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Transport Properties of Guest Molecules in Mesoporous SBA-15 Materials - A PFG NMR Study

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1. Introduction

Catalysts are among the most important materials in modern industry. Hundreds of millions of tonnes of catalysts per year are produced in order to convert “raw” materials into value-added products. Continuously new catalysts with improved chemical and optimized transport properties are developed. At the present time there is an increasing interest in SBA-15 type materials due to their unique internal porous structure, consisting of an array of straight non-intersecting channels with diameters of several nanometres where chemically active centres can be incorporated. Such pores should provide an increased rate of reactant supply and product removal from the catalyst. In the present work, the pulsed field gradient nuclear magnetic resonance (PFG NMR) method has been applied to study the mobility of guest molecules in SBA-15.

2. Experimental

The SBA-15 material under investigation was composed of porous particles of sausage U-like form with sizes of about 0.45 μm in diameter and of about 1 - 1.2 μm in length (fig.1). The SBA-15 particles contain the non-intersecting straight channels with a diameter of about 3 nm. The space between the particles forms macropores. Two types of materials, reference and modified ones, were investigated. In the latter, the vanadium-silicalite is assumed to be located in the mesopores of the SBA particles and on their surface.

The diffusivities of guest molecules in the SBA-15 samples have been measured using the home-built PFG NMR spectrometer operating at a ^1H resonance frequency of 400 MHz [1]. Two types of diffusion measurements covering different length-scale of molecular displacements were performed in order to clarify the influence of the macro- and mesopores on the transport properties of the reference and modified materials.

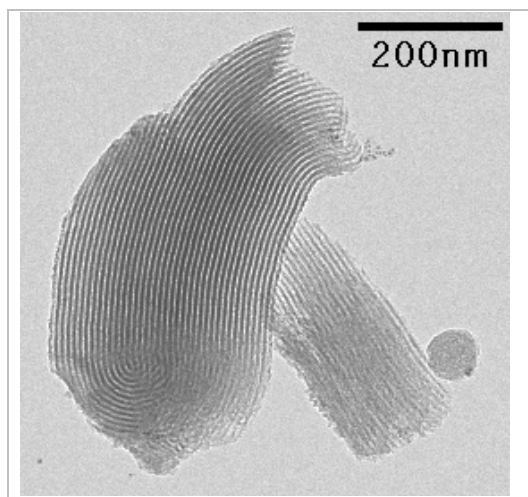


Fig.1. The TEM image of the SBA-15 particle.

By using the first type of experiments, we investigated the influence of the macropores on the molecular mobility in the SBA-15 material under study. In this case, the concentration of the molecules in pores and their self-diffusion coefficient were measured as a function of the external vapour pressure [2]. Under this condition, the molecular displacements were much larger than the size of the particles. The measured diffusivities were found being well correlated with the adsorption isotherms (fig.2) and nicely reflected the occurrence of hysteresis effects. The main result of these experiments is the observation of a fast exchange between the molecules in meso- and macropores on a time-scale of milliseconds. However, in the sample with the highest amount of vanadium this fast exchange was not registered. In our opinion, this might be a consequence of strong barriers on the particle surface.

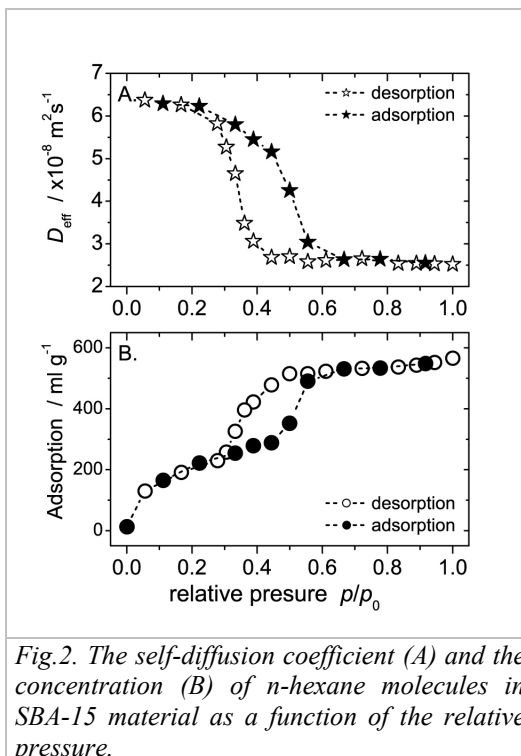


Fig.2. The self-diffusion coefficient (A) and the concentration (B) of *n*-hexane molecules in SBA-15 material as a function of the relative pressure.

The second type of experiments has been performed at sufficiently low temperatures with frozen liquid in the macropores in order to determine differences in the molecular diffusivities in the mesopores of the reference and of the modified materials. For all samples under study, no significant differences in the genuine intraparticle molecular diffusivities were found. From the observed dependence of the effective self-diffusion coefficient on the observation time we could determine an effective size of the SBA-15 particles: it was found that the particles in the samples modified by vanadiumsilicalite organize large agglomerates. In this case, molecules can travel from one individual particle to an adjacent one without crossing the macropores. Consequently, the mean lifetime of molecules in the mesopores of the modified samples is much larger than that in the reference material. The latter might be of importance for catalytic properties of such materials.

References

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- [2] R. Valiullin, P. Kortunov, J. Kärger, V. Timoshenko, *J. Chem. Phys.* 2004, 120: 11804.