



Structure of water in mesoporous organosilica by calorimetry and inelastic neutron scattering

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ABSTRACT

In this paper, we describe the preparation of mesoporous organosilica samples with hydrophilic or hydrophobic organic functionality inside the silica channel. We synthesized mesoporous organosilica of identical pore sizes based on two different organic surface functionality namely hydrophobic (based on octyltriethoxysilane OTES) and hydrophilic (3-aminopropyltriethoxysilane ATEs) and MCM-41 was used as a reference system. The structure of water/ice in those porous silica samples have been investigated over a range temperatures by differential scanning calorimetry (DSC) and inelastic neutron scattering (INS). INS study revealed that water confined in hydrophobic mesoporous organosilica shows vibrational behavior strongly different than bulk water. It consists of two states: water with strong and weak hydrogen bonds (with ratio 1:2.65, respectively), compared to ice-Ih. The corresponding O–O distances in these water states are 2.67 and 2.87 Å, which strongly differ compared to ice-Ih (2.76 Å). INS spectra for water in hydrophilic mesoporous organosilica ATEs show behavior similar to bulk water, but with greater degree of disorder.

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1. Introduction

The structural and dynamic properties of liquids [1–4] trapped within confined geometry and sizes of a porous solid have been subject of a considerable interest in recent years. In all these porous materials the most studied liquid is water [5–10]. Water plays an important role in many natural processes where it is confined in size or at contact with substrates. Water can be confined in rocks, biological cells, membranes and within proteins surfaces. The thermodynamical and the dynamical properties of water confined in size [11–13] and interaction between water molecules and surfaces are essential for our understanding of many natural processes for instance, the enzymatic activity of globular proteins or the functionality of biological membranes [14,15].

It is well known that water molecules form a great variety of hydrogen bond networks, i.e., pure water has many polymorphs, whose structures are varied by the interaction with surfaces. The structure and dynamics of water are modified by the presence of surfaces, via a modification of hydrogen bonding and also by alteration of molecular motion that depends on distance of water molecules from the surface. Therefore, a detailed description of these properties must take into account the nature of the surfaces and its affinity to form bonds with water molecules, and the hydration

level – in other words, the number of water layers. In order to discriminate between these effects, reliable model systems exhibiting hydrophilic or hydrophobic interactions with water are required. In this paper, we will present new results of water inside mesoporous hybrid materials containing functional organic groups inside both the framework and the pores channel. We will show that the confinement of water is strongly influenced by the nature of organic group incorporated in the wall surfaces. In the following, this water is defined as “confined” or “interfacial water” [16].

The effect of restricted geometry on the melting and freezing properties of water [10,17–19] in porous glasses have been extensively studied by various experimental techniques, in particular, calorimetry, dielectric spectroscopy [20,21], acoustic technique, NMR [22–24] and wide angles X-rays scattering and the dynamics of interfacial water is typically studied by inelastic neutron scattering [25–30]. Many studies of water in porous silica materials indicate the existence of two states of water molecules in the pores [31,32], viz., free pore water and water molecules bound to the pore walls [33]. Freezing of free pore water is reported to lead to cubic ice-Ic [34] instead of hexagonal ice-Ih [6,35] (crystallizing in bulk water), and is connected with a more or less pronounced thermal hysteresis [33,35,36]. This finding concerning the freezing of water in mesoporous silica materials is probably due to the ill-defined porosity of the used silica samples.

The discovery of a self-assembly synthetic pathway to periodic mesoporous silica, such as MCM-41 (Mobil Composition of Matter

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41), was recognized as significant finding in materials synthesis [37]. As a consequence of their uniform arrangement of mesopores and narrow mesopore size distributions, these materials are attractive for applications in chromatography, host-guest chemistry and catalysis. In the context of study the property of confined water, periodic mesoporous silica offers flexible model system that allows accurate adjustment of pore sizes and shape. Many studies on the physical property of liquids and particularly water were performed on periodic mesoporous silica [17,38].

While inorganic periodic mesoporous silica alone may be suitable for some applications, recently researchers realized that the properties of mesoporous materials could be modified by including organic groups in the channel spaces. Recently, a new class of materials, periodic mesoporous organosilicas (PMOs), has been reported [39–42]. These materials are unique compared to the first generation periodic mesoporous silica materials since the channel walls contain both organic and inorganic substances. This marriage of organic chemistry with inorganic materials chemistry offers fascinating new possibilities and applications. Organic precursors are easily varied to produce a wide range of materials with potentially interesting electronic, optical, charge-transport and magnetic properties.

The preparation of these materials involves the catalyzed hydrolysis of bis(trialkoxysilyl) organic precursors in the presence of a surfactant template. The presence of the organic moiety greatly influences the nature of the hydrolysis reaction and a number of new factors become important in the synthesis of these materials. Organic functionalization of these solids permits changes in the surface properties: hydrophilicity, hydrophobicity, binding to guest molecules and so on, and modification of the pore and the bulk properties of the confined water.

In this paper we present results on a study of physical property of water confined in PMOs materials. For this purpose we synthesized mesoporous organosilica based on two organic precursors (i) octyltriethoxysilane (OTES) and (ii) 3-aminopropyltriethoxysilane (ATES), the chemical structure of these organic precursors is shown in Table 1 of the supporting information file. Modifications in the properties of water in nanoporous materials depend on the distance of water molecules from the surface (i.e. pore size) and the nature of the surface. Therefore, a detailed description of water properties in nanoporous materials must take into account the nature of the pore surface and its affinity to form hydrogen bonds with water molecules. The above PMOs materials permit us to modify the surface properties of the nanoporous materials, e.g. hydrophilicity, and hydrophobicity or binding of various biomolecules. Therefore, we can utilize these PMOs materials as model systems to study the effect of the surfaces character on the structure and dynamics of water confined in size.

The physical properties of water in our PMOs samples and in common MCM-41 (for the sake of comparison) were studied using variety of methods such as: differential scanning calorimetry (DSC), inelastic neutron scattering (INS) and low temperature X-ray diffraction. It should be mentioned that in all these samples (PMO and MCM-41) the pore size and geometry were kept constant, namely hexagonal packing of cylindrical pores with uniform size, approximately 40 Å. This research focuses mainly of the influence of the nature of the pore surfaces on the physical properties of

water. As far as the authors know, the present work is the first one that deals with the thermodynamic properties of water in uniform porous materials as function of pore surfaces functionalisation.

2. Experimental methods

Materials: Sodium silicate solution (purum, >10% as NaOH, >27% as SiO₂) was purchased from Riedel-de Haën. Tetraethyl orthosilicate (TEOS, >98%), Triethoxy(octyl)silane (OTES, >97.5%) and (3-aminopropyl)triethoxysilane (ATES, 99%) were supplied by Aldrich. The quaternary ammonium surfactant compound (C₁₆TAB, >96%) was obtained from Fluka and used without further purification.

Synthesis of mesoporous silica MCM-41: MCM-41 mesoporous silica were prepared according to the well-known synthesis procedures reported by Beck et al. [37] (see supporting information).

Synthesis of PMOs: OTES and ATES inorganic-organic mesoporous silica with MCM-41-type architectures were synthesized at room temperature from mixtures containing constant molar ratio of a functionalized organotrialkoxysilane with tetraethoxysilane (TEOS) in the presence of the surfactant C₁₆TAB [41,43–47] (see Table 2 and details description of the PMOs preparation in the supporting information).

Surfactant-extraction: The surfactant template was removed from the organosilica materials through solvent extraction process. A 2 g sample of product was refluxed in 3 ml of (37 wt%) HCl and 200 ml of methanol for 1 day, collected by suction filtration, washed with water and dried in air at room temperature.

Characterization: Small-angle X-ray scattering (SAXS) patterns in a range of 2θ angles from 0.5° to 8° were recorded on a Bruker AXS D8 Advance Diffractometer (using Cu Kα λ = 1.5418 Å radiation) operating at 40kV/40 mA, with a graphite-reflected beam monochromator and variable divergence slits. Sorption isotherms of nitrogen at 77 K were measured by gas volumetry using a Quantachrome Autosorb-1 system. High Resolution Transmission electron microscopy (HR-TEM) images were acquired on a JEOL 840 instrument with an acceleration voltage of 200 kV.

Measurements: MCM-41 material and two types of mesoporous organosilicas were used as “confining materials” with average pore diameter of ~40 Å. Samples containing water were prepared by first immersing the silicates in distilled, deionized water for more than 12 h to fill the pores in the silica with water, and second by allowing water to escape from the saturated samples by slow evaporation at room temperature. After attainment of given water content, ≈10–20 mg of the sample was hermetically sealed in a high-pressure aluminum crucible covered with aluminum oxide on the surface to avoid entirely the reaction of water with aluminum. DSC with a Mettler Toledo DSC-822 equipped with a liquid nitrogen cooling system was used to measure the freezing and melting curves of ice in the silicates. All DSC measurements were carried out over the temperature range 203–298 K at a scanning rate of 2 K min⁻¹. At the end of each DSC measurement, a small hole was made in the crucible and it was then dried in an oven at 383 K to determine the mass of the water.

The INS spectra have been measured using HRMECS spectrometer installed at IPNS, ANL. The spectrometer is a direct geometry machine: the incoming neutrons have a fixed energy E_i , selected by a rotating chopper, and the energy analysis is made on scattered neutron time-of-flight. Under optimum conditions (large E_i and small scattering angles) the neutron momentum transfers at high energy transfers are relatively small; this made it possible to measure good quality INS spectra up to the highest excitation energies of around 450 meV. Experiments were carried out at low temperature, $T = 6$ K, to reduce multiphonon contribution and effect of the Debye–Waller factor. The measurements were done with $E_i = 80, 170$ and 600 meV to provide a good energy resolution

Table 1

Melting and freezing temperatures of water in the porous silica materials (values taken from the beginning of the peaks in the DSC curves).

| Material | 2R/nm | T_m /K | T_f /K |
|----------|-------|----------|----------|
| MCM-41 | 3.7 | 237 | 232 |
| ATES | 3.5 | 228 | – |
| OTES | 3.5 | 231 | 233 |

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