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Chemical exchange and spectral coalescence in low-hydration MCM-41 studied by proton NMR

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ABSTRACT

In Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) experiments, involving silica-based porous media, containing surface OH groups and water, it is generally observed that the water proton and OH group proton resonances tend to coalesce with increasing moisture content. It has been suggested that chemical exchange between protons of surface OH groups and water may not be the only mechanism producing the coalescence in the mesoporous material MCM-41. [Chem. Eur. J. 10 (2004) 5689] Here the importance of such exchange was investigated in MCM-41, hydrated to one water molecule per OH group, using low-field, static NMR relaxation techniques and high-field MAS NMR techniques. First the surface-water chemical exchange rate was estimated from two dimensional time domain NMR selective inversion recovery experiments. Second the exchange rate required to produce coalescence was estimated by modeling the exchange spectra using expected water proton NMR spectral positions and surface OH proton NMR spectral positions obtained from MAS experiments in dry MCM-41. The results suggest that the surface-water chemical exchange rate is too small to produce substantive proton NMR spectral coalescence in the MCM-41 material at this hydration level.

1. Introduction

Mesoporous MCM-41 [1], a member of the silica molecular sieve family, has attracted considerable interest over the last 10–15 years because of its large specific surface area, relative ease of synthesis and promise as an effective host for catalytic materials. In various applications the pore volume is filled with an aqueous medium; e.g. water with halogenated hydrocarbon and H_2 in palladized MCM-41 for the systematic design of ground water remediation schemes. In addition, the well defined pore shape of MCM-41 (hexagonal pore channels of uniform diameter) make this material an attractive model system for studies of water molecule dynamics, water phases and water-surface interactions in confined geometries. Nuclear Magnetic Resonance (NMR) has had important impact on these studies. Considerable literature exists on NMR of water in MCM-41, including reports on nuclear spin relaxation [2,3], diffusion [4], exchange and water molecule dynamics investigated by double quantum filtered NMR [5,6], hydrogen bonding details and origin of NMR chemical shifts and features in ^{1}H Magic Angle Spinning (MAS) NMR experiments [7–9], aspects of NMR observations during MCM-41 synthesis and Two-Dimensional (2D) NMR exchange experiments as a function of hydration [8], water phase behavior [10,11] and assignment of water deuteron NMR spectral components to deuterons belonging to water at single and hydrogen bonded surface hydroxyl groups [12].

In a number of MCM-41 hydration studies, using ^{1}H MAS NMR, it has been found that the surface OH proton resonances, seen in the 1–4 ppm NMR chemical shift region in dry MCM-41, largely disappear from this chemical shift range for hydration levels larger than that corresponding to about 1 water molecule per OH group (see [7–9,13]). A similar disappearance of surface OH proton resonances has also been observed in the mesoporous silica materials SBA-15 [7,9], controlled pore glass [14] and silica gel [15]. A reasonable explanation for this disappearance may appear to be that the OH proton NMR resonances coalesce with the water proton NMR resonance as a result of chemical exchange between water and surface OH hydrogens. However, it has been suggested [7] that in MCM-41 the observed proton resonance lines in this case are not resulting only from simple chemical exchange between surface protons and water protons, but also involve water molecule "surface hopping" that time averages chemical shift changes in both the water and OH group proton resonances. Such changes are produced by the making and breaking of hydrogen bonds as water molecules diffuse on the silica pore surface and visit OH groups. A first step in ascertaining the importance of the role played by surface-water chemical exchange is to measure the exchange rate involved. In this report such exchange is quantified in MCM-41 and its role in the coalescence of resonances and the disappearance of the OH resonances at low ppm values is discussed. A model,

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suggested in [7], involving time averaged chemical shift changes in both the water and OH group proton resonances as water molecules visit surface OH groups, is discussed.

2. Experimental

2.1. MCM-41 sample preparation

Procedures for the synthesis of MCM-41 and its characterization have been discussed extensively in the literature. In this work the method described in [1,16] was used. The MCM-41 surface was hydroxylated by fully saturating the material with deionized water and letting it stand for one week. Samples were dried by placing them in a 10^{-3} mbar vacuum at 353 K for 12 h. X-ray diffraction (XRD) measurements were carried out on the dry MCM-41 sample under the same conditions as reported elsewhere and the experimental results were essentially the same as reported in [16]. In addition, 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 $S = 1126\ \mathrm{m^2/g}$, which is in keeping with corresponding values for MCM-41 quoted in [1,16].

To hydrate a sample to a known water content, MCM-41 was placed into a pre-weighed NMR tube and dried under 10^{-3} mbar vacuum at 353 K for 16 h. The sample – NMR tube combination was then reweighed to ascertain the dry sample weight. The sample tube was opened to the air until a desired hydration level was reached and then sealed. Here the wet sample has a hydration level of 0.086 g water per gram of dry MCM-41. This, taken together with the signal amplitudes from known amounts of water and dry MCM-41 and the specific surface area of the material, indicates that the sample contains approximately one water molecule per OH group. We denote this as the "$n = 1$ sample".

2.2. NMR measurement

^{1}H MAS NMR spectra were recorded at 11.7 T using a Bruker DMX 500 spectrometer (Bruker BioSpin Ltd., Milton, Ontario). Experiments were performed using a Zirconia rotor of 4 mm O.D. A special rotor cap with O-ring, obtained from Wilmad LabGlass Company (Buena, New Jersey), was used to maintain the hydration level in the sample. 2D time domain NMR relaxation experiments [17] were performed with a home-built 30 MHz spectrometer using 7 mm O.D. thin walled NMR sample tubes (Wilmad LabGlass) that were flame-sealed to maintain hydration.

All chemical shifts, δ, are expressed in ppm, relative to DSS as an external reference.

3. Results and discussion

A typical ^{1}H MAS NMR spectrum for fully hydroxylated, dry MCM-41 is shown in Fig. 1. Two main proton peaks are observable in this spectrum. To decompose the spectrum into components, Lorentzian lines were fitted to the data using the Levenberg–Marquardt method [18]. The fit gives a sharp peak centered at 1.8 ppm and a broader peak of lower intensity, centered at 2.6 ppm. The areas and line widths of the peaks are expressed as percent of the total area under the spectrum and ppm, respectively, and are given in the caption, Fig. 1. This proton NMR spectrum is consistent with corresponding spectra in the literature where the proton chemical shifts at low and high ppm values have been assigned to protons of single hydroxyl groups and hydrogen bonded hydroxyl groups, respectively [8,12].

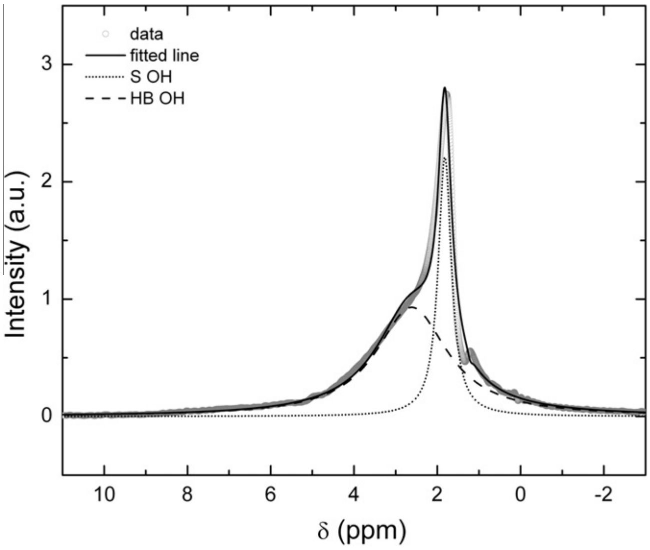

Fig. 1. ^{1}H MAS spectrum of dry, fully hydroxylated MCM-41, at room temperature and 10 K spinning rate. Two Lorentzian lines are fitted to the data; a narrow peak at 1.8 ppm with width of 190 Hz and relative area of 38% and a broader peak at 2.6 ppm with width of 1050 Hz and relative area of 62%.

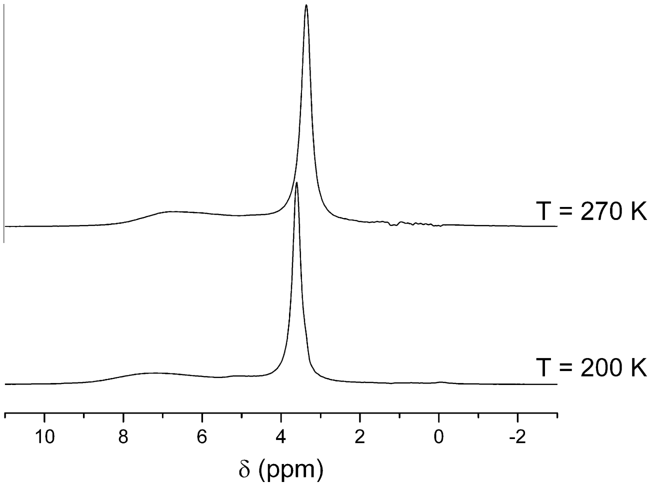

Fig. 2. ^{1}H MAS spectra of fully hydroxylated MCM-41 with hydration level $n = 1$, at 10 k spinning rate, recorded at 270 K and 200 K. The narrow peak represents 67% of the magnetization and the broad peak 33%.

Fig. 2 shows ^{1}H MAS NMR spectra for the fully hydroxylated MCM-41 sample, with hydration level $n = 1$, recorded at two different temperatures. Consider the spectrum for $T = 270$ K. The single OH (S–OH) group proton resonance seen at 1.8 ppm in the dry sample, Fig. 1, has disappeared completely from this spectral position in the hydrated sample. In addition, all, or at least a significant part, of the proton resonant signal associated with hydrogen bonded OH (HB–OH) group is no longer separately observable in the hydrated sample. Instead, a relatively narrow proton resonance line (width = 145 Hz), representing 67% of the magnetization, has appeared at 3.4 ppm and a much broader proton NMR peak (width = 1550 Hz) of lower intensity, representing 33% of magnetization, has appeared at about 6.1 ppm. Assignment of these proton resonances has been discussed in the literature [7–9,13] and is considered further below.

It may be noted that the general features of the ^{1}H MAS NMR spectra observed in hydrated MCM-41 also have been reported for the mesoscopic silica materials SBA-15 [7,9], controlled pore