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Combination of a Two-Zone Fluidized Bed Reactor with a Pd hollow fibre membrane for catalytic alkane dehydrogenation

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ABSTRACT

The combination of a Pd hollow fibre membrane with a Two-Zone Fluidized Bed Reactor (TZFBR) is described for catalytic dehydrogenation of propane. This configuration aims to combine the in situ catalyst regeneration provided by the TZFBR with the increased conversion that can be achieved with a Pd membrane, which removes hydrogen from the reactor, thus enhancing the reaction rate and in theory allowing even higher than equilibrium conversion. The experiments show that the Pd hollow fibre membrane acts effectively removing hydrogen from the reaction media and that with a Pt–Sn/Al_2O_3 catalyst the TZFBR can achieve steady state operation in spite of the increased coking of the catalyst. However, with this catalyst the quicker coke formation caused by the removal of hydrogen outweighs the beneficial effect of hydrogen removal and the yield achievable for a given feed is lower in the presence of the membrane. A conclusion from these results is that a catalyst with lower coke tendency is needed to apply this combination of Pd membrane and TZFBR.

1. Introduction

Membrane reactors are among the most powerful tools for achieving the targets of process intensification, i.e. to obtain cheaper, safer and more sustainable technologies. Although some excellent achievements have been obtained with polymeric membranes in low temperature applications [1,2], several difficulties have hindered the industrial application of membrane reactors using inorganic membranes [3]. In spite of these drawbacks, only inorganic membranes can withstand the high temperatures required in many catalytic reactions, which justifies the large efforts made worldwide to develop the different kinds of membrane reactors based on inorganic membranes, including metals [4], dense ceramics [5] and microporous materials [6,7].

The most widely studied inorganic membrane reactor is based on the removal of a reaction product through the membrane with the aim of achieving an increased conversion in a reaction with thermodynamically limited equilibrium conversion. Within this category, hydrogen removal using a Pd based membrane is the reactor type that has been most extensively studied. Early work on this topic was started by Gryaznov's group several decades ago [8], but Pd membrane reactors are still not being used industrially in large scale systems.

One of the main problems for the application of this kind of inorganic membrane reactor is the high cost of membranes. If a thin Pd layer is employed (a few micrometers thickness, e.g. 2 μm, as required by DOE for some applications) to increase the permeability and decrease the membrane price, the cost of the ceramic support becomes the main factor [4]. In this article a special type of Pd membrane supported on a ceramic hollow fibre will be employed. Hollow fibres provide a very high surface to volume ratio and therefore can exceed the performance achievable with Pd membranes deposited on tubular ceramic supports. In addition the smaller amount of ceramic material per unit of surface area may represent a significant cost reduction. Therefore such membranes are very promising for the development of membrane reactors. The manufacture of ceramic hollow fibres can be achieved through the spinning of a precursor mixture, in which ceramic particles are uniformly dispersed in a polymeric binder solution, and this has been employed for several applications [9].

A second limitation of membrane reactors and, in particular, those where hydrogen is removed to increase the conversion, is that the tendency to coke formation also increases. This fact has been observed in many cases, and because of the quick deactivation caused by coke, a continuous decrease in conversion is observed in the reactor [10–12].

The Two-Zone Fluid Bed Reactor (TZFBR) is a system designed to counteract the catalyst deactivation. In this reactor one of the reactants (usually a hydrocarbon) is fed at an intermediate point, while a second stream (usually containing an oxidizing reactant) is fed at

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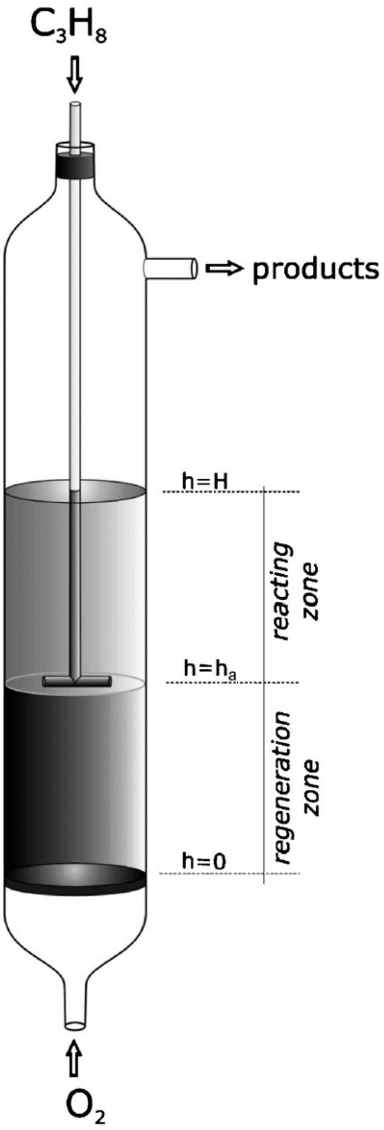

Fig. 1. Scheme of a TZFBR.

the bottom of the bed (see scheme in Fig. 1). In this way two zones with different atmosphere are created in the bed: a reducing zone, in the upper part, where the desired reaction takes place and coke is formed on the catalyst surface and an oxidizing environment in the lower part, where the catalyst is regenerated by coke combustion. A continuous circulation of solids between both zones is caused by the bubbles, characteristic of gas–solid fluidized bed reactors. Under suitable operating conditions, a steady state is achieved with most of the oxygen being consumed in the lower part of the bed. The TZFBR operation has been successfully tested in several dehydrogenation reactions (propane and butane dehydrogenation), using several catalysts [13–15]. The application of the TZFBR and related reaction systems for several catalytic processes, including also catalytic oxidation with the catalyst operating in redox mode, was discussed in a previous review [16]. One of the advantages provided by this type of reactor is the improved safety, since the reactants are not premixed and usually the oxygen concentration in the gas phase in the point where the hydrocarbon is fed is much smaller than that at the entry point of a conventional fixed bed with the same total feed. Anyway, in this work the amount of oxygen fed is so small that the mixture would be outside the flammability limits.

Fluid bed reactors have been employed combined with membranes in several works, but never in a situation where the bottom of the reactor was employed for catalyst regeneration, i.e. where the reacting hydrocarbon was absent in the lower zone of the bed. For example, Grace's group has been developing membrane fluid bed reactors for hydrogen production by methane steam reforming [17,18], but all the reactants were fed at the bottom of the reactor. This group has published recently a cold model of an internally circulating fluidized bed membrane reactor, where the reactants are fed at the bottom of the reactor and air is fed near the top, with the aim of burning the gases that have not permeate, and thus generating the heat required by the endothermic methane reforming [19]. Kuiper's group has also studied membrane fluid bed reactors for hydrogen production and CO_2 capture in a system with two reaction zones; in that case partial oxidation of methane was performed in the lower part of the reactor, using oxygen selective membranes, and steam reforming in the upper section (with hydrogen selective membranes) [20], but there was not solid circulation between both parts (in fact there were two reactors, one on top of the other). In this case coking was avoided by using a noble metal catalyst. An in-deep discussion of the potentials and the hurdles of fluid bed membrane reactors can be found elsewhere [21].

In this article we describe for the first time a combination of a TZFBR with a membrane reactor for the catalytic dehydrogenation of an alkane (propane) using a Pd hollow fibre membrane. This multifunctional reactor could provide a very desirable combination of advantages:

- The Pd membranes allow an increased conversion by removal of hydrogen.
- The TZFBR counteracts the increased deactivation caused by the lower hydrogen partial pressure.

The aim of this research was to explore the possibilities offered by this combination. The chosen reaction (propane dehydrogenation, $C_3H_8 \leftrightarrows C_3H_6 + H_2$) has been previously studied in membrane reactors [12] and TZFBR [14].

2. Experimental

The scheme of the TZFBR with membrane employed in this work is shown in Fig. 2. It consists of two cylindrical regions, the lower one with an internal diameter of 1.8 cm and the upper one 2.8 cm i.d. This change in the section of the TZFBR allows adapting the flow in each section to the requirements of the processes, which often need different gas flowrates in the oxidation and in the reaction sections, and constitutes an advantage over the use of reactors with a fixed diameter [22]. The reactor is made of quartz and a sintered quartz plate at the bottom acts as a gas distributor and supports the catalyst. The second gas entry allows feeding the hydrocarbon at an intermediate point of the bed. In reactors described in previous publications and in experiments without a membrane, this second entry was by means of a quartz tube. However, in this work, when a membrane requiring more space was inserted in the reactor, a quartz ring surrounded the reactor at an intermediate height and distributed the hydrocarbon that entered the bed through 6 small orifices in the wall.

The hydrogen selective membrane is a Pd membrane which is deposited directly on a porous alumina hollow fibre with a unique asymmetric structure. The asymmetric hollow fibre substrate is prepared via a phase-inversion/sintering technique [23]. The uniform spinning suspension was prepared by using alumina powders (1 μm:0.05 μm:0.01 μm = 7:2:1), N-methyl-2-pyrrolidone (NMP HPLC grade, Rathbone) as solvent, Arlacel P135 (Uniqema, UK) as well as Polyethersulfone (PESf, Radel A-300,

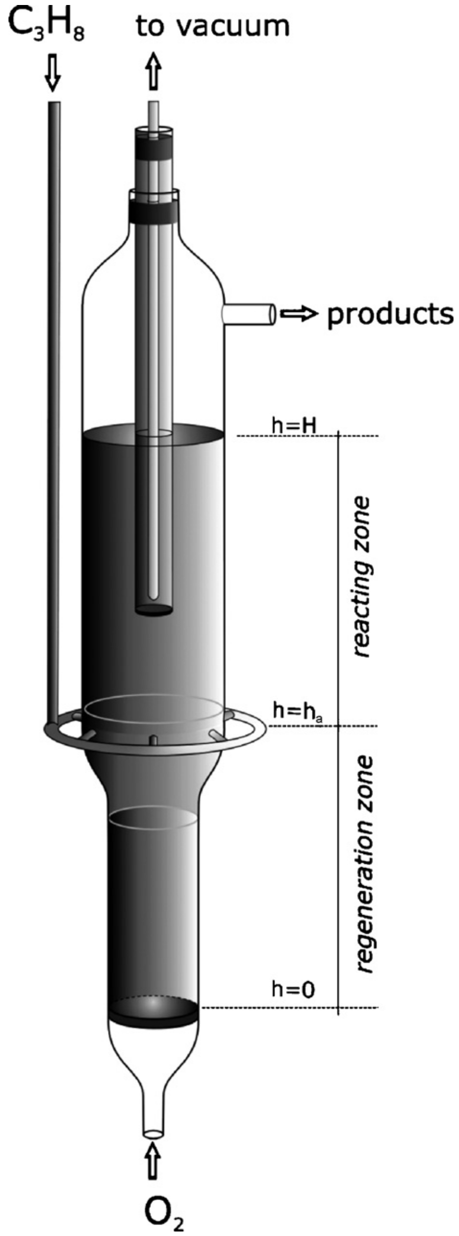

Fig. 2. Scheme of the TZFBR with a Pd hollow fibre ceramic employed in this article.

Table 1
Coating bath composition of Pd electroless plating.

Compounds	Pd bath
$Pd(NH_3)_4Cl_2·H_2O$ (g/L)	4
$Na_2EDTA·2H_2O$ (g/L)	40.1
NH_4OH (28%) (mL/L)	198
N_2H_4 (1 M) (mL/L)	5.6
pH	10–11
Temperature (K)	333

Ameco Performance, USA) as polymer additives. After degassing under vacuum for 2 h, the suspension was pressurized at 7–20 psig using nitrogen gas and was extruded through a tube-in-orifice spinneret (i.d. 1.2 mm, o.d. 3.0 mm) into an outer coagulation bath with an air-gap of 15 cm. DI water was used as the internal coagulant and the flow rate ranged from 10 to 30 mL/min. The resultant hollow fibre substrates were obtained by sintering the precursor fibres at 1723 K for 4 h with heating and cooling rates of 5 K/min. One end of the resultant substrates was sealed by glaze while the other end was kept open. The outer surface of the prepared substrates was coated with a thin and gas-tight layer of glaze with the exception of the part (about 6 cm in length) close to the sealed end of the fibre being left for electroless plating of Pd membrane. The Pd membranes were then coated directly onto the outer surface of asymmetric alumina hollow fibre substrates by an electroless plating technique [24]. Prior to the coating, the substrates were cleaned and activated by the conventional Pd–Sn activation procedure. The activation process consisted of successive immersion of the substrates in the tin (II) chloride ($SnCl_2$) solution and the palladium chloride ($PdCl_2$) solution at room temperature. Deionized water and 0.1 M HCl were used to rinse the samples between the immersions. The activation process was repeated 6 times, after which the substrate surface turned brown. The Pd membrane was then coated by using the plating bath with the composition listed in Table 1 [24]. The permeation of the resulting membrane is shown in Fig. 3, where the typical lineal dependence on the difference of the square root of hydrogen partial pressure, usually found for good quality membranes, is observed. Fig. 4 shows the structure of the membrane, with a unique asymmetric pore structure that is characterized by a thin, uniform sponge-like outer layer and a thick finger-like inner layer. Finger-like voids extend across approximately 80% of the fibre cross-section from a highly porous inner surface with the remaining

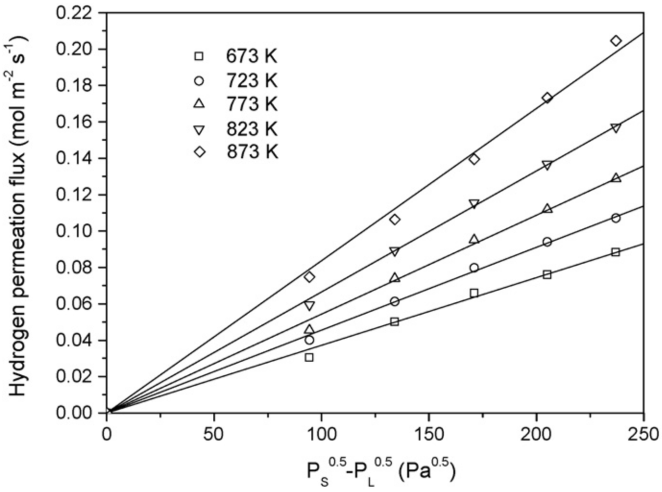

Fig. 3. Permeation of the Pd membrane supported on ceramic hollow fibres.

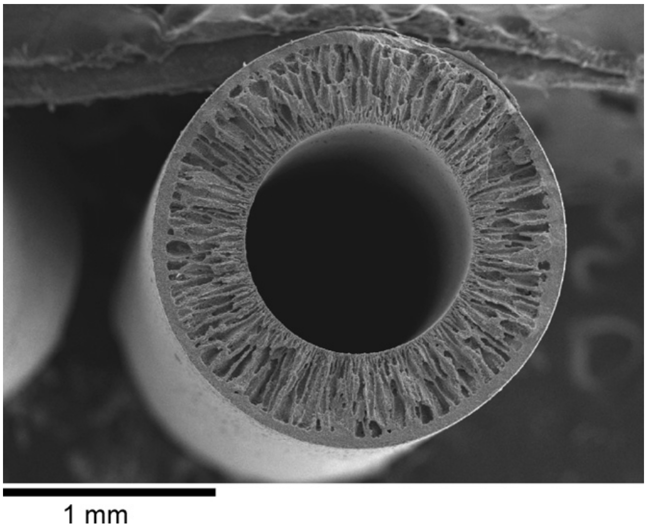

Fig. 4. SEM picture of the transversal section of the hollow fibre.

20% consisting of the sponge-like outer layer, forming a smooth and denser outer surface where a thin and defect-free Pd membrane is directly coated without using any extra modification on substrate surface.

In order to avoid the catalyst particles eroding the thin Pd membrane, it was located inside a porous alumina tube, 1 cm o.d., with the lower end closed with enamel and also enamelled in the upper zone, leaving a permeable length of 6 cm. This tube was highly permeable (c.a. 500 cm^3(STP) cm^{-2} min^{-1} bar^{-1} at room temperature), having a nominal pore size of 3 μm, and thus offered little resistance to the H_2 permeation. The hollow fibre was fixed inside this porous alumina tube with Teflon tape in the cold part of the tube (outside the reactor) and the alumina tube joined to the reactor with a silicon coupling sleeve.

The reactor was loaded with 15 g of a commercial Pt/Al_2O_3 catalyst (0.2 wt.% Pt, 0.2 wt.% Sn, 0.15 wt.% K, 150 m^2/g BET surface area), crushed and sieved to a particle size between 100 and 200 μm. Around 6 g were located in the bottom zone and 9 g in the upper zone. The minimum fluidization velocity, measured with nitrogen at 500 °C, was 12.5 cm^3(STP) cm^{-2} min^{-1}.

A vacuum pump (Varian DS102) was employed to remove the hydrogen permeated through the Pd membrane. The feed gases were mass flow controlled and the main exit stream (the retentate) was analyzed by gas chromatography. Usually the analysis was repeated several times, until a steady state was achieved. The flow rate of the stream at atmospheric pressure was measured with a bubble flow meter. It was not possible to measure the flow of hydrogen removed through the vacuum pump, and thus only the carbon balance was calculated. In all the experiments reported the carbon balance in steady state has an error lower than 2%, and usually lower than 1%.

3. Results

Pd hollow fibre membrane. Permeation tests of the prepared Pd membranes showed good H_2 flux (Fig. 3) and no N_2 permeation was observed. The permeation changes with the difference of the square root of hydrogen pressure as is usual with good quality Pd membranes, and this quality is also confirmed by the absence of noticeable N_2 permeation. Fig. 4 shows a SEM picture of the transversal section of the hollow fibre.

Experiments without membrane. A first series of experiments to test the application of the TZFBR with this catalyst and this reactor shape was made by varying the percentage of oxygen in the feed (%O_2, oxygen flow divided by the total flow fed to the reactor). The changes of propane conversion are shown in Fig. 5. In general a stable conversion was achieved after 30–60 min, showing that the coke formation rate in the upper zone was equal to the coke combustion rate in the lower zone. Only with the smallest amount of oxygen (1%) a continuous decrease in conversion is obtained. It seems that this small amount of oxygen is not enough to remove the coke formed, i.e. the total amount of coke formed per unit of time is larger than what can be removed by combustion with this flow of oxygen. The existence of a minimum flow of oxygen to achieve the steady state has also been found in previous works. The selectivity to propene varies between 77 and 95%, depending on the percentage of oxygen in the feed. Obviously, the larger the oxygen content in the feed, the higher the selectivity to CO_x. Only a small fraction of products (1–2%) corresponds to cracking (methane or ethene).

For each temperature there is an optimum percentage of oxygen that maximises the yield to propene. Fig. 6 shows this yield after 90 min of operation (in most cases corresponding to the steady state). It may be seen that there is a trend of having the optimum %O_2 at higher values as the temperature increases, which is related with the faster coke formation at higher temperatures.

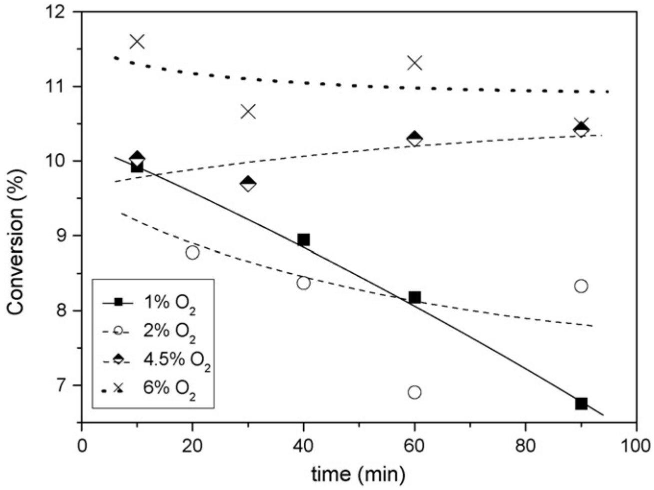

Fig. 5. Change of propane conversion along time in a TZFBR. Experimental conditions: T = 500 °C; %C_3H_8 = 81; different % of O_2 and Ar to balance. Regeneration zone: u_r (=u/u_{mf}) = 1.5; W_{cat} = 6 g. Reaction zone: u_r = 3; W_{cat} = 6 g.

Although some rigorous mathematical models of TZFBR have already been published [14,25,26], a simpler qualitative description will be more useful to explain these changes. Let us assume a TZFBR with fixed feed flow and weight of catalyst and consider the effect of changes in %O_2. Fig. 7 shows a qualitative plot of the global rate of coke formation (r_f, g s^{-1}) in the upper part of the bed and the global rate of coke combustion in the lower part of the bed (r_{comb}, g s^{-1}), vs. the mean coke content in the catalyst in the upper part (C_c, g coke(g catalyst)$^{-1}$). Of course r_f will vary with the amount of catalyst in the upper part of the bed, and will depend on the intrinsic rate of coke formation (g coke s^{-1}(g catalyst)$^{-1}$). For a given flow of gases, the exchange of solid between the lower and the upper part of the bed is constant, and therefore the amount of coke transported will increase with the coke content. The r_f vs. C_c line shows that the higher the coke content, the lower the coke formation rate (the catalyst is more deactivated). The r_{comb} vs. C_c line shows that for a given percentage of oxygen in the feed, the global rate of coke combustion increases with the available amount of coke, until all the oxygen is employed and then r_{comb} remains constant. If a steady state is achieved (which implies a dynamic equilibrium between coke formation and combustion) r_f and r_{comb}

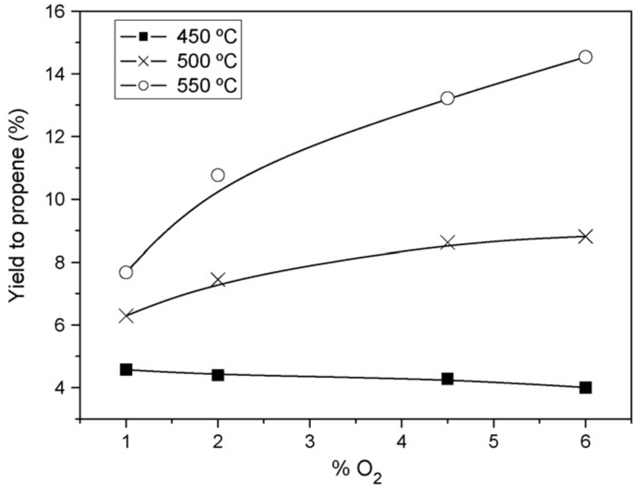

Fig. 6. Yield to propene vs. %O_2 curves at various temperatures. Experimental conditions: t = 90 min; %C_3H_8 = 81; different % of O_2 and Ar to balance; regeneration zone: u_r = 1.5; W_{cat} = 6 g. Reaction zone: u_r = 3; W_{cat} = 6 g.

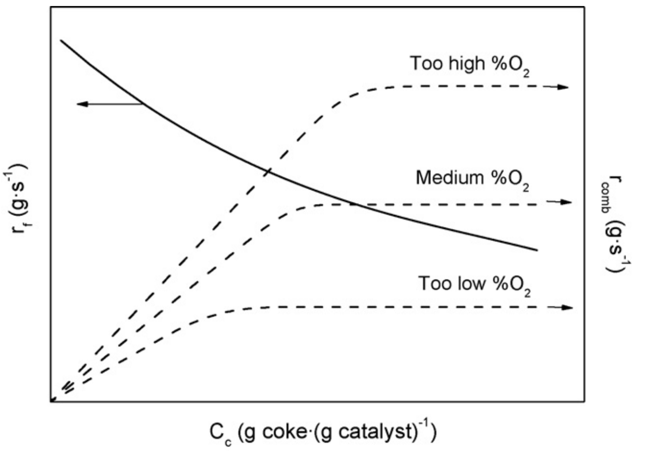

Fig. 7. Qualitative description of the coke formation and combustion processes in a TZFBR.

should be equal. As is exemplified in Fig. 7, at very low $\%O_2$ there is no steady state or else it is achieved with very high coke content (i.e. very low catalyst activity). At intermediate coke content the equilibrium between coke formation and coke combustion is achieved at lower C_c values as $\%O_2$ increases, as far as all the oxygen is consumed in the lower zone, i.e. the crossing of both lines occurs where r_{comb} vs. C_c is a horizontal line. If the percentage of oxygen in the feed is too high, the amount of coke transferred from the upper zone will not be enough to consume all the oxygen (this problem may also appear if the residence time in the lower zone was not enough) and some oxygen will reach the upper zone, where total hydrocarbon combustion can occur. This undesirable reaction will decrease the selectivity and could result in a lower yield to olefins.

The above qualitative description is consistent with the observed effect of the operating conditions shown in Fig. 6, is useful for understanding the observed trends and will help to explain the behaviour observed when the hydrogen selective membrane is inserted in the TZFBR.

Membrane and TZFBR. When the Pd membrane is inserted in the TZFBR, the removal of hydrogen from the reaction media can cause two important changes: (a) the reaction rate is increased, which favours larger propane conversion, being at least in theory possible to surpass the maximum conversion achievable in a conventional reactor (given by the thermodynamic equilibrium); (b) the lower the hydrogen partial pressure, the faster the coke formation, as has been previously observed in fixed bed membrane reactors [11,12].

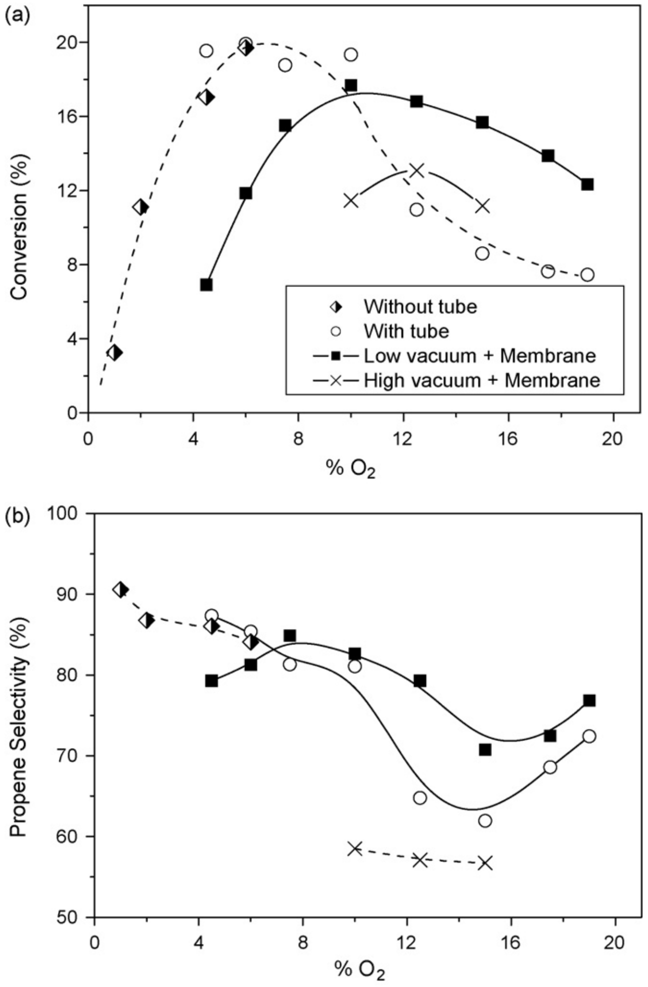

Fig. 8. Results in TZFBR with membrane, variable $\%O_2$ and comparison with TZFBR. (a) Conversion vs. $\%O_2$; (b) selectivity to propene vs. $\% O_2$. Experimental conditions: $T = 550\,^\circ C$; $t = 90$ min; $\%C_3H_8 = 81$; different % of O_2 and Ar to balance; regeneration zone: $u_r = 1.5$; $W_{cat} = 6$ g. Reaction zone: $u_r = 3$; $W_{cat} = 9$ g.

The experimental results are shown in Fig. 8. Propane conversion and selectivity to propene vs. percentage of oxygen in the feed are plotted for several operating conditions. The curves named “with tube” and “without tube” correspond to the operation in a TZFBR, with or without the insertion of a ceramic tube, respectively. This test was made in order to check the effect of the ceramic tube in the fluid dynamics and in the TZFBR performance. Although there is a small effect, the values obtained in the common region are quite similar, which implies that the changes in the solid flow pattern caused by the presence of a ceramic tube in the upper part of the bed do not change drastically the performance of the reactor. The data named as “low vacuum + membrane” correspond to a vacuum around 300 mbar (30 kPa) inside the membrane, and those named “high vacuum + membrane” are experiments where the pressure at the mouth of the membrane was 7 mbar (0.7 kPa). With 300 mbar the hydrogen removal will be very limited. In spite of this small driving force the hydrogen removal has a clear effect in the conversion vs. $\%O_2$ curve. The maximum conversion was obtained for a slightly higher oxygen percentage (10% instead of 5–8%) and the conversion in the maximum is slightly lower. When the membrane was operated with large vacuum, which means that the maximum hydrogen flux is obtained, the effect is even clearer: the maximum is achieved for around 12% oxygen in the feed and the conversion is slightly smaller than in the absence of a membrane. Similar trends were seen when the selectivity to propene was plotted vs. the percentage of oxygen in the feed: a small increase in selectivity is observed with low vacuum, and the lowest selectivity was obtained with high vacuum, probably because of the faster coke formation.

These results suggest that with this catalyst, the effect of the increased coke formation due to the removal of hydrogen surpasses the beneficial effect of the increased reaction rate. The faster coke formation is confirmed by the higher flow of oxygen at the point of maximum propene yield.

The effect of reaction temperature on the yield vs. $\%O_2$ curves is also clearly illustrative of the effect of faster reaction rates, both for dehydrogenation and for coking. It may be seen (Fig. 9) that at the lowest temperature (500 °C) the kinetics is so slow that a quite small yield was obtained; at a higher temperature (550 °C) the yield is larger, thanks to the faster kinetics, and increases with the $\%O_2$, as previously explained, up to a maximum value. At the highest temperature tested (600 °C) the faster deactivation by coke surpasses the beneficial effect of the faster dehydrogenation rate (and also the

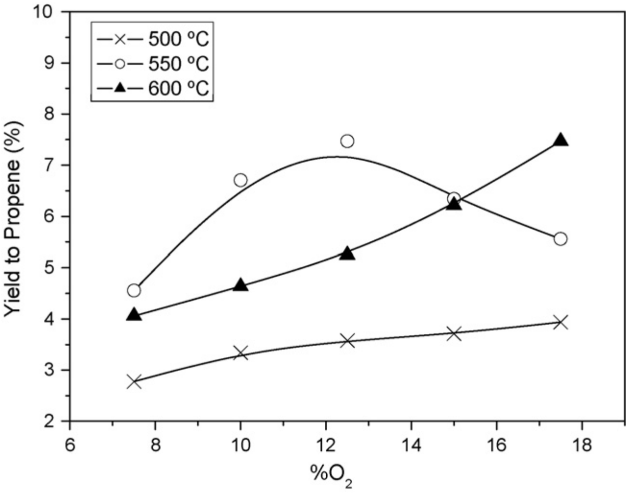

Fig. 9. Results in TZFBR with membrane at various temperatures. Experimental conditions: $t = 90$ min; %$C_3H_8 = 81$; variable % of O_2 and Ar to balance; regeneration zone: $u_r = 1.5$; $W_{cat} = 6$ g. Reaction zone: $u_r = 3$; $W_{cat} = 9$ g.

higher equilibrium conversion). The continuous increase of propylene yield with %O_2 suggests that a maximum should appear at %O_2 values over 18%, but such values have not been tested experimentally.

It is interesting to remark that in most cases (in spite of the faster coke formation caused by the hydrogen removal by the membrane) the TZFBR was able to achieve a steady state operation, although in general the conversion was lower than in the TZFBR without hydrogen removal, indicating higher coke content. In a conventional membrane reactor the conversion would decay continuously, without achieving a steady state. A final remark is that the Pd membrane supported on hollow ceramic fibre was able to withstand repeated heating and cooling cycles. The failure was produced by peeling of the Pd layer, after which the flow of gas through the ceramic support was so high that the experiment could not continue. However this failure was produced after 15 of such cycles, with around 50 h of operation at around 550 °C. Since in industrial operation the heating/cooling cycles would be a rare event, this performance is quite promising.

4. Conclusion

The use of Pd hollow fibre membrane in a TZFBR has been tested for the first time, using the catalytic dehydrogenation of an alkane (propane) as test reaction. The use of TZFBR allows a steady state operation to be obtained, even in the presence of the faster catalyst deactivation caused by the hydrogen removal by the membrane.

With the catalyst employed in this study the increase in coke formation caused a decline in yield, because the catalyst was more deactivated and also because of the lower selectivity to propene (coke is transformed to CO_x in the lower part of the reactor). Therefore the main conclusion from this research is that, even if the TZFBR can counteract partially the coke formation, a catalyst with slow coke formation is needed to take full advantage of the combination of a Pd membrane and a TZFBR.

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