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Control of transport properties with a microporous membrane reactor to enhance yields in dehydrogenation reactions

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Abstract

The dehydrogenation of isobutane has been studied in a membrane reactor using either a mesoporous alumina membrane or a microporous zeolite membrane. It has been shown that for both membranes an increase in the isobutene yield is observed when compared to a conventional reactor. However, these increases are related to two different phenomena: a complete mixing of reactants, products and sweep gas in the case of the mesoporous membrane and a continuous separation of hydrogen when the microporous zeolite membrane was used.

1. Introduction

The dehydrogenation of isobutane is an important reaction and a key step for producing isobutene, a raw material for the MTBE octane booster production. Some butanes dehydrogenation processes have been developed using a fluidized bed of platinum catalyst in the UOP process [1] or a fixed bed of a chromium based catalyst in the STAR process (Phillips Petroleum Co.) [2]. These processes generally use a feed of hydrogen in order to improve the catalyst stability and have a conversion limited by the thermodynamic equilibrium.

The removal of products from a reversible reaction system shifts the reaction towards the products side. This principle is the basis of the use of the membrane reactor for dehydrogenation reactions: the continuous and selective hydrogen removal will improve the yield of olefins [3–5]. Highly hydrogen selective dense, either palladium [6,7] or silica [8], membranes have been used for this purpose. This type of membrane shows a very high selectivity but a poor hydrogen permeability, which limits their application.

Others researchers studied dehydrogenation reactions with micro- or mesoporous alumina membranes [9,10] or Vycor glass membranes [11]. However, until now these membranes do not present a sufficient permselectivity for hydrogen and moreover, their stability at the high temperatures (573–773 K) required for alkanes dehydrogenation has to be improved.

Research efforts in order to increase membrane selectivity and permeability in gas separation processes have given a new and very attractive solution: zeolite membranes [12–14]. In fact, a membrane composed of a zeolite can theoretically

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Table 1
Membranes general characteristics

	Mean pore size	Thickness
α-Alumina support	12, 0.9, 0.2 μm	1500, 40, 20 μm
γ-Alumina membrane	3 nm	3 μm
Zeolitic membrane	0.6 nm	–

act as a molecular sieve giving good separation factors between hydrogen and hydrocarbons. Moreover, the thermal stability of zeolite is also an important and necessary characteristic for high temperatures dehydrogenation reactions. A new type of a recently patented [15] thermally stable composite silicalite/alumina membrane seemed to us to be a good candidate for membrane reactor applications.

The main goal of the present work is the experimental study of the performance of a catalytic membrane reactor in the isobutane dehydrogenation reaction. Two types of membrane have been compared: a mesoporous γ-alumina membrane and a microporous zeolite membrane. The reaction was performed using a fixed bed of an alkali-modified industrial catalyst.

2. Experimental

2.1. Materials

A commercial Pt-Sn/γ-Al_2O_3 catalyst was obtained from Procatalyse (CR-201). It contains 0.4 wt.-% Pt and 0.2 wt.-% Sn. Potassium (1.8 wt.-%) was added by impregnation in order to neutralise the acidic sites of the support in order to increase selectivity and stability. This solid was used in the form of cylindrical pellets (2 mm × 2 mm). Before each reaction, 1.7 g of the catalyst was introduced in the reactor and activated by hydrogen at 823 K for 2 h. The catalyst did not present any loss of activity under the experimental conditions studied.

Two types of membranes were used: a mesoporous γ-alumina membrane and a silicalite/alumina membrane. In both cases, they were supported on a macroporous α-alumina tube (supplied by SCT, US filters) of 25 cm length and 7 mm internal radius (see Table 1 for other characteristics). The support was enamelled at both ends before membrane deposition.

γ-alumina membranes were manufactured by dipping the support in a boehmite sol synthesised by the Yoldas method [15], followed by a firing at 823 K. Silicalite membranes were prepared by the method described in [16]. It consisted essentially of the hydrothermal synthesis of the silicalite in the macroporosity of the α-alumina support. The general characteristics of both types of membranes are given in Table 1.

2.2. Membrane reactor

The reactor is shown in Fig. 1. It consisted essentially of a stainless steel shell containing the membrane tube. Gases tightness between inner side and outer side of the membrane reactor was ensured by graphite seals (Le Carbone Lorraine). The reactor had two inlet and outlet streams and was heated by a heating cord. The catalyst bed was placed in the inner compartment of the reactor. The reactor temperature profile was measured by a thermocouple moving in a stainless steel tube

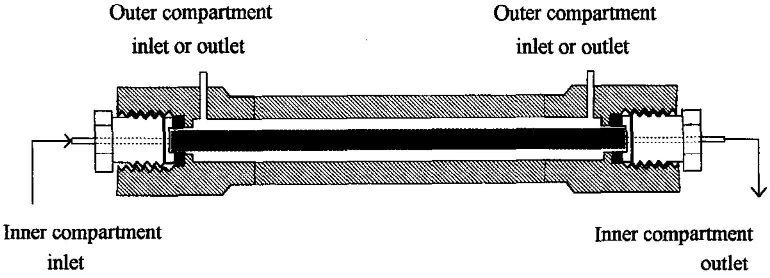

Fig. 1. Catalytic membrane reactor.

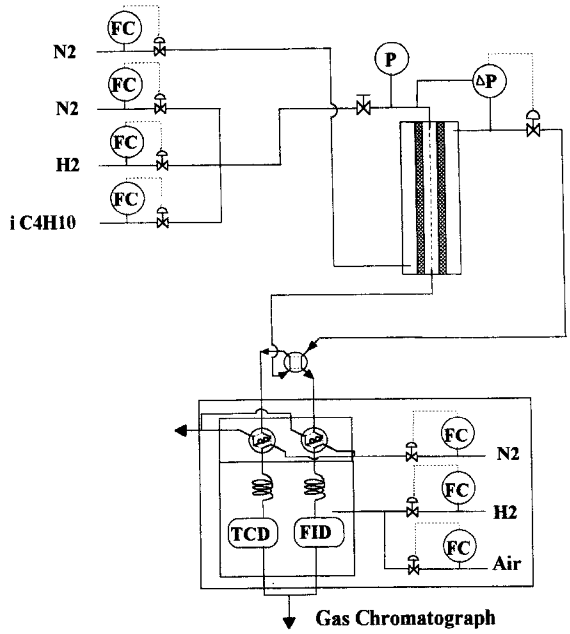

Fig. 2. Experimental set-up.

placed in the central axis of the inner compartment. The reactor was operated under quasi isothermal conditions with temperature gradients along the reactor length of about 5 K.

2.3. Experimental set-up

Fig. 2 presents a schematic diagram of the experimental set-up. The membrane reactor was supplied with a gas mixture (133 ml/min) of isobutane (16.0 vol.-%), hydrogen (19.2 vol.-%) and nitrogen in the inner compartment. Nitrogen (140 ml/min) was used as a sweep gas in the outer compartment. Gas flows were regulated by mass flow controllers and reactant and sweep feeds could be in a co-current or counter-current configuration. Reactants and products analysis was performed by gas chromatography, with FID and TCD detectors for hydrocarbons and hydrogen analysis.

In the present work, all the catalytic measurements have been performed at ca. 723 K. The differential pressure across the membrane was regulated by a Kämmer 80037Z automatic valve connected to a Keller DP232 differential manometer. In order to compensate the pressure drop created by the catalyst bed the differential pressure across the membrane was fixed to + 10.008 bar during all experiments.

Permeability measurements of single gases (N_2, H_2, i-C_4H_{10}) were also performed at 723 K, using a fixed bed of glass beads in order to simulate the catalytic bed. During permeabilities measurements, the transmembrane pressure was fixed and the permeate gas flow rate measured at different internal pressures.

3. Results and discussion

3.1. Permeability measurements

Fig. 3 and Fig. 4 show the change in hydrogen, isobutane and nitrogen permeabilities as a func-

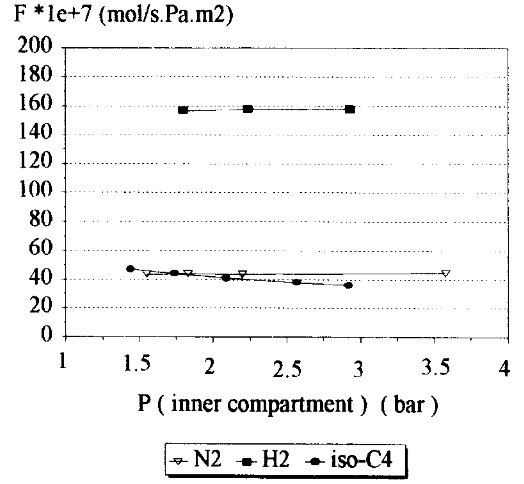

Fig. 3. Gas permeabilities vs. total pressure (γ-alumina membrane).

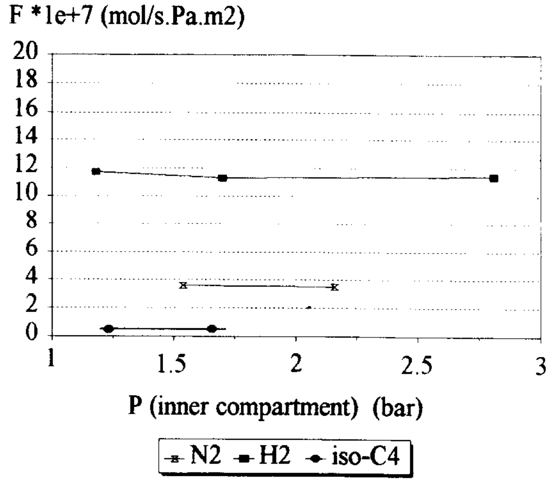

Fig. 4. Gas permeabilities vs. total pressure (zeolite membrane).

tion of the pressure for the γ-alumina and zeolite membranes, respectively.

For the γ-alumina membrane (Fig. 3), it can be observed that permeabilities do not increase with pressure. This result suggests that the membrane is defect-free since there is no viscous flow.

The experimental ratios of permeabilities H_2/N_2 and $H_2/i\text{-}C_4H_{10}$ are 3.6 and 4.0, respectively. According to Knudsen diffusion the corresponding theoretical values are 3.7 and 5.4. It can be then concluded that for H_2 and N_2, the mass transport is ensured by a Knudsen diffusion mechanism. This result is in good agreement with the physical characteristics of this membrane (mean pore size in the mesoporous range). In the case of isobutane, the permeability is higher than expected, probably due to surface diffusion, which can compete with Knudsen diffusion for condensable gases. This result was corroborated by Peureux [17] who studied the behaviour of isobutane permeability as a function of temperature for the same type of membrane.

For the zeolite membrane (Fig. 4), the permeabilities observed are much lower when compared with the γ-alumina membrane. However, for this membrane the total thickness of the separative layer is not clearly defined and then pure gases permeability values cannot be directly compared with the permeabilities obtained with the alumina membrane. Nevertheless the experimental ratios of the H_2/N_2 and $H_2/i\text{-}C_4H_{10}$ permeabilities are 3.0 and 30.0, respectively. These values indicate that the mass transfers through the zeolite membrane do not follow a Knudsen mechanism and that high separation factors for $H_2/i\text{-}C_4H_{10}$ mixtures should be obtained with this membrane.

3.2. Isobutane dehydrogenation reaction

The isobutane dehydrogenation reaction has been performed in the membrane reactor using the two types of membranes and the experimental conditions previously described. Three different configurations have been used:

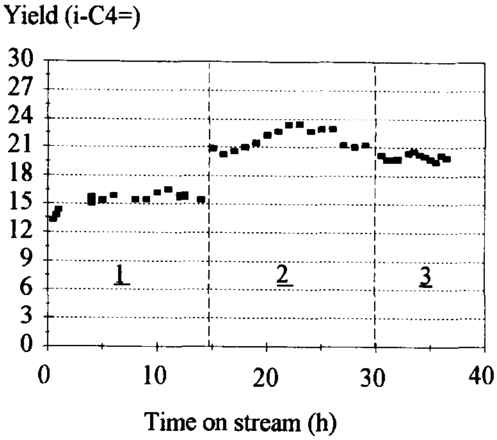

Fig. 5. Isobutene yield with fixed bed catalytic reactor (γ-alumina membrane) $T=733$ K. (1) No sweep gas; (2) co-current sweep gas; (3) counter-current sweep gas.

(1) no sweep gas, the entry and exit of the outer compartment are closed. This configuration simulates a conventional non-membrane reactor;

(2) co-current sweep gas in the outer compartment;

(3) counter-current sweep gas in the outer compartment.

The isobutane yields were calculated taking into account the gas analysis at the outlets of both compartments.

In the case of the $\gamma\text{-}Al_2O_3$ membrane, the isobutene yield for the three configurations is depicted in Fig. 5 as a function of time. It can be observed that in configuration 1 (non membrane reactor) the isobutene yield is very near the equilibrium yield as calculated for a conventional packed bed reactor for the same experimental conditions. When a sweep gas is used, the isobutene yield is higher than in configuration 1 (35% increase). When a counter-current sweep gas is used, the increase is a bit lower, which could be related to the more important loss of non reacted isobutane in the outer compartment (the percentages of the isobutane permeating through the γ-alumina membrane are respectively 34% and 44% in configurations 2 and 3).

Table 2 shows the comparative gas compositions at the reactor exits (co-current configuration). The most important fact is that, for the experimental conditions used here, the γ-alumina

Table 2
Gas compositions at the reactor exits with co-current sweep flow

	Compartment	γ-Alumina membrane (%)	Zeolite membrane (%)
Isobutane	Inner	6.45	10.6
	Outer	5.44	1.5
Isobutene	Inner	1.96	3.05
	Outer	1.5	0.33
Hydrogen	Inner	11.1	11.2
	Outer	11.1	10.5

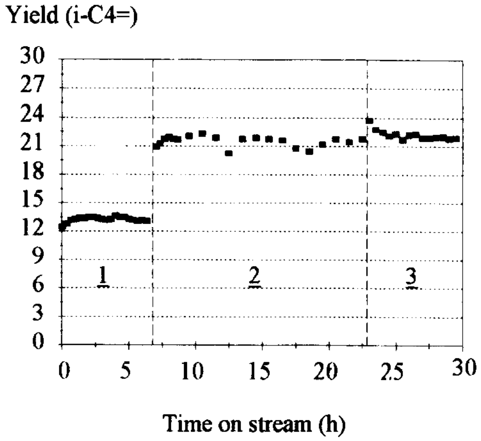

Fig. 6. Isobutene yield with fixed bed catalytic reactor (zeolite membrane) $T=723$ K. (1) No sweep gas; (2) co-current sweep gas; (3) counter-current sweep gas.

membrane is not able to separate hydrogen from hydrocarbons since the gas compositions in the inner and outer compartments are almost the same. This result suggests that the better isobutene yields (when compared with the conventional reactor, configuration 1) obtained with the γ-alumina membrane is a consequence of an equilibrium displacement by mixing the reacting feed with the sweep gas and not by a continuous separation of hydrogen. As a matter of fact, if a complete dilution of the reacting gases by the sweep gas is assumed (the concentrations of reactants being 8% for isobutane and 10% for hydrogen), the equilibrium conversion calculated at 723 K is 24%. This result was confirmed by Tayakout et al. [18] through a theoretical analysis developed for a catalytic membrane reactor using the same type of mesoporous alumina membrane.

In the case of the zeolite membrane (Fig. 6), it can be observed that the isobutene yield drastically increases (increase of 70%) when sweeping the outer compartment. The negative effect of the counter-current sweep gas is no more observed. The gas compositions at the reactor exits (Table 2) show an important separation factor between hydrogen and hydrocarbons (the ratio of the $H_2/i\text{-}C_4H_{10}$ transmembrane fluxes is 7 in the co-current configuration).

The loss of isobutane is limited for both reactor configurations (9%), suggesting that in the case of the zeolite membrane, the equilibrium displacement observed is not directly related to the above depicted dilution effect, but mainly to the continuous removal of the hydrogen produced during the reaction.

This interpretation was supported by gas separation experiments realised with the two different membranes. When a mixture of hydrogen, nitrogen and isobutane (with the same composition as the reactant mixture) is introduced in the inner compartment of the alumina membrane, the equilibrium in concentration between the two reactor compartments is obtained for the different gases. On the contrary, in the case of the zeolite membrane the isobutane concentration is almost the same between entrance and exit of the reactor inner compartment.

This work is now going on with the modelling of the zeolite membrane reactor in order to calculate the theoretical conversions for different configurations, gases flows and differential membrane pressure. This simulation will allow the optimisation of the isobutene yield in this type of reactor.

4. Conclusion

In the present experimental conditions, the isobutene yield is improved using either mesoporous or ultramicroporous membranes. However, the observed equilibrium displacements are consequences of two different phenomena. In the case of a mesoporous membrane, the observed increase in conversion is due to a mixing effect of reactants and sweep gas and not by a continuous separation of hydrogen as often reported in the literature. When an effective separative zeolite membrane is used, the equilibrium displacement by continuous product separation is really observed. Work in this area is going on by improving the performance of the zeolite membrane, by catalyst and reactor configuration optimisation and reactor modelling.

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