Application for Financial Support of a Proposal within a Package of Proposals
Submitted for Joint Evaluation by CNRS, DFG and EPSRC

Project 4: Diffusion Studies with Composite Zeolite Membranes

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Financial Support Requested from: DFG
1. General Information

1.1. Applicant
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1.2. Topic
Diffusion Studies with Composite Zeolite Membranes

1.3. Code Word
Diffusion by Membranes

1.4. Research Areas
Material Sciences
Chemical Engineering
Physical Chemistry
Interface Sciences

1.5. Scheduled Total Duration of Support
six years

1.6. Period of Support Applied for
three years

1.7. Begin of Support
April 2003

1.8. Summary
The work of this project is devoted to the determination of the diffusivities resulting from permeation measurements (i.e. of macroscopic and mesoscopic transport diffusivities measured under stationary conditions) for comparison with the diffusivities of comparable systems obtained by the other techniques available in the consortium. Moreover, the measurement of the time lag between the start of the permeation experiment with a completely unloaded membrane and the breakthrough of the permeate allows equivalent information under the initial transient conditions. Particular care is given to the investigation of the influence of as many parameters as possible, including loading, shape of the adsorption isotherm and temperature as well as the nature (size, composition) and the pretreatment conditions (activation, deterioration) of the zeolite membrane. It is the aim, therefore, of this project to use the zeolite-in-metal composite membranes as model membranes for diffusion studies. The zeolite crystals embedded into the metal matrix is the identical zeolite material used in the parallel diffusion studies. Provided that the preparation of the composite zeolite
membranes as described in Project 1 will be successful, we would have the unique possibility to (i) derive diffusion coefficients from stationary and instationary permeation experiments and to (ii) forecast the expected permeance of any industrial zeolite membrane, which will be most probably prepared by direct crystallization of a thin zeolite layer on a mesoporous support.

2. State of the Art, Own Activities in the Field

2.1. State of the Art

Since many processes in catalysis and separation technology employing zeolites are diffusion limited, the study of diffusion has become an important research topic. The correlation and interpretation of the transport coefficients derived from the zeolite membranes prepared with the standard zeolite material made in Project 1 would open the possibility to determine diffusion coefficients from stationary and instationary permeation measurements. Furthermore, the permeation data obtained on these model zeolite membranes (zeolite-in-metal composite) allow the forecast of the flux of technical zeolite membranes prepared by the direct crystallization of a continuous zeolite layer on a mesoporous metal or ceramic support.

As shown by the Delft group [1], the Generalised Maxwell-Stefan equation can describe the mass transport through a zeolite membrane. Very similar to the solubility - diffusivity theory applied for the description of mass transport through organic polymer membranes, mass transport through zeolite membranes is described by the interplay of diffusion and adsorption. The counteracting temperature dependences of adsorption and diffusion lead to a maximum of the permeance of single-component permeation if the heat of adsorption is larger than the activation energy for diffusion [2]. An analysis of the position of this maximum as a function of the temperature together with the adsorption isotherm data provides the activation energy of diffusion [3].

However, permeation through pore membranes must be treated in another way than permeation through organic polymer membranes. Whereas in polymer membranes the permeance can be increased by increasing the pressure difference across the membrane (according to the linear relationship between feed pressure and the solubility of the permeate in the polymer membrane over a wide pressure range), for zeolite membranes the pore volume, which can be filled, is restricted (the pore filling takes place according to the adsorption isotherm, which is in most cases non-linear, e.g. of Langmuir type, and only in the Henry regime at low partial pressure and at high temperatures a linear isotherm is found). Recently by the Delft group it was shown that only simple short chain-length alkanes on MFI zeolites follow a Langmuir type adsorption, but longer and branched alkanes exhibit a two-step adsorption behaviour, which is described by a dual-site Langmuir model [4]. Simulations have shown that the dual-site Langmuir model is due to the packing of the adsorbed molecules in the MFI channel network consisting of straight and sinusoidal pore segments interconnected by crossings [5]. It is concluded, therefore, that molecular diffusion becomes a function of the loading and the activation energy of diffusion will change when operating in these different adsorption regimes [6]. The interplay of diffusion and adsorption in the permeation on zeolite membranes has been described recently in a pioneering paper by MO and molecular dynamics calculations [7].
2.2. Own Activities in the Field

Prototypes of MFI and AFI zeolite-in-metal composite membranes have been developed and molecular permeation through these model membranes was studied [8]. Two types of permeation systems were investigated: If one of the binary-mixture components is larger than the pore size, molecular exclusion takes place and the permeating component behaves like in a single-file system. If both mixture components can pass the zeolite pore according to their size, a complicated temperature dependent interplay of mixture adsorption and mixture diffusion occurs. By comparing the single-component diffusion coefficients in one-dimensional pores (obtained on an AlPO4-5-in-nickel membrane) with those derived from ZSM-5-in-silver composite membranes it was found that the molecular mobility in the one-dimensional pore system of AlPO4-5 is orders of magnitude higher compared with the molecular mobility in the two-/three-dimensional MFI pore system [9]. Independent NMR pulsed field gradient studies came to a similar conclusion, namely that the diffusivity of an isolated molecule in a single-file system is two orders of magnitude larger than the largest intracrystalline diffusion coefficient in zeolites with 3-dimensional pore network so far observed [10].

3. Issues and Working Programme

The correlation and interpretation of the transport coefficients derived from supported zeolite membranes with corresponding data obtained on powder samples was so far not successful. It is the aim, therefore, of this project to prepare model membranes for diffusion studies, which are based on the identical zeolite material as used in the parallel diffusion studies by the other members of the consortium. It has been shown in the past that only preparation technologies without mechanical abrasion steps can be used in the preparation of zeolite-in-metal composite membranes. We could successfully bring large (>30 µm) individual zeolite crystals into metal foils using galvanic techniques. However, special treatment of the membranes thus prepared was necessary to remove additives from the galvanic bath such as surfactants, phosphates, cations etc. Besides the galvanic techniques, it is proposed, therefore, to apply gas phase deposition techniques such as sputtering of metal for the gas-tight sealing of zeolite crystals in combination with plasma etching.

The embedding techniques described in Project 1 will be focussed on the use of metal matrices since they are thermally more stable than polymers and allow oxidative regeneration of blocked membranes. The coefficients of thermal expansion between the zeolite and the metal matrix can be matched in certain temperature fields.

3.1. Issues

The work of this project is devoted to the determination of the diffusivities resulting from permeation measurements i.e. of macroscopic transport diffusivities measured under stationary and instationary conditions for comparison with the diffusivities of comparable systems obtained by the other techniques available in the consortium. Whereas under steady state permeation the permeation flux density is correlated with the diffusion coefficient according to the first Fick law, the time lag between the start of the permeation experiment with an unloaded membrane and the breakthrough of the permeates is similar to the instationary conditions described by the second Fick law and allows equivalent information under the initial transient conditions. Particular care is given to the investigation of the influence of as many parameters as possible, including loading and temperature as well as the nature (size, composition) and the pretreatment conditions (activation, deterioration) of the zeolite samples.
3.2. Working Programme

The permeation measurements start in the sequence as predetermined by the accessibility of the zeolite host materials indicated in tab.1 of the synthesis project (Project 1). In a following, second period of time, the measurements are repeated with identical or modified materials taking account of the findings by the other groups of the consortium.

Strictly speaking, the measurements within the project have to be carried out with two options, viz. the acquisition of diffusion data and the exclusion that these data might be corrupted by possible sources of error. It is this latter requirement, which has to be taken account of by involved consistency checks. In the present case they particularly include a simple check of the membrane quality by measuring the permeance of gas molecules of different size. In the case of an MFI membrane with a regular pore size of 0.55 nm methyl-tert-buthylether (MTB) with a kinetic molecular diameter of 0.63 nm or SF\textsubscript{6} with 0.65 nm are suitable probe molecules to prove the absence of defect sites. For FAU-type membranes with 0.75 nm pore width, 1,3,5 trisopropylbenzene with a diameter of 0.85 nm should be rejected by an intact FAU framework. The so-called permselectivity, i.e. the ratio of the single-component permeances of two components, of a component like n-hexane (0.43 nm) that can pass, e.g., an MFI membrane (0.55 nm) relative to a component like dimethylbutane (0.62 nm), which can pass the membrane only through defects of the regular zeolite structure, should be higher than 50.

Special concern will be given to the interplay of adsorption and diffusion in the description of the permeation of light alkanes through zeolite membranes. The adsorption parameters measured and modelled in the Projects 2 and 3 describe the temperature dependence of the adsorption capacity by fitted and empirically modified Langmuir equations with

$$q_i = (q_{sat,i} + \Theta T) \frac{K_i p_i}{1 + K_i p_i}$$

with

$$K_i = K_i^0 \exp \left[ \frac{Q_i}{RT} \right]$$

The symbols are as usual, the term $\Theta T$ accounts for the decreasing saturation capacity with temperature. It is expected that the adsorption of small molecules such as methane to propane in medium pore zeolites like MFI can be described by Langmuir type I behaviour [11]. For larger molecules such as n-butane, i-butane up to the heptanes, deviations from the type I behaviour are expected [12] and the adsorption behaviour should be described by a Double Langmuir model. The membrane permeation data will be described, therefore, by the Langmuir and Double Langmuir model.

Among the different models for diffusion in zeolites currently used, the chemical potential is assumed as the driving force for diffusion [13]. Zeolitic or configurational diffusion is described by

$$N_i = D_i \cdot q_{sat,i} \Delta \ln(1 - \Theta_i)$$

with

$$D_i = D_i^0 \exp \left[ \frac{-E_a}{RT} \right]$$
In this formula, $D_i$ is the corrected transport diffusion coefficient, which is assumed to approach the self-diffusion coefficients determined in Projects 6 and 7 by PFG NMR and QENS. The $N_i$ is the flux defined by Fick's first law of diffusion according to

$$N_i = -D_i \nabla c_i$$

Most of the membrane measurements are focused exclusively on steady state measurements. However, permeation measurements may also be made under transient conditions and such measurements can yield additional kinetic information. Pioneering work was done by the Delft group measuring the transient permeation behaviour of a 50%/50% binary mixture methane/n-butane on a silicalite-1 membrane at 25°C [14].

The solution of

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}$$

becomes for $t \to \infty$

$$N_{i,t} = \frac{D c}{L} \left( t - \frac{L^2}{6D} \right)$$

which is a straight line in the plot of the total permeate, $N_{i,t}$, versus $t$, with an intercept of time axis at $L^2/6D$ [15]. The consideration of adsorptive interaction according to the Henry adsorption regime $q=Kc$ gives a slightly modified expression.

In detail, we have the following working packages:

**Working package 1:** Erection of the permeation apparatus for measuring the single-component permeances by following (i) pressure increase and (ii) gas stream composition (Wicke Kallenbach methods)

**Working package 2:** Evaluation of the membranes prepared by single-component permeation measurements with molecules of different kinetic diameter

**Working package 3:** Determination of diffusion coefficients from instationary measurement (time-lag method) for single component gases and - for comparison - for binary mixtures of components with different adsorption behaviour

**Working package 4:** Determination of diffusion coefficients of single-component gases by monitoring the pressure increase under steady-state conditions in the permeate chamber using pressure detectors

**Working package 5:** Determination of the diffusion coefficient of single-component gases from Wicke Kallenbach measurements using the GC for the gas analysis on the permeate side of the membrane

Special attention is devoted to the following membrane types:
3.2.1. **NaCaA**

The understanding of mass transport in LTA systems is of basic importance for their application in selective adsorption processes. So far, no molecularly sieving LTA has been prepared. So the derivation of diffusion data from LTA-type membranes will be quite new. Vice versa, it will be tried to forecast the permeation behaviour of the LTA membrane from the diffusion data obtained by the other partners. In agreement with the choices of the other partners, the permeation studies will start with the series of n-alkanes with even carbon numbers from 4 to 14. Further extensions, both beyond this range and to odd carbon numbers, are to be discussed during the meetings. Within this range of n-alkanes, probably all techniques of the consortium might be applicable. Further on, diffusion studies shall be performed with methanol. Methanol in NaCaA was the first system, in which intracrystalline zeolitic transport diffusion could directly be observed.

3.2.2. **Cation-free LTA (GaPO₄, AlPO₄)**

If crystals > 20 µm will be obtained, the membrane preparation should be successful. The measurements will concentrate on the diffusivities of methane, ethane and n-butane. They will primarily be compared with those derived from ZLC (Project 3) as an alternative non-equilibrium technique, as well as with the self-diffusivities obtained by TZLC (Project 3), PFG NMR (Project 6) and QENS (Project 7).

3.2.3. **Silicalite-1/ZSM-5**

This permeation system is of special interest since the results obtained can be compared with both those of the other partners and with the results of other permeation studies. MFI-type membranes are the most often prepared zeolite membrane. In accordance with the other partners, again the measurements should start with the series of n-alkanes with even carbon numbers (4 to 20). Further on, measurements with isobutane (comparison with n-butane) and with methanol (good measuring conditions in the microscopic techniques) should be performed. Since the diffusivities in silicalite-1 and ZSM-5 are expected to be close to each other [15], the investigations might concentrate, at first, on silicalite.

3.2.4. **NaX/NaY**

Diffusion and permeation studies on FAU type membranes will be of special interest since there is up to now no FAU membrane with a continuous defect-free membrane layer. All the FAU type membranes prepared so far show no molecular sieve properties. An exception is made by the latest paper of Tsapatsis [16]. Diffusivities from permeation studies will be of special interest for the understanding of catalysis on Y type zeolites. The investigations should at first concentrate on the even n-alkanes from carbon number 4 to 14. Depending on the difference in the diffusivities in NaX and NaY, it might be feasible to concentrate on NaX (which offers better measuring condition, since it is available with sufficiently large crystallites). Again, for the sake of comparison with n-butane, also isobutane will be considered. In the present wide-pore zeolite the difference in the diffusivities is expected to be much smaller than with ZSM-5/silicalite-1. As a consequence of the specific cation-adsorbate interaction, dramatic differences between the diffusivities in NaX and NaY are expected for benzene, toluene and the xylenes, but not for cyclohexane.
3.2.5. **AlPO₂⁺⁻⁻⁻⁻⁻⁻⁵**

The preparation of this type of membrane requires a special orientation of the crystals perpendicular to the support surface. In the past this has been achieved by using electrical fields. It is an open question whether membrane preparation will be successful by using a perforated metal plate with holes, which may simultaneously host and orient the rod-shaped AlPO₄⁻⁻⁻⁻⁻⁻⁵ crystals. Considering two molecules, which should (isobutane) and should not (methane) exhibit the features of single-file diffusion, is of particular relevance for the comparison between equilibrium and non-equilibrium diffusion measurements. From the (conventional) theory one expects no substantial difference between the two measuring techniques in the case of normal diffusion, while the (apparent) diffusivities resulting from the equilibrium measurements of single-file systems should be dramatically smaller than the results of the uptake measurements. Thus, for the first time one might expect to find a system, where, e.g., the uptake diffusivities are much larger than the PFG NMR diffusivities. Again, methanol is of interest owing to its favourable measuring conditions in the microscopic techniques.

3.2.6. **Ferrierite**

Owing to the problems with the provision of a sufficiently large amount of zeolite material with equal and perfect crystals, the preparation of membranes of this type is not planned.

3.3. **References**

4. Requested Financial Support

4.1. Personnel
The person working in this sub-project will acquire a wide skill ranging from the erection of a non-standard permeation apparatus over analytical experience (how to handle a GC) to the interpretation and correlation of the permeation results on the basis of adsorption and diffusion measurements. It is proposed, therefore, to put a PhD student (BAT IIa/2) on this position.

4.2. Durable Equipments
It is foreseen to built an apparatus for measuring the single component permeances.

- 1 Turbomolecular pump (Balzers/Pfeiffer) 4 300 €
- T-regulation and thermo sensors (Juchheim) 4 500 €
- p-sensor, p-regulation, mass flow controller (MKS) 18 000 €
- Thermostated box 1 600 €
- Valves and fittings (Hoke) 3 200 €

The apparatus will allow both the determination of the permeance by (i) monitoring the pressure increase in the permeate volume and by (ii) applying the Wicke Kallenbach principle to measure the concentration of the permeating component in the sweep gas using a gas chromatograph. This GC is financed by another source.

4.3. Consumables
7000 € especially for gases and chemicals incl. small parts of the apparatus per year.

4.4. Travelling
The work within the package of projects depends on the quality of mutual exchange between the partners. This has to include the possibility of mutual visits in addition to the regular meetings (1000 € per year). Therefore, a total amount of 2000 € per year, corresponding to 6000 € for the total period of time is requested for, to support these visits and meetings.

4.5 Other Costs
For the support of conference participation (Annual German Zeolite Conferences, Conferences of the International Zeolite Association and Adsorption Association) an amount of 2000 € is requested for.

5. Requirements for the Success of the Application

5.1. Team Members
a) Prof. Dr. Jürgen Caro (applicant)
b) In October 2002 the group consists of 10 persons. Further 4 positions will be occupied by the end of 2002.
5.2. **Cooperation with Other Scientists**

The primary partners of cooperation are the members of the consortium. For special support and scientific exchange in the field of membrane preparation and diffusion measurement by them, cooperation with the following scientists is planned:

- F. Kapteijn and K. Jansen (Delft)
- M. Noack, P. Kölsch, R. Schäfer (Berlin-Adlershof)

The investigations shall be carried out in close contact with Prof. Dr. D. M. Ruthven, Univ. of Maine, USA, who he is going to stay in this laboratory as a 2002 Humboldt Awardee.

5.3. **Available Equipments**

- XRD for product identification
- Thermal analysis for controlled template removal
- SEM with FE and EDX for product characterization
- TEM for product characterization

5.4. **Support from the Own Budget**

From the budget of the institute an amount of about 3000 € may be used for ensuring the operating conditions of the equipments. The analytical equipment named in 5.3. can be used.

5.5. **Further Prerequisites**

The institute offers the working places for the co-workers, applied for, as well as the necessary laboratories. The infrastructure of the institute allows the use of data-networks and computer systems free of charge.

6. **Statements**

6.1. **Collaborative Research Centres (Sonderforschungsbereiche)**

The present application cannot be part of any of the existing collaborative research centres of the University.

6.2. **Application for Support by Different Sources**

I have never applied for financial support of this or a similar project. If I shall do so, I will immediately inform the German Science Foundation (DFG).

6.3. **Information to the University Representative of DFG (Vertrauensmann)**

The university representative of the DFG, Prof. Dr.-Ing. W. Zielke has been informed about this proposal.

7. **Signature**

Hannover, November 1, 2002