Masterthesis

MAS PFG NMR and ATR-FTIR diffusion measurements in porous coordination polymers

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1 Introduction

Porous solids are defined by voids in the solid matrix, without containing matter of the considered materials [1]. The ability of the pore walls to interact with atoms, ions and molecules, together with the capacity of the pore space to load or capture liquid and gas molecules, makes these materials important for today's technologies [2]. Traditionally, they are utilized mainly in catalysis, ion exchange and gas adsorption (for separation) [3]. Innovative applications like sensors, drug delivery and medical diagnosis are under development [2].

Porous coordination polymers, so-called metal-organic frameworks (MOF), are a relatively new class of crystalline microporous materials [4, 5, 6]. Generally, they consist of organic linker molecules and metal coordination centers, which form an ordered three-dimensional nanoporous network. The variety of possible linkers and coordination centers results in a large variety of matrix and pore space properties [7], which is interesting for fundamental research of host-guest interactions as well as technical applications [8].

Recently a breakthrough in the use of MOFs as catalysts was achieved by Kapteijn et. al [9] through the encapsulation of phosphotungstic acid inside MIL-101(Cr) (MIL, Matériel Institut Lavoisier) [6]. These new porous catalysts show superior conversion rates in a model reaction compared to conventional catalysts. This success has to be followed by further attempts to increase the reaction kinetics, for which the reaction mechanism and eventual reaction limiting steps have to be identified. The transport-diffusion behavior of the reactants and products inside the porous particles is known to be a rate determining step [10]. Thus, one part of this thesis was devoted to the investigation of transport-diffusion of the reactants of the aforementioned model reaction inside MIL-101(Cr). This research was performed during a three month internship in the group of Prof. Kapteijn at the Technical University Delft. Here, the time resolved Attenuated Total Reflection (ATR) FTIR spectroscopy technique (see [11] for details) was used.

Another stimulation on the field of MOFs was the synthesis of the MOF-5 framework by Li et. al [12] in 1999. This material is interesting for several reasons. It remains its framework integrity up to temperatures of 300°C in absence of stabilizing solvents [12]. Furthermore by exchanging synthetically the organic linkers of the structure, one may
scale the pore diameter gradually from 3.8 Å to 28.8 Å \[7\]. This shows that rational tailoring of porous materials for desired applications comes within reach \[8\].

First self-diffusion measurements of guest molecules in MOF-5 were performed by Stallmach et al. \[13\] using the pulsed field gradient NMR (PFG NMR) method. A follow up paper on benzene adsorbed at MOF-5 was prepared based on the work performed during this master thesis and is now submitted for publication \[14\]. It includes PFG NMR self-diffusion measurements of benzene adsorbed at MOF-5 at different benzene loadings and temperatures and is compared to state of the art molecular dynamics simulations in this system.

The PFG NMR technique is able to measure the self-diffusion of molecules directly inside a framework of porous materials without substantially disturbing the system \[15\]. In 1965, Stejskal and Tanner \[16\] proposed the use of pulsed field gradients in spin-echo NMR diffusion experiments, which allowed a broader applicability compared to the so far used constant gradient method \[17\]. Since then, many inventions of either pulse sequences, the mathematical apparatus and the experimental equipment continued to improve the technique steadily, as reviewed e.g. by Callaghan \[18\], Södermann et al. \[19\] and Stallmach and Galvosas \[15\]. For many applications, like separation and catalysis, it is desirable to know the diffusion behaviour especially of mixtures adsorbed at the porous materials. One way to obtain self-diffusivities of mixtures is to analyse separately the PFG NMR signals of the mixture components in the NMR spectrum. In the case of static NMR experiments this is often impossible, because \(^1\)H NMR resonance lines of adsorbed species are usually broad and thus impede the individual analysis due to likely overlaps.

In solid state NMR spectroscopy, there is a technique developed in 1959 by Andrew et al. \[20\] called magic-angle spinning (MAS), which significantly reduces line widths in NMR spectra. Rapid sample spinning at the magic-angle (54.7°) is used to reduce line-broadening caused by heteronuclear dipole-dipole interactions \[21\], chemical shift anisotropy \[22\] and internal magnetic field gradients \[23\]. Internal magnetic field gradients are the main cause of line broadening of molecules adsorbed at porous materials. Starting with the work of Maas et al. \[24\] in 1996, MAS probes were equipped with gradient coils for modulation suppression and coherence path selection \[25\]. Because the gradient coils are usually oriented coaxial with the sample spinning axis in magic-angle direction they are called ’magic-angle gradient’ coils \[24\].

A first combination of MAS NMR and PFG NMR using magic-angle gradient coils was reported by Weybright et al. in 1998 \[26\]. It was followed by self-diffusion studies in liquid-crystalline phases \[27\], lipid bilayers \[28\] and multilamellar liposomes \[29\]. Unfortunately the use of ’magic-angle gradients’ for studies of the self-diffusion of slow moving species was limited, because only low gradient strengths were achievable with
this coil design [25]. Using the combination of a microimaging gradient system with a narrow bore MAS probe, Pampel et. al [30] achieved a 10-fold increase in gradient strength compared to conventional MAS NMR systems. In recent years the scientific work in the field of MAS PFG NMR was mainly conducted using magic-angle gradients [31,32,33]. Only one paper by Pampel et. al in 2006 [34] revises the opportunities of their approach.

In this master thesis the combination of a micro-imaging system with a high resolution MAS probe at an Avance 400 spectrometer of the company Bruker had to be tested. In this context calibration of the hardware had to be performed and the necessary routines and protocols had to be prepared. The feasibility of this system had to be tested at the system benzene and n-hexane coadsorbed at MOF-5 in the context of the DFG priority program SPP1632 'Metal-organic frameworks', in the project 'Fundamental host guest interactions in MOFs'.

This contribution is divided into two main parts. The first part (chapter 2 to chapter 6) demonstrates the calibration and use of the MAS PFG NMR system for self-diffusion measurements. The second part (chapter B) reports about the transport-diffusion studies using time resolved ATR-FTIR spectroscopy.
2 Theory

2.1 MOF-5 framework

Li et al. [12] developed a new synthesis method for porous crystalline coordination polymers. The new material was named metal-organic framework 5 (MOF-5). Macroscopically it is a colourless crystal with density 0.59 g cm$^{-3}$ and a porosity of about 55%. It is built up of two main building blocks. The coordination centers are clusters, whose centers consist of a Zn$_4$O tetrahedron. The linkers can be seen as finite rods with chemical formula O$_2$–C–C$_6$H$_4$–C–O$_2$ (the outer oxygen atoms connect the linker and the attached coordination centers). Figure 2.1 shows the structure of the unit cell of MOF-5, which consists of two alternating kinds of cubic cells. Once the molds of the clusters point inside the cavity (A-cells) and once the vertices point inside (B-cells). The larger A-cells and smaller B-cells differ slightly in the accessible void space with 1.5 nm and 1.1 nm diameter spheres fitting inside, respectively.

![Figure 2.1: Structure of the unit cell of MOF-5 showing the two different cubic A- and B-cells. Once the molds of the Zn$_4$O tetrahedra point inside the cavity (A-cells) and once the vertices point inside (B-cells).](image)

2.2 Nuclear magnetization

In nuclei with unpaired nuclear spins there is a net nuclear spin characterized by the integer or half-integer number $I$ of the nucleus [18]. The spin is a property of micro par-
particles describing their intrinsic angular momentum, which leads to a magnetic moment 
\[ \mu_i = \gamma \hbar I_i, \] (2.1)
where \( \gamma \) denotes the gyromagnetic ratio, \( \hbar \) is Planck’s constant divided by \( 2\pi \) and \( I_i \) denotes the eigenvalues of component \( i \) of the nuclear spin operator \( \mathbf{I} \). If an external magnetic field \( \mathbf{B}_0 \) is applied along the \( z \)-axis with amplitude \( B_0 \), then the potential energy due to the Zeeman-interaction \( H \) is given by
\[ H = -\gamma \hbar B_0 I_z. \] (2.2)

\( I_z \) are the eigenvalues of the \( z \)-component of the nuclear spin operator \( \mathbf{I} \). For spin-\( \frac{1}{2} \)-systems such as \( ^{1}\text{H} \) and \( ^{13}\text{C} \), \( I_z \) can only attain the two discrete values \( I_z = \pm \frac{1}{2} \). In thermal equilibrium there is an excess occupation of the state \( I_z = \frac{1}{2} \) due to the Boltzmann distribution. Since Equation 2.1 relates the spin to the magnetic moment, the occupation excess leads to an excess of magnetic moments oriented along the applied magnetic field \( \mathbf{B}_0 \) and hence to a macroscopic nuclear magnetization of the sample
\[ M = (\sum \mu_+ \frac{1}{2} + \sum \mu_- \frac{1}{2}) e_z, \] (2.3)
with amplitude \( M_0 \). Each individual spin rotates about the direction of the applied magnetic field. Since the macroscopic magnetization is the sum of the individual spins, it is also precessing around \( \mathbf{B}_0 \). It’s precession angular frequency is called Larmor frequency and is given by
\[ \omega_0 = \gamma B_0. \] (2.4)
It corresponds to the frequency of an electromagnetic wave, which can generate transitions between the possible orientations of the nuclear spins in the external magnetic field.

### 2.3 Primary spin echo sequence

In NMR experiments the observable signal is proportional to the \( x-y \)-component of the magnetization \( \mathbf{M} \). Therefore one has to disturb the spin system from its thermal equilibrium and rotate the magnetization into the \( x-y \)-plane. This can be achieved by applying a resonant (\( \omega = \omega_0 \)) radio-frequency-pulse (rf-pulse) perpendicular to
the polarizing magnetic field $B_0$. The equation of motion of the local magnetization $M(r, t)$ under the influence of an applied magnetic field $B$ is given by the Bloch-Torrey equation \[15\]

$$\frac{\partial M(r, t)}{\partial t} = \gamma M \times B - \frac{M_z - M_0}{T_1} e_z - \frac{M_x e_x + M_y e_y}{T_2} + D \nabla^2 M,$$  \hspace{1cm} (2.5)

including the influence of the longitudinal ($T_1$) and transverse ($T_2$) relaxation as well as self-diffusion ($D$). In the absence of rf-magnetic fields, the first term of Equation 2.5 accounts for the torque exerted by the homogeneous magnetic field $B$ on the magnetization $M$. The second term with the relaxation time constant $T_1$ describes the restoration of thermal equilibrium, characterized by the magnetization $M_0$ directed along the longitudinal magnetic field $B_0$. This process involves an exchange of energy between the spin system and the surrounding thermal reservoir (called the lattice) and is therefore called spin-lattice, or longitudinal relaxation \[18\]. The lifetime of the transverse magnetization $M_{x,y}$ is largely determined by the third term of Equation 2.5 with the relaxation time constant $T_2$. This term is called the transverse relaxation, whereby nuclear spins come to thermal equilibrium among themselves. The energy exchange proceeds either directly between individual spins, or indirectly via the lattice. This leads to the relation $T_2 \leq T_1$. Finally the last term of Equation 2.5 accounts for the translational self-diffusion of the spin-bearing particles given by Fick’s second law \[15\]. By integrating the local magnetization $M(r, t)$ over the sample volume, one obtains the time-dependent magnetization $M(t)$.

Upon the application of rf-pulses perpendicular to the static magnetic field, the magnetization can be rotated out of its equilibrium orientation. Thereby the rf-pulse which rotates the magnetization by $90^\circ$ is called $\pi/2$ rf-pulse. Hence a $\pi$ rf-pulse rotates the magnetization by $180^\circ$. Now consider a sequence of a $\pi/2$ rf-pulse followed by $\pi$ rf-pulse after time period $\tau$, see Figure 2.2. This sequence is called primary spin echo sequence and was originally proposed by Hahn in 1950 \[37\]. The magnetization is rotated in the $x$-$y$-plane, where it dephases due to transverse relaxation ($T_2$ relaxation). If one would measure directly after the $\pi/2$ pulse, one would obtain a so called free induction decay (FID). The decay constant of the FID is called $T_2^\star$. Especially in systems with inhomogeneous magnetic fields, $T_2^\star$ is much shorter than the intrinsic $T_2$ value in such systems and the process is reversible. The FID may be recalled in a spin echo by application of a $\pi$ rf-pulse after a time $\tau$. This pulse adds a phase of $\phi = 180^\circ$ to all spins, but keeps their rotational direction and lets the magnetization rephase. The magnitude of the echo is reduced in comparison to the FID through transverse ($T_2$) relaxation and self-diffusion ($D$) of the spin-bearing particles.
2.4 Pulsed field gradient spin echo sequence

Stejskal and Tanner [16] proposed in 1965 the use of two pulsed field gradients (PFG) for labelling of the nuclear spins. Their approach is the so-called pulsed field gradient spin echo (PFG spin echo) sequence, see Figure 2.3. In comparison to the primary spin echo sequence discussed in section 2.3, there are two additional magnetic field gradients of amplitude $G$ and duration $\delta$. During the application of the first pulsed field gradient, the magnetic field $B$ depends on time and space. With the approximation that off-resonance magnetic field components perpendicular to $B_0$ can be neglected [15], the gradient only affects the $z$-component of $B(r, t)$ [15]

$$B_z(r, t) = B_0 + rG(t).$$

\[ (2.6) \]
At different positions $\mathbf{r}$ in the sample, the spins rotate with angular frequencies according to the local magnetic field $\mathbf{B}(\mathbf{r}, t)$, see Equation 2.4. This space dependent angular frequency is only present during the gradient application time $\delta$. After time $\delta$ there is a space dependent phase shift of the nuclear spins along the $z$-axis. The following $\pi$ rf-pulse effectively adds a phase shift of $\phi = 180^\circ$ to all spins, but keeps their rotational direction. This allows to refocus the spins with a second pulsed field gradient (if the spins with the respective phases remained at their places). If the second gradient has the same amplitude $G$ and duration $\delta$, the space dependent phase shift is deleted and the maximum magnetization is refocused in a spin echo at time $t_e$. If a particle changes its $z$-position due to self-diffusion during observation time $\Delta$, it carries its spin and hence the phase shift with it. Self-diffusion then leads to a redistribution of the phase shifts in space and thus to an incomplete refocussing through the second gradient pulse. The spin echo amplitude is therefore primarily sensitive to the mean squared displacement of the spin-bearing particles in $z$-direction during observation time $\Delta$.

The Bloch-Torrey equation (Equation 2.5), as the equation of motion, can be solved by a separation of variables ansatz [15], which yields a solution of the general form

$$M(t_e) = \Psi(t_e) R(t_e) M_0.$$

(2.7)

Here $M_0$ represents the initial magnetization, $R(t_e)$ denotes the signal decay due to transverse and longitudinal relaxation and $\Psi(t_e)$ denotes the attenuation due to self-diffusion. For the attenuation term $\Psi(t_e)$, one obtains a double integral

$$\Psi(t) = \exp \left\{ -D \gamma^2 \int_0^t dt' \left[ \int_0^{t'} dt'' G^*(t'') \right]^2 \right\}.$$

(2.8)

This equation depends on the self-diffusion coefficient $D$ and the effective magnetic field gradient $G^*(t)$. Since the $\pi$ rf-pulse inverts the effect of the magnetic field gradient on the accumulated magnetization phase, the effective gradient is given for the primary gradient spin echo sequence by

$$G^*(t) = \begin{cases} -G(t) & \text{for } t \leq \tau \\ +G(t) & \text{for } t > \tau. \end{cases}$$

(2.9)

Evaluation of the double integral of Equation 2.8 for a pair of rectangular gradient pulses yields

$$\Psi(t_e) = \exp \left\{ -D \gamma^2 \delta^2 \left( \Delta - \frac{1}{3} \delta \right) G^2 \right\}.$$

(2.10)
$G^2$ represents the square of the pulsed field gradient amplitude. It is important to note, that for the spectrometer system Avance 400 the gradient duration $\delta$ is always inserted for rectangular gradient shapes. If sine shaped gradients are applied, a new gradient duration $\delta'$ is internally calculated by

$$\delta' = \frac{\delta}{0.636},$$

(2.11)

which yields for the same gradient amplitudes $G$ the same gradient intensity as set for rectangular shaped gradients. Introducing the generalized gradient parameter $b$ with

$$b = (\gamma G \delta)^2 \left(\Delta - \frac{1}{3} \delta\right),$$

(2.12)

the equation for spin echo attenuation because of self-diffusion reads

$$\Psi(t_e) = \exp(-bD).$$

(2.13)

PFG NMR experiments are performed by varying the gradient strength $b$ and recording the resulting echo amplitude $M(b)$. For an experiment with all times fixed but only the gradient strength varied, relaxation leads to a constant attenuation factor and can be neglected in the analysis. Self-diffusion coefficients (3-dimensional case: $D = \langle r^2(\Delta) \rangle/(6\Delta)$) are obtained by analyzing the slope of the plot of $\ln(M(b)/M(0))$ versus $b$, where $M(0)$ is the reference value without applied pulsed gradients.

In multicomponent systems, where diffusion of the molecules carrying the nuclear spin under investigation may occur in different phases with different self-diffusion coefficients, the spin echo attenuation is given by a superposition of corresponding exponential terms. In the case of two phases A and B with diffusion coefficients $D_A$ and $D_B$, the spin echo attenuation can be decomposed into a sum of two exponentials [38, 39]

$$\frac{M(b)}{M(0)} = p_A \exp(-D_A b) + p_B \exp(-D_B b),$$

(2.14)

where $p_A$ and $p_B$ are the population of both phases.

### 2.5 Stimulated spin echo pulse sequence

Relaxation is often the limiting factor for time-dependent self-diffusion studies using PFG NMR. In order to reduce the influence of transverse relaxation, the magnetization is stored in the longitudinal direction during the $z$-storage time interval $\Delta'$, see Figure 2.4. At the time $\tau$ after beginning of the experiment, the second $\pi/2$ rf-pulse stores the magnetization along the longitudinal axis. The magnetization is recalled by
the third radio frequency pulse and rephased in a stimulated echo. During the storage period $\Delta'$ the magnetization is subject to $T_1$ relaxation which is usually longer than the $T_2$ relaxation. Hence, the region of larger observation times $\Delta$ becomes available, enabling one to investigate slow diffusion in samples with short $T_2$ relaxation. The signal intensity attenuation for the stimulated spin echo pulse sequence is given by

$$M(b) = \frac{M(0)}{\exp(-Db) \exp\left(-\frac{2\tau}{T_2}\right) \exp\left(-\frac{\Delta'}{T_1}\right)}.$$  \hspace{1cm} (2.15)

$T_1$ and $T_2$ are the longitudinal and transverse relaxation times of the spin system. $\tau$ and $\Delta'$ denote the storage intervals of magnetization in the $x$-$y$-plane and the $z$-direction respectively, see Figure 2.4.

### 2.6 Magic-angle spinning

One way to measure self-diffusivities of mixtures is to integrate the signal intensities of each component of the mixture in the Fourier transformed NMR signal. In case of static PFG NMR experiments in porous materials this is often impeded, because line broadening leads to partial overlaps of the NMR signals in the frequency domain. In 1959, Andrew et al. [20] used rapid sample spinning to reduce the line width in solid state NMR experiments. They showed that spinning of the samples at an angle of

$$\theta_{\text{MAS}} = \arccos\left(\frac{1}{\sqrt{3}}\right) = 54.7^\circ$$  \hspace{1cm} (2.16)
with the static magnetic field $B_0$ averages out dipole-dipole interactions.\cite{20}. This effect can be understood, when looking at the Hamiltonian of dipole-dipole interactions

$$H_D = \left( \frac{\omega_D}{2} \right) (3 \cos^2 \beta - 1)(3I_1I_2 - I_1I_2),$$  \hspace{1cm} (2.17)

where $\beta$ is the angle between the internuclear vector and the static magnetic field and $\omega_D$ is a constant determined by the strength of the dipolar coupling.\cite{21} The function $(3 \cos^2 \beta - 1)$ is related to the spherical harmonic $Y_{20}(\beta, \alpha)$. When the sample rotates about an axis which is inclined to the applied magnetic field, the time averaged hamiltonian is proportional to the angular part according to

$$H_D \propto (3 \cos^2 \theta - 1)Y_{20}(\beta', \alpha'),$$  \hspace{1cm} (2.18)

where $\theta$ denotes the angle between the sample spinning axis and the static magnetic field. At the angle $\theta_{\text{MAS}} = 54.7^\circ$ the average is zero. This averaging applies to dipolar coupling of heteronuclear species as well as dipolar broadening due to coupling of quadrupolar nuclei. $^1$H-$^1$H- dipolar broadening is usually not completely averaged out.

In addition chemical shift anisotropies can be averaged out. The chemical shift is also dependent on the orientation of the molecular framework in the magnetic field. In particular for sample spinning at the angle $\theta_{\text{MAS}}$, the sidebands in the frequency domain become symmetric. Rapid spinning decreases the intensity of the sidebands and increases the centerband intensity.\cite{21, 22}

In porous materials the NMR resonances are broadened by an internal nonuniform magnetic field (internal magnetic gradients) due to magnetic susceptibility mismatches between the solid matrix and the pore contents and residual anisotropies in the magnetic susceptibility like inclusions in the solid matrix. Magic-angle spinning is known to average out this effects, too.\cite{23}.\footnote{11}
3 Experimental

In this chapter the experimental equipment is described. This includes the specifications of the micro-imaging system as well as the high resolution MAS probe. Special attention is devoted to the standard settings of the spectrometer software Topspin 2.1 (pl6) and the peculiarities of the modular design of the MAS PFG NMR system. Additional information is given about the synthesis of the porous material MOF-5 as well as preparation and loading of the NMR samples.

3.1 Micro-imaging system

MAS PFG NMR studies were performed on a Bruker Avance 400 spectrometer, with a $^1\text{H}$ frequency of 400 MHz. The combination of the MAS and PFG NMR techniques in this work was realized by a similar setup using a micro-imaging system as proposed in [34]. Thus, opposite to former designs (e.g. Maas et. al [24]), insight into slow self-diffusion processes may be gained by the use of higher gradient strengths in a commercially available setup.

The Bruker Micro 2.5 imaging system was originally designed for imaging of small objects ($d_{\text{max}} = 30 \text{ mm}$). Figure 3.1 shows the Micro 2.5 probe consisting of the gradient system (top) and a narrow bore imaging probe containing the rf-part (bottom). The Micro 2.5 gradient system has to be inserted into a wide bore magnet ($d_{\text{m}} = 89 \text{ mm}$) and connected to the gradient amplifier as well as to a water cooling system. A probe, which contains the rf-wiring and mechanical tuning and matching, has to be inserted into the gradient system.

The gradient system is capable of applying gradient strengths of up to

$$G_{\text{max}} (x,y,z) = 1.5 \text{Tm}^{-1}$$  \hspace{1cm} (3.1)

in each coordinate direction, at a maximum current of $I = 60 \text{ A}$. Thus, for the magic angle direction the maximum gradient strength is

$$\left| \vec{G}_{\text{MAS, max}} \right| = \sqrt{3} G = 2.6 \text{Tm}^{-1}.$$  \hspace{1cm} (3.2)

The spectrometer software is Topspin 2.1 (pl6), works with predefined settings for the
Figure 3.1: The modular Micro 2.5 probe consisting of the gradient system (top, black sheathing) and the probe body (bottom). The gradient system has to be connected to the gradient amplifier and is equipped with water cooling. Rf-wiring and mechanical tuning and matching is placed inside the probe body.

application of magic-angle gradients. In the coordinate frame of the gradient system, the direction

$$G_{\text{MAS}} = \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} G .$$  \hspace{1cm} (3.3)

shown in Figure 3.2 needs to be matched to the orientation of the sample spinning axis in the MAS probe (presented in the next section).

3.2 High resolution MAS probe

The high resolution MAS probe for self-diffusion experiments was a commercially available narrow bore Bruker $^1$H/X MAS probe of the type HR MAS 400 SB DIFF BL4, see Figure 3.3. Inside the probe body there is the rf-wiring and the tunable capacitors for matching and tuning. At the foot of the probe and directed upwards there are the connections for the air pressure for the spinning of the sample. Downwards directed are the connections for optionally $^1$H and X-band (e.g. $^2$H and $^{13}$C) rf-signals. At the
Figure 3.2: Coordinate system of the gradient system with the direction of the magic angle as set from the default settings of the Topspin 2.6 software. $\theta_{\text{MAS}}$ denotes the magic-angle (54.7°) between the static magnetic field $B_0$ and the sample spinning axis. At the bottom there is a micrometer screw, which allows adjustment of the angle $\theta$ between sample spinning axis and the static magnetic field. The sample holder can be seen on top of the probe body and is shown in detail in Figure 3.4. Two sample holder positions are shown, in eject position (left) and inclined by the angle $\theta$ (right). Through the micrometer screw at the bottom of the probe body, the angle $\theta$ can be set continuously in a range of 60° starting from 5° with respect to $B_0$. For our experiments the angle has to be set to $\theta_{\text{MAS}} = 54.7°$.

3.3 MOF samples for NMR studies

3.3.1 MOF-5 Synthesis

Synthesis of the MOF-5 samples was done at the Ruhr University Bochum. It is based on the approach of Eddaoudi et al. [7] and was modified to yield the desired crystal quality. 0.665 g terephthalic acid and 3.14 g Zn(NO$_3$)$_2$·4H$_2$O were dissolved in 100 mL diethylformamide (DEF) under continuous stirring inside a closed vessel. This solution was kept at $T = 368\,\text{K}$ for 24 hours and at $T = 378\,\text{K}$ for additional 5 – 10 h to achieve the necessary crystal size. During this time cubic crystals were precipitating, which afterwards were decanted off the solvent. The crystals were washed several times with dimethylformamide (DMF) and with chloroform. Afterwards they were rinsed in benzene and dried at $T = 383\,\text{K}$ under dynamic vacuum for about 24 h. Macroscopically, the obtained MOF-5 crystals have a yellowish color and the crystal sizes are 0.2 mm to
3.3.2 Sample preparation for static and magic-angle spinning PFG NMR measurements

Adsorption of benzene for static measurements was done with about 90 mg of the MOF-5 samples, inside a NMR sample tube of 7.5 mm outer diameter. The sample tube was evacuated throughout the loading procedure. In order to remove water, residual solvents and air from the pore structure, the samples were slowly heated up to $T = 393 \text{ K}$, which was maintained for 48 h. After activation the samples were cooled down to room temperature and immersed into liquid nitrogen. At $T = 77 \text{ K}$ the samples were exposed to volumetrically determined amounts of benzene gas and the appropriate amount of benzene froze in. Consecutively, the glass tubes were sealed via ablation. A homogeneous distribution of benzene across the bed of MOF-5 in the sample tubes was ensured by storing the sealed samples for 24 h at room temperature before NMR measurements.

For MAS PFG NMR experiments the same procedure was applied, except for smaller glass tubes of 2.9 mm outer diameter. After ablation, this sample was inserted into a commercial MAS rotor of 4 mm outer diameter.

Three different loadings were studied. One single component sample was prepared with a loading of 10 benzene molecules per unit cell. Furthermore two mixture samples where used. First MOF-5 crystals were loaded with cyclohexane/benzene. Secondly,
loading was performed with $n$-hexane and benzene, such that a unit cell contains 15 and 13 molecules per unit cell, respectively.
4 Calibration of the Equipment

In this chapter it is described, how the 3D imaging system and the MAS probe are aligned in the superconducting magnet. In particular it is shown how the gradient axes were determined relative to the laboratory frame of reference with the help of magnetic resonance imaging (MRI). The Topspin 2.1 (pl6) software works with a predefined internal setting for the direction of the magic-angle gradient, see section 3.1 Equation 3.3. Thus most importantly, the sample spinning axis had to be aligned to this magic-angle gradient direction. A new method is presented, by which this problem can be solved in-situ with the sample of interest already in place. In the end of this chapter temperature measurements of the MAS sample at selected spinning frequencies are shown.

4.1 Determination of the gradient axes

In order to determine at which orientation the MAS probe had to be inserted into the gradient system, the gradient coordinates with respect to the laboratory frame of reference had to be identified. Therefore, spin density images of a phantom sample were acquired with a primary spin echo sequence with a slice selecting $\pi$ rf-pulse excitation and phase, read and slice gradients in orthogonal directions. Afterwards the images were compared with the knowledge of the sample orientation in the laboratory frame of reference.

The phantom sample consisted of a glass ware tube filled with water and a teflon sample (fixed with a plastic rod), see Figure 4.1 left. The cross-section of the teflon sample was 8 mm times 4 mm in size. Three sides of the sample were characterized by a specific number of wells in the teflon material. At one long side, there was a characteristic round notch.

In the following, grey to white areas of the images are associated with a high observable $^1$H spin density and the black areas are associated with a low spin density. There is no observable $^1$H NMR signal coming from the teflon sample, such that the only bright areas in the images come from the high $^1$H spin density of water. Furthermore the labels at the axes of the spin density images are given here for simplicity. At the time of acquisition they were unknown.

In order to determine the $z$-axis orientation, two spin density images were acquired.
Figure 4.1: Phantom sample consisting of a glass ware tube filled with water and a teflon sample held in place with a plastic rod. CuSO$_4$ is dissolved in the water for $T_1$ shortening.

At first an $x$-$y$ image with slice center at $z = 0$ mm was acquired, see Figure 4.2 left. In this image there is a black spot, which was assigned to the plastic rod. Then the setting was changed to the slice center at $z = -5$ mm and a second image was taken, see Figure 4.2 right. Since in this image the cross-section of the teflon sample can clearly be seen, it was concluded, that the $z$-axis of the gradient system agreed with the upward vertical direction in the laboratory frame.

For determination of the $y$-axis, two spin density images were taken in the $x$-$z$-plane with slice thickness 1 mm, see Figure 4.3. The white lines indicate the position and
slice thickness of the two images to the right. The middle and right represent images with slice centers at \( y = -1 \) mm and \( y = 3 \) mm, respectively. The image in the middle of Figure 4.3 shows three dark areas, where the right most of them is protruding out of the bright area and is slightly bend towards \((-x)\)-direction (white arrow). This is the plastic rod which keeps the sample in place. This dark area could only be seen in the slice at \( y = -1 \) mm. It was concluded, that the round notch of the teflon sample pointed towards \((-y)\)-direction of the gradient system. Additionally Figure 4.3 (right image) shows four dark areas corresponding to the four edges of the teflon sample, confirming that the \( y \)-direction of the gradient system pointed from the round notch side towards the four edged side of the teflon sample.

The same procedure was applied to the \( x \)-direction, see left image in Figure 4.4. The three teflon edges pointing in \((-x)\)-direction correspond to the three dark areas in Figure 4.4 middle, whereas we see only two edges in Figure 4.4 right. Thus the \( x \)-direction points from the three edged side of the sample towards the two edged one. In general it can be concluded, that we deal with a right-handed system, where the knowledge of two of the directions determines third one.

With this knowledge the predefined magic-angle direction of the Topspin 2.1 (pl6) software with respect to the laboratory frame of reference could be identified in general. The sample spinning axis was aligned approximately to this direction by rotating the probe in the \( x-y \)-plane and adjusting the angle \( \theta \) with the micrometer screw, as described in section 3.2. However, if the sample spinning axis is not exactly aligned with the magic-angle gradient, diffusion experiments would yield erroneous results due to artifacts in the NMR signal and apparent movement of the particles due to rotation. Thus, exact calibration of the sample spinning axis orientation remained to be done.
4.2 Sample spinning axis calibration

There were two degrees of freedom of the sample spinning axis orientation. Given the special modular setup, azimutal alignment was necessary, see section 3.1. This may be done by free rotation of the MAS probe with respect to the surrounding gradient probe. Furthermore, the magic-angle $\theta$ between the sample spinning axis and the magnetic field $B_0$ is variable (see section 3.2) and had to be set to $\theta_{\text{MAS}} = 54.7^\circ$. Three methods and their respective pros and cons are described for this magic-angle calibration.

4.2.1 Azimutal alignment

By applying a constant magnetic field gradient during the primary spin echo pulse sequence (see Figure 4.5), one attains a frequency encoding in direction of the gradient $g_{\text{const}}$. The Fourier spectrum then shows a 1D profile of the sample along the gradient direction. Assuming a rodlike sample with homogeneous spin density, one would obtain

Figure 4.5: Primary spin echo sequence with an applied constant gradient $g_{\text{const}}$. 

and is described in the following section.
a 1D profile with maximal width and minimal signal intensity per frequency unit, if the sample was aligned with the gradient direction. Whereas in case of a perpendicular orientation rod axis to \( g_{\text{const}} \) the 1D Fourier spectrum would have minimal width and maximal signal intensity per frequency unit. Experimentally it is easier to decide when the minimal 1D Fourier profile width and maximal signal intensity is obtained, especially under low signal-to-noise conditions.

The desired sample spinning axis orientation was along the \( x-(−y) \)-diagonal, see section 3.1 and thus the direction of \( g_{\text{const}} \) was chosen to be perpendicular in direction

\[
g_{\text{const}} = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} G. \tag{4.1}
\]

The azimuthal position of the probe, and with it of the sample, was adjusted according to the minimal 1D profile width and maximum signal intensity per frequency unit, see Figure 4.6.

![Figure 4.6](image_url)

(a) On top view of the rotational degree of freedom in the \( x-y \)-plane for the sample inside the gradient system.

(b) Sample out of the \( x-(−y) \)-diagonal and its Fourier transform 1D profile.

(c) Sample aligned with the \( x-(−y) \)-diagonal and its Fourier transform 1D profile.

**Figure 4.6:** Alignment method of the sample along the \( x-(−y) \)-diagonal. The rotational degree of freedom of the sample inside the gradient system is shown on the left. In the middle there is an on top view of the \( x-y \)-plane with direction of the constant magnetic field gradient \( g_{\text{const}} \). The gradient \( g_{\text{const}} \) is applied perpendicular to the \( x-(−y) \)-diagonal. The 1D Fourier transform profile of a sample with homogeneous spin density is narrowest and signal intensity per frequency unit is maximal, when the sample spinning axis is exactly aligned perpendicular to the gradient direction.

### 4.2.2 Magic-angle calibration with imaging

The second degree of freedom was the angle \( \theta \) between the spinning axis and the magnetic field, see Figure 3.4 in section 3.2. First we aligned the sample in \( y \)-direction and
recorded sequential $y$–$z$ spin density images with different settings of the micrometer screw. From the measured angles in the images we extrapolated the angle versus setting at the micrometer screw. We achieved an approximate alignment, but this method was time consuming and not accurate enough, since the micrometer screw settings and the angle increment had no linear relationship.

### 4.2.3 Magic-angle calibration using quadrupolar nuclides

The classical approach to align the sample spinning axis with the magic-angle direction is to measure the NMR signal of a sample with quadrupolar nuclides [40]. The Fourier transform magic-angle spinning NMR spectra of quadrupolar nuclei exhibit many spinning sidebands, which can also be observed in the time domain NMR signal. Their width and intensities are very sensitive functions of the angle between the spinning axis and the magnetic field. Carefully applied, this method is capable of adjusting the spinning angle within $\pm 0.1^\circ$ of the magic angle. Most convenience was reported for the signal of $^{79}$Br from powdered KBr [40], which was therefore used in this work. In Figure 4.7 three different settings of the spinning angle and the corresponding NMR signals are plotted. The intensities of the sidebands rise from Figure 4.7 (a) (out of angle) to Figure 4.7 (b) (close to the magic-angle) up to the highest intensities when the spinning axis is best aligned with the magic-angle, Figure 4.7 (c). Besides the good accuracy, this method had the disadvantage that when the KBr sample was taken out, in order to insert the sample of interest, one had to take the MAS probe out of the magnet and reset the spinning angle. The mechanics of the probe body weren’t rigid enough to preserve the angle setting upon removal of the sample. That is the reason why a method was needed for the alignment of the spinning axis without changing samples.

![Figure 4.7: Calibration of the magic-angle with a KBr sample following the method of Frye et al. [40].](image-url)
4.2.4 Constant gradient magic-angle calibration

To our knowledge there was no method reported in the literature for the alignment of the magic-angle with the sample of interest (containing no quadrupolar nuclide) already in place. Thus this problem was approached similarly to the azimuthal alignment method, see subsection 4.2.1. A spin echo sequence with a constant magnetic field gradient perpendicular to the magic-angle direction was applied. Figure 4.8 provides a visualization of the orientation of this gradient relative to the magic-angle direction. The orthogonality of $g_{\text{const}}$ to the MAS direction can be proofed by showing that the scalar product of the respective gradient directions notation is zero

$$G_{\text{MAS}} \cdot g_{\text{const}} = \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} \cdot \begin{pmatrix} -1 \\ 1 \\ 2 \end{pmatrix} = 0.$$ (4.2)

The Fourier transform 1D profile of the sample was observed continuously during turning of the micrometer screw. As described in subsection 4.2.1 the maximal signal height was reached, when the sample was aligned perpendicular to the gradient direction (and thus along the magic-angle direction). Since the sample was spinned at a frequency of 5 kHz, the 1D Fourier transform profile was modulated with corresponding sidebands with 5 kHz separation. The intensity of the centerband as well as the overall signal intensity was a very sensitive function of the angle $\theta$ and growed considerably close to the magic-angle in a similar manner as observed with the KBr method, see Figure 4.9. The final setting of the micrometer screw was compared to the method observing only the NMR signal of KBr. The settings agreed well leading to the conclusion that the
constant gradient approach is able to adjust the magic-angle within the same accuracy range like the conventional method of Frye and Maciel [40].

### 4.3 Temperature calibration

In magic-angle spinning NMR measurements the temperature of the sample may deviate from the ambient temperature in the probe. Rapid spinning causes friction between air and the rotor, which elevates the temperature of the sample. Therefore temperature calibration is important. One common procedure is to measure the chemical shift difference \( \Delta \delta \) between the lines in the \(^1\)H NMR spectrum corresponding to the CH\(_3\) group and the OH group of methanol [41]. At higher temperatures the extent of hydrogen bonding is lower and the resonance frequency for the OH group shifts to lower frequencies towards the CH\(_3\) group, see Figure 4.10. Van Geet [42] was the first who reported a temperature calibration function of quadratic form. Here an adapted version applicable for all spectrometer frequencies was used [43].

\[
T = -23.832(\Delta \delta)^2 - 29.46\Delta \delta + 403.0.
\] (4.3)

In Equation 4.3 the temperature is given in K and the chemical shift difference \( \Delta \delta \) is inserted in ppm. Figure 4.11 illustrates the temperature of the sample at various spinning frequencies, while the ambient temperature inside the probe was \( T = 25°C \).
Figure 4.10: $^1$H NMR spectra of methanol at the spinning frequency $\nu = 3$ kHz (solid line) and $\nu = 10$ kHz (dashed line). There is a peak shift of the lines corresponding to the CH$_3$ group and the OH group, because of a higher temperature of the sample at higher spinning frequency.

Figure 4.11: Temperatures of the methanol sample spinned at frequencies from $\nu = 3$ kHz to $\nu = 10$ kHz.
5 Results and Discussion

5.1 Stochastic phase shift

After proper alignment and calibration the first diffusion measurement was performed using a mixture sample of benzene and cyclohexane adsorbed at MOF-5. The sequence used was the pulsed field gradient spin echo sequence (see section 2.4) with a gradient strength linearly increased from $G = 0 \text{Tm}^{-1}$ up to $G_{\text{max}} = 2.6 \text{Tm}^{-1}$ in 32 steps, with a gradient duration of the sine shaped gradients of $\delta' = 3.14 \text{ms}$ and an observation time of $\Delta = 15 \text{ms}$. The sample was spinned at 10 kHz. Each spectrum was acquired by accumulating 16 scans.

The NMR spectra obtained at each of the 32 gradient strength values are plotted in Figure 5.1. The peak of cyclohexane appears at a chemical shift of $\delta_{\text{cyc}} = 1.3 \text{ppm}$ and benzene appears at $\delta_{\text{benz}} = 7.2 \text{ppm}$.

In order to obtain spin echo attenuation curves of cyclohexane and benzene separately, the signal intensities of their respective peaks were integrated for each gradient step. The intensity of the first peak was taken as the reference value at zero gradient strength. The obtained spin echo attenuation curves are plotted in Figure 5.2. Especially the attenuation curve of cyclohexane exhibits random jumps in signal intensity. Additionally both attenuation curves are modulated at higher gradient strength values and therefore deviate from a smooth decline.

![Figure 5.1: Fourier transform NMR spectra of cyclohexane ($\delta_{\text{cyc}} = 1.3 \text{ppm}$) and benzene ($\delta_{\text{benz}} = 7.2 \text{ppm}$) adsorbed at MOF-5 for various gradient strengths $G$.](image)
Figure 5.2: Comparison of spin echo attenuation curves of benzene (+) and cyclohexane (*) obtained by integrating the peak intensities of each component separately.

Detailed analysis of the single spectra at various gradient steps revealed that the jumps in intensity were caused by sudden phase shifts during acquisition of the spectra, whereas the modulations come from continuous phase shifts, see Figure 5.3. In this measurement the first phase shift jump occurred at a gradient strength of $G = 1.85 \text{Tm}^{-1}$ and caused a peak split in the spectrum, see Figure 5.3 bottom left. Then the phase shift persisted up to gradient strength $G = 2.26 \text{Tm}^{-1}$ and jumped back leaving another splitted peak, see Figure 5.3 bottom right. Splitting of the peaks indicated that the phase shift occurred during acquisition of one of the 16 scans. This behavior was also apparent in other measurements and occurred randomly at various gradient strengths.

As the origin of this stochastic phase shift a lead fracture was found at one of the rf-cables, see Figure 3.4. This fracture was probably caused by movement of the sample holder when the magic-angle was reset to the eject position in order to take out the samples. The cable in these cases is bend very strongly and might suffer fractures in the future as well.

5.2 Continuous phase shift

When the lead fracture was fixed, the continuous phase shift in the PGSE experiments remained. As possible source of strong eddy currents, a copper foil, which was wrapped around the sample holder was removed. In addition, the rotor mechanics were stabilized with air pressure, in order to exclude any vibrations affecting the NMR signals. However, the phase shifts and hence the modulations in the spin echo attenuation curves
Figure 5.3: Spectra of benzene and cyclohexane adsorbed at MOF-5 at various gradient steps. Shown is only the peak of cyclohexane. There is a continuous phase shift with increasing gradient strength overlapped by a stochastic phase shift occurring at gradient step $G = 1.85 \text{Tm}^{-1}$ and jumping back at $G = 2.26 \text{Tm}^{-1}$.

did not vanish. In the following discussion the sample used for error detection was high vacuum grease. This sample was chosen, because it has a very high viscosity and therefore a low self-diffusion coefficient, which allows free parameter choice up to high gradient values with long observation times, without alternating the spin echo signal intensity too much.

There were indications that the modulations were stronger at high gradient strength values. The influence of the gradients on the magnetization during acquisition of the NMR signal and on the application of the rf-pulses had to be investigated. Therefore the free induction decay (FID) of a sequence consisting of a pulsed field gradient followed by a $\pi/2$ rf-pulse was used, see Figure 5.4. The FID was recorded for variable gradient

Figure 5.4: Pulse sequence consisting of a pulsed field gradient with maximal gradient strength $G_{\text{max}}$ and a $\pi/2$ rf-pulse in variable distance $\tau_{\text{sep}}$. 
to rf-pulse separation times $\tau_{\text{sep}}$, while the gradient strength was set to the highest possible value $G_{\text{max}} = 2.6 \text{Tm}^{-1}$ with a gradient duration of the sine shaped gradients of $\delta' = 0.79 \text{ms}$. Figure 5.5 shows the Fourier transform NMR spectra of four selected gradient to rf-pulse separation times.

All spectra were phased according to the reference spectrum at $\tau_{\text{sep}} = 5 \text{s}$. If there were no influences of the gradient pulse on the rf-pulse, all other spectra would be the same. But the minimal distance for an undisturbed spectrum was found to be $\tau_{\text{sep}} = 5 \text{ms}$, whereas for smaller separations the spectra start to show phase distortions ($\tau_{\text{sep}} = 0.75 \text{ms}$) and even exhibit severe distortions at separation values as low as $\tau_{\text{sep}} = 0.1 \text{ms}$. For a longer gradient duration of $\delta = 2 \text{ms}$ the safe separation between gradient pulse and rf-pulse was in the same range of $\tau_{\text{sep}} = 5 \text{ms}$, but the phase shifts were weaker for spectra measured below this value. One possible source of these phase shifts might be a $B_0$ drift caused by eddy currents in metal structures due to the gradient pulses.

Figure 5.5: Spectra of high vacuum grease at various gradient to $\pi/2$ rf-pulse separations $\tau_{\text{sep}}$.

5.3 Feasible MAS PFG NMR diffusion parameters

Based on the knowledge of a minimal gradient to rf-pulse separation, a set of feasible parameters for the $^1\text{H}$ MAS PFG NMR diffusion studies were identified and tested in preparation of this master thesis. Using the stimulated spin echo sequence
the pulsed field gradient width of the sine shaped gradients was varied in between $0.79 \text{ ms} \leq \delta' \leq 7.08 \text{ ms}$. The rf-pulse separation had to be adjusted following the relation

$$\tau \geq \tau_{\text{sep}} + \delta'.$$

(5.1)

Accordingly, the tested range of rf-pulse separations included values in between $6 \text{ ms} \leq \tau \leq 13 \text{ ms}$. Observation times were in the range $15 \text{ ms} \leq \Delta \leq 500 \text{ ms}$.

### 5.4 Comparison of static and magic-angle spinning diffusion measurements

In order to show the feasibility of the MAS PFG NMR self-diffusion measurements up to highest gradient strength values, these measurements were compared to static PFG NMR measurements. The same sample of high vacuum grease was used. The sequence used was the stimulated spin echo pulse sequence (see section 2.5). The gradient strength was linearly increased from $G = 0 \text{ Tm}^{-1}$ up to $G_{\text{max}} = 2.6 \text{ Tm}^{-1}$ in 8 steps, with a gradient duration of $\delta' = 7.08 \text{ ms}$. The rf-pulse separation was $\tau = 13 \text{ ms}$, while the observation time used was $\Delta = 500 \text{ ms}$. Each spectrum was acquired by accumulating 32 scans and the sample was spinned at $5 \text{ kHz}$. Static PFG NMR self-diffusion reference measurements were performed on the home built NMR spectrometer FEGRIS FT [44] (1H frequency 400 MHz).

One typical source of error in PFG NMR experiments is that the time integrals of a pair of pulsed field gradients are not identical (i.e. they are mismatched) [45]. As a proof of the absence of gradient mismatches, the spin echo attenuation in the time domain was recorded using a stimulated spin echo sequence equipped with a small read gradient as reported by Callaghan et. al [46], see Figure 5.6. In the presence of small read gradients, possible gradient mismatches would manifest themselves by jumps in the echo time, i.e. the time at which the spin echo attains its maximum. It is important to note that the spin echo times would always be the same in the absence of a read gradient, but the echo amplitudes might be varied due to gradient mismatches.

![Figure 5.6: Stimulated spin echo sequence equipped with a read gradient $g_{\text{read}}$ optimized for 1D Fourier transform profile of the sample.](image-url)
The magnitudes of the spin echos in the time domain measured with magic-angle spinning for all gradient steps are shown in [Figure 5.7]. The spin echo amplitudes occurred all at the same acquisition time, which proved the absence of gradient mismatches. The low signal-to-noise ratio of the spin echo data is due to small sample volume in connection with low transverse relaxation time $T_2$. Thus when measuring samples with short $T_2$ values the minimal rf-separation time $\tau_{\text{sep}}$ might complicate measurements.

There are two different data analysis methods considered here for MAS PFG NMR experiments, which have to yield the same results. The first way is to extract the signal intensity by taking the maximum point of the magnitude of the spin echos in the time domain measurements. The second one is by integration of the signal intensity in the Fourier transformed data of the real part of the complex NMR signal. Here the use of the real part of the NMR signal is important, because magnitude data show broader lines, through which some signals might overlap and hamper the use of MAS PFG NMR.

In order to check for consistency of the MAS PFG NMR experiments with an established PFG NMR system, the spin echo attenuations were compared to static measurements at the spectrometer FEGRIS FT ($^1\text{H}$ frequency 400 MHz) using similar parameters as described above.

The spin echo attenuation curves for the static data and the two different data analysis methods used for the magic-angle spinning data are plotted in [Figure 5.8]. The spin echo attenuation of the method using maximum points of the spin echos agree for the static and the MAS PFG NMR experiments. The error in the case of magic-angle
spinning data is much higher, because the signal-to-noise ratio (see Figure 5.7) is lower due to a much smaller sample volume. Integration of the signal intensity in the Fourier transform spectra also yields the same results within the experimental uncertainty.

5.5 Benzene adsorbed at MOF-5

Before any mixture sample of unknown self-diffusion behavior was studied, the MAS PFG NMR performance was checked using a well known porous system. The system of choice was MOF-5 loaded with 10 benzene molecules per unit cell, because it was investigated extensively before [13, 14, 47]. Here, the pulse sequence used was the stimulated spin echo pulse sequence, where the gradient strength was linearly increased from $G = 0.07 \text{Tm}^{-1}$ up to $G_{\text{max}} = 2.6 \text{Tm}^{-1}$, while the gradient duration was $\delta' = 0.79 \text{ms}$. Observation time was chosen to be $\Delta = 40 \text{ms}$ and the sample was spun at 5 kHz. The rf-pulse separation was $\tau = 6 \text{ms}$.

As a precondition for a successful measurement the time domain data in the presence of small read gradients (see section 5.4) were recorded to check for eventual occurring gradient mismatches. All echos attained their maximum amplitude at the same time (not shown), which confirmed the absence of gradient mismatches. Integration in the frequency domain of the benzene peak yielded the spin echo attenuation curve plotted in Figure 5.9. As described in Stallmach et. al [13] the spin echo attenuation curves of the
Figure 5.9: Biexponential fit of the spin echo attenuation curve of MOF-5 loaded with 10 benzene molecules per unit cell. Results are two diffusion coefficients \( D_A = 2.35 \times 10^{-9} \text{m}^2\text{s}^{-1} \) with fraction \( p_A = 0.54 \) and \( D_B = 0.12 \times 10^{-9} \text{m}^2\text{s}^{-1} \) with fraction \( p_B = 0.46 \).

system benzene at MOF-5 deviate from linearity, which indicates a distribution of self-diffusion coefficients, see also [14]. In both contributions [13, 14] the slow self-diffusion coefficient is assigned to molecules hindered by residual solvent molecules in the pure MOF-5 structure. It is argumented that the fast self-diffusion coefficient represents the mobility of molecules in an undisturbed MOF-5 lattice. Thus, only the fast diffusion coefficient will be compared.

In the MAS PFG NMR measurements the biexponential fit of the data yields a fast self-diffusion coefficient of \( D_A = 2.35 \times 10^{-9} \text{m}^2\text{s}^{-1} \) with fraction \( p_A = 0.54 \). This value matches the static self-diffusion coefficient of \( D_{\text{static}} = 2.2 \times 10^{-9} \text{m}^2\text{s}^{-1} \) and its fraction \( p_{A,\text{static}} = 0.54 \) given in [14] as well as data obtained by molecular dynamics simulations [47] within the experimental uncertainty.

5.6 Benzene and n-hexane coadsorbed at MOF-5

First measurements of a mixture sample were performed with n-hexane and benzene coadsorbed at MOF-5. Loading was performed with n-hexane and benzene, such that one unit cell contains 15 and 13 molecules per unit cell, respectively. The pulse sequence used was the stimulated spin echo sequence with gradient strengths up to \( G_{\text{max}} = 2.6 \text{Tm}^{-1} \), sample spinning at 5 kHz, gradient duration \( \delta' = 0.79 \text{ms} \), diffusion time \( \Delta = 100 \text{ms} \) and rf-pulse separation \( \tau = 6 \text{ms} \). The sample temperature for
the spinning frequency used here is about 300 K, see section 4.3. Figure 5.10 shows the frequency domain of the spin echo attenuations. The spectra were referenced to the benzene peak at $\delta = 7.16$ ppm. Figure 5.11 shows the spin echoes obtained with time domain measurements in the presence of a small read gradient. All echoes attain their maximum at the same acquisition time, which again proves absence of gradient mismatches.

The spin echo attenuation curves were obtained by integrating the signal intensity in the frequency domain for the benzene peak and the n-hexane peak separately. The biexponential fit of the two components yields two self-diffusion coefficients per component, see Table 5.1. Comparison with the single component benzene adsorbed at
Figure 5.12: Biexponential fit of the spin echo attenuation in the frequency domain of MOF-5 loaded with benzene and n-hexane. Data was obtained by integrating the signal intensity in the frequency domain for the benzene peak and the n-hexane peak separately.

<table>
<thead>
<tr>
<th></th>
<th>$D_A$ [$10^{-9}$ m$^2$s$^{-1}$]</th>
<th>$D_B$ [$10^{-9}$ m$^2$s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.71</td>
<td>0.05</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.86</td>
<td>0.08</td>
</tr>
</tbody>
</table>

MOF-5 as presented in section 5.5 (loading of 10 molecules per unit cell) shows that the self-diffusion coefficient in the mixture sample is reduced by a factor of approximately three. Similar slow down effects were observed earlier in Hertel et. al (submitted) [14]. Figure 5.13 shows the self-diffusion coefficients at selected loadings as a function of temperature obtained by PFG NMR spectroscopy and MD simulations [14]. For low loadings of 6 and 10 benzene molecules per unit cell and a temperature of $T = 298$ K, there is an agreement between the results obtained by both methods. When increasing the loading from 10 to 20 molecules per unit cell of MOF-5, the experimental diffusion data drop by a factor of about three, while current molecular dynamics (MD) simulations predict slightly increasing diffusion coefficients for this range of loadings.

Using Monte Carlo and MD simulations, Krishna and van Baten [48] discussed recently the formation of clusters of small adsorbed molecules in several microporous materials at subcritical temperatures. Since all NMR measurements were performed well below the critical temperature of benzene ($T_c = 562$ K [49]), clustering of benzene...
in the MOF-5 pore space might be possible as well. It is obvious that it is more difficult for a cluster of benzene molecules to move through the pore network than for single benzene molecules. Comparison with the concentration dependent self-diffusion data in Figure 5.13 shows that clustering might occur in the range of 10 to 20 molecules per unit cell.

In this master thesis the sample temperature of 300 K is equally well below the critical temperatures of benzene as well as n-hexane \( T_c = 507.6 \text{ K} \) \[^49\]. The effective loading of 28 \((n\text{-hexane plus benzene})\) molecules per unit cell lies in the range assigned to cluster formation in \[^14\]. Thus it might be possible, that clustering of the molecules caused the low self-diffusion coefficients compared to the single component data obtained for benzene in \[^5.5\]. Such information about self-diffusion of mixtures was not available before and might help to improve future MD simulations.
6 Summary

In a multitude of applications it is important to know the self-diffusion behavior of mixtures adsorbed at microporous materials. Conventional MAS PFG NMR studies using a 'magic-angle gradient' coil are limited to the study of fast diffusing species due to low achievable gradient strengths.

In this work a commercially available micro-imaging system was combined successfully with a narrow bore MAS probe. This modular design has the advantage of a 10-fold higher gradient strength compared to 'magic-angle gradient' coil designs and thus allows the investigation of self-diffusion of slow moving species in mixtures.

Due to the modular design it was important to find procedures and to write test protocols to align the 3D imaging system and the MAS probe inside the superconducting magnet. The gradient axes with respect to the laboratory frame of reference were determined using magnetic resonance imaging.

A constant gradient method is proposed and tested, which allows the alignment of the sample spinning axis in azimuthal direction as well as the magic-angle, in-situ with the sample of interest already in place. This method yields an accuracy similar to the standard method of Frye and Maciel [40]. This procedure is described in detail in a manuscript submitted to the New Journal of Physics [50].

Possible pitfalls during the application of the special modular setup were lead fractures at the sample holder due to mechanical stress during sample changing. Necessary improvements also included to fix the sample holder mechanics with air pressure and the removal of a copper foil as a possible source of eddy currents. Most importantly, it was shown that the minimal time period between gradient pulses and rf-pulses is $\tau_{\text{sep}} = 5 \text{ ms}$ for this particular setup.

First successful self-diffusion experiments were conducted using a high vacuum grease sample. Due to its high viscosity and thus a low self-diffusion coefficient, this sample was suited to test the system up to highest gradient strengths and durations. As a precondition for successful self-diffusion measurements, gradient mismatches had to be excluded. This was achieved by using a stimulated echo sequence equipped with a small read gradient. It is shown that MAS PFG NMR self-diffusion measurements yield the same results as static measurements using two different data analysis methods. Integration of the signal intensity in the Fourier transform NMR spectra yielded the
same results as analyzing the amplitude of the spin echos.

The self-diffusivity of benzene adsorbed at MOF-5 was determined to be $D_A = 2.35 \times 10^{-9} \, \text{m}^2 \text{s}^{-1}$, which is consistent with diffusion data ($D_{\text{static}} = 2.2 \times 10^{-9} \, \text{m}^2 \text{s}^{-1}$) in a second manuscript submitted to the European Physical Journal Applied Physics [14].

The MAS PFG NMR measurements of the mixture sample n-hexane and benzene coadsorbed at MOF-5 yield two self-diffusivities per component. They are a factor of three lower than the single component self-diffusivity of benzene adsorbed at MOF-5. This behavior is explained by recently reported clustering of small molecules adsorbed at microporous materials at subcritical temperatures. Evidence of clustering in single component systems was found earlier using static PFG NMR experiments and is described in the submitted manuscript [14]. Such information about self-diffusion of mixtures was not available before and might help to improve future MD simulations.

Within the scope of the DFG priority program 1632 'Metal Organic Frameworks', and the project 'Fundamental host guest interactions in MOFs' there will be extended experiments using mixtures adsorbed at metal-organic frameworks.
# A Appendix

## A.1 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflection Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>DEF</td>
<td>Diethylformamide</td>
</tr>
<tr>
<td>DFG</td>
<td>Deutsche Forschungsgemeinschaft</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>FEGRIS</td>
<td>Feldgradientenimpulsspektrometer</td>
</tr>
<tr>
<td>FID</td>
<td>Free induction decay</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic-angle spinning</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>MIL-101</td>
<td>Matérial Institut Lavoisier 101</td>
</tr>
<tr>
<td>MOF-5</td>
<td>Metal-organic framework 5</td>
</tr>
<tr>
<td>MRI</td>
<td>Magnetic resonance imaging</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PFG</td>
<td>Pulsed field gradient</td>
</tr>
<tr>
<td>PGSE</td>
<td>Pulsed gradient spin echo sequence</td>
</tr>
<tr>
<td>PGSTE</td>
<td>Pulsed gradient stimulated spin echo sequence</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
</tbody>
</table>
A.2 Symbols

\( \delta \) gradient pulse width of rectangular shaped gradient pulse
\( \delta' \) gradient pulse width of sine shaped gradient pulse
\( \Delta \) diffusion time
\( \gamma \) gyromagnetic ratio
\( \mu \) magnetic moment
\( \nu \) spinning frequency of the sample
\( \omega_0 \) Larmor frequency
\( \Psi \) spin echo attenuation due to self-diffusion
\( \tau \) rf-pulse separation
\( \tau_{\text{sep}} \) separation time between pulsed field gradient and rf-pulse
\( \theta \) angle between sample spinning axis and static magnetic field
\( b \) generalized gradient parameter
\( B \) magnetic field
\( D \) self-diffusion coefficient
\( g \) gradient strength of constant gradients
\( G \) gradient strength of pulsed field gradients
\( G_{\text{MAS}} \) pulsed field gradient in magic-angle direction
\( H \) potential energy
\( I_i \) eigenvalues of the spin operator
\( M \) magnetization
\( p_i \) fraction of molecules in phase \( i \)
\( t \) time
\( T \) temperature
\( T_1 \) longitudinal relaxation time
\( T_2 \) transverse relaxation time
\( T_c \) critical temperature
\( t_e \) spin echo time
B ATR-FTIR diffusion studies

B.1 Introduction to ATR-FTIR diffusion studies

Recently a breakthrough in the use of MOFs as catalysts was achieved by Kapteijn et. al [9] through the encapsulation of phosphotungstic acid inside MIL-101(Cr) (MIL, Matérial Institut Lavoisier) [6].

These new porous catalysts show superior conversion rates in the Knoevenagel condensation reaction (see Figure B.1) compared to conventional catalysts. This success has to be followed by further attempts to increase the reaction kinetics, for which the reaction mechanism and eventual reaction limiting steps have to be identified. The transport-diffusion behavior of the reactants and products inside the porous particles is known to be a rate determining step [10]. Thus, this part of the master thesis was devoted to the investigation of transport-diffusion of the reactants (benzaldehyde (BA) and ethyl cyanoacetate (ECA)) of the aforementioned Knoevenagel condensation reaction inside MIL-101(Cr). The theoretical work and the experiments were performed during a 3 month internship in the group of Prof. Kapteijn at the Technical University Delft.

Conventional techniques such as PFG NMR or elastic neutron scattering are limited to studies of either self-diffusion, or conditions far from reaction conditions. Other approaches using batch systems using e.g. gas chromatography bear the disadvantage that they are time consuming and one needs a lot of material to perform the measurements. In-situ Attenuated Total Reflection (ATR) FTIR spectroscopy has been shown to be a powerful technique to determine the reaction mechanisms by revealing transition states [11] and the time evolution of the concentrations of the reaction species.

Figure B.1: Knoevenagel condensation reaction. The reaction of benzaldehyde (BA) with ethyl cyanoacetate (ECA) yields ethyl-α-cyanocinnamate under the release of water.
In this work the ATR-FTIR technique is employed to perform transport-diffusion studies through the sequential measurement of the concentration of guest molecules in the liquid solution. Based on this information, the time constants of the uptake by the porous particles had to be determined. The resulting transport-diffusion coefficients had to be used to evaluate the Weisz-Prater criterion, which is a measure to decide whether the reaction is reaction limited or diffusion limited.

**B.2 Theory**

**B.2.1 MIL-101 framework**

With the synthesis of MIL-101(Cr) a promising candidate for catalysis applications was provided. It shows thermal stability up to 300 °C and withstands solvents like water, ethanol and toluene. Macroscopically MIL-101(Cr) is a crystalline green powder with the chemical formula \(\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}[\text{O}_2\text{C}–\text{C}_6\text{H}_4–(\text{CO}_2)]_3n\text{H}_2\text{O} (n \approx 25)\). The structure of MIL-101(Cr) is built up from so-called supertetrahedra, see Figure B.2. Each supertetrahedron is made by the linkage of trimeric chromium(III) octahedral clusters and benzene-1,4-dicarboxylate (bdc) linkers. These supertetrahedra are the building units of one unit cell (\(a \approx 89\) Å), which consists of 12 middle cages (internal diameter \(d = 29\) Å) and 6 big cages (internal diameter \(d = 34\) Å). The middle cages are connected through pentagonal windows with a free diameter of 12 Å while the large cages have both pentagonal and larger hexagonal windows of 14.5 Å × 16 Å free diameter, see Figure B.2.

**B.2.2 ATR-FTIR principle**

The ATR-FTIR technique is based on Fourier Transform Infrared spectroscopy (FTIR). Instead of sending the infrared beam through a sample, it is guided through an optical
fiber into a crystal with high refractive index. The infrared beam is multiple times totally reflected inside the crystal, see Figure B.3. At one interface the crystal is in contact with a material of interest, e.g. a liquid solution. At the interface between the solution and the ATR crystal there is an evanescent wave protruding into the liquid. The interaction of this evanescent wave with the molecules of the solution leads to absorption of IR energy by characteristic absorption bands. By analyzing the outgoing IR beam one gains information about the absorbing material. The penetration depth \( d_p \) of the evanescent waves can be calculated via

\[
d_p = \frac{\lambda}{2\pi n_1 \sin^2(\theta) - n_2^2},
\]

with \( \lambda \) being the wavelength, \( n_1 \) the crystal refractive index, \( n_2 \) the refractive index of contact medium and \( \theta \) the incident angle. The penetration depth for a silicon crystal in contact with toluene (\( \theta = 60^\circ \)) is in between 0.85\( \mu \)m (650 cm\(^{-1}\)) and 0.2\( \mu \)m (2800 cm\(^{-1}\)).

**B.2.3 ATR-FTIR setup**

It was aimed to perform transport-diffusion studies through the sequential measurement of the concentration of guest molecules in the liquid solution. Based on this information, the uptake in terms of transport-diffusion coefficients by the porous particles had to be determined. Figure B.4 shows a schematic representation of the experimental setup. The ATR crystal is attached to a metallic probe, with an optical fiber inside, which guides the ingoing and outgoing infrared beams. The probe was immersed into the solution with the MIL-101 particles inside. The solution was kept at a predefined
Figure B.4: Setup for the ATR-FTIR diffusion measurements. ATR-FTIR probe immersed in the solvent with MIL-101 particles. The sealed flask is immersed in a heat bath and allows nitrogen purging. Guest substances are injected using a syringe.

temperature through a heat bath surrounding the flask. The flask is kept air tight and allows for nitrogen purging. The magnetic stirrer ensured a homogeneous concentration in the solution, while the MIL-101 particles had to be dispersed to take up the molecules. The guest molecules were injected into the solution via a syringe and then the concentration of the guest molecules was measured at predefined time intervals.

B.2.4 Concentration measurements with ATR-FTIR spectroscopy

Concentration measurements using the ATR-FTIR technique were performed by integrating the area of a characteristic peak of the substance of interest. Best results were obtained using peaks that did not overlap with peaks of the solvent or of the MOF crystals. For our solution (MIL-101(Cr) in toluene) the most decent peak for benzaldehyde was situated at $\nu = 1710\, \text{cm}^{-1}$ and for ethyl cyanoacetate it was at $\nu = 1757\, \text{cm}^{-1}$.

Figure B.5 shows the absorption band at $1710\, \text{cm}^{-1}$ (characteristic for benzaldehyde) at various instants of time. In order to calculate the concentration of benzaldehyde at these times, one may integrate the area of this peak with a two point baseline. The resulting intensity of absorbed light at this specific band is directly proportional to the concentration of benzaldehyde in the liquid. It has to be taken into account that the concentration drops through the uptake by the porous particles during the acquisition time (typically $\Delta t = 15\, \text{s}$) of one spectrum and thus the calculated concentration resembles the value at half the time interval (after $\Delta t = 7.5\, \text{s}$).
Figure B.5: Characteristic peak of BA at $\nu = 1710 \text{ cm}^{-1}$ at various times. Before injection (solid), just after injection (dashed), 30 min after injection (dotted) and 60 min after injection (dash-dotted).

Figure B.6 shows the calibration curve of the ATR-FTIR equipment for the solution of benzaldehyde in toluene. The intensity of the two point baseline integration of the characteristic peaks is plotted against the calculated concentrations. The concentrations used for calibration were chosen to be in the range expected for the diffusion experiments. The equation relating the concentration $c$ to the integral intensity $I$ reads

$$ c = b I , $$

where $b$ denotes the calibration constant. The calibration constants were obtained by a linear fit of intensity versus concentration, see Figure B.6. For benzaldehyde the fit yielded $b = 147 \times 10^{-6} \text{ mol ml}^{-1}$ and for ethyl cyanoacetate it was $b = 1.4 \times 10^{-4} \text{ mol ml}^{-1}$.

### B.2.5 Model for transport-diffusion

One goal of these studies was to find an effective transport-diffusion coefficient of reactants entering the MOF particles. As a first approximation the particles can be assumed to be of spherical shape. Secondly they are immersed in a finite volume bath. The fundamental equation to be solved is Fick’s 2nd law for a sphere assuming a constant diffusion coefficient.

$$ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) , $$

(B.3)
Figure B.6: Linear fit of concentration of benzaldehyde in toluene versus peak intensity obtained by two point baseline integration of the characteristic peak of benzaldehyde at $\nu = 1710 \text{cm}^{-1}$.

with $c$ denoting the concentration, $D$ the diffusion coefficient, $t$ time and $r$ radius of the particle. The rate at which solute leaves the solution is equal to the rate at which it enters the sphere.

$$l \frac{\partial c}{\partial t} = \mp D \frac{\partial c}{\partial r}, \quad r = \pm a, \quad t > 0,$$

where $l$ is the length of the bath and $a$ is the radius of the sphere. Initially the sphere is free from solute which translates into the initial condition

$$c = 0, \quad -a < r < a, \quad t = 0.$$

A solution for this partial differential equation can be found in J. Crank’s ‘The Mathematics of Diffusion’ [51]. One feasible expression of the solution is given by the infinite sum

$$\frac{M_t}{M_{\text{inf}}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1) \exp(-Dq_n^2 t/a^2)}{9 + 9\alpha + q_n^2 \alpha^2}.$$

Here $M_t$ is the total amount of solute inside the sphere after time $t$, the $q_n$s are the roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}$$

and $\alpha = 3V/(4\pi a^3)$ is the ratio of the volumes of solution and sphere.
B.3 Experimental

B.3.1 ATR-FTIR equipment and procedure

Infrared spectra were measured using a ReactIR iC 10 spectrometer (Mettler Toledo) equipped with an AgX 95 mm × 1.5 m Fiber (Silver Halide) probe interface and a liquid nitrogen cooled MCT detector. Spectra were recorded by averaging 30 scans at a resolution of 4 cm\(^{-1}\). The SiComp (silicon) crystal allowed a bandwidth of 2800 cm\(^{-1}\) to 650 cm\(^{-1}\).

The following procedure was applied throughout all measurements. After weighing the dried MOF the amount of toluene and guest substance which had to be added was calculated, such that the concentrations were on the order of 10\% of the conditions used for Knoevenagel condensation in Juan-Alcaniz et. al \[9\]. For later calculations the amount of toluene was calculated that had to be added in order to fill the pores of the MOF (wetting amount). Consecutively the remaining amount of toluene was added. The solution was heated up to 64°C and the flask was purged with nitrogen for at least 5 min. After switching on the stirring, the guest molecules were injected and data acquisition was started. Spectra were acquired continuously averaging 30 scans (15 s). In order to quantify the amount of injected molecules, the syringe was weighed before and after injection. After each measurement the samples were dried at 433 K for at least 24 h.

B.3.2 MOF samples for ATR-FTIR studies

B.3.2.1 MIL-101 syntheses

MIL-101(Cr) was hydrothermally synthesized (autogenous pressure) from a mixture of 1.63 g of Chromium (III) Nitrate (Cr(NO\(_3\))\(_3\)\(\cdot\)3\(\cdot\)9H\(_2\)O, 97\%), (0.56 g as 80 wt\%) 0.7 g of Terephthalic Acid (C\(_6\)H\(_4\)\(\cdot\)1, 4-(CO\(_2\)H)\(_2\), 97\%), 0.20 g of Hydrofluoric Acid (HF, 40\%) and 20 g of distilled Water (H\(_2\)O) inside a teflon autoclave. The mixture was heated for 8 h at 493 K (220°C) in a static oven. After this period the autoclave was cooled down. This procedure was done under water and atmosphere pressure during 1h. The crystalline MIL-101(Cr) product in the solution is doubly filtered off using two glass filters with a pore size in between 40 µm and 100 µm to remove free Terephthalic Acid. Then a solvothermal treatment is sequentally performed using Ethanol (95\% EtOH with 5\% Water) at 353 K for 24 h. The resulting solid is soaked in 1M of NH\(_4\)F solution at 343 K for 24 h and immediately filtered and washed with hot water. The solid was finally dried overnight at 423 K under air atmosphere.
B.3.2.2 PTA Encapsulation

Encapsulation of Phosphotungstic acid (PTA) was achieved by adding 1.5/0.8 g of PTA to the previously described mixture and 20 g of deionized water $\text{H}_2\text{O}$. The crystalline MIL-101(Cr) with phosphotungstic acid encapsulated as product in the solution is doubly filtered off using two glass filters with a pore size in between 40 $\mu$m and 100 $\mu$m to remove the free Terephthalic Acid. Then the washing procedure was performed as described above. In this work we investigated one sample of pure MIL-101(Cr) (0 wt%) and two encapsulated samples with 20 wt% and 50 wt% loading of PTA respectively.

B.4 ATR-FTIR results and discussion

First measurements showed that the peaks of terephthalate linkers were changing throughout the experiment, see Figure B.7. One reason for the increasing background might be the sticking of MOF material to the ATR crystal. Since this signal is partly overlapping with the characteristic peaks for benzaldehyde and ethyl cyanoacetate, this influence had to be excluded by integration with a two point baseline, see subsection B.2.4. This way it was assured to follow the time evolution of the intensity of the absorption band characteristic for the guest molecules most accurately.

One may wonder whether the sticking of MOF material at the crystal itself was a process, which decreased the intensity of the guest substances peaks and thus if one had to account for this influence on the peak area in addition to diffusion. In order to quantify this influence an experiment was performed after saturation of the benzaldehyde concentration in an diffusion experiment, see Figure B.8. Stirring was

![Figure B.7: ATR-FTIR spectra of the solution of MIL-101 particles and benzaldehyde in toluene taken at 1 min (blue) 2 min (green) and 5 h (red) after injection of benzaldehyde.](image)
Figure B.8: Time evolution of the intensity of the characteristic peak of benzaldehyde (blue) at 1710 cm\(^{-1}\) compared to the intensity of terephthalate (green). After equilibrium in a diffusion experiment, the stirring was switched off. The probe was taken out for cleaning and was then reimmersed in the solution. The first 4 min were measured without stirring, after 4 min the stirring was switched on again.

switched off and the probe was taken out for cleaning. After reimmersing the probe, only the solution was measured without stirring for the first 4 min. Afterwards stirring was switched on, see Figure B.8. It can clearly be seen that the peak intensity associated to terephthalate of the MIL-101(Cr) lattice increases with time, while there is no significant influence on the signal intensity of benzaldehyde. In fact the integrated area of the benzaldehyde peak did not change at all. This is why the sticking of MOF material at the ATR crystal interface when analyzing the uptake curves was not taken into account in the diffusion model.

For a quantitative description and modelling of the uptake curves, the initial intensity before any uptake had taken place had to be known. The first data point was an insufficient measure of the initial concentration, since the minimum time interval for the first datapoint with our equipment was 7.5 s, during which a significant portion of uptake had already taken place. Thus a hypothetical initial intensity was calculated using

\[
I = \frac{n_{\text{guest}}}{(V_{\text{tol}} - V_{\text{wet}} + V_{\text{guest}})b}
\]  

(B.8)

where \(n_{\text{guest}}\) denotes the number of moles of injected guest molecules, \(V_{\text{tol}}\) the volume of added toluene, \(V_{\text{wet}}\) is the amount of toluene that does not contribute to the bulk phase since it is filling the pores of the MIL-101(Cr) and \(b\) is the calibration constant obtained by calibrating the ATR-FTIR equipment, see subsection B.3.4.

One crucial parameter for the model of the uptake curves is the crystal size. SEM images showed two domains of crystal sizes. For MIL-101(Cr) loaded with 20 wt% of
PTA the diameter of the bigger crystals were ranging from $d = 0.8 \, \mu m$ to $d = 4 \, \mu m$ (Figure B.9) whereas the diameter of the smaller crystals were in the range of $d = 0.1 \, \mu m$ to $0.3 \, \mu m$ (Figure B.10). The model had to be adapted to these two mean diameters.

**Figure B.9:** Scanning Electron Microscopy image of MIL-101 loaded with 20 wt% of PTA. Domain of larger crystals observable with a magnification of $1000 \times$. The diameter of the crystals range from $d = 0.8 \, \mu m$ to $d = 4 \, \mu m$.

**Figure B.10:** Scanning Electron Microscopy image of MIL-101(Cr) loaded with 20 wt% of PTA. Domain of smaller crystals observable with a magnification of $25000 \times$. The diameter of the crystals range from $d = 0.2 \, \mu m$ to $d = 0.4 \, \mu m$.

Therefore one also had to provide the model with an estimate of the fractional uptake of the small crystals compared to the uptake of the big crystals. The fit of the experimental data for benzaldehyde diffusing inside MIL-101(Cr) 20 wt% dissolved in toluene yielded a transport diffusion coefficient of $D = 1.1 \times 10^{-16} \, m^2 s^{-1}$, see Figure B.11. The mean diameter of the smaller crystals was assumed to be $d_s = 0.2 \, \mu m$ and for the big crystals $d_b = 2.4 \, \mu m$. In a later experiment the uptake kinetics were found to be much slower, see Figure B.12. The benzaldehyde concentration did not attain equilibrium after $t = 1.5 \, h$ while in the first experiment the benzaldehyde concentration was already in equilibrium after $t = 30 \, min$. Table B.1 shows the parameters for the
Figure B.11: Fit of the experimental data for the uptake of benzaldehyde by MIL-101(Cr) loaded with 20 wt% of PTA. Experimental (open triangles) and fit (solid line) agreed best using an effective transport diffusion coefficient of $D_{\text{eff}} = 1.1 \times 10^{-16}\, \text{m}^2\, \text{s}^{-1}$, assuming two mean crystal sizes of $d_s = 0.2\, \mu\text{m}$ and $d_b = 2.4\, \mu\text{m}$.

A reasonable fit of the second measurement could only be achieved by significantly increasing the bigger mean diameter of the particles, see Figure B.12. Since SEM images indicated the occurrence of agglomerates of MOF particles from 2.4 µm to 3.6 µm, it might be that agglomerates caused a prolonged uptake process through longer diffusion paths until the porous particles were finally saturated. This would imply that the agglomerates were better dissolved during the first measurement than the second one. An argument supporting this hypothesis is that the fractional uptake of the smaller particles decreased, while it increased for the

Table B.1: Comparison of the parameters of the fit of experimental data obtained for two consecutive experiments with benzaldehyde diffusing inside MIL-101(Cr) 20 wt%. $D_{\text{eff}}$ denotes the effective diffusion coefficient, $d_s$ the mean diameter of the small crystals, $d_b$ the mean diameter of the big crystals, $p_s$ the fractional uptake of benzaldehyde by the small crystals, $p_b$ the fractional uptake of benzaldehyde by the big crystals

<table>
<thead>
<tr>
<th>measurement:</th>
<th>BA</th>
<th>BA reprod</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{eff}}[10^{-16}, \text{m}^2, \text{s}^{-1}]$</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>$d_s[\mu\text{m}]$</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$d_b[\mu\text{m}]$</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>$p_s$</td>
<td>0.42</td>
<td>0.19</td>
</tr>
<tr>
<td>$p_b$</td>
<td>0.25</td>
<td>0.29</td>
</tr>
</tbody>
</table>
Figure B.12: Reproducibility test for the uptake experiment of benzaldehyde by MIL-101(Cr) loaded with 20 wt% of PTA. The fit (solid line) of the experimental data (open circles) yielded the same effective transport diffusion coefficient \( D = 1.1 \times 10^{-16} \text{m}^2\text{s}^{-1} \), while the mean diameter the larger crystals had to be increased to \( d_b = 3.6 \mu\text{m} \).

the bigger particles, which would be expected since the amount of smaller crystals decreases by the formation of agglomerates. In order to prevent this effect one could try to sonicate the samples before the measurements. This would dissolve the agglomerates and therefore allow to measure at the same conditions in each experiment. A second approach would be to filter the crystals and to measure with one diameter only. Another source of uncertainty might have been that the SEM experiments were restricted to experiments in the gas phase, where the agglomerates might behave differently than in the liquid phase. Thus it is proposed to measure the particle size distribution with dynamic light scattering in the liquid phase, which should provide crystal sizes closer to the ATR-FTIR diffusion studies.

Figure B.13 shows the time evolution of the concentration of ECA in the experiment with MIL-101(Cr) 50 wt% PTA. For this sample dynamic light scattering (DLS) data was available. Since the uptake curve is steep in comparison to the MIL-101(Cr) 20 wt% PTA experiments, it was assumed that agglomerates were absent and that the diameters given by DLS could be taken. The fit of the data yielded an effective transport diffusion coefficient of \( D_{\text{eff}} = 5 \times 10^{-17} \text{m}^2\text{s}^{-1} \). Comparison with the uptake experiment for BA shows no significant differences, see Figure B.14.

The fit of the data for ECA and BA gave identical diffusion coefficients, see Table B.2. Of course the molecular structure of these two molecules would suggest different mobilities, but with the time resolution (15 s) the ATR equipment we were not able to measure...
Figure B.13: Fit of the experimental data for the uptake experiment of ethyl cyanoacetate by MIL-101(Cr) 50 wt%. The fit (solid line) of the experimental data (open squares) yielded an effective transport diffusion coefficient of $D = 5 \times 10^{-17} \text{m}^2\text{s}^{-1}$ assuming two mean crystal sizes of $d_s = 0.2 \text{µm}$ and $d_b = 1.2 \text{µm}$.

these differences. Comparison of the diffusivities for different loadings with PTA shows that for the loading with 50 wt% PTA ($D_{\text{eff}} = 0.5 \times 10^{-16} \text{m}^2\text{s}^{-1}$) the molecules were much less mobile than for the loading with 20 wt% PTA ($D_{\text{eff}} = 1.1 \times 10^{-16} \text{m}^2\text{s}^{-1}$). One reason might be an increased blocking of the pore windows by PTA in case of higher loadings.

The Weisz-Prater criterion is an inequality used to estimate the influence of pore diffusion and reaction rates in heterogeneous catalytic reactions. If the criterion is satisfied, pore diffusion limitations are likely to be negligible [10]. For spherical particles

Table B.2: Comparison of the parameters of the fit of experimental data for benzaldehyde and ethyl cyanoacetate at MIL-101(Cr) loaded with 50 wt% of PTA. $D_{\text{eff}}$ effective diffusion coefficient, $d_s$ mean diameter of the small crystals, $d_b$ mean diameter of the big crystals, $p_s$ fractional uptake of benzaldehyde by the small crystals, $p_b$ fractional uptake of benzaldehyde by the big crystals

<table>
<thead>
<tr>
<th>guest molec.:</th>
<th>BA</th>
<th>ECA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{eff}} \left[10^{-16} \text{m}^2\text{s}^{-1}\right]$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$d_s [\text{µm}]$</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$d_b [\text{µm}]$</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$p_s$</td>
<td>0.37</td>
<td>0.38</td>
</tr>
<tr>
<td>$p_b$</td>
<td>0.08</td>
<td>0.07</td>
</tr>
</tbody>
</table>
and reactions of first order it reads

$$ \phi = \frac{L^2 r_{obs} \rho}{D_{eff} c_s} < 1, $$

(B.9)

where $L = d/6$ denotes the characteristic length of the catalyst particles, $r_{obs}$ is the observed reaction rate, $\rho$ is the density of the catalyst and the denominator is determined by the effective diffusion $D_{eff}$ and the surface concentration of the reactant $c_s$ in the beginning of the reaction.

**Table B.3:** Weisz-Prater modulus evaluated for the samples MIL-101(Cr) 50 wt% PTA and MIL-101(Cr) 20 wt% PTA for the small and big crystals respectively.

<table>
<thead>
<tr>
<th>sample</th>
<th>20 wt%</th>
<th>50 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>small</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>big</td>
<td>2.7</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Table B.3 shows the values of the Weisz-Prater modulus for the measurements of BA and ECA at MIL-101(Cr) 20 wt% PTA and at MIL-101(Cr) 50 wt% PTA for the small and the big crystals respectively. For both samples the Weisz modulus for the small crystals is smaller than one, which indicates that the reaction is catalyzed without significant diffusion limitations. For the big crystals however the criterion is not fulfilled, which is an indication of a diffusion limited reaction. This means that for applications
it would be better to synthesize smaller crystals. Furthermore the Weisz modulus is larger in case of the sample loaded with 50 wt% of PTA. This might be an indication that, less activity was observed for this sample in the reaction experiments reported in [9] because of diffusion limitations.

**B.5 ATR-FTIR conclusions**

The ATR-FTIR spectroscopy technique was successfully applied to study the transport-diffusion of benzaldehyde and ethyl cyanoacetate from a solution in toluene inside MIL-101(Cr) particles. The MIL-101(Cr) samples were synthesized with phosphotungstic acid encapsulated in their cages. Two loadings were investigated in detail 50 wt% PTA and 20 wt% PTA. Since there is evidence of MOF material sticking to the ATR probe, the peaks of the IR spectra had to be integrated with a two point baseline to yield correct values for the concentration of the guest molecules in solution. SEM images showed two domains of crystal sizes. Thus the model for the uptake curves had to be modified to account for two mean crystal diameters.

For the samples with 20 wt% PTA the model could only be fitted by increasing the second mean diameter well above the observed diameter in the SEM images. This behaviour is attributed to the agglomeration of MOF particles during the drying procedure in between the experiments. This effect was not observed for MIL-101(Cr) loaded with 50 wt% PTA. The effective diffusion coefficient for BA and ECA in MIL-101(Cr) 50 wt% PTA at $T = 60 \, ^\circ\text{C}$ was found to be $D_{\text{eff}} = 5 \times 10^{-17} \, \text{m}^2 \, \text{s}^{-1}$ while for the sample with 20 wt% PTA the value was found to be the double $D_{\text{eff}} = 1.1 \times 10^{-16} \, \text{m}^2 \, \text{s}^{-1}$. The lower mobility in case of 50 wt% PTA might be caused by increased hindering of the entering molecules by PTA cluster units sitting in the windows of the MIL-101(Cr) cages.

Application of the Weisz-Prater criterion shows that for small crystals there is no significant transport limitation for the reactants in the Knoevenagel condensation, while in the larger crystals the reaction is probably limited by diffusion. Furthermore the values of the Weisz modulus are higher for the MIL-101(Cr) 50 wt% PTA sample, which indicates that diffusion limitations increase with higher loading of PTA. This might be the reason for less activity of these samples reported in [9].

The technique was feasible in measuring the uptake curves for two components by catalyst particles. The strengths of this approach are the reduction of the experimental work and the needed amounts of catalyst and reactants compared to the analysis of the concentration by the gas chromatography method. Secondly ATR-FTIR can be applied at reaction conditions and therefore it yields diffusion coefficients much more interesting for engineering purposes. However it was not achieved to resolve diffusion
differences between the two reactants benzaldehyde and ethyl cyanoacetate. This is attributed to the low time resolution during the first minute of the experiments.

In order to check for differences in the diffusion behaviour of the individual molecular species, techniques like PFG NMR and neutron diffraction would have to be applied, which are sensitive on much smaller timescales.
Bibliography


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Heartly thanks I would like to express towards my family who is always there for me and shares the good as well as the hard times in life with me.
D Statement of Authenticity

I hereby declare that I have written the attached document alone with only the sources and aids listed therein.

Leipzig, September 2010

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Leipzig, September 2010