Temperature and hydration dependence of proton MAS NMR spectra in MCM-41: Model based on motion induced chemical shift averaging

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ABSTRACT

The proton MAS NMR spectra in MCM-41 at low hydration levels (less than hydration amounting to one water molecule per surface hydroxyl group) show complex proton resonance peak structures, with hydroxyl proton resonances seen in dry MCM-41 disappearing as water is introduced into the pores and new peaks appearing, representing water and hydrated silanol groups. Surface hydroxyl group–water molecule chemical exchange and chemical shift averaging brought about by a water molecule visiting different surface hydrogen bonding sites have been proposed as possible causes for the observed spectral changes. In this report a simple model based on chemical shift averaging, due to the making and breaking of hydrogen bonds as water molecules move on the MCM-41 surface, is shown to fully reproduce the NMR spectra, both as a function of hydration and temperature. Surface proton–water proton chemical exchange is not required in this model at low hydration levels.

1. Introduction

Over the past two decades mesoporous MCM-41 [1] has received considerable attention due to its large potential in industrial applications arising from its large specific surface area, relative ease of synthesis, and its well defined pore shape (hexagonal pore channels of uniform diameter). The material also serves as a model system for studies of water molecule dynamics, water phases, and water–surface interactions in confined geometries. Nuclear Magnetic Resonance (NMR) has enjoyed considerable success in these studies and has been applied to characterize different hydration sites on the MCM-41 surface, study various interactions between water molecules and surface hydroxyl groups, observe phase changes of water inside the pores and study chemical exchange in this material [2–15]. As the hydration level is increased in the MCM-41 material from the dry state, it has been found that the surface OH proton resonances seen in the 1–4 ppm region begin to disappear, and are no longer visible at hydration levels above approximately 0.2 monolayer surface coverage [6]. A monolayer is the amount of water needed to cover the pore surface of the material with one layer of water molecules, where each water molecule is assumed to occupy a $0.3 \times 0.3 \ nm^2$ area on the surface. Both chemical exchange and the

surface hopping of water molecules, resulting in the coalescence of water proton and surface OH proton resonances, have been put forth as explanations for the apparent disappearance of the surface hydroxyl group proton resonances [6,7]. In the present study a model for chemical shift averaging is applied that involves chemical shift changes in the water proton and OH group proton resonances resulting from the making and breaking of hydrogen bonds as water molecules undergo translational and rotational motion on the surface. The model is able to reproduce the experimental ^1H MAS NMR spectra for hydration levels up to 0.2 monolayers, and over a temperature range of 200–325 K, without the need for surface OH proton–water proton magnetization exchange brought about by chemical exchange between surface OH groups and water molecules. Definitive spectral assignment for the resonances associated with hydrated and unhydrated hydroxyl groups, as well as the water protons, has been achieved.

2. Experimental

The details regarding the synthesis and characterization of MCM-41 have been discussed extensively in the literature [1,16]. In this work, the MCM-41 material was obtained from Sigma-Aldrich Canada (Oakville, Ontario). Nitrogen adsorption and desorption measurements were carried out on a Quantochrome Autosorb automated gas sorption system at 77 K with an out-gas

temperature of 473 K. From these measurements it was deduced that the specific surface area for our samples was $S = 1132$ m^2/g. To hydroxylate the MCM-41 surface, the material was fully saturated with deionized water, and allowed to stand for one week. The samples were placed in a 10^{-6} bar vacuum, at 350 K, for 12 h to dry.

In order to hydrate the samples to a desired water content, dry, hydroxylated MCM-41 was placed into a pre-weighed NMR tube. The sample tube was opened to the air for a fixed amount of time and the corresponding hydration level by weight was determined. Hydration levels of up to roughly 0.2 monolayers are studied. At this hydration level the ratio of water molecules to surface silanol groups is approximately 1:1. This ratio was determined from the signal amplitudes of known amounts of water, dry MCM-41, and hydrated samples.

The ^{1}H MAS NMR experiments were performed at 11.7 T with a spinning rate of 10 kHz. The spectra were recorded using a Bruker DMX 500 spectrometer (Bruker BioSpin Ltd, Milton, Ontario). The NMR tube used was a zirconia rotor of 4 mm O.D., which was fitted with a special rotor cap with O-ring (Wilmad LabGlass Company, Buena, New Jersey) in order to maintain the desired hydration level. A Bruker BVT3000 temperature controller maintained the sample at the desired temperature to within 0.2°, over the temperature range 200–325 K.

All chemical shifts, δ, are expressed in ppm, relative to tetramethyl silane (TMS) as an external reference.

3. Results and discussion

3.1. Chemical shift averaging model

A starting point for the present modeling of spectra in hydrated MCM-41 is the consideration of the spectrum in dry MCM-41 shown in Fig. 1. It is well established that the surface of dry, hydroxylated MCM-41 contains both single and hydrogen bonded silanols [17]. The two main peaks in the spectrum in Fig. 1 are fitted to Lorentzian lines using the Levenberg–Marquardt method [18]. This spectrum is consistent with other spectra in the literature where the peaks at 1.8 ppm and 2.6 ppm have been assigned to single and hydrogen bonded hydroxyl groups (S–OH and HB–OH groups, respectively), representing 38% and 62% of the signal, respectively [7,13]. In what follows it is assumed that the proton resonances of hydroxyl groups that remain unhydrated
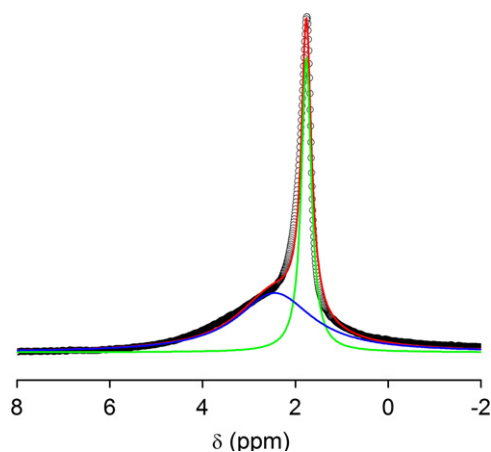

Fig. 1. ^{1}H MAS spectrum (open circles) of dry, hydroxylated MCM-41 at 293 K. The deconvolution is also shown: green – single hydroxyl group protons, blue – hydrogen bonded hydroxyl group protons, red, combined, fitted spectrum. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

as water is introduced into the pores of the MCM-41 material remain unchanged.

Upon the addition of water, all of the possible hydrogen bonding (H-bonding) configurations that may exist between the water molecules and the various silanol configurations present on the MCM-41 surface must be considered. Such configurations have been discussed previously [6,7]. In the present model it is assumed that a water molecule will make only one or two H-bonds to the surface. Water–silanol configurations, which lead to three or more H-bonds between water and the surface, are assumed to be unlikely. A simple model for the silica surface is based on random, intersecting silica fragments such as β-cristobalite [19]. However, the silanol density predicted by this model is 4.5–8 OH/nm^2, depending on the crystalline plane in consideration, whereas the silanol density in MCM-41 is known to be ~ 3.5 OH/nm^2 [20]. More detailed surface models exist that consider mixtures of siliceous crystallites made up of cristobalite, tridymite, and eddingtonite [20,21]. In the present model we consider the MCM-41 surface to be made up of β-cristobalite fragments, where the silanol species are roughly 0.5 nm apart [19,21]. The resulting water–silanol configurations and associated proton chemical shifts are shown in Fig. 2. It is assumed that hydration to the H-bonded OH groups occurs only through formation of a H-bond between water and the oxygen of a HB–OH group (see Fig. 2). The basis for this assumption is that all hydrogen atoms, forming H-bonds in the HB–OH group chain, are involved in H-bonding to their maximum capacity, whereas the oxygen atoms still have one or two orbitals available for water–OH group hydrogen bond formation. To a first approximation, this will leave the chemical shift of the HB–OH group protons unaltered.

Thus far, a model hydration surface has been created in terms of hydrogen bonding sites for water molecules. The isolated single silanol groups present three H-bonding sites (the hydrogen and the two free orbitals of the oxygen). At one end of any HB–OH group chain the OH (C of Fig. 3) will have its hydrogen not H-bonded to another OH group. Within the present context of spectral assignment the resonance of the proton of this hydrogen will appear as part of the S–OH proton resonance peak. This OH group would present only two hydrogen bonding sites for water (one each on oxygen and hydrogen atoms of C in Fig. 3). In what follows we make the assumption that the number of such OH groups terminating the H-bonded chains is small relative to the number of isolated S–OH groups, so that we can approximate the number of H-bonding sites per S–OH group available for water bonding as three. At the opposite end of any HB–OH group chain the OH group presents two H-bonding sites for water (on the oxygen of A, Fig. 3). We make the simplifying assumption that the number of such terminating OH groups is small in comparison to the number of non-terminating OH groups in HB–OH group chains. An OH group (B of Fig. 3) of a HB–OH group chain, not at the end of the chain, presents only one H-bonding site for water. From the dry spectrum (Fig. 1) of MCM-41 it was found that the ratio of hydrogen bonded silanols to single silanols is approximately 3:2. Therefore we take the ratio of the number of hydrogen bonding sites associated with single silanols to that for hydrogen bonding sites associated with hydrogen bonded silanols to be 2:1.

With the possible surface H-bonding sites and water molecule–OH group bonding configurations specified, the effect of motion of the water molecules on the observed proton NMR spectra needs to be considered. As the water molecules diffuse on the surface in a random fashion, making H-bonds in the different configurations presented, deshielding of the various protons involved occurs. A key aspect in this connection is the length scale traversed by water molecules on a time scale of the order of the inverse of the frequency separation between resonances of