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Nitrobenzene liquid-phase hydrogenation in a membrane reactor

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Abstract

This work presents the potentialities of a catalytic membrane reactor in a gas–liquid–solid reaction. A catalytic membrane has been prepared via well-controlled platinum deposition within the porous framework of a γ-Al_2O_3 mesoporous membrane. The hydrogenation of nitrobenzene to aniline has been performed using the catalytic membrane as an active gas–liquid contactor. Some operating parameters controlling the membrane reactor performance have been explored and compared with the behaviour of conventional reactors.

1. Introduction

The catalytic hydrogenation of polyfunctional molecules is a key step in the preparation of various fine chemicals. According to literature data [1], this is at best achieved using gas–liquid–solid (GLS) processes. Batch reactors are often very efficient, but a high pressure is generally required in order to improve the hydrogen mass transfer and stirring is necessary to improve GLS contacts. Trickle bed reactors are currently developed in industrial processes, but these systems present some disadvantages because the liquid film covering the solid catalyst pellets increases the resistance to external transfer of the gaseous reactant. Moreover, a preferential path can be formed which brings about poor contacts between the three phases: the presence of uncontrolled areas leading to hot spots is often observed.

Consequently, there has been considerable interest in the implementation of new types of reactor for gas–liquid–solid applications. It has been suggested recently [2] that a catalytic membrane reactor can be an efficient alternative to improve the contact between gas, liquid and solid because the volatile reactant does not have to diffuse through a liquid film covering the solid catalyst, as in conventional reactors. Following this principle, the hydrogenation of α-methylstyrene with a Pd–alumina catalytic membrane has been selected as a test reaction and a rate enhancement factor of 20 was obtained when comparing the membrane reactor to a model fixed-bed reactor [3].

The aim of the present work is to explore the potentialities of a catalytic membrane reactor in a gas–liquid–solid process. The hydrogenation of nitrobenzene was chosen as a model reaction and its kinetics established in a conventional slurry reactor under chemically controlled conditions. A first order with respect to the hydrogen pressure, an order with respect to nitrobenzene near zero and an apparent activation energy of about 45 $kJ \cdot mole^{-1}$ were obtained [4].

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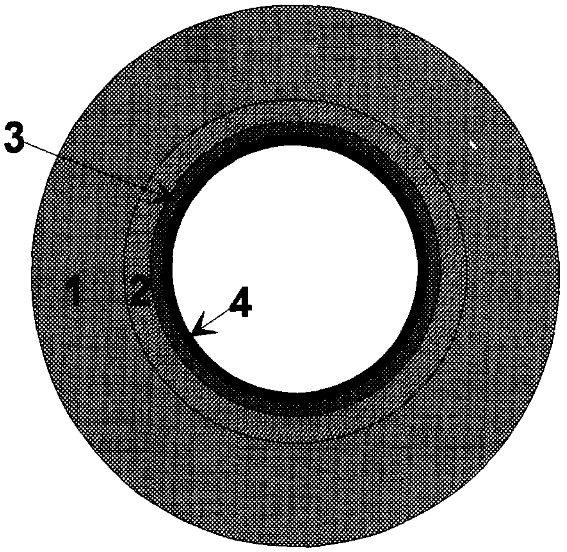

Fig. 1. Schematic of a cross-section of a tubular-shaped commercial membrane: SCT Membralox T1-70. Layers 1, 2 and 3 are made of α-Al_2O_3 and have respective thicknesses of: 1500, 40, 20 μm and average pore sizes of: 12, 0.9, 0.2 μm. Layer 4 is made of γ-Al_2O_3 and has a thickness of ca. 3 μm and average pore size of 5, 10 or 25 nm.

2. Experimental

2.1. Catalytic membrane

Starting materials were commercial SCT-US Filter (T1 70) porous alumina tubes made of a thin toplayer of mesoporous γ-Al_2O_3 deposited on a support made of several α-Al_2O_3 macroporous layers (Fig. 1) [5]. These tubes are enamelled at their ends (on 1 cm) in order to ensure tight connections. Different membranes with average pore sizes of 5, 10 and 25 nm have been used.

The platinum was deposited by ionic exchange with hexachloroplatinic acid [6] and activated by reduction in a hydrogen flow at 673 K. Well-dispersed platinum particles were deposited in the γ-Al_2O_3 toplayer with homogeneous loading profiles [7]. Table 1 gives some data concerning the active membranes used in this study.

2.2. Catalytic membrane reactor and experimental set-up

The hydrogenation of nitrobenzene was carried out in a membrane reactor especially designed for gas–liquid experiments (Fig. 2). The tubular catalytic membrane divides the reactor in two parts in which are separately introduced gas or liquid reactants.

Due to the asymmetrical character of the porous tube, the experimental set-up (Fig. 3) allows to feed the reactants either in the inner or the outer

Table 1
General characteristics of the catalytic membranes

Membrane average pore size (nm)	Membrane specific area (m^2g^{-1})	Membrane thickness (μm)	Pt loading (wt.-%) Pt/Pt + γAl_2O_3	Average Pt particle size (nm)
5	150	2	1.5	1.5
10	80	2	1.2	1.5
25	40	2	1.2	1.5

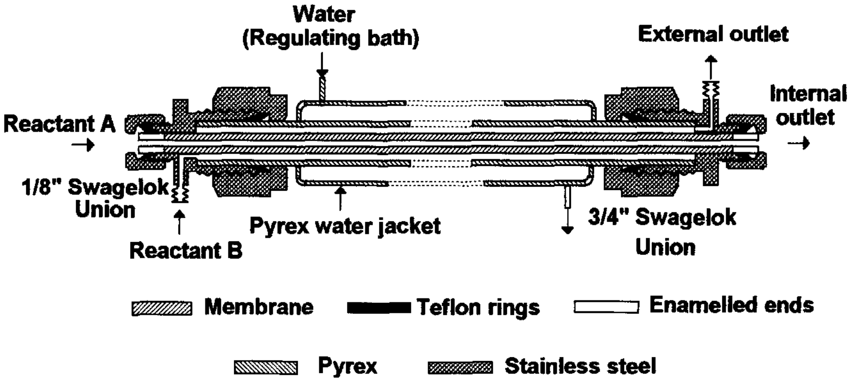

Fig. 2. Catalytic membrane reactor for three-phase applications.

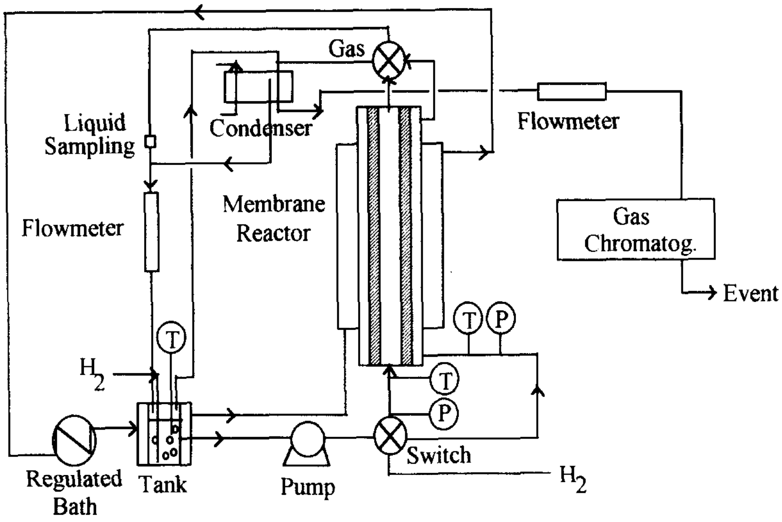

Fig. 3. Three-phase membrane reactor — experimental set-up.

compartment. The liquid phase is recirculated via a stirred tank where the reactant is heated and different gases can be introduced in order to saturate the liquid. The transmembrane differential pressure is controlled and for the experimental conditions used no liquid leakage was observed on the gas side.

The reaction rate and the products distribution were followed by repetitive sampling and gas chromatographic analysis.

2.3. Experimental conditions

Typically, a catalytic membrane of 25 cm length (0.3 to 0.6 mg Pt depending on the sample) was placed in the reactor and a mixture of 150 cm^3 ethanol and 10 cm^3 nitrobenzene was introduced in the recycle vessel. The rate of the recycle pump is about 1.6 $cm^3 s^{-1}$. The reaction temperature varies between 298 and 333 K and gas pressures up to $5 \cdot 10^5$ Pa can be used (this pressure corresponds in fact to the differential pressure, as the recycle pump only works at atmospheric pressure).

2.4. Catalytic membrane characterisation

Samples were characterised after catalytic evaluation by means of chemical titration (Pt loading), TEM (Pt average particle size), SEM (thickness of the γ-Al_2O_3 layer) and gas permeability measurements in order to compare the performance of the different catalytic membranes and calculate areal activities (per unit area of active metallic surface).

3. Results

3.1. Catalytic membrane characterisation

Whatever the type of membrane (thickness, pore size), the average size of the Pt particles is near 1.5 nm and is not affected by the catalytic test. Gas permeability measurements also suggest that the transport properties of the porous framework of the catalytic membrane are not affected by catalytic tests.

3.2. Catalytic studies

The catalytic membrane appears very stable; long duration tests (up to 100 h cumulative time on stream) do not show significant changes in the catalytic performance.

As indicated above and due to the asymmetrical character of the membrane, two modes of feeding the reactants have been explored (Fig. 4). In mode 1, the gas (hydrogen) is introduced in the outer compartment (permeate side, as named in separation processes) and the liquid in the outer

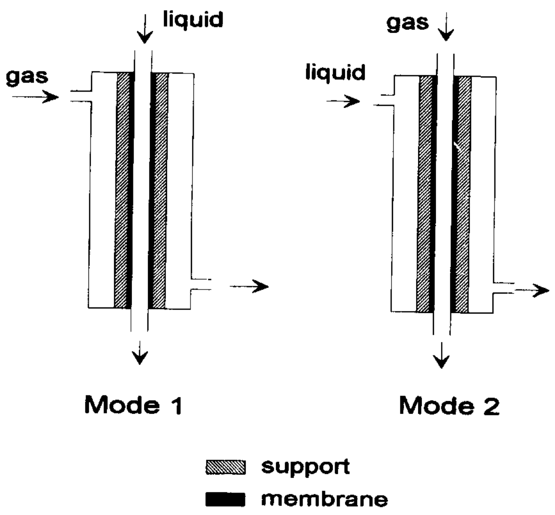

Fig. 4. The two modes of reactants introduction.

compartment (retentate side). In mode 2, the feeds are inverted.

Fig. 5a and Fig. 5b give the effect of reaction temperature on the areal activity as a function of the average pore size of the membrane for modes 1 and 2. In mode 1 (Fig. 5a), an increase of reaction temperature has only a limited effect on the activity, whatever the pore size. On the contrary, when mode 2 (Fig. 5b) is used, a clear positive effect is observed when membranes with pores of 10 and 25 nm are used.

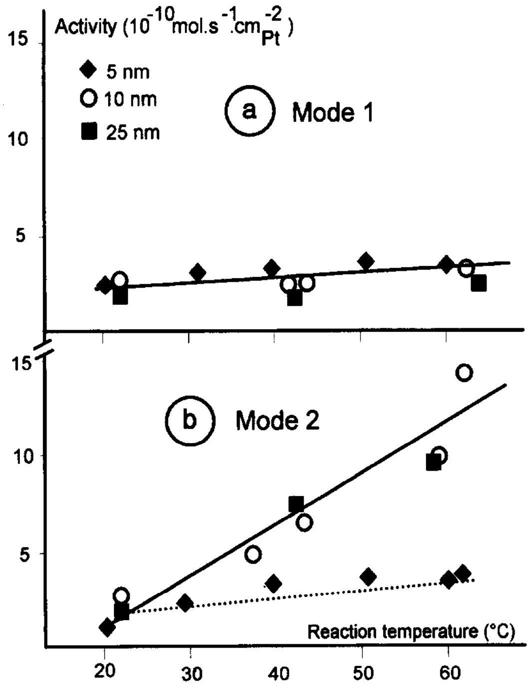

Fig. 5. Temperature dependence of the activity as a function of membrane pore size and mode of introduction.

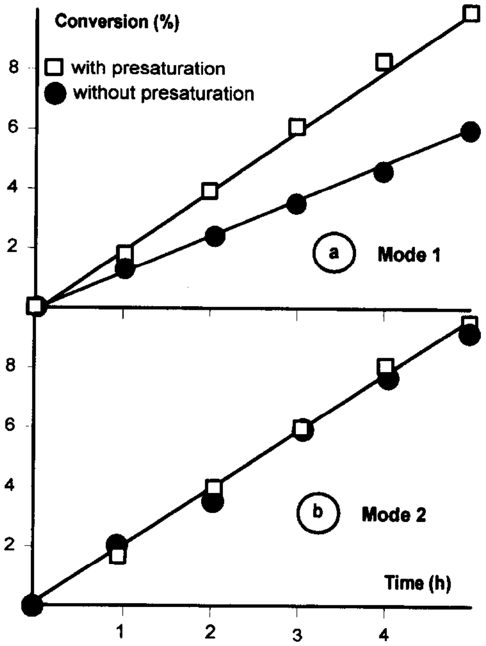

Fig. 6. Conversion with or without liquid phase presaturation (5 nm membrane).

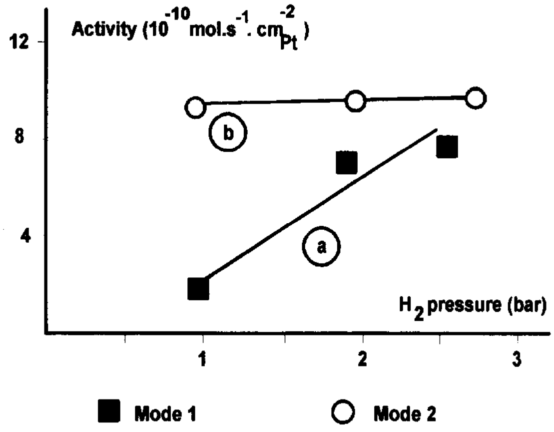

Fig. 7. Activity as a function of the hydrogen pressure.

Fig. 6a and Fig. 6b compare in modes 1 and 2 the activity of a Pt/γ-Al_2O_3 (5 nm) membrane when the liquid phase is presaturated with H_2 or not. The presaturation is achieved by bubbling H_2 in the recycle vessel (and is replaced by N_2 when non-presaturated liquid is used).

Fig. 7a and Fig. 7b show the effect of the H_2 pressure on the activity of a Pt/γ-Al_2O_3 (10 nm) membrane for the two modes of reactants introduction. In mode 1 the catalytic activity clearly increases with the H_2 pressure, in opposition to mode 2 where the activity is not modified.

4. Discussion

The absence of change in the Pt particle size distribution and in permeabilities measurements well agrees with the absence of deactivation of the catalytic membrane as observed in our experimental conditions (low temperatures of reaction).

As mentioned above, the behaviour of the catalytic membrane reactor strongly depends on the mode of feeding of the reactants.

4.1. Mode 1

As far as the influence of the reaction temperature is concerned (Fig. 5a and Fig. 5b), in mode 1 (liquid in the inner compartment, gas in the outer one) the apparent activation energy deduced from the experimental data is near 15 $kJ \cdot mole^{-1}$ (Fig. 5a), whatever the pore size of the catalytic membrane. This low value suggests a conversion controlled by diffusional limitations. For the same mode 1, Fig. 6a shows that the activity is clearly enhanced when a presaturated liquid is used, which indicates that a significant part of the reacting hydrogen comes from the liquid phase and that diffusion processes of H_2 may play an important role. Moreover, Fig. 7 (curve a) shows that the activity is proportional to the hydrogen pressure in good keeping with a control of the conversion by the H_2 transfer.

Let us now consider the multilayered porous structure of the tube during the reaction: due to capillary forces the liquid phase will fill up all the porous framework (i.e. support + membrane). In mode 1 (gas in the outer compartment) gaseous hydrogen will have to diffuse through the support before attaining the active phase located in the membrane (see Fig. 4). A rough calculation of the maximum diffusing flux of reacting hydrogen which can be expected for the experimental conditions used has been made. This calculation takes into account the two following diffusion processes: (i) H_2 coming from the gas phase and diffusing through the porous structure and (ii) H_2 coming from the presaturated liquid and diffusing through a 200 μm immobile liquid film at the surface of the toplayer. The maximum expected diffusing flux is obtained when the H_2 concentration in the catalytic layer is zero. This calculation implies an hydrogenation rate of nitrobenzene very similar to the experimental catalytic data (agreement within 30%).

All these considerations suggest that in mode 1, the whole process for all samples studied is controlled by diffusional limitations of hydrogen.

4.2. Mode 2

In mode 2 (Fig. 5b), the effect of the reaction temperature on the activity clearly depends on the average pore size of the catalytic membrane.

The behaviour of the membrane with a pore size of 5 nm is very similar in both modes (very low apparent activation energy) and diffusional processes probably control the activity. These limitations have been attributed to the diffusion of nitrobenzene in the porous structure of the γ-Al_2O_3 membrane: as a matter of fact the kinetic order with respect to nitrobenzene is positive and increases with the reaction temperature (the order is 0.3 at 20°C and 0.6 at 60°C).

In good agreement with the hypothesis above, when membranes with larger pores (i.e. 10 and 25 nm) are used (which corresponds to a decrease of diffusional limitations in the liquid phase), the activity strongly depends on the reaction temperature (Fig. 5b) and the corresponding apparent activation energy, $E_a = 37$ kJ/mole, tends to the value observed in conventional reactors under a chemically controlled regime (i.e. $E_a = 45$ kJ/mole, [4]). For these membranes the regime is then near-chemically controlled, which agrees with the fact that when the Pt loading is higher than those reported in Table 1, E_a is under 20 kJ/mole.

Fig. 6 reveals another difference between the two modes: in mode 2, the conversion is not affected by the presaturation of the liquid phase (curve b), which suggests that all or almost all of the reacting hydrogen comes from the gas phase, which is in opposition with what is observed in mode 1. This suggests that the H_2 transfer from the gas phase to the catalyst is very efficient.

This easy transfer has been confirmed by studying the effect of the H_2 pressure on the catalytic activity. As can be seen in Fig. 7, curve b, the activity is unchanged in mode 2 when increasing the H_2 pressure. This corresponds to a kinetic order for H_2 equal to zero: for these conditions hydrogen is not a kinetically limiting reactant, which is generally not the case when conventional three-phase reactors are used in liquid phase hydrogenation. Indeed for the same reaction, using a slurry reactor and a Pt/Al_2O_3 powder catalyst prepared with an alumina support with the same textural properties as the membrane, a kinetic order with respect to H_2 equal to 1 is obtained under a chemically controlled regime and for similar operating conditions [4].

This order 0 for H_2 has been observed whatever the average pore size (5 to 25 nm) of the alumina membrane. However, for the 25 nm sample, the activity suddenly drops for H_2 pressures above ca 2.5 bars and in the same time bubbles appear in the liquid phase. This activity drop has been attributed to the differential pressure which becomes high enough to empty the largest pores of the membrane. The gas–liquid interface is then displaced from the (active) toplayer which results in a less active system.

The difference in kinetic orders with respect to H_2 between the membrane reactor (order 0) and a conventional slurry reactor (order 1) suggests that the H_2 coverage of the platinum active surface is much higher in the membrane reactor and does not limit the reaction, which is not the case in the stirred tank reactor.

The modelling of this membrane reactor in nitrobenzene hydrogenation has been carried out for the two modes of introducing the reactants and the experimental results fit well with the simulation data [4].

5. Conclusion

A membrane supporting in its porous network a catalyst may act as an active contactor between gaseous and liquid reactants. The design of the catalytic membrane (pore size diameter, catalyst loading) and the operating conditions of the membrane reactor are important parameters which govern the mass transfers and the resulting performance. The conditions for which the gaseous reactant is, at variance with conventional three-phase reactors, not kinetically limiting have been determined. For these conditions, the kinetic order with respect to the gaseous reactant is indeed zero.

Due to its unique ability to transfer the gas to the active solid phase in the presence of a liquid, the catalytic membrane reactor appears to be a very good alternative when this transfer strongly limits the catalytic conversion. Other potential interests of catalytic membrane reactors for three-phase reactions are (i) they do not require permselective materials and then state-of-the-art mesoporous materials are suitable, (ii) due to the generally limited range of operating temperatures in three-phase reactions, there should be no problem with the thermal stability of the membrane and (iii) the catalyst is part of the reactor and its recovery does not need any separation from the liquid medium (as is the case in conventional slurry reactors); this specific configuration should also limit catalyst losses and allow in-situ regenerations.

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