Joint application for financial support of a

Package of Research Projects

on

Diffusion in Zeolites

by
CNRS (France)
DFG (Germany)
EPSRC (United Kingdom)
NSF (USA)

Extension for the Period from 2006-2009

Stefano Brandani, London
Jürgen Caro, Hannover
Hervé Jobic, Villeurbanne
Jörg Kärger and Petrik Galvosas, Leipzig
Johannes Lercher and Andreas Jentys, München
Ferdi Schüth and Wolfgang Schmidt, Mülheim
Dhananjai B. Shah, Cleveland
Reiner Staudt, Leipzig
Jens Weitkamp, Stuttgart
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(J. Caro, extension of funding by DFG requested through this proposal)

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(R. Staudt, extension of funding by DFG requested through this proposal)

Project 3: ZLC and Tracer(T)-ZLC Diffusion Studies with Zeolites
(S. Brandani, extension of funding by EPSRC, to be applied for)

Project 4: Diffusion Studies with Composite Zeolite Membranes
(D.B. Shah, funding by NSF, to be applied for)

Project 5: Studying Zeolitic Diffusion by Interference and IR Microscopy
(J. Kärger, extension of funding by DFG requested through this proposal)

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(P. Galvosas and J. Kärger, extension of funding by DFG requested through this proposal)

Project 7: QENS Studies of Zeolitic Diffusion
(H. Jobic, extension of funding by CNRS, to be applied for)

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(A. Jentys and J. Lercher, DFG funding requested through this proposal)
General Introduction

1. Motivation

The introduction of novel routes of synthesis and the refinement of established ones gave rise to an explosion in the variety of nanoporous materials [1]. This unprecedented wealth of structure types, their manifold application for basic industrial technologies as heterogeneous catalysis [2] and mass separation [3], their potentials for the development of new technologies [4] and - last but not least - their unique role as a model system of fundamental research of molecules under confinement have placed nanoporous host-guest systems among the top systems of interest in current research.

The rate of molecular transportation, i.e. the intrinsic diffusivity, is one of the key quantities characterizing such systems. In many practical applications, including mass conversion and separation, intracrystalline diffusion may represent an important step within the total processes, controlling its overall performance. On the other hand, diffusion is among the most general, omnipresent phenomena of nature and hence of particular relevance for fundamental research.

Most remarkably, some 70 years ago, the first systematic investigations of zeolites as the still most prominent class of substances among the nanoporous materials, did also include studies of molecular diffusion [5]. However, irrespective of this long history, our knowledge of this very basic process for both fundamental research and practical application is still by far not satisfactory: Though intracrystalline (intraparticle) diffusion was identified as the rate-limiting process in many technical applications of nanoporous materials [1, 2, 6-8] and was in the focus of myriads of theoretical studies [9-11], the experimental evidence about the relevant coefficients continued to be highly contradictory [12].

The need for a solution of this problem is emphasized by the continuously increasing publication numbers in the field. They include sophisticated theoretical approaches [13-21] in need of adequately reliable experiments, challenging projects considering technological aspects of zeolitic diffusion [22-27], novel principles of diffusion measurement [28-31], diffusion anomalies [32-39] and an overwhelming number of "new" systems to be investigated [40-51], including the risk of new misinterpretations as long as the "old" problems are still unsolved.

It has become obvious that an eventual clarification of this problem necessitates a concerted cooperation of the experts of the - highly sophisticated - measuring techniques, based on the availability of a specially designed material basis. The present initiative strives to meet both requirements, i.e. to ensure a concerted application of the most important techniques of diffusion measurement to identical zeolite specimens.

The chart on page 2 provides an overview of the techniques comprehended in this initiative and their specification with respect to the length scales of direct observation of mass transfer and to the physical situation under which the experiments are performed.

In a first period of activities, this novel route of attacking the long-lasting problem of "zeolitic diffusion" proved to be seminal and led to first important results. With the present application for extension we ask for the option to fully exploit the potential of the research network established during the first period of support. The extension of our work aims at a final
(which means in particular an exemplarily quantified) clarification of the origin of the large differences in the messages of the different measuring techniques, including the correlation with the structural peculiarities giving rise to these differences.

Further on, recognizing the challenges of theory and the demands of practical applications which generally imply multi-component rather than single-component sorption [52, 53], also multi-component diffusion studies are envisaged, aiming at a generalization of the explored limiting steps in molecular transportation to multi-component systems.

2. Main Achievements of the First Period of Support

2.1. Material Basis

In collaboration between the Hannover Group (funded within the package) and the groups in Mülheim and Stuttgart (associates), a sound basis of identical material for all partners could be established. This basis also includes options to deliberately modify the surface of the zeolite crystallites. They aim at the formation of well-defined surface resistances or - vice versa - at abolishing surface resistances possibly resulting in the course of synthesis and/or template removal. The spectrum of zeolites so far available includes silicalite-1, ferrierite, NaCaA and NaX, with maximum crystal sizes, depending on the structure type, between 50 \( \mu m \) up to more than 100 \( \mu m \), which represents a unique, unprecedented starting point for the activities of the research groups comprised within the present package of applications. The zeolite-providing groups showed high flexibility and followed the requests for materials and modifications emerging in the joint work within the group to the best of the given options.

2.2. Results of Measurement

2.2.1. Deviations from the "Ideal" Zeolite Structure

The microscopic diffusion studies with zeolites revealed a multitude of deviations from the ideal zeolite structure, in particular in zeolites of type MFI, LTA and FER [54-57]. In this way, for the first time experimental evidence in favour of a particular hypothesis [58] to explain differences in the measured diffusivities could be provided. This explanation is based on the fact that in the presence of additional transport barriers the resulting diffusivities are the larger the shorter are the displacements followed by the different measuring techniques.

2.2.2. Non-monotonic Chain-length Dependence

The systematic investigation of the interrelation between the diffusivities determined by different techniques provided new insight into the chain-length dependence of the guest diffusivities in nanoporous host materials. For the first time in real (and reliable) experiments (notably by QENS), over a certain range of chain lengths, the diffusivity was found to increase with increasing chain lengths [59-61]. This phenomenon (under quite different terms like "window effect"[62], "resonant diffusion" [63] or "levitation effect"[64]) is among the most celebrated topics of molecular modelling in zeolites.

2.2.3. Combining Magic Angle Spinning and Pulsed Field Gradients in MAS PFG NMR

First measurements by MAS PFG NMR did successfully exploit the advantages of magic angle spinning (MAS, viz. enlarged observation times and highly resolved spectra) with pulsed field gradient NMR. For the first time, selective diffusion measurements in zeolites...
with as many as four components have become possible [65] and the spectrum of guest molecules accessible by observation has been notably enhanced [66].

2.2.4. Diffusion Measurements by Microscopically Recording Transient Sorption

Further methodological development of interference microscopy and measurement with materials specially synthesized for diffusion measurement led to first measurements of orientation-dependent diffusivities based on a microscopic application of Fick’s first and second laws, viz. in MOF manganese formate (confirming the regime of strict one-dimensional diffusion), in ferrierite where - due to selected surface blockage - the two-dimensional channel system is found to give rise to one-dimensional diffusion and in SAPO STA-7 materials where for the first time the three principal elements of the diffusion tensor could be simultaneously observed during molecular uptake. A 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 has been submitted to Angew. Chem. Int. Ed., see also [67]. The publications "Measurement and analysis of internal concentration profiles in nanoporous materials" by J. Kärger, P. Kortunov, S. Vasenkov, L. Heinke, C. Chmelik, D. Tzoulaki, D. B. Shah, R. A. Rakoczy, Y. Traa, J. Weitkamp and "Direct measurement of orientation-dependent diffusion in nanoporous crystallites" by P. Kortunov, M. J. Castro, D. Tzoulaki, J. Kärger, and P. A. Wright are in preparation, see also [68].

2.3. Dissemination and Scientific Exchange

The collaboration initiated within the present package of applications has developed in permanent exchange with the scientific community in the field. The means of exchange include the (DFG- and NWO-funded) International Research Training Group "Diffusion in Porous Materials" (see www.pore-diffusion.org) and the EC Network of Excellence "INSIDE-PORES" (see www.pores.gr), offering excellent prerequisites for the acquirement of supplementary zeolite material, for the comparison of the measured diffusion data with theoretical predictions and for their practical exploitation.

An even further reaching interaction is realized via the national (German, French and British) Zeolite Associations and the diffusion-dedicated website "Diffusion Fundamentals"(see www.diffusion-fundamentals.org) including the Diffusion Online Journal. The poster prizes delivered during the 18th German Zeolite Conference (Hannover, 1 - 3 March) and the First Workshop of INSIDE PORES (Montpellier, 19 - 23 March 2006 [69]) were rewarded to presentations out of this consortium.

In addition, the Diffusion Fundamentals Conference, Leipzig, 2005, [70] jointly organized with the German Physical Society, the Society of German Chemists, the German Bunsen Society and DECHEMA, served as an excellent stage to disseminate the results obtained within the consortium and, simultaneously, to provide evidence on the benefit of this very special type of international collaboration. We are happy that the international (and highly interdisciplinary) community of researchers will come together again in August 2007 when F. Brandani and J. Kärger, members of the consortium, will organize Diffusion Fundamentals II in L’Aquila, Italy.

Together with the funding of our group meetings by DFG, these dissemination activities facilitated the involvement of other groups and techniques, e.g. the Thermal Frequency Response method, into our past activities and notably contributed to the option to reinforce our further activities by involving further partners, viz. the groups in Munich (FR measurements) and Cleveland (single-crystal membrane permeation) for complementing our
experimental basis and the groups in Athens and Amsterdam for accompanying theoretical studies.

Within Germany, and even for interested participants from abroad, the 607th DECHEMA Colloquium "New horizons for diffusion research in nanoporous materials: Experiments, Theory and Application", scheduled for October 26th, 2006, will provide an excellent occasion to disseminate the outcome of the present collaboration. Presentations of the consortium (J. Kärger: Diffusion in zeolites - a never-ending story?, H. Jobic: Diffusion studies by QENS - measurements approaching the "ideal" situation, J. Caro: Ideal vs. real zeolite structure: options to discriminate, S. Brandani: Studying "macroscopic" aspects of diffusion) shall be accompanied by a talk highlighting the interdependence with theory (D. Theodorou: Correlating molecular modelling and experimental diffusivities) and contributions from industry (D. M. Ruthven: From diffusion research to industrial application, J. Oppermann: Mass transfer coefficients determined from break-through experiments, with U. Müller, BASF, chairing the colloquium)

3. Primary Issues for the Period of Extension

3.1. Quantitative Correlation of the Differences in the Diffusivities with their Structural Origins

Though first evidence has been provided that the differences in the results of the different measuring techniques may be related to the differences in the observed space and time scales, the rigor proof of this assumption is still missing. Such a rigor proof has to include:

3.1.1 merging of the PFG NMR and QENS self-diffusivities in the 10...100 nm range,
3.1.2 coinciding messages of microscopic (PFG NMR in the transition range from intracrystalline to long-range diffusion), mesoscopic (single-crystal permeation) and macroscopic (ZLC, FR, uptake/release) studies about the magnitude of surface permeability,
3.1.3 quantitative correlation of transport phenomena observed at equilibrium (QENS, PFG NMR, TZLC) and non-equilibrium (single-crystal permeation, ZLC, FR, uptake/release) under the conditions of diffusion limitation and (surface) barrier limitation.

3.2. Genuine Zeolitic Diffusivities

There is an urgent demand from both theory and application that for at least a few nanoporous host - guest systems diffusivity data coinciding for different measuring techniques are provided. Tab. 1 summarizes those host-guest systems which, following our application for the first period of support, shall be in the focus of such studies

<table>
<thead>
<tr>
<th></th>
<th>methanol</th>
<th>methane/ethane</th>
<th>n-alkanes</th>
<th>branched alkanes</th>
<th>aromatics</th>
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<tbody>
<tr>
<td>LTA</td>
<td>×</td>
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<td></td>
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<tr>
<td>Silicalite-1</td>
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<td>×</td>
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<tr>
<td>NaX</td>
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Tab.1: Compilation of the host systems and guest molecules primarily under consideration
3.3. Maintenance, Solidification and Extension of the Material Basis

Even before the detection of internal and external transport resistances in zeolites with the present studies, zeolites have been well-known as a type of matter, the state of which may be easily affected by both the way of synthesis and post-synthesis treatment. The availability of a reliable material basis is hence one of the key issues to be cared for within the application package. This means in particular and primarily the synthesis of zeolite specimens, as specified in tab. 1, with a smallest possible variation width in their properties. Properties of supreme relevance for the diffusion studies include crystal size, x-ray diffraction patterns and sorption capacities which may be determined by standard procedures. Moreover, each of these samples should also be comparable with respect to the existence and intensity of additional transport resistances which can only be explored by the diffusion measurements themselves.

As a particular challenge, zeolite synthesis and post-synthesis treatment should as well include the option of exclusion or deliberate formation of transport resistances (possibly occurring on the crystal surface and in the crystal bulk phase), acting in addition to the genuine zeolite pore structure.

The exploration of synthesis routes leading (i) to zeolite crystal structures exhibiting an ideal one-dimensional channel structure and (ii) to cation-free zeolites of type LTA remain in the focus of our synthesis activities. This may turn out to be a too ambiguous goal since we are not aware of any synthesis procedure described in the literature which has lead to crystals of the required ideal structure (see, e.g. the description of our diffusion studies with such systems in [71]) nor did our own attempts over the period of the last three years lead to such materials.

The accessibility of also these particular host systems, however, would be of great benefit for two important features of a theoretical, first-principles treatment of molecular diffusion under confinement. This concerns (i) the exploration of the interplay between normal diffusion and single-file diffusion in one-dimensional channel systems [72] and (ii) the availability of diffusion data for a host system, the properties of which are expected to provide ideal conditions for comparison between theory and experiment. These properties include the absence of cations (and hence of the need to care for the often cumbersome electrostatic interaction in the simulations) and the cubic symmetry. Moreover, as a consequence of the pronounced role of the "windows" between adjacent supercages for molecular propagation, due to entropic reasons in some cases molecular diffusion may be expected to be slowed down with increasing temperature [73]. Experimental observation and confirmation of this effect would doubtlessly represent an outstanding detection.

3.4. Diffusion Measurement with Multicomponent Systems

In essentially all practical applications nanoporous host systems accommodate mixtures rather than a single guest species. Under these conditions completely new effects, including the cross effects between different components, become relevant. The extension of the present concept to multi-component systems is most rewarding, therefore, from the view points of both fundamental research and application.

In contrast to single-component diffusion in zeolites which is completely described by only two parameters, viz. the coefficients of self-diffusion and of transport diffusion (and their
dependencies on concentration and temperature), multi-component diffusion within systems comprising \( n \) different types of guest molecules has to be described by matrices with \( n \times n \) elements, with each element depending on temperature and the concentration of each individual component present in the mixture [74-76]. Moreover, one has to have in mind that in our studies additional transport resistances rather than genuine intracrystalline diffusion were in many cases found to be rate determining for molecular propagation and that only with the present investigations a first systematic study of the nature of these resistances and their dependence on the guest molecule (including temperature and concentration) has been initiated. Therefore, these very first systematic comparative studies of multicomponent diffusion will be restricted to the limiting cases of self-diffusion (as accessible by - incoherent - QENS and PFG NMR, as well as by tracer ZLC and tracer IR microscopy) and of co- and counter-diffusion, observable by uptake/release measurements, ZLC, (Thermal) Frequency Response, IR microscopy and single-crystal permeation under two-component adsorption. In principle, this type of measurement may be performed with each of the host systems with any combination of the indicated guest molecules. Owing to the large size of the available crystallites and the large spectrum of suitable guest molecules, this type of experiments is planned to start with silicalite-1.

The envisaged availability of the complete set of diffusion data, viz. the (single-component) transport diffusivities and self-diffusivities of either of the considered components and the coefficients of co-, counter and self-diffusion under two-component adsorption provide a unique and unprecedented basis for the development and confirmation of theoretical approaches by molecular modelling. These options shall in particular be exploited within the Dutch-German International Research Training Group (R. Krishna, B. Smit, S. Fritzsche) and via the EC-funded long-term relations with D. Theodorou, Athens (NoE and Marie Curie Programme of 6th framework)

### 4. Guidelines of Cooperation

The consortium which with this package of applications asks for an extension of support, fulfils in an ideal way the requirements for a final clarification of the long-lasting problem of diffusion in zeolites, viz. expertness in the various fields of diffusion measurements, covering the total spectrum of microscopic, mesoscopic and macroscopic observation, associated with the option of zeolite synthesis and modification as a joint, reliable and purpose-directed material basis for these investigations.

The main results of the collaboration attained over the first period of support are summarized in section 2. From them, the primary tasks as listed in section 3 are derived. We are convinced that they provide a sound and reliable basis for providing the final, experimentally based clarification of the long-standing problem of molecular diffusion in nanoporous materials.
As over the first period, DFG is asked for sponsoring five research projects, including the option of regular meetings of the whole consortium twice per year. These projects include

**Synthesis of Zeolite Crystallites** (by J. Caro, Hannover, extension of previous funding)

**Transient and Equilibrium Measurement of Sorption on Zeolites** (by R. Staudt, Leipzig, extension of previous funding)

**Studying Zeolitic Diffusion by Interference and IR Microscopy** (by J. Kärger, Leipzig, extension of previous funding)

**PFG NMR Studies of Zeolitic Diffusion** (by P. Galvosas and J. Kärger, Leipzig, extension of previous funding) and

**Measuring Zeolitic Diffusion by the Frequency Response (FR) Technique**
(by A. Jentys and J. Lercher, München, new project replacing the former membrane project handled by J. Caro, Hannover, which is now continued by D. B. Shah, Cleveland)

The package of applications is completed by projects devoted to

**ZLC and Tracer(T)-ZLC Diffusion Studies with Zeolites** (S. Brandani, London, extension of previous funding by EPSRC to be applied for),

**Diffusion Studies with Composite Membranes** (D.B. Shah, Cleveland, presently awardee of a Mercator Professorship at Leipzig University, in continuation of J.Caro's project of the first period, funding by NSF to be applied for) and

**QENS Studies of Zeolitic Diffusion** (H. Jobic, Villeurbanne, extension of previous funding by CNRS to be applied for).

Furtheron, in the fields of

**Zeolite Synthesis, Modification and Characterization** the consortium may rely on the involvement of the MPI für Kohlenforschung, Mülheim, (F. Schüth, W. Schmidt) and the Institute of Chemical Technology, Stuttgart (J. Weitkamp) which continue to be involved in the consortium without additional funding.

In this formation, the consortium disposes of the most important techniques of diffusion measurement in nanoporous materials, including

**Frequency Response**
**Interference Microscopy**
**IR Microscopy**
**Membrane Permeation**
**Pulsed Field Gradient NMR**
**Quasi-Elastic Neutron Scattering**
**Thermal Frequency Response**
**Uptake and Release**
**Zero Length Column.**

During the last period, within the consortium with respect to the experimental basis for diffusion measurement particular progress has been made in Quasi-Elastic Neutron Scattering
(option of the simultaneous determination of transport diffusion, self-diffusion) \[59, 61, 77, 78\], in uptake and release measurements (response times of about 1 s and operation with mono-crystalline layers), in interference microscopy (first microscopic application of Fick's laws to transient diffusion) \[67, 68\] and in PFG NMR (introduction of MAS PFG NMR) \[65, 66\].

Approving a joint application by J. Kärger and J. Weitkamp, DFG has granted an IR imaging system (Hyperion 3000, Bruker) which is expected to be available in October 2006. With an effective pixel size of \(2.7\times2.7 \, \mu m^2\) and a time resolution down to 1 s it provides the consortium with unprecedented options for monitoring the evolution of intracrystalline concentration profiles.

In the comparative diffusion studies of n-alkanes in zeolites NaCaA and silicalite-1, which were in the centre of the activities of the research group \[59-61, 79-81\], PFG NMR could not overcome the limitations, imposed on the conventional application of this technique towards larger chain lengths. Stimulated by this deficiency in comparison with the other techniques, our activities also included efforts for a further development of PFG NMR methodology. In a series of experiments the great benefit of a combination of PFG NMR with the magic angle spinning technique (MAS NMR) was explored \[65, 66, 82\]. It could be demonstrated that a combination of PFG and MAS NMR notably releases the narrow limitations of conventional PFG NMR diffusion measurements of zeolite host-guest systems at relatively low mobilities \[66\] and that, moreover, in this way the options for multi-component diffusion measurements are significantly improved\[65\]. The option of magic angle spinning is excluded for our home-built high-intensity field gradient PFG NMR diffusion spectrometers FEGRIS FT and FEGRIS NT \[83-85\]. For our commercial BRUKER spectrometers AVANCE 400 and 750, in turn, we do not dispose of the necessary gradient units. As specified there in more detail, therefore, project 6 includes the application for DFG funding of the relevant device as a special investment for the consortium.

The availability of an unprecedented assortment of measuring devices has made the international research group an attractive place for visiting scientists who, in turn, significantly contributed (and are still going to contribute) to the scientific outcome of the consortium. This assessment concerns both experimentalists like D. M. Ruthven (University of Maine, Humboldt Research Awardee 2003/2004) and D. B. Shah (Cleveland University, Mercator Professorship 2005/2006) and theoreticians like R. Krishna (Amsterdam) and D. Theodorou (Athens), who are in a particularly close contact with the activities of the consortium via the Dutch-German International Research Training Group "Diffusion in Porous Media" and the EC NoE "INSIDE-PORES", respectively. Their involvement in the DEHEMA Colloquium "New horizons for diffusion research in nanoporous materials: Experiments, Theory and Application" on October 26\textsuperscript{th}, 2006 (see section 2.3.), which is also thought as an event for reporting the progress of the work within the consortium is particularly appreciated.
5. **Consortium-Induced Additional Benefit**

After decades of futile efforts to unveil the origin of the huge discrepancies between the results of different techniques on zeolitic diffusion for numerous systems, with the present package of proposals the first attempt to solve this problem by the coordinated, simultaneous application of the different techniques within a consortium of research groups, which dispose of the most important and most advanced measuring techniques, has been initiated. The diversity and the technical requirements of the various measuring techniques necessitate a high specialization, which cannot be afforded by a single group for all relevant methods. The simultaneous application of different techniques by different groups, however, can only be successful within a network of close cooperation. Only on the basis of detailed agreement on the systems to be considered, including the conditions of sample preparation and the parameters of measurement, a reliable and reasonable comparison between the results of different techniques is possible. While the lack of such coordination again and again prevented a satisfactory clarification of the discrepancies between the different literature data, the first results of the international research group indicate that, owing to the novel options provided via the present initiative, these deficiencies are overcome.

With the involvement of worldwide leading groups in zeolite synthesis (Hannover, Mülheim, Stuttgart) the consortium may perform their measurements with specimens stemming from one and the same source, as a primary prerequisite of the comparability of the attained results. Moreover, this involvement has been shown to ensure the immediate feedback between zeolite synthesis, diffusion measurement and zeolite modification as a unique chance to optimise the zeolite samples according to the requirements of the measurements and to reveal correlations between synthesis- and modification-generated structural features of the samples and their diffusion properties.

The groups brought together in the consortium are in the forefront of the development and application of the most important measuring techniques of zeolitic diffusion. For the second period of funding, requested for by this package of applications, this potential has been reinforced by the involvement of further groups. Their joint activities overcome the main deficiencies of previous work, which most probably has been the crucial obstacle in solving a long-standing problem.

6. **References**


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