

7

Molecular Sieves

Science and Technology

Editors: H. G. Karge · J. Weitkamp

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Vol. 7, 2008

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Adsorption and Diffusion

Editors: Hellmut G. Karge · Jens Weitkamp

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S. Brandani · M. Eic · E. J. M. Hensen · H. Jobic · A. M. de Jong

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R. A. van Santen · L. Song

Molecular Sieves – Science and Technology will be devoted to all kinds of microporous crystalline solids with emphasis on zeolites. Classical aluminosilicate zeolites as well as microporous silica will typically be covered; titaniumsilicate, alumophosphates, gallophosphates, silicoalumophosphates, and metalloalumophosphates are also within the scope of the series. It will address such important items as hydrothermal synthesis, structures and structure determination, post-synthesis modifications such as ion exchange or dealumination, characterization by all kinds of chemical and physico-chemical methods including spectroscopic techniques, acidity and basicity, hydrophilic vs. hydrophobic surface properties, theory and modelling, sorption and diffusion, host-guest interactions, zeolites as detergent builders, as catalysts in petroleum refining and petrochemical processes, and in the manufacture of organic intermediates, separation and purification processes, zeolites in environmental protection. As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers for *Molecular Sieves* are accepted in English. In references *Molecular Sieves* is abbreviated *Mol Sieves* and is cited as a journal. Springer WWW home page: springer.com
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Molecular Sieves

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Preface to the Series

Following Springer's successful series *Catalysis – Science and Technology*, this series of monographs has been entitled *Molecular Sieves – Science and Technology*. It will cover, in a comprehensive manner, all aspects of the science and application of zeolites and related microporous and mesoporous materials.

After about 50 years of prosperous research, molecular sieves have gained a firm and important position in modern materials science, and we are witnessing an ever increasing number of industrial applications. In addition to the more traditional and still prevailing applications of zeolites as water softeners in laundry detergents, as adsorbents for drying, purification and separation purposes, and as catalysts in the petroleum refining, petrochemical and chemical industries, novel uses of molecular sieves are being sought in numerous laboratories.

By the beginning of 1999, the Structure Commission of the International Zeolite Association had approved approximately 120 different zeolite structures which, altogether, cover the span of pore diameters from about 0.3 nm to 2 nm. The dimensions of virtually all molecules (except macromolecules) chemists are concerned with fall into this same range. It is this coincidence of molecular dimensions and pore widths which makes zeolites so unique in adsorption and catalysis and enables molecular sieving and shape-selective catalysis. Bearing in mind that each zeolite structure can be modified by a plethora of post-synthesis techniques, an almost infinite variety of molecular sieve materials are nowadays at the researcher's and engineer's disposal. In many instances this will allow the properties of a zeolite to be tailored to a desired application. Likewise, remarkable progress has been made in the characterization of molecular sieve materials by spectroscopic and other physico-chemical techniques, and this is particularly true for structure determination. During the last decade, we have seen impressive progress in the application of quantum mechanical *ab initio* and other theoretical methods to zeolite science. The results enable us to obtain a deeper understanding of physical and chemical properties of zeolites and may render possible reliable predictions of their behavior. All in all, the science and application of zeolites is a flourishing and exciting field of interdisciplinary research which has reached a high level of sophistication and a certain degree of maturity.

The editors believe that, at the turn of the century, the time has come to collect and present the huge knowledge on zeolite molecular sieves. *Molecular Sieves – Science and Technology* is meant as a handbook of zeolites, and the term “zeolites” is to be understood in the broadest sense of the word. While, throughout the handbook, some emphasis will be placed on the more traditional aluminosilicate zeolites with eight-, ten- and twelve-membered ring pore openings, materials with other chemical compositions and narrower and larger pores (such as sodalite, clathrasils, $\text{AlPO}_4\text{-8}$, VPI-5 or cloverite) will be covered as well. Also included are microporous forms of silica (e.g., silicalite-1 or -2), alumophosphates, gallophosphates, silicoalumophosphates and titaniumsilicalites etc. Finally, zeolite-like amorphous mesoporous materials with ordered pore systems, especially those belonging to the M41S series, will be covered. Among other topics related to the science and application of molecular sieves, the book series will put emphasis on such important items as: the preparation of zeolites by hydrothermal synthesis; zeolite structures and methods for structure determination; post-synthesis modification by, e.g., ion exchange, dealumination or chemical vapor deposition; the characterization by all kinds of physico-chemical and chemical techniques; the acidic and basic properties of molecular sieves; their hydrophilic or hydrophobic surface properties; theory and modelling; sorption and diffusion in microporous and mesoporous materials; host/guest interactions; zeolites as detergent builders; separation and purification processes using molecular sieve adsorbents; zeolites as catalysts in petroleum refining, in petrochemical processes and in the manufacture of organic chemicals; zeolites in environmental protection; novel applications of molecular sieve materials.

The handbook will appear over several years with a total of ten to fifteen volumes. Each volume of the series will be devoted to a specific sub-field of the fundamentals or application of molecular sieve materials and contain five to ten articles authored by renowned experts upon invitation by the editors. These articles are meant to present the state of the art from a scientific and, where applicable, from an industrial point of view, to discuss critical pivotal issues and to outline future directions of research and development in this sub-field. To this end, the series is intended as an up-to-date highly sophisticated collection of information for those who have already been dealing with zeolites in industry or at academic institutions. Moreover, by emphasizing the description and critical assessment of experimental techniques which have been used in molecular sieve science, the series is also meant as a guide for newcomers, enabling them to collect reliable and relevant experimental data.

The editors would like to take this opportunity to express their sincere gratitude to the authors who spent much time and great effort on their chapters. It is our hope that *Molecular Sieves – Science and Technology* turns out to be

both a valuable handbook the advanced researcher will regularly consult and a useful guide for newcomers to the fascinating world of microporous and mesoporous materials.

Hellmut G. Karge
Jens Weitkamp

Preface to Volume 7

Sorption into, release from and diffusion inside microporous and mesoporous materials are of paramount interest in view of separation processes and catalysis by zeolites and related structures. Thus, volume 7 of the handbook-like series “Molecular Sieves – Science and Technology” is exclusively devoted to the phenomena of adsorption into, desorption out of and diffusion in the pores of zeolite crystallites.

Fundamentals of sorption and sorption kinetics by zeolites are described and analyzed in the first Chapter which was written by D. M. Ruthven. It includes the treatment of the sorption equilibrium in microporous solids as described by basic laws as well as the discussion of appropriate models such as the Ideal Langmuir Model for mono- and multi-component systems, the Dual-Site Langmuir Model, the Unilan and Toth Model, and the Simplified Statistical Model. Similarly, the Gibbs Adsorption Isotherm, the Dubinin–Polanyi Theory, and the Ideal Adsorbed Solution Theory are discussed. With respect to sorption kinetics, the cases of self-diffusion and transport diffusion are discriminated, their relationship is analyzed and, in this context, the Maxwell–Stefan Model discussed. Finally, basic aspects of measurements of micropore diffusion both under equilibrium and non-equilibrium conditions are elucidated. The important role of micropore diffusion in separation and catalytic processes is illustrated.

The discussion of experimental techniques for diffusion measurements especially under non-equilibrium conditions is continued in Chapter 2 which is co-authored by D. M. Ruthven, St. Brandani, and M. Eic. Results obtained by uptake rate measurements using evaluation of, for example, piezometric (pressure change), chromatographic, frequency response (FR), zero-length column (ZLC), membrane permeation, and effectiveness factor experiments or employing temporal analysis of products (TAP) are critically analyzed. A review of experimental diffusivity data for selected systems presents examples of both consistencies and discrepancies between “microscopic” measurements, for example, pulsed-field gradient NMR (PFG NMR) or quasi-elastic neutron scattering (QENS) on the one side and “macroscopic” determination of diffusivities by uptake techniques as listed above on the other. Possible origins of discrepancies are addressed. This chapter closes with a brief treatment of diffusion in bi-porous structures such as mesoporous silica materials.

Diffusion measurements by NMR spectrometry represent the most prominent methods for determining the rate of migration of molecules in the framework of zeolites under equilibrium conditions. The fundamentals of the pulsed-field gradient (PFG) NMR method, i.e. the measuring principle, the range of applicability, and its limitations are described in Chapter 3, which was contributed by J. Kärger. The PFG NMR method belongs to the category of “microscopic” methods, in that it operates on a sub-crystal scale (cf. Chapter 1). The non-invasive NMR technique is able to yield valuable information about the elementary steps of diffusion, especially about mean jump and reorientation times. Furthermore, PFG NMR allows, as shown in this chapter, studying particular phenomena of diffusion in zeolites such as long-range diffusion, additional diffusion resistances (surface barriers), structure-related diffusion, and diffusion under transient conditions. Complementarily to Chapter 2, the last section of Chapter 3 provides a detailed comparison of PFG NMR results with those of other techniques, which is particularly important in view of the two broad classes of diffusion measurements in zeolites, viz. experiments under macroscopic equilibrium (“self-diffusion”) by “microscopic” techniques and under non-equilibrium conditions, i.e. under concentration differences (“transport diffusion”) via “macroscopic” methods.

In Chapter 4, H. G. Karge and J. Kärger describe diffusion measurements by means of macro-infrared Fourier transform spectroscopy (Macro-FTIR), micro-infrared Fourier transform spectroscopy (Micro-FTIR, employing a so-called IR microscope), and interference microscopy (diffusion interference microscopy, DIFM). The FTIR methods enables studies of mono- and multi-component diffusion, especially in the case of slowly migrating species ($D < 10^{-3} \text{ m}^2 \text{ s}^{-1}$). In the case of bi-component diffusion with chemically different diffusants such as, for example, benzene and ethylbenzene, for the first time diffusivities were determined upon co- and counter-diffusion. The novel diffusion interference microscopy (DIFM) has proven to be a most powerful tool for studying phenomena of adsorption on and diffusion in zeolites, especially when combined with “FTIR microscopy.” In single crystals of zeolites, it enables the determination of concentration profiles with a very good local resolution and provides, inter alia, structural data, for example, information about the role of boundaries and intergrowth effects. From the analysis of transient concentration profiles occurring during uptake or release of sorbate molecules, diffusivity data and their concentration dependence as well as information about surface resistances, permeabilities, and sticking probabilities may be obtained.

Similar to the PFG NMR method, neutron scattering techniques are successfully employed for the determination of diffusivities under equilibrium conditions. These techniques and their application are discussed in Chapter 5 by H. Jobic. Particularly efficient is a novel combination of quasi-elastic neutron scattering (QENS) and a neutron spin-echo technique (NSE), which considerably expands the range of accessible diffusivities, viz. down to $10^{-14} \text{ m}^2 \text{ s}^{-1}$, so

that the range is now the same as that of PFG NMR (cf. Chapter 3). Although hydrogen has the largest neutron cross section, the neutron scattering technique is no longer restricted to the study of hydrogen-containing molecules. For instance, the self-diffusivities of hydrocarbons may be measured with the hydrogen-containing and the transport diffusivity with the deuterated molecules.

An ingenious method for measurements of adsorption on and diffusion in zeolites was available on the advent of the so-called frequency response spectroscopy (FR). L. Song and L. V. C. Rees have contributed Chapter 6 of this volume, which is exclusively devoted to the FR method. With great regret we have to announce that L.V.C. Rees, who pioneered the application of this technique in zeolite science and technology, passed away in 2006. Theory, experimental principles, and applications of FR with respect to the investigation of diffusivities in micropores and bi-dispersed porous solids are reviewed. The diffusive behavior of hydrocarbons and other sorbates in microporous crystallites and related pellets is analyzed. The high potential of the FR method for elucidating multi-kinetic mechanisms is demonstrated when surface resistances, surface barriers, or subtle differences in molecular shape and size of the diffusing species play a role.

E. J. M. Hensen, A. M. de Jong, and R. A. van Santen have written Chapter 7, which introduces the tracer exchange positron emission profiling (TEX-PEP) as an attractive technique for in-situ investigations, for example, in a stainless steel reactor, of the adsorption and diffusive properties of hydrocarbons in zeolites under chemical steady-state conditions. Self-diffusion coefficients of hydrocarbons, labeled by proton-emitting ^{11}C at finite loadings and even in the presence of another unlabeled alkane, may be extracted. The method is illustrated by adsorption and diffusion measurements of linear (n-hexane) and branched (2-methylpentane) alkanes in H-ZSM-5 and silicalite-1.

The closing Chapter 8 is authored by J. Kärger and deals with the so-called single-file diffusion. Single-file diffusion occurs when a mutual passage of diffusants in zeolites with one-dimensional channels is excluded. The chapter provides a thorough analytical treatment and informative discussion of experimental studies by PFG NMR, QENS, ZLC, FR, and permeation methods. Monte-Carlo simulations and analytical approaches reveal striking peculiarities in single-file systems of finite length.

Thus, Volume 7 of the series “Molecular Sieves – Science and Technology” presents descriptions, critical analyses, and illustrative examples of applications of the most important methods for investigations of sorption and sorption kinetics in zeolite systems and related materials. The editors hope that the volume will be helpful for researchers as well as technologists who are confronted with the important phenomena of adsorption and diffusion in microporous materials as they occur, for instance, in separation processes and catalysis.

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