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Combining macroscopic and microscopic diffusion studies in zeolites using NMR techniques

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Abstract

In this study the zero length column (ZLC) technique is extended to the case where the decay of the adsorbed phase concentration is observed directly by nuclear magnetic resonance (NMR). An adsorption–desorption apparatus compatible with a 400-MHz NMR spectrometer was developed. It operates with nitrogen or helium as the inert purge gas. The column of the adsorbent material is placed in the sensitive region of the superconducting magnet and the rf coil of the NMR spectrometer.

The time scales of the adsorption and desorption processes depend on concentration, temperature and crystal shape and are found to be in the range of 1–10 min. From the desorption branch, the non-equilibrium ZLC-NMR measurements yield intracrystalline diffusion coefficients in the range of 10^{-13} to 10^{-11} m^2/s for different alkanes in silicalite-1. These values are always found to be smaller than the values measured by pulsed field gradient NMR under equilibrium condition indicating that there must be additional transport resistance at the external surface of these silicalite-1 zeolite crystals.

Keywords: Diffusion; Porous media; Pulsed field gradient; Zeolites; ZLC

1. Introduction

The relation between the diffusivities obtained under equilibrium and non-equilibrium conditions in microporous materials—particularly in zeolites—is still an open problem of fundamental research. There are many rather contradictory results obtained by these two approaches [1]. One reason of this deficiency is clearly the fact that most of the laboratories working in the field of zeolitic diffusion are specialized in either equilibrium or non-equilibrium measurements. Hence, there are very few systems presented in the literature that have been equally thoroughly investigated by both equilibrium and non-equilibrium measurements.

Pulsed field gradient nuclear magnetic resonance (PFG NMR) studies [2] are now the most prominent equilibrium method for diffusion measurements. The application of this technique to molecules adsorbed in microporous materials such as zeolites has been pioneered in our laboratory [1]. In order to bridge the gap between the diffusion experiments performed under equilibrium and non-equilibrium conditions, we developed a methodology that allows us to use NMR as a detector for the adsorbed phase concentration in non-equilibrium diffusion studies. As a first step we decided to use the zero length column (ZLC) chromatography approach [1,3] to determine transport diffusion coefficients from the time dependence of the adsorbed phase concentration in a small bed of microporous materials, which is monitored by NMR. The experimental equipment, theoretical approaches and first results of these ZLC-NMR studies are presented in this paper. They are compared with the results of PFG NMR measurements performed with the same column of the microporous materials.

2. Equilibrium diffusion studies by PFG NMR

Pulsed field gradient NMR diffusion studies are a versatile tool to measure the Brownian (thermal) motion of molecules over distances from about 0.1 up to 100 μm. The technique measures the mean square displacement of the

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molecules carrying the nuclear spin under observation during a time interval Δ (observation time). This observation time is defined in the pulse sequence by the distance between the applied pulsed field gradients, which decode and read the position of the molecules. By stepwise increasing the intensity of these pulsed field gradients the amplitude of the spin echo observed in these experiments is reduced by

$$\psi(\delta g, \Delta) = \exp\{-\gamma^2\delta^2 g^2 D(4\Delta + 6\tau - 2\delta/3)\}, \tag{1}$$

where γ denotes the gyromagnetic ratio and δ and g are the width and the intensity of the pulsed field gradients, respectively.

D is the self-diffusion coefficient, which is related via Einstein equation to the mean square displacement. The above equation applies for the 13-interval PFG NMR pulse sequence [4], which is the preferred method for NMR diffusion studies in porous (heterogeneous) systems, where internal field gradients may occur. This PFG NMR technique does not require a macroscopic concentration gradient in order to measure the diffusivity. Therefore, it represents an equilibrium technique for diffusion studies.

3. Non-equilibrium diffusion measurements by ZLC

The ZLC technique has been widely used to determine intracrystalline or intraparticle diffusion in zeolite-based adsorbents. For gaseous systems it can be used for measuring transport diffusivities at zero loading [3], self-diffusivities (Tracer ZLC) [5] and transport diffusivities in mixtures [6]. The theoretical aspects of the technique have been extensively studied [3,5–14]. In a conventional ZLC experiment, a small sample of adsorbent (~1 mg) is exposed to an adsorbate at known partial pressure in an inert carrier stream. The sample is then purged with a stream of the pure carrier and the decay of the sorbate concentration in the effluent is followed. The basic assumption of the ZLC method is that there is no overall gradient of sorbate concentration through the cell. In other words, it can be assumed that it behaves as a perfectly mixed cell. Other assumptions are spherical particles of radius R, isothermal system and linear equilibrium at the particle surface. The general solution for the time dependence of the concentration of the gas phase $c(t)$ to such a system is given by [7]

$$\frac{c}{c_0} = \sum \frac{2L}{\beta_n^2 + \left(1 - L + \gamma\beta_n^2\right) + L - 1 + \gamma\beta_n^2} \exp\left(-\beta_n^2 \frac{D}{R^2} t\right), \tag{2}$$

where β_n are the positive roots of

$$\beta_n \cot\beta_n + L - \gamma\beta_n^2 = 0, \tag{3}$$

with

$$L = \frac{1}{3}\frac{F}{KV_\mathrm{s}}\frac{R^2}{D} \tag{4}$$

and

$$\gamma = \frac{1}{3}\frac{V_\mathrm{f}}{KV_\mathrm{s}}. \tag{5}$$

In these equations c_0 represents the initial steady value of $c(t)$, D is the transport diffusion coefficient, F represents the purge volumetric flow rate, K the dimensionless Henry law constant, V_f and V_s represent, respectively, the fluid and the solid volume in the ZLC cell.In gaseous systems $\gamma \rightarrow 0$ and Eq. (2) reduces to

$$\frac{c}{c_0} = \sum_{n=1}^{\infty} \frac{2L}{\beta_n^2 + L(L-1)} \exp\left(-\beta_n^2 \frac{D}{R^2} t\right). \tag{6}$$

The parameter L can be viewed as the ratio between the diffusional time (R^2/D) and the contact time (KV_s/F). If $L<1$, the desorption rate is determined by convection under equilibrium conditions (equilibrium control). For $L>5$ the desorption rate is controlled by the diffusion of the sorbate out of the particle (kinetic control). Since L is proportional to the purge volumetric flow rate (F), runs at different flow rates have to be made to verify that the system is kinetically controlled. This procedure ensures reliable measurements of diffusion coefficients.

In our study, measurements were carried out by following the decay of the adsorbed phase concentration (based on the intensity of the NMR signal). In this case the solution to the system (equivalent to Eq. (2)) is given by [15]

$$\frac{\bar{q}}{q_0} = \sum_{n=1}^{\infty} \frac{6L^2}{\beta_n^2(\beta_n^2 + L(L-1))} \exp\left(-\beta_n^2 \frac{D}{R^2} t\right), \tag{7}$$

where $\bar{q}$ is the average adsorbed phase concentration over the zeolite crystal, q_0 is the value of $\bar{q}$ in equilibrium with c_0.

4. Method of combined equilibrium and non-equilibrium diffusion studies

A schematic of the ZLC-NMR apparatus is shown in Fig. 1. The column placed within the 400 MHz NMR spectrometer equipped with a superconducting magnet consists of two concentric glass tubes approximately 120 cm long. A short bed of silicalite-1 (~25 mg) is placed at the bottom of the inner tube within the rf coil of the NMR probe. The sorbate tank is equipped with a two-stage pressure regulator. The experiment consists of exposing the zeolitic bed to a stream of carrier gas (N_2) regulated with a rotameter (max 2l/min N_2) and containing a certain amount of sorbate regulated by varying the outlet pressure of the pressure regulator. After passing through the bed the gas stream exits the column through the outer tube. The soap bubble flow meter is used to measure the volumetric flow rate of the stream leaving the column. After switching on the sorbate flow through the column the increase of the adsorbed phase concentration is monitored by the increase of the NMR signal amplitude. Reaching the equilibrium concentration manifests itself by a constant, nonzero NMR signal amplitude. For the system isobutane/silicalite-1 this