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NMR relaxation and diffusion studies of methane and carbon dioxide in nanoporous ZIF-8 and ZSM-58

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ABSTRACT

The ^{1}H and ^{13}C relaxation times of methane and carbon dioxide adsorbed in nanoporous ZIF-8 increase with loading and exceed the values of the bulk gases at the corresponding equilibrium pressure. The surface relaxation for the adsorbed molecules was determined by plotting the relaxation rates as function of inverse density. Longitudinal surface relaxivities of $(3.1 \pm 0.7) \times 10^{-10}\ \mathrm{m \cdot s^{-1}}$ for CH_4 at 125 MHz and of $(1.22 \pm 0.07) \times 10^{-10}\ \mathrm{m \cdot s^{-1}}$ for $^{13}CO_2$ at 100.6 MHz were obtained in ZIF-8. This approach applied to zeolite ZSM-58 yields much higher, density dependent surface relaxivities of $0.7 - 5.4 \times 10^{-8}\ \mathrm{m \cdot s^{-1}}$ for methane. In ZIF-8, the self-diffusion coefficients of both gases are in the range of $10^{-10}\ \mathrm{m^2 \cdot s^{-1}}$ and do not depend significantly on density. In ZSM-58, there is a two orders of magnitude difference in the diffusivities of both gases, which is caused by the small 8-ring windows of this zeolite.

1. Introduction

Synthetic zeolites and metal–organic frameworks are high-tech nanoporous materials with applications e.g., in separation, gas storage and catalysis [1–4]. The shape and size of their nanometer-sized pores, which are embedded in a crystalline solid network, are generally known from crystallographic methods. The pores often allow only small molecules to enter and move through the pore system while the motion of larger molecules is retarded. The mobility of the guest molecules is influenced via interactions with the internal pore-matrix interface. It may be studied non-destructively by NMR techniques.

The pore surface-to-volume ratio (S_V) as a measure of the size of the interface is high in nanoporous materials. It represents an important parameter for NMR investigations since the pore-matrix interface mediates the host–guest interaction. In macroporous systems, were liquid pore fluids saturate the pore space one often finds a proportionality between the relaxation rate (T_s^{-1}) added by the host–guest interaction and the pore surface-to-volume ratio: $T_s^{-1} = \varrho_s \cdot S_V$ [5–9]. The surface relaxivity parameter ϱ_s may then be used to characterize the host–guest interaction.

In this study, methane and carbon dioxide adsorbed in the SiO_2 zeolite ZSM-58 [10] and in the zeolitic zink 2-methyl-imidazolate ($Zn(MeIM)_2$) framework ZIF-8 [11] are investigated by ^{1}H and ^{13}C NMR. Several reports propose the application of both nanoporous materials for membrane-based gas separation processes [12–16]. ZSM-58 and ZIF-8 belong to the DDR and SOD zeolite structure types with two- and three-dimensionally interconnected pore systems, respectively. Although the chemical compositions of their solid matrices are different, the size of their pore cavities and especially the open diameter of the windows connecting these cavities are similar (see Table 1). In both pore systems, narrow windows form the connections between the pore cavities. The respective window diameters are mainly determined by the oxygen atoms and the 2-methyl-imidazolate molecules in ZSM-58 and ZIF-8, respectively.

Due to the well described pore characteristics both materials may be used to study fundamental aspects of NMR responses from small molecules in nanoporous materials. With this contribution we show, how host–guest interaction influence the relaxation and molecular diffusion in these two nanoporous materials. We will report surface relaxivities for adsorbed carbon dioxide and methane and we demonstrate the size selectivity of the windows for molecular self-diffusion in both systems.

2. Materials and methods

The synthesis and post synthesis characterization of the ZSM-58 and the ZIF-8 samples investigated in this study are described in detail in Refs. [17,18], respectively. For NMR sample preparation, gravimetrically determined amounts of the adsorbent materials were introduced in NMR sample tubes. The materials were heated under vacuum to remove residual solvents, templates, moisture

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Table 1
Comparison of specific pore volumes V_m, specific surface areas S_m, pore surface-to-volume ratios S_V, diameters of cavities and diameters of windows for zeolith ZSM-58 and MOF ZIF-8.

	V_m $\mathrm{cm^3 \cdot g^{-1}}$	S_m $\mathrm{m^2 \cdot g^{-1}}$	S_V $\mathrm{m^2 \cdot m^{-3}}$	d_p 10^{-10} m	d_w 10^{-10} m
ZSM-58 [17,33]	0.55	~ 290	0.53×10^9	7.7	3.7
ZIF-8 [11,34]	0.66	~ 1970	2.94×10^9	11.6	3.4

and air from the pore space. Subsequently, volumetrically determined amounts of methane and ^{13}C enriched carbon dioxide were chilled to the adsorbent bed using liquid nitrogen. Finally, the NMR sample tubes were sealed by ablation. The samples were prepared in pressure resistant NMR sample tubes of 8.0 mm outer diameter. At the target loadings $a(p)$, the equilibrium pressures p of the gas phase above the adsorbent beds varied between 1 bar $\leqslant p \leqslant$ 18 bar for CH_4 and 2 bar $\leqslant p \leqslant$ 28 bar for CO_2, respectively.

The adsorbed amounts were determined using the single component adsorption isotherms for methane and carbon dioxide as given in [17] for ZSM-58 and [18] for ZIF-8. Since the specific pore volumes V_m ($\mathrm{cm^3 \cdot g^{-1}}$) of ZSM-58 and ZIF-8 are known, the pressure dependent adsorbed amounts $a(p)$ can be used to calculate the density of the adsorbed phase in the pore space $\rho(p) = a(p) \times V_m^{-1}$. These densities are used to compare the relaxation and diffusion behavior of the adsorbed phases with that of the gas phase at the respective density and pressure.

NMR measurements of relaxation and self-diffusion were performed at 125 MHz ^{1}H resonance frequency and 100.6 MHz ^{13}C resonance frequency, using home-built NMR spectrometers [19]. Longitudinal relaxation times (T_1) were measured in ZIF-8 and ZSM-58 as function of loading using the inversion recovery (IR) NMR pulse sequence [20]. Diffusion measurements were performed in both nanoporous materials using the PFG NMR set-up as described in [19,21]. Details of the experimental procedures for the ^{1}H NMR diffusion measurements with ZIF-8 correspond to those published in Ref. [18]. For the discussion of the results, diffusion data from our own previous studies [18,17] were incorporated. Additional ^{1}H NMR studies at low-field and elevated pressures (up to 100 bar) were carried out for methane in ZIF-8 with the instrumentation described in [22]. Transverse relaxation time distributions $p(T_2)$ and two-dimensional $T_2 - T_1$ correlation were measured by the CPMG [23,24] and the IR-CPMG sequences [25] at 5.06 MHz resonance frequency, respectively.

3. Results and discussion

The low-field NMR studies of methane in ZIF-8, which are presented in the Supporting information (Figs. S1 and S2) show in agreement with previous investigations [22] that for pressures below 50 bar the transverse and longitudinal relaxation times of intracrystalline adsorbed methane exceed the corresponding values measured for the pure gas phase. Additionally, these relaxation times are found to increase with pressure. At a first glance, these observations contradict the general assumption that additional interactions with the solid matrix of the porous material shorten the relaxation times compared to the bulk phase of the pore fluid.

The additional interactions of the adsorbed methane with the ZIF-8 lattice become only obvious if the relaxation rates are analyzed as function of the density in the adsorbed phase [22]. This has its reason in the well-known density dependence of the gas phase relaxation times, where the longitudinal and transverse relaxation times of methane increase with increasing pressure and density, respectively [26,27]. The physical reason is the spin rotation relaxation mechanism and the shortening of the corresponding correlation time with increasing density. Obviously, the molecules change more often their rotational state due to mutual collisions, if the density increases. Since adsorbed phases have generally higher densities than gas phases at the same pressure, the same intermolecular guest–guest interaction increase also the relaxation time in the adsorbed phase. However, additional interaction with the host lattice will alter the density dependence of the relaxation times from that of the pure gas phase. E.g., inter- and intra-molecular dipole–dipole interaction as well as a change of the rotational dynamics at adsorption sites were discussed by Riehl and Koch [28] as relaxation mechanisms for methane adsorbed in a monolayer at graphitized carbon black at low temperatures.

Assuming that for our high-field studies at room temperature in ZIF-8 and ZSM-58 the known density dependence of the longitudinal relaxation of methane $T_1^g(\rho)$ and an additional relaxation at the inner surface $\varrho_s \cdot S_V$, which is proportional to the surface-to-volume ratio S_V, act as parallel relaxation mechanisms one obtains for the density dependence of the adsorbed phase longitudinal relaxation time $T_1^{ads}(\rho)$ [5,6,29]:

$$\frac{1}{T_1^{ads}(\rho)} = \varrho_s \cdot S_V + \frac{1}{T_1^g(\rho)} \tag{1}$$

The bulk methane relaxation is governed by the spin rotation relaxation mechanism. It may be approximated by $T_1^g(\rho) = \alpha\rho$, where α takes the value of $27.86\ \mathrm{s \cdot (g \cdot cm^{-3})^{-1}}$ [26,27,22]. Thus, one may expect an increase of the relaxation rate with inverse density of the adsorbed phase:

$$\frac{1}{T_1^{ads}(\rho)} = \varrho_s \cdot S_V + \frac{1}{\alpha\rho} \tag{2}$$

Fig. 1 shows that the ^{1}H longitudinal relaxation rate of adsorbed methane measured at 125 MHz ^{1}H resonance frequency increases with inverse density with the same rate as in the bulk methane gas. At a given molecular density, the constant off-set represents the surface relaxation effect by the ZIF-8 pores. It may be estimated by the extrapolation of the linear dependence plotted in Fig. 1 to infinite density ($\rho^{-1} \to 0$). A value of $\varrho_s \cdot S_V = (0.91 \pm 0.20)\ \mathrm{s^{-1}}$ was obtained, which yields a surface relaxivity of $\varrho_s = (3.1 \pm 0.7) \times 10^{-10}\ \mathrm{m \cdot s^{-1}}$ for methane. This value confirms well with our previous result for a surface relaxivity in ZIF-8, which was measured over a substantially smaller range of densities [22].

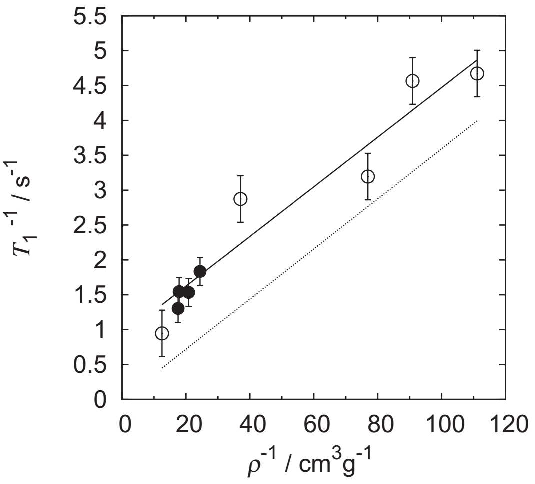

Fig. 1. Relaxation rates (^{1}H at 125 MHz) of methane adsorbed in ZIF-8 compared to the pure gas phase at equal densities (dashed line [26,27,22]). The presentation as function of inverse density ρ^{-1} in the pore space and in the gas phase, respectively, illustrates the surface relaxation effect in the ZIF-8 nanopores. ○ this work; ● data from [18].