diffusion-fundamentals

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

Evidence for Subdomains in Large Crystals of NaX Zeolite

Ziad Adem, Flavien Guenneau, Marie-Anne Springuel-Huet, Antoine Gédéon

Laboratoire Systèmes Interfaciaux à l'Echelle Nanométrique, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05 (France), E-mail : ziad.adem@etu.upmc.fr

1. Introduction

Pulsed Field Gradient (PFG) NMR has proved to be a valuable tool to probe the intracrystalline diffusion of molecules adsorbed in microporous materials [1].

It is well-known that the purely intracrystalline diffusivity D_{intra} can only be attained, if the root mean square (rms) displacement of the molecules during the observation time is much smaller than the diameter of the crystallites. If it is not the case, a fraction of the diffusing molecules will feel the influence of the interface between the intra- and the inter-particle space. For PFG NMR measurements this condition requires the use of large-size crystals (typically more than 20 µm) which are rarely available commercially. The aim of this work was to exploit such a PFG-friendly sample of NaX zeolite and to follow the influence on D_{intra} of a wide variety of parameters such as the temperature, the nature of the adsorbate and its concentration.

2. Theory

In a PFG experiment, and in the ideal situation of normal self-diffusion, the coefficient D can be calculated from the equation [1] :

$$A = A_0 \exp\left[-\gamma^2 g^2 \delta^2 D(\Delta - \delta/3)\right] \quad (1)$$

where A is the amplitude of the NMR signal (spin echo), γ the gyromagnetic ratio of the nucleus under investigation, g the amplitude, δ the duration and Δ the separation of the gradient pulses. In general, owing to the high mobility of adsorbed molecules, the pore system of microporous materials can be considered as a homogeneous medium and the previous equation remains valid.

In the case of a totally reflecting interface, the measured effective diffusion coefficient is smaller than the genuine one and depends on the observation time, Δ. For small values of Δ it should follow the equation [2,3] :

$$D(\Delta)/D_0 = 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V} \sqrt{D_0 \Delta} + \beta \frac{S}{V} D_0 \Delta \quad (2)$$

3. Materials and methods

The NaX crystals with a silicon-to-aluminum ratio of 1.2 were kindly provided by Pr. Bao Lian Su (Université de Namur, Belgique). The scanning electron microscopy pictures (Fig. 1) show a close-to-perfect icosahedral geometry with crystal diameters around 80 µm. The sample was placed in a glass tube of 10 mm od equipped

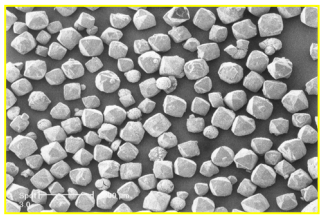

Fig. 1 : SEM micrograph of the NaX sample

with a Young valve. It was carefully dehydrated at a temperature of 400°C under vacuum and filled with a quantity of adsorbate corresponding to 2 molecules per supercage.

The experiments were run on a Bruker DSX spectrometer operating at a proton NMR frequency of 300 MHz. The probe was a Bruker Diff30, coupled with a 40 A current amplifier, leading to a maximum gradient value of 12 Tm^{-1}. We used the conventional spin echo (PFGSE) sequence for the smallest values of the observation time Δ, and switched as soon as possible to the stimulated echo variant (PFGSTE) to take advantage of the long T_1.

4. Results and discussion

Apart from the very first values, the variation of the effective diffusion coefficient with the square-root of the observation time for n-hexane follows a linear trend (Fig. 2). This is a clear sign of the existence of some restriction inside our sample. Fitting the values between 7.5 and 25 ms to Eq. 2 one obtains a genuine intracrystalline diffusion coefficient of 1.45×10^{-10} m^2s^{-1} which is notably smaller than the value found in the literature for a similar system [4]. By approaching the shape of the restricting region by a sphere, its radius is found to be 5 µm, in complete disagreement with the size of the crystallites. This suggests that some defects like local dislocations were produced during the synthesis but remained invisible on the SEM micrographs.

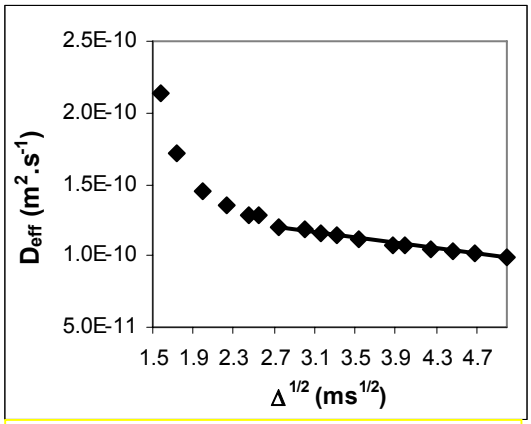

Fig. 2 : Effective diffusivity of n-hexane in zeolite NaX at 293 K as a function of observation time.

5. Conclusion

The first experiments on large-crystal NaX zeolites revealed that the sample was not homogeneous from the point of view of diffusion. The continuity of the porous system does not seem to exceed a few micrometers in contradiction with the other characterization techniques. Further experiments are in progress to confirm this result, by varying the temperature or changing the adsorbate.

References

[1] J. Kärger and D. M. Ruthven *Diffusion in zeolites and other microporous solids*; Wiley Interscience: New York, 1992.

[2] P.P. Mitra, P.N. Sen, L.M. Schwarz, Phys. Rev. B 47 (1993) 8565-8574.

[3] L.L. Latour, P.P. Mitra, R.L. Kleinberg, C.H. Sotak, J. Magn. Reson. A 101 (1993), 342-346.

[4] J. Kärger, F. Stallmach, S. Vasenkov, Magn. Reson. Imaging 21 (2003) 185-191.