Water Transport in Periodic Mesoporous Organosilica Materials

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ABSTRACT: Water transport in periodic mesoporous organosilicas (PMOs) was studied using pulsed field gradient NMR. A series of isogeometric PMO materials with different chemical compositions of the pore walls were investigated and compared to a purely siliceous MCM-41 material with an identical pore size. The long-range water diffusivities measured were found to be largely controlled by the macroscopic textural properties of the materials, namely, by the particle geometry and a degree of the particle agglomeration, and by thermodynamic conditions under which the experiments were performed. It is shown that their combined effect caused water molecules either to propagate predominantly along the capillary-condensed water domains or to frequently alternate their trajectories between these domains and the water phase in the interparticle space. Because the transport rates in these two regimes differ substantially, it is suggested that by a purposeful choice of the PMO composition, both the long-range transport rate and the chemical functionality can deliberately be tuned.

■ INTRODUCTION

Diffusive mass transfer is the most ubiquitous phenomenon in nature and is often a decisive step in various biological and physicochemical processes.1,2 Among them, water transport in nanoporous solids has long been in the focus of scientific research with the main intentions being to understand and to control the rates of water propagation under different thermodynamic conditions.3–12 Concerning different strategies serving for these goals, purposeful designs of the pore system and of the pore surface chemistry are most widely explored. Along the former route, the correlations between the pore space morphology and molecular dynamics are exploited to manipulate the diffusive transport. The structural details of the pore space in this case are effectively combined into a geometric tortuosity factor reflecting slowing down of the diffusion rate as compared to the bulk liquids.

On decreasing the pore dimensions to the meso- or micropore ranges, in addition to purely steric or geometric effects,13 strong confinement gives rise to additional mechanisms affecting the molecular mobilities. Thus, in the extreme cases, with the most prominent example being zeolitic materials,14 tight confinements may elevate the role of the intermolecular interactions so that they become the key factor determining diffusive transport. As an example, in the pore channels with the pore diameters comparable to the molecular diameters, such that the molecules cannot bypass each other, the emergence of the single-file diffusion regime severely affects the transport rates. On the other hand, in mesoporous materials with the pore sizes in the range between 2 and 50 nm, molecular ordering can alter the local mobilities.15

The presence of the pore walls can affect the rates of water transport in two ways. First of all, the surface field exerted by the pore walls can result in the position-dependent mobilities across the pore.16 In particular, it is widely discussed that water mobilities in the first hydration shells differ notably from those in the layers further apart from the pore walls. Alternatively, surface interactions may alter the phase state of water in the intrapore spaces. It has found many experimental evidences that the phase state and transport under these circumstances are strongly coupled.10,19–21 This coupling is of a particular interest for an efficient manipulation of the water transport. Thus, it is speculated that the phase-state oscillations in hydrophobic pores, as induced by the external pressure changes, may be responsible for directed water transport through biological membranes.22 Hence, experimental studies of water dynamics in the pore channels with tunable surface chemistry and under different thermodynamic conditions are of immediate interest for improving our understanding of water behavior in nanochannels. Among them, a quantitative differentiation between the effects of polarity and of pure steric effects is the most challenging one.23

On considering transport in complex materials, the textural complexity present over different length scales is fingerprinted

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in molecular transport, rendering it length scale-dependent or heterogeneous.24,25 Because the majority of the mesoporous materials is typically found in a powder form, two important transport modes need to be distinguished. On the length scales below the particle dimensions, the intraparticle diffusion rates are mostly determined by the geometry and pore wall chemistry of the material under study.26 This transport mode is of importance for the processes in which the local mass transfer controls the surface-facilitated reactions or contributes to the confinement-facilitated molecular separation. On the larger length scales exceeding dimensions of the individual particles, the overall transport rates are different from the intraparticle one. These rates are often referred to as the long-range diffusion rates and result as a combined effect of the diffusive resistances in the intra- and interparticle spaces and of the physical mechanisms responsible for the mass transfer between the two spaces.27 Notably, all of these phenomena depend on thermodynamic conditions.20,28 Often the long-range transport is a rate-determining step and needs to be appropriately tuned in order to yield high efficiency or performance of the overall process. Hence, in addition to understanding diffusion on a single pore level, explorations of the long-range transport turn out to be challenging and warrant thorough experimental studies.

Periodic mesoporous organosilicas (PMOs) are ideal model systems because they combine the highly ordered pore structure of the well-known M41S phases29 with the variety of different surface chemistry within the pores. PMOs are synthesized using bis-silylated precursors of the form (RO)3Si–R–Si(OR)n, where R is an organic bridging group which can be altered according to the desired surface properties. Recently, water molecules confined within the pores of a benzene-bridged PMO were shown to diffuse and rotate with a smaller activation energy compared to water in the pores of pure siliceous MCM-41 because of the different interfacial interactions.30 Furthermore, PMOs with an aromatic bridging group may exhibit a molecular-scale periodicity or “quasicrystalline arrangement” within the pore walls.31 This allows a periodically alternating surface chemistry along the pore channel, caused by arrays of silica and aromatic organic groups. Because of the endless possibilities for the organic bridging function, the surface chemistry of PMOs can be fine-tuned. For example, when going from a benzene bridging group to a biphenyl bridge, the organic hydrocarbon part becomes larger and thus the overall pore wall gets more hydrophobic.32 When going from a benzene bridge to a divinylaniline one, the amino function offers the possibility of forming hydrogen bonds with water, thus making the material considerably more hydrophilic again.

In this work, we employed MCM-41 silica and benzene- (B), biphenyl- (BP), and divinylaniline-bridged (A) PMO materials with cylindrical pore morphology and with the pore diameter of 3.3 nm as ideal model systems to explore the impact of chemical composition on the properties of spatially confined water. The synthesis procedure and the structural properties as probed by a number of conventional characterization techniques are thoroughly described in the Supporting Information. We performed the pulsed field gradient (PFG) NMR studies of the water transport in these materials at two distinct thermodynamic conditions corresponding to (i) the interparticle space containing the water vapor phase and with (ii) the interparticle space blocked by the ice phase.

**METHODS**

PFG NMR. The 1H PFG NMR diffusion experiments33,34 were performed using a home-built NMR spectrometer operating at a 100 MHz resonance frequency for protons. The high values of the magnetic field gradients up to 35 T/m were applied.35 This allowed (i) to keep the time intervals in the NMR pulse sequences during which the nuclear magnetic magnetization evolved in the transverse plane relatively short (several milliseconds) and (ii) to assess very small diffusivities down to $10^{-12}$ m$^2$/s. The 13-interval pulse sequence,36 with the pairs of the magnetic field gradient pulses of different polarities applied in the encoding and decoding time intervals, was used with the primary goal to minimize the perturbing effects caused by the strong gradient pulses. Diffusion experiments with different diffusion times $t$ between 10 and 160 ms were performed in order to check whether the diffusion process probed was normal (the mean square displacements linearly growing with $t$) or some deviations were caused because of the complexity of the material organization (leading, e.g., to the observation of restricted diffusion with the mean square displacements growing as $t^a$ with $a < 1$).

The spin-echo signal intensities $S$ measured using this method are directly related to the so-called diffusion propagator $P(z,t)$. The latter is the probability density function to find a displacement $z$, namely, the projection of the displacement vector onto the $z$-axis along which the magnetic field gradient is applied, during a given diffusion time interval $t$. The relationship between $S$ and $P(z,t)$ is given by

$$S(q, t) = S(0, t) \int_0^\infty P(z, t) e^{-iqz} dz$$

where $q \equiv \gamma g$ is the wave number, $\gamma$ is the gyromagnetic ratio for protons, $\delta$ and $g$ are the effective length and strength of the magnetic field gradient pulses, respectively. This simple functional dependency allows to probe directly the properties of the diffusion process by measuring $S$ as a function of $q$ at fixed $t$. For normal diffusion, that is, when the propagator is of Gaussian form, eq 1 transforms to

$$S(q, t) = S(0, t) e^{-Dq^2t}$$

with $D = (z^2)/(2t)$ being the diffusivity. Any deviation of $S(q,t)$ from the exponential form signals about either non-Gaussian statistics of the molecular displacements (anomalous diffusion38) or distribution of the diffusivities over the sample volume (multiphase or multicompartment diffusion). In the latter case, there are different molecular ensembles (often referred to as “phases”, which does not necessarily imply thermodynamic phases) in the sample with different translational mobilities. In this case, $S(q,t)$ can be described by a weighted sum of eq 2

$$S(q, t) = S(0, t) \sum_i p_i e^{-D_i q^2t}$$

where $p_i$ and $D_i$ are the relative fractions and diffusivities of the nuclear spins in the phase $i$, respectively. Equation 3 is also valid if the different phases refer to the spatially extended regions in which molecules have different diffusivities and there is no molecular exchange between these regions. The occurrence of molecular exchange between different ensembles can be unveiled by performing the diffusion experiments using different diffusion times. If during the diffusion times, $t$, molecules can explore different regions with different
diffusivities, \( p_i \) in eq 3 becomes functions of the diffusion time.\(^{21}\) Note that in eq 3, we have implied no nuclear magnetic relaxation weighting for different phases. In our experiments, the applicability of this assumption is ensured by maintaining the transverse relaxation time intervals in the NMR pulse sequences substantially short. For multiphase systems (in the sense of eq 3), the average diffusivity

\[
D_{av} = \sum_i p_i D_i
\]

is a useful concept to characterize the overall transport. It can be easily obtained by approaching eq 2 to the low-\( q \) part of \( S(q,t) \).\(^{21}\)

**RESULTS AND DISCUSSION**

Vapor Phase in the Interparticle Space. The experimental studies of the water transport have been performed under two distinct conditions. In the first series of the diffusion experiments, only the mesopore space has been filled with the capillary-condensed water. This has been achieved by equilibrating the samples with water vapor at 80% relative humidity. The water sorption isotherms (see Figure 3 of the Supporting Information) reveal that at this vapor pressure, (i) all cylindrical mesopores are completely filled by water and (ii) some small amount of water (less than 10%) may be found between the particles.

Even though the mesopore structure in all materials studied is identical (except the pore wall chemical composition), the primarily measured NMR spin-echo diffusion attenuation functions \( S(q,t) \) revealed dramatic differences in the water transport behaviors. As an example, Figure 1 shows \( S(q,t) \) measured for different samples at the temperature of \(-20^\circ\)C. The first distinct feature observed is that while \( S(q,t) \) for MCM-41 and A-PMO is of an exponential form as given by eq 2, that for B-PMO and BP-PMO follows the pattern of eq 3. In the latter samples, the diffusion process exhibits features typical of multiphase systems, namely, the occurrence of molecular ensembles with different diffusivities. Second, the water diffusivities in, for example, MCM-41 and A-PMO, differ by more than 1 order of magnitude. In the B-PMO and BP-PMO samples, the average diffusivities as well are substantially higher than that in the A-PMO sample.

In order to unveil these differences obtained, the transport mechanisms need to be established. To do this, we have performed the diffusion experiments at different temperatures. The spin-echo diffusion attenuations obtained were analyzed in the same way, as indicated in Figure 1, and the final results are shown in Figure 2. It turns out that the temperature dependencies of the diffusivities for the A-PMO sample and for all other samples exhibit different activation energies \( E_a \) for diffusion. Whereas in A-PMO, \( E_a \approx 18 \) kJ/mol, which is typical for diffusion in bulk liquid water, diffusion in three other samples exhibits a notably higher activation energy \( E_a \approx 42 \) kJ/mol. This activation energy is close to the heat of water vaporization, and this finding is a hint to understand different transport patterns observed in the experiments.

All samples under study are found in a powder form composed of small particles traversed by the tubular mesopores. The particle sizes are typically in the range of several hundreds of nanometers. The particles may further agglomerate. Because the samples were saturated with water at 80% humidity, the space formed between the particles contains mostly the water vapor phase. The outer surface of the particles is covered by a thin, few monolayer thick water film, and the contact points between the particles may also contain water films. During the diffusion time intervals used in the experiments, the molecular trajectories may alternate between the vapor and condensed phases. Indeed, the water molecules
approaching the water film on the external particle surface may desorb, perform either Knudsen flights or molecular diffusion in the vapor phase, and then be adsorbed again. The alternation frequency depends on the thermodynamic conditions, on the water diffusivities in the different phases, and the spatial extensions of the domains of different phases. As a result, the diffusion process, as seen by PFG NMR, becomes strongly dependent on the relationship between the diffusion time $t$ and the lifetimes $\tau$ of molecules in different phases.\(^{39}\)

Under the conditions of the slow exchange ($\tau \gg t$), $S(q,t)$ is well-approached by eq 3. However, because the fraction $p_v$ of water molecules in the vapor phase is substantially lower than $p_l$ in the capillary-condensed phase, $S(q,t)$ apparently exhibits a monoeponential shape. Thus, the measured $S(q,t)$ reflects the diffusion behavior in the capillary-condensed phase only. Hence, by fitting eq 2 to the experimental data, one obtains the diffusivity in the condensed phase. In another limit of the fast molecular exchange ($\tau \ll t$) during the diffusion times $t$ applied, the molecular trajectories alternate frequently between the two phases. Hence, the diffusivity may be described by a single average diffusivity given by eq 4. Once again, $S(q,t)$ turns out to be the exponential function as given by eq 2, but now with the diffusivity $D_{\text{av}}$. In the intermediate exchange regime, $S(q,t)$ can be approximated by eq 3 with the time-dependent $p_v(t)$. Notably, the low-$q$ behavior of $S(q,t)$ in this regime remains irrespective of the diffusion time $t$ with the slope being proportional to eq 4.\(^{21}\)

These scenarios discussed may now be used to explain the experimental observations made in our experiments. It turns out that, under the conditions under which our experiments were performed, the diffusion behavior probed in the MCM-41 and A-PMO samples may be classified to belong to the fast and slow exchange regimes, respectively. In the former case, the diffusivity probed, $D_{\text{av}}$ is given by the sum of two terms, $D_{\text{av}} \approx p_v D_v + D_l$. Here, $p_v \ll 1$ and $p_l = 1 - p_v \approx 1$ are the relative fractions of water molecules in the vapor and liquid phases, respectively, and $D_v$ and $D_l$ are their respective diffusivities. Irrespective of the fact that $p_v \ll 1$, the notably higher diffusivity $D_v \gg D_l$ ensures that the term $p_v D_v$ has a dominant contribution to $D_{\text{av}}$. This is further supported by the data of Figure 2 revealing that the activation energy for diffusion in this sample is close to the heat of water vaporization $\Delta H_{\text{vap}} \approx 42$ kJ/mol. Indeed, because $D_l$ only weakly depends on $T$, namely, $D_l \propto \sqrt{T}$ in the Knudsen and molecular diffusion regimes, the temperature dependency of $D_{\text{av}}$ is controlled by $p_v \propto \exp(-\Delta H_{\text{vap}}/RT)$, where $R$ is the universal gas constant.

In contrast, in the A-PMO sample, the experimental conditions correspond to that of the slow exchange regime. Hence, according to the discussion presented above, the slope of the spin-echo diffusion attenuation functions reflects the diffusivity in the capillary-condensed phase, $D_v$. Once again, this is found to be in a good agreement with the temperature dependency obtained for this sample and revealing the activation energy for diffusion to be close to that of bulk water. An important question is why the two samples show such distinct behaviors? We anticipate that this difference is determined by the textural properties of these materials. The electron microscopy studies (see Figures S4 and S5 of the Supporting Information) reveal that the MCM-41 silica material is composed of the loosely connected and well-dispersed particles. At the same time, the A-PMO particles tend to form large agglomerates. The water sorption isotherms (Figure S3, Supporting Information) also support this by revealing that upon the completion of the capillary condensation in the cylindrical channels, the isotherm for MCM-41 silica at high relative humidities is found to be more flat than that for the A-PMO sample. This indicates that the particle agglomeration leads to higher interparticle mesoporosity. During the shortest diffusion times of 10 ms and the lowest temperatures used in our experiments, the water molecules displace by the distances about $\sqrt{D_{\text{av}}t} \approx 1 \mu$m. This exceeds notably the dimension of the individual MCM-41 particles. Hence, because of a poor contact between the crystals and because of small particle size, many adsorption–desorption cycles occur during the diffusion times and the transport rate becomes notably accelerated by the fast diffusion in the vapor phase. In contrast, in the agglomerates of A-PMO, the formation of a well-developed network of capillary-condensed water ensures an efficient transfer of water molecules between the particles via the liquid bridges. In this case, a relatively low interfacial area between the condensed and vapor phases suppresses the molecular exchange rates between the two phases. As a result, $S(q,t)$ is found to follow eq 3, but with the component associated with the vapor phase being not resolved in the experiment due to a very low $p_v$.

Interestingly, the onset of the intermediate exchange regime is observed in the A-PMO sample upon increasing the temperature above 20 °C. This is evident in Figure 3, showing the appearance of a notable fraction of water molecules possessing the diffusivities higher than that in the condensed phase. This fraction is found to increase with increasing diffusion time, which is a typical feature of the molecular exchange process. Quite generally, this finding implies that with increasing temperature, water molecules initially residing in the condensed phase perform more and more frequent excursions to the vapor phase. Both increasing density of the vapor phase and increasing diffusivity in the condensed phase with increasing temperature contribute to the enhancement of the exchange process.

On inspecting Figure 3, one may note that the diffusivity associated with the slow diffusing component in $S(q,t)$ (as
reflected by the different slopes of the broken lines in Figure 3) decreases with increasing diffusion time. This is an indication of a non-Gaussian character of the diffusion process. In the sample under study, this can be caused either by the partially reflecting boundary conditions at the external boundary of the A-PMO agglomerates 28 or by a fractal-like organization of the capillary-condensed water network within the agglomerates. 40 In our opinion, the former scenario is more favorable. Indeed, because of a substantial difference of the densities in the gaseous and liquid phases, water molecules approaching the liquid—vapor interface perform many unsuccessful attempts to desorb before they finally succeed to escape the liquid phase. 28 This gives rise to the restricted diffusion phenomenon within the agglomerates. The analysis of the time-dependent diffusivities (see the Supporting Information) yields the average restriction size on the order of several micrometers, 34 which may be indicative of the average agglomerate size.

In line with the previous discussion, the transport behavior in the B-PMO and BP-PMO samples can be classified to belong to the intermediate exchange regime in the whole temperature range studied. Both the shapes of the diffusion attenuation functions (shown in Figure 1 for one particular temperature) and the temperature dependencies of the average diffusivities shown in Figure 2 support this scenario. Similar to that of the MCM-41 sample, the average diffusivities in these samples are dominated by fast diffusion in the vapor phase and are well-approximated by \( D_v \approx p_v D_v \). By reasonably assuming that the diffusivities \( D_v \) in the vapor phase in all of these samples are close to each other (this is indeed true for molecular diffusion in the vapor phase), the difference of \( D_v \) in these three samples becomes thus determined by the differences in \( p_v \). The estimates of \( p_v \) (see Table S3 in the Supporting Information) in these samples based on their textural properties and at the relative humidities studied nicely corroborate this hypothesis. Moreover, the scanning electron microscopy (SEM) images evidence that on considering their textural properties, these two samples thought to show some agglomeration, but as not pronounced as in the A-PMO sample.

**Ice Phase in the Interparticle Space.** The discussion presented in the preceding section revealed that in the majority of the samples containing vapor phase in their intercrystalline spaces (except the A-PMO sample), the long-range transport was notably contributed by diffusion in the vapor phase. To learn more about the mass-transfer patterns in the condensed phase and on the effect of chemical composition of the pore walls on the overall water transport, it would be beneficial to exclude the transport mode through the vapor phase. This can be done by providing excess liquid, so that the interparticle space will also contain water, and by subsequent freezing out the interparticle water. In this way, the interparticle space containing ice becomes excluded for molecular transport, whereas the mesopores will still contain liquid water because of a strong suppression of the freezing temperatures in small mesopores. 32,41–43

Figure 4 shows the results on water diffusivities in two samples, A-PMO and B-PMO, obtained upon increasing the temperature starting from \(-45^\circ C\). The experimental procedure was as follows. The samples contained water in an amount equal to twice of the mesopore volume. Thus, all mesopores and the interparticle space were filled with liquid water. First, the samples were cooled down, and the freezing process was monitored by measuring the NMR spin-echo signal intensity with the echo time of several milliseconds. The signal intensity dropped stepwise at temperatures between \(-10^\circ C\) and \(-20^\circ C\). Because the nuclear transverse relaxation times in ice are notably shorter than that in liquid water, the signal drop was an indication of freezing occurring in the samples. 44 Notably, a small NMR spin-echo signal remained however observable down to \(-45^\circ C\).

In the samples without excess water, no indications of freezing were observed upon cooling down. When no excess water was provided, the water in small mesopores remained in the supercooled state down to the lowest temperatures used in our experiments. This is caused by strong suppression of homogeneous ice nucleation because of strong confinements. However, in the samples with excess water, ice readily nucleated in the interparticle space filled with water. This resulted in complete freezing of water between the particles. At the same time, as proven by our experimental observations, water in the A-PMO and B-PMO channels remained in the mobile, liquidlike state, giving rise to an NMR signal surviving the transverse nuclear magnetic relaxation filter of the NMR spin-echo pulse sequence.

On heating the samples starting from \(-45^\circ C\), the diffusivities in the A-PMO and B-PMO samples first increased monotonically and then exhibited a stepwise increase at a temperature very close to \(0^\circ C\). At this temperature, the frozen ice between the particles melted and the diffusivities measured became comparable to that of bulk water. For comparison, the diffusivities of bulk water are also shown in Figure 4 by the solid line. The slightly lower values for the diffusivities measured in our experiments are caused by the steric restrictions both in the intra- and interparticle spaces. The most interesting region in Figure 4 refers, however, to the temperatures at which the interparticle water was found in the frozen state. Only this part will be discussed in what follows.

The diffusivities of supercooled water measured in the A-PMO and B-PMO samples between \(-45^\circ C\) and \(0^\circ C\) are found to be notably (up to 2 orders of magnitude) lower than the diffusivities of bulk water extrapolated to these temperatures. Remarkably, this dramatic difference is found to be irrespective of the phase state in the interparticle space, as evidenced by the data of Figure 4. Indeed, the experiments reveal the almost identical diffusivities for the capillary-condensed water in the presence of either ice or vapor phase between the particles. These (long-range) diffusivities result as a combined effect of

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Diffusivities of the slow diffusing component in the A-PMO (open circles) and B-PMO (open squares) samples saturated with water at 80% relative humidity and for the A-PMO (filled circles) and B-PMO (filled squares) samples obtained when the samples contained excess water in the frozen state.
diffusion within the particles and of water migration between the particles within the agglomerates. Under both conditions, with the vapor or ice phases between the particles, the water transport between the particles takes place along a thin, several monolayers thick water film found on the external surface of the individual particles and between them. In the case of the frozen intraparticle water, such layers between ice and solid are known to remain down to very low temperatures.\textsuperscript{45} It turns out that these layers in the two cases considered have similar impact on the long-range water transport.

Another intriguing question is why these diffusivities measured are so different from the bulk water diffusivities? According to the literature data, in the mesopore channels, such as in the channels of MCM-41, the water diffusivities are typically only slightly lower than that of the bulk ones. For example, quasielastic neutron scattering (QENS) studies revealed the water diffusivities in MCM-41 on the order of \(10^{-9} \text{ m}^2/\text{s}\), which is only two times lower than the bulk diffusivity.\textsuperscript{36} In contrast to QENS probing the molecular dynamics on the sub-nanometer length scale, PFG NMR probe displacements over the distances up to several micrometers.\textsuperscript{47}

We anticipate that this is a particular architecture of the agglomerates and of their constitutes, namely, of the particles traversed by a parallel set of the tubular pores, which gives rise to a dramatic slowing down of the effective, long-range diffusivities. Indeed, when a molecule approaches an opening of a tubular mesopore, it may either diffuse back into the same pore or perform an excursion along the water film on the external boundary of the particle. In the latter case, it enters with a high probability another pore nearby the original one. In either case, the molecular displacements acquired in the initial pore before approaching the pore opening will effectively be reduced by the molecular displacement in the secondary pore. This situation is exemplified in Figure 5a. When, however, the interparticle space is filled with water, such as at temperatures above 0 °C in Figure 4, the molecular trajectories become efficiently randomized because of an increased probability to approach another particle with different orientations of the intraparticle channels (see Figure 5b) rather than entering a channel in the original particle. A similar effect has earlier been reported for bimodal porous solids with the gaseous phase filling one of the pore spaces.\textsuperscript{28} With the broken persistency of the molecular trajectories, the effective diffusivities become comparable to the bulk diffusivities.

The difference observed for the diffusivities in the A-PMO and B-PMO materials in Figure 4 can be related either to slowing down of the intraparticle diffusivities due to a strong hydrogen bonding in the A-PMO channels or to a specific architecture of the agglomerates as revealed by the SEM study.

To answer this question further studies using materials with identical textural properties are needed and will be in the focus of our subsequent work.

### CONCLUSIONS

Because of a number of favorable properties, mesoporous materials are attracting an increasing interest for being used in practical applications. Transport of guest species in these materials often plays a key role in many processes. A wide spectrum of the synthesis approaches of mesoporous solids results in a respective large spectrum of materials with different architectures of their mesopore spaces, chemical compositions of the pore walls, and macroscopic textural properties. All of these details can strongly influence water transport. In this work, we have studied water diffusion in a family of isometric PMOs with tubular pores using PFG NMR. The main intention was to establish the transport mechanisms and to find correlations between the pore wall chemistry and water diffusion. Indeed, the experiments revealed substantial differences in the transport patterns for materials prepared using different aromatic bridging units, that is, with different pore wall polarities. A thorough analysis of the diffusion behavior studied over a length scale from hundreds of nanometers to several micrometers, at different temperatures, and different water concentrations revealed that the experimentally observed difference originates primarily from different textural properties of these materials. The latter includes the particle morphology and their agglomeration. The conclusions drawn from the diffusion analysis and the transport mechanisms conceived were further corroborated by the SEM studies of the material structure.

In particular, in the MCM-41 silica, showing a relatively weak agglomeration, a sufficiently high surface-to-volume ratio of the particles renders the water molecular lifetimes in the particles substantially shorter than the experimental time. This results in the frequent excursions of the water molecules to the vapor phase and thus leads to an efficient mass transfer through the MCM-41 material enhanced by fast diffusion in the interparticle space. If the material synthesis involves organic bridging units, a more pronounced agglomeration causes molecular diffusion in the capillary-condensed water to become the dominant mass-transfer mechanism. As demonstrated by our experimental findings, in both cases, the overall water transport depends strongly on the phase state of water in the interparticle space.

Though the results obtained revealed the dominant role of the macroscopic organization of the PMO materials on the water transport, they also suggest the strategies how the effects of the mesopore geometry and of the mesopore wall polarity can complementarily be probed using PFG NMR. For this purpose, the macroscopic structure of the PMO materials obtained with different organic linkers should be kept intact. This can, for example, be achieved by exploiting monodisperse spherical PMOs.\textsuperscript{28-31} In this case, the particle morphology will remain identical and finer details in the transport behavior can be analyzed more accurately. As a final remark, the experimental findings presented in this work demonstrate that by a careful choice of the material chemical composition, the two important dynamic properties, namely, the long-range water transport and the local intrapore water mobility, can simultaneously be optimized.
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