

# Diffusion of cyclohexane in native and surface-modified mesoporous glasses

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**Abstract** Diffusion of cyclohexane in mesoporous silica materials with different degrees of surface silanization has been probed by means of pulsed field gradient nuclear magnetic resonance. The self-diffusion coefficients have been measured at various pore fillings from about 10% of one monolayer coverage to complete pore saturation by the capillary-condensed phase. It is found that the surface modification, namely grafting of dimethyloctadecylmethoxysilane molecules to the silica surface, reduces diffusivities of guest molecules as compared to the native sample. The contribution of the Knudsen molecular diffusion to the measured diffusivity has been assessed using the model of fast molecular exchange between the adsorbed phase on the pore walls and the molecules in the gaseous phase in the pore interior. The diffusivity data were correlated with the degree of the surface modification, with the latter being probed by measuring  $^1\text{H}$  and  $^{13}\text{C}$  spectra using magic angle spinning (MAS) solid state NMR, nitrogen adsorption and thermogravimetry.

**Keywords** Adsorption · Surface modification · Diffusion · Mesopores · NMR

## 1 Introduction

Behavior of molecular ensembles confined to pores of mesoporous silica materials is a matter of continuous research over the last decades (Hansen et al. 1996a, 1996b; Hwang et al. 2001; Vyalikh et al. 2005). Since these host materials provide relatively high transport rates for guest entities and simultaneously the physico-chemical properties of the intrapore surfaces of these materials can be chemically modified (Anwander et al. 2000; Whilton et al. 1999), mesoporous silica catalysts are considered as promising candidates for novel catalytic applications. This has initiated a few recent studies of the dynamics of guest molecules in mesoporous silica (Aksnes and Gjerdaker 1999; Gedat et al. 2001; Shenderovich et al. 2003). A set of NMR techniques have been utilized to establish an influence of the pore geometry, of the degree of the pore filling and of the surface properties on dynamics and phase behavior of confined molecular species in mesoporous Sorbsil (Aksnes and Gjerdaker 1999), MCM-41 (Gedat et al. 2001) and SBA-15 (Shenderovich et al. 2003) materials, as only a few representative examples.

Upon variation of the fluid content in mesopores, the character of the diffusion processes may change significantly (Valiullin et al. 2004, 2005a). In part, this is related to the fact that the fluid phase state may change (Valiullin et al. 2009), which ultimately will lead to a respective transition in the mechanisms of molecular propagation. Thus, for low adsorption, corresponding to one monolayer surface coverages or less, the molecular diffusion is determined by two microscopic mechanisms, namely (i) hopping-like surface diffusion along the inner surface of the adsorbent (Dvoyashkin et al. 2009; Valiullin et al. 2005b), and (ii) diffusion through the gaseous phase in the pore interior, known as Knudsen diffusion (Knudsen 1909;

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Pollard and Present 1948). At higher pore loadings, corresponding to the region of multilayer adsorption, the character of diffusion of such multilayered molecules may differ from that at sub-monolayer coverages (Choi et al. 2001). In the range of capillary-condensation, the transport pattern is predominantly determined by the pore-space geometry, such as pore-size distribution, interconnectivity of the neighboring pores, and surface roughness (Choi et al. 2001; Dvoyashkin et al. 2007; Malek and Coppens 2001; Sapoval et al. 1996; Valiullin and Skirda 2001).

In the present work, we study diffusion of cyclohexane as a guest molecule in the mesopores of the Controlled Pore Glass (CPG) at various degrees of the pore loadings. As an essential point, we have studied the effect of the surface silanization on the transport properties of the guest molecules. The surface modification was monitored using  $^1\text{H}$  and  $^{13}\text{C}$  cross-polarization MAS NMR spectroscopy (Sutra et al. 1999), nitrogen adsorption and thermogravimetry. A comprehensive diffusion analysis may help to better understand the relative contributions of different transport modes to the overall transport of organic molecules in random silicas with different surface properties for their further optimal use in technical applications.

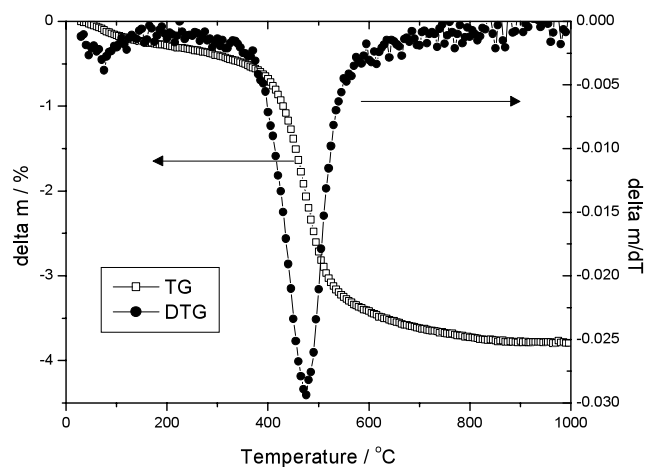
## 2 Experimental

### 2.1 Material

The CPG 10-75 supplied by Fluka is a common solid support having amorphous pore network (Ciesla and Schüth 1999). It consists of a highly interconnected pore network and has a narrow pore size distribution with an average pore diameter of 8.1 nm and with a porosity of 57%. The cross-section of pores of CPG is approximately circular and, therefore, its structure may be represented by a network of cylindrical pores. The specific surface area provided by manufacturer is  $182\text{ m}^2/\text{g}$  and the specific pore volume is  $0.47\text{ cm}^3/\text{g}$ . Before modification, in order to remove organic impurities, the glass particles were stored in 30%  $\text{H}_2\text{O}_2$  solution during 4 hours at 400 K.

### 2.2 Standard procedure for the surface modification

Before modification the porous glass samples were activated at 673 K for 2 hours to remove the physisorbed water. The reactions of porous glass with different amounts of dimethyloctadecylmethoxysilane were carried out in dried toluene at 383 K for 24 hours in teflon containers (1g CPG + 2 ml toluene + 0.0803 g (sample-1), 0.1544 g (sample-2), 0.2241 g (sample-3) and 0.3034 g (sample-4) silane). After the reaction, the samples were washed with 40 ml hot toluene and dried in vacuum at 343 K for 24 hours.



**Fig. 1** Thermogravimetry (*squares*) and its temperature derivative (*circles*) graphs of the sample-3

**Table 1** Textural parameters of the modified samples obtained by nitrogen adsorption

Sample number	BET-surface / $\text{m}^2/\text{g}$	Volume / $\text{cm}^3/\text{g}$	Pore width / nm (BJH <sub>des</sub> )
Original	174	0.60	98
1	153	0.52	91
2	149	0.51	92
3	140	0.48	88
4	145	0.50	88

To obtain the surface density of the bonded silane groups, the samples were investigated by means of thermogravimetry and nitrogen adsorption (ASAP2000). Thermogravimetric measurements were carried out in helium with a heating rate of 10 K/min. As shown in Fig. 1, the silane molecules were decomposed at about 700 K. From the mass difference, the number of silane molecules bonded on the surface was calculated.

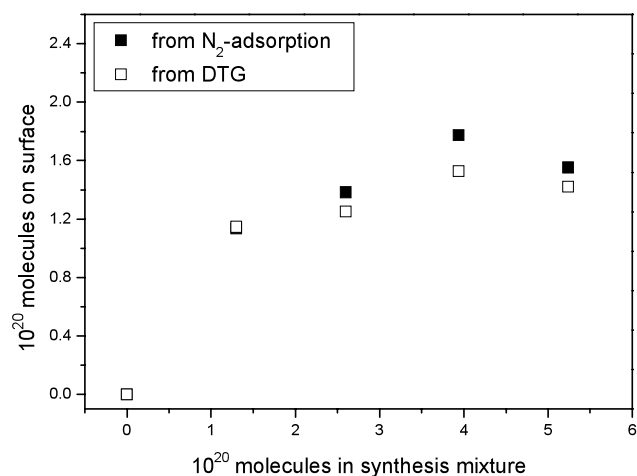
Data on textural parameters of the original and modified samples are given in Table 1 as revealed by nitrogen adsorption. The number of silane molecules on the surface was derived assuming a molecular volume of  $413\text{ cm}^3/\text{g}$  for  $\text{SiC}_{20}\text{H}_{44}$ . The calculated occupation of OH-groups by silane molecules are summarized in Table 2 (OH-concentration of the original surface is  $3.94 \cdot 10^{20}\text{ g}^{-1}$ ). The correlation between the number of silane molecules in the synthesis mixture and the surface silane groups is given in Fig. 2.

### 2.3 MAS NMR characterization

The samples for MAS NMR measurements were prepared by heating 11 mg of the porous glass in glass tubes of 3 mm

**Table 2** Data on percentage of OH groups substituted by grafted dimethyloctadecylmethoxysilane as derived from thermogravimetry and nitrogen adsorption experiments

Sample number	Thermogravimetry / %	Adsorption / %
Original	taken as 0%	taken as 0%
1	29.1	28.7
2	31.8	35.1
3	38.8	45.0
4	36.1	39.4

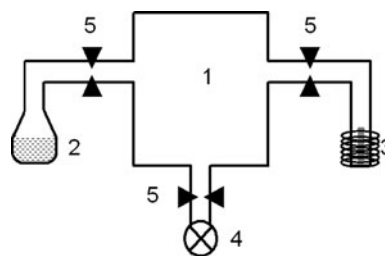
**Fig. 2** Calculated number of surface bonded silane molecules in dependence on the number in the synthesis mixture

outer diameter. The CPG porous glass without surface modification was activated by an increase of the temperature from 298 K to 673 K at a rate of 10 K h<sup>-1</sup>. Further, the samples were maintained at 673 K for 24 h under vacuum. The modified CPGs were activated by an increase of the temperature from 298 K to 353 K.

NMR measurements were performed on a Bruker AVANCE 400 spectrometer equipped with a double-resonance magic angle spinning (MAS) probe. Zirconia rotors (4 mm outer diameter) with the inserted sealed glass tube were spun at 10 kHz. <sup>1</sup>H MAS NMR spectra were recorded by the Hahn-echo pulse sequence ( $\pi/2-\tau-\pi-\tau$ -acquire), where  $\tau$  equals to one rotor period (100  $\mu$ s). The excitation pulse length ( $\pi/2$ ) was 1.2  $\mu$ s and repetition time was 5 s. The <sup>13</sup>C MAS NMR spectra were recorded by the cross-polarization sequence using  $\pi/2$  proton pulse duration of 3  $\mu$ s, contact time of 5 ms and repetition time of 4 s. For each <sup>13</sup>C MAS NMR spectrum 14 000 scans were accumulated.

#### 2.4 Pore loading and PFG NMR diffusion measurements

The procedure of saturation of the porous material by guest molecules was similar to that described elsewhere (Valiullin

**Fig. 3** Scheme of the adsorption facility used for preparation of a certain pore loading. (1) reservoir with prepared pressure, (2) flask with liquid cyclohexane, (3) NMR tube with porous material, (4) turbomolecular pump, (5) valves

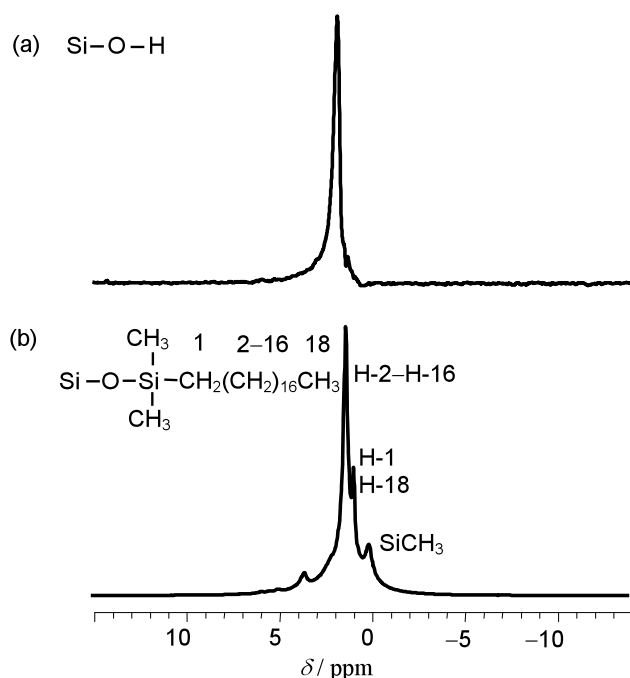
et al. 2004). The long glass NMR tube with CPG was connected to a reservoir with a volume notably exceeding that of the total pore volume (Fig. 3). First, the reservoir was filled with a gas under study. The gas pressure was controlled using a high precision pressure gauge ( $\pm 10^{-6}$  bar). Thereafter, the gas in the reservoir was brought into contact with the porous glass. The amount of adsorbed liquid was controlled by measuring the <sup>1</sup>H NMR free induction decay signal intensity (Valiullin et al. 2004). Thus, by increase or decrease of the gas pressure in the reservoir, giving a certain time for the equilibration, the respective adsorption and desorption isotherms could be measured.

Simultaneously with the measurements of the amount adsorbed, diffusion experiments were performed on a Bruker NMR spectrometer operating at a 400 MHz resonance frequency on protons. The spectrometer was equipped with a home-built PFG unit allowing to perform a spatial encoding and decoding of positions of probe molecules and producing a maximal  $z$ -gradient strength  $\sim 35$  T/m in a 7 mm o.d. NMR tube (Galvosas et al. 2001). In order to suppress effects of the internal magnetic fields, originating from the susceptibility difference between the fluid and the solid framework, and to minimize undesirable eddy-current effects in diffusion measurements, the 13-interval stimulated echo pulse sequence with bipolar gradients has been applied (Wu et al. 1995). The typical parameters of the pulse sequence used were: time interval between the first and the second  $\pi/2$  radio-frequency pulses 1500  $\mu$ s, duration of the gradient pulses 600  $\mu$ s, and diffusion time 10 ms. Temperature during measurements was kept at 297 K.

### 3 Results and discussion

#### 3.1 Surface characterization

A detailed structural characterization of the chemically modified Si-OH surfaces was performed by means of solid-state <sup>1</sup>H MAS NMR. The <sup>1</sup>H MAS NMR spectrum of the original CPG is shown in Fig. 4a. The spectral line at about



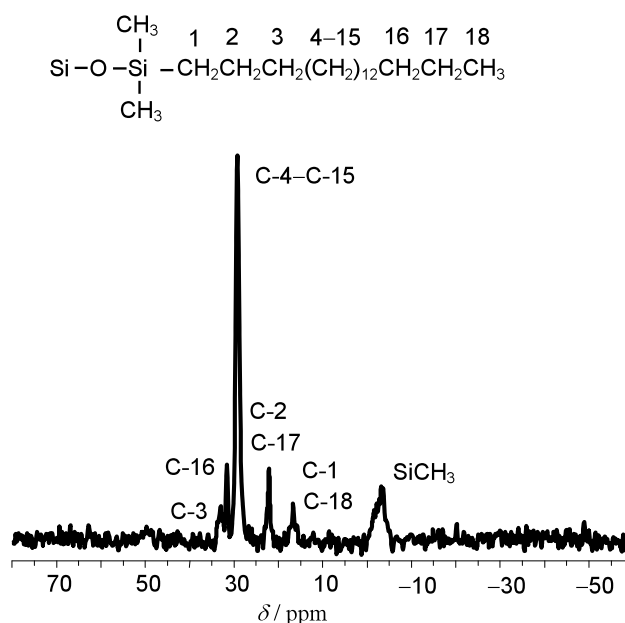
**Fig. 4**  $^1\text{H}$  MAS NMR spectra of the (a) CPG without surface modification and (b) CPG chemically modified (sample-4)

1.8 ppm can be assigned to the OH groups directly bonded to the silicon atom. The integral intensity of this peak has allowed estimating the amount of OH groups per unit area. Using the data on the specific surface area, provided by the manufacturer, a value of 2 OH groups per  $1\text{ nm}^2$  has been derived. This surface concentration was further used for derivation of a required concentration of dimethyloctadecylmethoxysilane in solution for the surface modification.

In case of the CPG chemically modified with the dimethyloctadecylmethoxysilane, the signal of the chain methylene protons at 1.3 ppm dominates the spectrum (see Fig. 4b). Besides this very intense signal, a small sharp spectral line from the terminal methyl group can be detected at 0.8 ppm, while a broad resonance with low intensity at approximately 0 ppm shows the presence of the methyl groups directly bonded to the silicon atom. A small peak at 3.5 ppm shows residual water on the CPG surface.

The  $^{13}\text{C}$  MAS NMR can also be used in the investigation of bonded phases and, in contrast to  $^1\text{H}$  MAS NMR, more detailed structural information can be obtained. The  $^{13}\text{C}$  solid-state NMR spectrum of the modified CPG is shown in Fig. 5. The assignment in the spectra is as follows: C-1/C-18, 16.5 ppm; C-2/C-17, 22.1 ppm; C-3, 33.2 ppm; C-16, 31.6 ppm;  $\text{SiCH}_3$ , -3.3 ppm and for the main carbon chain, C-4–C-15, 29.2 ppm.

Similar  $^1\text{H}$  MAS NMR and  $^{13}\text{C}$  MAS NMR spectra were acquired for the CPG, having different degrees of surface modification (Sample 1–3). Given that the spectra for all samples were recorded and processed under the same con-

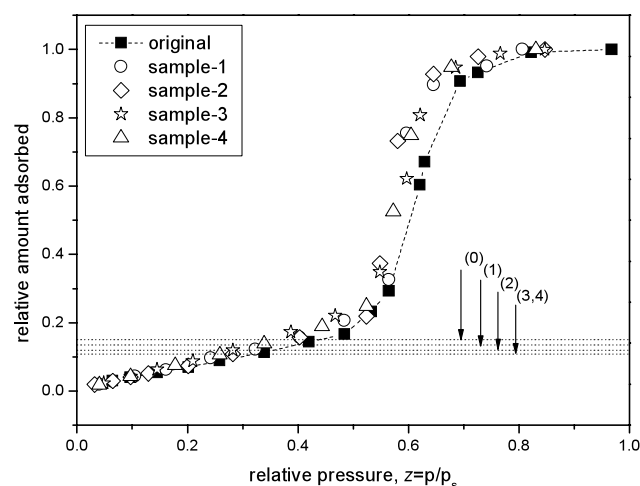


**Fig. 5**  $^{13}\text{C}$  MAS NMR spectrum of the sample-4

ditions, the total intensities of the  $^1\text{H}$  MAS NMR spectra can be compared. The  $^1\text{H}$  MAS NMR spectra reveal no correlation between proton loading and total intensity. With the higher proton loading the integral of spectra for all samples remains unchanged. In the case of  $^{13}\text{C}$  MAS NMR spectra, the comparison is simplified by the fact that the more resolved spectra were obtained. The intensity of the line related to main carbon chain (C-4–C-15) should increase in proportion to the degree of the surface modification. As the  $^{13}\text{C}$  MAS NMR spectra show, the intensity also remains unchanged for all modified samples (samples-1–4). These results are in good agreement with the results which are shown in Table 2.

### 3.2 Desorption isotherms

Figure 6 shows the relative amount of cyclohexane adsorbed at a certain vapor pressure on the desorption branch. The shape of the isotherms (the adsorption branch is not shown) is of type IV according to the 1985 IUPAC classification and is typical for mesoporous solids with relatively narrow pore size distribution. All modified samples reveal a very similar desorption behavior. At a relative vapor pressure  $z_{des}^{orig} \approx 0.63$  (where  $z = P/P_s$ ,  $P$  is the pressure in the reservoir and  $P_s$  is the saturated vapor pressure) for the original material and  $z_{des}^{mod} \approx 0.58$  for all modified samples a well-pronounced desorption knee is observed. The observed small difference in the capillary evaporation pressures might be caused by the presence of long grafted molecules on the surface of the modified samples. These polymer molecules change the initial pore space in a way to incorporate brush-



**Fig. 6** Isotherms for cyclohexane in original (solid squares) and modified (open symbols) samples measured on desorption branch. Dashed line is to guide the eye. Dotted horizontal lines show calculated values for amount adsorbed which is required to cover the surface by a monolayer assuming 0% for original sample, 35% for sample-1, 68% for sample-2 and 100% for samples-3,4 conversion

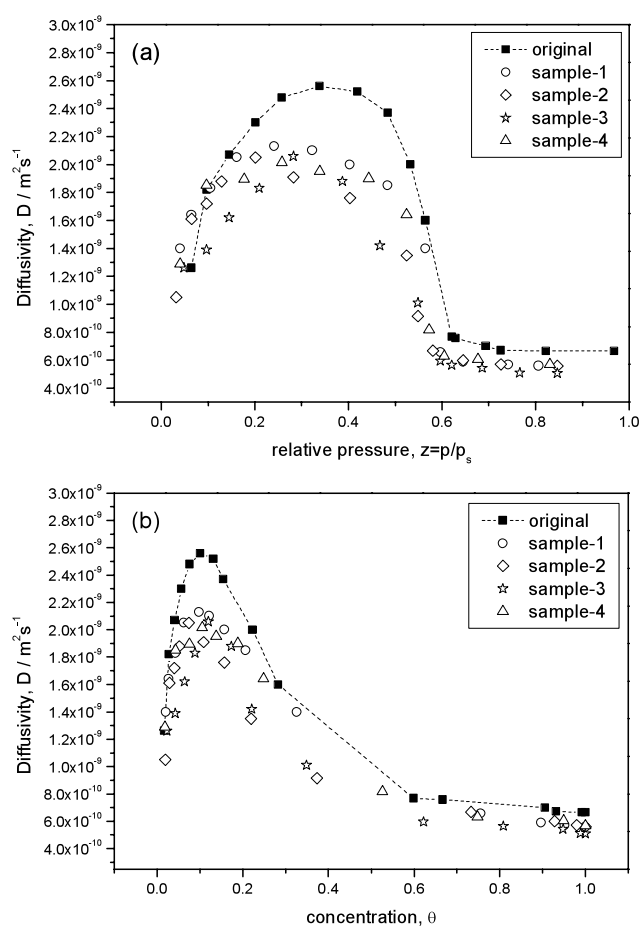
like structures, which may render the evaporation transition to lower pressures.

Simple calculations allow estimating the amount of the adsorbed molecules corresponding to one monolayer surface coverage. Assuming cylindrical pore geometry, the ratio of the volume occupied by one monolayer to the total pore volume is given by  $V_{mon}/V_{tot} = (4dd_0 - d_0^2)/d^2$ , where  $d = 8.1$  nm is the pore diameter and  $d_0 = 0.6$  nm is the kinetic diameter of a cyclohexane molecule. For the modified samples, the surface is affected by the end-capped polymers. Thus, the effective surface of the original porous glass is reduced by a factor of  $0.042 \text{ nm}^2$  per one grafted polymer. The calculations were performed assuming 35% (sample 1), 68% (sample 2) and 100% (samples 3, 4) conversions of OH groups (see Table 2). The result is presented by horizontal dotted lines in Fig. 6 and reveals that the grafting process only slightly changes the inner surface: the value of the pore filling, corresponding to one monolayer coverage, lies in a range between 0.15 and 0.11 for all samples.

### 3.3 Diffusion

The self-diffusion coefficients  $D$  measured at different values of  $z$  are presented in Fig. 7a. A more informative representation, showing diffusivities of Fig. 7a plotted versus the amount adsorbed, is shown in Fig. 7b. To do this, the relative pressures of Fig. 7a have been related to  $\theta$  by the use of the desorption isotherms (Fig. 6).

Qualitatively, the measured diffusivities show a similar behavior for all samples and reveal three pronounced regimes with decreasing pore loading. They include: (i) plateau-like dependency in the range of pore loadings from



**Fig. 7** Experimentally measured self-diffusion coefficients vs the relative pressure  $z$  (a) and vs the concentration  $\theta$  (b) for cyclohexane in CPGs. The dashed lines are given as an eye guide

1 to about 0.6, (ii) increase of  $D$  from  $\theta = 0.6$  to 0.15 and (iii) sharp decrease of  $D$  for pore loadings less than 0.15. By interrelating these regions with the shape of the isotherm shown in Fig. 6, it is evident that these pore fillings coincide with the regions of capillary-condensed phase, onset of the evaporation transition and the region of the sub-monolayer surface coverage, respectively. Thus, the initial increase in diffusivities starting from  $\theta = 0.6$  might be reasonably attributed to the appearance of the gaseous phase in the pore interior, where the diffusion process is much faster as compared to diffusion in the liquid phase. It has to be noted that with a diffusion time of 10 ms, as used in the experiments, and a self-diffusion coefficient  $D \approx 10^{-9} \text{ m}^2/\text{s}$ , the molecules travel distances of the order of a few micrometers. Thus, during this time they perform many cycles of alternating displacements in the gaseous and liquid phases.

The problem of fast molecular exchange between adsorbed and gaseous phases has been analyzed by Kärger



et al. (1988). Within this model, the effective diffusivity  $D$  consists of two terms:

$$D = p_g D_g + p_l D_l \quad (1)$$

where  $p_g$ ,  $p_l$  and  $D_g$ ,  $D_l$  are the relative fractions of the molecules and their diffusivities in the gaseous and liquid phases, respectively. In Valiullin et al. (2004) it has been shown, that  $p_g$  can be expressed as

$$p_g = \frac{1 - \theta}{\theta} \frac{z(\theta) P_s M}{\rho R T}. \quad (2)$$

Here,  $M$  is the molar mass,  $\rho$  is the liquid density,  $T$  is the temperature.

Assuming cylindrical pore geometry, one can assess the contribution of the diffusion through the vapor phase  $p_g D_g$  considering the Knudsen diffusion regime of diffusion in the gaseous phase in the mesopores. Burganos (1998) has derived an analytical solution for the diffusion coefficient in the Knudsen regime,  $D_K$ , in a porous medium with a porosity  $\varphi$  and a tortuosity factor  $\tau$ . According to this approach:

$$\frac{D_K}{D^*} = \frac{4\varphi^2}{\tau} \frac{1}{d} \left( \frac{S}{V} \right)^{-1} \quad (3)$$

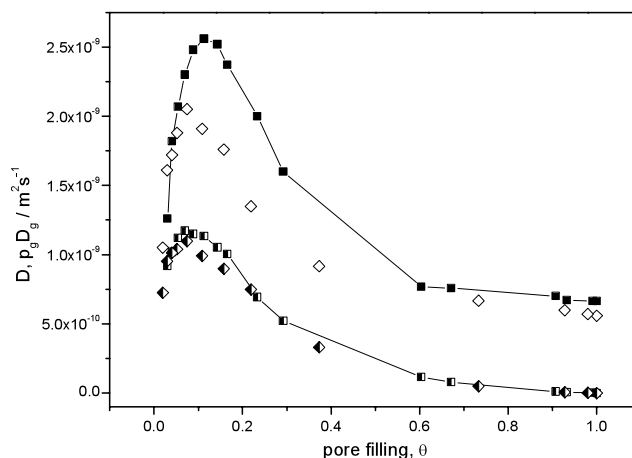
where  $D^*$  is the Knudsen diffusivity in an infinite cylindrical tube of diameter  $d$ ,  $S/V$  is the pore surface-to-volume ratio. The tortuosity factor for CPG has been determined experimentally as

$$\tau = \frac{D(\theta \rightarrow 1)}{D_0} \quad (4)$$

where  $D_0 = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$  is the bulk diffusivity of cyclohexane at 297 K. Taking account of the decrease of the effective pore diameter due to the adsorbed molecules on the pore walls,  $D^*$  can be given as (Valiullin et al. 2004)

$$D^* = \frac{d\sqrt{1-\theta}}{3} \sqrt{\frac{8RT}{\pi\mu}}. \quad (5)$$

The values of  $p_g D_g$  as resulting from these calculations are presented in Fig. 8 and compared with the experimental data for the overall diffusivities. The term  $p_g D_g$  is found to be comparable with the values of measured diffusivities, differing by factor of about 2.5 for the original and by factor of 2 for the modified samples at one monolayer coverage. This means that overall mass transfer is notably affected by the Knudsen mechanism of diffusion. For smaller pore sizes, the influence of the Knudsen diffusion on the overall transport has to be lower. This tendency is in a good agreement with other experimental data obtained on materials with 3.6 nm (Valiullin et al. 2005a) and 10 nm pore sizes (Valiullin et al. 2004). The dramatic difference in effective diffusivities  $D$  for the original and modified samples in the range



**Fig. 8** Comparison of the experimental diffusivities  $D$  for the original (filled squares) and modified (sample-2, diamonds) samples (see Fig. 7b) with the theoretical estimate of the contribution from the gaseous phase on the basis of the porosity data and the adsorption isotherms presented in Fig. 6 (half filled squares and diamonds represent original and modified samples, respectively)

of the pore loadings close to one monolayer surface coverage  $\theta \approx 0.15$ , where  $p_g D_g$  passes the maximum, is probably caused by the grafted polymers which, in turn, should lead to a reduction in the Knudsen diffusivity. In case of the modified samples such parameters as porosity  $\varphi$ , tortuosity  $\tau$  and pore surface-to-volume ratio  $S/V$  may differ as compared to these values for the original material. More detailed analytical treatment in this case is not trivial, because the exact spatial distribution of the grafted polymers at various loadings is unknown.

Further decrease of the pore loading from  $\theta \approx 0.15$  towards smaller  $\theta$  leads to a strong decrease of the effective diffusivity. This is a direct consequence of the hopping diffusion mechanism along the heterogeneous surface and severe confinement to which the molecules are subjected with further decreasing loading. Depending on the binding energy distribution of the adsorption sites, the fraction of molecules occupying highly adsorptive sites is higher for lower surface coverages, leading to increasing diffusivity with increasing pore loading. In recent papers (Dvoyashkin et al. 2009; Valiullin et al. 2005b) such surface diffusion processes have been studied in great detail.

## 4 Conclusions

Transport properties of cyclohexane in Controlled Pore Glass 10-75 before and after modification by grafting of dimethyloctadecylmethoxysilane to the surface has been performed by means of PFG NMR. For each pore filling the exact values of the self-diffusivities have been provided. In both the non-modified and modified glasses significant

contributions of Knudsen diffusion have been observed, although, in the modified glasses it was slightly reduced due to the presence of the grafted long-chain molecules. Combination of the results of nitrogen adsorption, thermogravimetry and MAS NMR has thus been shown to provide quantitative information on the modification processes, which allows to control the degree of modification in a precise way. Altogether, the results of the present studies may be of high relevance in such applications as heterogeneous catalysis and separation.

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