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Olefins catalytic oligomerization on new composites of beta-zeolite films supported on α-Al_2O_3 membranes

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1. Introduction

Petrochemical refining processes use homogeneous catalysts to carry out oligomerization of light olefins to obtain high value materials, such as polyethylene [1], polypropylene, etc. Alternatively, oligomerization of light olefins within the range from C_3 to C_5 may lead to high octane fuel precursors. Heterogeneous catalysts are used to limit the chain length to a monomer unit, as in the production of the propylene tetramer (TPC) [2], such as Selectopool [3] and Dimersol [4], among others. All these systems have used a variety of catalysts comprising of liquid acids impregnated on solid supports. Currently, alternative materials having an inherent surface acidity, namely HY and H-ZSM-5 zeolites [5] and sulphated metal oxides, are being investigated though the main drawback in these systems is their high deactivation rate. This is due to coke deposition, which forms either during subsequent oligomerization and hydrocarbon dehydrogenation reactions, or from catalytic cracking of long chain species [6]. Therefore, there is a need for developing new materials with higher stability and resistance to deactivation derived from undesirable coking. In this respect, a new class of materials and devices are being developed, based on composite materials made with porous inorganic membranes and catalytic active components confined within the porous system of the membrane. With a membrane, it becomes possible to combine both selective diffusion and catalytic reaction effects. Other potential uses involve the selective control of reagents feed needed to promote effective contact among gaseous and liquid phases [8]. Some reviews on this topic have been published by Armor [9]; Hsieh [10]; Saracco and Specchia [11]. Such features are clearly advantageous in order to achieve modification of the chemical equilibrium in a catalytic reaction, as demonstrated recently for catalytic dehydrogenation [7] of paraffins. Membrane reactors may move a reactions equilibrium to increase the yield of product of interest, by preferential removal of the reactive intermediate product, preventing its reaction further in consecutive reaction networks. The specific characteristics of zeolite membranes, with small and uniform pores, make them ideal candidates to integrate reaction and selective separation.

The aim of the present work is to explore the yield increase of branched octane of *i*-butene oligomerization, for the production of substituted benzene and/or MTBE additives in high-octane gasoline. The oligomerization reaction produces *i*-octene from *i*-C_4=, and also undesired C_{12}= or/and C_{16}= compounds. The control of the residence time of reactant in the membrane pores increases the C_8= selectivity and yield. A second important goal is to reduce the deactivation of the catalytic membrane. If *i*-C_4= remains for a long time in the pores, its oligomerization produces long-chain hydrocarbons which block the pores and deactivates the catalyst.

2. Experimental

The supported zeolite phase was synthesised following the conditions reported earlier [12], based upon an initial composition expressed as:

$$3.20Na_2O : 1.62K_2O : 1Al_2O_3 : 90SiO_2 : 22.5(TEA)_2O : 1080H_2O.$$

The gel-like phase was used as a precursor of the crystalline zeolite phase by introducing it in the pore system of the γ-alumina washcoat supported on the tubular α-Al_2O_3 membrane (CT 01070 from the Societé de Ceramiques SCT, France). These inorganic membranes have a total length (axial) of about 25 cm and i/o diameters of 0.65 and 1 cm, respectively, together with a narrow pore size distribution, showing a maximum around 5 nm, Fig. 1.

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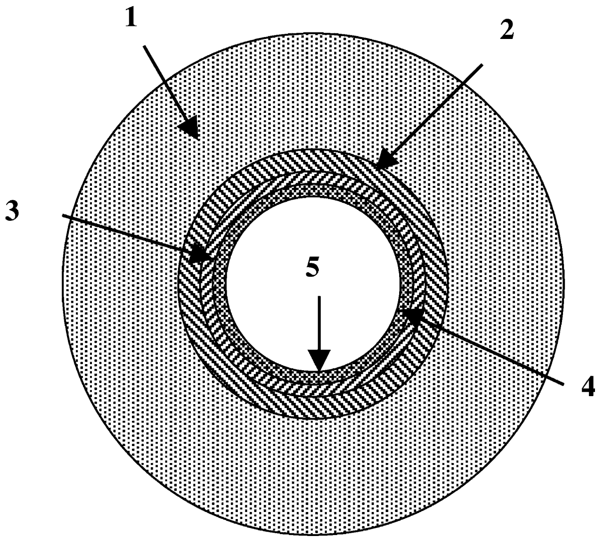


Fig. 1. Cross-section of membrane SCT Membralox T1 70. Layers 1–3 are made of α-Al_2O_3. Layer no. 4 is γ-Al_2O_3 and layer no. 5 is beta-zeolite.

The precursor gel was prepared using sodium hydroxide (>99%) dissolved in bidistilled water, aluminium (99.9%), TEAOH (35%), potassium hydroxide and silica powder. After crystallisation, the zeolite was exchanged in an aqueous solution of ammonium salts (NH_4NO_3), at $T = 363$ K, then the composite material was dried for 24 h at 363 K. The calcination proceeded for 3 h at 823 K, using a temperature ramp of about 2 K min^{-1}.

These materials were tested for the catalytic oligomerization of i-C_4 olefins. The membrane reactor consisted of an external cylindrical stainless steel container which contained a ceramic membrane inside. Two Teflon fittings permitted positioning the ceramic body into the metallic cylinder (Fig. 2). This assembly was divided into two chambers, the outer one being used for feeding the gas phase (*i*-butene), while the inner chamber was used for collecting the permeate, i.e. the final. The reactants cross the porous membrane, within which, their catalytic transformation occurs.

The input and product streams followed the path illustrated in Fig. 2. The *i*-butene (>99.999% purity) passed through the fine control valves which regulate the overall flow. The pressure is monitored by means of a transducer Cole-Parmer, Mod. 07356, which is placed at the reactor inlet, while the reaction zone was surrounded by an electrical furnace having three heating zones. The reaction temperature was monitored by means of a West 2054 controller, while the hydrocarbon analysis was performed in a GC fitted with FID (HP5890 Series II Plus) and a capillary column (HP PONA, 50 m × 0.2 mm × 0.5 μm).

A comparative study was made on the performance of the zeolite membrane versus a reference material constituted by pure beta-zeolite (PQ). One hundred milligram of zeolite was used in a fixed-bed reactor at WHSV of 0.96 min^{-1}. The membrane reactor used a similar WHSV of 0.97 min^{-1}. The operating conditions involved *i*-butene being introduced at temperatures in the range from 323 to 423 K. The olefin was fed continuously through the annular space of the reactor i.e. from 20 to 60 ml min^{-1}, while the products were recovered for analysis from the internal section. The main products of the reaction above this temperature range were C_4 dimers and trimers, i.e. C_8= to C_{12}=.

3. Results and discussion

Fig. 3 illustrates typical X-ray diffractograms corresponding to a zeolite synthesised under the conditions mentioned earlier. The main peak appearing at $2\theta = 22.37$, with an interplanar *d*-spacing $d_{hkl} = 0.397$ nm, in the composite system (zeolite on membrane) corresponds to the highest peak in our reference (i.e. powdered beta-zeolite, from PQ Corp.). The diffraction patterns for the sample with a SiO_2/Al_2O_3 ratio 90, presented two peaks above $2\theta = 21.57$ and 36.3. These peaks could be identified to the intermediate phase present during the zeolite film formation. These peaks are not present for the sample with SiO_2/Al_2O_3 ratio 60, indicating that the film formed on the support has the structure of a beta-zeolite. The scanning electron micrographs of the zeolitic films indicated that, it is constituted by grains in a polycrystalline network. The grains have a rather uniform size, around 0.35 μm, whereas, the zeolite film thickness above 3.5 μm. Fig. 4A is a SEM micrograph which corresponds to a front view of the zeolitic film supported on the

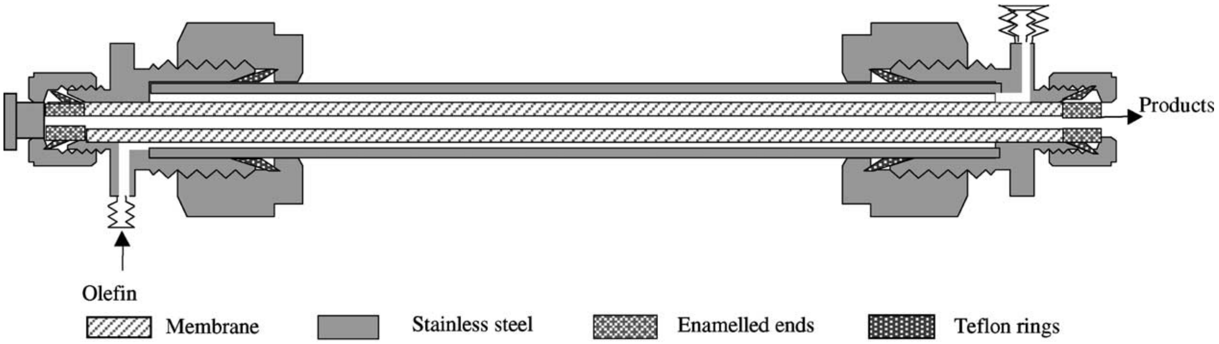


Fig. 2. Catalytic membrane reactor for the oligomerization of olefins and feed trajectories in the membrane reactor.

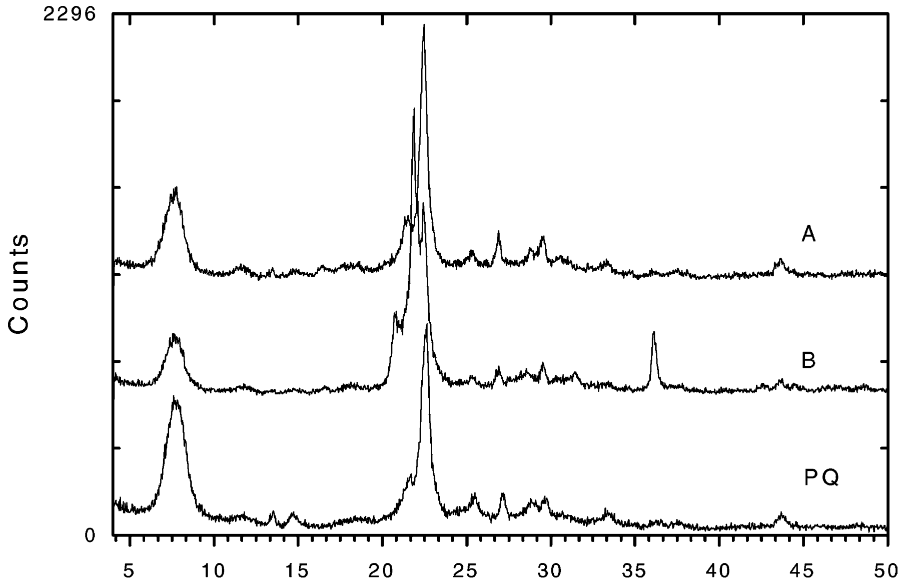


Fig. 3. X-ray diffraction patterns of beta-zeolite film, SiO_2/Al_2O_3 ratios 60 and 90 (A and B), and a reference commercial beta from PQ.

ceramic substrates. Fig. 4B is a side view of the composite material showing the stacking of layers formed by the ceramic membrane at the bottom, then the γ-Al_2O_3 washcoat and the zeolitic phase at the top. The weight of the zeolite film is 118 mg. It was determined by the weight increase of the support after syntheses.

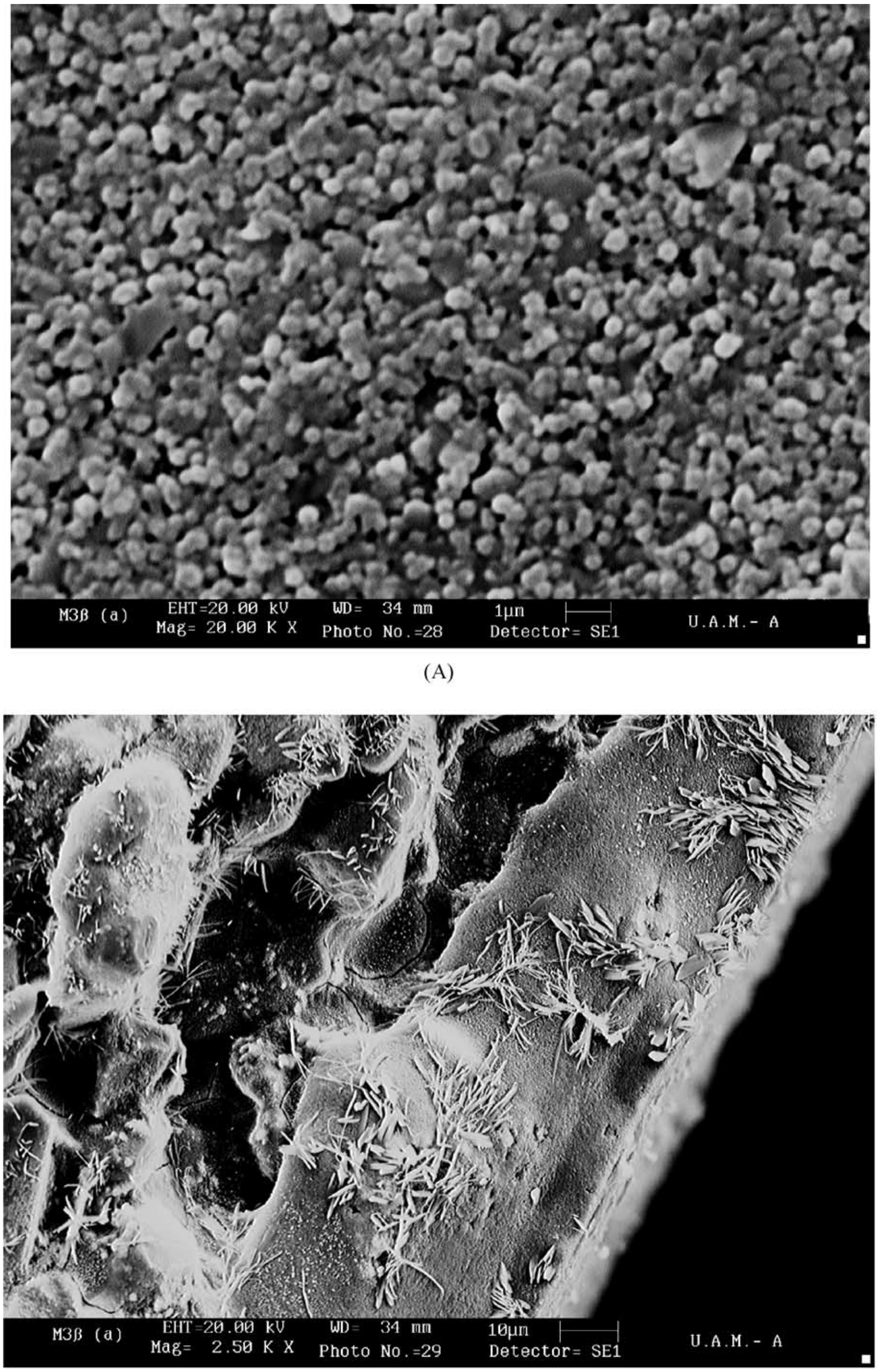
The catalytic properties of the composite system (zeolite films deposited on the ceramic tubular membrane) are described in detail elsewhere [12]. The catalyst surface area and average pore diameter were determined by a volumetric method (BET) and the total acidity using TPD ammonia desorption. The main physical and chemical properties of the membrane are summarised in Table 1.

Concerning the permeation of *i*-butene and butene through beta-zeolite membranes, the rates were determined as shown in Fig. 5 for the zeolite in the sodium form. The permeation rate for the support (41×10^{-7} mol Pa^{-1} m^{-2} s^{-1}), after drying at 423 K over night is about 35 time greater compared to composite membranes and is not presented in Fig. 5. Both species permeance increases with temperature, with a maximum around 500 K. The permeation rates are indicative of a gas diffusion mechanism. The shape of the curve suggests most of the gas diffuses predominantly through the zeolite pores [13].

The performance comparison between the membrane and fixed-bed reactors was carried out at atmospheric pressure, with a temperature of 373 K and a volumetric flow of 30 ml min^{-1}. Under these conditions the WHSVs were similar for both reactors. The initial C_8= production rate was 1.4×10^{-4} mol s^{-1} g^{-1} for the fixed-bed reactor and 1.2×10^{-4} mol s^{-1} g^{-1} for catalytic membrane reactor. Fig. 6A shows, for the membrane reactor, the conversion of the *i*-C_4= was stable during the 168 h reaction period, with constant volumetric flow and temperature, with no apparent decay in the conversion rate. In the fixed-bed reactor the conversion was similar to that achieved in the membrane reactor for the first minutes, but the deactivation rate was more significant. After only 4 h under the stream, the zeolite bed was completed deactivated. In this case, gradual plugging and high-pressure drop were observed. Also, long chain hydrocarbon species were observed on the surface of the zeolite, causing fouling of the pores and blocking active sites and/or pores. Long chain species were not observed in the catalytic membrane. An increase in the overall flow at constant temperature causes a back pressure acting on the membrane. Fig. 6B shows that the conversion is constant as a function of reactant flow. This result suggests a diffusion control regime for the conditions applied, while Fig. 6C shows that the selectivity decreases gradually in the flow range between 20 and 40 ml min^{-1}. Fig. 6D and E present the results for conversion rate and selectivity obtained with a constant volumetric flow of *i*-butene, having a value of 30 ml min^{-1}, in the reaction temperature range from 323 to 423 K. For *i*-C_4=, the increasing temperature favours the conversion to C_8= from about 10% up to approximately 65%. Note that for the same temperature range, the selectivity increases, most notably from approximately from 53 to 63%. For these type of reactions (series reactions), the membrane provides effective short contact times because of the zeolite film thickness being in the range of only a few micrometres. Therefore, the reactants can be forced

Table 1
Main properties of the zeolitic membrane

Pore diameter	1.4 nm
Surface area	473 m^2 g^{-1}
Total acidity	300 μmol g^{-1}
Crystal size	350 nm



(A)

(B)

Fig. 4. SEM front view (A) and side view (B) of the zeolitic film supported on the ceramic membrane.

to pass through the catalytic pores. However, in powder zeolites in a fixed bed, the contact time is more important because the depth of catalyst is of the order of a few millimetres. This advantage allows us to enhance the selectivity towards C_8= dimers, while limiting the fraction of products in the range between C_{12}= and C_{16}= oligomers. The reactivation of the system was studied in separate experiments consisting of suppressing the i-C_4= input through the membrane, then leaving the remaining i-C_4= within the membrane pores for 12 h total deactivation was observed. However, after exposing it to an air flow stream at 723 K, the system was totally reactivated. A second step consisted in substituting the i-C_4= feed by N_2, purging the i-C_4= trapped inside the membrane pores, thus avoiding secondary reactions, which led to maintaining the activity level.

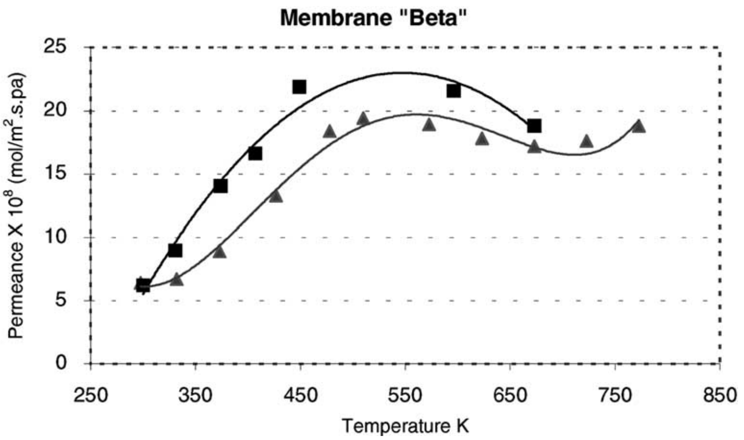


Fig. 5. The *n*-butene and *i*-butene membrane gas permeation.

Finally, the unreacted i-C_4 coming out of the membrane reactor was mostly vented, though, if necessary it could be fed through the system again. Alternatively, it could feed a second membrane reactor for further reaction.

Other reactor configurations for this reaction may include a packed bed inert membrane reactor. This case could also be described as an extractor. In this case, the catalyst bed is packed inside or outside a membrane tube. The i-C_4= may be fed via the reaction side and the products are removed at the permeate side. A second configuration may be a catalytic membrane reactor in which a sweep gas flowing through the permeate side. This could improve the

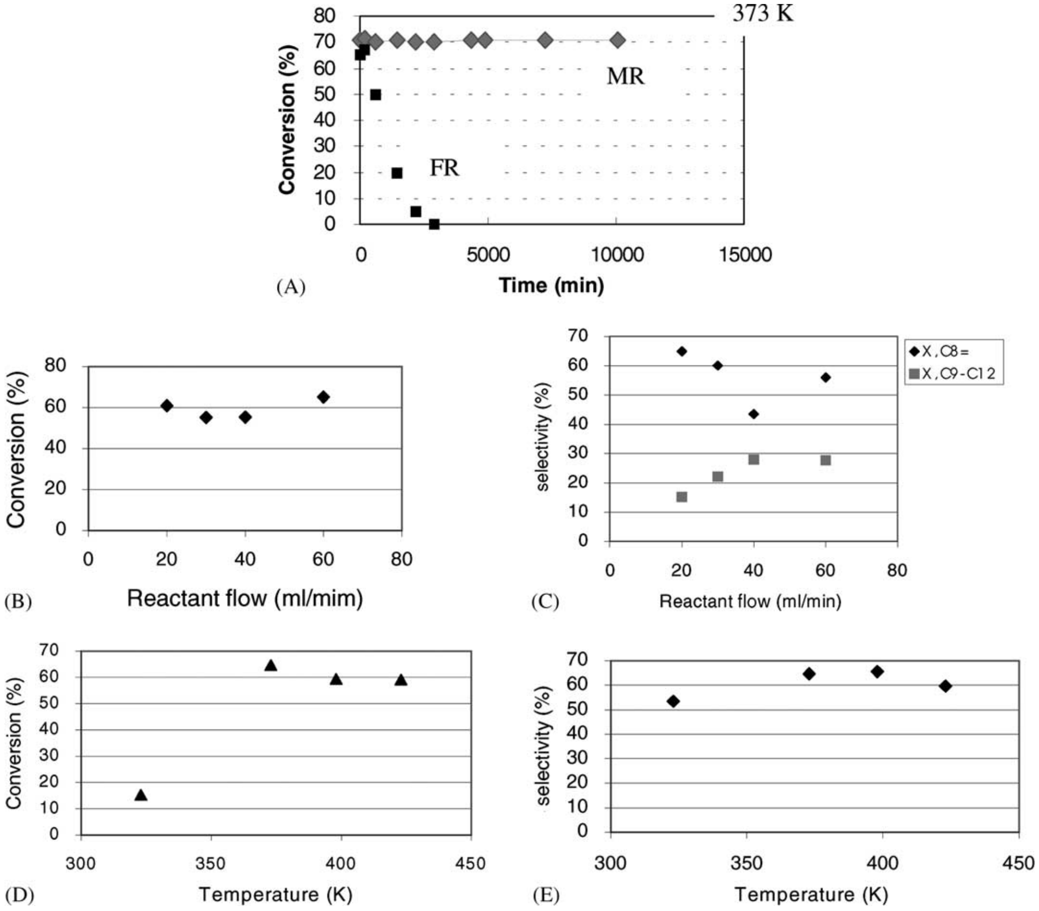


Fig. 6. Comparison between membrane reactor (MR) and fixed-bed reactor (FR) (A).Catalytic properties of the composite system (zeolite film + porous ceramic membrane), within the temperature interval 323–423 K. Selectivity (C and E) and total conversion of i-C_4= (B and D). The conversion and selectivity correspond to the amount of *i*-butene depletion or product formation (C_8= or C_{12}=), respectively.

permeation of products by a lower molar fraction of permeating species.

4. Conclusions

The synthesis of beta-zeolite films on a ceramic membrane support (i.e. γ-Al_2O_3) was carried out as expected. The catalytic properties of these alumina-zeolite composite systems were tested using the *i*-butene oligomerization reaction, which is an acid-promoted reaction. The membrane was used as a thin catalytic layer and the reactants were forced to permeate through it. A good control of the residence time of different species could be obtained; hence, this may increase the selectivity to the intermediate products C_8= by reducing the occurrence of undesirable secondary reactions. The preliminary studies obtained yields for C_8= close to 60% above 370 K.

For this application, the membrane does not provide any separation function, but it is capable of being used as an efficient contact medium, especially one in which short residence time can be controlled.

Compared to a conventional fixed-bed zeolite catalyst, which under similar conditions deactivates easily, the beta membrane reactor shows no deactivation. Also excellent activity is maintained with fast intermediate product removal.

Upon reuse the catalytic membrane was found to be chemically and thermally stable.

Acknowledgements

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