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Adsorption Hysteresis Phenomena in Mesopores

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1. Introduction

The adsorption hysteresis behaviour in mesoporous materials is usually related to capillary condensation and the metastability of the gaseous phase under mesoscalic confinement. Since the first observation and description of this phenomenon by Szigmondy (1911), a lot of experimental and theoretical work has been done in order to understand the underlying mechanisms [1-3]. In spite of the progress in theoretical approaches and experimental techniques, the internal dynamics of fluids in the pores are still poorly understood.

Generally, the hysteretic behaviour results from an inhomogeneous distribution of the fluid within the porous matrix on a length scale typically of the order of the pore size, which in a complex irreversible way depends on the external conditions (e.g., gas pressure, temperature). Consequently, these inhomogeneities may result in different dynamical properties of the fluids in pores being determined by the external conditions and the history how this particular state has been attained.

Common way to study the adsorption processes is the adsorption/desorption and the scanning curves experiments with incomplete filling/draining circles. The experiments are performed by stepwise changing of the external driving force (pressure) and measuring the amount adsorbed after the system is apparently equilibrated. Under assumption of an adsorption model one can explain the shape of the isotherms. However, the adsorption experiment does not contain any information about the internal microscopic processes, thus it does not allow any conclusions about the distribution of the adsorbate inside the pores. Probing of the self-diffusivity for different amount adsorbed and sorption history can provide the desired additional information about the mechanism leading to the hysteresis behaviour of the molecules inside the pores.

Pulsed field gradient (PFG) NMR is a powerful technique to measure both the macroscopic (amount adsorbed) and the microscopic properties (self-diffusion coefficient) of the molecules confined in porous materials.

2. Results and Conclusion

In **Figure 1**, the adsorption hysteresis is presented for the case of cyclohexane in Vycor porous glass at 297K. The corresponding self-diffusion coefficients measured directly by PFG NMR are also presented on the top of the figure. One can see the dependence of the self-diffusivities on both the external parameters and the history how the state has been attained.

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In [4], Woo and Monson provide a very comprehensive picture of the equilibrium and the dynamics of fluids confined in disordered mesoporous glasses. They have studied a lattice gas with disordered, spatially correlated site dilution and with an additional, non-random attractive interaction between the fluid and the solid surface. The evolution of the system, i.e. the redistribution of the liquid/gas phase, is suggested to be dominated by the presence of the ragged free-energy landscape characterized by a plenty of local minima. Different distributions of the liquid and gaseous phases in the pores are reflected by different self-diffusivities at the same amount adsorbed (Figure 2). This difference can be explained by the differences in the morphology of the liquid-gas interface and their different influences on the exchange rate.

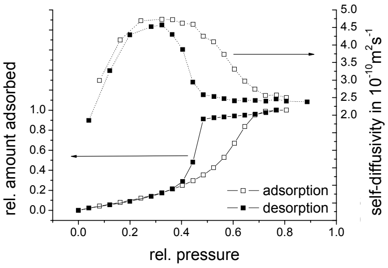

Figure 1: Hysteresis behavior of the amount adsorbed and corresponding self-diffusivities

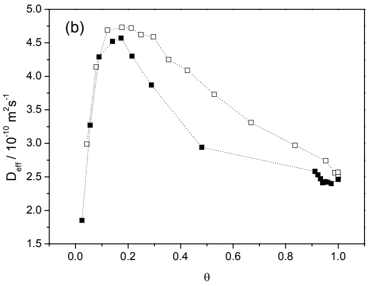

Figure 2: Self-diffusivity vs. concentration

The relaxation of the system towards the global free-energy minimum is controlled by crossing of the energy barriers. This process is essentially activated in nature and usually exceeds the experimental time scale by orders of magnitude. This extremely slow density redistribution which controls the molecular uptake has been predicted theoretically and observed in our experiments as well. In Figure 3, uptake kinetics are presented inside and outside the hysteresis region. Obviously, in the range of the hysteresis loop, the redistribution mechanism dominates the uptake whereas outside the hysteresis loop the uptake is rather diffusion-limited. The former is an activated process introducing a logarithmic time.

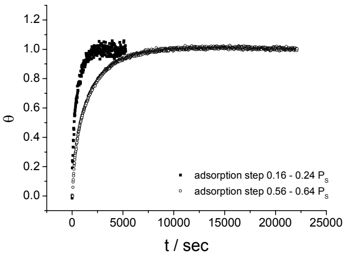

Figure 3: Uptake kinetics inside and outside of the hysteresis loop

The vastly different time scales of these two mechanisms are the main reason why hysteresis loops are reproducible.

References

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