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Probing the Evolution of Water Clusters During Hydration of the Solid Acid Catalyst H-ZSM-5

Kenneth D.M. Harris[1*], Mingcan Xu[1], John Meurig Thomas[1,2]

1 School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, Wales

2 Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, England

* Author for correspondence: HarrisKDM@cardiff.ac.uk

Abstract

A technique developed recently for *in situ* solid-state ^{1}H NMR studies of adsorption processes is applied to probe hydration of the solid acid catalyst H-ZSM-5, yielding information on the interaction between the adsorbed water molecules and Brønsted acid sites on the H-ZSM-5 host material. Quantitative analysis of the results from the *in situ* experiment allows the average size of water clusters associated with the Brønsted acid sites to be determined directly, and suggests that there is a preference to form clusters comprising 5 – 6 water molecules. The *in situ* ^{1}H NMR data also provide insights on kinetic aspects of the adsorption process.

Introduction

Zeolites are essential catalysts for many important industrial processes [1-10]. An important aspect of the catalytic role of these microporous aluminosilicate materials is the fact that they contain Brønsted acid sites, while another important aspect is the concept of "shape selectivity", in which the course of a reaction can be governed by the geometric properties of the channels and cavities within the zeolite framework. In the H-form of a zeolite, the Brønsted acid site is the bridging hydroxyl group between SiO_4 and AlO_4 tetrahedra, and there is one Brønsted acid site for each aluminium atom in the framework. The overall density of Brønsted acid sites therefore depends on the Si/Al ratio (although we note that the density of Brønsted acid sites may not necessarily be uniform throughout the material). We focus here on the widely studied zeolite ZSM-5 in its H-form, denoted H-ZSM-5. The framework structure of ZSM-5 comprises straight channels of diameter *ca*. 0.51 – 0.56 nm and zigzag channels of diameter *ca*. 0.54 – 0.56 nm. The two types of channel intersect each other, giving rise to a three dimensional network of inter-connected channels.

Although the hydration of zeolitic solids has been studied for many years, including some notable early contributions [1,11-13], several aspects of the hydration of these materials remain to be understood. Fortunately, the continual development of new experimental approaches provides opportunities to advance an understanding of this subject. The specific focus of the present work is to probe the interaction of adsorbed water molecules with Brønsted acid sites in zeolitic solids, and to assess the extent of aggregation of water molecules at these sites. An important question is whether well-defined clusters of water molecules are associated with the Brønsted acid sites, and if so, to establish the structural evolution of such water clusters during the adsorption process. We focus specifically on the adsorption of water in a dehydrated sample of H-ZSM-5, and we exploit a solid-state NMR technique that has been developed recently for *in situ* studies of absorption processes [14-16]. This technique allows NMR spectra to be recorded as a function of time during the adsorption process, and may be exploited to identify the specific sites involved in the adsorption process and to probe the evolution of the populations of these sites as a function of time. We demonstrate here that this technique can yield quantitative insights concerning the aggregation of water molecules at the Brønsted acid sites of H-ZSM-5.

Brief Resumé of the *In Situ* Solid-State NMR Technique

The experimental set-up for the *in situ* solid-state NMR technique [14] is shown in Figure 1. A powder sample of the material on which the adsorption is to take place (in this case dehydrated H-ZSM-5) is loaded into a solid-state NMR rotor, and a sealed glass capillary tube containing the species to be adsorbed (in this case water) is also inserted into the rotor. The NMR rotor is then subjected to rapid sample spinning (i.e. magic angle spinning, MAS) that is required for recording high-resolution solid-state NMR spectra [17-19]. The centripetal force produced by the sample spinning is sufficient to break the glass capillary tube, thus releasing the water within the rotor and triggering the process of hydration of the H-ZSM-5 host material. As water is a solid in the temperature regime relevant to the present work (see below), the adsorption of water within the H-ZSM-5 sample proceeds *via* the vapour phase [20]. The high-resolution solid-state NMR spectrum (in the present case, ^{1}H NMR) is recorded immediately after stable sample spinning is attained. Because the adsorption process is triggered by bringing the adsorbate and adsorbent directly into contact inside the NMR rotor, the adsorption process can be monitored from the very earliest stages, and the subsequent evolution of the adsorbed states of the water molecules (identified from the NMR spectrum) can be mapped as a function of time. The time-resolution of the experiment is dictated by the time to record an individual NMR spectrum (*ca*. 10 minutes for ^{1}H NMR spectra under the conditions used here). In order to follow the time-dependence of the adsorption process, the rate of adsorption may be adjusted by carrying out the experiment at a suitable temperature (in the present case 183 K).

Experimental Details

The sample of H-ZSM-5 used in the present work was prepared by dehydration [at 200 ºC for 12 hours under vacuum (*ca*. 10^{-3} mbar)] followed by deammoniation [at 450 ºC for 12 hours under vacuum (*ca*. 10^{-3} mbar)] of a sample of the ammonium form of ZSM-5. The sample of the ammonium form of ZSM-5 was purchased from Zeolyst (SiO_2/Al_2O_3 = 23; residual Na^+ corresponding to Na_2O wt.% = 0.05). Given the known mass of the sample of H-ZSM-5 used in our experiment and the known Si/Al ratio, the total number of Brønsted acid sites within the sample is estimated to be N_B^{total} = 3.99×10^{-5} mol. As discussed in the Appendix, this value is required to establish an absolute scaling of the ^{1}H NMR spectra.

A known amount of deionized water (5 mg) was sealed in a glass capillary tube of 0.7 mm diameter (Capillary Tube Supplies Ltd). A known amount of H-ZSM-5 (30 mg) and the sealed glass capillary tube were transferred to a MAS NMR rotor (4 mm diameter) in a glove box under a flow of nitrogen gas. Solid-state ^{1}H MAS NMR experiments were carried out on a Chemagnetics CMX-Infinity 300 spectrometer (^{1}H frequency, 300.146 MHz). In the *in situ* solid-state ^{1}H NMR experiment, the MAS NMR rotor containing the H-ZSM-5 sample and water (inside the capillary tube) was maintained at 183 K for at least 30 min (with no MAS) before triggering the adsorption process by subjecting the rotor to MAS at 12 kHz. As soon as stable MAS was attained (after *ca*. 1 min), ^{1}H MAS NMR spectra were recorded. The recycle delay was 10 s and 64 scans were accumulated for each ^{1}H MAS NMR spectrum (total time to record each spectrum *ca*. 640 s).

Results and Discussion

It is well-established [22] that dehydrated H-ZSM-5 gives rise to ^{1}H NMR resonances at 4.3 ppm and 1.7 ppm, assigned to the Brønsted acid sites and silanol groups (SiOH) respectively. A broad signal is also observed at *ca*. 7 ppm, and is assigned to another type of bridging hydroxyl group which interacts with other oxygen atoms of the H-ZSM-5 framework [22-24]. We refer to these bridging hydroxyl groups as "framework-interacting" bridging hydroxyl groups (as distinct from the "free" Brønsted acid sites that give rise to the resonance at 4.3 ppm).

The first ^{1}H MAS NMR spectrum recorded in our *in situ* study, immediately after the start of the adsorption process (Figure 2a,b), exhibits only the resonances at 1.7 ppm, 4.3 ppm and *ca*. 7 ppm characteristic of dehydrated H-ZSM-5 discussed above. As time progresses during the adsorption process, the intensity of the original resonance due to "free" Brønsted acid sites (at 4.3 ppm) decreases, and simultaneously a new resonance emerges and grows at 7.2 ppm (Figure 2a,c). The new resonance at 7.2 ppm is overlapped with the broad resonance at *ca*. 7 ppm (assigned to "framework-interacting" bridging hydroxyl groups) present in the original sample of dehydrated H-ZSM-5.

The isotropic ^{1}H chemical shift of the new ^{1}H resonance at 7.2 ppm is different from that for physically adsorbed water molecules in other silica-based materials [for example, the siliceous nanoporous material MCM-41 (3.8 ppm [15]) and silica gel (3.5 ppm [25])] and is different from that for water molecules interacting with silanol groups (5.4 ppm [15]). The fact that the observed ^{1}H

resonance for water is at significantly lower field (7.2 ppm) is consistent with the water molecules interacting with Brønsted acid sites (as also discussed previously [26]). Although the water molecules interacting with the Brønsted acid sites may encompass a range of structurally distinguishable environments (for example, occupying different sites within clusters of water molecules, as discussed below), individual ^{1}H resonances for different water environments are not resolved. In this regard, we note that the ^{1}H resonances are intrinsically broad as a consequence of strong ^{1}H–^{1}H dipolar coupling. In addition, we cannot rule out the possibility that exchange of water molecules occurs among different water environments, such that only an averaged ^{1}H resonance is observed for all the water molecules that interact with a given Brønsted acid site. Thus, the observed ^{1}H resonance at 7.2 ppm subsumes the signals due to all the water molecules that interact with Brønsted acid sites. The position of this resonance shifts only slightly (to higher field) as the amount of adsorbed water increases. Throughout the adsorption process, there is no evidence from the ^{1}H NMR spectrum for the emergence of any other new peaks representing other water environments within the H-ZSM-5 host structure.

In the original sample of dehydrated H-ZSM-5, the ^{1}H resonance at 4.3 ppm represents "free" Brønsted acid sites that do not interact with any guest molecules nor with framework oxygen atoms. The intensity of this resonance decreases as a function of time during the hydration process, indicating that the ^{1}H resonance for Brønsted acid sites that interact with water molecules ("hydrated" Brønsted acid sites) is shifted from 4.3 ppm. As the only ^{1}H resonance that increases in intensity during the hydration process is the resonance at 7.2 ppm (already assigned to water molecules), it must be deduced that the hydrated Brønsted acid sites *also* contribute to this resonance (it is well established that the ^{1}H chemical shift for Brønsted acid sites engaged in hydrogen bonding interactions with guest molecules [22,26-28] is significantly higher than that for "free" Brønsted acid sites) Thus, the ^{1}H resonance at 7.2 ppm comprises unresolved contributions from adsorbed water molecules interacting with Brønsted acid sites, the hydrated Brønsted acid sites, and the "framework-interacting" bridging hydroxyl groups (at *ca*. 7 ppm). We note that the ^{1}H chemical shift (1.7 ppm) and intensity of the resonance for the silanol groups remain constant throughout the hydration process (see Figure 3).

To establish more detailed insights on the hydration process, we now consider the time-dependence of the number of water molecules that interact with Brønsted acid sites (denoted N_w)

and the time-dependence of the number of hydrated Brønsted acid sites (denoted N_{BH}). Details of the procedure to extract values of $N_w(t)$ and $N_{BH}(t)$ from quantitative lineshape analysis of the *in situ* ^{1}H NMR spectra are elaborated in the Appendix.

Plots of $N_w(t)$ *versus* time and $N_{BH}(t)$ *versus* time are shown in Figure 3, and plots of $N_w(t)/N_{BH}(t)$ *versus* time and $N_w(t)/N_{BH}(t)$ *versus* $N_{BH}(t)/N_B^{total}$ are shown in Figures 4 and 5 respectively. Clearly, N_w/N_{BH} represents the average number of water molecules that interact with each hydrated Brønsted acid site, and N_{BH}/N_B^{total} represents the fraction of Brønsted acid sites that are hydrated. At early stages of the adsorption process, the values of both N_w and N_{BH} are low, and the fluctuation in these values (due to uncertainties in the lineshape fitting process) is comparable to the values themselves. This fact is evident from the data at low values of time (less than *ca*. 30000 s) in Figure 3. As a consequence, at low values of time, the values of N_w/N_{BH} exhibit large fluctuations. For this reason, Figures 4 and 5 show only the values of N_w/N_{BH} corresponding to times greater than 25000 s.

As shown in Figure 3, both N_w and N_{BH} increase linearly as a function of time. At about 29000 s, there is an abrupt change in the rate of increase of N_w and also (although to a lesser extent) a change in the rate of increase of N_{BH}. At the time of the abrupt change in the rate of adsorption (i.e. dN_w/dt), the loading of water is *ca*. 0.88 wt. % and the fraction of Brønsted acid sites that are hydrated (i.e. N_{BH}/N_B^{total}) is *ca*. 0.17. Given the abrupt change in the rate of adsorption at *ca*. 29000 s, the hydration process may be considered in terms of two regimes. In the first regime (up to *ca*. 29000 s), the rate of increase of N_w is 4.52×10^{-10} mol s^{-1} and the rate of increase of N_{BH} is 8.48×10^{-11} mol s^{-1}. In the second regime (after *ca*. 29000 s), the rate of increase of N_w is 3.04×10^{-9} mol s^{-1} and the rate of increase of N_{BH} is 4.65×10^{-10} mol s^{-1}. The total duration of the experiment was 59200 s. At the end of the experiment, the fraction of hydrated Brønsted acid sites (N_{BH}/N_B^{total}) is 0.49, and the total amount of adsorbed water corresponds to *ca*. 6.2 wt. % (representing *ca*. 37 % of the total amount of water introduced into the NMR rotor at the start of the *in situ* NMR experiment).

At present, we have not yet established whether the abrupt change in the rate of adsorption observed at *ca*. 29000 s in Figure 3 is an intrinsic feature of the adsorption process in this system or a consequence of the specific experimental conditions under which the adsorption process was carried out. With regard to the latter, it is conceivable that the abrupt increase in dN_w/dt may be related to changes in water vapour pressure inside the MAS NMR rotor, although for our current experimental

set-up, we have no means of monitoring the water vapour pressure inside the MAS NMR rotor during the *in situ* NMR experiment.

The ratio N_w/N_{BH} represents the average number of water molecules associated with each *hydrated* Brønsted acid site, and the time-dependence of this ratio is shown in Figure 4. As discussed above, values of N_w/N_{BH} exhibit significant scatter at low values of time, but from *ca*. 25000 s and throughout the second regime of the adsorption process, the value of N_w/N_{BH} fluctuates about a constant value of approximately $N_w/N_{BH} \approx 5 - 6$ (see Figure 4). At the end of the experiment, the average cluster size (averaged over the period of time from 50000 s to 59200 s) is $N_w/N_{BH} = 5.4$.

At the end of the *in situ* ^{1}H NMR experiment, 49 % of the Brønsted acid sites are hydrated. The fact that the average number of water molecules associated with each hydrated Brønsted acid site is as high as 5.4, while 51 % of Brønsted acid sites remain "free" (i.e. non-hydrated), indicates that the distribution of water molecules among the Brønsted acid sites is distinctly non-uniform. Importantly, as shown in Figures 4 and 5, the same distribution comprising hydrated Brønsted acid sites associated with an average of 5 – 6 water molecules and non-hydrated Brønsted acid sites persists throughout the majority of the hydration process (at least from *ca*. 30000 s until the end of the experiment), while only the relative amounts of hydrated and non-hydrated Brønsted acid sites changes. These observations are fully consistent with a hydration model involving a significant preference for the formation of clusters of water molecules of a specific preferred size interacting with the Brønsted acid sites, rather than the hydration of all Brønsted acid site uniformly. Although N_w/N_{BH} represents an average number of water molecules associated with each hydrated Brønsted acid site (and does not provide information on the actual *distribution* of sizes of water clusters), the time-evolution of N_w/N_{BH} nevertheless provides a strong constraint in understanding mechanistic aspects of the adsorption process, and serves as basis to rule out a range of alternative hydration models.

For example, we first consider an alternative hydration model in which a range of different cluster sizes may exist during the hydration process. In this case, the distribution of cluster sizes at a given stage of the process would depend on the rate at which water molecules become available for growth (i.e. the rate of water adsorption) and the relative rates of growth of clusters of different sizes n (in each case to form the cluster of increased size n+1). For such a model, the distribution of cluster sizes (and hence the average cluster size N_w/N_{BH}) may be expected to show a complicated time dependence, but the value of N_w/N_{BH} should nevertheless exhibit a monotonic increase as the total

amount of adsorbed water increases. Second, we consider another type of model involving the hydration of all Brønsted acid sites initially by a single water molecule, followed by hydration of all Brønsted acid sites by a second water molecule, and so on. In this case, the value of N_w/N_{BH} should remain constant at $N_w/N_{BH} = 1$ up to the point at which the fraction of hydrated Brønsted acid sites reaches $N_{BH}/N_B^{total} = 1$. Clearly, the time-evolution of N_w/N_{BH} and N_{BH}/N_B^{total} for both of these alternative models would be different from that observed in the present work (Figure 5).

A relevant issue in the hydration of zeolites in the H-form is the extent to which proton transfer occurs from the Brønsted acid sites to the water molecules. In the present case, proton transfer from a Brønsted acid site to the cluster of water molecules $(H_2O)_n$ with which it interacts would form a protonated cluster $H(H_2O)_n^+$, giving rise to an ion-pair species with a negatively charged site on the framework. Alternatively, the Brønsted acid site may be engaged in hydrogen bonding to the water cluster $(H_2O)_n$ without proton transfer. From previous studies, the ^{1}H chemical shift of a protonated water molecule is expected to be in the region *ca.* 7 – 12 ppm [26], and thus the observed ^{1}H chemical shift for the adsorbed water molecules in H-ZSM-5 (7.2 ppm) may be consistent with some degree of protonation of the water clusters. In this regard, we note that the proton affinities of clusters of water molecules are higher than that of a single water molecule [29,30], and proton transfer may therefore be more favourable for water clusters of the size implicated here than for an individual water molecule. Although the ^{1}H resonance at 7.2 ppm shifts very slightly (to higher field) as the adsorption progresses, there is no evidence for any significant change in the protonation state of the water clusters (which may be expected to cause a significant shift in this resonance) during the hydration process. This observation is again consistent with a hydration model in which the size of water clusters remains approximately constant (while the number of such water clusters increases) throughout the hydration process. As discussed above, the ^{1}H resonance at 7.2 ppm includes contributions from ^{1}H nuclei in *both* the adsorbed water molecules and the hydrated Brønsted acid sites. Thus, our analysis of the time-dependence of the hydration process (see Appendix) and our conclusions concerning the clustering of water molecules at the Brønsted acid sites still hold irrespective of the extent of proton transfer between the hydrated Brønsted acid sites and the water clusters.

Concluding Remarks

In conclusion, our *in situ* solid-state ^{1}H NMR study of the hydration of H-ZSM-5 is fully consistent with a model in which there is a significant preference for the formation of clusters of well-defined size (comprising 5 or 6 water molecules) interacting with each hydrated Brønsted acid site. Importantly, while the number of hydrated Brønsted acid sites increases continuously throughout the hydration process, the average cluster size remains essentially constant, suggesting that a specific favourable cluster size is formed in preference, for example, to a uniform hydration of all available Brønsted acid sites. Clearly, the size and shape of the space available inside the H-ZSM-5 host structure may dictate the maximum size of water clusters that can be formed in the region of a given Brønsted acid site.

While the results reported here indicate that the *cluster size distribution* is distinctly non-uniform, with the Brønsted acid sites either being hydrated by clusters comprising 5 or 6 water molecules or remaining non-hydrated, the technique employed in the present work does not provide any information on the *spatial distribution* of the water clusters within the H-ZSM-5 host structure, nor any information on the way in which the spatial distribution of the water clusters varies as a function of time. Depending on the rate of diffusion of water molecules into and through the H-ZSM-5 host structure and the rate of growth of water clusters at the Brønsted acid sites, it is reasonable to expect that the spatial distribution of the water clusters may change in a well-defined manner as a function of time during the hydration process, while maintaining an essentially constant cluster size distribution, as reported above. We also note that, while the size distribution of the water clusters interacting with the Brønsted acid sites is dominated by clusters comprising 5 – 6 water molecules, the existence of small populations of transient clusters comprising between 1 and 4 water molecules cannot be discounted, as such water clusters may well represent intermediates during the formation of clusters of the preferred size (i.e. 5 – 6 water molecules) at the Brønsted acid sites.

We note that adsorption water in H-ZSM-5 has also been studied previously by equilibrium gravimetric measurements [31], and the reported results are also consistent with the formation of small clusters of water molecules (comprising *ca*. 4 water molecules) associated with each Brønsted acid site. However, we emphasize that our *in situ* NMR technique allows details of changes in the interactions involving the water molecules to be studied as a function of time during the adsorption process, rather than simply measuring the total amount of water adsorbed in the equilibrium state of

the system. Thus, as discussed above, our *in situ* NMR technique allows the relative amounts of hydrated and non-hydrated Brønsted acid sites to be quantified, giving access to quantities (e.g. N_w/N_{BH}) that are inaccessible by the type of gravimetric approach reported in ref. 31. We emphasize that our ability to determine N_w/N_{BH}, and to probe the variation of N_w/N_{BH} during the adsorption process, are key aspects of our analysis. In addition, while studies of the final equilibrium state of an absorption process can provide valuable information, we emphasize that our *in situ* NMR technique allows the evolution of the adsorption process to be studied from its earliest stages until the equilibrium state is reached. The time-dependence of N_w/N_{BH} conveys significant insights concerning the clustering of water molecules during the adsorption process, which could not be established simply by observing the final equilibrium state of the system.

Finally, we note that ^{1}H multiple quantum NMR techniques have been exploited [32] (together with ^{129}Xe NMR) in order to probe the distribution of guest molecules in zeolites (demonstrated for the case of hexamethylbenzene in zeolite Na-Y), and in particular to "count" the number of ^{1}H nuclei involved in guest clusters. Clearly, the combination of ^{1}H multiple quantum NMR together with the *in situ* strategy employed in the present work should create interesting prospects for future studies of changes in the clustering of guest molecules within a zeolite as a function of time during adsorption processes.

Acknowledgements

We are grateful to Cardiff University for financial support.

Appendix

We define $N_w(t)$ as the number of water molecules that interact with Brønsted acid sites at time t, $N_{BH}(t)$ as the number of hydrated Brønsted acid sites (i.e. Brønsted acid sites that interact with water molecules), $N_{BF}(t)$ as the number of "free" Brønsted acid sites (giving rise to the ^{1}H resonance at 4.3 ppm), and N_{BI} as the number of "framework-interacting" bridging hydroxyl groups (giving rise to the ^{1}H resonance at *ca*. 7 ppm in the original sample of H-ZSM-5). We make the reasonable assumption that the adsorbed water molecules preferentially interact with the "free" Brønsted acid sites (which are not already engaged in any hydrogen bonding interactions) rather than with the "framework-interacting" bridging hydroxyl groups (which are already engaged in such interactions with framework oxygen atoms). On this basis, N_{BI} remains constant during the hydration process, whereas N_{BH} and N_{BF} vary as a function of time.

In the following discussion, $I_\Sigma(t)$ denotes the total integral of the ^{1}H NMR spectrum recorded at time t, $I_{4.3}(t)$ denotes the integral of the ^{1}H resonance at 4.3 ppm, and $I_{7.2}(t)$ denotes the integral of the ^{1}H resonance at 7.2 ppm (which also includes the broad resonance at *ca*. 7 ppm present in the original sample of dehydrated H-ZSM-5).

As the ^{1}H resonance at 4.3 ppm is assigned as "free" Brønsted acid sites, the integral of this resonance $I_{4.3}(t)$ is proportional to $N_{BF}(t)$:

$$I_{4.3}(t) = S\, N_{BF}(t) \qquad (1)$$

where S denotes the scaling factor between the number of ^{1}H nuclei and signal intensity.

As the signal observed in the ^{1}H NMR spectrum at 7.2 ppm includes the unresolved ^{1}H resonances due to the adsorbed water molecules, hydrated Brønsted acid sites and "framework-interacting" bridging hydroxyl groups (*ca*. 7 ppm), the integral of this resonance $I_{7.2}(t)$ is:

$$I_{7.2}(t) = S\, \{2N_w(t) + N_{BH}(t) + N_{BI}\} \qquad (2)$$

with the factor of 2 arising because each water molecule has two ^{1}H nuclei.

The total number of Brønsted acid sites is independent of time, and is given by:

$$N_B^{\text{total}} = N_{BF}(t) + N_{BH}(t) + N_{BI} \qquad (3)$$

For the original sample of dehydrated H-ZSM-5 (i.e. at $t = 0$), $N_{BH}(0) = N_w(0) = 0$, and therefore:

$$N_B^{total} = N_{BF}(0) + N_{BI} \quad (4)$$

And at $t = 0$, the integral of the signal at 7.2 ppm is:

$$I_{7.2}(0) = S\, N_{BI} \quad (5)$$

The total integral of the ^{1}H resonances at 4.3 ppm and *ca*. 7 ppm at $t = 0$ is therefore:

$$I_{4.3}(0) + I_{7.2}(0) = S\, \{N_{BF}(0) + N_{BI}\} = S\, N_B^{total} \quad (6)$$

As discussed in the main text, N_B^{total} is known independently of the ^{1}H NMR data, and the scaling factor S is therefore determined directly from:

$$S = \{I_{4.3}(0) + I_{7.2}(0)\} / N_B^{total} \quad (7)$$

The total integral of the ^{1}H NMR spectrum at time t is (where N_{SiOH} denotes the number of silanol groups):

$$I_\Sigma(t) = S\, \{N_{BF}(t) + N_{BH}(t) + N_{BI} + 2\, N_w(t) + N_{SiOH}\} \quad (8)$$

$$I_\Sigma(t) = S\, \{N_B^{total} + 2\, N_w(t) + N_{SiOH}\} \quad (9)$$

and at $t = 0$, the total integral is

$$I_\Sigma(0) = S\, \{N_B^{total} + N_{SiOH}\} \quad (10)$$

Thus, recalling that N_B^{total} and N_{SiOH} are independent of time, $N_w(t)$ is determined directly from:

$$N_w(t) = \{I_\Sigma(t) - I_\Sigma(0)\} / 2\,S \quad (11)$$

By rearranging equation (3),

$$N_{BH}(t) = N_B^{\text{total}} - N_{BI} - N_{BF}(t) \quad (12)$$

At $t = 0$, $N_{BH}(0) = 0$, and thus

$$N_{BF}(0) = N_B^{\text{total}} - N_{BI} \quad (13)$$

Hence, we have

$$N_{BH}(t) = N_{BF}(0) - N_{BF}(t) \quad (14)$$

and by using equation (1), which relates $N_{BF}(t)$ to $I_{4.3}(t)$, we obtain:

$$N_{BH}(t) = \{I_{4.3}(0) - I_{4.3}(t)\} / S \quad (15)$$

The values of $N_w(t)$ and $N_{BH}(t)$ reported in Figures 3 – 5 were determined using equations (11) and (15) respectively.

Figure Captions for On-line Version (Colour)

Figure 1 Schematic illustration of the set-up for the *in situ* adsorption experiment inside a solid-state NMR rotor.

Figure 2 (a) Stack plot of all *in situ* ^{1}H MAS NMR spectra recorded as a function of time during the adsorption of water in H-ZSM-5 at 183 K (time resolution 640 s per spectrum). Individual ^{1}H MAS NMR spectra are also shown: (b) the first spectrum recorded (representing essentially the sample of dehydrated H-ZSM-5), and (c) the spectrum recorded at 8.3 h.

Figure 3 Results from quantitative lineshape fitting of the *in situ* ^{1}H MAS NMR spectra recorded as a function of time at 183 K during the adsorption process. Blue diamonds: total amount of water adsorbed (N_w). Purple triangles: total amount of Brønsted acid sites that interact with water molecules (N_{BH}). Red squares: total amount of silanol groups (N_{SiOH}).

Figure 4 The ratio N_w/N_{BH} (the average number of water molecules per hydrated Brønsted acid site) as a function of time, established from the *in situ* ^{1}H MAS NMR spectra recorded at 183 K. As discussed in the text, the data shown are from t = 25000 s – 59200 s.

Figure 5 The ratio N_w/N_{BH} plotted *versus* N_{BH}/N_B^{total} (the fraction of Brønsted acid sites that are hydrated), established from the *in situ* ^{1}H MAS NMR spectra recorded at 183 K. As discussed in the text, the data shown correspond to t = 25000 s – 59200 s.

Figure Captions for Printed Version (Black/White)

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Figure 1

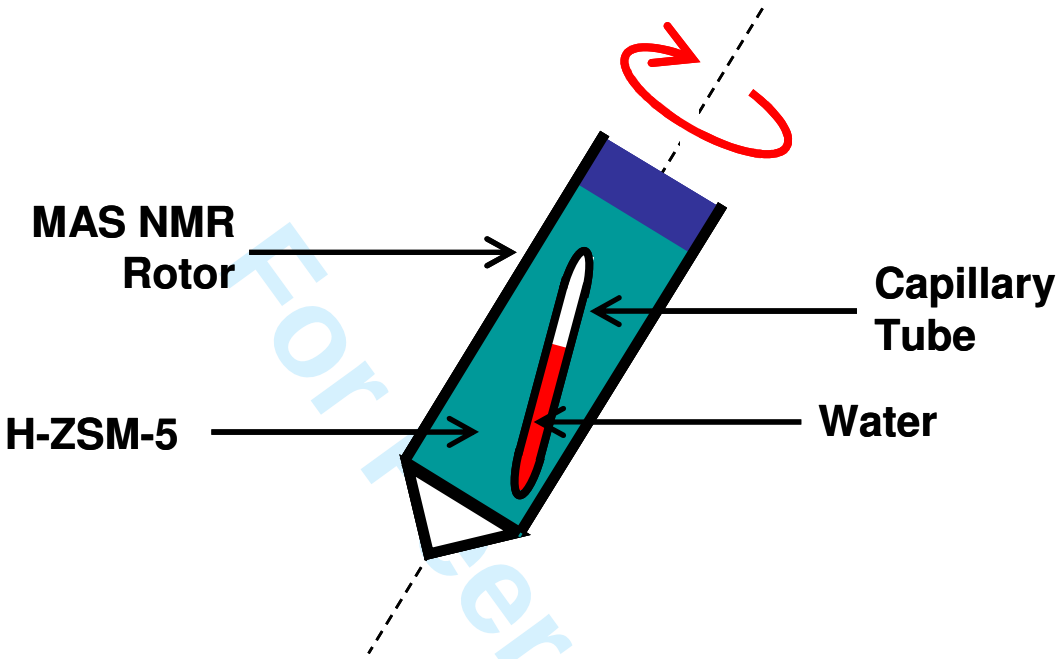

Figure 2

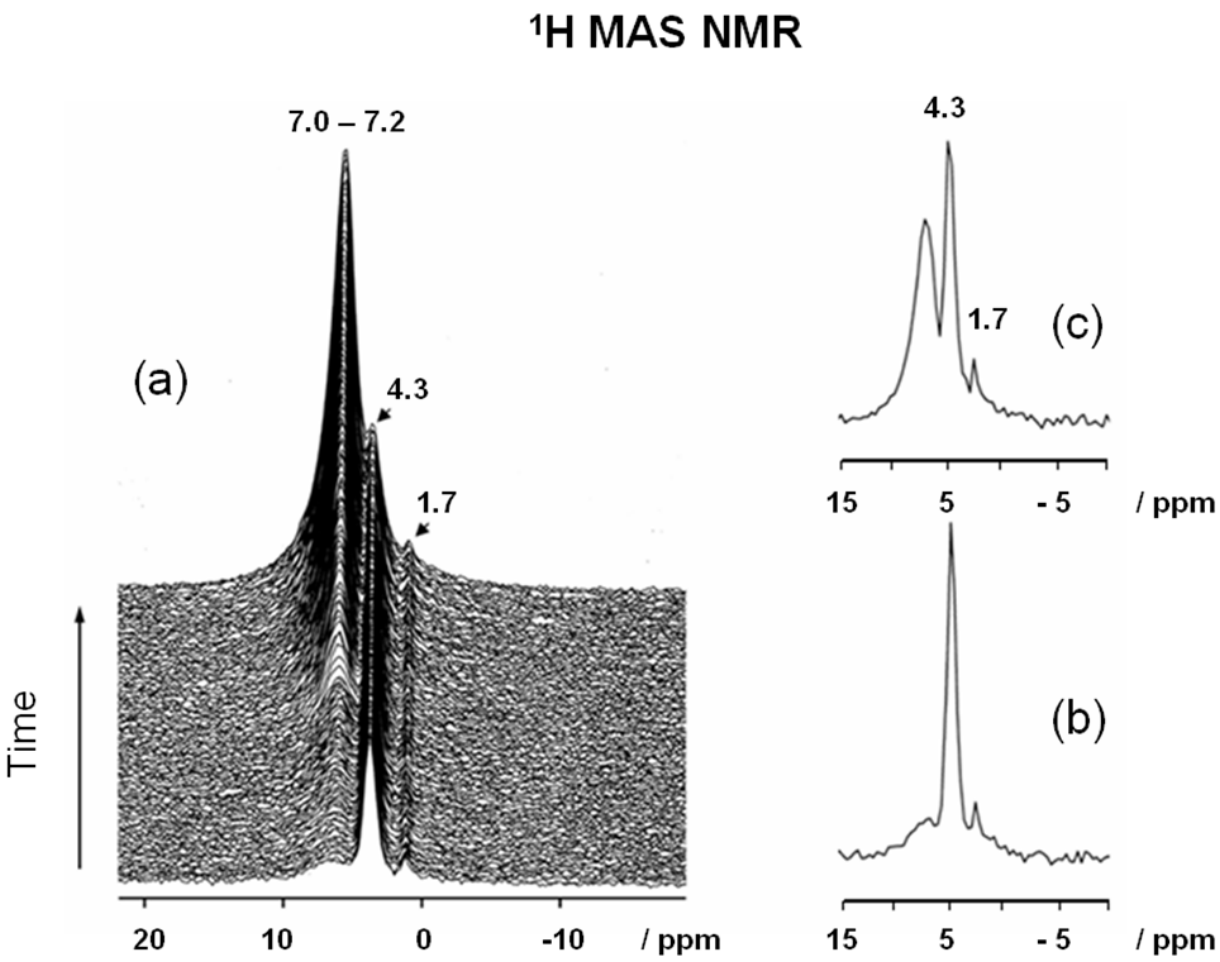

Figure 3

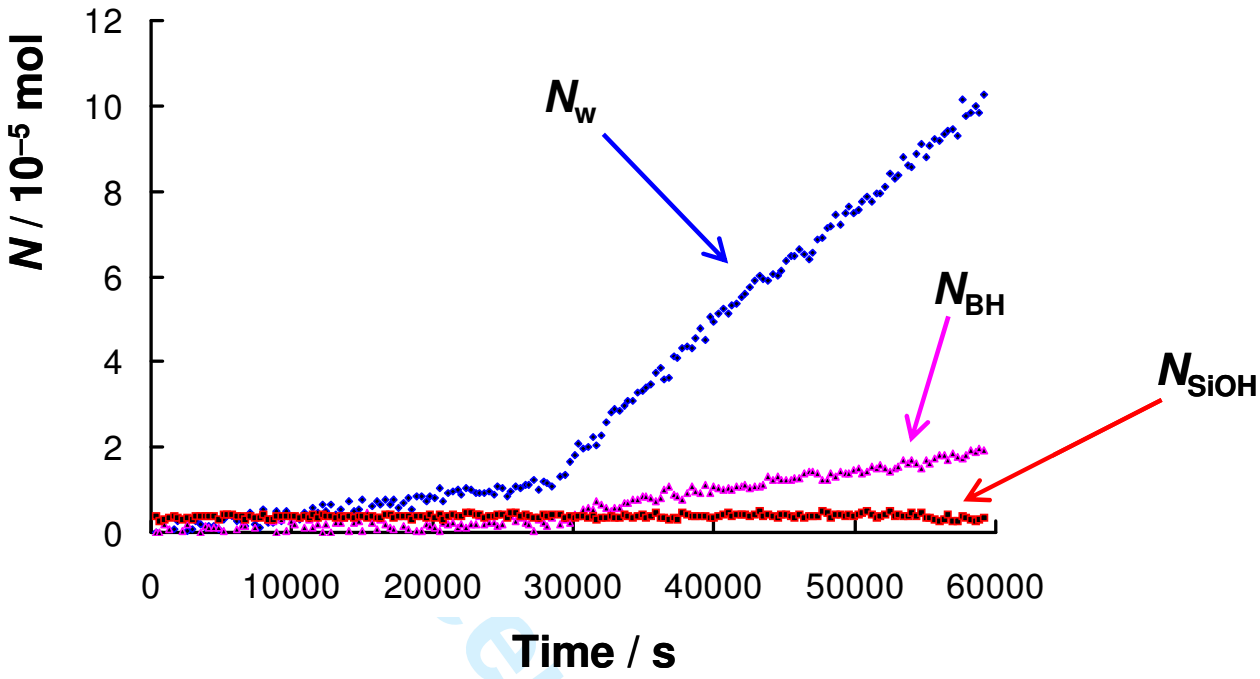

Figure 4

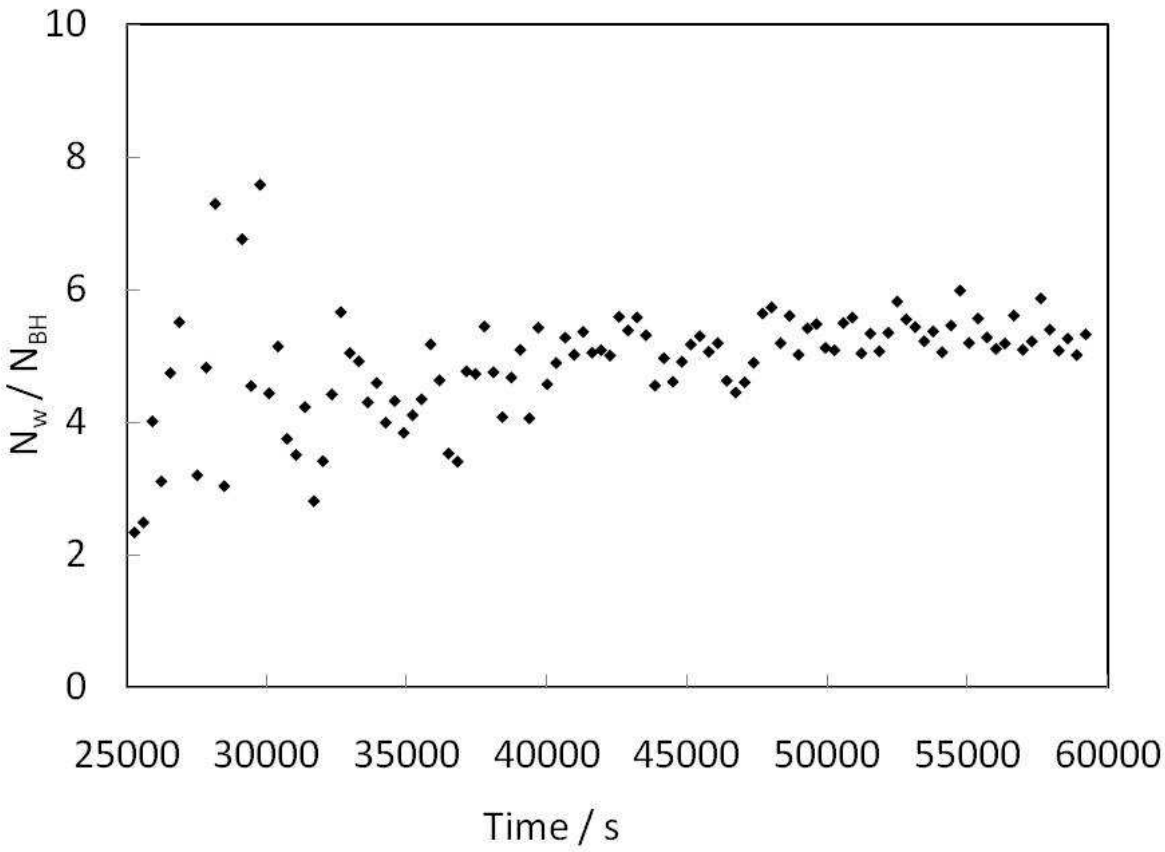

Figure 5