

## Self-Diffusion of Methyl Oleate in Mesoporous Materials with SBA-16 Structure

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### 1. Introduction

The existence of a 3-dimensional system of relatively large pores makes mesoporous silica of the SBA-16 type to be an attractive candidate as a catalyst support for catalytic production of biodiesel, viz. fatty acid methyl esters. Using these materials for the catalytic production of biodiesel from triglycerides, which can be extracted from marine algae, shows potential for addressing increasing needs in fuels. Understanding transport properties of such relatively large sorbate molecules in the pore system of SBA-16 is of high importance for catalysis in this type of materials. Here we report the synthesis of the BTEB (viz., 1,4-bis (trithoxysilyl)-benzene) SBA-16 material and the properties of methyl oleate self-diffusion in this material at room temperature. The diffusion studies were performed using pulsed field gradient (PFG) NMR at high magnetic field (17.6 T) and high magnetic field gradients (up to 30 T/m). Application of high field and high gradients allowed using natural abundance <sup>13</sup>C PFG NMR, in addition to a more traditional <sup>1</sup>H PFG NMR. PFG NMR measurements resulted in obtaining quantitative knowledge of methyl oleate self-diffusion inside BTEB SBA-16 particles.

### 2. Experimental

The synthesis of periodic mesoporous benzene-silica materials with crystal-like pore walls has been reported in Ref. 1. The detailed synthesis procedures used in this work were adapted from Ref. 2. The structure of the synthesized BTEB SBA-16\_100 material was characterized by BET, TEM, SEM and SAXS. The pores structure of SBA-16 is shown in Fig. 1a.

<sup>1</sup>H and <sup>13</sup>C PFG NMR diffusion measurements were performed using a wide bore 17.6 T Bruker Biospin Spectrometer. Magnetic field gradients were generated using diff60 diffusion probe (Bruker Biospin). Diffusion studies were carried out using the PFG NMR stimulated echo pulse sequence with eddy current delay and by the 13-interval PFG NMR sequence with bipolar gradients. The former and the latter sequences were used for measurements using <sup>1</sup>H and <sup>13</sup>C PFG NMR, respectively. Sorbate diffusivities were obtained from PFG NMR attenuation curves, viz. dependencies of the intensity of the PFG NMR signal on the amplitude of the magnetic field gradients.

For preparation of PFG NMR samples ~100 mg of BTEB SBA-16\_100 material was introduced into a 5 mm NMR tube. The NMR tube was connected to a custom-made vacuum system and the sample was activated (i.e. made water-free) by keeping it under high vacuum at around 110°C for 24 hours. After activation sufficient amount of methyl

oleate was added to fill all particle pores and also all gaps between the particles with the liquid sorbate. The tubes were flame-sealed after the loading.

### 3. Results and Discussions

The measured  $^1\text{H}$  and  $^{13}\text{C}$  PFG NMR attenuation curves for diffusion of methyl oleate in the sample of BTEB SBA-16\_100 showed non-monoexponential behaviour characteristic to the existence of more than a single diffusivity. Examples of the attenuation curves measured for different diffusion times are shown in Fig.1b. The observed PFG NMR data are explained by the existence of a superposition of a relatively fast diffusion of methyl oleate in the macropores / liquid phase of the sample and a much slower diffusion inside the porous particles. These results allowed estimating the intraparticle diffusivity of methyl oleate in the sample of BTEB SBA-16\_100.

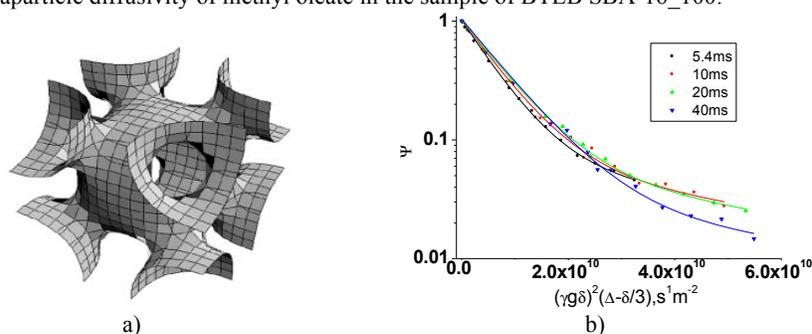


Figure 1. a) Direct image of 3D pore structure of SBA-16 [3]. b)  $^{13}\text{C}$  PFG NMR attenuation curves measured for diffusion of methyl oleate in BTEB SBA-16\_100 for different diffusion times.

### 4. Conclusion

Our results demonstrate feasibility of diffusion studies of large sorbate molecules in SBA-16 materials using combined application of  $^1\text{H}$  and  $^{13}\text{C}$  PFG NMR.

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