

NMR Studies on Silica Monoliths - Diffusion in a Hierarchical Pore Structure

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1. Introduction

For many applications in chromatography and separation, porous materials with a structure-in-structure fashion are desirable. For such applications, silica monoliths were synthesized which have a trimodal, hierarchical pore structure [1]. It consists of three different interconnected pore domains with pore diameters (measured by Hg-porosimetry) in the range of a few microns (macropores), 18 nm and about 2-3 nm (mesopores and micropores). In this study, we investigated transverse relaxation times (T_2) and self-diffusion of methanol, benzene and water (loadings: 25%, 50%, 90-100% pore filling) in two silica monoliths, which differ mainly in the diameter of their macropores (JHS-002-02 $d_{\text{JHS}}=3 \mu\text{m}$; CL-14, $d_{\text{CL}}=24 \mu\text{m}$).

2. Transverse relaxation times and self-diffusion studies

The transverse relaxation times were measured with the conventional CPMG NMR pulse sequence [2] and analysed via an inverse Laplace transformation. The self-diffusion of methanol, benzene and water adsorbed in the monoliths was measured using the pulsed field gradient (PFG) NMR technique [3] and analysed via a biexponential diffusion model [4]. The PFG NMR measurements were carried out for different observation times ($\Delta=5\text{-}20\text{ms}$) in a temperature range of 298 K to 330 K.

The T_2 -relaxation time distributions (Fig. 1) show three regions of transverse relaxation times (peaks) corresponding to the three pore domains. However, the areas under the different peaks do not correspond to the specific pore volumes, which were measured by Hg-porosimetry. This indicates an exchange of the pore fluid molecules between the three pore domains. The PFG NMR data (Fig. 2) show that the self-diffusion coefficients (SDC) of water, benzene and methanol in JHS-002-02 (small macropores) decrease with increasing loading. In contrast, the corresponding SDC of the pore fluids in CL-14 (large macropores) increase with increasing loading. This behavior may be explained with a different rate of exchange between the gas and the liquid phase of the pore fluids in the two different monoliths. Because of the small macropores in JHS-002-02, the liquid/vapor interface is large allowing a fast exchange of the molecules between the gas and the liquid phase. Due to the larger macropores at CL-14, the exchange rate between gas and liquid phase is significantly smaller, which reduces the contribution of the gas phase to the molecular self-diffusion in the pore space.

The temperature-dependent SDC measurements shown in Fig. 3 support this idea. For both monoliths, the measured activation energies for water are significantly higher than the activation energy of liquid water (16 kJ/mol)[5]. Compared to CL-14, the higher

value of the activation energy of water in JHS-002-02 indicates a stronger contribution of the exchange through the liquid/gas interface to the self-diffusion process inside the pore system.

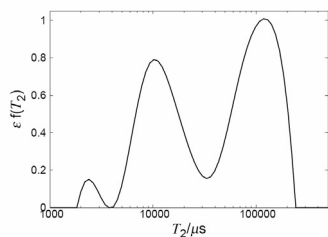


Fig. 1. T_2 -relaxation time distribution for water in CL-14 at 100% pore filling.

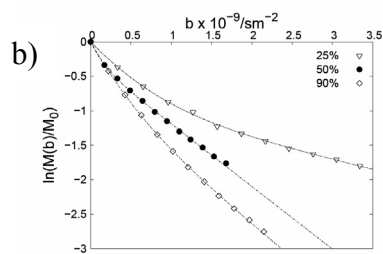
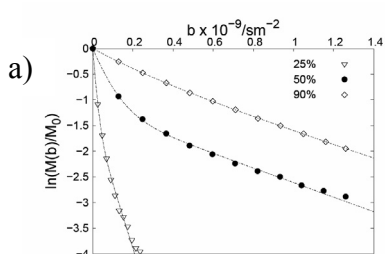


Fig. 2. Semi-logarithmic plots of the PFG NMR spin echo attenuation of methanol in a) JHS-002-02 and b) CL-14 for different loadings (25%, 50%, 90% pore filling).

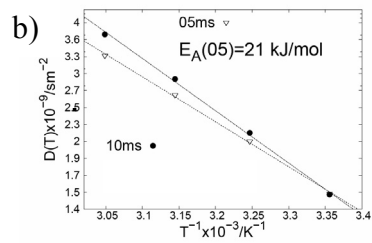
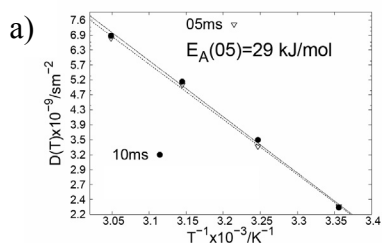


Fig. 3. Temperature-dependent self-diffusion coefficients of water in a) JHS-002-02 and b) CL-14 as obtained by ^1H PFG NMR studies.

References

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