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Pulsed field gradient NMR study of surface diffusion in mesoporous adsorbents

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ABSTRACT

Surface diffusion of *n*-heptane in two mesoporous adsorbents with different morphologies of the pore network, namely Vycor random porous glass and porous silicon with linear pores, have been studied using pulsed field gradient NMR. The experimentally obtained diffusivities revealed increasing mobility of guest molecules with increasing surface coverage, indicating heterogeneity of the surface properties. The diffusion studies at different temperatures have further confirmed this hypothesis. The activation energies for surface diffusion turned out to be a function of surface coverage. The experimental results obtained are analyzed using a model of surface diffusion taking account of a distribution of the transition rates.

1. Introduction

By high transport properties and high surface area, mesoporous materials are presently becoming an important ingredient of chemical industry. The efficiency of these materials is further determined by flexible tunability of their structure and surface functionality, offering remarkable options for the process-oriented optimization of their properties. While surface treatment is mostly used to provide a required chemical functionality, the structural details largely affect dynamical behavior of confined guest species. Concerning structural properties, these materials may generally be subdivided onto two groups, *viz.* with ordered and disordered pore networks. The most prominent representatives of the first group, which are typically produced via supramolecular templating, are well-known MCM-41 [1] and SBA-15 [2] materials. The second group is amply typified by porous glasses, resulting from, e.g., sol–gel or phase separation processes [3,4]. During the last decade, a rich variety of novel mesoporous materials with quite different morphologies of the pore networks and chemical compositions of the solid framework have been synthesized [5,6]. In turn, this necessitates further development of analytical techniques for their structural characterization [7]. In addition, the optimal use of these materials in applications exploiting their advanced transport properties demands establishing detailed structure–dynamics relationships, similar to those obtained for a large family of microporous adsorbents [8,9].

Among different mechanisms of molecular transport, surface diffusion plays a significant role, sometime being the dominating mechanism of the mass transfer through porous solids. Quite generally, it may be associated with a thermally-activated hopping motion of the guest molecules along the surfaces. Being one of the key points for understanding chemical reactions or processes of crystal growth, this phenomenon has been extensively explored (see, e.g., reviews [10–12]). However, it turns out that accurate theoretical treatments of surface diffusion is possible only in some limiting cases, such as for particle ensembles on homogeneous surfaces with a solely hard-core intermolecular interaction. The analysis is much more complicated for the heterogeneous surfaces. While the analysis is still possible for single particles on lattices with frozen disorder, the particle ensembles can be hardly treated [13,14]. Under certain assumptions about the microscopic nature of the jump process, however, some general properties can be obtained [15–17]. Much progress in the understanding of surface diffusion have been attained using computer simulation methods. Illuminating some general patterns in the diffusion behavior, these studies simultaneously shown a very reach behavior depending on the involved intermolecular and adsorbate–substrate interactions, distributions of site and/or barrier energies, temperature and concentration of particles [18–21].

For experimental studies of surface diffusion, two different approaches are commonly used. One of them is based on the creation of a gradient of the chemical potential (e.g., via pressure or concentration gradients) and measuring the resulting fluxes. In this way, the so-called chemical diffusion coefficient is measured, which contains information about both single-molecule and cooperative modes of the molecular transport. Another approach is designed to operate under the equilibrium conditions by, e.g., "labeling" a molecule and following its trajectory [22–25]. This type of experiments typically yields tracer diffusivity (also referred to as self-diffusivity). Exactly this quantity is also probed by pulsed field gradient nuclear magnetic resonance (PFG NMR)

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[26–28] used in this work. Importantly, this method allows to non-invasively measure the ensemble-averaged molecular mean squared displacements. This, first of all, substantially broadens the experimental possibilities to address various aspects of diffusion in porous materials [29] and, in particular, of surface diffusion. In addition, the thus obtained data may provide a good basis for comparison with the data of the single particle tracking techniques [22–25]. Thus, it has been recently anticipated that these two approaches may, under certain conditions, yield non-equivalent information [30,31].

In our previous work, we have demonstrated that PFG NMR can be successfully applied to study surface diffusion in mesoporous materials [32]. In particular, surface diffusivities of two organic molecules have been measured as a function of surface coverage in mesoporous silicon. The results obtained have revealed an inhomogeneity of the surface properties. An additional evidence for this was provided by the measured activation energies for diffusion for three samples with different surface coverages. Although the qualitative explanation was satisfactory, some interesting questions remained unexplored. First of all, it is unclear what kind of heterogeneity, chemical or geometrical, accounts for the observed phenomenon. Secondly, the activations energies were measured only for three different concentrations that reveals only qualitative behavior. A more detailed information on this quantity may yield deeper insight into the microscopic details of the surface diffusion process. To address these issues, we studied the surface diffusion process in two mesoporous materials with different morphologies of the porous space, namely Vycor random porous glass and porous silicon with linear pores. This allowed us to address the influence of the pore space morphology on the surface diffusivities. In addition, by measuring the activation energies for diffusion in a broad range of the surface coverages, we demonstrate a competitive effect of different mechanism affecting the process of surface diffusion.

Finally, we would like to mention that due to strong dependence of the surface diffusivity on adsorbate–substrate interaction, the macroscopic observables, such as molecular displacements probed by PFG NMR, have fingerprints of the surface properties. Hence, being properly analyzed, the data on surface diffusion may provide unique information on surface characteristics not accessible by other techniques. For example, site energy distribution can be assessed using the measurements of gas adsorption [33]. However, these data may hardly distinguish different surface topographies, i.e., how the sites with different adsorption energies are distributed over the surface. It has long been anticipated that combined adsorption–diffusion studies may help to reconstruct the surface topography [19]. The relevant experimental data, however, are rarely available in the literature. In this respect, we hope that the results of the present study may further contribute to this issue.

2. Materials and methods

One of the goals of this work was to check how the pore space morphology may affect process of the surface diffusion of guest molecules. This has determined our choice of two well-known representatives of the mesoporous materials with different pore structures. The first of them is Vycor porous glass [4], having a very networked 3D structure of the porous space with an average pore diameter of about 5 nm. In contrast to Vycor, the second material, mesoporous silicon, was produced to have linear pores with the similar average pore diameter. Importantly for PFG NMR studies, both materials are monolithic ones. The Vycor porous glass used was purchased in a rod-like form with a length of 1 cm and a diameter of 3 mm. The thickness of the used mesoporous silicon films exceeded 200 μm.

The mesoporous silicon sample [34] was prepared by electrochemical etching of the single-crystalline (100)-oriented p-type Si wafers with a resistivity of $(2-5)\times10^{-3}\ \Omega$ cm. The electrolyte contained HF (48%) and C_2H_5OH in a ratio of 1:1. The porous silicon films were grown using an anodization current density j of 20 mA/cm^2. With these parameters, the linear pores with the average pore diameter of about 6 nm grow perpendicularly to the substrate surface [35]. After the mesoporous silicon film had been formed, it was removed from the substrate by means of an electropolishing step with j = 700 mA/cm^2 applied for 2–3 s. For the chemical stabilization of the surface, it was thermally oxidized at T = 570 K in ambient atmosphere during 3 h. Vycor porous glass (#7930) was purchased from Corning Inc., Corning, NY, USA. Before the use, following recommendations of the manufacturer the samples were cleaned by boiling in 35% H_2O_2 for a several hours. For the further measurements, the porous silicon films have been stacked in a glass NMR tube. In this way, we ensured that the direction in which the molecular displacements have been detected using PFG NMR coincided with the pore axes in the porous silicon.

The samples with different surface coverages c, also referred to as concentrations, have been prepared by adsorption from the gas phase prepared to have a given vapor pressure P. The actual values of c were estimated using the data on the preliminarily measured amounts adsorbed as a function of the external gas pressure. Fig. 1 shows such normalized data for n-heptane (which further was used for the diffusion studies) in Vycor and porous silicon at T = 298 K. The data shown have been obtained by measuring the signal intensities S of the ^{1}H NMR free induction decay [36,32]. It reflects the total amount of protons and, hence, of the adsorbed molecules in the sample. Before the measurements, we have made sure that T_2-weighting effect upon changing the pore loading are minimal [32]. The relative amount adsorbed θ in the pores at a given pressure was obtained by the normalization of the respective S with respect to that at the full pore saturation. The latter corresponds to the equilibrium with the gas at a pressure slightly below of the saturated vapor pressure P_s. To convert θ to the corresponding surface concentration c, the low-pressure part of the adsorption isotherms were fitted to BET equation to obtain θ_1, namely the relative amount required to cover the surface by one monomolecular layer. Consequently, c results as θ/θ_1.

The PFG NMR diffusion experiments have been performed on a NMR spectrometer operating at a 400 MHz resonance frequency on

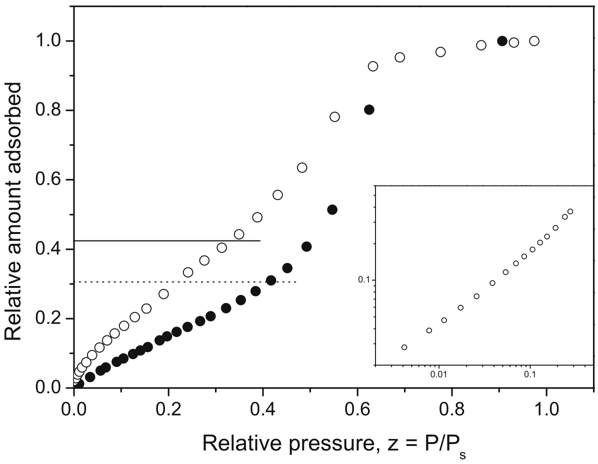

Fig. 1. Normalized adsorption isotherms for n-heptane in Vycor (open circles) and porous silicon (filled circles) measured at T = 298 K. The solid and dashed lines show the monolayer coverages θ_1 obtained by fitting the BET equation to the data up to $z\approx0.5$ for Vycor and porous silicon, respectively. The inset shows the double-logarithmic plot of the same data for Vycor for $z\leqslant0.4$.