Anisotropic Self-Diffusion of Guest Molecules in $Zn_2(bdc)_2dabco$

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1. Introduction

Non-invasive pulsed field gradient (PFG) NMR self-diffusion studies [1] are a powerful tool to elucidate host-guest interactions in MOFs [2,3]. Experimental (PFG) NMR self-diffusion studies on benzene adsorbed in the well-known Zinc-based metal organic framework MOF-5 show for relatively low loading (less than 20 molecules per unit cell) good agreement with data obtained by MD simulations [2,4,6]. Zinc-based MOFs provide good conditions for further studies of host-guest interactions based on the comparison of data obtained by experimental PFG NMR methods on one side and theoretical MD Simulation on the other. Therefore, zinc-based MOF $Zn_2(bdc)_2dabco$ [6] is a promising candidate to investigate host-guest interactions in microporous materials. $Zn_2(bdc)_2dabco$ consists of zincoxide-clusters in a paddlewheel configuration and two different linkers (Terephthalic acid, dabco). This build-up forms channels with a size of 7.5 Å, which are interlinked by windows of 4 Å. In a first step we measured self-diffusion coefficients of benzene and CO_2 via PFG NMR.

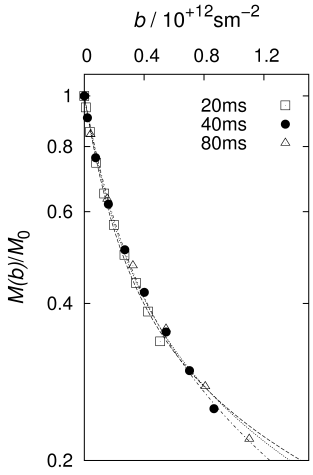

Fig. 1: Spin-echo attenuation curve of benzene in $Zn_2(bdc)_2dabco$ for 20, 40 and 80 ms Diffusion time.

2. Results

PFG NMR experiments of benzene adsorbed in $Zn_2(bdc)_2dabco$ (see Fig. 1) do not show a simple mono-exponential behaviour of the spin-echo attenuation curve. These are in the case of $Zn_2(bdc)_2dabco$ most likely caused by an anisotropic diffusion behaviour due to the pore channels in the $Zn_2(bdc)_2dabco$ crystals. The analysis of the spin-echo attenuation using a model of Callaghan et al. [7] for anisotropic self-diffusion yields self-diffusion coefficients of $1 \cdot 10^{-11}$ m^2/s along the channels and $3 \cdot 10^{-13}$ m^2/s perpendicular to the channels.

Self-diffusion studies on CO_2 adsorbed in $Zn_2(bdc)_2dabco$ show a strictly mono-exponential behaviour of the spin-echo attenuation curve. The corresponding self-diffusion coefficient is $6 \cdot 10^{-9}$ m^2/s.

The different diffusion behaviour of the two species of guest molecules may be attributed to the different hydrodynamic radii of benzene and CO_2. The smaller CO_2

molecules are able to pass the windows between the channels without obstructions, but the benzene molecules are restricted during a jump from one channel to the other.

The next step will be the implementation of MD simulations of benzene and CO_2 in $Zn_2(bdc)_2dabco$ to verify the conclusions of the experimental (PFG) NMR studies.

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