

## Correlating phase state and transport in hierarchical mesoporous materials

**Philipp Zeigermann<sup>\*</sup>, Dirk Mehlhorn, Jörg Kärger, Rustem Valiullin**

Faculty of Physics and Earth Sciences, Universität Leipzig, Leipzig, Germany

<sup>\*</sup>zeigermann@physik.uni-leipzig.de

The pulsed field gradient technique of NMR (PFG NMR) is applied to explore molecular diffusion in different specimens of zeolite NaCaA, notably in samples containing hierarchical pore systems, as well in a silica material with an ordered, bimodal mesopore structure. In the hierarchical zeolites the diffusivities in the two pore spaces are measured separately from each other by 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. It is shown that the presence of the mesopores may give rise to dramatically enhanced intra-crystalline diffusivities while a blockage of the mesopores reduces the intra-crystalline diffusivities by an order of magnitude [1]. The well-defined pore structure of a bimodal mesoporous glass allowed for a quantitative analysis of the diffusion process in a medium with spatially-ordered distribution of the fluid density for a broad range of the gas-liquid equilibria. The measured diffusion data were interpreted in terms of effective diffusivities, which were determined within a microscopic model considering long-range molecular trajectories constructed by assembling the alternating pieces of displacement in the two constituting pore spaces. It has further been found that for the system under study, in particular, and for mesoporous materials with multiple porosities, in general, this generalized model simplifies to the conventional fast-exchange model used in the literature. Thus, not only justification of the applicability of the fast-exchange model to a diversity of mesoporous materials was provided, but also the diffusion parameters entering the fast-exchange model were exactly defined. The equation resulting in this way was found to nicely reproduce the experimentally determined diffusivities, establishing a methodology for targeted fine-tuning of transport properties of fluids in hierarchical materials with multiple porosities [2].

This work was supported by the DFG (FOR 877).

### References

- [1] D. Mehlhorn, R. Valiullin, J. Kärger, K. Cho, R. Ryoo: *Exploring the hierarchy of transport phenomena in hierarchical pore systems by NMR diffusion measurement*. Microporous Mesoporous Mat. **164**, 273–279 (2012)
- [2] P. Zeigermann, S. Naumov, S. Mascotto, J. Kärger, B.M. Smarsly, R. Valiullin: *Diffusion in hierarchical mesoporous materials: Applicability and generalization of the fast-exchange diffusion model*. Langmuir **28**, 3621–3632 (2012)