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Permeation and separation behaviour of a silicalite-1 membrane

F. Kapteijn *, W.J.W. Bakker, J. van de Graaf, G. Zheng, J. Poppe, J.A. Moulijn

Chemical Engineering Department, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Abstract

The permeation behaviour of single component and binary mixtures of hydrogen, n-butane and carbon dioxide through a silicalite-1 membrane as a function of temperature (steady state) and time (transient) are presented. Multicomponent permeation can be well described by the Generalized Maxwell–Stefan equations.

1. Introduction

In the process and chemical industry, in the area of catalytic conversions, one is faced with several aspects that engineers have to cope with in the design and control of catalytic reactor systems. Several processes are limited by thermodynamics, like ammonia and methanol synthesis, water-gas shift, dehydrogenation and isomerization. In spite of high catalytic activities one cannot beat the thermodynamic limits per single pass through the reactor. Other processes are highly exothermal, like oxidation and hydrogenation, and low feed concentrations and good heat transfer measures have to be used to avoid hot spots in the catalyst bed and runaways. Some processes suffer from low selectivities due to the occurrence of consecutive or parallel reactions, like in selective oxidation and hydrogenation reactions. Since, in general, chemical transformations are accompanied by heat effects, good measures have to be taken to transfer heat to or from the catalyst bed. Sometimes in plants chemical products are formed by endothermal reactions, while they are subsequently used in exothermal conversions, which means that large amounts of sensible heat are pumped around.

The application of an emerging new type of catalytic reactor, the catalytic membrane reactor, offers in principle a way out of these dilemmas engineers are confronted with. Fig. 1 indicates schematically some configurations that can be applied to the above-mentioned cases. In reactor I products are selectively removed from the reaction mixture, thus allowing higher single pass conversions by 'shifting' the equilibrium and higher selectivities by the removal of the desired, valua-

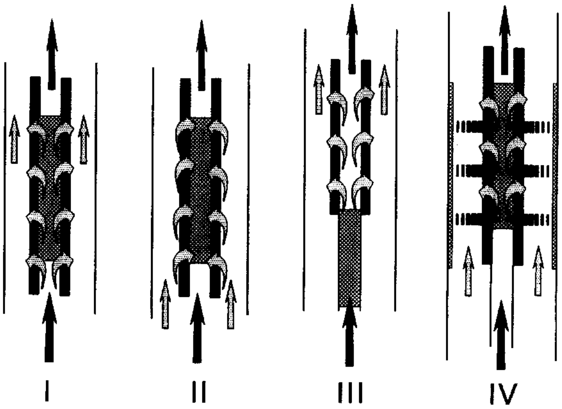

Fig. 1. Configurations of hybrid catalytic membrane reactors.

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* Corresponding author.

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ble intermediate products. Reactor II can handle reactions in which for reasons of exothermicity or reaction selectivity the reactants cannot be fed to the catalyst bed completely mixed. Here, a selective membrane controls the feed rate of one of the components to the reaction mixture over the whole length of the reactor. Configuration III allows the direct separation of the reaction mixture in the reactor environment, without the need of heat exchange and coupled unit operations, lowering the size of the equipment. Reactor IV is an example of reaction coupling. In the inner catalyst an endothermal reaction takes place, e.g. the production of hydrogen, which permeates selectively through the membrane to the outer catalyst where it reacts exothermally with the reactant fed through the annular space, e.g. an oxidation reaction. The heat produced by this reaction is transferred through the membrane by conduction and provides the endothermal reaction with heat. This idea might be applied in fuel cells where steam reforming can be combined with the oxidation of hydrogen to produce electricity. In all these cases it can be envisaged that the membrane itself is the catalytic medium or is coated with catalytic material.

Characteristic features of these membranes are that they need to be perm-selective and thermostable and allow fluxes that are compatible with the catalytic conversion rates.

- Thermostability is only achieved with inorganic materials, including carbon, since polymeric membranes are limited to temperatures of 400–500 K.
- Perm-selectivity with inorganic materials is in general obtained when they are porous, having pore sizes below 10 nm down to those of molecular dimensions (zeolites). In these regimes Knudsen diffusion, surface diffusion and zeolitic diffusion takes place which allows a selective transport of components.

Knudsen diffusivity yields, at maximum, separation selectivities proportional to the square root of the ratio of the molar masses of two components. This limits the applicability since isomers cannot be separated and the selectivity of components of nearly equal masses is small. The application of zeolites as membrane material looks quite promising, since molecules of sizes larger than that of the zeolite pores are not expected to permeate (molecular sieving), while those molecules that enter the pore system experience permanently the force field of the zeolitic structure, which might be quite different for various components and zeolitic materials. Moreover, zeolites can be made catalytically active themselves.

Unfortunately, however, hardly any data is available at present on the permeation of components through zeolitic membranes, the fluxes and selectivities in mixtures and the mechanisms of transport. This is mainly due to the fact that only recently zeolitic membranes, based on silicalite-1 and ZSM-5, were synthesised successfully and were proven to work [1,2].

In this paper we report on some permeation results obtained with a silicalite-1 membrane which have relevance to catalytic applications and are characteristic examples of the behaviour of this material. An interpretation and modeling will be given of unary and binary permeation, which is the first step that has to be understood before a successful application in catalytic reactors is possible.

2. Experimental

The asymmetric membrane (diameter 3 cm) consists of a continuous layer (40 μm) of intergrown silicalite-1 crystals on top of a sintered stainless steel support [1,3,4]. Permeation measurements were carried out with a Wicke–Kallenbach diffusion cell, where at one side of the membrane the gas mixture under investigation flows, while at the other side helium is used as sweep gas to remove the permeated components. The partial pressure (below 1 bar) was varied by dilution with helium. All reported experiments were carried out at 1 bar pressure at both sides of the membrane and at temperatures between 300 and 673 K. The gases used are hydrogen, carbon dioxide and n-butane and mixtures of the latter two with hydrogen. This gives an indication of some phenomena that will occur during (de)-hydrogenation reactions of C_4 molecules and in the water-gas shift reaction.

Adsorption measurements were carried out in a conventional volumetric apparatus at 300 K, using silicalite-1 prepared under similar conditions as the membrane.

3. Results

Fig. 2a presents the development of single component permeation fluxes of hydrogen and n-butane at room temperature at 0.95 and 0.05 bar partial pressure, respectively, as a function of time upon switching the feed gas from helium to the feed mixture. Fig. 2b contains the results for a 95:5 mixture of these components, while Fig. 2c shows the adsorption data of these components as a function of their partial pressure at room temperature. In the unary experiments the steady state hydrogen permeation flux is about 20 times larger than that of n-butane at the applied conditions, whereas in the binary system it has dropped by a factor of more than a hundred while the n-butane flux remained unaltered. In the latter experiment the hydrogen permeates first and appears at the same time as in the unary experiment, but then drops quickly and reaches its final, low value as the n-butane appears. A n-butane selectivity of more than 100 over hydrogen is found. Similar trends have been found for methane/n-butane mixtures. From the adsorption data it is clear that n-butane has already a high fractional occupancy at 5 kPa pressure, while hydrogen only adsorbs weakly. Apparently, adsorption properties contribute appreciably to the permeation behaviour of mixtures.

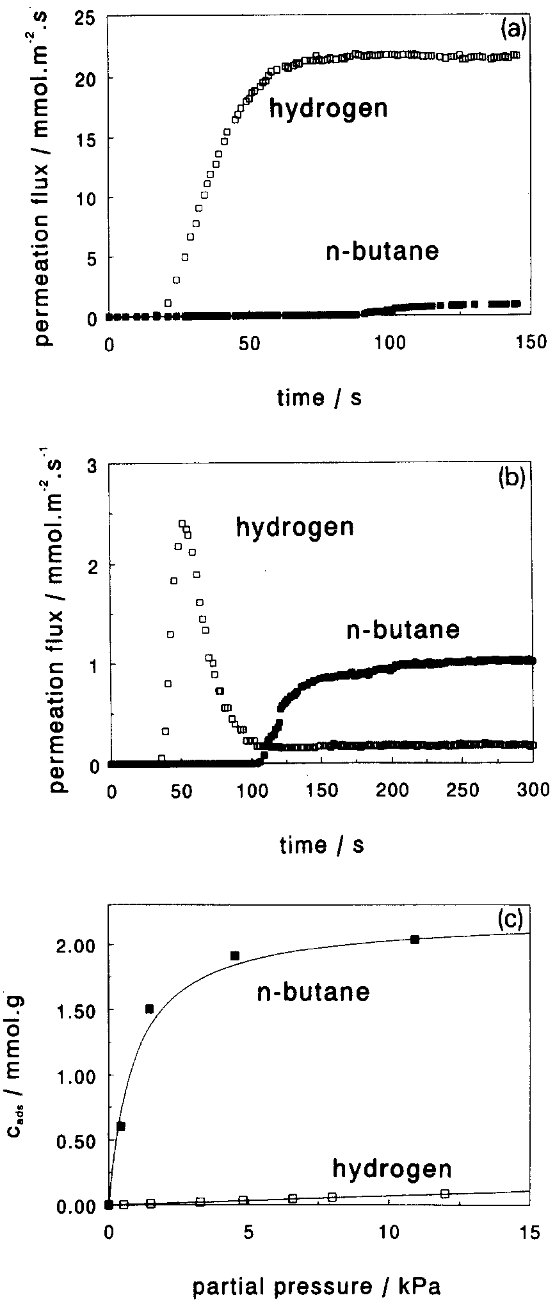


Fig. 2. (a) Unary permeation flux as a function of time for hydrogen (95 kPa) and n-butane (5 kPa) at 300 K, adapted from Ref. [4]. (b) Transient permeation flux development for a mixture of hydrogen (95 kPa) and n-butane (5 kPa) at 300 K, adapted from Ref. [4]. (c) Adsorption isotherms of hydrogen and n-butane on silicalite-1 at 300 K.

The same picture arises for a 1:1 mixture of hydrogen and carbon dioxide (Fig. 3). While in the unary permeation runs hydrogen at 0.5 bar is somewhat slower than carbon dioxide, in the mixture carbon dioxide permeates by a factor of 12 faster than hydrogen. Also in this case it was observed that carbon dioxide adsorbs stronger than hydrogen, although less extreme than for n-butane.

The temperature dependency of the permeation of binary mixtures (1:1) is presented in Fig. 4

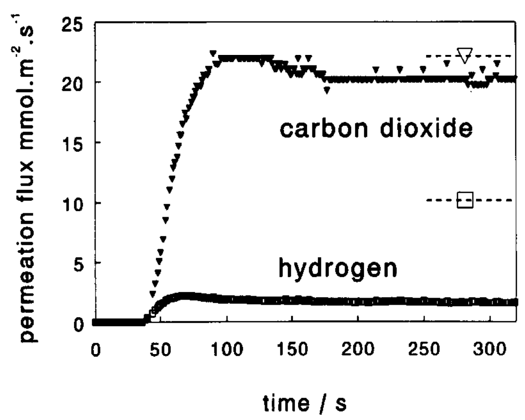
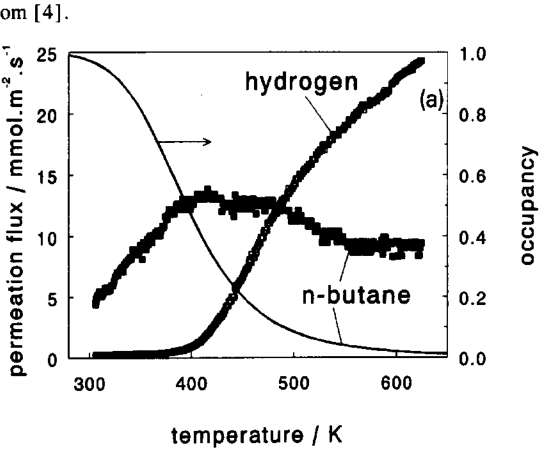


Fig. 3. Development of permeation fluxes of a mixture of H_2 and CO_2 (both 50 kPa) at 300 K. Indicated are unary levels, adapted from [4].



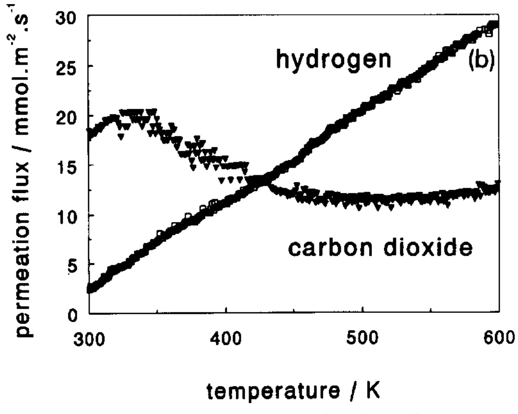


Fig. 4. (a) Permeation fluxes as a function of temperature for a mixture of hydrogen and n-butane (both 50 kPa), adapted from Refs. [4,6]. (b) Permeation fluxes as a function of temperature for a hydrogen/carbon dioxide mixture (both 50 kPa), adapted from Ref. [4].

(Fig. 4a for hydrogen/n-butane and Fig. 4b for hydrogen/carbon dioxide). At room temperature n-butane permeates preferentially and hydrogen hardly permeates. At increasing temperatures the n-butane flux increases, passes through a maximum at about 430 K, decreases and levels off around 600 K The hydrogen flux starts to increase noticeably above 400 K when the n-butane flux has reached its highest value. At 480 K it equals that of n-butane and at 600 K it has become about 2.5 times as high. In the case of the hydrogen/carbon dioxide mixture a similar trend is observed, on the understanding that carbon dioxide reaches its maximum already at 330 K and hydrogen exhibits only a nearly linear increase as a function of temperature. Also in this case the perm-selectivity reverses as a function of temperature. At low temperature the stronger adsorbing component permeates preferentially, while at high temperature hydrogen does, so an inversion of the selectivity takes place. It can be noted that for n-butane the results, at 0.5 bar partial pressure, were identical in the case of a unary experiment or a in binary mixture with methane.

4. Discussion

The permeation results indicate that through silicalite-1 membranes high fluxes are possible, depending on temperature and partial pressures of the components involved. Of course the membrane thickness itself is also a controlling factor.

The presence of a second component that adsorbs at the zeolite under the applied conditions affects the flux of the first component and can nearly completely suppress it. This behaviour in binary permeation is strongly determined by the competitive adsorption of the components. These results clearly demonstrate that single component permeation data cannot be applied as such to predict the selectivities of components in the permeation of mixtures.

The binary data as a function of the temperature show that permeation selectivities vary considerably and can even reverse. So, temperature is an important control parameter in optimizing separation performance.

The modelling of these unary and binary permeation results is based on the Generalized Maxwell–Stefan (GMS) equations, adapted for zeolitic diffusion by Krishna [5]. In this model the driving force for movement of a species is the gradient of its thermodynamic potential across the membrane, which is counter-balanced by the friction this species experiences, due to its movement, with the zeolite wall ('vacancies') and with other species by counter-exchange.

Based on Langmuir adsorption behaviour, which often describes adsorption in silicalite-1 well, given by Eq. (1), this GMS approach results in Eq. (2) for unary permeation. In this approach adsorption equilibrium is assumed at both sides of the membrane, while the permeation through the membrane is the rate determining process.

$$\theta_i = \frac{c_i}{c_i^{\mathrm{sat}}} = \frac{K_i p_i}{1 + \sum_{j=1}^{n} K_j p_j} \qquad (1)$$

$$N_1 = -c_1^{\mathrm{sat}} \rho \epsilon \frac{D_1}{1-\theta_1} \nabla\theta_1 = c_1^{\mathrm{sat}} \rho \epsilon D_1 \nabla \ln(1-\theta_1) \qquad (2)$$

where c_i^{sat} represents the saturation concentration of component i in the zeolite (mol/kg), ρ the density of the zeolite (1800 kg/m^3), ϵ the porosity of the support layer (0.4) which is partially impermeable, and θ_i the fractional occupancy by component i, given by Eq. (1). For a binary system, assuming 'single file diffusion' without counter-exchange in the zeolite [5], Eq. (3) can be derived which indicates the mutual influence of the species on each other fluxes.

$$N_1 = -\rho \epsilon c_1^{\mathrm{sat}} \frac{D_1}{(1-\theta_1-\theta_2)} \{(1-\theta_2)\nabla\theta_1 + \theta_1 \nabla\theta_2\}$$

$$N_2 = -\rho \epsilon c_2^{\mathrm{sat}} \frac{D_2}{(1-\theta_1-\theta_2)} \{(1-\theta_1)\nabla\theta_2 + \theta_2 \nabla\theta_1\} \qquad (3)$$

Both flux expressions contain the so-called Maxwell–Stefan diffusivity D_i (m^2/s). Here, 'single file' diffusion indicates that molecules cannot pass each other in the zeolite channels, resulting in the absence of a mutual interaction term represented by D_{ij}. Of course, in the two-dimensional pore network of silicalite-1 it is possible for molecules to pass each other.

The single component permeation of C_1–C_4 alkanes could well be described by Eq. (2), including the temperature dependent n-butane permeation flux in Fig. 4a [6,7]. The occupancies at both sides of the membrane were calculated from measured adsorption isotherms. Subsequently, application of Eq. (2) yields values of the Maxwell–Stefan diffusivity. At high temperatures or at low occupancies this relation can be simplified to Eq. (4) where the flux has become proportional to the partial pressure gradient, valid in the so-called Henry region.

$$N_1 = -c_1^{\mathrm{sat}} K_1 \rho \epsilon D_1 \nabla p_1 \qquad (4)$$

A Fickian diffusion description failed, due to the strongly varying values of the Fickian diffusivity, especially at high occupancies [6,7]. This is clear from the term $D_1/(1-\theta_1)$ in Eq. (2) which, in fact, represents the Fickian diffusivity. The values obtained for the MS diffusivity compare excellently with the transport diffusivities obtained by other techniques [6,7].

Binary permeation data for ethane/ethene and propane/propene mixtures could be well described by Eqs. (3), using the diffusivity values obtained by unary permeation experiments. To this purpose the single component adsorption data were used to calculate the multicomponent occupancies. Diffusivities can be calculated from the binary experimental data by integration of the one-dimensional differential Eqs. (3). Expressions as in Eq. (5) are obtained.

$$C = -\nabla \ln(1-\theta_t) = \frac{\ln\left(\frac{1-\theta_{1\mathrm{f}}-\theta_{2\mathrm{f}}}{1-\theta_{1\mathrm{p}}-\theta_{2\mathrm{p}}}\right)}{d_{\mathrm{m}}}$$

$$= A_1 + A_2 = \frac{-N_1}{c_1^{\mathrm{sat}} \rho \epsilon D_1} + \frac{-N_2}{c_2^{\mathrm{sat}} \rho \epsilon D_2}$$

$$A_1 = \frac{-N_1}{c_1^{\mathrm{sat}} \rho \epsilon D_1} = C \cdot \left\{ \frac{\theta_{1\mathrm{p}} - \theta_{1\mathrm{f}} \cdot \exp(-C \cdot d_{\mathrm{m}})}{1 - \exp(-C \cdot d_{\mathrm{m}})} \right\} \tag{5}$$

Here the subscripts f, p and t refer to the feed, permeate and total occupancies, d_{m} is the membrane thickness.

These results demonstrate the applicability of the GMS theory to describe the permeation through silicalite membranes. This can easily be extended to multicomponent systems [5]. The single file diffusion model has the advantage that it contains only the diffusivities of the individual components, which can be determined by unary permeation experiments. To apply the GMS equations to multicomponent permeation further only good data or good descriptions for the multicomponent adsorption is needed. The multicomponent Langmuir adsorption model, Eq. (1), and the Ideal Adsorbed Solution (IAS) model have been shown to give good results.

5. Conclusions

Unary and binary permeation experiments through a silicalite-1 membrane have demonstrated that the permeation flux and separation selectivity are governed by the temperature, partial pressure and adsorption behaviour of the participating components. Strongly adsorbing molecules can completely block the permeation of another, weakly adsorbing one. The Generalized Maxwell–Stefan equations provide a good basis for the description of the multicomponent permeation behaviour with this type of membrane.

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