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Catalysis with membranes or catalytic membranes?

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Abstract

This paper considers the application of inorganic membranes in conjunction with catalysis and discusses attempts which have been made to affect changes in the yields and product distributions in a number of catalytic reactions with a number of different conformations of catalyst and membrane. Various possible reactor conformations are first considered and then some results obtained for catalytically-active perm-selective membranes are presented to illustrate some of the problems encountered with such membranes. The use of non-perm-selective wall-and-tube reactors is then considered. Finally, the results of model calculations are presented which show that the most promising confirmation for the use of perm-selective membranes is one in which the membrane and catalyst are in separate units and external recirculation of reactants and products is carried out.

1. Introduction

The subject of catalytic membranes has attracted much interest over the last decade or so. Part of the work in this area with which one of the current authors has been associated was inspired by the development [1] of stable perm-selective inorganic membranes with pore openings down to micron size which are capable of giving separation of gases of different molecular weights as a result of Knudsen diffusion (rate of diffusion inversely proportional to the square root of the molecular weights of the diffusing species). It was recognised that the use of these membranes in combination with various catalysts, either within or in contact with the membrane, might lead to advantages in comparison with the use of those catalysts alone, and so a research project was embarked upon to examine some of these possibilities. Other work involving the use of non-perm-selective porous tubes containing active catalytic phases was also embarked upon, the catalysts being prepared using deposition techniques similar to those used in earlier work [2].

This paper first discusses the various possible modes of use of membranes in catalysis. It then reviews some of the work carried out by one of the authors and his coworkers using perm-selective membranes, discussing the background philosophy and objectives of the research and the degree to which these objectives were achieved. The paper also considers work on the preparation and use of catalytic systems in which the catalyst is located in the walls of tubes containing macropores, the so-called porous-wall reactor, in which no selective diffusion takes place. Finally, it also considers the use of a configuration in which a perm-selective membrane is physically located away from the catalyst in a continuous feed recirculation reactor system.

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2. Possible modes of operation of perm-selective membrane reactors

In this paper, the term 'membrane' is used to imply a perm-selective porous barrier between two enclosures which allows more rapid diffusion through it of one type of molecule than of another. The ideal membrane for use in a membrane reactor system would be one which is totally selective to one component of the reaction mixture. For example, a membrane composed of palladium or one of its alloys gives rise to completely selective diffusion of hydrogen; when such a membrane is combined with a suitable catalyst, it can be used to extract the hydrogen produced, for example, in a dehydrogenation reaction, allowing the equilibrium to be displaced towards the products, e.g.:

$$C_nH_{2n+2} \Leftrightarrow C_nH_{2n} + H_2 \qquad (1)$$

The use of membrane reactors with palladium membranes was pioneered by Gryaznov and his colleagues in Moscow [3]. The use of palladium, however, suffers from a number of disadvantages. For example, the rate of diffusion of hydrogen in palladium is relatively slow under realistic operation conditions and so very high membrane areas or very thin, and hence fragile, foils will have to be used; furthermore, hydrogen diffusion in palladium depends strongly upon the ability of the palladium surface to dissociate molecular hydrogen into atoms and this dissociation step can be retarded by other components of the reaction mixture or be completely poisoned by impurities. Palladium also has the limitation of a rather low melting point and this limits its use to relatively low-temperature reactions if the membrane and catalyst are in close proximity. Other metals such as tantalum or titanium may offer some advantages over palladium in this respect.

Inorganic membranes composed of microporous γ-alumina (pore diameters less than ca. 5 nm) supported on a macroporous material such as α-alumina [1] have been developed largely for gas-separation purposes, for example to separate hydrogen from carbon dioxide; assuming that only Knudsen diffusion can occur, the separation factor for such a mixture should be the inverse of the ratio of the square roots of the molecular weights of the two molecules, in this case 4.0. These membranes are stable up to relatively high temperatures, at least the temperature at which the γ-modification begins to transform into other more crystalline forms of alumina (ca. 600°C). Hence, their use can be considered in processes operating up to such temperatures. Furthermore, as γ-alumina has a relatively very high specific surface area and is frequently used as a catalyst support, the membrane itself can in principle be used as a support for a variety of catalytic components. It has recently been demonstrated that other oxides such as silica and titania can also be used to form membranes with pore sizes similar to those obtainable with γ-alumina. The work using these membranes was planned to demonstrate some possible configurations for the use of such membranes in which advantage could be taken of the diffusion properties of the membranes. The concepts to be described below take

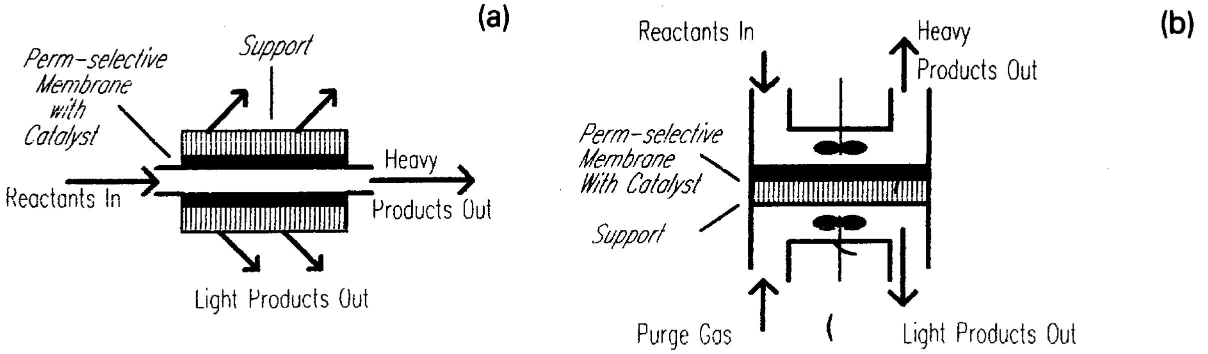

Fig. 1. Schematic representation of catalytic membrane reactors with: (a) cylindrical membrane and (b) flat plate-shaped membrane.

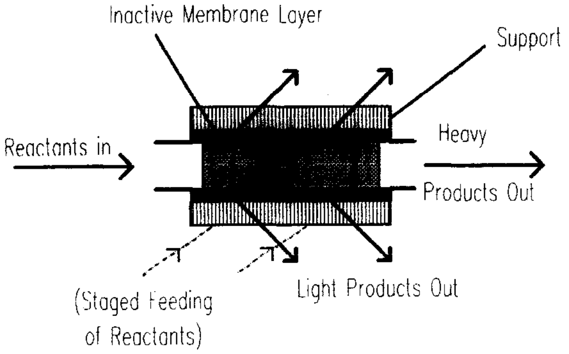

Fig. 2. Schematic representation of an inactive membrane reactor with a separate catalyst operated in the plug-flow mode; the membrane is used either to remove lighter products or to allow staged addition of reactants.

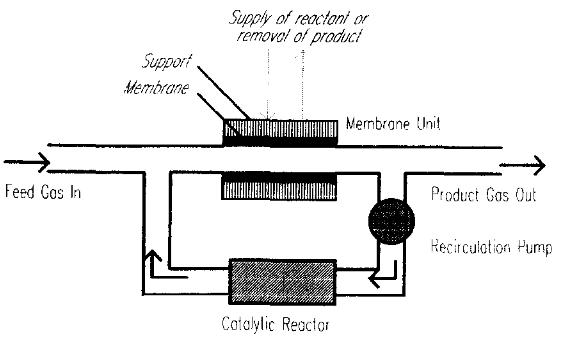

Fig. 3. Schematic representation of a system with separate catalytic reactor and membrane unit with recirculation of reactants and products. The membrane can be used either for the selective removal of a light product (e.g. hydrogen) or the addition of a reactant (e.g. oxygen).

advantage of the ability of the membranes to act as catalyst supports and/or to allow the diffusion of reactants to the membrane or diffusion of the products away from the membrane and in some cases also to give some molecular separation of the components in the gas mixtures.

Fig. 1 shows schematically the concept of the catalyst in the membrane. The membrane may be in the form of a cylindrical tube and the microporous separation layer is on either the inside or outside wall; in this case, the reactor may be operated as a plug-flow system (Fig. 1a). Alternatively, the membrane may be in the form of a flat plate, in which case the system is best thought of as a pair of continuous stirred-tank reactors (Fig. 1b); this will generally be the case if low flow rates are used through both sides of the reactor. In either of these two configurations, it is possible to feed the reactants together to one side of the membrane or to feed them separately from either side of the membrane; similarly, the products may emerge from one or other or both sides of the membrane or they may undergo some degree of separation by the membrane.

Fig. 2 shows schematically the situation which appertains if a separate catalyst is placed in contact with the membrane rather than in it; as in the situation where the catalyst is in the membrane (Fig. 1), the membrane may be in the form of a tube or as a flat plate. In this case, it would be normal that the reactants would be co-fed, as adequate mixing (especially radial) of the reactants throughout the catalyst bed is unlikely if one of the reactants is fed through the membrane; however, if it was advantageous to the reaction in question to have staged mixing of one of the reactants (e.g. in a selective oxidation reaction in which low partial pressures of oxygen favour higher selectivity), one of the reactants can be fed through the membrane.

Fig. 3 shows a conformation in which recirculation of reactants and products are carried out using a membrane and a separate catalyst. The membrane and catalyst are shown as separate units but it is also possible to have the catalyst and membrane together in a single unit, as in Fig. 2 but with external circulation. As will be discussed further in Section 4, there appear to be some significant advantages to the separation of the membrane and the reactor, at least in a situation in which Knudsen separation occurs and in which it is desired to remove a light product (e.g. H_2) preferentially; there would not be so much advantage if the membrane were totally selective to one or other product (e.g. H_2 through Pd). As in the case discussed in the previous paragraph (see Fig. 2), there could also be some advantageous situations in which one of the reactants (e.g. oxygen) was fed through the membrane.

3. Experimental testing of the catalytic membrane concept

3.1. Methanol oxidation over a silver-doped membrane catalyst [4]

Prior to the work to be summarised here, Lefferts et al. [5] had previously carried out a study of the selective oxidation of methanol with molecular oxygen over massive crystalline silver catalysts of the type used commercially for the production of formaldehyde by the Borden process; this reaction is carried out with an excess of methanol over oxygen and the reaction is a combination of dehydrogenation and oxidative dehydrogenation (reactions 2 and 3, respectively):

$$CH_3OH \rightarrow CH_2O + H_2 \quad (2)$$

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \quad (3)$$

In addition to these reactions, total oxidation to CO and CO_2 occurs by consecutive and parallel steps. When an oxygen-treated catalyst was exposed to methanol alone, it was found that formaldehyde was produced selectively but that the oxygen was gradually removed; when the oxygen had all reacted, the catalyst no longer exhibited any catalytic activity. It was concluded that reactions (2) and (3) occur over sites associated with strongly bonded sub-surface oxygen species which are probably located at dislocations in the silver surface. As long as this type of oxygen is available below the surface, the silver is capable of carrying out reaction (2) selectively. The presence of weakly adsorbed oxygen species favours the formation of CO and CO_2. Attempts to improve the behaviour of the massive silver catalysts by introducing more defects gave improvements in behaviour but these were short-lived as the defects gradually disappeared during use. Supported silver was much less selective than massive silver, presumably due to unselective reaction occurring on the surface of the support.

It was decided to try out the concept of the membrane reactor with a silver catalyst incorporated in the membrane using a system in which the two sides of the membrane are considered to be stirred tank reactors (Fig. 1b). By introducing the methanol from one side of the membrane and the oxygen from the other, it was hoped that it would be possible to maintain a high concentration of the sub-surface oxygen described above in the absence of significant amounts of weakly adsorbed or gas-phase oxygen. Silver was deposited in the microporous layer of the membrane structure using a method similar to that used previously for the preparation of α-alumina-based nickel catalysts: a solution of silver nitrate and urea was hydrolysed at 90°C within the pores to give AgOH (or Ag_2O) and this was then decomposed at 400°C to give metallic silver:

$$2AgNO_3 + CO(NH_2)_2 + 4H_2O$$

$$\rightarrow \underset{\underset{2Ag}{\downarrow}}{2AgOH} + 2NH_4NO_3 + H_2CO_3 \quad (4)$$

It was shown by scanning electron microscopy that the silver was concentrated in the pores of the thin microporous membrane layer rather than in the wider pores of the α-alumina support structure and that the particle diameters were about 17 nm.

Experiments were carried out in the temperature range 100 to 500°C in which a flow of 8% methanol in helium was admitted to one side of the membrane and a flow of up to 4% oxygen in helium was added to the other side. Table 1 gives some typical results for an unmodified membrane and for membranes with two different silver loadings in the microporous layers.

Reaction with the unmodified membrane started at a temperature just below 200°C and reached a value of 75% at 500°C. The primary

Table 1
Methanol conversions and selectivities to formaldehyde for different silver concentrations in the microporous membrane layer

Silver content (wt.-%)	Conversion at 250°C (%)	Selectivity at 250°C (%)	Conversion at 300°C (%)	Selectivity at 300°C (%)
0	4	0	10	1–2
15	12	25	25	20
67	15	53.5	30	35.7

product at low temperatures was dimethyl ether and the secondary product was CO; as the temperature was increased, the selectivity to the ether decreased and that to CO and also methane and formaldehyde increased, the latter two products decreasing once more at the highest temperatures examined. The highest selectivity to formaldehyde (ca. 16%) was found at 450°C.

When silver was incorporated in the membrane, the conversion of methanol started at a temperature just above 100°C and reached 50% at 380°C, the highest temperature examined. The predominant product was CO over the whole temperature range. Of the other products, formaldehyde was predominant at the lowest temperatures but CO_2 and dimethyl ether became more significant at higher temperatures. As can be seen from the results of Table 1, the selectivity to formaldehyde was increased by increasing the concentration of silver in the membrane layer, particularly at lower temperatures.

The conversions and selectivities achieved were much lower than those achieved using massive silver catalysts [5]. Although this is probably partly due to the fact that the massive catalysts were studied at higher temperatures under conditions when 100% oxygen conversions were achieved and such conditions could not be achieved in the membrane reactor without destroying the membrane layer, much of the difference observed was probably due to the presence of the γ-alumina membrane layer; γ-alumina catalyses the dehydration of methanol to form dimethylether. The high concentrations of CO found for the unmodified and Ag-modified membranes are probably due to unimolecular decomposition reactions of the formaldehyde in the micropores of the membrane.

3.2. Dehydrogenation reactions [6]

Two sets of experiments were carried out to test the use of perm-selective membrane in dehydrogenation reactions. In the first of these, a 1-g sample of EuroPt-1 (6.2 wt.-% Pt on SiO_2 [7]) mixed with 0.5 g of quartz was placed above the membrane layer in the reactor and a mixture of 10% of butane in He was flowed over the catalyst (20 cm^3 min^{-1}); the support side of the membrane assembly was purged with pure He (80 cm^3 min^{-1}). Table 2 summarises the results obtained, comparing the data obtained with equal pressures either side of the membrane with data obtained with a slight pressure differential of ca. 0.15 bar across the membrane; also shown for comparison purposes are results obtained under equivalent flow conditions with normal plug-flow conditions.

Table 2
Conversions and selectivities for the dehydrogenation of butane to butenes over Pt/SiO_2 catalyst in contact with a γ-Al_2O_3 membrane at 400 and 500°C without and with a slight over-pressure (ca. 0.15 bar); data for a conventional plug-flow reactor are also shown for comparison purposes

Conditions	Conversion at 400°C (%)	Selectivity at 400°C (%)	Conversion at 500°C (%)	Selectivity at 500°C (%)
Membrane separation Zero pressure diff.	7	ca. 55	9	45–50
Membrane separation 0.15 bar pressure difference	11	80	15	60
Normal plug-flow reactor	5	50	9	40

It can be seen that the selectivity to the butenes was under no circumstances 100%; the other products were methane and smaller amounts of ethane and ethylene. In addition to hydrogen, small quantities of butane and the butenes were found at the support side of the reactor. The conversions and selectivities were not very dependent on *W/F*. During use, severe carbon deposition occurred on the catalyst and no activity could be observed after ca. 60 min of operation. Assuming only the butenes as products, the thermodynamically calculated conversions of butane at 400 and 500°C would be ca. 3 and 16%, respectively. Hence, it would appear that under our conditions of operation, thermodynamic equilibrium may have been reached at 400°C in the plug-flow reactor at 400°C but not in the same reactor at 500°C. However, because the selectivity to other products was not measured accurately (using a mass-spectrometer), the equilibrium conversions taking these products into account could not be calculated. We were only able to conclude that the use of a membrane without a pressure differential gave a slight improvement in conversion and that a slight pressure differential gave a greater improvement. In principle, if it possible to use a catalyst which does not suffer from carbon deposition and which is selective for the production of butenes, the use of a membrane should therefore give improved conversions (see, for example, Ref. [8]).

Similar experiments to those reported above for butane were carried out using 1 g of a ZnO catalyst [9] (again diluted with 0.5 g of quartz) for the dehydrogenation of methanol at 500°C. In a normal plug-flow reactor using the conditions given above, the conversion was 15% and the selectivity to formaldehyde was 80%, the balance being CO. The thermodynamically calculated conversion at this temperature is 80% and so we can assume that the reaction is still far from equilibrium under these conditions and that any effects observed in the presence of a membrane will be largely kinetic in origin. When the catalyst was placed in the membrane reactor, it was necessary to apply a slight positive pressure of He to the support side of the membrane; if this was not done, the formaldehyde formed penetrated into the pores of the membrane and decomposed to CO and hydrogen. With this positive pressure, a conversion of 25% was measured and there was only a slight decrease in the selectivity to formaldehyde (ca. 75%). Hence, it would appear that the selective withdrawal of hydrogen has increased the rate of the dehydrogenation reaction by about 65%.

It can thus be concluded that some advantages were found in the experiments reported above compared to experiments without a membrane. However, the results were complicated by problems of selectivity and the occurrence of undesirable reactions on the membrane surface. It would seem that the use of membrane reactor systems will require very careful control of the characteristics of the membrane and catalyst as well as the reaction conditions in order to benefit from the use of such a system. The following sections give brief descriptions of alternative systems involving porous tubes (which may or may not be permselective) where control of the reaction system is likely to be more easily achieved.

4. The porous wall reactor concept

This concept is illustrated in Fig. 4. In this case, the catalyst is incorporated in the wall of a porous tube which is then placed within another non-porous tube. One reactant gas is introduced from within the porous tube and the other from the outside. The two reactants then meet within the tube wall, in direct contact with the catalyst, and the flow of reactants can be controlled in such a way that 100% reaction occurs within the wall.

The concept of the porous wall reactor is likely to be of greatest interest in reactions such as the removal of NO_x by selective catalytic reduction (SCR) with ammonia [10]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (5)$$

or the Claus reaction [11]:

$$2H_2S + SO_2 \rightarrow 3/8S_8 + 2H_2O \qquad (6)$$

As long as the rate of chemical reaction is high compared with the rates of diffusion of the two reactants, the latter will determine the profile of reactants and products within the wall and a range of different concentrations of reactant can be tolerated before there is breakthrough of one or other reactant to the other side of the wall. For example, in the de-NO_x reaction, the reactor can in principle tolerate relatively large variations in the concen-

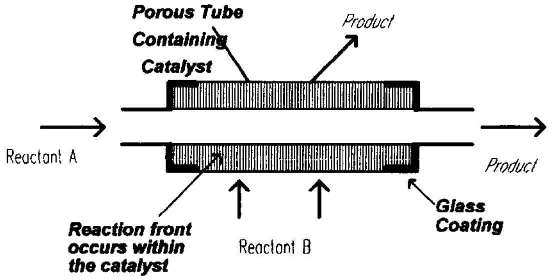

Fig. 4. Concept of the porous-tube reactor; in this case, the tube contains the catalyst and acts only as a means of separating the two reactants.

tration of NO_x in the stack-gas to be treated before breakthrough of the ammonia reductant to the stack-gas occurs. Dosing of ammonia to the porous tubes is thus relatively straightforward and does not require the elaborate control needed for more conventional reactors. The parameters determining the operation of the concept have been examined in detail by Sloot [10].

Our work in this area has been concerned with the design of suitable catalysts for the de-NO_x reaction [12]. As commercial SCR catalysts are generally composed of vanadia on titania, our materials, which have not been optimised, were prepared by hydrolysis by atmospheric water vapour of $Ti(OC_2H_5)_4$ and $VOCl_3$; these were taken up, in a volume ratio of 4:1, in an α-alumina tube glass-coated at both extremities so that a 2-cm section was uncoated in the centre of the tube. The tube containing the mixture of hydroxides thus obtained was then calcined at 450°C to form the oxides, the all-over process being described by the following equations:

$$Ti(OC_2H_5)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_2H_5OH \quad (7)$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (8)$$

and

$$VOCl_3 + 4H_2O \rightarrow V(OH)_5 + 3HCl \quad (9)$$

$$V(OH)_5 \rightarrow V_2O_5 + 5H_2O \quad (10)$$

The resultant materials were tested in a system which allowed the introduction of a mixture of NO (750 to 1500 ppm) in an oxygen (2 vol.-%) / He mixture on one side, at a flow rate of 60 cm^3 (STP) min^{-1}, and a mixture of NH_3 (750–1500 ppm) in He on the other, at the same flow rate. The conversions and slips of the two reactants were measured for tube temperatures in the range 200–300°C.

Under the conditions tested, the catalyst sample prepared as above did not give 100% conversion of the NO; nor was slip of the reactants to the other side of the porous wall fully prevented. For example, at a temperature of 200°C and with 1500 ppm of ammonia and 1500 ppm of NO, the conversion of ammonia was approximately 33% and that of NO was approximately 50%. Under these conditions, only about 10 ppm of NO was found in the ammonia-containing stream and about 110 ppm of ammonia was found in the NO-containing stream. As would be expected, increasing the partial pressure of NO while keeping that of ammonia constant caused a decrease in the ammonia slip and an increase in the NO slip. It was also found that an increase of the total pressure at the NO-containing side of the reactor from 1.0 to 1.1 bar caused a decrease in the ammonia slip to 68 ppm. Surprisingly, rather than improving the situation, increasing the reaction temperature caused a lowering in the conversions and an increase in the degrees of slip obtained. Clearly there is significant room for further optimisation of the preparation of the catalyst to improve the conversions and decrease the slip of reactants. Nevertheless, the results are encouraging and further work on the concept is justified.

5. Separate reactor and membrane with recirculation

We have already discussed above (Section 2) examples of the use of separate catalysts combined with membrane separation to remove hydrogen formed in dehydrogenation reactions. We shall now argue that there are significant advantages to gained by using separate membrane and catalyst using recirculation of reactants and products in such reactions. As an example, we consider the water-gas shift reaction:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (11)$$

The aim of our work on this reaction [13] is to drive the equilibrium as far as possible to the right so that a hydrogen-rich fuel is produced on the support side of the membrane assembly; the work is part of a larger project on the production of such hydrogen-rich fuel for use in a gas turbine [14]. For the purposes of this paper, we take a very simple model and consider two situations: (i) a

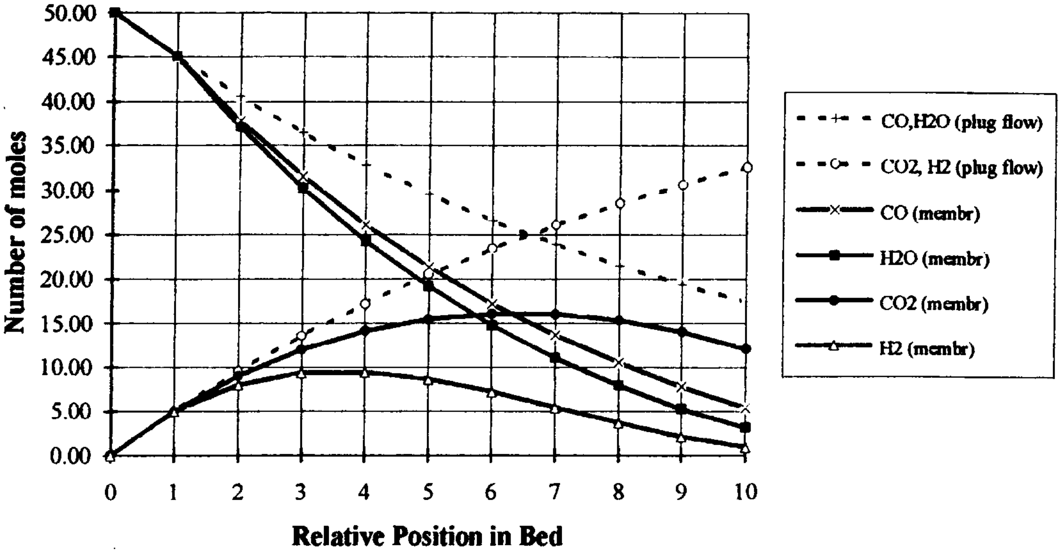

Fig. 5. Profiles of the relative concentrations of reactants and products through the catalyst bed for the water-gas shift reaction without and with a membrane; see text.

plug-flow reactor of which the walls are a membrane and within which the catalyst is located (see Fig. 2); and (ii) a continuously stirred-tank reactor with external recirculation and a separate membrane (see Fig. 3). We calculate for each, using a number of simplifying assumptions, the composition of the gases in the reactor and on the other side of the membrane (permeate) for various conversions of the reactants.

(i) *Plug-flow membrane reactor with separate catalyst.* For our calculation, we assume first-order behaviour with respect to CO and equal input concentrations of hydrogen and CO; as a simplification, we assume that the reaction is irreversible. We then consider that the bed is divided into a series of increments corresponding to 10% reaction of the input concentration of the CO and that each of these increments is followed by an equivalent section of membrane through which separation occurs by Knudsen diffusion; in the results shown here, we assume that the rate of diffusion of hydrogen is such that 50% of the hydrogen produced in the first element of the bed diffuses through the membrane and that the rates of diffusion of the other gases in the reaction mixture are determined only by Knudsen diffusion, i.e. they are inversely proportional to the molecular masses. Finally, we assume that the rates of counter-diffusion are negligible, a situation which will in practice only be achieved if the total pressure on the support side of the membrane is much lower than that on the side of the catalyst or if a purge gas flowing with high velocity is used and there is no counter-diffusion of this purge gas. Further refinement of the model (e.g. using shorter increments of bed for each element and considering different diffusion rates and/or the use of a purge gas and permitting back-diffusion of all components) produces results which differ in some respects from the data presented below; however, the all-over conclusions are similar [13]. The effects of the reversibility of the reaction have not yet been considered.

Fig. 5 shows the concentration profiles through the catalyst bed calculated according to this model for the situations without and with a membrane; the former is the normal profile for a first order reaction. When a membrane is introduced, the relative concentrations of all the reactants and products decrease. As hydrogen has the highest diffusion coefficient, the loss of hydrogen is the greatest. However, as the concentrations of CO and water are highest near the beginning of the bed, the loss of these molecules through the membrane is quite significant.

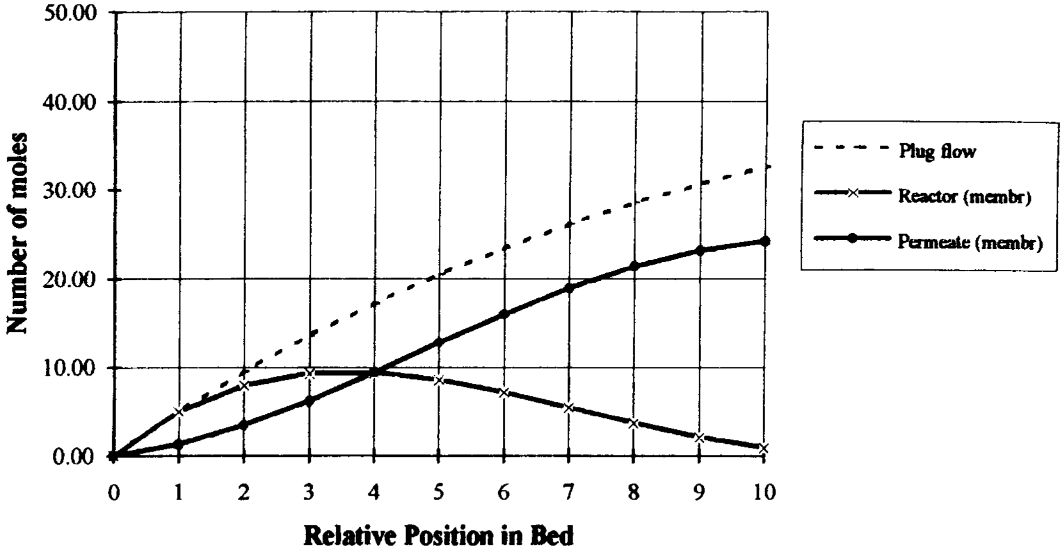

Fig. 6. Profiles of the percentage hydrogen through the catalyst bed and in the permeate for the water-gas shift reaction without and with a membrane; see text.

Fig. 6 shows the percentage of hydrogen at various positions in the bed for the data shown in Fig. 5. It can be seen that the percentage of hydrogen in the eluate stream is always below that in the normal reactor and that it becomes somewhat closer to that of the normal reactor at higher conversions. The absolute concentrations of hydrogen in the eluate stream are at all positions in the bed significantly lower than those in a normal plug-flow reactor. Further refinement of the model [13] confirms these general conclusions for a variety of different relative diffusion rates; the effect of using shorter elements of bed in the calculations is to cause a significant drop in the percentage of hydrogen in the eluate stream. The only conceivable advantage of the conformation considered is that the conversions of CO achievable in the membrane reactor may be somewhat higher than those in the conventional plug-flow reactor because of equilibrium constrictions. We plan to consider this our refinement of the model [13].

(ii) *Recirculation reactor with separate catalyst and membrane unit.* The results of the calculation of the percentages of hydrogen in the reactor side and in the eluate stream for the reactor system of Fig. 3 are compared in Fig. 7 for different degrees of conversion of CO with the percentages of hydrogen which would be obtained in a plug-flow reactor. Similar assumptions are made concerning the rates of diffusion of reactants and products as were made in the previous section; further, it is assumed that the rate of recirculation of reactants and products is very high compared with the all-over flow through the reactor so that the concentrations are the same throughout the reactor and membrane assembly. Results are given for three different porosities (in the ratio 1:2:3); only the results for the exit from the reactor are affected by this variable as the composition of the permeate remains the same. It can be seen that the concentrations of hydrogen in the eluate stream are now in all cases higher than those in the reactor effluent or those which would be obtained with a normal plug-flow reactor. It should be noted that these results do not depend on any assumption concerning the kinetics or reversibility of the reaction. The reason for the improvement compared with the results outlined in the previous section is that the gas mixture entering the membrane assembly is always much richer in hydrogen than in the corresponding position in the plug-flow reactor. The concentrations of hydrogen in the eluate stream are always higher than those in the effluent of the reactor and are also much higher than the corresponding concentrations in the effluent from a plug-flow reactor at the equivalent con-

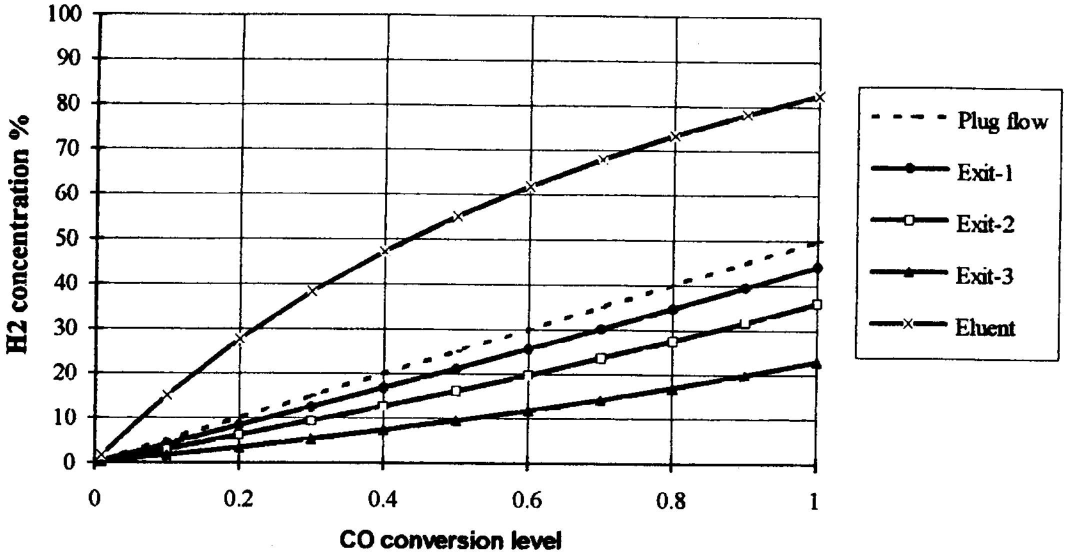

Fig. 7. Comparison of the hydrogen concentrations obtained at various conversions for the water-gas shift reaction carried out in a recirculation reactor with a separate membrane separation unit. For comparison purposes are shown the concentrations which would be obtained in a plug-flow reactor at the same conversions. For details, see text.

versions. We are currently refining the model further to allow for lower rates of recirculation (i.e. incomplete mixing). We are also carrying out experiments to show whether our conclusions are correct in practice. Clearly, there are significant practical advantages in such a reactor conformation compared with one in which the catalyst is included in the membrane assembly. For example, the relative rates of reaction and diffusion can be controlled independently, e.g. by varying the temperature of the reactor or the size of the membrane unit. Furthermore, as the membrane unit does not need to be at the same temperature as the catalytic reactor, problems of membrane stability and sealing of the membrane tubes are less significant than when the catalyst is in the membrane tube. It is clear that from an engineering point of view it is undesirable to have large temperature gradients and that it may be difficult to have significant recirculation without such gradients. However, it is unlikely that these difficulties will be more significant than those of membrane stability, etc. Hence, the substantial potential increases in hydrogen yields for reactions such as that considered may warrant the investment required for such reactors.

6. Conclusions

This paper summarises work on the use of membrane reactors with which one of the authors has been associated and then considers the advantages of using a system in which the catalyst and membrane are in separate units and recirculation is used. The results of a simplified model show that this conformation gives much better separation of a hydrogen-rich stream than does a reactor in which the membrane and catalyst are in the same unit. Further work on this subject is in progress [13].

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