Quantifying the adsorption of flowing gas mixtures in porous materials by remote detection NMR

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Abstract

Traditional adsorption measurements are carried out at static conditions for a single gas component, and multi-component adsorption measurements are challenging and time-consuming. Here we introduce an efficient remote detection NMR method for *in situ* analysis of adsorption of flowing gas in mesoporous materials. We investigated adsorption of continuously flowing propane and propene gases as well as their mixture in packed beds of controlled pore glass and silica gel materials. Remote detection provided from 300 to 700 -fold sensitivity enhancement as compared to a direct experiment carried out by a large coil around the packed bed. The unique time-of-flight information obtained using this method was utilized in flow velocity determination, and the velocities were converted into amount of adsorbed gas. As the detection was performed outside the packed bed region, the spectra were not influenced by the porous materials. Because resonances of each gas component were well-resolved in the spectra, the amount of adsorption of each gas component could be determined from the same data, measured in a few minutes.

Keywords:

Remote detection NMR

Adsorption

Mesoporous materials

Flow

Microfluidics

1. Introduction

Gas adsorption phenomena play fundamental role in technological and industrial processes [1]. Most of the processes proceed through stages of multi-component adsorption. Therefore, it is vital to understand multi-component gas adsorption in porous materials. Traditionally adsorption isotherms are measured in static equilibria conditions for a single gas component only, and the measurement of a multi-component adsorption isotherm is very challenging and time-consuming. Because in most of the applications gases are flowing through porous materials, the static measurements may give inaccurate view for the adsorption phenomena of the dynamic systems.

Nuclear magnetic resonance (NMR) spectroscopy is an exceptionally versatile method in chemical analysis, providing spectroscopic, dynamic and spatial information [2,3]. The method provides detailed information about pore size distribution, morphology, diffusion and adsorption phenomena, chemical exchange etc. [4-13] NMR has also been exploited in the determination of the amount of adsorbed gas in static conditions by measuring the amplitude of a gas signal in the region outside the porous material, and converting it into the amount of substance by means of a calibration curve [14,15]. The most well-known application of NMR, magnetic resonance imaging (MRI), has been utilized for the determination of spatially resolved concentration profiles and adsorption isotherms of gases in porous materials *in situ* [16-18].

The weakness of NMR is that it is a relatively insensitive method. This problem becomes emphasized once gases are investigated because they have much lower densities than liquids. Furthermore, in many cases, such as in microreactors and microfluidics [19], the size of an overall device is much larger than the volume that contains porous material, leading to a very low filling factor of the NMR coil that

surrounds the device with the gas. Remote detection (RD) NMR [20] offers a remedy for these issues. In the method, spectroscopic or spatial information is encoded into spin coherences of a fluid by a large coil positioned around the sample, but the signal is detected outside the sample, once the fluid has flown out, with a much smaller and a significantly more sensitive coil having an optimal filling factor. The method may improve the sensitivity of the experiment by several orders of magnitude as compared to the direct signal detection with the coil around the sample. On the other hand, it inflicts one additional dimension, because the spectral or spatial encoding is done in indirect fashion. The method provides also highly useful time-of-flight (TOF) information, because the spins encoded in different parts of the sample arrive at different time to the detector. This can be utilized, e.g., in TOF flow imaging [21]. RD NMR has been used to image flow through porous materials [22] and membranes [23], microfluidic devices [24-26], rocks [21], wood [27], as well as for chemical reaction imaging [28-30].

Recently, we used RD NMR, along with parahydrogen-induced polarization, to image chemical reactions in microfluidic packed bed reactors [28]. Because of the TOF information, RD NMR images offer a straightforward way to determine flow velocity in a capillary tube. We observed an initially surprising phenomenon: the flow velocity in the packed bed region was lower than in the empty tube region, although it should be higher, if the gas concentration were unchanged, because solid porous material occupies a significant amount of the tube volume in the packed bed region. We found that this is a consequence of significant adsorption of gas on the surface of the porous material, making the average gas concentration in the packed bed region much higher than in the empty tube region.

In this work, we investigate systematically this phenomenon using propane and

propene gas, their mixtures as well as various controlled pore glass and silica gel mesoporous materials. We show that the method makes it possible to determine the amount of gas adsorbed in porous materials *in situ*, while the gas is flowing through the material, like in many technologically relevant applications. Because the NMR signal is detected outside the sample, a well-resolved NMR spectrum is observed without the inhomogeneity issues or background signals arising from the porous material. In the case of multi-component flow, the spectrum enables the quantification of the adsorption for each gas component simultaneously.

2. Theory

Z encoded TOF RD NMR images (see Fig. 1c) reveal how long is the travel time of gas from a particular z position to the detection coil. Because in the current system the tubing is aligned along the z axis (see Fig. 1a), the images provide a straightforward way to quantify the flow velocities at the packed bed and empty capillary regions.

Based on the mass balance, *i.e.*, knowing that the number of gas molecules travelling through a capillary cross-section is equal in the packed-bed and empty capillary regions, we derived the following equation for the amount of adsorbed molecules per unit of the surface area of the porous material (see the Supporting Information of [28]):

$$n_{ua} = \frac{P}{sRT} \left[\left(\frac{d_o^2 u_o}{d_p^2 u_p} - \phi \right) \frac{1 + v_{pore} \rho_{solid}}{(1 - \phi) \rho_{solid}} - v_{pore} \right] \quad (1)$$

Here, u_p and u_o are the flow velocities in the packed-bed region and outlet tubing (the empty capillary region), respectively, which can be determined from the z

encoded TOF RD NMR images. Parameters d_p and d_o are the inner diameters of the packed-bed and outlet capillaries. P is the gas pressure, T is the temperature, R is the universal gas constant, s is the specific surface area of the porous material, ϕ is the porosity produced by the voids between the particles, v_{pore} is the specific pore volume and ρ_{solid} is the density of the solid skeleton of the particles (2.23 g/cm³ [31]). Values of the parameters in Eq. (1) for the materials studied in this work are shown in the Electronic Supplementary Information (ESI). Eq. (1) assumes that the pressure drop is insignificant inside the measurement region. This has turned out to be a good approximation, because the resistance of the gas flow is very small [28].

Fig. 1. (a) Experimental setup of the RD NMR gas adsorption measurements. (b) Pulse sequence of the z encoded TOF RD NMR imaging experiment. (c) Z encoded TOF RD NMR image of propane flowing through CPG237 mesoporous material at room temperature. The slopes indicated by black dashed lines show the flow velocities in the packed bed and empty outlet capillary regions.

3. Results and discussion

3.1 Single gas adsorption

Z encoded TOF RD NMR image of propane flowing through CPG237 mesoporous material measured at room temperature is shown in Fig. 1c (see Materials and methods in ESI). The slopes of the pattern, denoted by black dashed lines in the image, indicate the flow velocities in the packed bed and empty outlet capillary regions. The slope is smaller in the packed bed region than in the outlet capillary, although the inner diameters of the packed bed and outlet capillaries were equal. This is a consequence of significant adsorption of the gas on the surface of the porous material. The flow velocities in the packed bed and outlet capillary regions, given by the slopes, were 5.1 and 10.7 cm/s, respectively. The width of the amplitude pattern in the image is relatively narrow, showing that dispersion of gas is low. This is a consequence of fast diffusional mixing of flow lamellas in the narrow (inner diameter: 0.50 mm) capillaries [28]. It also indicates that the exchange between gas inside the porous material and free gas is fast as compared to the travel time through the packed-bed; otherwise significant dispersion would be expected.

RD NMR analysis was carried out for four different mesoporous materials, CPG81, CPG115, CPG237 and SG100, using two different gases, propane and propene. The flow velocities in the packed-bed and outlet capillaries were determined from the z encoded TOF images, and they were converted into the amount of adsorbed gas per unit of the surface area of the porous material, n_{ua} , by using Eq. 1. The results, along with the reference values given by standard, static adsorption measurements, are shown in Figs. 2a, 2b and S4 in ESI. The values given by the RD NMR analysis are on the same order of magnitude with the reference values, showing that the method works. However,

the RD NMR values are systematically slightly lower than the reference values. We interpret that this is a consequence of the fact that gas is flowing in the RD NMR experiment, while the reference experiments were performed in static conditions. The results imply that the smaller pore size (and surface area), the larger the difference between the RD NMR and reference experiments.

In RD NMR analysis, we assumed that the gas pressure in the packed bed is equal to the pressure in the gas cylinder. In principle, neglecting the pressure drop in the flow system will result in overestimated adsorption values (contrary to observed). However, the gas was led to the packed bed through a relatively large (as compared to the packed bed) 1/16" capillary, and flow resistance of gas in such a capillary is very small. Therefore, the assumption about negligible pressure drop should be a good approximation.

Significant flow resistance in the packed bed would also lead to wrong results in the analysis. If the flow resistance was high, the flow velocity would be smaller in the upper part of the packed bed than in the lower part, and curved signal pattern, instead of linear, would be observed in the z encoded TOF RD NMR images. However, because the observed pattern is linear (see Fig. 1c), the flow resistance in the packed bed appears to be insignificant.

If the travel time of some gas molecules from the packed bed to the detector would be much longer than T_1 relaxation time of the molecules, these molecules would not be observed in the RD NMR experiments, leading to wrong results in the analysis. In principle, one could imagine that some of the molecules could be stuck in small pores deep inside the particles for a long time. However, this would result in a significant dispersion of gas molecules. Contrary to this, the narrow signal pattern in the

z encoded RD NMR images (see Fig. 1c) implies that the dispersion is small. Therefore, the time-scale of the adsorption-desorption processes has to be much smaller than the travel time of the gas molecules through the packed bed.

The discussion above implies that the observed lower amount of adsorbed gas in the RD NMR analysis as compared to the static reference measurements is not an artefact of the method, but it is a true phenomenon arising from the effect of flow. The results emphasize the significance of the novel RD NMR adsorption measurement method: Because flow has a significant effect on the amount of adsorbed gas, it is extremely important to be able to quantify adsorption in dynamic (not only static as in the standard adsorption measurements) conditions, because in many everyday technological applications, gas is flowing through porous materials, and the efficiency of the device is dependent on the amount of adsorbed gas in those conditions.

Fig. 2. Amount of propane (a) and propene (b) adsorbed on the surface of porous materials. Standard, static adsorption measurements (REF) are shown by open symbols, and RD NMR measurements with flowing gas are indicated with filled symbols.

Reference values for silica gel (surface area 751 m²/g) were taken from ref. [32]. (c) RD NMR adsorption measurements for the mixture of propane and propene (1:1 ratio) in CPG81. Total pressure of the gas mixture (not partial pressures of the gas components) is shown on the horizontal axis.

4.2 Two component gas adsorption

Adsorption of a mixture of propane and propene was also investigated with RD NMR. The spectrum measured by the detection coil is shown in Fig. S3 in ESI. Although the line width is rather large (about 60 Hz) due to the short residence time of the gas in the detection coil and shimming issues, the signals of propane and propene are well-resolved (but not the J coupling splittings). Because the detection is performed outside the sample, the spectrum is not affected by the background signals and susceptibility issues arising from the porous materials. In contrast, the propane and propene signals are not resolved in the spectrum measured directly from the porous material region (see Fig. S3 in ESI) due to the susceptibility issues, and therefore adsorption measurements of the mixture with standard NMR spectroscopy are not feasible.

Because the signals of the gas components are resolved in the detection coil spectra, z encoded TOF images of each component could be processed from the data of a single, relatively short RD NMR experiment (experiment time 8 min). The flow velocities were determined from the slopes, like in single gas component experiments, and they were converted into the amount of adsorbed gas using Eq. 1 (in this case, P is the partial pressure of the gas component, not the total pressure). The results are shown in Fig. 2c and Fig. S5 in ESI. In general, the observed amount of adsorbed propene is

higher than that of propane, which is reasonable, because the adsorption affinity of pure propene is also higher than that of propane (see Figs. 2a and 2b). However, there is a single exception: at the total pressure of 8 bar, the amount of adsorbed propane is larger than that of propene in CPG81. This is probably a consequence of the partial condensation of propane in the small pores, because the vapor pressure of propane (8.5 bar) is lower than that of propene and close to the total pressure of the gas mixture. The adsorption amount for each subcomponent is smaller than in the case of single component adsorption due to competing adsorption: many adsorption sites are occupied by the second gas compound.

5. Conclusions

This study shows that RD NMR can be used for *in situ* quantification of adsorption of gases flowing through porous materials. RD NMR provides a significant, 300-700 -fold sensitivity gain and unique TOF information utilized in the adsorption analysis. Because the signal is detected outside the sample, the spectra are not affected by the susceptibility issues and background signals arising from the porous material. In the case of multicomponent gas mixture, the signals of each component are resolved in the spectrum (contrary to the spectrum measured directly from the porous material region), and adsorption of each component can be quantified from a single measurement data acquired in a few minutes, as demonstrated using mixtures of propene and propane. Therefore, RD NMR is a powerful tool for the investigation of competing adsorption in porous materials in conditions relevant to various technological applications.

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Graphical abstract

Highlights

- Novel remote detection NMR based method for quantifying the amount of adsorbed gas
- *In situ* monitoring of adsorption of gas flowing through mesoporous materials
- Fast quantification of multicomponent gas adsorption

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Electronic Supplementary Information (ESI) to the article

Quantifying the adsorption of flowing gas mixtures in porous materials by remote detection NMR

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1. Materials and methods

1.1 Materials

Adsorption of propane, propene and their mixtures in controlled pore glass (CPG, from Millipore) and silica gel (SG, from Merck) mesoporous materials was studied in this work. Three CPG materials with the pore diameters of 81, 115 and 237 Å (referred to as CPG81, CPG115 and CPG237, respectively) as well as one SG material with the pore diameter of 100 Å (referred to as SG100) were investigated. In the RD NMR experiments, the porous materials were packed inside a cylindrical 1/32" PEEK capillary with the inner diameter of 0.50 mm for CPG and 0.41 mm for SG samples. The length of the packed bed varied between 15-26 mm. Before the RD NMR experiments, the samples were kept in vacuum at 50°C overnight in order to remove moisture and other impurities. The properties of the materials, announced by the manufacturers, and the packed beds are shown in Table S1.

The inter-particle volume V_{ip} was calculated for each packed bed by subtracting the volumes of the solid skeleton and pores from the overall volume of the packed bed sample, V_s , based on the measured mass of porous material inside the packed bed capillary volume and information provided by the manufacturers. Thereafter, the interparticle porosity ϕ was calculated by the following equation:

$$\phi = \frac{V_{ip}}{V_s}. \quad (2)$$

Table S1

Properties of the controlled pore glass (CPG) and silica gel (SG) mesoporous materials, announced by the manufacturers, and the packed beds used in the RD NMR experiments.

Sample	Mean pore diameter (Å)*	Pore volume (cc/g)*	Surface area (m ² /g)*	Particle size (μm)*	Sample mass (mg)	Sample column length (mm)	Inter-particle porosity, ϕ
SG100	100	0.9-1.2	270-370	63-200	0.8	15	0.364
CPG81	81	0.49	197	125-177	2.48	23	0.486
CPG115	115	0.49	119.5	125-177	2.05	19	0.484
CPG237	237	0.95	78.8	125-177	2.13	26	0.419

*Values announced by manufacturers

1.2 RD NMR experiments

RD NMR measurements were performed with Bruker Avance III 300 and Bruker DSX 300 wide bore magnets equipped with imaging systems. Both spectrometers operate at 300 MHz proton resonance frequency. Spatial encoding was carried out with a Bruker Micro 2.5 imaging probe, using a radiofrequency (RF) insert with the inner diameter of 25 mm and height of 70 mm. The height of the bird cage coil of the RF insert is 35 mm. The packed bed was mounted inside the encoding coil with a sample holder made of Teflon (see Figs. 1a and S1) and connected to the outlet capillary. In the case of the CPG samples, the same 1/32" capillary was used as an outlet capillary as in the packed bed, but in the case of the SG sample the outlet capillary was smaller, 360 μm in diameter. A home-made detection probe was pushed inside the hollow interior of the imaging probe body. The detection microsolenoid coil was wound around the outlet capillary out of 120 μm thick copper wire. The length of the coil was 3 mm. The coil was positioned ca. 10 mm below the bottom edge of the encoding coil with

the help of a 3D printed coil holder (see Fig. S2).

Fig. S1. Image of the double probe RD NMR setup with a packed-bed sample.

Fig. S2. Left and middle: 3D printed coil holder prototype (Reprap printer, ABS material). The version used in the RD NMR experiments was printed using stereolithography method (Formlabs Form II, standard clear resin GPCL02) to ensure better print resolution and channel accuracy. Right: Similar coil holder made of Teflon. This photo illustrates how the outlet tubing and detection coil was mounted in the holders.

The pulse sequence of a z encoded TOF RD NMR imaging experiment is shown in Fig. 1b. In the beginning of the experiment, the spins inside the encoding coil were excited by a $\pi/2$ pulse, and the initial position of the spins was labelled into spin coherences by a z gradient pulse similarly as in the phase encoding in conventional MRI [1]. Thereafter the encoding was stored as a longitudinal magnetization in order to prevent dephasing when the gas was flowing out of the sample. Finally, the signal was read by a train of detection coil $\pi/2$ pulses. Based on the principle of reciprocity [2], we estimated that the detection coils around the 1/32" and 360 μm capillaries were 320 and 690 times more sensitive than the encoding coil. This significant sensitivity gain enabled flow imaging in spite of the small channel dimensions and low density of gas.

The length of the z gradient pulse was 250 μs (ramp time 50 μs), and the delay Δ was 300 μs (including the gradient pulse and gradient stabilization delays). The number of consecutive FIDs collected during one scan was 40 and the time resolution (the time between the beginnings of successive FIDs) was 22 ms. The number of accumulated scans was 8. The field of view in the z direction was 40 mm and the resolution was 0.64 mm. The total experimental time was 8 min.

Propane and propene gases (purity > 99.5%) were used in the experiments, and the experiments were

carried out with individual gases as well as their binary mixtures. Before experiments, either a single gas or a mixture of propane and propene were added to a 1L cylinder. In the mixtures, propane:propene ratio was either 1:1 or 1:2. The total absolute pressure of the gas was about 8 bar. The mixture was allowed to settle for about 30 minutes prior the experiments. In the beginning of the experiment, the gas was released to flow through the packed-bed. Gas flow rate was controlled by a valve at the end of the flow system. The pressure in the whole flow system was approximately equal to the pressure of the cylinder, because the pressure drop needed for the gas flow was very small. Between successive experiments, a certain amount of gas was released from the cylinder in order to achieve a desired lower gas pressure for the next experiment. Probed pressure range for propane and propene was 8-1.25 and 5-1.25 bar, respectively, and 8-1.25 bar for the mixtures. The experiments were performed at room temperature.

1.3 Reference static gas adsorption experiments

In order to get reference values for the RD NMR adsorption analysis, traditional adsorption isotherm measurements [3] were carried out for CPG115 and CPG237 materials. The material under investigation was placed in a 10 mm NMR sample tube (inner diameter 8 mm, volume of an empty tube 9.38 ml), and the height of the sample pillar was about 5 cm. Gas was added to the sample tube from a container with the volume of 46 ml. Volume of the connection between the container and sample tube was 0.84 ml. There were also additional connections to vacuum and a gas cylinder from the container.

Before the reference adsorption measurements, materials were kept in vacuum at 50°C overnight, similarly as before RD NMR experiments, in order to get comparable conditions. The adsorption experiments were carried out at room temperature, similarly to the RD NMR experiments. First, 0.05 bar of gas was added to the container. Then the gas was admitted to the sample and the pressure drop was recorded after the equilibrium delay of 10-20 min. Then the process was repeated with a step of 0.2 bar until the final pressure of 2.95 bar. The total measurement time of the adsorption isotherm data was 3-4 h. The adsorption isotherm was calculated in a standard way based on the results [3].

2. Supplementary results

Fig. S3. Black solid line: ^1H NMR spectrum of the mixture of propane and propene (1:2 ratio, total pressure of 6.75 bar) flowing through the RD NMR setup, measured with the detection coil (8 scans) outside the packed-bed region. For the comparison, ^1H NMR spectra of propane (blue dotted line) as well as a mixture of propane and propene (red dashed line) adsorbed in CPG115 in a 10 mm sample tube (static, no flow, 1 bar) observed from the region of the porous material with a 10 mm BBO probe (1 scan) are shown in the figure. The components of the mixture are well resolved in the detection coil spectrum, but they are not resolved in the direct spectrum because of susceptibility issues caused by the porous material. Therefore, the figure illustrates nicely how the RD approach improves chemical resolution in the adsorption experiments, because the spectra are detected outside the sample region. T_1 and T_2 relaxation times of propane adsorbed in CPG115 were determined to be 680 and 14 ms, respectively. T_2^* was on the order of 3 ms. These are typical values for gases, and therefore adsorption analysis of many other gases should be well feasible with the proposed RD approach. For the free gas in the outlet capillary, the T_1 relaxation time is probably slightly longer and T_2 significantly longer than for the adsorbed gas inside the packed bed.

Fig. S4. Amount of propane (a) and propene (b and c) adsorbed on the surface of porous materials. Standard, static adsorption measurements (REF) are shown by open symbols, and RD NMR measurements with flowing gas are indicated with filled symbols.

Fig. S5. RD NMR adsorption measurements for the mixture of propane and propene. (a) Adsorbent is CPG81, and propane:propene ratio is 1:1. (b) Adsorbent is CPG115, and propane:propene ratio is 1:1. (c) Adsorbent is CPG237, and propane:propene ratio is 1:2. Total pressure of the gas mixture (not partial pressures of the gas components) is shown on the horizontal axis.

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