Communication

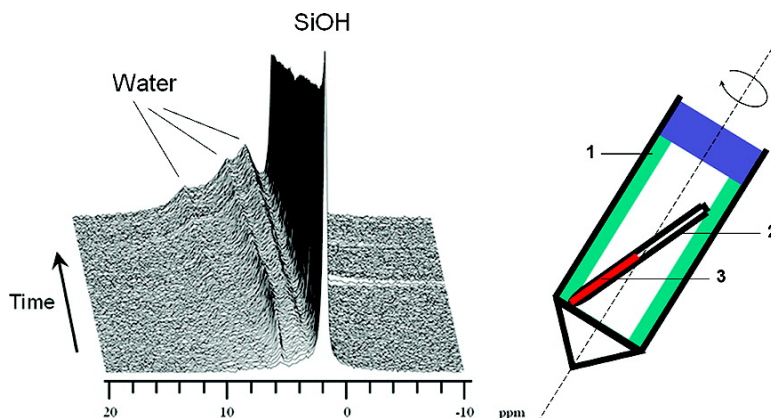# Mapping the Evolution of Adsorption of Water in Nanoporous Silica by in situ Solid-State H NMR Spectroscopy

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Mapping the Evolution of Adsorption of Water in Nanoporous Silica by in situ Solid-State ^{1}H NMR Spectroscopy

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An important fundamental question in nanoscience is whether molecules in confined nanoporous spaces exhibit properties that differ significantly from those in the bulk,[1] and it is essential that appropriate techniques are available to answer this question. A key topic in this regard is the study of water molecules in nanoporous spaces. To date, however, studies of structural transitions and dynamics of water in nanoporous structures have focused on systems under equilibrium conditions[2] and thus have not provided information on the structural evolution of the water molecules adsorbed within the nanopores prior to the establishment of equilibrium. To address this issue, we apply a recently developed technique for in situ solid-state NMR studies of adsorption processes, in order to map the structural evolution of water adsorbed in nanoporous voids within a widely used siliceous host material[3] known as MCM-41, which contains hydrophilic nanopores of typical diameter ca. 3 nm and has been used in a range of applications, including catalysis.[4]

Although solid-state NMR is used widely in chemistry and materials science, its adaptation for in situ studies of adsorption processes is associated with specific technical challenges, both because the sample is located in a confined and relatively inaccessible space inside the NMR magnet and because high-resolution solid-state NMR usually involves rapid sample rotation. Although progress has been made[5] in the development of solid-state NMR techniques for in situ studies of adsorption, we recently proposed[6] a new experimental strategy with the specific feature of enabling the very earliest stages of the adsorption process to be probed directly. In this strategy, the species to be adsorbed is sealed in a glass capillary and inserted into the solid-state NMR rotor together with the host material on which the adsorption is to take place. The adsorption process is triggered by magic angle spinning (MAS), which exerts a significant centripetal force on the sample[7] leading to breakage of the glass capillary. As a result, the species to be adsorbed is brought in direct contact with the nanoporous host material, in situ within the solid-state NMR rotor. The NMR spectrum may be recorded immediately at the start of the adsorption process, and the time resolution then depends solely on the time required to record an individual NMR spectrum. To slow down the adsorption process, and hence to allow the earliest stages of adsorption to be probed within the time resolution of the technique, it can be advantageous to work at low temperature. If the species to be adsorbed is a solid at the temperature of the experiment, the adsorption occurs via the vapor phase. Although the vapor pressure can be very low for solids at low temperature (e.g., the equilibrium vapor pressure of ice[8] at 183 K is ca. 10^{-2} Pa), the vapor phase nevertheless provides a vehicle for transport of molecules from the solid state to the adsorbed state.

To extend the application of this technique into a new domain of time resolution, we focus here on ^{1}H NMR studies (which provide time resolution of the order of a few hundred seconds) of the evolution of the adsorption of water within the siliceous nanoporous host material MCM-41. Separate experiments were carried out for samples of water with natural ^{1}H/^{2}H isotopic abundances, denoted water-h_2, and deuterated water (Aldrich; 99.9% [2]H), denoted water-d_2. The sample of MCM-41 (with natural ^{1}H/^{2}H isotopic abundances in the silanol groups) was dehydrated under vacuum at 723 K for 12 h. For the separate experiments involving water-h_2 and water-d_2, the water (ca. 5 mg) was sealed in a glass capillary (0.7 mm diameter) which was loaded together with the powder of dehydrated MCM-41 (ca. 15 mg) inside a MAS NMR rotor (4 mm diameter).[9,10] The rotor was then inserted into the solid-state NMR spectrometer (Chemagnetics CMX Infinity 300; ^{1}H frequency, 300.146 MHz) at ambient temperature, cooled to 183 K, and kept at 183 K for ca. 30 min to allow thermal equilibration. Sample spinning was then started, breaking the capillary tube and releasing water (via the vapor phase) for adsorption inside the MCM-41 host material. Once MAS was stable at 12 kHz (within 60 s), ^{1}H NMR spectra were recorded using a direct $\pi/2$ pulse with recycle delay 10 s. At 183 K, 32 scans were accumulated for each spectrum (corresponding to a total time of ca. 320 s per spectrum).

In situ ^{1}H NMR spectra for water-h_2/MCM-41 and water-d_2/MCM-41, recorded as a function of time at 183 K, are shown in Figure 1. First, it is relevant to note that, immediately after breakage of the capillary at 183 K, most of the water in the NMR rotor must be present as ice, but the ^{1}H NMR signal from bulk ice is too broad (ca. 50 kHz[11]) to be observable using normal MAS NMR conditions of the type employed in the present work.[12] For reference, the ^{1}H chemical shift for ice is in the range of 6.4 to 7.4 ppm depending on temperature.[13]

For water-h_2/MCM-41, four signals are observed (Figure 1a,b). The strong signal at 1.7 ppm, present from the start of the process, is due to isolated silanol groups on the MCM-41 framework [as discussed below, the concentration of silanol groups in the MCM-41 sample used in the present work has been determined to be ca. 2.53 mmol g^{-1} (after dehydration)]. The signal at 5.4 ppm, which also increases in intensity with time, is assigned as water molecules hydrogen bonded to silanol groups. This signal is also observed for water-d_2/MCM-41, and its appearance immediately after the start of the adsorption process suggests that this water environment undergoes facile [1]H–[2]H exchange (Figure 1c). For both water-h_2/MCM-41 and water-d_2/MCM-41, this signal broadens after ca. 6 h, as discussed below. The broad signal at ca. 3.8 ppm, which increases in intensity with time, is assigned as physically adsorbed water-h_2. This signal is not present for water-d_2/MCM-41 (Figure 1c), indicating that no significant [1]H–[2]H exchange occurs for this water environment, and hence that these water molecules do not
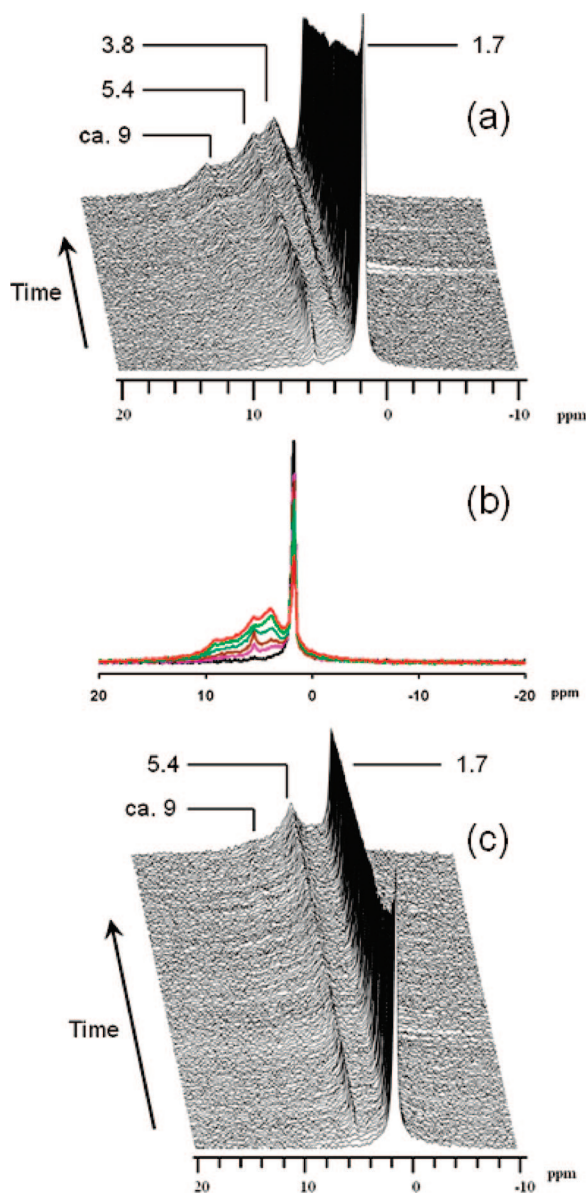
Figure 1. In situ ^1H NMR spectra recorded as a function of time during adsorption of water-h_2 on MCM-41 at 183 K: (a) stack plot of all data recorded, with time resolution of 320 s per spectrum, and (b) selected spectra recorded at 320 s (black), 2240 s (lilac), 4480 s (brown), 15 360 s (blue), 31 680 s (green), and 46 080 s (red). (c) In situ ^1H NMR spectra recorded as a function of time during adsorption of water-d_2 on MCM-41 at 183 K (time resolution 320 s per spectrum). The total time of the experiments was 12.8 h for (a) and 12.2 h for (c).

interact significantly with silanol groups. The ^1H NMR chemical shift is close to that (3.5 ppm) for physically adsorbed water on silica gel.[14]

At the start of the adsorption for water-h_2/MCM-41, the signal at 5.4 ppm dominates over the signal at 3.8 ppm, suggesting that, at this stage of the process, most water molecules become adsorbed on readily accessible silanol groups (e.g., near the apertures of the nanopores). The relative amount of physically adsorbed water (at 3.8 ppm) then grows steadily with time because the number of readily accessible silanol groups is limited.

Later in the adsorption process for water-h_2/MCM-41, and after establishing significant populations of physically adsorbed water-h_2 (3.8 ppm) and water-h_2 hydrogen bonded to silanol groups (5.4 ppm), an additional signal emerges at ca. 9 ppm. This signal is also observed for water-d_2/MCM-41, indicating that the water

molecules giving rise to it have undergone $^1H-^2H$ exchange (either direct $^1H-^2H$ exchange with silanol groups, or involving water molecules that previously underwent direct $^1H-^2H$ exchange with silanol groups). The emergence of the signal at ca. 9 ppm seems to coincide with broadening of the signal at 5.4 ppm, suggesting possible exchange of water between these sites. Although we cannot definitively assign the water environment at ca. 9 ppm, its emergence in the later stages of the adsorption may suggest that it arises from formation of larger water aggregates (e.g., clusters or adsorbed multilayers) and may represent a distribution of such environments.[15] Clearly, the ^1H chemical shift for such aggregates may differ from those of isolated water molecules adsorbed on MCM-41 (as observed early in the adsorption process) and bulk phases of water, although the high value of the ^1H chemical shift for this environment may be indicative that such aggregates are protonated (arising from proton exchange from the silanol groups).

Figure 2 shows ^1H NMR spectra for water-d_2/MCM-41 on increasing temperature from 193 to 273 K (after being at 183 K for over 12 h). Clearly, the intensity of the signal at 5.4 ppm increases significantly. At 223 K, the line width of this signal decreases abruptly, suggesting that a significant structural change occurs for this water environment, consistent with previous reports of a "phase transition" (at 240[2e] or 232 K[16]) for adsorbed water in MCM-41. The ^1H chemical shift also decreases as temperature is increased, toward that of bulk liquid water, and thus the "phase transition" may represent the transformation of the water in the nanopores from a number of relatively rigid environments to a more liquid-like phase. The intensities of the signals at 1.7 and ca. 9 ppm decrease as temperature is increased, becoming unobservable by 273 K. At 273 K, all ^1H environments in the material presumably undergo fast exchange on the time scale of the measurement, giving rise to a single narrow line close to that of bulk liquid water.

In addition to characterization of the redistribution of water molecules among different water environments as a function of time and temperature, as discussed above, the experiments carried out here also provide access to quantitative information on the kinetics of the adsorption process itself. Thus, appropriate integration of the ^1H NMR spectra recorded as a function of time yields the total amount of water adsorbed in the MCM-41 host material relative to the amount of ^1H sites present originally (in the silanol groups) in the MCM-41. As quantification of the concentration of silanol groups in the MCM-41 material used in the present work, an external reference is required containing a known amount of hydroxyl groups per unit mass. For this purpose, a sample of zeolite ZSM-5 with independently known Si/Al ratio (11.5), which corresponds to a concentration of bridging hydroxyl groups of 1.33 mmol g^{-1}, was used. Quantitative comparison of the ^1H NMR spectra recorded for a known mass of this ZSM-5 sample and a known mass of the MCM-41 sample used in the present work (before adsorption of water) indicated a silanol group concentration in the MCM-41 sample of 2.53 mmol g^{-1}. Integration of the ^1H NMR spectra recorded subsequently following adsorption of water on the MCM-41 host material was then used to deduce the total amount of water relative to the amount of MCM-41. Such analysis of the ^1H NMR spectra recorded as a function of time during the adsorption process at 183 K has been used to determine the kinetics of the total amount of water adsorbed, as shown in Figure 3. First, it is clear that the adsorption proceeds in two stages with different rates. Thus, there is an initial period of rapid adsorption up to ca. 1 wt % water, followed by a period of slower adsorption which proceeds throughout the remainder of the experiment (total time 12.8 h). Second, both regimes of the adsorption process are
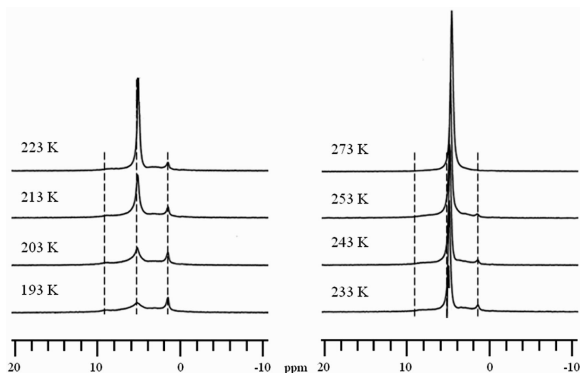
Figure 2. ^1H NMR spectra recorded on increasing temperature after adsorption of water-d_2 on MCM-41 at 183 K (and being held at 183 K for 12 h). Vertical dashed lines are at 9.0, 5.4, and 1.7 ppm.
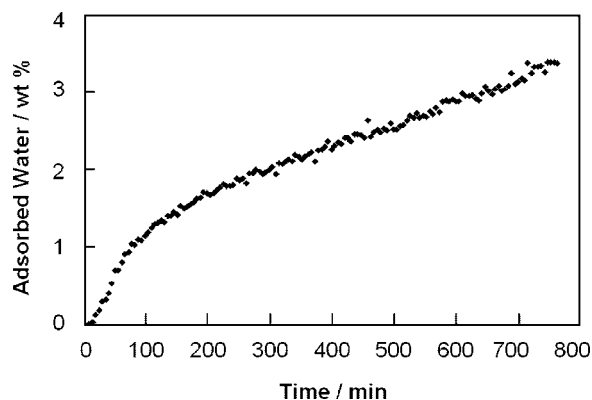

Figure 3. Total amount (expressed as wt %) of water adsorbed in MCM-41 as a function of time at 183 K, established from the ^1H NMR spectra recorded in situ during the adsorption process.

associated with a linear increase in the amount of water as a function of time, with the initial regime of rapid adsorption corresponding to a rate of 1.6×10^{-2} wt % min^{-1} and the subsequent regime of slower adsorption corresponding to a rate of 2.9×10^{-3} wt % min^{-1}. We suggest that the more rapid initial regime may be associated with water molecules populating the easily accessible adsorption sites near the entrance to the pores of the host material, with the implication that, once these sites are occupied, subsequent adsorption becomes hindered. The fact that the adsorption process exhibits linear time dependence in both regimes is consistent with the overall kinetics being governed by processes at the gas−solid interface (rather than, for example, diffusion within the pores) and under the assumption that the pressure of the water vapor inside the rotor remains constant[17] throughout the experiment.

While the ^1H NMR spectra allow the total amount of water adsorbed inside the pores of the MCM-41 host material to be established as a function of time, as discussed above, the rates of redistribution of the populations of the individual water sites cannot be established reliably from these spectra, as a consequence of the severe overlap of the peaks representing the different water sites. It is also relevant to note that the relatively abrupt change in the rate of water adsorption at ca. 1 wt %, corresponding to the transition from the initial rapid regime of water adsorption to the subsequent slower regime, is not associated with any abrupt change in the distribution of water molecules among the different adsorption sites (i.e., no abrupt change is observed at the corresponding value of time in the ^1H NMR spectra shown in Figure 1a).

In summary, this work demonstrates that, in the adsorption of water on the nanoporous material MCM-41, different water environments are populated at different stages of the process and reveals insights regarding the sequence in which these environments become populated and the exchange of water molecules between them. In contrast, ex situ studies of adsorption processes (e.g., with adsorption carried out external to the NMR spectrometer) cannot reveal such information. Clearly, the technique developed here for probing the sites populated at the very earliest stages of adsorption processes, and the subsequent evolution of the populations of these sites, creates new opportunities for investigating adsorption processes at an unprecedented level of detail. Furthermore, this work has also revealed new insights on aspects of the kinetics of the adsorption process, including the discovery that the adsorption occurs in two well-defined regimes corresponding to an initial regime of rapid adsorption and a subsequent regime of slower adsorption. In both regimes, the amount of water adsorbed increases linearly with time, and the ^1H NMR technique allows quantitative information on the rates of adsorption in these regimes to be established.

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(10) Unlike the procedure described previously,[6] the MCM-41 sample was *not* subjected, in a preliminary step, to fast spinning to form a cylindrical void along the axis of the rotor, prior to inserting the capillary tube.
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