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The use of membrane reactors for catalytic *n*-butane oxidation to maleic anhydride with a butane-rich feed

Erzeng Xue*, Julian Ross

Centre for Environmental Research, College of Science, University of Limerick, Limerick, Ireland

Abstract

Selective oxidation of *n*-butane to maleic anhydride was studied using a tubular ceramic membrane reactor loaded with a commercial VPO catalyst and under both O_2-rich and butane-rich feed conditions. The study was carried out using a configuration by which butane was fed to the inner tube (tube-side) where the catalyst was mounted and O_2 was fed either entirely to the outer tube (shell-side) or distributed in a certain ratio between the tube- and shell-sides with a variation of the pressure difference across the membrane, ΔP. It was observed that the use of a butane-rich feed under this configuration gives a higher maleic anhydride yield and that both ΔP values and the way feed O_2 was distributed can have a significant effect on the reaction rate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Membrane reactors; Maleic anhydride; Butane-rich feed

1. Introduction

Conversion of *n*-butane (*n*B) to maleic anhydride (MA) by means of VPO catalysts is a unique catalytic reaction in terms of conversion of an alkane directly to an oxygenate [1]. The current industrial processes are mostly operated using a feed containing 1–2% of *n*B in air in order to avoid the danger of operating the process in the flammable region. Large volume of air (∼80% of N_2) goes through the process which by no means is economical [1–6]. Alternatively, an *n*B-rich stream can be used as feed and the reaction is operated in the region above the upper flammable limit of the *n*B and oxygen (O_2) mixture. This has been explored in some earlier works [7–9]. Since O_2 is consumed faster during the butane oxidation than *n*B, there is little risk of entering the flammable region as the reaction proceeds [9].

Recent development in the synthesis of ceramic membranes has opened a new frontier for research and development of both existing and new industrial catalytic processes. Applying membrane reactor technology in combination with the use of *n*B-rich feed to the *n*B oxidation to MA represents one of these challenges [8–11]. There are several advantages associated with the use of membrane reactors over that of conventional reactors such as a fixed-bed reactor in terms of controlling a reaction process. For instance, partial pressures of the reactants, such as those of O_2 and *n*B in the *n*B oxidation process, in the reaction zone can be regulated to a certain extent by supplying one of the reactants through a properly selected membrane and by proper selection of the operating parameters for the reactor since the mass transfer through a membrane is a function of the membrane permeability and selectivity, the feed mode and feed composition, and the

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* Corresponding author. Tel.: +353-61-202-684;
fax: +353-61-202-602.
E-mail address: erzeng.xue@ul.ie (E. Xue).

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pressure difference across the membrane (ΔP). These parameters can be independently tuned to meet the specific requirements of a reaction process and for a given catalyst. Some of these considerations in relation to the *n*B oxidation to MA have been discussed in our earlier works [9].

In this paper the results of our recent study on the catalytic oxidation of *n*B to MA using a membrane reactor are reported. The performance of a membrane reactor operated using an *n*B-rich feed is evaluated and compared with that using an O_2-rich feed. Various ways of introducing O_2 to the reactor and the effect of the operation pressure across the membrane on the reaction rate and MA yield are also examined.

2. Experimental

A commercial α-Al_2O_3 membrane tube (T1.70, US Filter-SCT) of dimension ϕ_{in}/ϕ_{out}=7/10 mm and 150 mm long (enamelled 25 mm at each end) was used for this study. The membrane was modified with zeolite prior to use to obtain a desired pore size distribution, typical permeation rate being in the range 10^{-7}–10^{-8} mol (m^2 s Pa)$^{-1}$ [12]. The membrane tube was mounted in a specially designed stainless steel chamber acting as a membrane reactor which allowed gases to be fed to the tube- and shell-sides in several ways. The effluent gases from tube- and shell-sides could either be mixed or separate before being analysed. The operation pressure on the tube-side was atmospheric and the pressure on the shell-side was controlled to obtain the desired pressure differences across the membrane.

A commercial VPO catalyst supplied by DuPont Iberica S.A., Spain, was used for this study. The catalyst was prepared using a method similar to that described in literature [13–14] had a BET surface area of 10 m^2 g^{-1} and was pre-activated in N_2 at 750°C. The powder-formed catalyst was pressed to disk, then crushed and sieved to obtain grains of sizes between 0.1 and 0.3 mm. To reduce the risk of hot-spot formation in the catalyst bed during the reaction, the VPO catalyst (2 g) was diluted with quartz grains (2 g) of the same sizes. The mixture was packed in the inner tube of the membrane.

The test system consists of a set of mass flow controllers to deliver the required feed mixture, a membrane reactor in a furnace with temperature control and an on-line sample analysis. The connecting lines were heated to above 100°C to avoid any possible condensation of water (H_2O) and MA produced. Several non-return valves and pressure relief valves were also in place to ensure safe operation. The analysis was performed with a Hewlett Packard 5890 II GC equipped with two 6-way sampling valves and two columns (Carboxen 1000 and Paraplot Q). All the components in the gas streams before and after reactions were determined. Helium (He) was used as the internal standard to correct any volume change before and after the reaction as well as any offset caused by variation of ambient temperature and pressure.

The catalyst was normally pre-treated, aged in the reaction mixture at 400°C overnight prior to taking experimental data. The data reported here are the average values of several samples taken under each set of conditions and are expressed as the rates of O_2 or butane consumption in units of mmol g^{-1} s^{-1}.

3. Results and discussion

3.1. Comparison of the performance of the membrane reactor operated in a co-feed mode and that using different feeds

Fig. 1 shows the results of *n*B and O_2 consumption rates and Fig. 2 shows the corresponding MA selectivity and yield as a function of the reaction

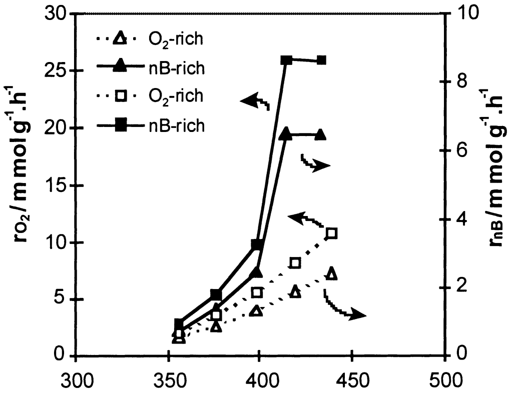

Fig. 1. Rates of *n*B and O_2 consumption (r_{O_2} r_{nB}) as a function of temperature using an O_2-rich feed and an *n*B-rich feed (see text for the experimental conditions).

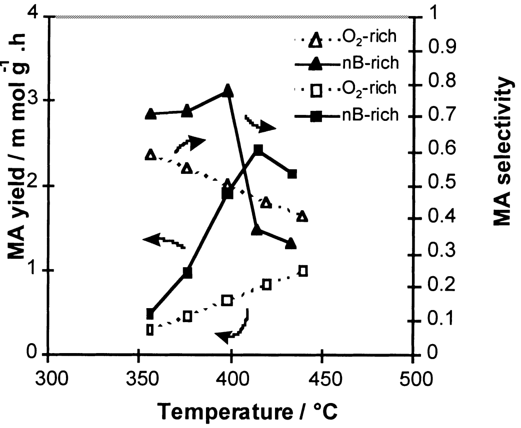

Fig. 2. MA selectivity and yield as a function of temperature using an O_2-rich feed and an *n*B-rich feed (see text for the experimental conditions).

temperature using an O_2-rich feed and an *n*B-rich feed, respectively. Both the experiments were conducted in the membrane reactor with all gases fed to the tube-side only and with the inlet and outlet valves of the shell-side fully closed (co-feed mode). This arrangement may have resulted in a small fraction of the feed gas at the short distance after entering the tube-side slipping through the membrane to the shell-side and then diffusing back to the tube-side before exiting the reactor because of the presence of a small pressure drop over the catalyst bed; however, considering the fact that the pressure drop over the catalyst bed was generally very small, being less than 3 kPa, and that all other operating parameters were kept the same (except the feed composition) during the experiments, the comparison may be regarded as being valid for the conditions concerned. The feed volume flow was 100 ml (STP) min^{-1} in both cases; the feed compositions used were O_2/*n*B/CO_2/He=20%/2%/65%/13% for the O_2-rich feed and O_2/*n*B/CO/CO_2/He=20%/15%/5%/55%/5% for the *n*B-rich feed.

With either feed, the rates of *n*B and O_2 consumption increase as the reaction temperature increases, and so does the MA yield. In the case of using *n*B-rich feed, the rates of *n*B and O_2 were levelled off at high temperatures because of the complete consumption of the feed O_2. It is seen that using the *n*B-rich feed gives much higher rates of *n*B and O_2 consumption as well as MA yield than using the O_2-rich feed. The MA selectivity was also different. In the case of using O_2-rich feed, the MA selectivity decreases continuously as temperature increases; however, the MA yield with the use of *n*B-rich feed shows no sign of decreasing at temperatures lower than 400°C. A sharp decrease in MA selectivity at high temperatures for the *n*B-rich feed was due to the fact that O_2 in the feed was totally consumed at these temperatures which led to the cracking of *n*B to occur. These results demonstrate clearly that under these test conditions, using an *n*B-rich feed is beneficial for the reactions concerned.

3.2. The effect of transmembrane pressure difference on the reactor performance with various feed compositions

When the gases are to be fed separately to tube- and shell-sides, new operation parameters emerge. On either side of the membrane, the feed volume flow, the feed composition and operation pressures can be varied. A systematic approach is required to determine the effects of all these operation parameters. In this work we limit our experiments to certain fixed conditions that were to use a constant overall feed composition (O_2/*n*B/CO/CO_2/He=20%/15%/5%/55%/5%) and fixed volume flows for the tube-side feed (55 ml min^{-1}) and for the shell-side feed (45 ml min^{-1}). For all the experiments total *n*B to be fed to the reactor (15 ml min^{-1}) was fed to tube-side only; the O_2 (a total feed rate of 20 ml min^{-1}), on the other hand, was either fed to shell-side alone or divided into two streams and fed separately to the shell-side and to the tube-side. The compositions of feed to the tube-side and to the shell-side were therefore varied depending on how much O_2 was fed to the tube-side and how much to the shell-side. For each set of fixed feed compositions, the operation pressure on the shell-side was regulated so that a desired pressure difference across the membrane (ΔP) was obtained and the rates of *n*B and O_2 consumption and MA selectivity were measured.

Fig. 3 shows typical results of O_2 consumption rates at various temperatures as a function of transmembrane pressure difference (ΔP) with all O_2 fed to the shell-side only. (The data of *n*B consumption rates and MA yield follow the same trend as that of O_2 and are omitted here.) The values of ΔP were calculated based on the difference between the shell-side pres-

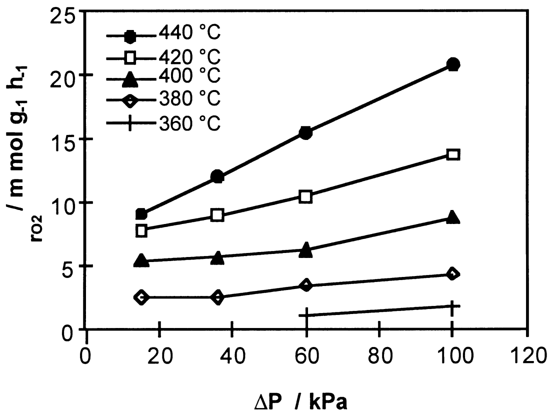

Fig. 3. Rates of O_2 consumption r_{O_2} at various temperatures as a function of the transmembrane pressure difference (see text for the experimental conditions).

sure and the average pressure in the catalyst bed on the tube-side. The pressure drop across catalyst bed varied very little in these experiments, being typically in the range 1–3 kPa. The figure shows that the reaction rates increase as ΔP increases for this feed arrangement. This observation is in line with the findings in a separate study of the reaction kinetics for the catalyst used. In the kinetic studies, it was found that the rate of reaction under *n*B-rich feed conditions can approximately be expressed as

$$r = kp_{O_2}^{\alpha} p_{nB}^{\beta}$$

The values of α and β vary with the feed compositions and operation conditions, being generally in the range of 0.5–1.0 and 0–0.5 with respect to O_2 and *n*B, respectively. An increase of partial pressure of O_2 in the catalyst bed would therefore have a stronger positive effect on the reaction rate than that of *n*B. This is what is happening here. When ΔP rises, which is the driving force for the mass transport from the tube-side to shell-side, the partial pressure of O_2 on the tube-side is therefore increased, hence the conversion levels increase.

Fig. 4 presents the results of the experiments with varying O_2 distribution between the tube-feed and the shell-feed (only O_2 conversions are plotted here and the same trend was observed for *n*B conversions and MA yield). Three different ways of feeding O_2 were examined and compared, these being: O_2 to shell/ O_2 to tube=20/0, 15/5 and 10/10 ml min^{-1}. When all the O_2 was fed to shell-side only (solid diamonds), an increase in ΔP leads to an increase in the rates of O_2 conversions at all temperatures, the dependence of reaction rates on ΔP being more pronounced at higher temperatures. As with this feed arrangement, the O_2 in the reaction zone relies completely on the rate of O_2 supply from the shell-side, which is directly proportional to the transmembrane pressure difference ΔP. At higher temperatures the rate of O_2 supply through membrane becomes the rate limiting factor for the overall conversion, thus a small increase of ΔP can lead to a large increase in the overall rate of reaction. When 25% of the total O_2 was fed to the tube-side (open squares, O_2 to shell/tube=15/5 ml min^{-1}), the dependence of reaction rate on the ΔP appears to diminish at low temperatures; the O_2 consumption rates also become higher for low ΔP than in the case of feeding all O_2 to the shell-side. This is mainly due to the fact that a portion of O_2 was fed to the tube-side together with the *n*B which makes better use of the first part of the catalyst bed than in the first case, especially when ΔP is low. At high tem-

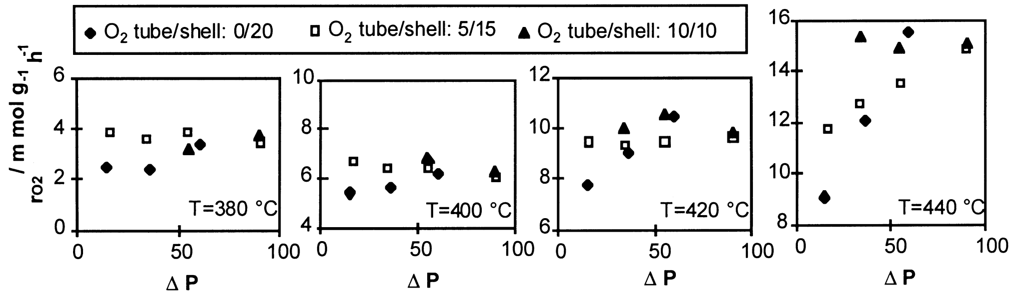

Fig. 4. O_2 consumption rates for three different feed compositions as a function of ΔP at temperatures between 380 and 420°C.

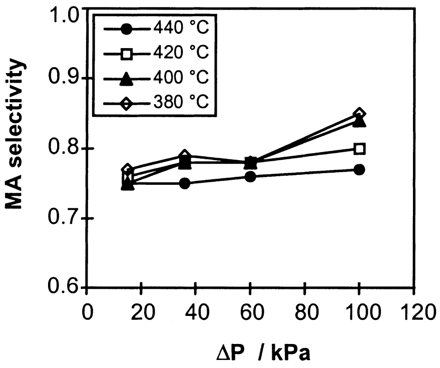

Fig. 5. MA selectivity at different temperatures as a function of the transmembrane pressure difference (corresponding to the experiments as shown in Fig. 3).

perature, however, the reaction proceeds faster, demanding more O_2 than that already in the tube-feed plus that transferred through membrane at low ΔP, an increase of ΔP results in a rise of the overall conversion rate. When ΔP is higher, the amount of O_2 in the reaction mixture becomes in excess of that demanded by the reaction and the rate of reaction will then dictate the overall rate of conversion. When half of the total O_2 is supplied through the tube-side (O_2 to shell/tube=10/10 ml min^{-1}, solid triangles), the dependence of the O_2 consumption rates on ΔP disappears completely. As the highest O_2 conversion achievable in this system is just a little more than 50%, the initial O_2 feed to the tube-side plus that diffused through the membrane from the shell-side will then provide enough O_2 required by the reaction, thus an increase of ΔP will no longer produce a positive influence on the reaction rate. The actual concentration profiles in the catalyst bed may be very complicated, because of the presence of multi-components diffusing through the membrane into and out of the reaction zone along with the complicated reaction kinetics.

In general, the selectivity to MA varies with the reaction temperature becoming lower at higher temperatures. In the case of feeding O_2 to shell-side only, the selectivity at a fixed temperature appears to increase slightly as the ΔP increases. This is shown in Fig. 5 (the MA selectivity data shown in this figure correspond to the experiments shown in Fig. 3). When the reactor was operated with the O_2 being fed to both the tube-side and the shell-side, there was very little change of MA selectivity values.

The use of a membrane in this context is nothing more than an O_2 distributor. However, the work reported here demonstrates that the performance of a membrane reactor is affected by many parameters such as feed distribution between the tube- and the shell-sides of membrane and the operation pressures. The presence of these parameters along with others such as membrane permeability and selectivity makes membrane reactors more complicated than conventional reactors such as a fixed-bed reactor, therefore requires a more careful and systematic way to approach. However, this also implies that process designers have extra freedoms in optimising the operation conditions of a membrane reactor and in catalyst selection. Some parameters may be independently tuned for a given catalytic reaction and for a given catalyst. A detailed discussion of the use of membrane reactors and their advantages for the catalytic *n*-butane oxidation to MA reaction is given elsewhere [9].

4. Conclusions

Catalytic oxidation of *n*-butane to MA can be achieved using membrane reactors by feeding *n*-butane to the one side (tube) of membrane on which a catalyst is mounted and adding O_2 to the other side (shell) and distributing O_2 through the membrane to the reaction zone. A comparative study with this configuration and with the feed added to the tube-side only shows that using a butane-rich feed gives better conversions and MA yield than an O_2-rich feed. For a catalyst having positive dependence of the O_2 partial pressure in kinetics and the reaction is operated with a butane-rich feed, the supply of O_2 to the reaction zone is critical, which can be achieved either by increasing the transmembrane pressure (ΔP) in the case of all O_2 being fed to the shell-side or by co-feeding a portion of O_2 together with butane to the tube-side. When all the O_2 is fed to the shell-side, MA selectivity was found to increase slightly with ΔP.

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