Application for Extension of Financial Support of

Project 8:
Measuring Zeolitic Diffusion by the
Frequency Response (FR) Technique

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.   Applicants

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1.2.   Topic

Measuring Zeolitic Diffusion by the Frequency Response (FR) Technique

1.3.   Code Word

Diffusion by FR technique

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

1.5.   Scheduled Total Duration of Support
three years

1.6.   Period of Support Applied for

three years

1.7.   Total Period of Support

three years, beginning from November 2006

1.8. Summary

With this project, we are going to reinforce our research group with a technique of great versatility and manifold practical use for the investigation of dynamic phenomena. In the hierarchy of the experimental techniques coming together in our research group it occupies the "most macroscopic" position. This means, that in comparison with all other techniques the mathematical formalism between the primary experimental data and the elementary processes, which shall be unveiled by these measurements, is the most expensive one. The risk of misinterpretations inherent to such constellations, however, is generally overcompensated by the multitude of information resulting from this technique. Its evidence may be even further strengthened by combination with the thermal frequency response technique, as well accessible within the research group via our French partners (see project 7).

The inclusion of this new project without the need for enlargement of the personnel budget offered by DFG during the first period has become possible since Prof. DB Shah, Cleveland, Ohio, presently Mercator-Professorship awardee at Leipzig University and the world-wide top scientist in the field of single-crystal permeation, will continue the activities in the field of single-crystal membrane preparation and permeation, for which the Hannover group has cared during the first period.

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

2.1. State of the Art

In a Frequency Response (FR) experiment the pressure of the sorbate is periodically varied over the sample by applying a volume modulation to a closed system [1, 2]. While for the empty system the pressure modulation varies at the same frequency as the volume perturbation (180° out of phase), over a porous sample a change in the phase and the amplitude of the (pressure) response to (pressure) modulation is observed [1, 2]. The measurement of diffusion coefficients by the frequency response method is based on measuring the pressure response as function of the frequency of the pressure perturbation [3, 4]. The characteristic parameters of the frequency response experiment, i.e., the phase lag ($\Phi_{Z\text{-}B}$) and amplitudes (P_B and P_Z) obtained experimentally from the pressure response, are described by [5]:

in-phase: $(P_B/P_Z) \cos \Phi_{Z\text{-}B} - 1 = K \, \delta_c$

out-of-phase: $(P_B/P_Z) \sin \Phi_{Z\text{-}B} = K \, \delta_s$

$$\delta_c = (1/\eta)[(\sinh\eta + \sin\eta)/(\cosh\eta + \cos\eta)]$$
$$\delta_s = (1/\eta)[(\sinh\eta - \sin\eta)/(\cosh\eta - \cos\eta)]$$
$$\eta = (\omega L^2/2D)^{1/2}$$

$\Phi_{Z\text{-}B}$ is the difference between the phase lags in the presence and absence of the zeolite, P_B and P_Z the relative amplitudes of the pressure during the volume change in the absence and in the presence of the zeolite, ω the angular frequency of the volume modulation, D the diffusion coefficient and L the diameter of zeolite crystals. δ_c and δ_s, which are functions of the diffusion coefficient, are known as the in-phase and out-of-phase characteristic functions, respectively. K is a constant related to the gradient of the sorption isotherm at the equilibrium pressure p_e:

$$K = (RT_0/V_e)(dQ_e/dp_e),$$

where T_0 is the temperature, V_e the system volume, Q_e the equilibrium amount sorbed and p_e the equilibrium partial pressure. The in-phase and out-of-phase functions obtained from the experimental measurements over the frequency range can be fitted to obtain the diffusion coefficients [6, 7].

Reports in the literature describe the use of the frequency response method for studying the diffusion of linear, branched and cyclic alkanes [8-13], alkyl substitutes benzene molecules[8, 14-17], ammonia [18-20] and of noble gasses [21] in zeolites[22].

In comparison to the other methods for diffusion measurement the frequency response method offers the following advantages. (i) Only a small perturbation to the sorption equilibrium is applied, therefore, the concentration of the sorbed phase remains almost constant. By varying the equilibrium pressure before the experiment the diffusion coefficient can be determined as a function of the surface coverage. (ii) The compression and expansion cycles in the frequency response method give rise to both adsorption and desorption pressure responses in a single experiment. Thus, differences in the diffusion mechanisms for the two processes can be detected. (iii) The method is capable of separating two simultaneously occurring diffusion processes if the respective diffusivities differ by half an order of magnitude [5]. (iv) In principle, frequency enhancement allows the extension of the effective observation times to arbitrarily small values, as a unique feature among the macroscopic measuring techniques.

In a typical frequency response experiment the response to volume perturbation is followed by monitoring the pressure modulation inside the system with highly accurate pressure gauges [23, 24] or by measuring the temperature response of the sample by infrared measurements [25, 26]. Although a theoretical first-order approach to studying multi-component sorption by the frequency response method is described in the literature [27], to the best of our knowledge the diffusion of multi-component mixtures was not experimentally studied by the frequency response method so far. In their theoretical work, Sun *et al.* [27] show that the frequency response method should allow to differentiate between the diffusion of C_2H_6 and CO_2 in zeolite 4A. For these two molecules the difference between the diffusion coefficients, i.e., two orders of magnitude, is sufficient to differentiate between the two contributions using an integral signal such as the pressure response. However, for molecules with similar diffusion coefficients, e.g., xylene isomers or alkanes, spectroscopic methods with sufficiently high time resolution (i.e., rapid scan IR spectroscopy or mass spectroscopy) will be necessary to follow the partial pressure modulations of the individual components in the gas phase, thus allowing to monitor the uptake of the individual components out of a multi-component gas phase mixture.

2.2.   Own Activities in the Field

Over the last few years, sorption, diffusion and surface permeation as the relevant constituents of molecular transport were extensively studied for alkanes and aromatics in narrow- and medium-pore zeolites.

The sorption of alkanes in zeolites was investigated using calorimetry, gravimetry, and *in situ* infrared spectroscopy [28, 29]. At temperatures below 373 K, alkanes are found to be adsorbed localized on the strong Brønsted acid sites (bridging Si-OH-Al groups) *via* hydrogen bonding of the dipole induced in the alkane and the hydroxyl group. Two n-alkanes, but only one iso-alkane, interact simultaneously with Brønsted acid sites of H-MFI. The heat of sorption decreases in the sequence H-MFI > H-MOR > H-FAU because of the weaker undirected interaction in a larger pore. With increasing size of the hydrocarbon, the heat of adsorption increases primarily due to an increase in the dispersion forces. The linear relationships between the enthalpies and the entropies of sorption suggest that the interaction

is of similar nature for all hydrocarbons and characteristic for a particular pore size and shape of the zeolite.

For branched alkanes (i. e, 2,2-dimethylalkanes on the medium-pore zeolites FER and TON) the sorption on the outer surface and in the pore mouths of the zeolite crystals was studied [30]. At low coverage, all three dimethylalkanes were found to be adsorbed in parallel to the outer surface. As the coverage increases, additional 2,2-dimethylpentane and 2,2-dimethylhexane molecules are additionally adsorbed with the propyl and butyl groups pointing into the pore. Also, a large fraction of the 2,2-dimethylpentane and 2,2-dimethylhexane molecules, initially adsorbed parallel to the outer surface, rearrange into this sorption structure.

For benzene, the energetic and entropic contributions controlling the sorption on acidic (H/ZSM-5) and non-acidic (Silicalite-1) MFI type materials were studied using gravimetry, calorimetry and *in situ* IR spectroscopy to describe the qualitative and quantitative interactions of the aromatic molecules with the pores and the functional groups [31]. A model describing the sorption isotherms was derived, which indicated the presence of sterically constrained sorption structures for benzene in MFI type materials. The non-directed interaction of benzene with the pore walls controls the sorption energetically, while the directed interaction with the bridging hydroxy groups contributed only to a minor degree. Benzene located close to SiOHAl groups formed perturbed hydroxy groups, their wavenumber reflects the local sorption geometry of benzene as well as the acid strength of the hydroxy group and the base strength of benzene.

The diffusion of benzene and alkyl-substituted isomers was studied by uptake experiments followed by IR spectroscopy [32] and related to the shape selectivity in toluene alkylation with methanol and ethylene over HZSM-5 and the xylene isomerization. Post-synthesis surface silylation was found to significantly increase the para-selectivity of the zeolites, while significant changes in xylene diffusivities were not observed. Additionally, the silylation of ZSM-5 zeolite with tetraethylorthosilicate blocked active sites on the external zeolite surface [33].

The frequency response method was successfully applied to describe the diffusivities of toluene in HZSM-5 zeolites before and after silylation by chemical liquid deposition of tetraethoxysilane (TEOS) [34]. Two diffusion processes were identified by the frequency response method in both materials and tentatively assigned to the diffusion of toluene in the straight and sinusoidal channels of the zeolites. The differences in toluene diffusivities were associated with the tortuosity of the diffusion pathways in the sinusoidal channels and connected transport barriers. Silylation of the zeolite leads to a decrease in toluene diffusivities in the straight and sinusoidal channels of the zeolites. In addition, the relative importance of transport in the sinusoidal channels increases after the modification, while the total uptake remains unaffected. In contrast to earlier interpretations invoking the narrowing of the pores, the effect of surface modification is associated for the first time with arbitrary blocking of pore entrances, thus enhancing the tortuosity of possible diffusion pathways. A scheme of the novel model for describing the diffusion of toluene in H/ZSM-5 is shown in figure 1.
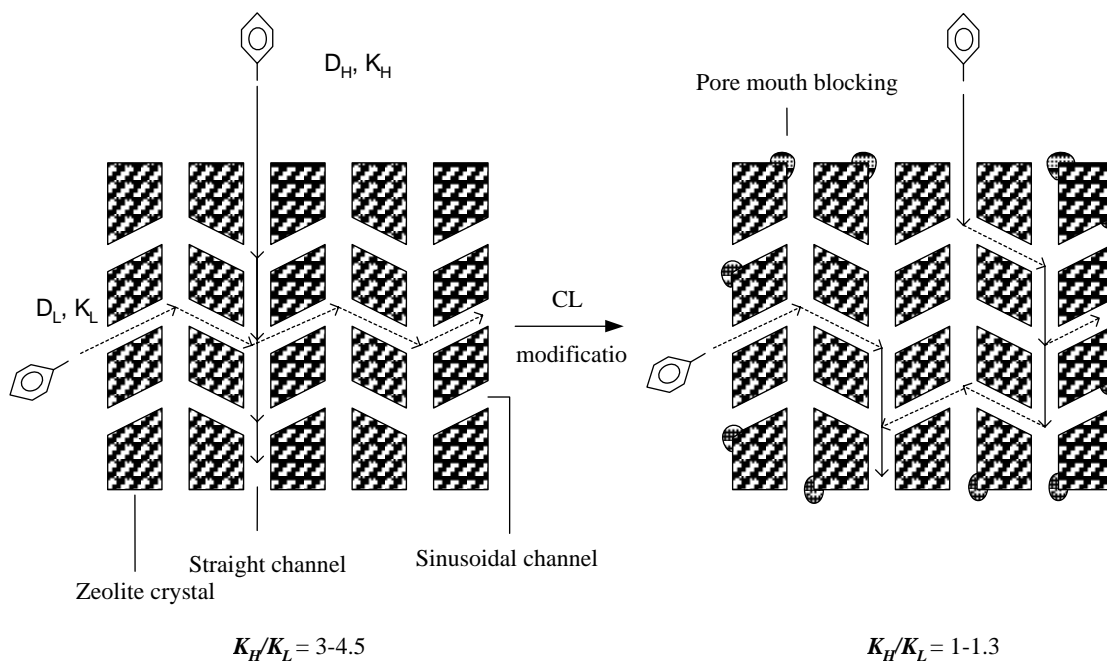
Figure 1:   Scheme of the diffusion pathways of toluene in H/ZSM-5 before and after
             modification with TEOS. The dashed lines denote the slow diffusion process and the
             solid line denote the fast diffusion process.

The elementary steps of sorption and transport of benzene, toluene, and o- and p-xylene from
the gas phase to hydroxy groups of zeolite H/ZSM-5 on the outer surface (SiOH groups) and
in the pores (SiOHAl groups) were studied using pressure modulations followed by fast time-
resolved IR spectroscopy [35]. Sorption on these acid sites occur *via* a common physisorbed
state on the outer surface. The equilibration of the molecules in this state was fast compared
to the sorption rates on SiOH and SiOHA1 groups. The relative rates of equilibration of
functional groups with the aromatic molecules suggest that the aromatic molecules move
freely on the outer surface of the crystals before reversibly binding to OH groups, entering the
micropores or desorbing. Molecules able to enter the pores (benzene, toluene, p-xylene) are
faster adsorbed on SiOHA1 groups than on SiOH groups. If the access of the molecules into
the pores is sterically constrained (o-xylene), the rate of adsorption on the remaining
accessible SiOH groups is strongly enhanced.

3.   Issues and Working Programme

3.1.   Issues

Within the project, the work will be divided into two parts. In the **first part** the frequency-
response method will be used to study the diffusion of the target molecules (see table in the
project introduction) in zeolites consisting of non uni-dimensional pore systems. The
frequency response technique has proven its potential for measuring diffusion coefficients of
hydrocarbon molecules inside the pores of microporous molecular sieves, where is was shown
that diffusion processes within the two channels can be differentiated up to differences in the
diffusion coefficients of less than one order of magnitude [34].

In the **second part** of the project the frequency response experiments will be extended to study the multi-component diffusion of molecules in zeolites. In the typical FR experiment the diffusion process is followed by monitoring the changes in pressure, which does not allow to differentiate between the uptake of different species. Within the project we will attach a small volume gas cell to the vacuum system of the frequency response system, which will be used to measure the concentration of the molecules in the gas phase using rapid scan IR spectroscopy.

3.2.   Working Programme

3.2.1. *Diffusion in Non-unidimensional Pores Studied by the Frequency Response Method*

Within the materials studied in this project Silicalite-1 (10 MR 5.1 Å × 5.5 Å and 10 MR 5.3 Å × 5.6 Å) and Ferrierite (10 MR 4.2 Å × 5.4 Å and 8 MR 3.5 Å × 4.8 Å) have pore systems consisting of two intersecting channels, while LTA (8 MR 4.1 Å × 4.1 Å), NaX (12 MR 7.4 Å × 7.4 Å) represent a three-dimensional network and AFI (12 MR 7.3 Å × 7.3 Å) contains uni-dimensional channels.

For the diffusion of toluene in MFI we have already shown by means of structure by the frequency-response method that the dimensions of the pores, just like the tortuosity of the channels, influences the diffusion processes [28, 34]. Within the project we plan to extend these experiments to the diffusion of xylene isomers and benzene in Silicalite-1, NaX and AFI and to the diffusion of linear and branched alkanes in Ferrierite and LTA, the materials with the smaller pore diameters, in correlation with the equivalent toluene studies of the partners.

From these experiments it will be possible to differentiate between the effects of pore diameter, channel intersections and transport barriers on the outer surface on the molecular diffusion. These experiments will complement our previous sorption studies of aromatic molecules [31] and alkanes [28, 30] on zeolites as well as the transport studies of aromatic molecules in MFI [35] and contribute to the description of the transport and sorption processes involved in technical applications such as sorption and catalytic reactions. As a very important issue, in direct comparison with the results of the other techniques applied to one and the same zeolite material within the consortium, it has to be clarified why in previous FR studies [9] the diffusivities obtained by this technique tend to be much closer to the microscopically determined values than to the results of the other macroscopic methods [36].

In addition, these experiments are necessary for the second part where the multi-component diffusion of aromatic molecules and of n- and iso-alkanes will be studied.

3.2.2. *Multi-component Diffusion of Molecules in Zeolite Pores Studied by the Frequency Response Method*

The application of zeolites in separation by sorption and (shape selective) catalysts typically involves the transport and sorption of two or more molecules, which might be reactants and/or products, in the zeolite pores. In this part of the project we plan to develop a strategy to detect the concentration of two (or more) molecules in the gas phase during the frequency response experiments using IR spectroscopy. An estimation of the intensity of the characteristic bands of toluene and xylene in gas phase, based on reference spectra measured in a multiple reflection gas cell with 1 m length, indicates that IR spectra containing about 500 to 1000 interferograms will have a sufficient signal-to-noise ratio to differentiate concentration

changes in the order of 1 ppm (which corresponds to a partial pressure change of 10^{-3} mbar). Based on this estimation a low volume multiple reflection IR cell, which can be directly connected to the vacuum system of the frequency response system, will be necessary. Two parameters will determine the design: (i) the volume of the cell has to be as low as possible to minimize the required volume displacement in the bellow system necessary to obtain the desired pressure step (typically 2-5 %) and (ii) a sufficient optical path length to detect the characteristic bands of the molecules from the gas phase spectra. In addition, the high frequencies (up to 1 Hz) of the typical frequency response experiment will require to use the rapid scan mode and a low spectral resolution (8 – 16 cm^{-1}) to measure the spectra of the molecules in the gas phase. Therefore, in the first part of this work-package characteristic bands in the IR spectra, which will allow to differentiate between benzene, toluene and o-, m-, p-xylene and iso- and n-alkanes, have to be identified. For the series of aromatic molecules these species can be differentiated from the bands in the region at 1650-1350 cm^{-1} or 850 – 650 cm^{-1}. The separation of n- and iso-alkanes might not be possible from the intensities of the -CH_3 and –CH_2 vibrations, therefore, as an alternative, one component will be used in the deuterated form, which will allow to differentiate between the two molecules using the intensities of the –CH and -CD vibrations. However, this will require a careful study of the influence of isotope effects and of isotope exchange reactions during the sorption/diffusion processes.

With this technique, we plan to study the multi-component diffusion of xylene isomers in Silicalte-1 and of n- and i-C_6 in small pore zeolites. Both examples are of significant technological interest as they are the basis for (shape) selective isomerization reactions.

3.2.3 Two-component Diffusion in One-dimensional Pore Systems

The confinement to displacements into one direction, in parallel with the option to attain arbitrarily small observation times (just, by choosing sufficiently high frequencies), makes the FR technique a unique tool for tracing the transition between single-file behavior and ordinary diffusion. Since for single-component systems non-equilibrium measurements do not reveal any particularities of single-file systems, in comparison with normal 1D diffusion [37] FR experiments of this type have to be performed under the condition of two-component adsorption, with differing single-component diffusivities. Just depending on the probability that adjacent molecules may pass each other, by an appropriate selection of the frequency the limiting cases of either single-file diffusion (mutual passages during cycle duration rather unlikely) or normal diffusion (many passages possible) may be realized. Since molecular passages may indicate imperfections in the crystal structure, in combination with the microscopic techniques available in the consortium FR measurements may notably contribute to a better understanding of both the real structure of the zeolite host systems and the elementary steps of molecular propagation in their interior.

3.3. References

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4. Requested Financial Support

4.1. Personnel

1 PhD student ¾ BAT IIa position

For the position in the project a student with a strong background in chemical engineering is required. Therefore, the position has to be at a typical level for students in this field.

4.2. Durable Equipments

Multiple reflection gas cell   15,000.-

As outlined, a small volume multiple reflection gas cell will be required to obtain a sufficient intensity of the IR bands of the characteristic bands in the gas phase IR spectra. From the intensity of the gas phase spectra of the xylene isomers (obtained from BRUKER) we have estimated a required optical path length in the order of 100 cm to be able to detect the changes in the gas phase concentration during the pressure steps. For the project the purchase of the cell from Bruker or Infrard Analysis is planned.

Software for data analysis
Grams/AI + Grams 3D   950.-
Mathcad 13   800.-

Within the Munich group Grams/AI is used for the analysis of the IR spectra. At present we have 5 licenses for this program, however, the analysis of the time-resolved IR spectra will be very time consuming and therefore an additional license of this program is required.

For the analysis of the Frequency Response data (requiring Fourier transformation and non-linear fitting) the program MathCad will be used.

4.3. Consumables (costs for the entire project period)

Gasses and chemicals for sorption   9000.-
(ultra-high purity)

Spare parts for the vacuum system (valves and sealings, oil for pumps)   4500.-

4.4. *Traveling*

Implying that the group meetings are ensured by central funding, the travelling budget has primarily to be used for keeping personal contact with other laboratories in the field of FR sorption measurement, in particular for conference participation (Annual German Zeolite Conferences, Conferences of the International Zeolite Association and Adsorption Association). Therefore, a total amount of 2000 €per year, corresponding to 6000 €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. Johannes A. Lercher (applicant)
b) PD Dr. Andreas Jentys (applicant)
c) Dr. Yongzhong Zhu (Material synthesis)
d) MSc. Rino Mukti (Support for FR Experiments)
e) Dipl. Chem (F.H.) Xaver Hecht (technical support)
f) Dipl. Chem. (F.H.) Martin Neukamm (technical support)
g) Anderas Marx (technical support)

5.2. Cooperation with other Scientists

The primary partners of cooperation are the members of the consortium. For special support and scientific exchange in the field of adsorption equilibria and transient adsorption measurements, cooperation with the following scientists is planned:

Prof. Randall Q. Snurr, Department of Chemical Engineering, Northwestern University
Prof. Julian Gale, Univ. Perth, Australia.
Dr. G. Onyestyak, Hungarian Acad Sci, Budapest, Hungary.

5.3. Available Equipments

Frequency response system for diffusion studies (detection of pressure)
Frequency response system with (rapid scan) IR detection of surface species (Bruker 66v)
Microbalance/Calorimeter (Setaram)
IR system for sorption experiments from vacuum and carrier gas (Bruker IFS 88)
IR system for *in situ* reaction studies on the solid-gas interface
IR system with ATR unit for *in situ* reaction studies on the liquid-gas interface
Laser-Raman system for catalyst characterization
XRD system (Philips X'Pert Pro System)
Calvet Calorimeter for liquid phase sorption experiments
6 Vacuum systems for catalyst characterization
16 microreactor setups (partially in multi-reactor configuration)
Workstations and software for simulations of structures and dynamic processes

5.4. Support from the Own Budget

From the budget of the institute an amount of about 3000 €per year may be used for ensuring the operating conditions of the equipments.

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 the library, 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

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

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

The university representative of the DFG, Herr Prof. Dr. R. Bulirsch, has been informed about this proposal.

7. Signatures

Munich, June 19, 2006

PD Dr. Andreas Jentys   Prof. Dr. Johannes Lercher