Characterization of functionalized chromatographic mesoporous silica materials: Coupling water adsorption and intrusion with NMR-relaxometry

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Abstract

Silica particles are widely used as a support material for chemically-bound stationary phases in chromatographic separation processes. The tuning of textural properties and surface chemistry of stationary phase materials (SPMs) is crucial to enhance their selectivity to certain compounds and the efficiency of the separation process. Silica supports have the advantage that their surface can be modified with a large variety of hydrophilic and hydrophobic functional groups, but their influence on the silica surface properties has not been evaluated in detail. In this sense, the contact angle is a key parameter for the assessment of surface chemistry but its quantification in the pore walls is particularly challenging and requires a combination of various tools and experimental techniques. In this work we demonstrate that by combining water adsorption and intrusion measurements is possible to derive reliable information of the effective contact angle $\theta$ of adsorbed water for wetting ($\theta = 0^\circ$), partial wetting ($\theta < 90^\circ$), and non-wetting situations ($\theta > 90^\circ$) observed on the pore walls of the SPMs under study. Furthermore, NMR relaxometry experiments reveal that the $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$-ratio can be correlated with the effective adsorption strength of water on the surface. Indeed, we find a linear correlation between the negative inverse of the $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ -ratio (-$T_{2,\text{ads.film}}/T_{1,\text{ads.film}}$) with the contact angle determined from water vapor adsorption and intrusion experiments for the investigated SPMs. Our work clearly demonstrates for the first time that water vapor adsorption experiments and novel water intrusion technique coupled with NMR relaxometry can be used as complementary techniques to quantitatively analyze the wettability behavior and surface chemistry of nanoporous materials.

1 Introduction

Chromatography is a widely used technique for the separation of organic and inorganic compounds and substances, e.g., amino acids, proteins, nucleic acids, hydrocarbons, and carbohydrates. Process design and optimization of chromatographic separations requires the tuning of the selectivity of the chromatographic stationary phase material (SPM) in relation to the specific compounds of interest. Porous silica particles are commonly used as SPMs in chromatography column applications. In fact, more than 90 % of modern high-performance liquid chromatography (HPLC) columns are packed with porous silica particles due to their good mechanical strength, high chemical and thermal stability, controllable pore structure and surface area, as well as a relatively easy modification with functional groups to induce different polarities [1–3]. Improvements of such SPMs are crucial for process design and optimization in order to achieve an efficient chromatographic separation. Textural properties such as specific surface area, pore size and pore volume may affect selectivity, the transport properties, and hence, efficiency of the separation process. In addition, the surface chemistry of the silica plays an important role since it can enhance the affinity and selectivity to certain compounds. Thus, an effective approach for improving the separation efficiency is based on tuning the surface composition of the SPMs. One of the advantages of using silica as SPM is that its surface contains active silanol groups (Si-OH, free OH groups of the silica), which enables the modification of the surface chemistry by grafting different types of functional groups and silanes to create monomeric or polymeric bonded phases. This controllable and tailorable way of modifying the silica surface polarity results in enhancing its utility as SPMs in separation processes. For example, the silica surface is functionalized with hydrophobic compounds, e.g., C8 chains, for reversed-phase chromatography in order to achieve high selective adsorption and good retention of hydrophobic, usually organic compounds [4–6]. A large variety of different
surface functional groups is available, which drastically modifies its properties depending on the nature of the organic moiety.

Up to now, there is little comprehension on the influence of the functional groups on the final textural and chemical properties of the functionalized SPM. A detailed assessment of texture and surface chemistry of porous functionalized stationary phase materials, especially the quantification of the surface chemistry inside the pores is very challenging and requires the combination of different tools [7].

Within this context we suggest here to combine for the first time advanced physisorption and water intrusion techniques with NMR relaxometry to assess important aspects of the surface chemistry of SPMS with focus on their hydrophilicity/hydrophobic nature.

A useful quantification of the latter is by determining the contact angle of suitable adsorbed liquid on surfaces. For nonporous surfaces, droplet contact angles can be directly obtained by optical and tensiometry methods, e.g. the Wilhelmy technique [8,9] and the sessile drop technique [10]. However, determining the contact angle within the pore walls is more challenging as the application of the above mentioned macroscopic experimental techniques is not possible to nanoporous materials.

To address this challenge, methodologies based on advanced adsorption have been applied which allow for assessing surface heterogeneity including hydrophilicity/hydrophobicity of the pore walls by using a variety of adsorptives of different polarity and sensitivity to surface functional groups [11–13]. Particularly, the use of water vapor adsorption for surface chemistry and pore structure characterization has been investigated [8,11,14–19], however the interpretation of water adsorption isotherms is not straightforward as they are affected by both surface chemistry as well as pore size and structure. To differentiate between surface chemistry and textural effects on water adsorption isotherms, it is beneficial to compare these with adsorption isotherms of completely wetting fluids, which are not that sensitive to details of the surface chemistry, e.g. Ar adsorption at 87 K [12] and coupled with the application of dedicated methods based on non-local-density functional theory (NLDFT) allows for a reliable assessment of textural properties such as surface area and pore size (pore size/volume distribution). This provides now the basis for deriving reliable information from water adsorption for surface chemistry assessment, but determining the contact angle within the pore walls is more challenging as the application of the above mentioned macroscopic experimental techniques on nonporous surfaces. A suitable approach consists on deriving the contact angle of water on pore surfaces based on water adsorption in combination with the Kelvin equation if the pore size (and pore size distribution) is known [14,15,18,20]. However, the determination of the correct equilibrium contact angle from water sorption isotherms, which exhibit often hysteresis, requires a detailed understanding of the contributions to hysteresis and can, contrary to the work presented in these papers, not be calculated from the adsorption branch. In fact, the choice of adsorption branch for deriving the contact angle is not straightforward, because the pressure where pore condensation/filling occurs is delayed due to metastable pore fluid (i.e. nucleating barriers associated with condensation/pore filling), while the desorption branch of the hysteresis loop reflects in the absence of pore network effects (e.g., pore blocking, cavitation) the liquid-vapor equilibrium transition, and hence should be the basis for assessing the effective, equilibrium contact angle of an adsorbed water phase. [21]. However, the application of this methodology is limited to wetting and partially wetting surfaces with a contact angle $\theta$ between 0° and 90°. We therefore combine the water vapor adsorption experiments with water intrusion/extrusion experiments for non-wetting surfaces ($0 > 90°$). In this case, the contact angle can be determined with the Washburn equation [21] by applying hydraulic pressure to force the water inside of the pores.
In addition to water vapor adsorption and water intrusion experiments, we have shown that NMR relaxometry measurements can be a complementary tool for the fast assessment and quantification of the surface chemistry of nanoporous materials. We have shown recently that the ratio of spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation time ($T_1/T_2$-ratio) is characteristic for the wetting behavior of adsorbates on silica and carbons surfaces [22]. The relaxation time ratio has been used in the petrochemical industry to analyze the wetting behavior of oil in sedimentary rocks, e.g. [23,24]. In addition, it was demonstrated that the $T_1/T_2$-ratio of catalysts in contact with different liquids can be associated with the effective interaction strength between these liquids and the catalyst surface [25–27]. Furthermore, they showed a linear correlation between the negative inverse relaxation time ratio ($-T_2/T_1$) of different porous materials with the adsorption energy $E_{ads}$ determined from temperature programmed desorption (TPD) experiments [28–30]. However, the specific surface area of the material under study may also affect the $T_1/T_2$ ratio as the specific surface area has a stronger effect on $T_2$ relaxation compared to $T_1$ relaxation [22,31]. In order to address this problem, we therefore suggest here to use the ratio of specific surface relaxivities ($k_{a,2}/k_{a,1}$) as an indicator for surface chemistry effects as this value is similar to the relaxation time ratio $T_{1,ads.film}/T_{2,ads.film}$ of the adsorbed liquid film on the pore surface and hence, independent of the specific surface area of the material under study and solely affected by the surface chemistry. This comprehensive surface chemistry assessment presented in this study is complemented by solid-state NMR spectroscopy under Magic Angle Spinning (MAS), which is an extremely powerful technique to probe surface site density and structure in both pristine and functionalized stationary phase materials [32].

Hence, in this work we demonstrate the applicability of this powerful experimental toolbox for both the textural and surface chemistry characterization, with a focus on hydrophobicity/hydrophilicity, on mesoporous silica material, functionalized with 5 different organic moieties, which are commercially used as SPMs in chromatography. The functional groups used to modify the surface chemistry are illustrated Table 1. We demonstrate that it is possible to derive, by combining water adsorption and intrusion experiments reliable information of the effective contact angle $\theta$ of adsorbed water for wetting ($\theta = 0^\circ$), partial wetting ($\theta < 90^\circ$), and non-wetting situations ($\theta > 90^\circ$) observed on the pore walls of the SPMs under study. Further, NMR relaxometry measurements of selected SPMs immersed in water reveal that the $T_{1,ads.film}/T_{2,ads.film}$-ratio can be correlated with the effective adsorption strength of water on the surface. Indeed, we find a linear correlation between the negative inverse of the $T_{1,ads}/T_{2,ads}$-ratio ($-T_{2,ads}/T_{1,ads}$) with the contact angle determined from water vapor adsorption and intrusion experiments for the investigated SPMs. Our work clearly demonstrates for the first time that water vapor adsorption experiments and novel water intrusion technique coupled with NMR relaxometry can be used as complementary techniques to quantitatively analyze the wettability behavior and surface chemistry of nanoporous materials.

2 Material and Methods

In this work, 5 commercially available stationary phase silicas with different surface functional groups obtained from Advanced Materials Technology (AMT) were investigated as shown in Table 1: Pristine silica (AMT pristine), silica functionalized with glycan (AMT glycan), silica functionalized with pentafluorophenylpropylsilane (AMT PFP), silica functionalized with C8 (AMT C8) and silica functionalized with C18 (AMT C18). The surface chemistry of each silica is different based on the functional groups on its surface. Table 1 shows an overview of the silica SPMs and their corresponding functional groups.
Table 1: Evaluated silica SPMs with their corresponding functional groups

<table>
<thead>
<tr>
<th>Silica</th>
<th>Functional group</th>
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<tbody>
<tr>
<td>AMT pristine</td>
<td>-</td>
</tr>
<tr>
<td>AMT C18</td>
<td>(CH₂)₁₇-CH₃ dimethyloctadecylsilane</td>
</tr>
<tr>
<td>AMT C8</td>
<td>(CH₂)₇-CH₃ dimethyloctylsilane</td>
</tr>
<tr>
<td>AMT PFP</td>
<td>(CH₂)₃-C₆F₆ pentafluorophenylpropylsilane</td>
</tr>
<tr>
<td>AMT Glycan</td>
<td>R-(CH)₅-(OH)₅</td>
</tr>
</tbody>
</table>

2.1 Textural characterization by gas adsorption

High resolution gas adsorption measurements were performed on a commercial Autosorb iQ automatic volumetric adsorption analyzer from Anton Paar (QuantaTec, Boynton Beach, FL, USA) equipped with 1, 10 and 1000 Torr transducers. AMT pristine was degassed at 150 °C for 12 h under vacuum prior to all gas adsorption experiments. The functionalized SPMs were degassed at 120 °C for 12 h under vacuum in order to not modify the surface chemistry due to the removal or degradation of the functional groups. Textural properties were analyzed using a combination of argon (Ar 6.0 purchased from AirLiquide) 87 K and nitrogen 77 K adsorption experiments. Argon (87 K) isotherms were measured in a relative pressure range of approx. 10⁻⁵ up to 1 for each material. Network characteristics of the SPMs were analyzed by comparing the pore size distributions determined from the adsorption and desorption branch of the material using a dedicated metastable and equilibrium non-local density functional theory (NLDFT) kernel assuming cylindrical pores.

2.2 Investigation of surface chemistry by water vapor adsorption experiments

The evaluated silica materials can be classified depending on their surface chemistry and interaction with water as hydrophilic and hydrophobic (high and low water affinity respectively). For the first case, water pore filling takes place at pressures below water saturation pressure (p<p₀), whereas for the second one, water must be forced to get into the pores by applying pressures highly above saturation pressure (p>p₀). Hence, two experimental methodologies were used in order to determine the effective contact angle: water adsorption isotherms for hydrophilic silica and water intrusion measurements for hydrophobic silica.

The determination of the effective contact angle of water within the pores from water adsorption measurements on (partially) wetting silica (contact angle <90°) was done by utilizing the Kelvin equation (eq.1) which correlates the pressure where the equilibrium vapor-liquid phase transition occurs with the pore diameter (under the assumption of a cylindrical pore geometry).

\[
\ln\left(\frac{p}{p_{sat}}\right)_{cap} = -\frac{2\gamma V_c \cos \theta}{(r - t_m)RT}
\]

(1)
where \( \gamma \) is the bulk surface tension of water, \( V_L \) is the bulk molar volume of water, \( \theta \) is the contact angle of water on the silica pore walls, \( r \) is the pore radius obtained from the argon sorption measurements, \( R \) is the universal gas constant, \( T \) is the temperature of the isotherm and \( t_m \) corresponds to the statistical thickness of the adsorbed water layer. Hence, based on the known textural properties the effective contact angle can be calculated.

For this calculation, the pore radius was previously obtained by applying the BJH method to the desorption branch of the argon 87K data. The multilayer thickness formed prior to capillary condensation was determined by applying the Generalized Halsey equation, (eq. 2) to a reference non porous silica material (a controlled pore silica glass, Schott) with similar surface composition to the evaluated silica:

\[
t_m = a \left( \frac{1}{\ln \left( \frac{p}{p_0} \right)} \right)^{1/b}
\]  

(2)

where \( a \) and \( b \) are characteristics constants for the given adsorption system and temperature. Such parameters were determined from the controlled pore silica glass and used for the AMT silica. For the case of water, the thickness was calculated by assuming a fully hydroxylated surface on the silica materials.

Generalized Halsey equation was applied to the multilayer region in the \( p/p_0 \) range of 0.2-0.7 and 0.2-0.8 for argon and water sorption respectively to determine the thickness of the evaluated silica. Lastly, \( p/p_0 \) from eq.1 was chosen at the inflection point of the water desorption branch corresponding to the mode of the pore size distribution.

Water adsorption experiments were performed at 298 K with a dedicated volumetric (manometric) vapor sorption analyzer Vstar (Anton Paar QuantaTec) in the relative pressure range of \( p/p_0 = 0.005 \) up to 0.99. AMT pristine was degassed at 150 °C, while the functionalized SPMs were degassed at 120 °C for 12 h under vacuum prior to the adsorption experiments.

Water adsorption experiments were performed on a fresh sample from the same homogeneous batch that was used for Ar adsorption experiments. A second cycle (without any additional thermal treatment) was measured for the same sample in order to evaluate the hydroxylation of the surface after the first cycle.

2.3 Investigation of surface chemistry by water intrusion measurements

The determination of the contact angle of water on non-wetting surfaces (contact angle > 90°) is based on water intrusion/extrusion experiments. In this case, hydraulic pressure (\( p_h \)) is applied to intrude the non-wetting liquid water into the pores of a porous material. The contact angle can be determined from the Washburn equation (eq.3) [21], if the pore radius (\( r \)) is known (from Ar adsorption measurements):

\[
p_h = -\frac{2\gamma_{lv} \cos \theta}{r}
\]

(3)

where \( \gamma_{lv} \) is the surface tension, \( r \) the pore radius and \( \theta \) the effective contact angle. For highly curved surfaces, the surface tension may depend on the curvature. However, based on older works it seems that such corrections are only needed when the radius of the curvature approaches molecular dimensions [33,34].
Water intrusion experiments were performed using a poremaster 60 (Anton Paar, Germany) and sealed polymer envelopes, containing water and the hydrophobic C18 silica. For the preparation of the polymer envelopes, highly purified water with a conductivity of 0.060 mS m\(^{-1}\) was degassed with helium for at least 5 minutes. The porous material was then introduced into a prepared polymer envelope. Additionally, water in a large excess compared to the mesopore volume was carefully pipetted into the envelope. Finally, the envelope was sealed under vacuum. The vacuum was drawn until the boiling pressure of water (ambient temperature) was reached. After that, the sample was introduced into the cell of the mercury porosimeter. All measurements were performed using the smallest motor speed, using the autospeed mode. For the high pressure measurements, starting at 20 psi, 2 cycles were always measured. All intrusion measurements were performed at room temperature (~25 °C).

The polymer envelope and the water both show significant compressibility effects upon pressurization. Therefore, we apply a compressibility correction. The compressibility of the polymer is accounted for by a reference measurement, in which solely the polymer envelope is pressurized in the porosimeter. The compressibility of water is accounted for by utilizing the bulk modulus of water at 25 °C, calculated via the density and the speed of sound [35]. Detailed information about the compressibility correction is provided in the supplementary information.

During preparation of the polymer envelope, the mass of the polymer and water is recorded. This mass is used to scale the reference curves of water and polymer accordingly to obtain a compressibility corrected water intrusion curve.

2.4 Surface chemistry investigation by NMR relaxometry

The surface chemistry of three selected hydrophilic as well as hydrophobic SPMs (AMT pristine, AMT Glycan and AMT C18) was investigated based on the \(T_{1,\text{ads}}/T_{2,\text{ads}}\)-ratio determined from NMR relaxometry experiments. This method is based on the different relaxation behavior of molecules in contact with a surface compared to those in the bulk phase (or “free” liquid). Liquid near a (nanoporous) particle surface exhibits a much shorter relaxation time compared to the bulk fluid due to the reduction of rotational and translational molecular mobility of the adsorbed liquid molecules [36]. The specific surface area as well as the surface chemistry of the material under study affects the relaxation time reduction. In the fast diffusion regime, the relaxation time can be described by the two-fraction-fast-exchange-model [37]:

\[
\frac{1}{T_i} = \frac{1}{T_{i,\text{bulk}}} + k_{a,i} \frac{S \cdot V_{\text{solid}}}{V_{\text{liquid}}} \tag{4}
\]

Here, \(T_i\) is the relaxation time of the porous material immersed in the liquid phase, \(T_{i,\text{bulk}}\) is the relaxation time of the pure bulk liquid with \(i=1\) for spin-lattice and \(i=2\) for spin-spin relaxation. \(S\) is the specific surface area of the porous material under study, \(V_{\text{liquid}}\) is the volume of liquid in the sample and \(V_{\text{solid}}\) the volume of the nanoporous material under study. The parameter \(k_{a,i}\) is the specific surface relaxivity and is a measure for the relaxation time reduction of liquid at the particle surface:

\[
k_{a,i} = \lambda_{\text{ads, film}} \cdot \rho_{\text{solid}} \cdot \left( \frac{1}{T_{i,\text{ads, film}}} - \frac{1}{T_{i,\text{bulk}}} \right) \tag{5}
\]

\(\lambda_{\text{ads, film}}\) describes the thickness of the adsorbed liquid film, \(T_{i,\text{ads, film}}\) the corresponding relaxation time of the adsorbed liquid film and \(\rho_{\text{solid}}\) the skeletal density of the material under study. Please note, this definition can be transformed to the definition of surface relaxivity \(\rho_t = \frac{\lambda_{\text{ads, film}}}{T_{i,\text{ads, film}}}\) by Davis et al. [38] assuming that \(T_{i,\text{ads, film}} \ll T_{i,\text{bulk}}\) and by shifting the skeletal density from eq. 3 to eq. 2.
Fairhurst et al. showed a dependence between the T2 reduction and the interaction strength of different fluids in contact with the surface of zinc oxide powders [39]. However, the relaxation time is affected by surface chemistry as well as surface area and confinement effects and the relaxation time can therefore not be interpreted in a straightforward way for the quantification of the surface chemistry of different nanoporous materials. D’Agostino et al. suggested to use the ratio of spin-lattice to spin-spin relaxation time as a measure for the effective interaction strength between liquids and porous materials surfaces [25–27]. They found a linear correlation between the inverse relaxation time ratio (−T2/T1) and the desorption enthalpy determined from TPD measurements for water saturated samples [28–30]. Our previous experiments confirmed that the T1/T2 ratio can be coupled with the interaction strength of adsorbates on surfaces [22]. However, the effect of the specific surface area on T1 is less pronounced compared to T2, i.e. a stronger relaxation time reduction can be observed for T2 [22,31]. To neglect the effect of the T1/T2 ratio on textural properties, we suggest to use the ratio of specific surface relaxivities k_{a,2}/k_{a,1}, which can be simplified to the ratio of relaxation times in the adsorbed liquid film T_{1,ads}/T_{2,ads} assuming that T_{i,ads,film} ≪ T_{i,bulk}:

\[
\frac{k_{a,2}}{k_{a,1}} = \frac{\lambda_{ads} \cdot \rho_{solid} \cdot \left( \frac{1}{T_{2,ads}} - \frac{1}{T_{2,bulk}} \right)}{\frac{1}{T_{1,ads}} - \frac{1}{T_{1,bulk}}} \approx \frac{T_{1,ads}}{T_{2,ads}}
\]

(6)

In this work, the ratio of specific surface relaxivities was determined for the samples AMT pristine, AMT Glycan and AMT C18. For this, the SPMs were immersed in deionized water (Milipore water made with a PURELAB flex 2 by ELGA LabWater) prior to NMR relaxation measurements at a concentration of approx. 20 wt%. The SPMs were left in water for at least 24 h to ensure complete hydroxylation of the surface. Homogeneous suspension were prepared by mixing the samples in an ultrasonic bath (Branson 1510) for 2 h and stirring for 30 min at approx. 700 rpm.

For the samples AMT pristine and AMT Glycan, both samples were left until the particles formed a clearly visible sediment and the excess liquid was removed with a pipette. Additional excess bulk water was removed by keeping the samples in a drying oven at 80 °C for 30 min. Afterwards, the samples were immediately transferred to 10 mm NMR tubes (Bruker) and relaxation times were measured with a benchtop NMR device (Bruker minispec mq20). The temperature of the device was stabilized at 25 °C during the measurements. The inversion recovery pulse sequence was used for the determination of the spin-lattice relaxation time T1. The Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used for the determination of the spin-spin relaxation time T2 (see the Supporting Information for more details).

For the sample AMT C18, a fast separation of the water and solid powder was visible due to the hydrophobic nature of this sample. In this case, the solid powder was swimming on top of the liquid water phase as soon as the stirring stopped. This upper powder was transferred to a 10 mm NMR tube and relaxation times were measured in the same way as for AMT pristine and AMT Glycan. In this case, the water will most-likely not be inside of the pores but between the particles. However, as we assume the external surface chemistry to be identical with the internal surface chemistry, the T_{1,ads}/T_{2,ads}-ratio can still be used as a measure of surface chemistry effects.

For all 3 samples, the weight of the water saturated solid powder in the NMR tube was determined. After the NMR measurements, the samples in the NMR tubes were degassed under vacuum at 150 °C for 12 h by connecting the NMR tubes to a Xeriprep (Anton Paar). Finally, the weight of the dry powder was determined after degassing.
2.5 Solid-state NMR spectra under Magic Angle Spinning were acquired on a 500 MHz (11.7 T) DD2 Varian spectrometer at a $^1$H resonance frequency of 499.86 MHz. Samples were activated at 120°C for 12 hours and packed into 1.6 mm zirconia rotors under argon atmosphere. An MAS rate of 20 kHz was used. For background suppression, a DEPTH sequence was applied, consisting of a 90° pulse (100 kHz) followed by two 180° pulses (100 kHz) with a combined CYCLOPS and EXORCYCLE phase scheme [40–42]. 16 scans were accumulated.

3 Results and Discussion

3.1 Textural characterization

A comprehensive textural characterization of AMT pristine as well as the functionalized AMT materials was obtained by an advanced gas adsorption methodology based on a combination of argon 87 K and N₂ 77 K (see Figure 1a) in combination with pore size/volume analysis by applying a dedicated non-local density functional theory (NLDFT) method (Figure 1b and Figure 1c) assuming cylindrical pores. All samples exhibit a type IVa isotherm characteristic of mesoporous materials [43]. The shape of the hysteresis, which can be classified as a combination of H1 and H2 type (the adsorption-desorption branches are not completely parallel), suggests that the majority of mesopores are freely accessible to the external surface without restrictions, but still a fraction of larger mesopores is restricted by smaller pores (ink-bottle pores) [43]. A detailed analysis and comprehension of the pore network and connectivity is later on discussed in Figure 2.

Figure 1: a) Ar 87 K adsorption isotherms for the evaluated SPMs. Full symbols represent the adsorption branch and open symbols represent desorption branch. b) Cumulative pore volume and c) Differential pore size distribution for the evaluated samples by applying a dedicated NLDFT cylindrical equilibrium kernel to the desorption branch.
Figure 1b exhibits the cumulative pore volume for all samples, which clearly shows that the materials don’t show any microporosity. AMT pristine has the highest Ar uptake, thus leading to the largest total pore volume. The pore size distribution for this material is rather broad with mesopores in the range between 5 and 17 nm. The incorporation of the functional groups into the silica leads to a clear decrease of the pore volume but also of the mesopore size. For the latter case, a clear shift of the mean mesopore size can be observed in the pore size distribution (Figure 1c) for all functionalized SPMs compared to AMT pristine (calculated from the desorption branch). As mentioned before, the hysteresis helps to understand the pore connectivity of a material by evaluating the vapour/liquid phase transition in the adsorption/desorption process. For this analysis, pore size distributions were calculated from the Ar 87 K adsorption branch using a dedicated NLDFT metastable adsorption kernel and from the Ar 87 K desorption branch using a dedicated NLDFT equilibrium kernel (see Figure 2a) [44,45].

Figure 2: Differential pore size distribution a) using a dedicated NLDFT metastable kernel and equilibrium kernel to the Ar at 87 K adsorption and desorption branch, respectively and b) using a dedicated NLDFT equilibrium kernel to the Ar 87 K and N2 at 77 K desorption branch

Two assessments can be clearly distinguished in the pore size distribution. Firstly, for pores smaller than 9 nm, a small shift of the pore size distribution determined from the adsorption branch to smaller pore sizes is observed compared to the pore size distribution from the desorption branch. Such shift can be attributed to initiated/advanced condensation, i.e. the effective nucleation barrier associated with the nucleation of the liquid phase is reduced in an interconnected pore network resulting in a phase transition at a relative pressure smaller than the corresponding relative pressure with the spinodal of the fluid in these pores [44]. The occurrence of initiated condensation is known to exist in highly connected 3D pore networks [46,47]. For these pores, the desorption branch reflects thermodynamic equilibrium and the pore size can be determined in a straightforward way from the desorption branch. On the other hand, for pores larger than 12 nm, a shift of the pore size distribution determined from the desorption branch to smaller pore sizes can be observed, meaning that such larger cavities empty via pore blocking. Taking into account that in this complex 3D pore network system, during adsorption the pores are filled prior to the spinodal (initiated condensation), whereas during desorption most of the pores empty in an equilibrium liquid to vapor transition (only a small minority of large pores empty via pore blocking), the pore size distribution can be reliably determined from the desorption branch of the N2 77 K and Ar 87 K isotherms. The confirmation of the emptying of such large mesopores by pore blocking is shown in Figure 2b. Since the
pressure at which evaporation occurs is ruled by the size of the necks, the pore size distribution determined from the desorption branch is independent of the chosen adsorptive [44] and indeed, Figure 2b exhibits a very good agreement of the pore size distributions obtained from Ar 87 K and N$_2$ 77 K desorption branches.

Molecular simulations were carried out on model systems with non-standard pore geometries to provide further insight into the pore filling mechanism. A relatively good match with the experimental Ar adsorption isotherm was found for a system containing a missing cylinder in an array of hexagonally packed cylinders of amorphous silica, forming small and large pores with the diameter of large pore being 9 nm (see Figure 3). At low pressure (panel A), the Ar atoms adsorb first onto the corners of small and large cavities. As the pressure increases, the smaller cavity is filled (panel B) before the system reaches the monolayer capacity given by the BET method (panel C) indicating that the BET surface area analysis may overpredict the probe-accessible surface area. At the intermediate pressure range, the shape of the cross-sectional area of the cavity gradually turns from a hexagon to a circle (panels D and E). This behavior is driven by the liquid-vapor surface tension that leads to the Ar multi-layer to arrange in a manner that reduces the surface area of the cavity. The simulated isotherm shows a sharp step, indicating that the pore size distribution of the model is narrower than for the AMT silica. Overall, the agreement between the simulated and the experimental isotherms at the low and intermediate pressure range points to contributions from non-convex pore shapes for capturing the adsorption behavior.

![Figure 3: Simulated (blue squares) and experimental (red circles) Ar adsorption isotherms. The inset shows snapshots at reduced pressures of 0.01 (A), 0.1 (B), 0.2 (C), 0.5 (D), 0.6 (E), and 0.8 (F); Ar atoms are depicted as pink spheres; amorphous silica is depicted as points with silicon in yellow and oxygen in red.](image)

Table 2 summarizes the textural properties of the three samples. The BET surface area was calculated by taking a relative pressure range between 0.05 and 0.3 and assuming a cross sectional area of 0.142 and 0.162 nm$^2$ for Ar at 87 K and N$_2$ at 77 K, respectively. The pore volume was determined with NLDFT from the Ar and N$_2$ adsorption isotherms.
Table 2: Summary of the textural properties of the evaluated SPMs

<table>
<thead>
<tr>
<th>SPM</th>
<th>S_{BET} Ar 87K / m^2g^{-1}</th>
<th>S_{BET} N2 77K / m^2g^{-1}</th>
<th>Pore volume Ar 87K / cm^3g^{-1}</th>
<th>Pore volume N2 77K / cm^3g^{-1}</th>
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<td>AMT pristine</td>
<td>109</td>
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<td>0.26</td>
<td>0.26</td>
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<tr>
<td>AMT C18</td>
<td>60</td>
<td>61</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>AMT C8</td>
<td>89</td>
<td>91</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>AMT PFP</td>
<td>87</td>
<td>92</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>AMT glycan</td>
<td>93</td>
<td>104</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 2 reveals a clear effect of the surface chemistry of the different SPMs when comparing the BET surface area determined with Ar and N2 adsorption on the polar and non-polar surfaces. Whereas the surface area with Ar and N2 gives similar values on non-polar silicas (AMT C18, AMT C8, AMT PFP), a large difference can be observed for polar surfaces (AMT pristine and AMT glycan). In the last decades, N2 was always considered as the standard adsorptive for the textural characterization of nanoporous materials. However, more recently it was recognized that nitrogen has some limitations in its use, primarily due to N2’s quadrupole moment (caused by higher electron density on the ends of the N2 molecule), which leads to specific interactions with polar surface functional groups or exposed ions on material surfaces. These specific interactions between the N2 molecule and the material’s surface can lead to different orientations of the N2 molecule on the surface of polar materials leading to uncertainty in the cross-sectional area used for BET surface area calculations. In fact, this uncertainty in the assumed cross-sectional area can result in a reported N2 BET surface area which differs from the true surface area of the material by as much as 20 % if the standard cross-sectional area of 0.162 nm² is used for N2 [43,48]. In contrast, Argon is the recommended adsorptive for surface area determination by IUPAC. First, Ar is monoatomic and, therefore, has a consistent orientation on the surface of the material. This allows for unambiguity in Ar’s cross-sectional area used for surface area calculations. Also, Ar lacks a dipole or quadrupole moment, thus it eliminates possible interactions with any surface functional groups or exposed ions present in these materials. As a result, since there are no specific interactions depending on the material’s surface chemistry, there is a direct correlation between the Ar pore filling pressure and the pore size of the material.

The high degree of hydrophobicity of AMT C8 and AMT C18 is confirmed by ¹H solid-state NMR spectra under Magic Angle Spinning (MAS) of these samples (Figure 4). In pristine silica, after activation, a main resonance at 1.8 ppm can be seen, which can be attributed to isolated silanol groups at the surface. At the same time, a smaller signal of adsorbed water can be found between 2.4 and 4.5 ppm [49]. Note that this set of samples was activated at 120 °C only in order to avoid thermal degradation of the alkyl grafting. This relatively low activation temperature may yield a small residual amount of adsorbed water. In the ¹H MAS NMR spectrum of AMT C18, the resonance of isolated silanols is completely missing, showing that these groups have been completely replaced by alkyl grafting. In AMT C8, a tiny fraction of silanol groups is still visible at 1.8 ppm. Yet, since N2 and Ar physisorption isotherms are extremely coherent for this material, too, we consider that these few residual silanol sites are practically inaccessible for Ar or N2 physisorption under the given conditions.
3.2 Surface chemistry

The comprehensive detailed analysis of the surface chemistry of the 5 investigated SPMs will be shown in the following by combining water vapor adsorption experiments with water intrusion/extrusion and NMR relaxometry measurements.

3.2.1 Water vapor adsorption

Surface chemistry can be assessed by the comparison of adsorptives exhibiting different wettability. Argon at 87 K leads to a complete wetting adsorbate (effective contact angle is zero) independent of the effective surface chemistry. However, water adsorption is sensitive to the underlying surface chemistry. In fact, the water adsorption mechanism is produced by the formation of clusters, which nucleate onto the most energetic surface sites of the material. After clustering nucleation, such clusters continue growing around the polar sites and generating bigger droplet agglomerates, in contrast to argon adsorption, in which an adsorbed layer is formed along the surface prior to capillary condensation. Therefore, the effect of the silica SPM surface chemistry was evaluated by measuring water adsorption isotherms at 298 K (Figure 5a).
The measured water isotherms confirm as before mentioned that water adsorption on porous materials does not only depend on the pore volume and pore size but specially on the surface chemistry, thus water is only strongly adsorbed at the active and most energetic sites in which later on clustering formation happens. For the case of silica materials, such active sites correspond to hydroxyl groups on the surface (Si-OH). The presence of hydrogen-bonded silanols is expected to render the surface more hydrophilic. AMT pristine and AMT glycan show a type IVa isotherm with a complete mesopore filling due to their high OH content. On the contrary, AMT C8, AMT C18 and AMT PFP only show a very low water uptake since the hydroxyl groups on the surface have been replaced by hydrophobic ligands (C8, C18 and PFP respectively). Hence, for these samples the water-surface interactions are too weak and not sufficient to form water cluster onto the surface. This observation is very interesting and proves the importance of using water as a powerful tool for surface chemistry characterization on porous materials. Even though the overall silica samples exhibit similar surface area and significant mesopore volume based on Ar 87 K adsorption measurements, water can only be adsorbed and fill the pores on polar materials (AMT pristine and AMT glycan), whereas the pores cannot be filled for non-polar surfaces.

The silanol content of a pristine silica surface varies depending on many factors such as the synthesis conditions, temperature of calcination, post synthesis treatment, (e.g. silica exposed to a water saturated environment). Thus, water sorption isotherms on pristine silica materials can look very different depending on such silanol groups. In this sense, previous works on pristine SBA-15 and MCM-41 silica demonstrated that water adsorption measurements resulted in the hydroxylation of the surface during the first water cycle [17]. However, for AMT pristine, Figure 5b clearly shows that no re-hydroxylation of the surface takes place during the first cycle of the water adsorption measurement, which is reflected in the perfect agreement of the adsorption and desorption branch at low relative pressures and the good reproducibility of the first cycle in following cycles. Hence, the sample AMT pristine was already completely hydroxylated in the beginning of the measurement.

Effective contact angles on AMT pristine and AMT glycan from water sorption measurements were found to be ca. 3° and ca. 34°, respectively. The calculation of the contact angle is previously explained at the section 2 (materials and methods). As expected, pristine silica shows a contact angle very close to 0°, indicative of a fully wetting surface, due to the highly hydrophilic surface character of the silica. Interestingly, AMT glycan shows a contact angle substantially higher despite the fact that this silica is functionalized with a hydrophilic molecule which contains a big number of –OH groups. A similar trend is observed in the NMR relaxometry experiment when comparing both silica (Figure 9b).

3.2.2 Water intrusion/extrusion measurements

For AMT C8, C18 and PFP, capillary condensation was not observed at relative pressures below bulk coexistence ($p/p_0 < 1$) as expected due to the hydrophobic nature ($\theta > 90°$) of the surface functionalization. To obtain the effective contact angles, a novel methodology based on water intrusion was applied to the three SPM. During water intrusion, similar to mercury intrusion, hydraulic pressure is applied on water to form a liquid phase inside the pores. The intrusion/extrusion curves are shown in Figure 6.

After accounting for compressibility, a clear and distinct intrusion step with a successive plateau is obtained for all 3 investigated SPM. The intrusion step occurs at 24.6 MPa for AMT C8, 24.4 MPa for AMT C18 and 17.5 MPa for AMT PFP. Interestingly, while for AMT C8 and AMT C18 we observe extrusion of water from the pores at 3.1 and 1.3 MPa, for AMT PFP no extrusion is observed when returning to ambient pressure. Subsequent cycles on AMT PFP did not show any intrusion into the mesopores. Pioneering work from Fadeev et. al [50] on several
hydrophobic silicas showed that for C8 silicas (with a similar pore diameter) the intrusion and extrusion pressures were at 23.0 and 3.1 MPa, in great correspondence with our results here. Their work also contained water intrusion measurements on silicas functionalized with short chain, fluorinated alkyl groups. Here, similar to our results, no extrusion was observed. It has to be noted, that their functional groups did not include an aromatic ring as it is present for AMT PFP.

![Figure 6: Water intrusion/extrusion curves on AMT PFP, AMT C18 and AMT C8 for the uncorrected and the compressibility corrected case. AMT C18 and AMT C8 are shifted for 500 and 1000 mm$^3$ g$^{-1}$ for better visibility.](image)

The corrected intrusion curve can then be used to obtain the effective contact angles. This is done by evaluating the pore size distribution of the water intrusion branch with the Washburn equation (eq. 3) and fitting it to the benchmark distribution obtained by the argon adsorption using the contact angle as a variable. In analogy to the Washburn equation, the BJH approach (modified kelvin equation) is applied to the desorption branch of the argon isotherm to obtain the corresponding pore size distribution. The obtained fits are shown in Figure 7. The distributions obtained from the water intrusion are slightly broader than those obtained by the argon data. This might reflect differences of the orientation of the bulky organic groups of the 3 SPM at these experimental conditions (highly pressurized water at 25 °C and argon vapor at 87 K). The obtained effective contact angles are with 119 ° and 120 ° very similar for C8 and C18.

This finding is in good correspondence to experiments done by Fadeev and coworkers, showing no significant effect of alkyl chain length on the effective contact angle of water for hydrophobized flat silicon surfaces. Here, they measured a macroscopic droplet and reported an advancing contact angle of 110 ° [51]. Lefevre et. al. [52] have reported also 120 ° for a MCM-41 functionalized with n-octyl-dimethylchlorosilane (C8) while using a water intrusion experimental setup and the Washburn equation (eq 3). AMT PFP has with 114 ° a lower effective contact angle indicating the slightly less hydrophobic nature of the samples. In previous work [50], it was also observed that fluorinated hydrocarbons provide a less hydrophobic surface than non-fluorinated hydrocarbon functionalized surfaces. Additionally, the aromatic nature of AMT PFP might contribute to a slightly higher polarity and thus to the lower effective contact angle of water.
Figure 7: Fit of pore size distribution obtained via the Washburn equation and the water intrusion curves using the contact angle as a variable to the pore size distribution obtained from the argon isotherm via the BJH method (modified Kelvin equation).

3.2.3 NMR relaxometry

For the investigation of the surface chemistry by NMR relaxometry, first T₁ and T₂ calibration lines are generated to calculate the specific surface relaxivities by using the bulk water relaxation times and the relaxation times of water saturated samples (Figure 8a,b). The specific surface area on the x-axis of the calibration plots is determined from Ar 87 K (Table 2).

Figure 9a shows the ratio of the specific surface relaxivities $k_{a,2}/k_{a,1}$, which is equal to the $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$-ratio. One can clearly see that the interaction strength between water and AMT pristine is the strongest one, which is in line with the observations of the water vapor adsorption experiments. The hydrophobic nature of AMT C18 is clearly represented in the small $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$-ratio, which agrees well with the large contact angle determined with water intrusion results. The three investigated SPMs vary mainly in their surface functional groups,
textural properties such as the pore size distribution are similar. Hence, we can neglect confinement effects that could affect the specific surface relaxivities in this case. However, future studies are required to systematically investigate how pore size and geometry affect the specific spin-lattice and spin-spin surface relaxivities and hence, the $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ ratio.

3.2.4 Comparison of water vapor adsorption, water intrusion and NMR relaxometry measurements

The comprehensive surface chemistry assessment in this study is based on the application of water vapor adsorption, water intrusion/extrusion and NMR relaxometry. The correlation of the water contact angle with the $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ ratio determined with NMR relaxometry is shown in Figure 9a. We can clearly see that the most hydrophilic sample is AMT pristine as it shows a contact angle close to zero and the highest $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ ratio. The hydrophobic nature of AMT C18 is reflected in the large contact angle of ~125° and the comparatively small $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ ratio. Indeed, a linear correlation can be found between the contact angle and the inverse relaxation time ratio $-T_{2,\text{ads.film}}/T_{1,\text{ads.film}}$ (Figure 9b), clearly indicating that both values can be used complementary to analyze the wettablity and surface chemistry characteristics of porous materials. NMR relaxometry might be advantageous for fast surface chemistry characterization due to shorter measurement times compared to water vapor adsorption experiments, i.e. the measurement of $T_1$ and $T_2$ only takes a couple of minutes.

![Figure 2: Correlation between the contact angle determined with water vapor adsorption and water intrusion, respectively with (a) the $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ ratio and (b) the negative inverse relaxation time ratio $-T_{2,\text{ads.film}}/T_{1,\text{ads.film}}$](image)

4 Conclusions

This study shows the comprehensive textural and surface chemistry characterization of porous silica particles, modified with different surface functional groups, by utilizing a combination of fluids, which completely wet the surface independent of its surface chemistry (i.e. Ar 87 K) and fluids, which are wetting, partially wetting or non-wetting depending on the surface chemistry (i.e. water). Water vapor adsorption as well as NMR relaxometry clearly confirm that AMT pristine and AMT glycan are hydrophilic, with AMT pristine having a slightly smaller contact angle and higher $T_{1,\text{ads.film}}/T_{2,\text{ads.film}}$ ratio, respectively, than AMT glycan. In contrast, the hydrophobic nature of the samples AMT C8, AMT C18 and AMT PFP is confirmed by water vapor adsorption experiments and further quantified by water intrusion and NMR relaxometry measurements. Indeed, we find a linear correlation between the contact angle determined from water vapor adsorption and water intrusion experiments with the negative inverse relaxation time ratio $-T_{2,\text{ads.film}}/T_{1,\text{ads.film}}$. Further, NMR relaxometry is shown to be a powerful and unique tool for the fast assessment of surface chemistry as $T_1$ and $T_2$ measurements only take between 3 and 20 min. The comprehension of the textural and surface chemistry is crucial for material synthesis, process design and have a direct impact into the transport properties, selectivity to certain compounds and separation efficiency of chromatographic separation processes etc. Our work clearly demonstrates for the first time that water vapor adsorption experiments and novel water intrusion technique coupled with NMR
relaxometry can be used as complementary techniques to quantitatively analyze the wettability behavior and surface chemistry of nanoporous materials

5 Acknowledgements

The work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 416229255 – SFB 1411 as well as Project-ID 431791331 - SFB 1452. The molecular simulation work was supported by the Chemical Measurement & Imaging program, with co-funding from the Interfacial Engineering program, of the National Science Foundation (CHE-2003246).

6 References


