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High-pressure low-field ^{1}H NMR relaxometry in nanoporous materials

Carsten Horch, Stefan Schlayer, Frank Stallmach *

University of Leipzig, Faculty for Physics and Earth Sciences, Linnstrae 5, 04103 Leipzig, Germany

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ABSTRACT

A low-field NMR sensor with NdFeB permanent magnets ($B_0 = 118$ mT) and a pressure cell made of PEEK (4 cm outer diameter) were designed for ^{1}H relaxation time studies of adsorbed molecules at pressures of up to 300 bar. The system was used to investigate methane uptake of microporous metal–organic frameworks and nanoporous activated carbon. T_2 relaxation time distribution of pure methane and of methane under co-adsorption of carbon dioxide show that the host–guest interaction lead to a relaxation time contrasts, which may be used to distinguish between the gas phase and the different adsorbed phases of methane. Adsorption isotherms, exchange of methane between adsorbent particles and the surrounding gas phase, successive displacement of methane from adsorption sites by co-adsorption of carbon dioxide and CO_2/CH_4 adsorption separation factors were determined from the observed NMR relaxation time distributions.

1. Introduction

Low-field ^{1}H NMR relaxometry has proven to be a powerful tool for non-destructive characterization of pore space properties of fluid saturated porous materials [1–3]. The method is based on the enhancement of the relaxation processes of the hydrogen containing fluid molecules interacting with the inner surface of the porous materials. In the case of fast diffusional exchange between the fluid molecules at the surface layer and the molecules in the pore body, the total relaxation rates $T_{1/2}^{-1}$ are found to be proportional to the pore surface-to-volume ratio S/V and the relaxation times become a measure for the pore size R_p [4,5].

This non-destructive inside into the pore structure and the fluid matrix interaction led to a number of successful applications. They include mobil NMR such as, e.g., down-hole logging [6,7] and investigation of damages on arts [8], but also laboratory based studies with relatively cost efficient bench-top NMR instrumentation on rock cores [9–11], soils, construction materials [2,12], food and cosmetic products [13].

Most low-field NMR studies are performed with permanent magnets generating the polarizing magnetic field. Besides of just using opposing pieces of such permanent magnets with the sensitive volume in between the two blocks of magnets such as, e.g., demonstrated in [2,8], an interesting alternative arrangement is the so-called Halbach array [14]. It was employed by Hills et al. and Blümler and co workers [15,16] to construct customized NMR sensors. For inside-out low-field NMR investigations, singles-side sensors like the NMR mouse and NMR skin sensor [17,18], but also sensors with circular sensitive volume around the central permanent magnets like the designs proposed by Jackson et al. and Mardon et al. [19,20] are known.

In most of the above mentioned applications, the porous materials investigated belong rather to macroporous systems ($R_p > 50$ nm, according to the IUPAC classification) or they contain at least a large fraction of such macropores. Simple molecular fluids like liquid water or hydrocarbons remain liquid-like in the body of the macropores. This means that one generally observes $T_2 \lesssim T_1$ with T_2 being only slightly smaller than T_1. T_2 may be shortened additionally due to diffusion in external magnetic field gradients of the NMR sensor or in internal field gradients caused by susceptibility differences between pore and matrix space.

With respect to the relaxation times in micro-($R_p \leqslant 2$ nm) and mesoporous systems ($2 \text{ nm} < R_p \leqslant 50$ nm), the situation is different. Especially micropores are too small that free liquid phases may be formed in the center of the pore body. However, due to their dispersive (van-der-Waals type) interaction with the pore wall, the fluid molecules develop an adsorbed phase at the pore-matrix interface which dominates the relaxation behavior.

In the present study we explore the opportunity to use cost efficient low-field NMR relaxometry to study gas adsorption in microporous and mesoporous adsorbents. As adsorbent particles we investigate a new type of spherically shaped micro- and mesoporous activated carbon [21] as well as the crystalline microporous metal–organic frameworks CuBTC [22] and ZIF-8 [23]. All materials are meanwhile available as commercial adsorbents. They have very different organic and inorganic matrix properties and pore sizes. As

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* Corresponding author. Fax: +49 341 973 2549.
E-mail address: stallmac@physik.uni-leipzig.de (F. Stallmach).
URL: http://www.uni-leipzig.de/~gfp/ (F. Stallmach).

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adsorbent molecule and ^{1}H NMR probe of the inner surface we choose methane. It is potentially interesting for gas purification and gas storage applications and its pressure dependent relaxation times in the gas and liquid phases are known from literature [24–27].

Recent spectroscopic studies in activated carbon showed a distinct chemical shift of adsorbed hydrogen allowing one to distinguish between adsorbed and gas phase hydrogen in the high-resolution ^{1}H NMR spectrum at pressures up to 100 bar [28]. For our purpose of low-field ^{1}H NMR porosimetry with methane, we developed an NMR sensor and a compatible pressure cell operating at up to 300 bar. Although the adsorbed phases in the porous hosts are generally in exchange with the gas phase in the surrounding pore network and the interparticle void space, respectively, we will show that there remains a sufficient relaxation time contrast to the free gas phase to distinguish between these phases.

Additionally, it should be noted that the interactions of methane with the inner surfaces of porous materials are generally week. In other words, methane may be considered as a non-wetting pore fluid. After impregnation into the porous host at elevated pressure, it can easily be removed from the inner surface of the porous material. Thus, by using pressurized methane as probe of the pore structure, the non-destructive nature of low-field ^{1}H NMR porosimetry is extended to materials which do not contain water or liquid hydrocarbons as their natural pore fluids or which would be irreversibly contaminated by those pore liquids.

2. Instrumentation for high-pressure adsorption studies in low-field NMR

2.1. High-pressure adsorption apparatus

For adsorption measurements with innovative microporous and mesoporous adsorbent materials at elevated static gas pressures a joint system for sample activation, gas loading and NMR measurements was designed and constructed on a wooden table. Stainless steel tubing, valves, electro-resistive pressure transducers (accuracy ±2%) as well as the gas reservoir and the manually operated pressure generator from the commercial high pressure system taper seal (HiP, Erie, PA, USA) were arranged and fixed on top of the table to allow sample preparation with single component gases and gas mixtures (see Fig. 1). All tubings connectors and valves are rated for maximum pressure of 1035 bar. The manually operated high-pressure generator (pump) and the gas reservoir, which serves also as volume for producing the desired gas mixtures, are rated for a maximum pressure of 350 bar.

The gases are delivered via three different inlet stages (see Fig. 1). Methane and carbon dioxide or other gases are supplied via gas cylinders, the third stage is usually connected to dry nitrogen gas from the lab gas supply. It is used for purging, cleaning and pressure tests of the system.

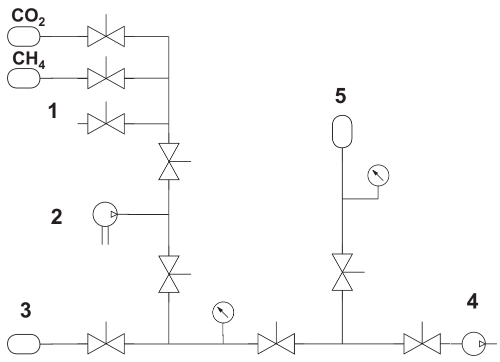

Fig. 1. Set-up of the high-pressure loading station: gas inlets (1), high-pressure generator (2), gas reservoir (3), vacuum pump (4) and NMR pressure cell (5).

The center element of the high-pressure adsorption set-up is the NMR compatible pressure cell. Based upon our own experiences in building customized small-diameter NMR pressure cells for high-field application [29] and on earlier work of Behr et al. [30], who designed a 5 cm o.d. pressure cell for MRI applications, we decided to use the non-metallic high-strength plastic PEEK (polyethyletherketone, Quadrant Engineering Plastic Products). PEEK proved to be suited with respect to both tensile strength ($S = 115$ MPa) and low background ^{1}H NMR signal. It is relatively easy to machine in the workshop to the desired shape.

To safely operate this cell at the target pressure of 300 bar at room temperature, the dimensions of the cylindrical vessel were calculated to withstand a pressure of 1000 bar. With the target inner diameter of $d_i = 2$ cm, which corresponds to the maximum sample diameter, the outer diameter of the pressure cell was determined to be $d_a = 4$ cm. For this calculation, the equation $p_{max} = S * ((d_a/d_i)^2 - 1)$, was applied, which is generally used in engineering to calculate the pressure resistances of tubes and pipes [31]. This approach is in agreement with good engineering practice required for design and operation of small-volume experimental pressure equipment. It is in accordance with the safety regulations of the European Commission concerning pressure equipment (see directive 97/23/EC [32]). The pressure cell is about 14 cm long to allow easy access and positioning in the NMR sensor. The top of the cell has an increased diameter of 5 cm. It is sealed by a stainless steel cover which carries the inlet tubing and the connection to the pressure transducer. The stainless steel cover is connected to the PEEK NMR pressure cell by 6 screws (4 mm diameter, 30 mm length). An O-ring seal squeezed into mutually fitting notches ensures long time gas-tightness.

Since gases for relaxation time measurements need to be free of paramagnetic oxygen (see, e.g., Gerritsma and Trappeniers [24] for methane) and microporous adsorbates generally need to be activated at elevated temperatures under vacuum, the system is equipped with a vacuum pump to remove residual gases, moisture and air from the system. Additionally, the NMR sample cell may be mildly heated in an oven during sample activation. During operation at elevated pressures the sample cell is fixed below the table and the NMR sensor (see below) is moved to accommodate the cell. The pressure cell and the NMR sensor are confined in a shielded space below the wooden table in order to protect the operator and the lab environment.

2.2. Low-field benchtop NMR sensor

The low-field NMR sensor was designed to accommodate the pressure cell described above. It should easily be moved to the pressure cells fixed below the gas loading station. The polarizing static magnetic field of the sensor is generated by two pairs of two NdFeB permanent magnet plates ($10 \times 10 \times 1.5$ cm^3 each) opposing each other (see Fig. 2). At the inside of the sensor the two pairs are enframed by shaped iron yokes (area of 10×20.5 cm^2 each). The center parts of these inner yokes are placed in a distance of 6.5 cm from each other. Each permanent magnet arrangement carries an additional iron yoke on its back side ($10 \times 20.5 \times 0.8$ cm^3 each). The curvature of the inner iron yokes were optimized for strength and homogeneity of the polarizing magnetic flux density B_0 over the cylindric sample volume. The calculations were performed by finite element simulations using COMSOL software (COMSOL AB, Sweden) [33].

This arrangement of permanent magnets and iron yokes yields a transverse relaxation time T_2^* of 135 μs for a cylindrical water sample with 2 cm diameter and 2 cm length (see Fig. 3a). The