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Use of membrane reactors for the oxidation of butane to maleic anhydride under high butane concentrations

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Abstract

The oxidation of butane to maleic anhydride (MA) has been carried out in an inert membrane reactor, where a mesoporous membrane was used to distribute oxygen to a fixed bed of VPO catalyst. The study was carried out using relatively high butane/oxygen ratios (up to seven times higher than those currently used in industrial practice), some of which would have been in the explosive range if fed to a fixed bed reactor. The maximum MA yields obtained were respectively 17.7 and 14.2% for 5 and 10% total butane concentrations in the feed.

Keywords: Maleic anhydride; Inert membrane reactor; Butane oxidation

1. Introduction

The process of selective oxidation of butane to maleic anhydride (MA) over VPO catalysts has been intensively studied in recent years. The main part of this research effort has been devoted to the development of new promoted catalysts (see for instance the review by Hutchings [1]), while process alternatives based on reactors different from the conventional fixed bed (fluidized beds, riser reactors [2]), have been less studied.

Butane concentrations in the feed stream of industrial reactors are usually between 1 and 2% by volume of butane in air, in order to remain below the lower flammability limit. However, in principle it is also possible to operate above the upper flammability limit, by maintaining a high enough butane concentration, or below the minimum oxygen for explosion, with a sufficiently low oxygen concentration. Under the highly diluted conditions employed in industrial practice, recycle is not economically feasible, and unconverted butane is flared. On the other hand, the low concentration of butane in the feed stream increases the energy requirements of the operation, and results in a low concentration of MA at the exit of the reactor, with the associated increase in separation costs. Operation with a higher butane concentration in the feed would therefore be advantageous from the industrial point of view.

The problem of achieving reactor operation with a higher butane concentration in the feed while at the same time avoiding the flammability range can be solved by the use of inert membrane reactors (IMRs). In this reactor the membrane is used to distribute oxygen to a catalyst bed containing a butane-rich atmosphere, and reactor operation outside the explosion range becomes feasible for a wider range of butane/oxygen feed ratios. In addition, oxygen distribution can lead to an increase in the selectivity to the desired product by reducing the partial pressure of oxygen in the reactor: in selective oxidation of hydrocarbons, where both reactants and partial oxidation products can undergo deep oxidation to carbon

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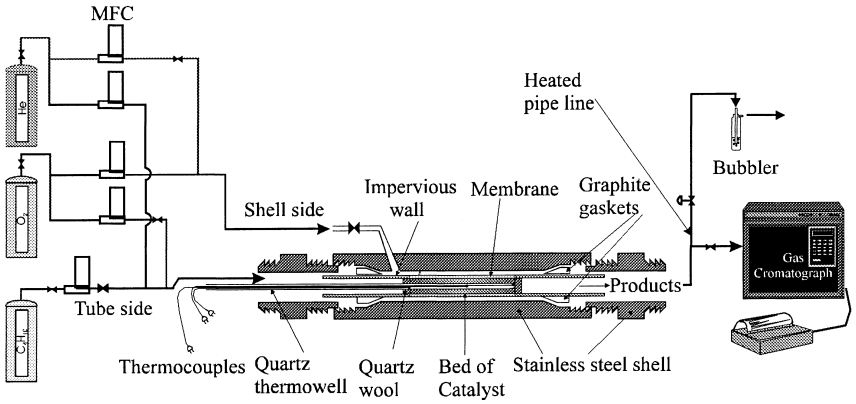

Fig. 1. Reaction system.

oxides, it is often found that reducing the partial pressure of oxygen results in higher selectivities [3]. This is often sufficient to increase yield, in spite of the lower hydrocarbon conversion that may be obtained with a reduced partial pressure of oxygen. In addition it has been found that, for many partial oxidation reactions, when operating at complete or nearly complete oxygen conversion, a reactor with a distributed oxygen feed uses the oxygen more efficiently, which leads not only to safer operation and higher selectivities [4–6], but also to higher hydrocarbon conversions [6].

In this work, an IMR has been used for the oxidation of butane to MA, with butane concentration in the 5–10% range. The effect of different operating variables and of the feed configuration on the selectivity and yield to MA has been investigated.

2. Experimental

2.1. Membrane reactor

A schematic drawing of the reaction system used is shown in Fig. 1, where the membrane reactor section has been enlarged in order to allow a more detailed view. The reactor consisted of a ceramic membrane enclosing a fixed bed of VPO catalyst in the tube side, to which oxygen was distributed from the shell side using the membrane pore network. Between 2.5 and 3 g of VPO catalyst were packed in the membrane tube side, forming a bed of annular cross-section, between the inner membrane wall and an axial quartz thermocouple well. Reaction took place at atmospheric pressure, and at temperatures between 375 and 450°C. Mass flow controllers were used to feed the different gases to the reactor. Butane was always fed to the tube side of the membrane, while the inert diluent (He) could be fed to either side or to both. Oxygen was usually fed to the shell side of the membrane, where it flowed at pressures of up to 4 bars; in a few experiments, part of the oxygen feed was diverted to the tube side, and premixed with butane at atmospheric pressure before entering the reactor. Unless otherwise indicated, the percentages of butane and oxygen given in this work refer to the overall feed to the membrane reactor, i.e., as if oxygen and butane were premixed at the reactor entrance.

The membrane plus catalyst was inserted in a stainless steel outer shell, and sealed using graphite gaskets, and the ensemble was heated by means of a three-zone furnace. External cooling was used to keep the graphite gaskets at least 150°C below the reaction temperature. The exit gases were analyzed by means of on-line gas chromatography, using three capillary columns in a single gas chromatograph equipped with TCD and FID detectors. Oxygen and carbon balance closures were usually better than ±5%.

The membranes used for oxygen distribution were obtained by modification of commercial tubular microfiltration membranes SCT, (Societé des Ceramiques Techniques, Tarbes, France). In this case the main concern was to achieve sufficient membrane inertness and a homogeneous oxygen distribution

throughout the bed. In order to obtain the desired permeation characteristics, the original Al_2O_3 tubes were subjected to several cycles of impregnation with either boehmite or silica sol, until the desired permeation flux was achieved, and the back permeation of butane to the shell side under typical reaction conditions was reduced to a sufficiently low level. Characteristic final loads in this work were 6 wt.% of γ-Al_2O_3 and 15 wt.% of SiO_2. After each impregnation cycle the membranes were dried and calcined (600°C for γ-Al_2O_3 and 800°C for SiO_2). Following the deposition of silica or alumina the membranes were doped with $LiNO_3$, in order to reduce their surface acidity, which contributes non-selectively to the reaction.

During the different stages of preparation the membranes were characterized by permeation experiments in a separate permeation unit. The final permeation flux in the γ-Al_2O_3 loaded membranes was typically one order of magnitude higher than in membranes where silica had been deposited. The Knudsen contribution was at least 60–70% in both types of membranes, and the back permeation of butane (measured in experiments without reaction, where nitrogen was used instead of oxygen) was <2% of the total butane feed.

2.2. Catalysts

Two different VPO catalysts were used in the experiments reported in this work. The first, termed catalyst A was prepared by DuPont, and the second (catalyst B) by Haldor Topsoe. Catalyst A was somewhat more active and selective than catalyst B. Both were prepared following specific recipes, within the framework of the European project BRPR-CT95-0046, and supplied as powder, already in an active form. The powder was pelletized, then crushed and sieved to a size of 160–320 μm, which formed the fixed bed on the tube side of the membrane reactor. It should be noted, however, that both of these catalysts were developed to work under conditions similar to those used in industrial practice (high oxygen and low butane concentrations), and their use in this work has taken place under very different conditions (butane concentrations 3–8 times higher). Further characterization and kinetic measurements on these catalysts will be published elsewhere.

XRD analysis performed using a Rigaku/Max System difractometer (Ni-filtered Cu Kα radiation, scan rate of $0.02^\circ\,s^{-1}$) showed that in both catalysts the prevailing phase was crystalline pyrophosphate, $(VO)_2P_2O_7$. The BET surface area determined from N_2 adsorption–desorption measurements (Pulse-Chemisorb 2700) was about 26 and 12 m^2/g for catalysts A and B, respectively.

3. Results and discussion

3.1. Stability of operation

In spite of the high butane concentrations employed, after a few hours on stream the performance of the catalyst in the membrane reactor was stable, giving steady conversion and product distribution. Regarding membrane stability, accelerated aging tests were carried in a separate unit, using steam/air mixtures at the reaction temperature. After 800 h under this mixture the membrane was still usable, with only a small increase in the permeation flux, in spite of a noticeable decrease in the surface area of the silica-loaded membranes. During reaction, the membrane reactor operated with a smooth (typically ±8°C) temperature profile, which is in contrast with the characteristic hot spot observed in the entrance region of fixed bed reactors, even with considerably leaner feeds. In addition, in many of the experiments reported below, the IMR operated under conditions that would have been within the explosive range had the butane and oxygen feeds been mixed at the reactor entrance.

3.2. Reaction results

3.2.1. Effect of temperature and space velocity

The temperature was varied between 375 and 450°C (Fig. 2). As could be expected, the butane and oxygen conversions increased markedly with temperature. The selectivity to MA increased up to 400°C, and then decreased, following a nearly threefold increase in butane conversion when the temperature was raised from 400 to 450°C. The temperature profiles were smooth in all cases, with maximum temperature deviations within the above quoted range, even at 450°C.

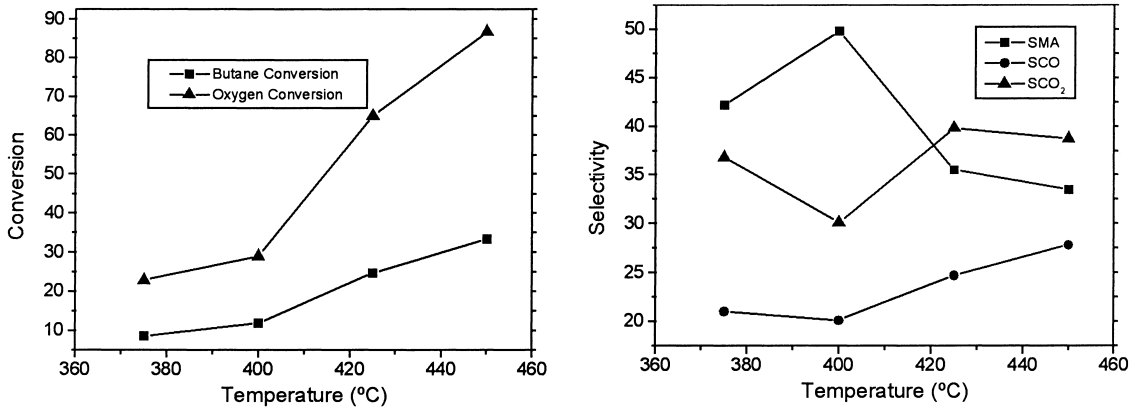

Fig. 2. Butane and oxygen conversions and MA selectivity as a function of temperature. Catalyst B, alumina-loaded membrane, GHSV = 2950 h^{-1}, 10% butane, 20% oxygen, Wcat = 2.55 g.

The selectivity–conversion tradeoff that is normally encountered in partial oxidation reactions was also observed when varying the total gas hourly space velocity (GHSV) by changing the total flow rate. Fig. 3 shows an almost linear decrease of the butane and oxygen conversions with GHSV, and a corresponding increase in MA selectivity. It may be noticed that the data in the figure extend over a 100% increase in the total flow rate to the reactor, which means that the flux of oxygen permeated across the membrane had to be doubled during the course of the experiment. With porous membranes the desired value of oxygen permeation can be obtained simply by adjusting the oxygen pressure on the shell side. This is an important advantage over dense oxygen-permeating membranes, where the permeation fluxes have a limited range.

3.3. Oxygen/hydrocarbon ratio

Fig. 4 shows the results of a series of experiments in which the overall feed to the reactor contained 10% of butane and increasing amounts of oxygen, while the amount of diluent was adjusted to keep the total flow rate constant. It can be seen that both the MA selectivity and yield increased as the oxygen concentration was increased. This is not surprising since the VPO catalysts used were similar to the commercial catalyst, that works well in oxidizing atmospheres. This means that in order to obtain good results, the oxygen to butane ratio in contact with the catalyst surface must be maintained above a certain limit (the usual commercial ratio is around 14).

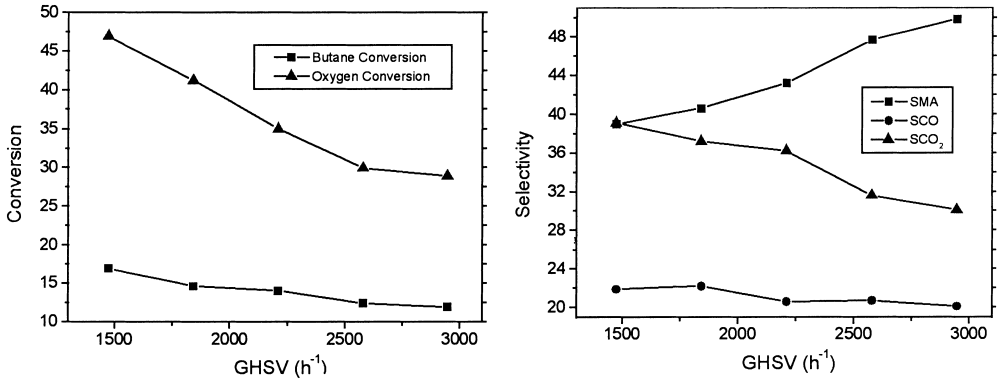

Fig. 3. Butane and oxygen conversions and MA selectivity as a function of GHSV. Catalyst B, alumina-loaded membrane, temperature = 400°C, 10% butane, 20% oxygen, Wcat = 2.55 g, variable total flow rate.

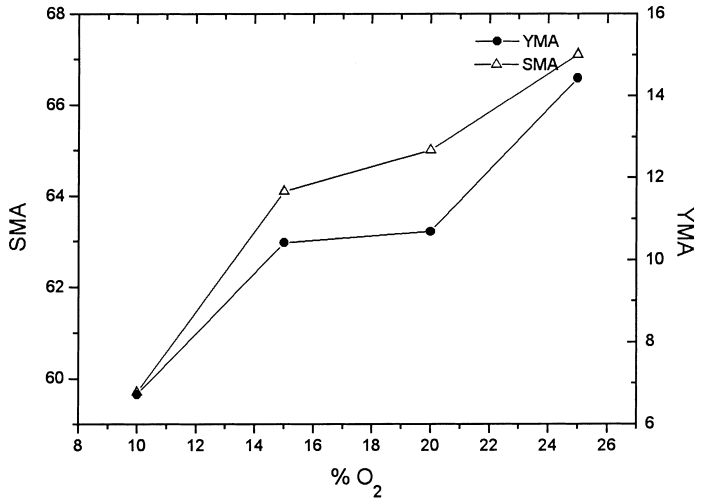

Fig. 4. Maleic anhydride selectivity and yield as a function of the oxygen concentration. Catalyst A, butane concentration: 10%, remainder He. Temperature = 400°C, Wcat = 2.55 g, GHSV 2950 h^{-1}.

The fact that the oxygen/butane ratio is the main parameter controlling reactor performance was confirmed in separate experiments run in a micro fixed bed reactor, in order to maintain more homogeneous conditions throughout the catalyst. The results shown in Table 1 were obtained at three different sets of experimental conditions (temperature, W/F). In the first two series the MA yield steadily improves as the oxygen to hydrocarbon ratio increases, while the selectivity shows little change. In order to maintain a selective catalyst surface a minimum value of the oxygen concentration is needed, which depends on the oxygen to butane feed ratio and also on the conversion reached in the reactor. The last two columns in Table 1 show that, if the oxygen concentration is depleted beyond a certain limit (e.g. by increasing W/F at low oxygen/butane ratios) the selectivity drops rapidly. The highest yield in Table 1 corresponds to an oxygen concentration of 20% and an oxygen to butane ratio of 10, which are close to those used in industrial practice.

The above described behavior is consistent with the data presented in Table 2, which were obtained in an IMR loaded with catalyst A. In these experiments the amount of oxygen fed to the reactor was kept constant, corresponding to an overall concentration of 20%, while the butane feed rate was varied. It can be seen that the selectivity to MA stayed at an approximately constant level (ca. 67%), while the MA yield increased from 11.3 to 17.7% as the butane concentration was reduced. It is also interesting to note that, because of safety considerations, none of the feed compositions in Table 2 could be used in a fixed bed reactor.

Table 1
Results of microreactor experiments carried out with catalyst A

W/F (mg cat/cm^3 min)	Temperature (°C)	O_2 (%)	O_2/butane	Butane conversion	O_2 conversion	MA selectivity	MA yield
17	380	10	1.1	7.5	29.8	68.1	5.10
17	380	10	2.2	12.6	29.1	65.1	8.21
17	380	20	4.4	15.5	15.4	65.5	10.13
17	380	20	10.0	28.8	12.1	63.7	18.33
7	400	16.3	1.7	6.5	15.4	67.6	4.41
7	400	16.7	2.4	8.1	13.7	66.2	5.37
7	400	16.8	8.2	16.3	8.8	67.6	11.03
3.3	400	10.6	0.6	11.0	98.0	12.0	1.32
2.6	400	10.6	0.6	9.2	98.0	14.0	1.29

Table 2
Reactor performance as a function of the butane concentration[a]

Butane (%)	SMA	SCO	SCO_2	XBut	XO_2	Yield MA
10	66.6	16	17.3	16.9	35.3	11.3
7.5	66.4	16.3	17.3	19.4	30.8	12.9
5	67	16.5	16.9	26.5	28.9	17.7

[a] Oxygen concentration: 20%, silica membrane. Other conditions as in Fig. 2.

3.4. Feed configuration

Because in the IMR oxygen is progressively distributed along the bed, the butane concentration is very high (very low oxygen to butane ratio) for the catalyst located near the bed entrance. It is therefore interesting to study the influence of feed configuration, i.e., the effect of shifting part of the oxygen (or He) from the shell to the tube side, in order to change the conditions at the reactor entrance. Fig. 5 shows the evolution of butane conversion and MA selectivity and yield as part of the oxygen feed was shifted from the shell to the tube side (the He feed was adjusted to keep flow rates constant in both sides). It can be seen that a moderate shift of the oxygen feed is beneficial: the butane conversion increased with only a slight decrease in selectivity. This caused the MA yield to increase, reaching a maximum when about 8 ml of oxygen were fed to the tube side. However, beyond a certain level of oxygen shift, the selectivity and MA yield rapidly drop, becoming zero when about 15 ml/min of oxygen were shifted from the shell to the tube side. A very similar behavior (not shown) was obtained for catalyst B.

The data in Fig. 5 indicate the need to supply enough oxygen to every reactor position: As more oxygen is shifted from the shell to the tube side, the catalyst in the entrance region of the reactor becomes more active and selective; initially this is enough to compensate the loss of performance of the catalyst in the remainder of the reactor, and the yield increases. However, as more oxygen is detracted from this zone, the catalyst becomes non-selective, and all the maleic produced in the entrance region is oxidized to CO and CO_2 as it travels further down the bed.

The effect of He shift from the shell to the tube side is less marked than that of oxygen, and results from a complex interaction of several factors. Fig. 6 shows that a maximum in the selectivity and yield was obtained when about 28% of the He feed (40 Nml/min) was supplied at the reactor entrance. The initial shift of the He feed was beneficial to dilute the concentration of the different species (especially that of butane) in the entrance region of the reactor, giving rise to an increase in selectivity. In this case however, unlike the oxygen-shift experiments, the total flows to shell and tube side were not kept constant: As He was shifted to the tube side, the total flow to the shell side was reduced by the same amount. The extent of back permeation (i.e., the permeation of the hydrocarbon in the tube side towards the shell side) increases as the total permeation flux from the shell side decreases. Because

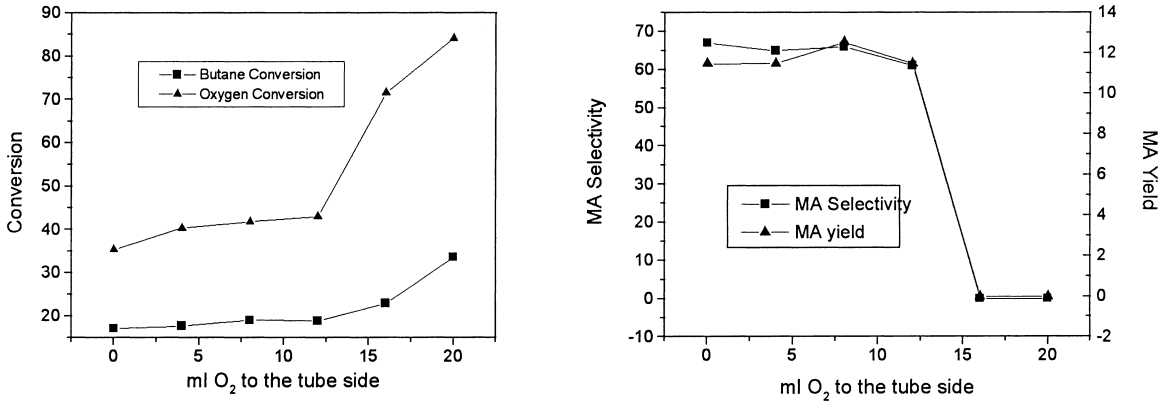

Fig. 5. Butane conversion and MA selectivity and yield as a function of the oxygen feed to the tube and shell sides. Temperature = 400°C, Wcat = 3.25 g. Total flow rate: 200 Nml/min (60 to tube side, 140 to shell side), A. Butane feed: 20 Nml/min (tube side), O_2 feed: 40 ml/min, distributed between tube and shell sides. He was also fed to both sides in variable proportions, in order to maintain constant flow rates to tube and shell sides.

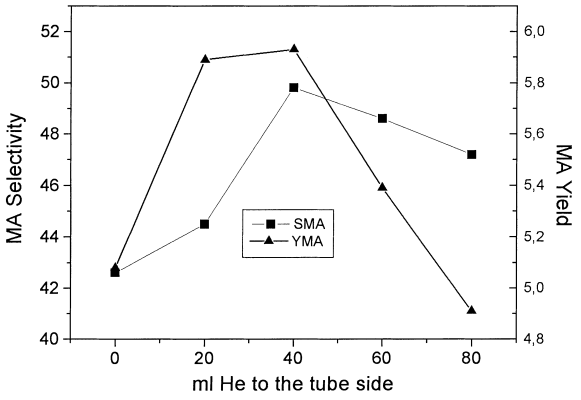

Fig. 6. MA selectivity and yield as a function of the He feed to the tube and shell sides. Temperature = 400°C, total flow rate: 200 Nml/min (20 Nml/min fed to the tube side, and 40 Nml of oxygen to the shell side), 2.55 g of catalyst B. Initially the total flow of He (140 Nml/min) was fed to the shell side.

the He diluent accounts for the greater part of the flux from the shell to the tube side, as He is shifted from the shell to the tube side, back permeation of butane (and especially of MA) to the shell side increases. This is detrimental to selectivity, contributing to the deep oxidation of MA. Therefore the initially beneficial effect of the He shift is eventually overcome by the effect of back permeation, and an optimum exists in the amount of He transferred to the tube side.

4. Concluding remarks

The inert membrane reactor (IMR) is a promising contactor to carry out the oxidation of butane to maleic anhydride. It allows safe operation with smooth temperature profiles, under conditions that are not possible in conventional fixed or fluidized bed reactors. Interesting MA yields were obtained in this work at relatively high butane concentrations: 17.7 and 14.2% for feeds containing 5 and 10% butane, respectively. This is so in spite of the fact that the catalysts used were intended to work under oxygen-rich conditions, which does not allow a full use of the oxygen-distributing capabilities of the IMR. Further improvements are likely with catalysts that are more tolerant to reducing environments. Also, additional development of the mode of contact is required to tailor it more closely to the specific characteristics of this process.

Acknowledgements

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