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

Project 1:
Synthesis of Zeolite Crystallites and Preparation of Composite Membranes for Diffusion Measurement

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Financial Support Requested from: DFG
1. **General Information**

1.1. **Applicant**
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1.2. **Topic**
Synthesis of Zeolite Crystallites and Preparation of Composite Membranes for Diffusion Measurement

1.3. **Code Word**
Zeolite Synthesis for Diffusion

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 present project cares for the material basis of the package of proposals devoted to the investigation of molecular diffusion in zeolites. On the one hand, this project has a service character to supply the project partners with high-quality and well-characterized zeolite material. On the other hand, novel routes in zeolite synthesis will be applied to control and fine-tune the crystal properties. The zeolite specimens produced within this project have to obey a number of requirements, which result from the conditions under which the different experimental techniques operate. They involve the crystal size, (which is expected to be varied over as large ranges as possible, in particular including large crystal sizes,) crystal homogeneity, crystal endurance under the conditions of sample preparation for the diffusion measurements and crystal composition with respect to the lattice atoms, the exchangeable cations and structure defects, which can result in external and internal transport resistances (barriers).

Zeolite synthesis shall be based on both conventional recipes as recommended by the Synthesis Commission of the International Zeolite Association [1] and on most recent novel developments including the application of crystallization seeds, compartmentalized gel preparation and microwave heating using concepts as temperature controlled nucleation-growth profiles, tailoring the crystal size and morphology by controlled growth conditions and continuous addition of fresh crystallization solution together with temperature changes.

Whereas in the beginning of the project the crystallization work will dominate, one year after the beginning of the project, the preparation of model zeolite membranes for diffusion measurements will be started. The correlation and interpretation of the transport coefficients derived from supported zeolite membrane layers with corresponding diffusion and adsorption data obtained on powder samples (cf. Project 4) would open the unique possibility to study molecular permeation on model membranes thus forecasting the permeance and selectivity for any zeolite membrane. 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. It has been shown that only preparation technologies without mechanical abrasion steps can be used. In the past, certain problems with flexible metal foils containing embedded zeolite crystals occurred. It is proposed, therefore, to apply (i) mechanically stable porous supports in combination with galvanic deposition techniques and to use (ii) gas phase deposition techniques such as sputtering for the gas-tight sealing of zeolite crystals in metal matrices in combination with plasma etching.

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

2.1. State of the Art

In the General Introduction to the package of projects the rather unsatisfactory situation with our present knowledge about zeolitic diffusion, i.e. about one of the key processes governing their practical application, was described. It was particularly demonstrated, how irrespective of a dramatic development in the measuring techniques over the last few years, so far all attempts of a generally acceptable explanation of the differences in the diffusivities obtained by different measuring techniques did fail. Summarizing all these previous activities, as their common main deficiency one has to criticize the lack of sufficient coherence between the activities in different fields involved. The present package of projects ensures such a coherence. It is the task of this project, to supply the necessary material basis for the work within the package. The synthesis work within the project is based on essentially two constituents:
2.1.1. Verified Syntheses of Zeolitic Materials

The collection of recipes, contained in the description of “Verified Syntheses of Zeolitic Materials” as published by the Synthesis Commission of the International Zeolite Association [1] represents a sound basis for the production of standard material, which has to be made available to all partners in the identical form and in sufficient quantities.

8 different zeolite structures will be crystallized in a high quality incl. a controlled variation of defect concentrations (from single crystals to twinned ones and highly intergrown specimens) with crystal size in relatively large amounts. In the leading synthesis groups worldwide, there exist in one group not more than 2 or 3 established recipes to prepare high-quality zeolite crystals of a certain structure type. We have the ambitious goal to prepare 8 different structure types ranging from silicates, aluminiumsilicates to aluminiumphosphates. This requires a scientific experience in this field of zeolite crystallization. The industrial crystallization of zeolites for classical applications such as adsorption, catalysis and ion exchange is oriented on the production of small µm-sized zeolite crystals to reduce diffusion problems. There exist numerous ways to reduce the mean crystal size. These small crystals are obtained in a shorter crystallization time, which meets economic demands, and these small crystals are usually of a narrow crystal size distribution [2].

However, the requirements on zeolite material to study the molecular diffusion are quite different from the standard recipes of the verified syntheses. Crystals of different size with a narrow size distribution and with a well-shaped crystal habit characteristic of the zeolite type under study are needed.

Using template-free synthesis procedures, defect-free but very small zeolite crystals are obtained as shown by Unger and Schüth [3]. Since intracrystalline defects influence the diffusion of guest molecules and alter the homogenous distribution of the guest molecules over the crystal in sorption equilibrium, special attention will be devoted in this project to the nature and impact of different defect structures. Besides single crystals, zeolite materials with different concentrations of defined defects will be prepared to demonstrate the influence of irregularities of the perfect molecular sieve structure on molecular transport.

2.1.2. Application of Novel Routes of Zeolite Synthesis

The special requirements of the techniques of diffusion measurements applied in the different projects require features of the zeolite material, which are beyond the scope of conventional recipes of zeolite synthesis. For this purpose, also novel routes of zeolite synthesis shall be introduced, which are expected to allow a broader variation of those features of the zeolite crystallites (e.g. size, size dispersion, content of defects, zeolite composition and lattice endurance), which are of relevance for the different measuring techniques.

The different syntheses will be based on IUPAC recommended “Verified syntheses of zeolitic materials”. However, these recipes describe the synthesis for a certain sol/gel composition usually in a 50ml tube without stirring, which give only a few mg of zeolite material, often with tiny (< 1 µm) crystals. Besides the modification of the recipe to get larger crystals (controlled variation of the batch composition; usually higher dilution with water and higher contents of template give larger crystals, since nucleation is suppressed relative to crystal growth) and crystals with stepwise modified defects (disturbing the crystallizing system by
stirring and addition of new feed), we have to solve a scale-up problem of the order of the factor 100 working with 1l autoclaves.

It is known that the crystal size and quality is influenced by the chemical composition of the crystallization batch, the source of the chemicals used for the preparation of the batch, and the way how the synthesis batch is prepared. Further parameters, which influence the crystallization and which can be used for the fine-tuning of the zeolite crystals, are ageing of the starting gel, the heating mode and heating source.

Relatively defect-free zeolite and zeolite-like molecular sieve crystals like the aluminium-phosphates can be prepared by hydrothermal synthesis [4]. However, serious problems are encountered in the preparation of large synthetic molecular sieve crystals, although natural zeolites can occur as large and well-shaped crystals. Simulating the geoteric conditions in a high-pressure crystallization, 6-ring zeolites could be prepared in good crystal quality as shown by Ghobarkar [5].

2.2. Preparation of zeolite composite membranes: State of the art

The direct crystallization of thin continuous zeolite layers on porous substrates such as ceramics or metal sinter plates is the most promising way to get a technical zeolite membrane for industrial application, which can be prepared on a large scale. However, the membranes so far developed exhibit intercrystalline mass transport through defects in the zeolite layer, which spoils the selectivity. On the other hand, these zeolite membrane layers are relatively thick polycrystalline and intergrown zeolite layers. Consequently, the evaluation of these membranes is quite difficult.

There are some attempts, therefore, to embed medium-sized and large zeolite single crystals of proven quality into a gas-tight matrix so that mass transport exclusively goes through the zeolite crystals. This situation is quite different from a zeolite composite membrane where tiny zeolite powder is suspended in a polymer matrix where mass transport takes place through the polymer with repeated diffusion ways through the embedded zeolites [6].

Hayhurst [7] sealed a selected zeolite crystal by an epoxy resin. Problems were the penetration of the epoxy resin into the zeolite pores, the impossibility of a thermal activation and the detection difficulties of the permeance since only one crystal was under study. The groups in Twente and Enschede tried to seal the void between crystals with water glass or a silica glue [8]. During drying and calcination cracks occurred. The Berlin group was relatively successful to seal the voids between the crystals by galvanic metal (Ag, Ni) deposition [9]. The problems, however, are that the preparation was based on silver lacquer on a glass plate as support and the metal film with the embedded zeolite crystals had to be removed (acetone) from the support. This flexible metal film was mechanically unstable and there were many unsuccessful preparations. Additionally, additives of the standard galvanic baths like surfactants and phosphate salts entered the zeolite crystals and could be hardly removed. A further problem was that the standard galvanic baths have a fixed pH in the acid region, which can damage the zeolites. Using magnetron sputtering, the Berlin group could successfully seal zeolite in metal matrices for diffusion and permeation studies [10].
2.3. Own Activities in the Field

J. Caro has an expertise in the crystallization, characterization and application of molecular sieve crystals, especially of aluminiumphosphate based ones. This is expressed by the fact that the standard recipe of the International Zeolite Association for the crystallization of AFI was submitted by Caro and Girnus [11].

Most innovative and successful was the first application of the microwave heating in the preparation of aluminiumphosphate molecular sieves, esp. of AFI type zeolites [12]. These synthesis products were used as the starting material for the production of molecular sieve membranes using different technologies for the embedding of the zeolite crystals in the metal matrix like galvanic techniques [13] or magnetron sputtering [14].

The use of the single-crystalline molecular sieves as non-linear optical material and as a host to orient rode-like molecules for polarization-dependent spectroscopy (Raman, UV-vis) gave direct information for the crystal quality and herewith a very valuable feedback for the molecular sieve crystallization [15].

More recently, J. Caro together with M. Noack was active in the crystallization of MFI layers on alumina supports for the preparation of supported zeolite membranes [16].

3. Issues and Working Programme

3.1. Issues

This project provides the material basis for the diffusion measurements within the package of projects, jointly submitted to CNRS, DFG and EPSRC. To satisfy the need of the various techniques with material from one and the same batch (which is highly desirable for the sake of comparability), in many cases an up-scaling of so-far used laboratory-scale syntheses is inevitable.

In parallel to the application of verified recipes of zeolite synthesis, novel synthesis routes shall be followed, which are expected to ensure a larger variability of those parameters, which are of relevance for the measurements. They include the variation of the crystal size, the dispersion of the crystal sizes, the content of defects, zeolite composition and lattice endurance.

The spectrum of zeolite specimens to be synthesized include
- NaCaA,
- Cation-free LTA (galliumphosphate and aluminiumphosphate isomorphs),
- Silicalite-1/ZSM-5,
- NaX/NaY,
- AlPO-5,
- Ferrierite.

Moreover, part of the synthesis work concerns zeolite membranes, which shall be produced with single crystals of proven quality, introduced into metallic matrices. By the use of these well-characterized zeolite materials it is ensured that in the different measuring techniques identical material is applied, so that a new quality of comparative measurements of zeolitic
diffusion is attained. Having the synthesis project within the Package of Proposals ensures the continuous direct contact between zeolite producer and zeolite user. The effect of special features of zeolite synthesis on the obtained diffusivities may thus be immediately implemented in the further strategy of zeolite synthesis.

<table>
<thead>
<tr>
<th>Aspired Date of Delivery</th>
<th>Zeolite Type</th>
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<tr>
<td></td>
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<td>Siegen</td>
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<tr>
<td>July 03</td>
<td>NaCaA</td>
<td>20</td>
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<td>Fall 03</td>
<td>LTA GaPO₄/AlPO₄</td>
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<tr>
<td>Fall 03</td>
<td>Silicalite-1</td>
<td>20</td>
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<tr>
<td>Jan. 04</td>
<td>ZSM-5</td>
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<tr>
<td>Spring 04</td>
<td>AlPO₄-5</td>
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<tr>
<td>Fall 04</td>
<td>Ferrierite</td>
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Tab. 1: Survey of the specimens of zeolite crystallites provided for the partners of the consortium as a first portion for the beginning of the experiments. About the fabrication of further material and its specification will be decided on the basis of the regular meetings of the consortium. So far, the synthesis of zeolites AlPO₄-5, Ferrierite and cation-free LTA has only been accomplished in extremely small amounts of the order of grammes, correspondingly, the amounts to be distributed among the partners can only care for a minimum need. The material sent to Stuttgart is planned for exploring catalytic test reactions (e.g. oxidation of n-alkanes in LTA with dispersed platinum and isomerization of alkanes in MFI) suitable for studying zeolitic diffusion on the basis of a variation of the effective intrinsic reactivity.

3.2. Working Programme: Crystallization of high-quality molecular sieve material for the project

Zeolite synthesis is scheduled to be carried out in the sequences of the following sections. It is this sequence, in which also the individual partners will investigate the diffusion properties of the different systems. About synthesis modifications and variation in zeolite treatment prior to the measurements will be decided during the half-yearly meetings of the consortium. The complete table of zeolite specimens provided within this project for the partners of the consortium is presented by tab. 1.

It is planned to work out the 8 (eight!) different syntheses of the molecular sieve structures in small 50 ml autoclaves and then to transform them into the 1 l scale. Even working with 1 l autoclaves, the amounts of zeolite necessary for the parallel studies, require several repeated crystallizations. For example, the standardized AFI synthesis gives 3 g product from ca. 110 g
of batch. Using a half-filled 1 l-autoclave, three subsequent crystallizations of 6 h each are necessary to give the 45 g product. For a larger AFI crystal size, more diluted gels with higher content of organic template will be used, which makes it necessary to conduct six runs in the 1l autoclave to give 45 g of product.

3.2.1. LTA (NaCaA)

Zeolite NaCaA is expected to be successfully applicable to all techniques available within the consortium for identical diffusants (probably the medium-chain-length n-alkanes). There is no other adsorbent, which provides similarly promising prospects. It is due to this reason that the work of the consortium is to start with this material.

The preparation will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by Thompson and Franklin [17]. By addition of triethanolamine, larger crystals will be obtained, which is correlated – unfortunately – with a broader particle size distribution [18].

By using a seeding technique it is hoped to solve the problem of the wide crystal size distribution. The seed crystals will be prepared in a microwave-supported preparation. Crystal growth will take place in a diluted sol batch far below the nucleation threshold with continuous addition of fresh sol solution. In time intervals the autoclave will be stirred.

3.2.2. LTA (Gallophosphate GaPO₄, Aluminiumphosphate AlPO₄, cation-free LTA)

Both the possibility of diffusion measurements free of the influence by exchangeable cations and the availability of MD-simulations for the self-diffusion of the short-chain-length (n-) alkanes (see, e.g., [19]) make diffusion studies with such materials highly desirable. MD-simulations of zeolitic diffusion in the absence of cations are considerably more reliable, since a number of complications (molecular interaction with the cations, position and movement of the cations, interaction of the cations with the lattice) do not occur in this case. The preparation of the gallophosphate with LTA structure will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by Kessler and Merrouche [20]. The synthesis of the aluminiumphosphate with LTA structure is based on a recipe submitted by Guth and Gies [20].

It is planned to do the preparation as a two-step synthesis completely in a microwave heating facility. In a first step, the seeds are prepared at a relatively low temperature level, than fresh solution is added and crystallization takes place at 140°C.

3.2.3. MFI (Silicalite-1 and ZSM-5)

Due to their brick-like shape, also the MFI-type zeolites are suitable for the direct observation of intracrystalline diffusion by IR and interference microscopy. Moreover, they may attain rather large particle sizes, which facilitate their investigation by transient methods. Their anisotropy and the fact that they generally do not exist as pure single crystals, however, substantially complicate diffusion analysis. The initially mentioned advantages and the very existence of defects in the structure as well as their practical relevance (application of ZSM-5 in heterogeneous catalysis) make this structure type a very important host system of the investigations.
The preparation of ZSM-5 will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by Lechert and Kleinwort [21]. High-alumina ZSM-5 is more difficult to prepare than the Al-free MFI structure silicalite-1. Often mordenite is found and it cannot be avoided. It is proposed, therefore, to focus at the beginning of the project on the MFI structure silicalite-1.

The preparation of silicalite-1 will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by Faust and Schott-Darie [22], which is based on [23]. In the silicalite-1 crystallization, all the experience gained in the optimization of MFI type silicalite-1 membranes varying the synthesis parameters can be used [24]. Benzene-1,2-diol will be used as an additional co-template. Silicalite-1 single crystals have been prepared in the presence of benzene-1,2-diol with a perfect morphology and in an appropriate crystal size ranging from 9x3x2 \( \mu \text{m}^3 \) to 165x30x30 \( \mu \text{m}^3 \), depending on the content of benzene-1,2-diol in the crystallization system. The concentration of the benzene-1,2-diol controls the morphology and the twinning of the well-shaped crystals [25]. The systematic variation of the crystallization parameters enabled the growth of well-shaped MFI crystals up to several hundred micrometers [26].

### 3.2.4. FAU (NaX/NaY)

X-type zeolites provide the largest crystallites among the zeolites of cubic structure. It is due to this reason and due to the (in comparison with all other types of zeolites so far investigated) most favourable measuring conditions for PFG NMR and QENS, that zeolitic adsorbate-adsorbent systems with zeolite X as the host system have been particularly carefully investigated. In fact, with zeolite X both reasonable agreement (viz. with methanol as a guest – see, e.g. [27]) and disagreement (viz., \textit{inter alia}, with benzene, see, e.g. [28]) between the (microscopic, equilibrium) PFG NMR and the (macroscopic, transient) sorption, ZLC and T-ZLC data have been observed. Important evidence about the nature of the observed diffusion phenomena may be deduced from a comparison of the diffusion data of unsaturated and saturated hydrocarbons, if the cation content (by applying X and Y zeolites) is changed.

The preparation will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by Lechert and Staelin [29].

The optimization of the synthesis parameters allows the growth of well-shaped single-crystals in stepwise sizes up to 210 - 245 \( \mu \text{m} \) [30].

### 3.2.5. AlPO\(_4\)5

Within the coordinated activities, zeolites of type AlPO\(_4\)5 are associated with a number of important issues. They concern in particular

- the special conditions under which molecular diffusion (“single-file diffusion” – see, e.g. [31]) has to proceed in one-dimensional channels,
- the most suitable measuring conditions for IR and interference microscopy, resulting from the fact that – supposing an intact channel system – the molecular profiles are directly observable, if the crystals are observed perpendicularly to the channel direction and
- the fact that irrespective of the perfect external appearance of the crystallites large intracrystalline ranges are found to be inaccessible by the guest molecules.
It is in particular the last item, which represents a special challenge for zeolite synthesis. Moreover, it is most likely to contain important information, how by internal interfaces molecular transport may be dramatically affected (and even - as in the given case - totally excluded).

The preparation will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by Caro and Girnus [32]. Large AlPO₄-5 crystals can be synthesized under conventional hydrothermal synthesis conditions using triethylamine as template [33]. Millimeter-sized CrAPO₄-5 and MgAPO₄-5 crystals with excellent morphology are obtained from concentrated gels containing HF [34]. These isotypic forms of AlPO₄-5 like CrAPO₄-5 are, e.g., known to possess – though far from being perfect - a better crystallinity. Very high-quality AlPO₄-5 crystals up to a length of 1.4 mm can be crystallized hydrothermally at a high dilution of the synthesis gel and by replacing the template triethylamine by tripropylamine [35]. The hydrothermal synthesis of silico-aluminiumphosphate molecular sieves is very sensitive to the synthesis conditions and the starting chemical sources. The incorporation of Si in the AFI framework (SAPO-5) controls the morphology and crystal size. By optimization of the hydrothermal synthesis, SAPO-5 crystals of well-shaped hexagonal rod-like morphology can be obtained [36].

3.2.6. Ferrierite

Zeolites of type ferrierite possess two mutually intersecting systems of parallel channels of different diameters. Therefore, depending on the size of the considered diffusants, both single-file behaviour (for molecular sizes intermediate between the two channel diameters) and normal diffusion through both channel types (for sufficiently small molecules) may be expected. In contrast to AlPO₄-5, which is of hexagonal, prismatic shape, ferrierite is available in the shape of thin platelets, with both channel systems in the platelet plane. It is a particular challenge for zeolite synthesis to ensure such a thickness of the platelets that internal concentration profiles become directly observable by IR and/or interference microscopy.

The preparation will be based on the recipe in the “Verified Syntheses of Zeolitic Materials” submitted by J. Dong [37]. Hydrothermal syntheses using different organic additives are reported in the literature, especially pyrrolidine [38] and tetra methyl ammonium cations [39]. Non-aqueous methods based on ethylenediamine plus triethylamine give good crystallinity, improved yield and larger crystals [40]. It will be tried to adopt the synthesis principle of large mordenite crystals in the presence of aliphatic alcohols to the ferrierite system. Under well-optimized conditions pure uniform and large single crystals were obtained. Single crystals of mordenite with different crystal sizes were obtained from the batch composition 0-4 ROH (aliphatic alcohol): 0.1 – 0.6 Na₂O : 0.002 – 0.02 Al₂O₃ : SiO₂ : 40 - H₂O can be obtained [41]. Furthermore, tetrahydrofuran as co-template will be used according to the paper “Synthesis of FER Type Zeolites in Presence of Tetrahydrofuran” [42]. In addition, some of the concepts proven for the MOR system will operate for the FER system as well [43].
3.3. **Working Programme: Preparation of zeolite composite membranes from well-characterized molecular sieve crystals**

In the beginning of the project the preparation work will be focussed on the crystallization of the different zeolite structures. 1 year after the beginning of the projects the preparation of model zeolite membranes by bringing selected zeolite crystals into a metal matrix for diffusion measurements will start.

The correlation and interpretation of the transport coefficients derived from supported zeolite membrane layers 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. It has been shown in the past that only preparation technologies without mechanical abrasion steps can be used. Because of the problems we had with 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 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 expansion between the zeolite and the metal matrix can be matched in certain temperature fields.

### 3.3.1 **Gas-tight embedding of zeolite in metal by galvanic techniques**

Good experience has been made with the embedding of individual MFI and AFI crystals in Ni or Ag foils by galvanic techniques using silver lacquer on a glass support for both (i) fixing the crystals during galvanic metal deposition and (ii) being the origin of the metal deposition where metal deposition starts. However, there are some technological problems to be solved. The metal foil with the embedded zeolite crystals has to be removed from the glass support (by using the solvent acetone) and then it has to be mounted in the permeation cell. Since the foil with the embedded crystals is flexible, often cracks between metal and zeolite were observed. Therefore, mechanically stable porous metal supports such as sinter metals will be used. The metal zeolite composite will not be removed from this support. Another problem of the past was the experience that aggregates of zeolite crystals could not be embedded perfectly. Inside the aggregate no galvanic metal deposition took place (pin hole). We will, therefore, in this project use metal plates with equidistant holes for the isolation of the crystals. Metal deposition can start from the metal grid.

### 3.3.2 **Gas-tight embedding of zeolite crystals by gas phase techniques such as sputtering and plasma etching**

Some problems of the galvanic techniques are the incorporation of additives of the galvanic standard baths such as tensides or phosphate salts in the zeolite structure. It is relatively difficult to remove them from the pores. Gas-phase deposition techniques such as sputtering can avoid these problems. A rotating sputter target or a rotating substrate have to be used for a homogeneous metal deposition. The thickness of the metal layer should be larger than the crystal dimension perpendicular to the support. In cooperation with the BAM Berlin we could show that the metal film is gas-tight indeed. For the deposition of such relatively thick layers high-power sputter units are necessary. After metal deposition, the top of the crystal has to be made free of metal for adsorption and permeation by anisotropic plasma etching. For a smooth surface this has to be made again on a rotating plate or with a rotating plasma source.
3.4. References for Chapter 2 and 3


5. H. Gobarkar, O. Schäf, P. Knauth, Angew. Chem. 113 (2001) 3948


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4. Requested Financial Support

4.1. Personnel

1 experienced PostDoc (BAT Iia) is needed to reach the goals of this ambitious synthesis programme as the most crucial part of the whole package. 8 different zeolite structures will be crystallized in a high quality incl. a controlled variation of defect concentrations (from single crystals to twinned ones and highly intergrown specimens) over longe ranges of crystal sizes in relative large amounts. In the leading synthesis groups worldwide, there exist in one group not more than 2 or 3 established recipes to prepare high-quality specimens of a certain structure type. We have the ambitious goal to prepare 8 different structure types ranging from silicates, aluminiumsilicates to aluminiumphosphates. This requires a scientific experience in this field of zeolite crystallization.
The different syntheses will be based on IUPAC recommended *Verified syntheses of zeolitic materials*. However, these recipes describe the synthesis for a certain sol/gel composition usually in a 50ml tube, which give a few mg of zeolite material, often with tiny (< 1 µm) crystals. Besides the modification of the recipe to get larger crystals (controlled variation of the batch composition; usually higher dilution with water and higher contents of template give larger crystals, since nucleation is suppressed relative to crystal growth) and crystals with stepwise modified defects (disturbing the crystallizing system by stirring and addition of new feed), we have to solve a scale-up problem of the order of the factor of 100 working with 1 l autoclaves.

1 PhD student (BAT Iia/2) is needed to follow novel non-established synthesis routes such as the use of microwave heating in combination with seed crystals, the application of micells and tensides. Special attention will be paid to establish a model for the influence of the crystallization parameters on the kind and concentration of structure defects (deviation from single crystal) found in the prepared zeolite crystals.

It is planned to work out the 8 different syntheses of the molecular sieve structures in small 50 ml autoclaves and then to transform them into the 1 l scale. Even working with 1 l autoclaves, the amounts of zeolite necessary for the parallel studies require several repeated crystallizations. For example, the standardized AFI synthesis gives 3 g product from ca. 110 g of batch. Using a half-filled 1l-autoclave, three subsequent crystallizations of 6 h each are necessary to give the 45 g product. For a larger AFI crystal size, more diluted gels with higher content of organic template will be used which makes it necessary to conduct six runs in the 1l autoclave to give 45 g of product.

### 4.2. Durable Equipments

#### 4.2.1. Crystallization of high-quality molecular sieve materials for the project

1 Parr autoclave 1l with magnetic stirring, pressure sensor, temperature sensor, heating device, addition of feed and removal of product during the crystallization 29 000 €

20 Parr autoclaves of 80 ml each 20 000 €

2 heating blocks for 80 ml Parr autoclaves 5 000 €

1 Microwave heating facility 20 000 €

#### 4.2.2. Preparation of zeolite composite-membranes

1 Simple galvanic device for metal deposition 4 500 €

1 Plasma burner 4 500 €

### 4.3. Consumables

Altogether 15,000 € per year. According to the recipes of “Verified syntheses…” only standard starting chemicals can be used. The scale up from the 80 ml to the 1l autoclave will require larger amounts of relative expensive chemicals, especially of organic template molecules. For modifying the standard recipes to control crystal size and defect concentrations, additional chemicals are needed.
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 3000 € 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 advice in particular areas of zeolite synthesis and membrane preparation, cooperation with the following scientists is planned:

Zeolite crystallization: P. Behrens (Hannover), W. Schwieger (Erlangen), F. Schüth (Mülheim), M. Noack and H. Kosslick (Berlin), J. Lercher and J. Kornatowski (München), K.K. Unger (Mainz).


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

Prof. Dr. Jürgen Caro