Application for Extension of Financial Support of

Project 1:
Synthesis of Zeolite Crystallites
for Diffusion Measurement

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

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1. General Information

1.1. Applicant

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1.2. Topic

Synthesis of Zeolite Crystallites 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, support by DFG since 2003

1.6. Period of Support Applied for

three years

1.7. Total Period of Support

support started November 2003,
extension requested starting from November 2006

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). The main activities during the second period will concern

(i) consolidation and maintenance of supply by these zeolite types, the synthesis routes of which have been established during the first period of support (viz. NaX, NaCaA),

(ii) progress in the structural verification and the intentional creation/abolishment of transport resistances operating in addition to the genuine zeolite bulk phase, located either on the surface of the zeolite crystallites ("surface barriers") or (e.g. in the form of stacking faults or twinning interfaces) in the crystallite interior,

(iii) exploration of novel synthesis routes to zeolite crystallites for 1D-diffusion studies and diffusion measurement in cubic, cation-free pore spaces, as two special cases of particular relevance for diffusion measurement and modelling, without the structural defects inherent so far to the recipes known from literature and

(iv) synthesis of selected extra-large zeolite crystals for single-crystal permeation studies, primarily concentrating on the set of host systems considered by the consortium, but with the option of trials with other zeolite types if they are easier to get grown as extra-large crystals.

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

2.1. State of the Art

The General Introduction to the package of requests for extension illustrates the rather unsatisfactory situation with our present knowledge about zeolitic diffusion, i.e. about one of the key processes governing their practical application. In parallel, it has been demonstrated that a continuously increasing number of publications emphasizes the great relevance of the topic. They include sophisticated theoretical approaches [1-9] in need of their proof by adequately reliable experiments, challenging technological projects based on aspects of zeolitic diffusion [10-15], novel principles of diffusion measurement [16-19], diffusion anomalies [20-27] and an overwhelming number of "new" systems to be investigated [28-39], with the inherent risk of new misinterpretations as long as the "old" problems are still unsolved.

In parallel, the progress made in this field due to the activities of the consortium during the first period of support has also been highlighted. This concerns in particular the great step ahead which has become possible owing to the availability of zeolite material for all partners as well has for research groups from outside who were involved in the activities of our groups, including D. Theodorou and T. Steriotis, Athens [40], O. Klepel, Leipzig [41], V. Bourdin, Paris [42], and J. Lercher and A. Jentys, Munich [43, 44], owing to both the activities within this project and the involvement of the groups of Mülheim and Stuttgart, complementing the available spectrum of materials.

2.2. Own Activities in the First Period

Standardized methods to synthesize zeolites A and X with variable crystal sizes and narrow size distributions have been established [45], employing concepts of slow release of reactants

and diffusion control in the crystallization systems using organic additives. Zeolite A of sizes of ca. 10, 20, 40 μm and zeolite X of ca. 50 and 80 μm have been synthesized in sufficient quantities, and have been made available for project partners for further diffusivity measurements [46, 47]. Results of adsorption and diffusion upon these materials begin to appear [48] .

Synthesis of aluminium phosphates molecular sieves has been one of the expertises of J. Caro. One of the established synthesis recipes is the verified synthesis of $AlPO_4$-5 as a standard of the International Zeolite Association. Further optimization of this recipe aiming at large quantity and high quality materials for diffusion measurements is currently carried out. We succeeded in the synthesis of large crystals with lengths up to 500 μm. Problems to be solved are broad distributions of crystal sizes and crystal intergrowths to various degrees.

Owing to support by the colleagues of the University of Stuttgart (J. Weitkamp, R. Gläser, C. Berger), a sophisticated method to synthesize large crystallites of zeolite Y up to 5 μm with variable Si/Al ratios has been established for the consortium [49]. The colleagues at MPI Mülheim (F. Schüth, W. Schmidt) helped us with large crystals of silicalite-1, including a thorough characterization of their microstructure and the option to separate single-crystal specimens from twinned crystals [50].

Furthermore, a method to build-up and to fine-tune the surface barriers of zeolites through liquid-gas-phase-deposition of tetraethyl orthosilicate (TEOS) has been set up. We have applied this method to build-up surface barriers on samples of 4A and 5A zeolites . Preliminary investigation of the project partners in Leipzig on these samples indicate that transport resistances due to surface barriers represent an important issue in understanding micropore diffusion processes. The publications "Quantifying surface barriers on nanoporous particles by pulsed field gradient NMR" by M. Krutyeva, D. Tzoulaki, C. Krause, S. Vasenkov, J. Kärger, X. Yang, and J. Caro, and "Surface barriers and their influence on transient sorption by A-type zeolites" by D. Tzoulaki, P. Kortunov, M. Krutyeva, S. Vasenkov, J. Kärger, X. Yang, and J. Caro are in preparation, see also [51, 52]. To explore the significance of surface barriers is gaining attention, and will be devoted more works in the whole project.

With respect to material characterizations, we have been developing a crystallographic method to determine the amounts, the positions and orientations of small guest molecules that are entrapped in void spaces of zeolites, and to extract information of possible host/guest interactions in such systems [53-55]. This method is applicable to the characterization of zeolite-based adsorbate/adsorbent complexes at equilibrium states [54, 56], and to understand the role of template molecules during zeolite crystallization [53, 55]. The publication "Solvothermal synthesis of silica-sodalite: effects of water, germanium and fluoride" by X. Yang, D. Albrecht, and J. Caro has been submitted in June 2006.

In order to expand the scope of available materials for micropore diffusion studies, in parallel, also research in the field of metal-organic-framework (MOF) materials has been performed. We successfully achieved the synthesis of a microporous manganese formate with a well developed crystal habit and large crystal sizes. The relationship between the crystal morphology and the 1D pore system could be revealed by Interference and IR microscopy. The publication "Oriented crystallisation on supports and anisotropic mass transport of the MOF manganese formate" by M. Arnold, P. Kortunov, D. J. Jones, Y. Nedellec, J. Kärger, and J. Caro is submitted to Angew. Chem. Int. Ed., see also [57]

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, EPSRC and NSF, with the request of respective support of the relevant groups. In continuation of the efforts during the first period and in contact with the partners of the groups in Mülheim and Stuttgart, the activities have to concentrate on both the application of verified recipes of zeolite synthesis and the exploration of novel synthesis routes 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, and have to meet the following, quite general aims:

1. Synthesis of microporous crystalline materials of the same zeolite framework type but different chemical compositions, such as metal aluminosilicate, aluminium phosphate, and pure-silica polymorphs.

2. Synthesis of standard zeolites of types LTA and FAU, incl. their modification by chemical treatment (surface barriers) or modifying the transport and adsorption behavior by ion-exchange.

By comprehending the expertise to synthesize a number of zeolite materials of different framework types with sufficient crystal sizes and well developed crystal habits, including zeolites A, X, ferrierite, silicalite-1, and AlPO4-5, a comparison and analysis of the values of molecular diffusivity in micropores, obtained by employing different measurement methods, becomes possible. The variety of framework types offers us a complaisant freedom to define beforehand the geometry of pores to be studied, one of the most profound parameters influencing diffusion and adsorption behaviors. However, beside pore geometry there are other equally important factors that are pivotal to molecular diffusion, such as physical and chemical heterogeneity of pore walls, i.e., defects and various chemical compositions; sometimes the indispensable co-existences of guest species in pores, e.g. extra-framework cations etc. The versatility of state-of-the-art chemistry of zeolites affords means to study those factors.

Recent developments in the "fluoride route" to synthesize high-silica and pure-silica zeolites facilitates large single crystals being defect-free [58, 59]. Our own research evidences that the same statement might apply as well to aluminosilicate zeolites [45] and zeotype aluminum phosphates AlPO4s [60]. This opens up a way to control the concentration or even to eliminate the existence of defects while governing morphologies during synthesis. Furthermore, holding the methodology and proficiency of High Resolution Transmission Electron Microscopy, we are able to characterize the type and quantity of defects, as well as other microscopic features of the structure, e.g. intergrows of crystals, interpenetrations of crystallographic planes, modulated sub-structures in a crystalline phase etc. These pieces of information about microstructures are highly precious, especially when unexpected diffusion/adsorption phenomena are observed and to be explicated by project partners.

The efforts during the first period of support revealed substantial difficulties in elaborating a technology for the fabrication of the aspired single-crystal membranes, see also section 2.2.1. of Project 4. 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 μm, which have been applied in the so far only successful attempts to produce single-crystal membranes [61-63]. 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 [64] shall be followed.

3.2. Working Programme: Crystallisation, Characterization and Modification of High-quality Zeolites for Diffusion Measurements Within the Consortium

Tab. 1 provides an overview of the key host materials for the comparative diffusion studies scheduled to be performed within the research group.

Lattice neutrality and all its benefits for simplifying simulation and modelling make it generally desirable to perform diffusion measurements with the cation-free zeolite isotypes. There are, however, three important reasons which make it necessary to as well include aluminosilicates in our considerations:

(i) They are the most frequently used zeolites in technology and science
(ii) The contents of cations allows an ideal variation of the host properties by cation exchange
(iii) In some cases, cation-free synthesis is associated with decisive deficiencies in the perfection of the crystal structure and unable to yield crystal sizes of the desired size. Therefore, in addition to the cation-free isotypes as the main target, tab. 1 also refers to some aluminosilicates.

Framework Type	Material	Remark	Pore Dimension
LTA	Aluminosilicate = Linde type A (optional: ZK-4 and zeolite alpha with Si/Al up to 5)	Variable Si/Al ratio	3D, 8-ring
	Pure SiO_2 = ITQ-29	Corma's LTA	
	Aluminium phosphate	Guth's $AlPO_4$	
MFI	Pure SiO_2 = silicalite-1	Pentasil	3D, 10-ring
	(optional: Aluminosilicate = ZSM-5)		
(optional:**MEL**)	Pure SiO_2 = silicalite-2		
	Aluminosilicate = ZSM-11		
FAU	Aluminosilicate Zeolite X	Variable Si/Al ratio	3D, 12-ring
	Aluminosilicate Zeolite Y		
FER	Pure SiO_2 ferrierite	Gies' invention	2D, 8 and 10-ring
	(optional: Aluminosilicate ferrierite)	Vaughan's work in 1966	
AFI	Aluminium phosphate = $AlPO_4$-5	Caro's standard	1D, 12-ring
	Aluminosilicate SSZ-24	Zones'	

Table 1: Host systems scheduled as key materials for the diffusion experiments planned to be performed within the research group

Similarly, in addition to MFI, among the pentasils also MEL-type zeolites are mentioned in tab. 1. If available with sufficiently large crystal sizes and with perfect habitus, their higher (viz. tetragonal) symmetry would notably facilitate the analysis of the diffusion experiments in comparison with MFI. This is a simple consequence of the fact that an accurate data analysis has to take account of diffusion anisotropy.

Following Tab. 1, the envisaged activities to care for the respective types of zeolite material are described in some more detail.

3.2.1 Target Material 1: LTA Framework

The framework type LTA defines a crystalline structure with a spherical cage that is accessible through six identical 8-ring windows opening isotropically in a 3D Cartesian coordinate system parallel to the directions of the axes. The diameter of the circular window is about 4.1 Å, a figure that varies with the chemical composition of type materials chosen.There are three known chemical designations for zeolitic materials with LTA type framework:

1) the sodium aluminosilicate zeolite Linde Type A [65], and its variations zeolite ZK-4and zeolite Alpha [66], both with higher Si/Al ratios up to 5;

2) the pure silica polymorph ITQ-29 recently reported by A. Corma et al.[67]; and

3) the aluminum phosphate molecular sieve synthesize by J.-L. Guth et al.[68].

We have optimized methods to synthesize the first variation of the aluminosilicate material in forms of large and uniform crystals with sizes up to ca. 40 μm. Since even this remarkably large size is still below the minimum extensions desirable for manufacturing reliable single-crystal membranes [61-63], particular concern shall be devoted to the synthesis of - at least a few - extra-large A-type zeolites (with, hopefully, sizes between 50 and 100 μm). Even if only a few crystallites may be provided, owing to interference and IR microscopy which as well operate with single crystallites, comparison with other techniques is possible. Moreover, with an output of a few milligrammes of such large crystals, application of the ZLC technique as the most sensitive macroscopic method shall become possible.

A real breakthrough has been achieved in the deliberate formation and modification of surface barriers by TEOS treatment. For the first time, ways to their quantification by both PFG NMR studies and interference microscopy could be explored, see section 2.2. By subjecting A-type zeolites of varying sizes to the thus approved procedures of surface modification, the material basis shall be created which allows a systematic application of all measuring techniques of the consortium, sensitive to surface barriers, to one and the same system. Comparison of the obtained results represents a crucial test of the compatibility of the techniques applied and of the working hypothesis that, subject to the same limiting conditions, all techniques of diffusion measurement should yield coinciding data.

According to literature, ITQ-29 can be synthesized with ca. 20 μm in size, and Guth's $AlPO_4$ is to be obtained with a size of ca. 80 μm. The aluminosilicate framework possesses a negative electronic charge, which is compensated by exchangeable cations located in the cages, while ITQ-29 and Guth's $AlPO_4$ are cation-free. These three materials represent a good set of samples which possess the same type of pore-geometry (not the same pore-geometry), and differ from each other in terms of pore-wall heterogeneity and extra-framework cations.

3.2.2. Target Material 2: MFI and MEL

Framework types MFI (ZSM-5 and silicalite-1) and MEL (ZSM-11) are pentasils constructed with 5-rings as secondary building units (SBU). Both structures exhibit three-dimensional 10-ring channels. MFI has two kinds of intersecting channels, a straight one of ca. 5.6 Å × 5.3 Å in size, a sinusoidal one of ca. 5.5 Å ×5.1 Å. MEL has only one type of straight channel of ca. 5.4 Å × 5.3 Å large, which is also accessible though 10-ring windows on wall sides. Both frameworks are available as samples of sodium aluminosilicate zeolites, of names ZSM-5 [69] and ZSM-11 [70], respectively; and as pure-silica polymorphs, silicalite-1 and silicalite-2 [71]. They are good examples of 3D medium rings among all microporous materials. In [72, 73], for the first time the interdependence of the principal elements of the diffusion tensor in such structures has been elaborated, in which the higher symmetry of MEL is shown to be of substantial advantage for a separate determination of the tensor elements. The Mülheim colleagues have established a method to prepare large single crystals of MFI type materials [50, 64]. Methods for MEL have to be developed.

3.2.3. Target Material 3: FAU

Both zeolite X and Y possess the framework type FAU, but with different Si/Al ratios. FAU has 3D cage systems with 12-ring windows of diameters at 7.4 Å. The building blocks of this structure is the same as in LTA, i.e., the sodalite cage. Therefore, it is always strategic to have samples of this structure in parallel with those of LTA in the diffusion measurements, and to compare the results. Moreover, X-type zeolites may be synthesized with the largest crystal sizes among systems of cubic symmetry. First successful attempts to synthesize Y-type zeolites with sizes up to the range of 10 micrometers [41, 49] have been performed by our Stuttgart colleagues.

3.2.4. Target Material 4: FER

Two perpendicularly intersecting straight channels define the FER structure. One of them opens with elliptical 10-rings of a size 5.4×4.2 Å, the other has 8-ring openings of 4.8 Å × 3.5 Å. Type materials are sodium aluminosilicate ferrierite [74] and pure-silica ferrierite [75]. A synthetic recipe to obtain large crystals of FER type aluminosilicate has been found within the frame of this project [76, 77]. In collaboration with the Stuttgart group, the further development of synthesis procedures leading to large pure-silica ferrierite crystallites is among the main activities of the next period, in particular with respect to the exploration of methods to tailor and to deliberately differentiate the accessibility of the two types of micro-channels.

3.2.5. Target Material 5: AFI

The framework type AFI illustrates a well-known example for 1D micropore structure. It describes a 12-ring straight channel of a diameter at ca. 7.3 Å. A standard synthetic recipe optimized by J. Caro produces large single crystals of zeotype aluminum phosphate AFI-AlPO4-5 [60]. An isostructural sodium aluminosilicate material named SSZ-24 is known, and obtainable as hexagonal rods of ca. 10 μm longitudinal extension, that are composed of thin plates on top of each other [78]. So far, all microscopic studies with such 1D zeolite structures did reveal dramatic deviations from the expected textbook structure where AFI-type zeolites have to be expected as "bundles of macaronis" of atomistic dimension [79-87]. Hence, for a successful performance of 1D diffusion experiments a further optimization of the present recipes is inevitable.

3.3.   References

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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. 6 different structure types, each with some modifications, have remained within the focus of the research group. They have to be crystallized in a high quality. The activities include a controlled variation of defect concentrations (from single crystals to twinned ones and highly intergrown specimens) over long ranges of crystal sizes in relatively large amounts, the deliberate formation and abolishment of additional transport resistances ("surface barriers") and their structural manifestation as possible by the methods of structure analysis. 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 6 different structure types ranging from silicates, aluminosilicates to aluminiumphosphates. This requires exceptional 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).

It is planned to work out the 6 different syntheses of the molecular sieve structures in small 100 ml autoclaves and then to transform them into the 1 l scale. We have to solve a scale-up problem of the factor of 10 working with 1 l autoclaves. 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

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 €

10 Parr autoclaves of 100 ml each   20 000 €
2 heating blocks for 100 ml Parr autoclaves   5 000 €

4.3. Consumables

Chemicals for Synthesis: 10,000 € per year. According to the recipes of "Verified syntheses of zeolitic materials" only standard starting chemicals can be used. The scale up from the 100 ml to the 1l autoclave will require larger amounts of relatively 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

Implying that the group meetings are ensured by central funding the travelling budget has primarily to be used for keeping personal contact with the relevant leading laboratories of zeolite synthesis, in particular with J. Kornatovski, W. Schmidt (Mülheim) and R. Gläser (Stuttgart), and for conference participation (Annual German Zeolite Conferences, Conferences of the International Zeolite Association and Adsorption Association). Therefore, a total amount of 2,000 € per year, corresponding to 6,000 € for the total period of time is requested for supporting visits and conference participation.

5. Requirements for the Success of the Application

5.1. Team Members

a) Prof. Dr. Jürgen Caro (applicant)
b) The research group of J. Caro consists of about 25 persons.

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, cooperation with the following scientists will be continued: P. Behrens (Hannover), W. Schwieger (Erlangen), W. Schmidt and J. Kornatowski (Mülheim), R. Gläser (Stuttgart), M. Noack (Berlin), K.K. Unger (Mainz), J.-L. Guth (Mulhouse), D. HJ. Olson (Piscataway).

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-worker, 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, June 19, 2006

Prof. Dr. Jürgen Caro