diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Exploring the Diffusion Properties of Pseudomorphic MCM-41 Materials by PFG NMR

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1. Introduction

Ordered mesoporous silicas such as micelle-templated silicas (MTS) feature unique textural properties in addition to their high surface area: narrow mesopore size distributions, controlled pore size and connectivity make them particularly suitable for chromatographic applications (size exclusion chromatography, HPLC and capillary gas chromatography). In these applications, the particle morphology has to be tailored at the micrometer scale and the preparation of mesoporous silicas in the form of discrete monodisperse spheres with tunable sizes has been possible using the concept of pseudomorphic transformation [1].

Considering the foreseen applications, mass transfer properties are of considerable importance for these materials. On this subject Pulsed Field Gradient (PFG) NMR has proved to be a successful tool to study the diffusion of various molecules in porous materials [2]. The aim of this work is to show that PFG can be used to characterize the diffusion properties of pseudomorphic samples of MCM-41 at different synthesis stages.

2. Materials and methods

The mesostructured material was obtained after a pseudomorphic transformation of pre-formed porous silicas* by the dissolution/recrystallization of commercial silica gel particles of definite size and spherical shape: Lichrosphere 60 (Merck), particle diameter of 12 µm and wide pore size distribution centered on 60 Å, and Sylopol (Grace/Davison) spheroidic-particle mean diameter of 50 µm and an average pore size of 160 Å. The materials obtained after various times of synthesis were carefully dehydrated under vacuum and an amount of hexane corresponding to 40% of the adsorption capacity was subsequently adsorbed for diffusion studies. The PFG experiments were run on a 300 MHz Bruker DSX spectrometer equipped with a Diff30 probe delivering a maximum gradient of 12 $T.m^{-1}$. To avoid any effect arising from the presence of internal field gradients the bipolar 13-interval pulse sequence was preferred. The observation time Δ was varied from 6.5 ms to 12 ms.

3. Results and discussion

The spin echo attenuation curves $\ln (I / I_0) = f(g^2)$ clearly show two components (Fig. 1 A). The initial steep decay is attributed to molecules diffusing, at least partly, in the interparticle space. The second part represents the diffusion of n-hexane in the porous

* The synthesis was carried out at the Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique (LMCCCO) at Montpellier, France

network of the particle. A simple linear analysis gives us the associated effective diffusion coefficient D_{eff}. The measured diffusivities exhibit a dependence on the observation time characteristic of restricted diffusion (Fig.1 B). For small values of Δ and in the case of a totally reflecting interface D_{eff} should follow the equation [3] :

$$D_{eff}(\Delta) / D_0 = 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V} \sqrt{D_0 \Delta} \quad (1)$$

The genuine intraparticle diffusion coefficient D_0 is obtained from a linear fit of the curves $D_{eff} = f(\Delta^{1/2})$. For the samples formed from Lichrosphere a single diffusion coefficient is observed for the silica-gel and the MCM-41 transformed material. However, the analysis of the *S*/*V* ratios shows the progress of the MTS region with the synthesis time, eventually leading to the complete transformation of the particles.

A more complex behaviour is observed for the Sylopol samples. This requires a multicomponent nonlinear fit of the whole attenuation curve to extract all diffusion coefficients. Two distinct intraparticle diffusion coefficients are obtained and attributed to different regions of the particles. One corresponds to the untransformed silica located in the core of the particle, the other to the MCM-41 domain on the particle outer shell. Whatever the synthesis time, the estimated diameter of the Sylopol core is 30 µm based on the *S*/*V* ratio of Eq. (1). In this case the pseudomorphic transformation is fast but somehow limited.

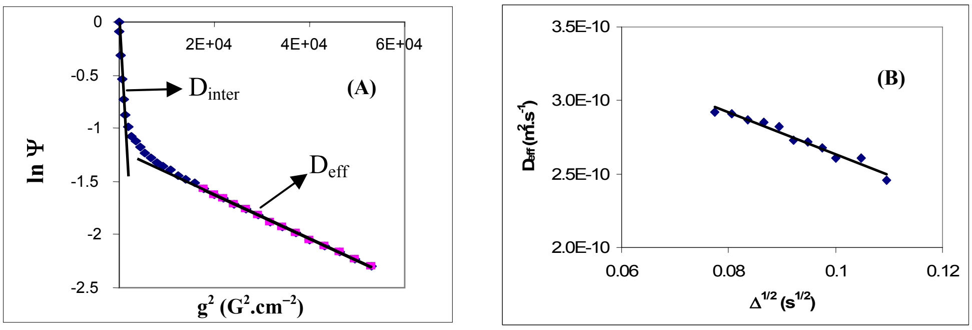

Fig. 1 : Spin-echo attenuation curve (A) and effective diffusivities (B) for n-hexane adsorbed in the pseudomorphic MCM-41 obtained from Lichrosphere 60 after 4 day synthesis. Δ = 9.5 ms

4. Conclusion

This preliminary study clearly shows the efficiency of PFG NMR to study innovative materials like pseudomorphic mesoporous silicas. This method gives not only information on the diffusion properties but also permits to gain insight into the internal structure of these materials at different stages of synthesis.

References

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