasing chemical reaction rate with a Pt/C catalyst

Preliminary results using a Pt/C catalyst and dioxane as a solvent are shown (Fig. 5). In spite of the two-fold increase in the rate of oxidation (as the flow rate of oxygen was changed) a similar behaviour was observed. In order to compare these two catalytic systems, the rates were expressed as turnover frequency (TOF), defined as:

$$\mathrm{TOF} = \frac{\dot{V}_{\mathrm{L}} c_{\mathrm{Ald,e}}}{n_{\mathrm{met}}}, \qquad (4)$$

where n_{met} is the number of moles of active metal catalyst in the channel.

Faster kinetics, and therefore faster release of energy did not influence the temperature profile in the reactor (isothermal operation was maintained due to effective heat transfer). Despite higher rates of reaction the process soon became limited by chemical kinetics and not by mass transfer.

4. Concluding remarks

The efficiency of multichannel and multifunctional packed bed reactors with characteristic size of 2–5 mm, manufactured based on the use of shims technology (Chart Heat Exchangers Ltd.) has been demonstrated. For a given catalyst particle size ($d_{\mathrm{P}} = 0.165$ mm) the selective oxidation of benzyl alcohol to benzaldehyde in a 3 mm × 3 mm channel resulted not only in the highest yield of benzaldehyde, but also the scatter in the experimental results (in terms of benzaldehyde concentration) was the smallest, indicating that stable reactor conditions has been achieved. The performance of the reactor was not affected strongly by the orientation of channels in the reactor (horizontal or vertical) as well as by the direction of flow (co current upward- or downward flow). This was probably due to the effectiveness of the mixing channels that had been incorporated into the structure, in combination with fortuitous two-phase flow patterns in the 3 mm × 3 mm channel. In this channel (3 mm × 3 mm), the dispersion of the gas phase in the form of small and ‘‘stable’’ bubbles was not influenced by gravitational forces.

For the Ru/Al_2O_3 catalyst, for the range of solvents tested, toluene was found to provide the best catalytic performance. The use of a dioxane/water mixture resulted in a 50% reduction in catalytic activity, and the use of NMP led to fast deactivation of the catalyst.

For the range of conditions tested, as gas flow rate is increased it is evident that the oxidation of benzyl alcohol becomes limited by chemical reaction. This is due to the efficient mass transfer not only in the mixing channel but also in the packed bed. This limitation was not changed significantly by increasing the chemical kinetics by a factor two (use of Pt/C catalyst in pure dioxane).

So far, the results of these experiments continue to be very encouraging, and therefore a 2 kg h^{-1} isolated product yield reactor is being constructed at the University of Bath, to show the viability of the multichannel multifunctional compact reactor technology for the manufacture of fine chemicals and pharmaceutical intermediates. This new design of reactor will be manufactured by Heatric, in accordance with the authors' design specifications.

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