Microporous and Mesoporous Materials 164 (2012) 273–279

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

# Exploring the hierarchy of transport phenomena in hierarchical pore systems by NMR diffusion measurement

Dirk Mehlhorn [a], Rustem Valiullin [a], Jörg Kärger [a,*], Kanghee Cho [b], Ryong Ryoo [b]

[a] Faculty of Physics and Earth Science, University of Leipzig, Linnéstr. 5, Leipzig D-04103, Germany
[b] Department of Chemistry and Graduate School of Nanoscience and Technology (WCU), KAIST, Daejeon 305-701, Republic of Korea

ARTICLE INFO

*Article history:*
Available online 7 July 2012

Dedicated to Prof. Dr. Jens Weitkamp on the occasion of his 70th birthday

*Keywords:*
Mesoporous zeolites
LTA
Diffusion
Hierarchical pore systems
Pulsed field gradient NMR

ABSTRACT

The pulsed field gradient technique of NMR (PFG NMR) is applied for exploring molecular diffusion in different specimens of zeolite NaCaA, notably in samples containing “hierarchical” pore systems where the micropores are traversed by mesopores. Choosing ethane (capable of permeating both micro- and mesopores) and cyclohexane (unable to penetrate the micropores) as guest molecules and varying purposefully the accessibility and mobility in the mesopores by temperature variation and pore blocking, the diffusivities in the two pore spaces are measured separately from each other. It is shown that the presence of the mesopores may give rise to dramatically enhanced intracrystalline diffusivities while a blockage of the mesopores reduces the intracrystalline diffusivities by an order of magnitude.

## 1. Introduction

In the middle of the last century, the introduction of nanoporous materials has revolutionized the technologies for product upgrading by mass separation [1] and mass conversion [2]. The worldwide annual benefit attained by such technologies in, e.g., only petrol refining is estimated to be of the order of 10 billion Euros [3]. With groundbreaking investigations in the field of heterogeneous catalysis [4], Jens Weitkamp has notably contributed to this impressive development. We dedicate this paper to him on the occasion of his 70th birthday, in appreciation of these contributions and in gratitude for many stimulating advices for our own work.

In the last few years, the requirement for sustainable, energy efficient and clean technologies has given rise to new orientations and developments in the fabrication, investigation and application of nanoporous materials. A substantial amount of these studies is dedicated to the solution of a problem inherent to the application of nanoporous materials quite in general: Their great potentials in shape-selective catalysis [2–4] and mass separation by molecular sieving and selective adsorption [1] results from the intimate contact between the guest molecules and the host surfaces, notably by choosing pore sizes as close as possible to the sizes of the involved molecules. One has to pay for this closeness with, in general, dramatically reduced guest diffusivities [5–8]. The gain in value-added products by molecular conversion or separation, however, can never exceed the relevant diffusion rates [8,9]. The closeness between molecular and pore sizes which, on the one hand side, is the prerequisite for the elementary processes leading to the desired processes, is thus found, on the other side, to limit their performance.

Among the various strategies developed for overcoming this dilemma, the fabrication of materials with hierarchical pore spaces has attracted particular attention. In such materials, a microporous (in general zeolitic) bulk phase, the “source” of the value-added products, is traversed by (or embedded in) a network of mesopores, the product of the relative micropore volume ($V_{\text{micro}}/V_{\text{total}}$) and the relative mesopore surface area ($S_{\text{meso}}/S_{\text{BET}}$) being known as the hierarchy factor [10]. The techniques applied in the fabrication of such ”mesoporous” zeolites include “hard” [11] and “soft” (supramolecular) [12–15] templating methods as well as post-synthetic dealumination or desilication [16–18].

It is well known that, due to huge differences in the results of different measuring techniques, the diffusivity in purely microporous materials remained, over decades, a mystery [19,20]. Only recently, owing to the combined application of “microscopic” techniques of diffusion measurement [8], notably Quasi-Elastic Neutron Scattering [21], pulsed field gradient NMR (PFG NMR) [22,23] and micro-imaging by IR and interference microscopy [24], the differences in the diffusivities obtained by different techniques could be referred to the influence of transport resistances

---

[*] Corresponding author.
*E-mail address:* kaerger@physik.uni-leipzig.de (J. Kärger).

1387-1811/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2012.06.049

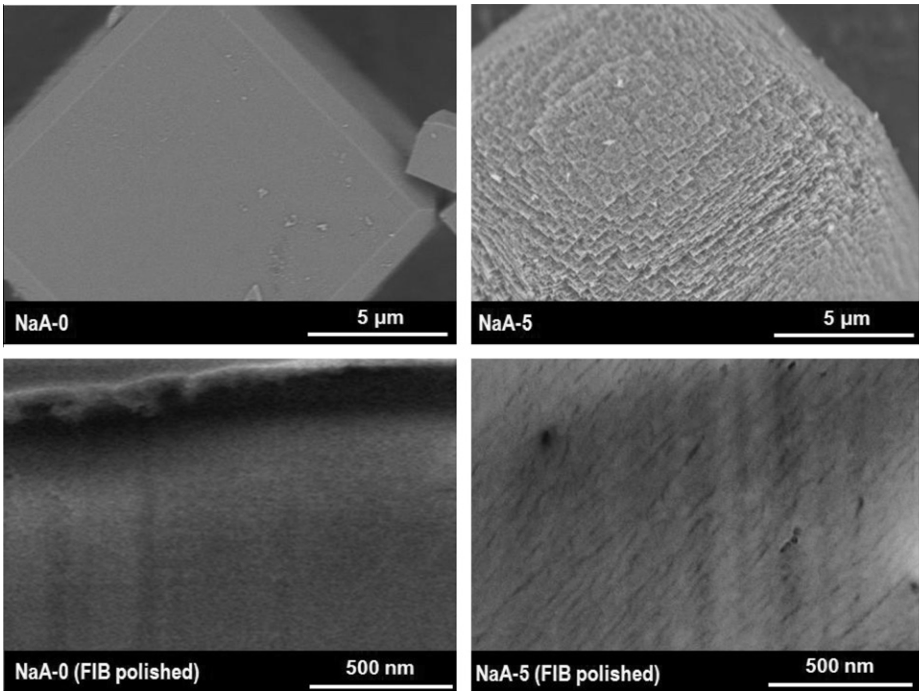

**Fig. 1.** SEM images of the purely microporous (NaA-0, left column) and a mesoporous (NaA-5, right column) LTA zeolite sample: top images were taken from the external surfaces of the calcined samples and the bottom images were taken after cross-sectional polishing by focused gallium ion beam. The dark, slant lines in the lower right image indicate the presence of mesopores in the cross-sectional cut.

acting in addition to the genuine pore structure which appear to be essentially omnipresent in the "real" structure of nanoporous materials [25,26]. A clear separation between the influences of these different types of transport resistances remains a challenging task of current diffusion research.

Similarly challenging is the situation with hierarchical pore systems. It is not unexpected, therefore, that first diffusion studies with mesoporous zeolites were only focused on the combined effect of the two pore systems on the rates of molecular uptake and intracrystalline molecular diffusion, including macroscopic uptake experiments [27] and microscopic diffusion measurements by PFG NMR [28–30]. In the present communication, we report about first PFG NMR diffusion studies aiming at a separate determination of the diffusion properties of the micro- and mesoporous spaces in zeolites with a hierarchical pore system.

## 2. Experimental

### 2.1. The material under study

The measurements have been performed with three specimens of calcium-exchanged zeolite LTA, one purely microporous (NaCaA-0) and two mesoporous ones with mesopore volumes of 0.110 $cm^3/g$ (NaCaA-2) and 0.218 $cm^3/g$ (NaCaA-5), respectively. The width of the mesopores is estimated to be about 5 nm. The SEM pictures shown in Fig. 1 provide an impression of their morphology.

Following the procedure described in detail in Ref. [31], the mesoporous zeolite LTA was synthesized under the presence of 3-(trimethoxysilyl)propylhexadecyldimethylammonium chloride (TPHAC) as an organosilane surfactant, giving rise to the formation of mesopores within the LTA microporous space. The numbers following 'Na(Ca)A-' in the sample names mean the mole percent of organosilane surfactant to entire silica species (silicate + organosilane) in the initial synthetic gel. Finally, 82% of the sodium ions were replaced by Ca2+ cation exchange.

Ref. [29] provides a summary of the results of previous PFG NMR diffusion studies of this material with propane as a guest molecule as well as further details of sample preparation and characterization. It was in particular confirmed that morphology, particle size and external/internal mesopore structure of all samples are maintained after calcination and ion-exchange treatments. In all samples, the mean crystal diameter was about 11 µm and proved to be big enough for allowing PFG NMR diffusion studies free of disturbing boundary effects.

### 2.2. PFG NMR diffusion measurements

Under the influence of a pair of field gradient pulses, applied in addition to the sequence of radio-frequency pulses giving rise to the formation of the NMR signal ("spin echo" of intensity $M$), signal attenuation obeys the relation [23,32,33]

$$M(\delta g)/M(0) \equiv \psi(\gamma\delta g, t) = \int_{-\infty}^{\infty} P(z,t)\cos(\gamma\delta gz)dz \qquad (1)$$

with $g$ and $\delta$ denoting, respectively, the amplitude and duration of the gradient pulses. $t$ stands for the observation time of the PFG NMR experiment, i.e., the time interval between the two gradient pulses (where, for simplicity, the pulse width $\delta$ is implied to be negligibly small in comparison with $t$). $\gamma$(=2.67 × $10^8\ T^{-1}\ s^{-1}$ for protons) is the gyromagnetic ratio. $P(z, t)$ denotes the probability that, during time $t$, an arbitrarily selected molecule within the sample is shifted over a distance $z$, i.e., in the direction of the applied field gradient. This interrelation between the signal attenuation curve $\psi(\gamma\delta g, t)$ and the "mean propagator" $P(z, t)$ [23,32–34] gives rise to the matchless versatility of PFG NMR for the exploration of molecular mass transfer in complex systems which, in this study, shall be exploited for an in-depth study of mass transfer in the two pore systems of mesoporous zeolites.

For molecules in an infinitely extended, isotropic medium the propagator is a Gaussian [8]