

# Membranes: On the interplay of Diffusion and Permeation and the Technical Consequences

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## 1. Zeolite membranes – state of the development

The first LTA membranes for hydrophilic pervaporations are going to enter the market. However, shape selective gas separation membranes are still in development. Since it is difficult to control simultaneously the individual steps of the *in situ* crystallisation, several techniques have been developed to facilitate nucleation and crystal growth on a ceramic or metal support. During the last few years for the controlled preparation of supported zeolite membranes seeding techniques (secondary growth) have been established. By decoupling the nucleation step (at high supersaturation) from the crystal growth (at low supersaturation), the seeds can grow in low concentrated solutions under suppression of secondary nucleation.

## 2. Mass transport through zeolite membranes

Molecular transport through zeolite membranes can be described by First Fickian Law with  $J = -D \text{ grad}c$ . In this model permeation is controlled by the interplay of diffusion and adsorption. Since diffusion is increased by temperature but the amount of adsorbed is reduced with increasing temperature, the two counter effects lead to a maximum of the flux as a function of temperature.

The transport behaviour of zeolite membranes is influenced by diffusion as follows:

### a) Anisotropic mass transport

If the crystal growth is anisotropic and we have randomly oriented seeds, those crystallites with their fastest growth direction pointing away from the seeded surface will grow more rapidly than crystallites in other orientations. Finally, the crystals with the fastest growth direction perpendicular to the plane of the membrane will dominate. For MFI crystals usually the c-axis is the longest dimension and, consequently, the c-axis is the fastest growth direction. Therefore, most MFI-membranes are c-oriented. From the study of the diffusion anisotropy of the MFI structure it can be expected, that permeation through c-oriented MFI membranes is less favourable [1,2].

### b) Grain boundaries

From prior studies it is known that grain boundaries perpendicular to the permeation flux represent diffusion barriers whereas grain boundaries parallel to the flux direction enhance mass transport but reduce the selectivity. There are no quantitative measurements so far.

## 3. Dehydrogenation of i-butane in a membrane reactor with MFI membrane

An MFI membrane was prepared by seeding supported crystallization. The reasonable  $H_2$ -selectivity of a hydrogen/i-butane mixture with a separation factor (SF)  $SF \approx 70$  in the binary mixture (50%/50%) with i-butane with a permeance of ca.  $1 \text{ m}^3 H_2 / \text{m}^2 \text{ h bar}$  at  $500^\circ\text{C}$  recommends this MFI membrane to support de-hydrogenations in a membrane reactor by selective  $H_2$  removal. It is remarkable, that no degradation during one week of operation at  $500^\circ\text{C}$  including 5 oxidative regenerations to burn off carbonaceous residues was observed. When the hydrogen is removed from the shell side of the reactor by a sweep gas or vacuum, the conversion increased by about 15%. This removal of the hydrogen has two positive effects in comparison with the classical fixed bed: the conversion of the i-butane is increased and, furthermore, the selectivity of the i-butene formation increases since the hydrogenolysis is suppressed. As a result, at the beginning of the reaction the i-butene yield in the membrane reactor is by ca. 1/3 higher as in the classical fixed bed [3]. However, as a result of the hydrogen removal, coking is promoted and after ca. 2 hrs time on stream the olefine yield of the membrane reactor drops under that of the classical fixed bed [4]. After an oxidative regeneration the former data are obtained.

## 4. Separation of xylene isomers by zeolite MFI membrane

The development of high-flux and high-selectivity MFI membranes for the xylene separation shows the importance of a certain channel orientation and the significance of a seeded growth of an oriented particle monolayer [5]. By using a trimer TPAOH as structure-directing agent, the appropriate balance between in-plane and out-of-plane growth could be achieved which results in a b-oriented

layer. Whereas a c-orientation results in an SF  $\approx$  1, b-orientation gives a xylene SF of ca. 500 at 200°C. It is interesting to note that in the latter case SF increases with increasing temperature. This experimental finding is characteristic of the interplay of adsorption and diffusion effects. At low temperatures the zeolite pores are filled to a certain degree and we have a *single file* like behaviour. That is to say that the more mobile p-xylene cannot move faster through the pore network than the less mobile o-xylene. This situation changes dramatically for lower pore filling at higher temperatures. Now the mobile p-xylene can move more or less independently from the presence of o-xylene. The separation was supported by a very small loading (total pressures  $p/p_s$  ca. 0.007). It is hoped to clear this experimental finding by diffusion studies.

## 5. Semi-technical application of zeolite LTA membranes in water/alcohol pervaporation pilot plants

Commercial zeolite membranes distributed by the Japanese company Mitsui [6] and most recently by the European alliance between Smart and Inocermic [7] consist of a hydrophilic LTA zeolite layer on a ceramic tubular support and are extremely powerful in the separation of water from organic solutions by pervaporation. Mitsui has recently installed pervaporation units in Brazil (3.000 l/d) and India (30.000 l/d) at an operation temperature of 130°C for the dehydration of bio ethanol using LTA membranes. The ethanol concentration in the feed is 93%, in the retentate it is 99.7%. In laboratory tests at 75°C the membrane performance for a 90% ethanol/10% water test mixture was determined to be 8 kg H<sub>2</sub>O/m<sup>2</sup>h with a separation factor SF<sub>H<sub>2</sub>O/ethanol</sub>  $\approx$  10.000 [40]. In alliance between Smart Chemicals Development and Inocermic GmbH LTA membranes are produced in a half-industrial scale in Germany. The membrane layer is inside  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> four-channel-supports thus protected against mechanical damage. Organic solutions can be dried to water levels down to 0.1% by pervaporation. A first plant for ethanol dehydration was realised in the UK, a second one with 100 m<sup>2</sup> membrane area is in construction.

## 6. Outlook

Several shape selective gas permeations are in the pilot phase (e.g. [8]). For a successful process development, the reliability and performance of the corresponding membranes must be improved. For studying the influence of grain boundaries and of the diffusion anisotropy, MFI model membranes have to be developed which allow the study of the mass transport behaviour of the membrane. For this reason selected well-characterized zeolite crystals shall be embedded gas-tight in a metal matrix [9-11]. The preparation steps are as follows: (i) Synthesis of a zeolite powder with a crystal size  $\geq$  20  $\mu$ m, (ii) isolation and orientation of the crystals on an electrically conducting support (e.g. Au sputtered ceramic or sintered metals), (iii) galvanic Ni or Ag deposition starting at the surface of the support. The zeolite crystals are insulators and remain, therefore, uncoated by the metal. These model membranes will allow the study of the anisotropic diffusion behaviour and of the influence of structure imperfections on molecular mass transport, thus supporting the development of high performance membranes for the industrial praxis.

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