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Oxidative dehydrogenation of propane in an inert membrane reactor

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Abstract

A study of the application of an inert membrane reactor (IMR) to the oxidative dehydrogenation of propane is presented. The performance of the IMR has been compared to that of a conventional fixed bed reactor using the same catalyst and operating conditions. Also, the effect of the membrane permeation properties on reactor performance has been investigated. Finally, a factorial design of experiments has been carried out in order to find the operating conditions that lead to a maximum propene yield. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; inert membrane reactor; Propane; Propene

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1. Introduction

A considerable amount of work has been devoted to the development of catalysts that provide a good selectivity to olefins in the oxidative dehydrogenation of paraffins. It has been found that one of the best catalytic systems in terms of activity, selectivity and stability of performance is V/MgO [1–4]. In addition to the development of better catalysts, the selectivity achieved at a given conversion can also be increased by employing modes of contact that are different from the conventional fixed bed reactor (e.g., [5–11]); among these are the dual-zone fluidized bed reactors that employ reducible catalysts, and membrane reactors, with which this work is concerned.

The oxidative dehydrogenation (ODH) of propane yields propene as the selective reaction product, although CO and CO_2 are also obtained through non-selective oxidations of both propane and propene. This is a typical example of a series–parallel oxidation network with an intermediate valuable product. In such systems it is often found that the use of a low partial pressure of oxygen often favours the selective vs. the non-selective reactions. The inert membrane reactor (IMR) configuration, where an inert ceramic membrane acts as an oxygen distributor to a fixed bed of catalyst has been used in different selective oxidation reactions [8–11]. Oxygen distribution using microporous (i.e., zeolite) membranes has already been employed for the ODH of propane, although relatively low propene yields were obtained [11]. This work will explore the possibility of using for this reaction IMRs based on mesoporous rather than microporous membranes.

2. Experimental

A V/MgO catalyst containing 24% V_2O_5 by weight was prepared by Haldor-Topsoe A/S, following specific recipes from the Institute de Recherches sur la Catalyse, within the framework of the European Project JOE3-CT95-0022. The experimental reaction system has been described previously (e.g., [12]). The catalyst bed (2.5–3.5 g, particle diameter be-

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tween 250 and 500 μm), was located inside a tubular ceramic membrane, which was sealed within a stainless steel shell by means of graphite gaskets. The reactor temperature and pressure were monitored at several points. All gas streams entering the reactor were mass-flow controlled, and the exit gases were analysed by on-line gas chromatography. Oxygen was always fed to the void space between the ceramic membrane and the shell, and the hydrocarbon to the internal side of the tube. The inert gas could be supplied with any of the reactants, giving rise to the two membrane reactor configurations that will be compared in this work: IMRHe + O_2 (Fig. 1b) when the inert gas is fed along with oxygen, and IMRO_2 (Fig. 1c) when the inert is premixed with propane. The system could also be operated as a conventional fixed bed reactor (Fig. 1a) by cofeeding all the reactants to the tube side and closing the valves on the shell side.

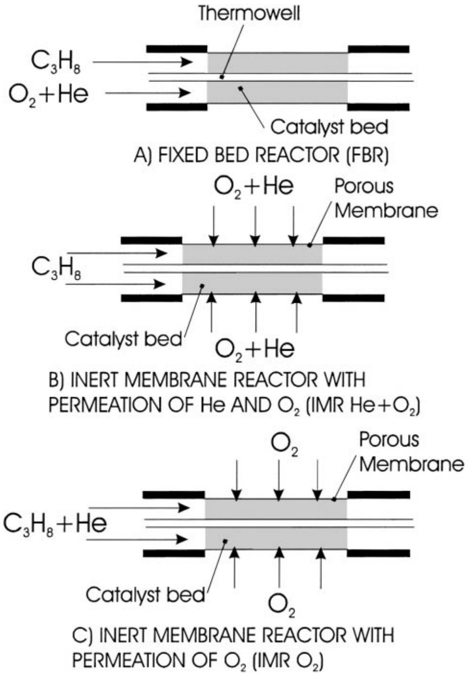

Fig. 1. Scheme of the different reactor configurations used in this work: (a) conventional fixed bed reactor (FBR), (b) inert membrane reactor with permeation of oxygen and inert gas from the shell side (IMRHe + O_2), and (c) inert membrane reactor with permeation of oxygen from the shell side (IMRO_2).

2.1. Membrane preparation

The ceramic membranes were prepared from alumina filtration tubes (SCT). These were modified by partially filling the pores with a suitable material in order to obtain a flow restriction during operation. This ensures a homogeneous distribution of oxygen along the reactor and minimises the back-permeation of propane. Membrane preparation involved the following steps:

1. impregnation with a silica or boehmite sol;
2. drying at 120°C for 2 h;
3. heating to 800°C at 2°C min^{-1}, then calcination at this temperature for 2 h;
4. steps 1–3 are repeated until the desired permeation rate is achieved;
5. impregnation with a lithium or sodium nitrate solution, to decrease the catalytic activity of the membrane, that is usually non-selective;
6. drying and calcination as in steps 2 and 3;
7. enamelling of both ends, leaving a 14 cm long permeable zone.

2.2. Membrane testing

Prior to use in the IMR, the membranes were subjected to the following measurements:

(i) The permeability of the membranes to nitrogen was measured at room temperature, as a function of the pressure drop across the membrane. This is useful to detect possible defects in the pore-filling process just described, which are evidenced by a significant increase of permeability and a high percentage of laminar flow contribution.

(ii) The intrinsic catalytic activity of the membrane (i.e., without V/MgO catalyst) was measured under reaction conditions. The propane conversion was found to be smaller than 3% at 550°C and close to 9% at 600°C.

3. Results and discussion

3.1. Effect of operating conditions

The effect of reaction temperature on the selectivity and conversion is shown in Fig. 2. As could be

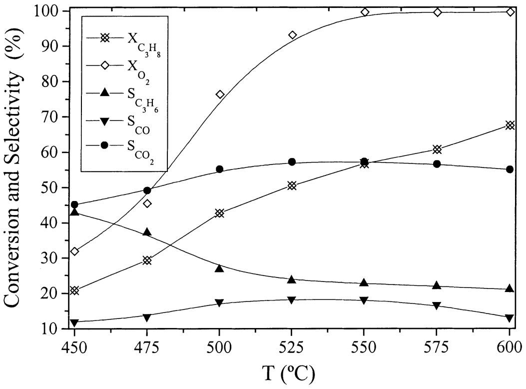

Fig. 2. Effect of reaction temperature for a sample containing 2.3 g of catalyst; total flow rate 200 N cm^3 min^{-1}; C_3H_8:O_2:He = 4:8:88; IMRHe + O_2.

expected, the propane conversion increases with temperature, at the same time the selectivity to propene decreases and the selectivity to carbon oxides increases slightly. The selectivity to cracking products (mainly ethene, and some ethane and methane at the highest temperatures) varies from 0.7% at 500°C to 2% at 550°C, and reaches 11% at 600°C.

Fig. 3 shows the results of experiments where the oxygen to propane ratio was varied, while keeping constant the rest of the experimental conditions. As the oxygen/propane ratio increases, a lower selectivity and a higher propane conversion are obtained. Because of these opposite trends, the propene yield goes through a maximum, which in Fig. 3 appears at values of the O_2/C_3H_8 ratio between 1 and 2, for all the temperatures tested.

3.2. Comparison of FBR, IMRO$_2$, and IMRHe + O$_2$

The main part of this work is concerned with the study of different reactor feed configurations. The two types of membrane reactor described above supply He to either the shell or the tube side of the membrane. Intermediate situations are depicted in Fig. 4, which shows the evolution of the yield to propene as the supply of inert diluent to the shell side is progressively shifted to the tube side, while keeping the same total flow rates of propane, He and O_2. The highest yields at any temperature were obtained for the IMRO$_2$, i.e., when all the He feed was supplied to the tube side of the reactor. This is related to the beneficial dilution effect of He, which in the IMRO$_2$ is made available from the reactor entrance. This effect is not due to a shift of equilibrium, since the yields are in this case controlled by the reaction kinetics.

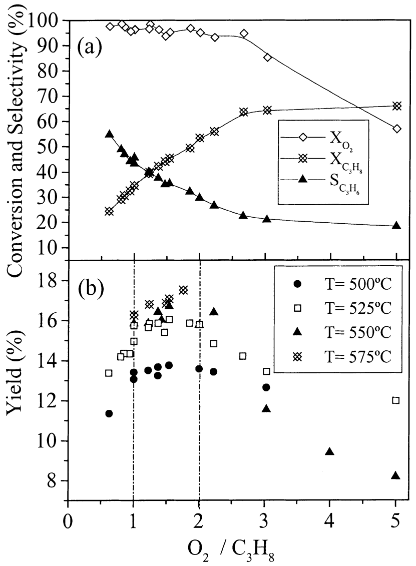

Fig. 3. Effect of the O_2/C_3H_8 ratio in the reactor feed for a sample containing 3.1 g of catalyst; total flow rate of 200 N cm^3 min^{-1}; IMRO$_2$; T = 525°C; (a) propane and oxygen conversions, and selectivity to propene, and (b) yields obtained at different temperatures; other conditions as in (a).

Below, the comparison between the results obtained with the IMRO$_2$, the IMRHe + O_2 and the fixed bed

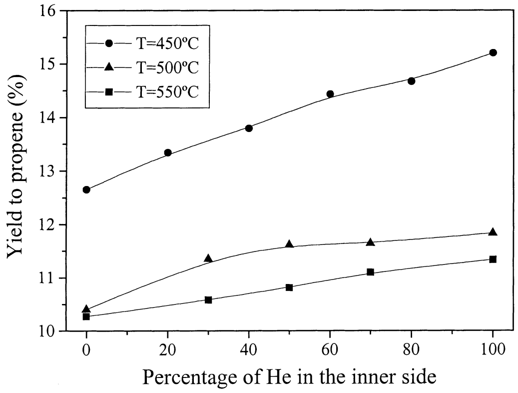

Fig. 4. Effect of the feed configuration of the inert diluent: from IMRHe + O_2 to IMRO$_2$. The He percentage indicates the fraction of the total flow of inert gas that is supplied to the tube side.

Table 1
Characteristics of the membranes used

Membrane	Pore-filling material (wt.%)	Alkaline dopant	Permeation length (cm)	Permeability ($cm^3 min^{-1} bar cm^2$)[a]
M1-A	γ-Al_2O_3 (5.5)	Li_2O	14.5	$20+6.9\,P$
M1-S	SiO_2 (8.3)	Li_2O	15.3	$9.1+3.7\,P$
M2-S	SiO_2 (16.3)	Na_2O	15.0	$0.1+2.6\,P$
M3-S	SiO_2 (15.1)	Na_2O	14.0	$4.1+2.3\,P$

[a] Note: P is the arithmetic mean of the total pressure at both sides of the membrane (bar).

reactor (FBR) configurations is presented. The temperature interval for this comparison was limited to a maximum temperature of 550°C. At higher operation temperatures hot spots developed in the FBR, even when substantial external refrigeration was provided. In contrast, the membrane reactor gave a much more stable performance, avoiding to a large extent the hot spots associated with FBR operation. Thus, in specific experiments run to assess the stability of operation in both types of reactors (not shown), hot spots of around 70°C were often observed in the entrance region of the FBR, while for the same conditions the maximum temperature deviation in the IMR remained close to 20°C.

The effect of membrane permeability on the performance of the membrane reactor has been studied by using four different membranes. The main characteristics of the membranes used are shown in Table 1. The permeability (measured at room temperature using N_2) is expressed as a lineal function of P, the arithmetic mean of the total pressure at both sides of the membrane. With membrane M1-A, impregnated with 5.5 wt.% of boehmite, the permeation flux is high, and there is almost no difference between the results obtained in the FBR and the IMR (Fig. 5). On the other hand, Fig. 6 shows the results obtained with membrane M1-S, where the permeability is considerably lower; it can be seen that the IMR gives a noticeably higher selectivity at a given conversion, compared to the FBR. With membrane M2-S, (Fig. 7) with an even lower permeability, the selectivity increase obtained with the $IMRO_2$ is very significant throughout the interval of propane conversion explored.

The experiments in Figs. 5–7 indicate that the membrane permeability must be low enough to maintain a homogeneous distribution of oxygen. Otherwise, with a low resistance to permeation, the pressure drop across the membrane and along the catalyst bed on the tube side become comparable, and preferential permeation takes place near the end of the catalyst bed. This results in an unfavourable oxygen distribution which does not improve the selectivity with respect to the FBR. Furthermore, a low resistance to permeation

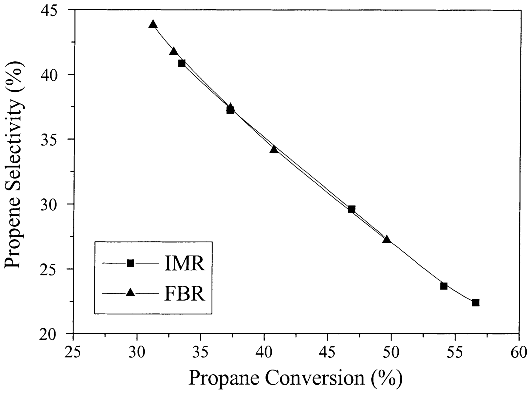

Fig. 5. Selectivity-conversion plot for fixed bed and inert membrane reactors. Membrane M1-A; 2.7 g of catalyst; $T=500$°C; $C_3H_8:O_2:He=4:8:88$; variable total flow rate.

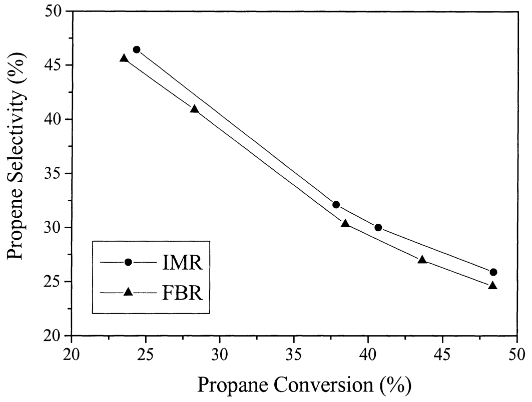

Fig. 6. Selectivity-conversion plot for fixed bed and inert membrane reactors. Membrane M1-S; 2.8 g of catalyst; $T=500$°C; $C_3H_8:O_2:He=4:8:88$; variable total flow rate.

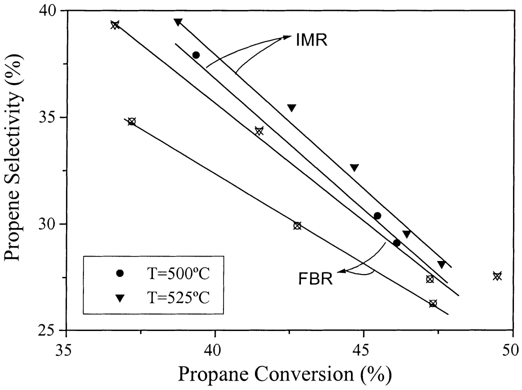

Fig. 7. Selectivity-conversion plot for fixed bed and inert membrane reactors at two different temperatures. Membrane M2-S; 2.9 g of catalyst; C_3H_8:O_2:He = 4:8:88; variable total flow rate.

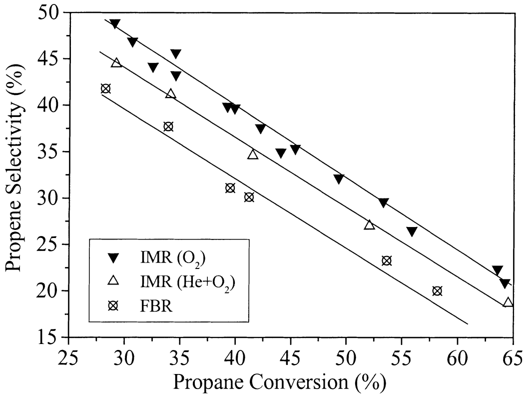

Fig. 8. Selectivity-conversion plot for fixed bed and inert membrane reactors. Membrane M3-S; 3.1 g of catalyst; $T = 525°C$; total flow rate 200 N cm^3 min^{-1}; variable C_3H_8/O_2 ratio.

often gives rise to considerable back-permeation of the hydrocarbon, a development that is deleterious to selectivity [13].

The above experiments were done by keeping constant the overall feed composition and varying the feed flow rate. Experiments with a constant flow rate and a variable propane to oxygen ratio are shown in Fig. 8. Again, it can be observed that the selectivity to propene was higher when oxygen was fed through the membrane (both IMRs), and the best results were obtained when He was fed along with propane to the membrane tube side (IMR O_2). This gives a roughly constant increase in the selectivity to propene (8–10% points, similar to that obtained in the experiments with variable flow rate) with respect to the FBR throughout the conversion range investigated. Fig. 8 also shows that a smaller improvement in selectivity was obtained with the IMRHe + O_2 configuration. This is consistent with the behaviour already shown, in Fig. 4: the beneficial (in terms of selectivity) effect of dilution is available from the reactor entrance for both the FBR and the IMRO_2, but not for the IMRHe + O_2; in this case, the high propane concentration at the reactor entrance increases the rate of the cracking and coke formation reactions; part of this coke is eventually burnt, increasing the selectivity to CO_x.

3.3. Reactor optimisation

The objective of this section was to find the optimum operating conditions for the reactor. For this, a factorial experimental design with four variables was used: temperature (T), gas flow rate (F), and the partial pressures of propane, $P(C_3H_8)$ and oxygen, $P(O_2)$ in the feed. The values used for each of the variables are given in Table 2, resulting in a total of 30 experiments (2^4 factorial experiments, plus eight star experiments, plus four repetitions of the central experiment and two of star experiments) which were carried out in random order.

The experimental data on propene yield were fitted to a function containing linear, squared and product (interaction) terms, as follows:

Table 2
Variables used in the factorial design of experiments, augmented with a star design

Variable	Central experiments	Factored experiments	Star experiments
Temperature T (K)	798	773, 823	748, 848
Total gas flow rate F (N cm^3 min^{-1})	200	100, 300	150, 250
Partial pressure of propane $P(C_3H_8)$ (kPa)	6.5	5, 8	3, 10
Partial pressure of oxygen $P(O_2)$ (kPa)	8.0	5, 11	4, 12

$$\begin{aligned}\text{Yield} = {} & A0 + A1\,T + A2\,F + A3\,P(\mathrm{C_3H_8}) \\ & + A4\,P(\mathrm{O_2}) + A11\,T^2 + A22\,F^2 \\ & + A33\,P(\mathrm{C_3H_8^2}) + A44\,P(\mathrm{O_2^2}) + A12\,T\,F \\ & + A13\,T\,P(\mathrm{C_3H_8}) + A14\,T\,P(\mathrm{O_2}) \\ & + A23\,F\,P(\mathrm{C_3H_8}) + A24\,F\,P(\mathrm{O_4}) \\ & + A34\,P(\mathrm{C_3H_8})P(\mathrm{O_2})\end{aligned}$$

While the *A* coefficients obtained from the fitting have no direct physical meaning, the above equation is useful as a tool for optimisation. This was carried out by evaluating the gradient of the objective function (propene yield) with respect to each of the experimental variables studied. The isoyield contour graphs illustrate the effect of each couple of variables studied. The $P(\mathrm{C_3H_8})$ vs. $P(\mathrm{O_2})$ graph (Fig. 9a) shows that the highest yields stay in a band around the diagonal (propane to oxygen ratio close to 1). This was confirmed with further experiments around the predicted maximum, which located the maximum yield at an oxygen/propane ratio near 1.25 at each temperature investigated. The study of the effect of temperature and gas flow showed that the maximum yield was obtained at intermediate flow rates, from 200 to 300 $\mathrm{cm^3\,min^{-1}}$, and at the highest temperatures in the interval studied (Fig. 9b).

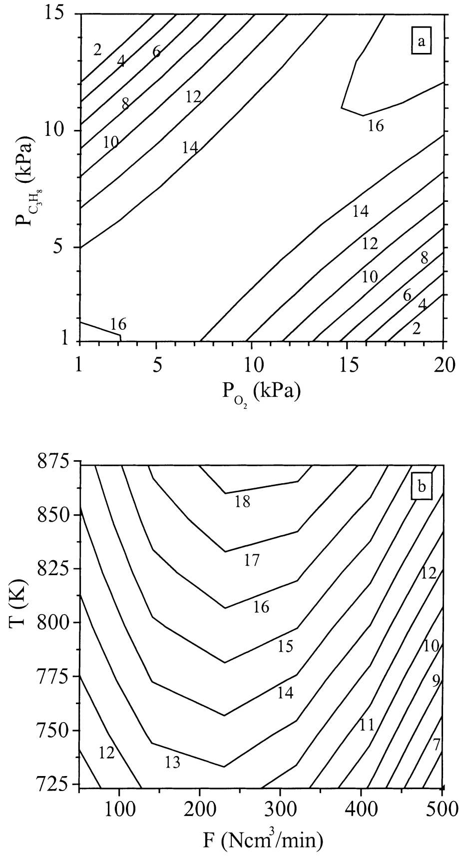

Fig. 9. Propene isoyield contour graphs: (a) partial pressure of oxygen vs. partial pressure of propane, and (b) temperature vs. gas flow rate.

The regression model agrees well with experimental results up to 560–570°C. In the upper temperature region of our study, thermal and non-oxidative catalytic dehydrogenation can be significant, leading to a deviation of the experimental data from predicted yields. Other contributing factors (e.g., temperature deviations, whose magnitude increase as temperature is raised), are also possible. The maximum yield experimentally observed (ca. 18%) was achieved at 575°C; further improvement was not obtained by increasing the temperature to 600°C.

4. Conclusions

A ceramic inert membrane reactor has been used as an efficient contactor in the oxidative dehydrogenation of propane (ODH). The inert membrane reactor can significantly improve the selectivity for a given propane conversion with respect to that obtained in a fixed bed reactor. A key factor for such improvement is the membrane permeability, that must be tailored to provide a homogeneous distribution of oxygen along the reactor and a suitable value of the permeation flux. Both were achieved with the composite silica/alumina membrane used in this study as oxygen distributors. Finally, it has been shown that, in addition to a higher selectivity, the membrane reactor gave more homogeneous temperature profiles, and an easier control of operation.

Acknowledgements

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