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Gas Transport in Aluminosilicate Nanotubes by Diffusion NMR

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Abstract

Diffusion of tetrafluoromethane in aluminosilicate nanotubes was studied by means of ^{13}C pulsed field gradient (PFG) NMR at 297 K. The measured data allow the estimation of the diffusivity of tetrafluoromethane inside the nanotubes as well as the diffusivity for these molecules undergoing fast exchange between many nanotubes. The results support the assumption about the one-dimensional nature of the tetrafluoromethane diffusion inside nanotubes.

Key words: PFG NMR, ^{13}C NMR, nanotubes, diffusion

1. Introduction

Information about diffusion of confined molecular species inside nanotube channels has high relevance due to potential applications of nanotube systems as sensors, catalysts, and membranes. Studies of transport in one-dimensional channels are also of high interest because of the possibility of an observation of the unique “single-file” type of diffusion [1]. In this contribution, we demonstrate the potential of ^{13}C pulsed field gradient (PFG) NMR at high magnetic field and high magnetic field gradients for investigations of transport of adsorbed gas molecules in novel aluminosilicate nanotubes.

2. Experimental

Single-walled aluminosilicate nanotubes were synthesized according to the protocol given in references [2, 3]. Tetraethoxysilane and Aluminum-tri-sec-butoxide mixture (1:2) was added dropwise to aqueous solution of 0.05M $HClO_4$ at 25 ˚C. After 18 hours of vigorous stirring, the solution temperature was increased to and kept constant at 95 ˚C

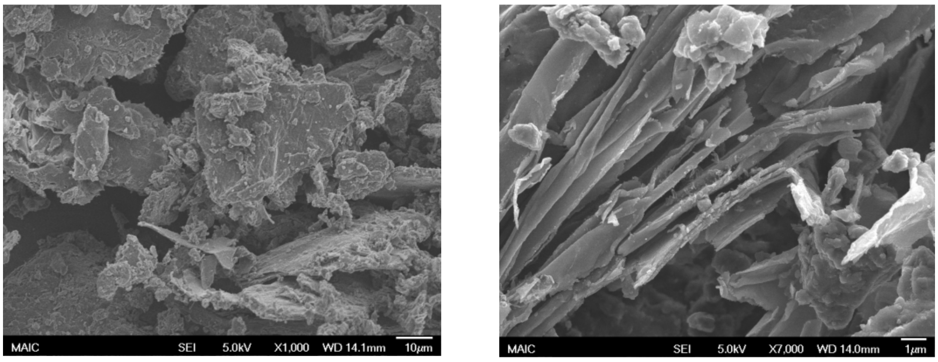

Fig. 1: SEM images of aluminosilicate SWNT bundles. The white scale bars represent 10 μm (left) and 1 μm (right).

for 4 days. At the end of 4 days, the nanotubes were first precipitated by addition of a 30 wt % ammonia solution, the resulting gel was then centrifuged and 10 N HCl was added dropwise to re-disperse the nanotubes. Nanotube dispersion solution then dialyzed against de-ionized water for 4 days using a 15 kiloDalton membrane to obtain a pure nanotube dispersion. Nanotube powder samples were prepared by freeze-drying pure nanotube dispersion solution at -50˚C for 5 days.

These nanotubes exhibit uniform channels having an outer diameter of around 2.2 nm and inner diameter ~1.0 nm. Fig.1 shows selected SEM images of the studied nanotube sample. The images show that nanotubes are packed into bundles revealing sandwich-like structures with sizes ranging from half a micrometer to a few tens of micrometers.

The aluminosilicate nanotube samples have been prepared using the following procedure. Around 150 mg of the nanotubes was placed into a 5 mm NMR tube with a medium wall thickness. The sample was activated under high vacuum (10^{-4} mbar) at 453 K. Following the sample activation, a fixed amount of ^{13}C-labelled CF_4 was cryogenically transferred into the NMR tube containing the sample. After loading, the tube was flame sealed and separated from the vacuum system. The resulting gas pressure inside the tube is estimated to be around 8 bar after equilibration at 298 K.

Diffusion measurements were performed using a 17.6 T Bruker BioSpin NMR spectrometer operating at a ^{13}C resonance frequency of 188.6 MHz. The spectrometer is equipped with the Diff60 probe and Great-60 gradient amplifier (Bruker BioSpin) capable of producing magnetic field gradients with the maximum amplitude of 30 T/m. Diffusion studies were performed using the stimulated echo sequence with the longitudinal eddy current delay (PGSTE LED) [4]. Diffusion data were obtained from PFG NMR attenuation curves, i.e. the dependence of the PFG NMR signal intensity on the amplitude of the magnetic field gradient. The signal intensity was obtained by integrating the area under the single line of the ^{13}C NMR spectrum of tetrafluoromethane. ^{13}C PFG NMR was employed instead of the more traditional ^{1}H PFG NMR to take advantage of the longer ^{13}C T_2 relaxation times that are typically observed for guest molecules confined in nanopores. Proton T_2 NMR relaxation times of molecules confined in nanopores tend to be very short due to intra-molecular and inter-molecular dipole-dipole interactions that are not completely averaged out by molecular motion as well as magnetic susceptibility effects. Such effects are reduced when using ^{13}C instead of ^{1}H NMR detection.

3. Results and Discussion

Fig. 2 presents ^{13}C PFG NMR attenuation curves for diffusion of CF_4 in the nanotube sample at 298 K. The attenuation curves were obtained for three different effective diffusion times (t_{eff}) – 4, 8 and 16 ms. These curves do not contain any contributions from the CF_4 diffusion in the gas phase above the bed of nanotube bundles. The bulk gas phase contributions, which were determined in separate experiments performed on an NMR tube containing only CF_4 gas at a comparable pressure, were subtracted away from the measured attenuation curves.

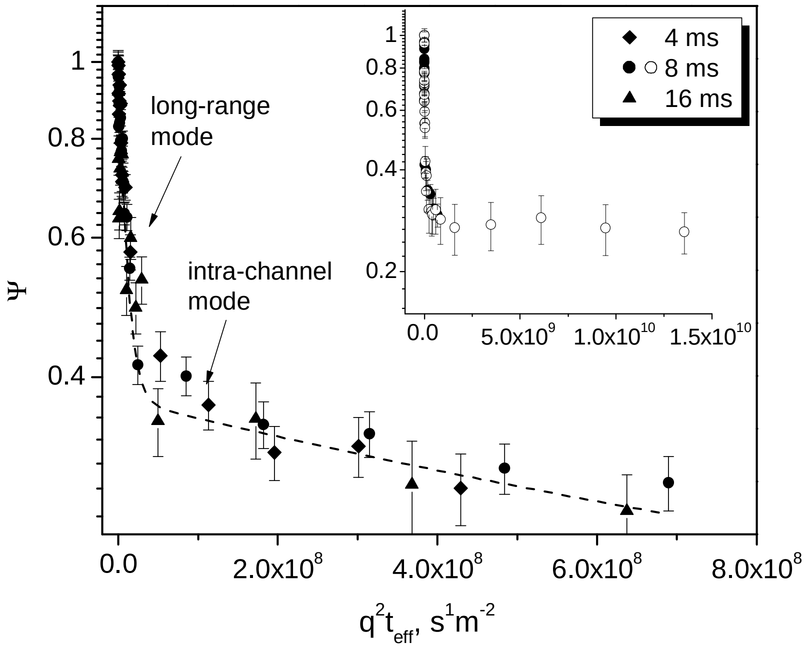

Fig. 2: Diffusion attenuations for tetrafluoromethane in aluminosilicate nanotubes obtained for different effective diffusion times. The dashed line represents the best fit result using Eq. (1). The inset shows the diffusion data for t_{eff} = 8 ms in the larger gradient range. The empty and filled circles in the insert show the attenuation curves measured for different delays between the first and second $\pi/2$ pulses of the PGSTE LED sequence (τ_1= 2.7 and 1.3 ms).

In the case of unrestricted and isotropic diffusion PFG NMR attenuation curves are expected to follow a mono-exponential behaviour, viz. $\psi_{is}(q,t_{eff}) = \exp(-q^2 t_{eff} D)$, where D is the self-diffusion coefficient, $q = \gamma g \delta$, γ is the gyromagnetic ratio for ^{13}C, δ denotes the duration of an applied gradient pulse with amplitude g, and t_{eff} is the effective diffusion time. The attenuation curves in Fig. 2 show significant deviations from such behaviour.

CF_4 molecules are expected to be able to pass one another inside nanotubes because the collision diameter of CF_4 (0.466 nm [5]) is smaller than the largest effective radius of the nanotubes (≥ 0.5 nm). Hence, the intra-nanotube transport of CF_4 molecules is expected to obey the mechanism of normal, *i.e.* Fickian, diffusion. Due to the presence of many short (≤ 1 µm) nanotubes (short as compared to the distances travelled by molecules during the observation time) and nanotube bundles in the studied sample, in addition to the intra-channel diffusion, we expect an ensemble of CF_4 molecules that diffuse according to the mechanism of the so-called long-range diffusion, i.e. diffusion leading to fast exchange [6] between the nanotube interiors and the surrounding gas phase between the nanotubes or nanotube bundles. Thus, the attenuation curve is expected to contain two terms:

$$\psi_{tot}(q,t_{eff}) = p_{lr}\exp(-q^2 t_{eff} D_{lr}) + (1 - p_{lr})\psi_{intra}(q,t_{eff}), \tag{1}$$

where p_{lr} represents the fraction of molecules performing long-range diffusion with diffusivity D_{lr}, and $(1 - p_{lr})$ is the fraction of adsorbed molecules never leaving the tubes during the observation time. For intra-channel diffusion within one-dimensional channels, which are randomly oriented, the attenuation function $\psi_{intra}(q,t_{eff})$, according to [7], can be expressed in the following form:

$$\psi_{intra}(q,t_{eff}) = \frac{1}{2}\sqrt{\pi}\exp(-q^2 t D_{\perp}) \times \frac{erf\left(\sqrt{q^2 t\left(D_{\parallel} - D_{\perp}\right)}\right)}{\sqrt{q^2 t\left(D_{\parallel} - D_{\perp}\right)}}, \tag{2}$$

where $D_{\parallel}$ and $D_{\perp}$ are the diffusivities along the directions parallel and perpendicular to the channel axis, respectively.

It was found that Eq. 1 can be used to obtain good fits to all of the experimental data (see dashed line in Fig. 2). The corresponding best fit parameters for all 3 diffusion times used were found to be the same within the experimental uncertainty ($D_{\parallel}$ =1.7·10^{-9} m^{2}s^{-1}, $D_{\perp}$ =1.0·10^{-13} m^{2}s^{-1}, D_{lr} =1.1·10^{-7} m^{2}s^{-1}, and p_{lr} =0.62). Using the Einstein relation [8], $\langle r^2 \rangle = 2D_{\parallel} t_{eff}$, the corresponding limiting values of the root mean square displacements for diffusion inside the nanotubes are estimated to be approximately 4 µm for 4 ms and 8 µm for 16 ms. These results are consistent with the observation of many sufficiently large (>10 µm) nanotube bundles in the studied sample (Fig. 1), where molecules can cover distances of up to 8 µm without leaving a nanotube channel. Our data indicate that, within the experimental uncertainty, the intra-channel diffusivity remains independent of diffusion time. Hence, we can conclude that this diffusivity value is not significantly influenced by possible additional transport resistances at the channel margins. The observed independence of the value of p_{lr} of diffusion time for the studied range of $t_{eff} \leq$ 16 ms can be explained by the existence of a broad distribution of nanotube bundle lengths. As a result, there is a fraction of sufficiently short nanotubes contributing to the long-range diffusion, while for other (longer) nanotubes the diffusion can be described as purely intra-channel. Finally, the observed independence of the long-range diffusivity of diffusion time suggests that the conditions of fast exchange between the short nanotubes and the surrounding gas phase are fulfilled for all studied diffusion times. PFG NMR measurements for $t_{eff} > 16$ ms were prevented by the decrease of the CF_4 signal due to T_1 NMR relaxation.

The diffusivity along the direction of the channels was found to be at least 4 orders of magnitude larger than that in the direction perpendicular to the channels, indicating that the density of defects that would allow diffusion of CF_4 molecules in the direction perpendicular to the channel direction is negligible.

In order to ule out a possible influence of magnetic susceptibility effects on the measured diffusion data, additional PFG NMR measurements were performed for the same effective diffusion time (t_{eff} = 8 ms) but with different values of the delays between the first and second $\pi/2$ pulses of the PGSTE LED sequence (τ_1= 2.7 and 1.3 ms). The observed coincidence of the PFG NMR attenuation curves measured for different values of τ_1 confirms that susceptibility effects are negligible under our measurement conditions [9].

4. Conclusions

^{13}C PFG NMR at high field and high gradients was used to study diffusion of tetrafluoromethane in novel aluminosilicate nanotubes. The data provide evidence for 1D diffusion within non-intersecting channels. The measured PFG NMR diffusion data yielded the self-diffusion coefficient of CF_4 along the channel direction in the nanotube interior as well as the corresponding diffusivity of CF_4 molecules undergoing fast exchange between many nanotubes.

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