

Application for Extension of Financial Support of

**Project 4:  
Diffusion Studies with  
Composite Zeolite Membranes**

as part of a package of proposals  
aspiring joint support by CNRS, DFG, EPSRC and NSF

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Financial support requested from: NSF

# **1. General Information**

## **1.1. Applicant**

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Professor Shah continues the DFG-funded activities of Prof. Caro, Hannover, performed during the first period under the (preceding) application's reference number: CA 147/10-1,2

## **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**

After three years of support by DFG, the responsibility of the activities in the field of diffusion measurement by membranes within the consortium is passed from Prof. Caro to Prof. Shah who cares for a continuation of the research efforts by support requested from NSF for (further) three years

## **1.6. Period of Support Applied for**

three years

## **1.7. Begin of Support**

support started November 2003,  
continuation by funding through NSF shall be requested, starting from November  
2006

## **1.8. Summary**

Following the overall mass transfer through an individual crystal, the information provided by single-crystal membrane permeation measurements is intermediate between those provided by interference microscopy, QENS and PFG NMR (being able to resolve the intracrystalline features of molecular transport) and the macroscopic techniques. Hence, as a mesoscopic technique, single-crystal permeation assumes a unique role among the techniques comprised within the package of application and is, moreover, the only non-equilibrium technique which may operate under stationary conditions.

The particular challenge of this project is the establishment of conditions which allow the comparability of the single-crystal permeation measurements with the other techniques. It turned out in both the previous activities within the project, that the original aim to develop a technology allowing the investigation of all major synthesis products within the consortium by the permeation technique is probably far too ambitious. This may be illustrated by the fact that even with the super-large MFI-type zeolite crystallites with all edge lengths of essentially more than 100  $\mu\text{m}$  used at Cleveland State University, even there, i.e. in the location of its cradle and the present stronghold of this technique, not more than about 10 % of produced membranes turn out to operate correctly.

Hence, deviating from the original intentions, the activities within this project will concentrate on the production of at least a few single-crystal zeolite membranes with - if necessary- highly selected zeolite crystals. The options for comparison with the other techniques of the consortium include interference microscopy as a microscopic non-equilibrium technique and IR microscopy, just intermediate between microscopic and mesoscopic, if only a few further crystals are available for comparative studies. With increasing amount of zeolite material available, starting with ZLC as the most modest method with respect to the amount needed, also the other techniques shall be applied. It is planned, to exploit the (probably not very numerous) properly working single-crystal membranes with a maximum of diffusion runs. This also concerns - in close correlation with the investigation of the analogous effect by interference spectroscopy - the discrimination between intracrystalline transport resistances and surface barriers.

The measurements will in particular include the options of co- and counter-diffusion, since, operating under stationary conditions, permeation studies offer far better conditions for the observation of these phenomena than transient non-equilibrium techniques.

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

### **2.1. State of the Art**

The development in diffusion research with zeolites and other microporous materials during the first period is in particular characterized by a real flood of studies dedicated to experimental studies of the permeation through zeolite membranes [1-6], their technical assessment [7-9] and theoretical studies by molecular modelling [10-12], including estimates about permeabilities on the surfaces [6, 13].

Though diffusion studies with membranes doubtlessly represent the largest group of diffusion studies in the field of zeolites and other nanoporous materials, also with respect to other issues there is a continuously increasing number of publications. They include sophisticated

theoretical approaches [14-22] in need of adequately reliable experiments, challenging projects considering technological aspects of zeolitic diffusion [23-28], novel principles of diffusion measurement [29-32], diffusion anomalies [33-40] and an overwhelming number of "new" systems to be investigated [41-52], including the risk of new misinterpretations as long as the "old" problems are still unsolved.

It should be emphasized that, irrespective of this great number of diffusion studies, in none of these efforts the phenomena experimentally observed during membrane permeation could unambiguously be attributed to well-defined transport phenomena occurring either in the zeolite bulk phase or at the interfaces within the membrane or at the membrane surface, i.e. due to the effect of external and internal diffusion barriers. Exactly this type of information, however, has to be provided by single-crystal permeation studies, where all heterogeneity problems inherent to polycrystalline membranes may be excluded.

As to our knowledge, however, efforts for advancement in the preparation of single-crystal membranes are only known from the groups in Hannover and Cleveland which, for the sake of efficiency, have agreed upon changing the baton within the consortium. The subsequent section 2.2. summarizes the efforts of the Hannover group to fabricate single-crystal membranes for the consortium and the outcome and provides, moreover, an overview of the experiences existing in this field at Cleveland State University

## 2.2. Own Activities in the Field and Results of the First Period

### 2.2.1. Activities at Hannover University During the First Period

#### A. Permeation Apparatus

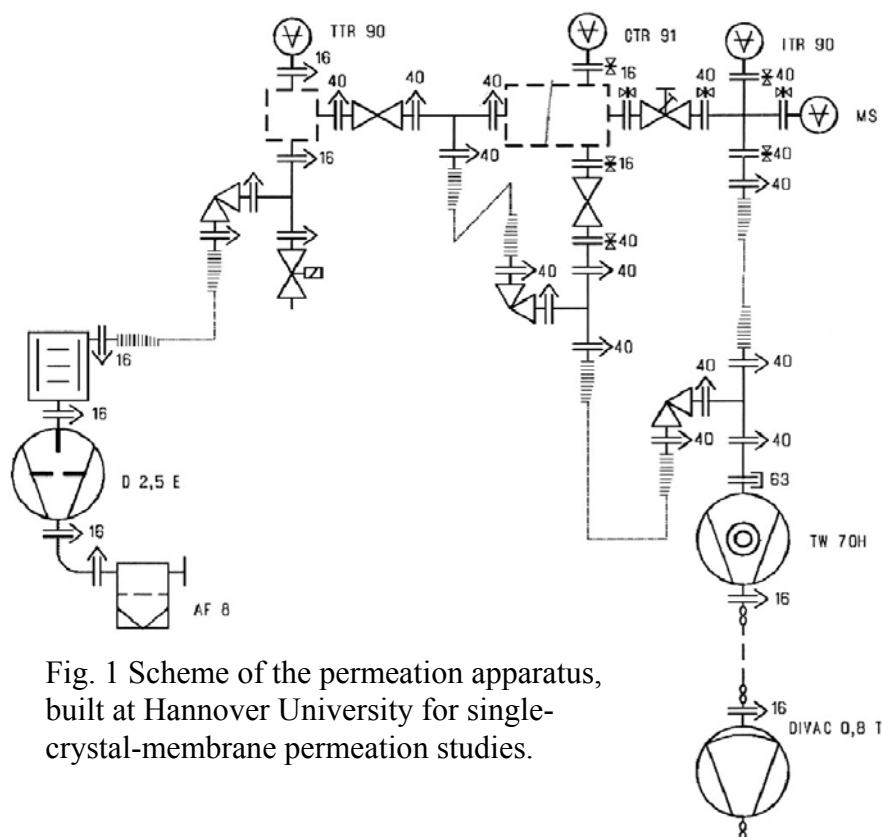


Fig. 1 Scheme of the permeation apparatus, built at Hannover University for single-crystal-membrane permeation studies.

Based on our experience, a permeation apparatus was designed and built according to the scheme in Fig. 1. This apparatus allows for measuring a steady increase in pressure on the permeate side of the membrane as long as the pressure on the feed side is much larger. Due to the much larger volume of the gas inlet system as compared to the cell below the membrane (40 l vs. 32 ml) and the high sensitivity of the capacitance pressure sensor in the cell ( $10^{-5}$  mbar), this is a reasonable assumption. The residual mass spectrometric gas analyzer can be used to examine the composition of gas mixtures permeating through the membrane. The cell itself and the residual gas analyzer can be heated in situ to remove adsorbed material from the inner walls of the vacuum system and to activate the membrane inside the cell.

### ***B. Membrane Preparation***

Novel attempts have been made to prepare model membranes which consist of several zeolite single crystals in a certain geometry embedded in a gas-tight sealing material. Different novel ways have been explored to prepare such membranes with zeolite LTA (Ca exchanged A) and FAU (type X) crystals embedded:

#### (i) Sputtering of inorganic material:

A few hundred zeolite crystals have been put on a porous alumina support in disc geometry with a radius of 9 mm. Then, several alternating layers of chromium and chromium-nitride have been sputtered on the zeolites and the support at Forschungszentrum für Oberflächentechnologie Witten. Unfortunately, these layers have proven to be extremely brittle and permeable, which did not allow their use as a sealing material for membranes.

#### (ii) Vapor deposition of silica and titania:

A few hundred zeolite crystals have been put on a porous alumina support. Then, a silica layer of about 1-3  $\mu\text{m}$  thickness has been vapor deposited on the supporting discs at the Department of Electrical Engineering of the University of Hannover, fixing the zeolite crystals to the surface. Afterwards, several alternating layers of silica and titania have been vapor deposited at Laser Zentrum Hannover. Again, these layers have turned out to have a high permeability and a low mechanical stability.

#### (iii) Rubber as sealing material:

Zeolite crystals have been embedded on a porous alumina support by using butyl rubber and styrene-butadiene rubber. Both rubbers have a low permeability against helium and nitrogen, and resist temperatures up to 180 °C. In order to remove the sealing material from the top of the crystals, the membranes have been polished. Unfortunately, small cracks between the crystals and the rubber have been produced, thus rendering the membrane useless, as the flux through these cracks has been much larger than that through the crystals. Attempts utilizing a novel mechanical force-free pulsed UV laser at the Institute of Mineralogy of the University of Hannover to remove the rubber on top of the crystals have been made. These attempts produced membranes with circular holes over about 100 zeolite A crystals each. However, there was massive leak rate of gas not passing through the crystals.

#### (iv) Smaller membranes with epoxy resin as sealing material:

Since many problems were caused by the O-ring pressing against the sealing material of the membrane inside the permeation apparatus and the large area of the alumina support discs, a new setup has been chosen consisting of an unsupported, circular membrane with a radius of either 0.5 or 1 mm inside a metal ring. In the preparation, several crystals are embedded in epoxy resin and hardened between 80 and 150 °C. The membrane has then been polished from both sides in order to remove the resin from the top and below the crystals.

(v) Research state:

After the time-consuming erection of the apparatus and the negative experiences with using inorganic sealing materials and different novel ways in membrane preparation, we are now able to prepare suitable zeolite membranes with large A- and X-type crystals embedded in epoxy resin. The problem with LTA (Ca ion exchanged A) membranes is that the in-situ dehydration in the apparatus turns out to be difficult. Microscopy shows that both sides of the zeolite crystals were apparently free of epoxy resin, and after heating the membrane inside the apparatus up to 200 °C under high vacuum, there is no measurable flux through the zeolite crystals. The reasons for this behavior are not clear. Zeolite FAU (X) is less hydrophilic than LTA and FAU shows larger pore diameters expecting higher permeation fluxes. Furthermore, since zeolite FAU (X) is with 70 µm of larger size than zeolite LTA with 40 µm, it should be easier to prepare FAU membranes. These experiments are still underway.

### ***C. Porous Silicon Wafers***

Parallel to the experiments with zeolite membranes, the established permeation apparatus has been exploited to examine the flux of helium through porous silicon wafers as part of a joint research project with the Institute of Experimental Physics of Leipzig University where these wafers have been produced by an etching technique. The flux through the wafers can now be measured reproducibly within about a 10% error range, which for the first time allows the determination of Knudsen diffusivities in tailored pores.

#### ***2.2.2. Activities in the Field at Cleveland State University***

The idea of fabricating a single crystal membrane and using permeation data from such membranes to determine micropore diffusivities was conceived at Cleveland State University in 1980's. Since then, it has undergone significant changes in methodology and design. The fabrication of single-crystal membranes required overcoming a number of problems such as synthesizing sufficiently large crystals, finding an appropriate epoxy to bind the crystal to the support, polishing the crystal carefully to make sure that both faces of the crystal are fully open and that there are no hairline cracks in the membrane. The single crystal membrane was placed in a diffusion cell that divided the set-up into two chambers. The pressure on the feed side was increased and the pressure rise in the permeate side was monitored and analysed. The static method was successfully used to measure intracrystalline diffusivities of n-alkanes [53], C<sub>4</sub> hydrocarbons [54], aromatics [55] and inert gases such as helium and argon [56].

This method, as designed, had several limitations, the biggest being that it could not be used to measure binary diffusivities. To correct this deficiency, the apparatus was modified to have flowing gases on the two sides of the membrane similar to the Wicke-Kallenbach diffusion cell, but, with a single crystal membrane. A sophisticated analysis system also had to be installed to accurately measure the small fluxes permeating through the single crystal membrane.

A comprehensive experimental program was initiated to study binary diffusion of n-alkanes. Since adsorption and diffusion are intimately connected with one another, pure component adsorption isotherms of C<sub>1</sub> to C<sub>10</sub> hydrocarbons were measured gravimetrically [57, 58]. Pure component diffusivities were determined from single crystal permeation [59, 60] and binary diffusivities of selected systems [61, 62]. We have also constructed a similar apparatus to perform experiments with single pellet membrane [63, 64]

### **3. Issues and Working Programme**

#### **3.1. Issues**

Being intermediate between the microscopic and macroscopic techniques and as the only technique of the consortium operating under stationary non-equilibrium conditions, single-crystal permeation assumes a prominent position within the research group. This concerns in particular the options of multi-component diffusion studies. Co- and counter-diffusion experiments by membranes can be performed in the most direct way, owing to the option of maintaining constant boundary conditions [61]. (In fact, with respect to the ease of the performance of two-component diffusion measurement, co- and counter-diffusion through single-crystal membranes is only matched by the option of selective self-diffusion measurement by QENS and (MAS) PFG NMR - if one disregards ZLC at vanishing concentrations).

The efforts during the first period of support revealed substantial difficulties in elaborating a technology for the fabrication of the aspired single-crystal membranes. It turned out in particular that there is probably no way to produce single-crystal membranes with crystal sizes below the range of about 100  $\mu\text{m}$ , which have applied in the so far only successful attempts to produce single-crystal membranes [6, 60, 61]. Hence, for improving the options for including single-crystal permeation studies into the arsenal of the group's measuring techniques, special care for the production of extra-large zeolite crystallites shall be taken. This concerns in particular the set of host materials considered by the consortium, but also other promising routes [65] shall be followed. Future activities for the fabrication of single-crystal membrane will therefore concentrate on those zeolite samples supplied within the consortium or by other cooperation, which - owing to their extra-large crystal size - offer best fabrication conditions. As a consequence, the realization of the subsequently presented working programme depends on the availability of the respective and suitable zeolite crystals and shall be cared for in the sequence of availability.

As a further peculiarity of this type of measurements, one must be aware of the poor conditions for zeolite activation, in particular of the rather limited range for temperature increase. This results from the requirement of (i) an ideally tight inclusion of the crystal into the otherwise completely impenetrable membrane and of (ii) the insurance of free access to and release from the crystal faces, respectively, on either sides of the membrane. This situation clearly favours the application of cation-free zeolites, which reduces the risk of complications due to the essentially unavoidable presence of traces of the omnipresent water molecules. Experiments with cation-containing zeolites should be performed, therefore, by deliberately involving certain levels of water content [66].

#### **3.2. Working Programme**

##### **3.2.1. LTA**

Irrespective of the fact, that during the first period of support for this particular host system the probably most intriguing result has been obtained, namely the deviations from a monotonic dependence of the diffusivities of the n-alkanes in zeolite NaCaA on the chain length [67, 68], as a consequence of the relatively small sizes of the A-type zeolite crystals so far available [65, 69] the fabrication of LTA single-crystal membranes shall only commence after single-crystal membranes with other crystal types, in particular MFI-type zeolites will have been produced.

### 3.2.2. *Silicalite-1/ZSM-5*

The technology for the fabrication of single-crystal membranes is farthest advanced for the LTI-type zeolites silicalite-1 and ZSM-5 [6, 13, 60, 61]. This type of zeolite is, therefore, an excellent candidate for the fabrication of single-crystal membranes and, thus, for comparative single-crystal permeation studies within the consortium. During the first period, in contrast to the findings with zeolite NaCaA, the diffusivity of the n-alkanes in MFI-type zeolites was found to decrease monotonically with increasing chain length [70, 71]. However, in both previous single-crystal permeation studies [60] and simulations by molecular modelling [14, 17, 26], similarly as with zeolite NaCaA, also indications for oscillating diffusivities with increasing chain lengths have been observed. The experimental reconsideration of this question by single-crystal permeation studies, as part of a concerted activity within the research group, is hence among the main tasks within this project. In addition, further experimental work is as well needed to clarify the possible influence of additional transport barriers on the crystal surfaces [6, 13].

In comparison with the n-alkanes, diffusion of branched n-alkanes and aromatics is notably reduced. While in the case of isobutane, still essentially all techniques of diffusion measurement are applicable (including PFG NMR with the option of MAS), the diffusion of longer iso-alkanes and the aromatics shall most likely be accessible by only the macroscopic techniques and IR- and interference microscopy. Both the practical impact of such studies and the option to directly trace the influence of compatibility ("commensurability") of channel architecture and molecular shape on diffusion [72-76] make such studies highly desirable.

Two-component (co- and counter-) diffusion studies shall in particular be performed with guest molecules vastly differing in their mobilities. In this way, the interrelation between the different diffusivities based on their microkinetic coupling (in addition to the omnipresent influence of (equilibrium) thermodynamics mediated by the two-component adsorption isotherms) is expected to appear in the most pronounced way.

In addition to the transport resistances with spacings in the  $\mu\text{m}$  range as detected by PFG NMR [77, 78] MFI-type zeolites are well known to possibly exhibit notable transport resistances at the interfaces between the individual compartments of the omnipresent intergrowths [79-84]. It is indispensable to take account of possible complications in permeation data analysis due to these resistances, which under the conditions of single-crystal permeation may influence the overall result much more significantly than in all the other techniques applied. With this background, attempts to incorporate the ideally-single-crystal material produced by W. Schmidt et al., Mülheim, deserve particular attention.

### 3.2.3. *NaX*

Among all so far considered nanoporous materials, the large-pore zeolite NaX allows PFG NMR and QENS measurements over the largest spectrum of guest molecules, including in particular n-alkanes, branched alkanes, aromatics and methanol. Most interestingly, in previous studies only with methanol as a guest molecule [85, 86] macroscopic and microscopic studies revealed satisfactory agreement. The reconsideration of this problem, in particular for benzene/toluene as a standard molecule of previous studies [87-91] and for the n-alkanes is among the key issues of this project. Since X-type zeolites have already been synthesized with crystal sizes up to the range of 100  $\mu\text{m}$ , they are among the promising candidates for the fabrication of single-crystal membranes. As a drawback of membrane-



permeation studies with this type of crystal one must be aware of the hydrophilic properties of NaX, which complicate their activation and, hence, impair the options of comparison with the results of other techniques.

As a further complication, on analysing the diffusivity data one must be aware of the octahedral shape of typical NaX-type crystals. As a consequence, it might be complicated if not even impossible to fabricate single-crystal membranes in such a way that the zeolite cross section through the membrane remains constant. As a very important consequence of this situation (which has been overlooked in the, as to our knowledge, so far only single-crystal permeation studies with zeolite NaX [92]), the distribution of molecular concentrations over the crystal is additionally affected, which has to be taken account of in a strict analytical treatment of the experiment.

Similarly as with zeolites MFI, two-component (co- and counter-) diffusion studies shall in particular be performed with guest molecules vastly differing in their mobilities since in this way the interrelation between the different diffusivities based on their microkinetic coupling should appear particularly distinctly.

#### **3.2.4. Ferrierite**

The ferrierite crystals applied in the network consist of plates with areas in the range of  $100\ \mu\text{m} \times 100\ \mu\text{m}$  and thicknesses in the range of tens of micrometers. It is on the edges of these plates where the channel openings are expected. Tightly incorporating such crystals into otherwise impenetrable membranes (with the channel openings with either the eight- or the ten-membered rings on the membrane faces) would mean an ideal means for one-dimensional diffusion studies, complementing the studies so far performed by interference and IR microscopy [93].

#### **3.2.5. $AlPO_4-5$**

Tightly incorporating AFI-type crystals into otherwise impenetrable membranes with channel direction perpendicular to the plane of the membrane would provide an ideal means for one-dimensional permeation studies. These studies would include the intriguing options of single-file and dual-mode diffusion, which for two-component diffusion would lead to a perfect slaving of the fast molecules by the more slowly diffusing ones, with interesting practical applications, e.g. for reducing cold-start HC emissions from automotive exhaust, as suggested in [94].

Moreover, the envisaged single-crystal permeation studies would provide the only option to directly check channel permeabilities. Hence, in combination with studies by IR and interference microscopy, which have been shown to be sensitive to microscopic diffusivities [95], permeation studies could significantly contribute to elucidate the real structure of AFI-type crystallites, including the exploration and quantification of internal transport resistances. In combination with the efforts of the synthesis groups - the present activities will contribute to the exploration of synthesis routes which may lead to defect-free AFI-type zeolites, which may in fact be understood as bundles of macaronis of atomistic dimension.

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## **4. Financial Support**

secured by NSF

## **5. Requirements for the Success of the Application**

### **5.1. Team Members**

Prof. O. Talu (Cleveland State University)  
PhD student

### **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:

- Prof. F. Kapteijn and Prof. K. Jansen (Delft)
- Dr. M. Noack (Berlin-Adlershof)
- Prof. J. Caro (University of Hanover)

In data analysis we shall cooperate with

- Prof. R. Krishna (University of Amsterdam)

### **5.2. Available Equipments**

Wet chemistry accessories (chemicals), ovens;  
Polishing machine for fabrication of single crystal membrane;  
Optical microscopes, SEM for characterization;  
Micromeritics surface area and porosimetry analyser;  
Single crystal Wicke-Kallenbach permeation set up with automated GC-MS analysis;  
Single pellet Wicke-Kallenbach permeation set up;  
Low pressure Cahn Microbalance for equilibrium measurements at low pressures;  
High pressure gravimetric balance for equilibrium measurements at high pressures;  
2 Volumetric binary equilibrium measurement system.

### **5.4. Support from the Own Budget**

full support is sought from NSF

### **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. Signature**

Cleveland, June 19, 2006



Prof. Dr. D. B. Shah