The Delft silicalite-1 membrane: peculiar permeation and counter-intuitive separation phenomena

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Abstract

An overview is given of the permeation and separation phenomena obtained with a silicalite-1 membrane developed at the TUDelft in the group of Van Bekkum. Peculiar permeation characteristics are observed for single component permeation where the flux passes through a maximum and a minimum as a function of the temperature. Moreover, the silicalite-1 framework is rather flexible that it allows permeation of branched and dibranched molecules. In the separation of mixtures the size of a molecule is only important if it approaches that of the pore. For molecules that easily fit into the pores adsorption is the dominant factor in separation: weakly adsorbing components are rejected by strongly adsorbing species, giving rise to sometimes high separation factors. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolites can be described as porous crystalline materials. This implies a rather regular structure of the matrix with uniform pore sizes. Application for size and shape selective chemical and physical processes is therefore quite obvious and tempting. Zeolite films would be ideal as permselective layers in membrane separation in view of the expected molecular sieving: too large molecules are rejected and absolute separations could be possible. Moreover, separations at elevated temperatures, where polymeric materials fail, become possible with zeolites.

As is well-known to the experienced experimentalist zeolite synthesis is still a rather empirical activity in which a lot of chemical feeling and experience is needed, so synthesis of zeolite membranes is not quite obvious. Two counteracting requirements are asked for, a thin layer, to achieve sufficiently high fluxes, and a defect free layer, to achieve high separation efficiencies. Layer thicknesses should preferably be in the order of less than one micrometer, so a support is needed to give strength to the zeolite layer. Porous ceramic and stainless steel supports can be used for high temperature applications.

The group of Van Bekkum/Jansen with their extensive experience in zeolite synthesis and thin zeolite coatings on smooth silicon single crystal surfaces was one of the first to report in

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the open literature a supported zeolite layer with real membrane properties [1–3]. Sintered stainless steel with a toplayer of fine sintered stainless steel wool was used as a support. A continuous layer of intergrown silicalite-1 crystals constituted the permselective membrane layer, firmly bonded to the stainless steel. Moreover, this asymmetric membrane could be reproduced. The stainless steel has the advantage over the nowadays frequently used porous α-alumina that mounting in installations at elevated temperatures is in principle much easier.

In this overview, we summarize the exciting permeation and separation results that have been obtained with this membrane [4–11].

2. Experimental

The present day used membrane is in fact a UHV flange adapted for mounting in the permeation cell. The flange contains the membrane in its centre. This is a layer of silicalite-1 grown on an asymmetric sintered stainless steel support with a coarse support layer and a fine top layer of stainless steel wool Fig. 1. Two methods are being used for determination of the permeation characteristics of the membrane: the batch method and the Wicke–Kallenbach (WK) method [12] Fig. 2. In the batch method a calibrated volume is filled with a pure compo-

Fig. 2. Experimental methods to determine permeation through membranes: (a) Batch method; (b) Wicke–Kallenbach (WK) method.

nent up to a pressure of 300 kPa. The gases are allowed to permeate through the membrane while at the other side, the permeate side 'vacuum' is drawn by means of a membrane pump (100 Pa). The pressure is recorded as a function of time. This yields the permeation flux of that component. In the WK method at one side of the membrane, the feed side, a pure gas or a mixture flows over the membrane while at the other side, the permeate side, a sweep gas is used, generally helium or argon, which sweeps away the permeated molecules. Both the feed and permeate mixtures are analysed by a mass spectrometer or a GC. Due to the asymmetry of the membrane the silicalite-1 layer can either face the feed or the permeate side.

The batch method yields directly single component permeation data over a pressure range. It is less suited for mixtures since the composition of a mixture in the volume may change as a function of time. The WK method is suited for both single component as well as for mixture permeation due to the continuous supply of the feed mixture. Of course, the presence of the sweep gas, which is absent in the batch method, may affect the permeation characteristics.

3. Results and interpretation

Directly after membrane synthesis the tetrapropylammonium template is still present and has to be removed by calcination in air. This can be used to check the leak tightness of the membrane, which is an important parameter for
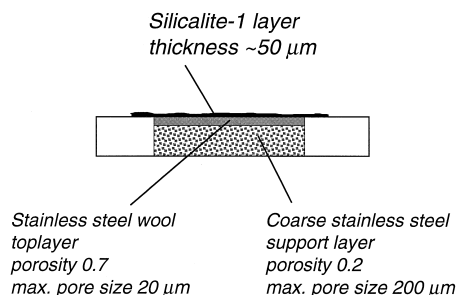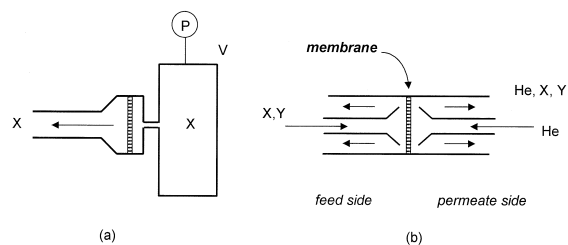

Fig. 1. Schematic representation of the membrane disk with the zeolite toplayer and the composite support consisting of a thin layer of metal wool and a macroporous layer of sintered stainless steel particles.

the separation performance. Krypton is added to the calcination air and its permeation in the WK cell is followed as a function of the temperature, which is slowly increased (1 K/min) to avoid damage to the membrane. The membrane consists of a layer of ~ 50 μm thickness of intergrown crystals. A typical breakthrough of krypton is shown in Fig. 3. Initially, the membrane is impermeable for krypton, but around 625 K some permeation is visible, but the bulk permeation, corresponding with the template removal is around 650 K. The minor permeation at lower temperatures may indicate the presence of some defects in the membrane, but, in view of all results gathered up to now, these must be small and of molecular sizes, although somewhat larger than the silicalite-1 pores (~ 0.51–0.54 nm).

Single component permeation measured in the WK cell are presented in Fig. 4 for the *n*-alkanes up to C4 as a function of the temperature. Here, the flux is not reported, but the permeance, which is the flux divided by the partial pressure difference of that component over the membrane. This is to account for the fact that in some cases the fluxes are that high that this difference may change considerably over the temperature range or to account for back-permeation of the sweep gas, which also causes concentration changes. Moreover, this makes the behaviour of different components more comparable. One can observe a general trend that a component permeance passes
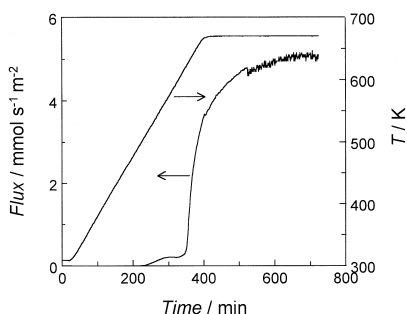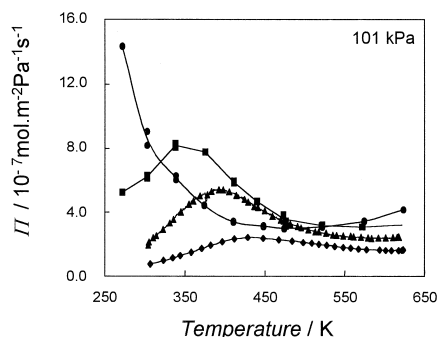

Fig. 4. Permeances Π of different hydrocarbons as a function of temperature by WK method, after Ref. [11]. Feed: 101 kPa of the pure component; Sweep gas: 101 kPa helium. ($\bullet$) methane, ($\blacksquare$) ethane, ($\blacktriangle$) propane, ($\blacklozenge$) *n*-butane.

through a maximum at lower temperature and rises again at higher temperatures. The position of these maximum and minimum shifts to higher temperatures with increasing carbon number. Adsorption phenomena determine this maximum. At low temperatures the silicalite-1 is nearly completely filled with the permeating component and the diffusion of the adsorbed component is controlling the permeation. With increasing temperature this activated diffusion increases leading to higher permeances. At the same time, however, the amount adsorbed will decrease due to the higher temperature. At a certain temperature the amount adsorbed decreases faster than the diffusivity increases and the permeance passes through a maximum and decreases at higher temperatures. The increase at still higher temperatures is explained in terms of a type of activated Knudsen type diffusion [4,13], although this is subject to ongoing discussions.

In Fig. 5, the results of three different ways of measuring are shown and it is obvious that the position of the maximum is method dependent! This makes comparison of results of different studies not easy. In Fig. 5, the WK cell was used with the silicalite-1 layer facing the feed side (C) or facing the permeate side (B), and compared with the batch method where vacuum was drawn (A). The latter yielded the maximum at the lowest temperature and the
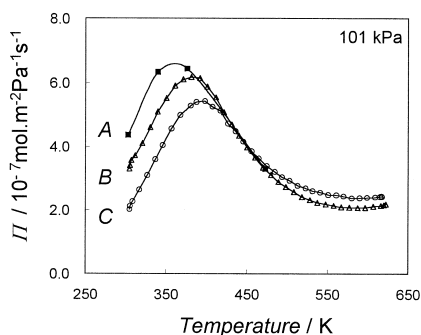

Fig. 3. Breakthrough flux of krypton during calcination of the synthesised silicalite-1 membrane in air in the WK cell.

Fig. 5. Permeance Π of propane (feed 101 kPa propane) as a function of temperature for different experimental conditions, after Ref. [11]. (○) WK method, membrane on feed side (sweep 101 kPa helium); (△) WK method, membrane on permeate side (sweep 101 kPa helium); (■) Batch method, membrane on feed side (permeate side vacuum).

highest permeance. Concentration gradients over the stainless steel layers due to the limited molecular diffusion have to be accounted for and cannot be neglected. In fact, the membrane is exposed to different local concentrations, which explains the different results. If one properly accounts for the diffusion phenomena, which is in principle straightforward, then similar diffusivity values can be obtained for the three methods [11].

The effect of the experimental method is further explored in Fig. 6 for an isothermal permeation of ethane at 473 K in the batch method and the WK method. In the latter method two sweep gases are used: helium and argon. The temperature of 473 K was chosen to allow

back permeation of the sweep gas, which does not occur at low temperatures due to the blocking effect of the alkane (see below). In addition, adsorption of argon in the silicalite-1 was avoided. Corrections were made for the partial pressure differences over the membrane by representing the data in terms of permeances. For the batch method the highest values are obtained with only a slight decrease due to still some adsorption phenomena at higher pressures. The constant permeance indicates that the membrane has no large defects. Since no other component is present these represent the true single component permeation data. The permeances measured by the WK method with helium or argon as sweep gas are lower, although at higher ethane pressures they seem to converge. Analysis of the feed side ('retentate') showed that helium and argon are able to permeate in opposite direction, especially at lower pressures. Apparently, this back permeation hampers that of ethane. This hampering is molecule dependent. So it is very important to be able to describe this phenomenon before one can interpret quantitatively permeation data from the WK method in terms of diffusivities.

The data presented below are further all recorded using the WK method since they comprise mixtures.

In Fig. 7, unary and mixture data are given for the transient permeation of *n*-butane and hydrogen. The membrane is in a step change
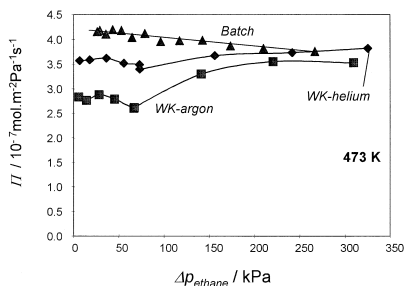

Fig. 6. Effect of the sweep gas on the permeation behavior of ethane at 473 K using the WK method, after Ref. [11]. Permeate pressure 101 kPa, sweep gas: (■) helium, (◆) argon. Included are also data of the batch method (▲) with vacuum at permeate side.
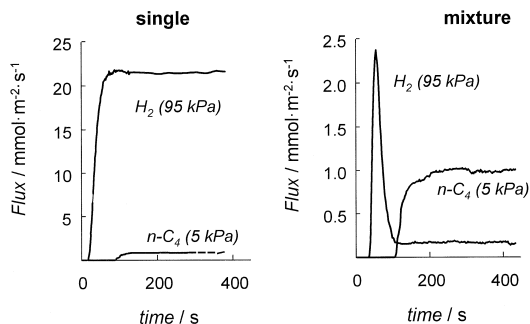

Fig. 7. Transient single component (left) and mixture (right) permeation fluxes of *n*-butane (5 kPa) and hydrogen (95 kPa) at 300 K upon a concentration step from helium to the feed mixture, after Ref. [5].

exposed to a feed mixture and the transient permeation of these components is followed as a function of time. As single component hydrogen permeates much faster than the *n*-butane, but in the mixture the latter goes faster, even in spite of its lower concentration. It is not affected by the presence of hydrogen, while hydrogen is affected by *n*-butane. In the initial period one observes a fast permeation of hydrogen which seems to enter quickly into the silicalite, but after some time the pores are completely blocked by the strongly adsorbing *n*-butane. This results in a selectivity of over 100 for *n*-butane. Steady state data for a 1:1 mixture are given in Fig. 8 as a function of temperature. One even sees here a reversal of the separation behaviour. At high temperatures, where *n*-butane does not adsorb so strongly any more, hydrogen has a chance to permeate through the membrane. Thus, temperature can be used to control the selectivity. Although hydrogen permeates faster at high temperatures the membrane does not reach the Knudsen selectivity at these conditions.

Apart from temperature, composition also determines strongly the permeation/separation behaviour. Fig. 9 exemplifies this for a methane/ethane mixture. As a single component methane permeates faster than ethane (solid lines), but in a mixture (dashed lines) ethane is the fastest and hardly affected by the presence

Fig. 9. Permeation fluxes of ethane and methane at 300 K as a function of the partial pressure, after Refs. [22,23]. Solid lines single component (diluted with helium to 100 kPa total pressure), dashed curves mixture data (total pressure 100 kPa).

of methane. On the other hand methane is strongly hindered by the presence of ethane. Methane is less hindered only at low concentrations of ethane. Also these phenomena stem from the competitive adsorption of both components, ethane adsorbing stronger than methane. It stresses the importance to have good adsorption data of these components and, may be even more important for modeling purposes, to have good models to describe multicomponent adsorption.

Up to now molecules that fit into the pores of the silicalite-1 have been considered. Branched molecules are bulkier and even exceed the size of the pores. Figs. 10 and 11 give data of the permeation of *n*-butane and *i*-butane and *neo*-pentane. As single component *i*-butane has difficulties in permeating through the membrane
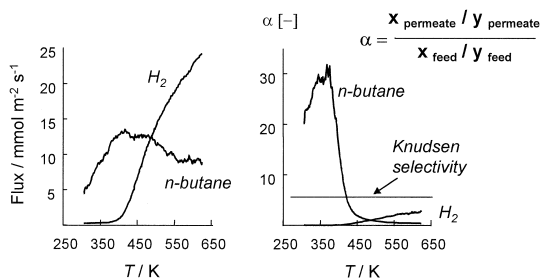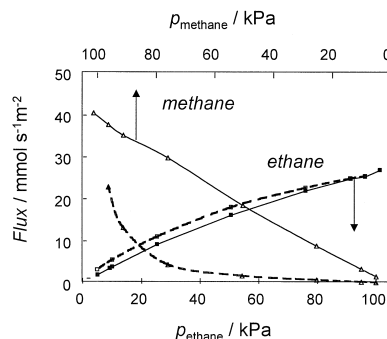

Fig. 8. Steady state permeation fluxes of a mixture of *n*-butane (50 kPa) and hydrogen (50 kPa) as a function of temperature (left), and the corresponding permeation selectivities (right) with respect to *n*-butane and with respect to hydrogen (lower curve). Indicated is the Knudsen separation selectivity level with respect to hydrogen.
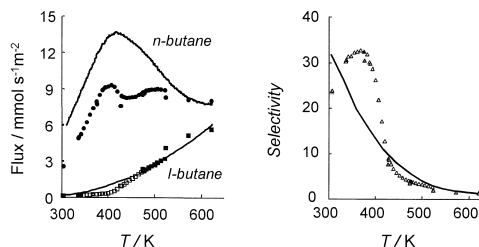

Fig. 10. Permeation fluxes of *n*-butane and *i*-butane as a function of temperature at 50 kPa partial pressure (left) and the corresponding permeation selectivity with respect to *n*-butane (right), after Refs. [22–24]. Solid curve unary data (diluted with helium), symbols for 1:1 mixture.

and has no maximum permeation as the normal alkanes have. It is merely an activated permeation. The interpretation is that the heat of adsorption of *i*-butane is lower than the activation energy for diffusion, so their combined effect does not result in a maximum. This in contrast with the normal alkanes where the opposite holds. In a mixture the branched molecules are even more hindered due to the presence of the other component *n*-butane. Only when the latter passes through its maximum, i.e., where its occupancy in the zeolite decreases appreciably, then the other molecules are able to permeate. Depending on the concentrations large values for the *n*-butane selectivity can be found. It is quite clear from Fig. 10 that the mixture data give a different selectivity behaviour as a function of the temperature than what is predicted on the basis of the single component data. This stresses the need to investigate mixtures and not to rely blindly on single component data. The fact that the branched molecules can permeate indicates that the framework of silicalite-1 is not rigid, especially at higher temperatures. This flexibility allows the permeation of bulky molecules.

The last example deals with the polar character of both the silicalite-1 and the molecules under investigation. Fig. 12 shows in a pervaporation experiment the preferential permeation of ethanol in an ethanol/water mixture. Due to the hydrophobic nature of the silicalite-1 the less hydrophilic molecule is able to permeate faster, although in this case the selectivity is strongly

Fig. 12. Pervaporation fluxes of water and ethanol at 300 K as a function of the mol fraction ethanol in the liquid mixture (left axis) and the corresponding separation selectivity for ethanol (right axis).

concentration dependent. Selectivities can even be improved by modifying the silicalite-1 surface, making it more hydrophobic.

4. General conclusions

The permeation and separation behaviour of the silicalite-1 membrane was not predicted a priori. It was expected that for example in the hydrogen/*n*-butane mixture the smaller hydrogen would permeate much faster than the bigger and longer *n*-butane molecule. Experiments demonstrated just the opposite and many experiments were performed to check this counter-intuitive behaviour. A posteriori this could be simply explained on the basis of adsorption phenomena. More of these surprising phenomena have been described above. They can be summarized by the following trends in permeation and separation behaviour.

· Permeation of molecules that can pass through the pores of silicalite-1 (~ 0.51–0.55 nm) is governed by their adsorption characteristics in the silicalite-1 and their intrinsic diffusivity which is highly dependent on the operation conditions. These characteristics can lead to peculiar effects in the permeation fluxes. As a function of the temperature it increases, passes through a maximum, decreases and can even pass through a minimum and increase again. This behaviour has been modeled based on the Maxwell–Stefan theory for multicomponent dif-
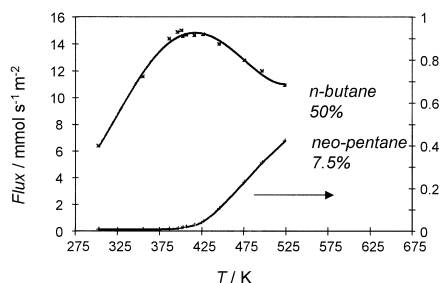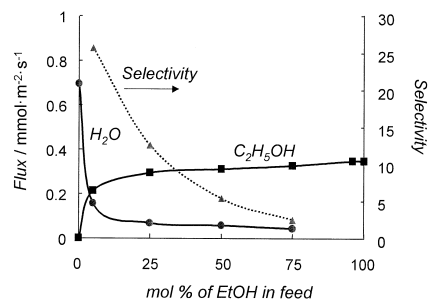

Fig. 11. Permeation fluxes of *n*-butane (50 kPa) and *neo*-pentane (7.5 kPa) as a function of the temperature in a mixture (dilution with helium to 100 kPa total pressure).

fusion, but now applied to diffusion in zeolitic materials [9].

· Molecules that are of the size of the pores and larger have problems in entering the zeolite, but still exhibit some permeation. Fluxes are appreciably lower than for smaller size molecules. Typical examples are SF_6, isobutane, isooctane and benzene derivatives [4,14–16]. The silicalite-1 framework is sufficiently flexible to allow permeation of these molecules. This results in an activated permeation behaviour.

· Very large molecules do not permeate. These can be used to test the quality of the membrane. Examples are triethylamine (TEA, 0.74 nm) and 1,3,5-triisopropylbenzene (TIPB, 0.93 nm) and perfluorobutylamine (1.02 nm) [17].

· Shape selectivity is observed for mixtures of molecules that fit easily in the silicalite-1 pores and those that are of the pore size or larger [16]. Also a strong temperature dependency exists.

· At high loading the zeolite is filled with molecules to such an extent that there is no opportunity to pass each other in the pores (single file diffusion) or via parallel channels, so all molecules are expected to permeate at the same rate. Selectivities are now only determined at the entrance in the membrane and differences in intrinsic diffusivities do not play a separating role. This can explain results of Funke et al. [14,15].

· At low loading (Henry regime) molecules will permeate independently of the presence of each other. For a simple Langmuir type adsorption it can be shown [9] that the permeation flux is proportional to the product of the adsorption equilibrium constant and the diffusivity:

$$N_i \propto K_i D_i \nabla p_i$$

Since stronger adsorbing molecules will have lower diffusivities these two parameters will balance out to a certain extent. In this situation the separation of isomers, which will adsorb to similar extents, that experience shape selectivi-

ties, will be promising [18]. An optimum in temperature, however, has to be sought with respect to selectivity and permeation fluxes. The latter will increase with temperature, but selectivity will decrease due to the higher activation energy for diffusion of the most hindered component.

At high temperatures the interaction of the molecules with the zeolitic pore walls has decreased such that adsorption is negligible. Molecules move freely through the zeolite, but still experience the geometric constraints of the pores and the presence of the Van der Waals force field. This is described by a kind of activated Knudsen diffusion [19], which accounts for the increasing trend of the unary permeation at higher temperatures.

The hydrophobic nature of the silicalite-1 leads to pervaporation selectivities in favour of organics in water–organics mixtures [20,21].

The pioneering work of the group van Bekkum/Jansen in the area of zeolite membranes has triggered a lot of new and interesting research. But in spite of the efforts in this area it is still in its infancy and numerous challenges are open for further research and development.

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