Experimental report

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Proposal: **6-07-10** **Council:** 4/2016

Title: Ordering of water confined in hydrophilic nanopores – low temperature investigation

Research area: Materials

This proposal is a new proposal

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Samples: AlPO4-54*xH2O

Instrument	Requested days	Allocated days	From	To
D4	5	5	02/12/2016	07/12/2016

Abstract:

We propose the first neutron diffraction measurements on AlPO4-54•xH2O at low temperature, in the temperature range of 10-300 K. AlPO4-54*xH2O (hexagonal VFI structure, space group P63, a=18.9678(13) A and c=8.0997(4) A, Al18P18O72*47H2O) exhibits 1-D pores along the c direction, which are among the largest pores known for zeolites and aluminophosphates, with a diameter of 12.7 A in which H2O molecules form a disordered hydrogen-bonded network at ambient temperature. AlPO4-54*xH2O is an ideal system to probe nanoconfined water. The ordering dependence of its nanoconfined water has been studied by single-crystal X-ray diffraction, which obviously could not detect hydrogen. The experiment proposed here will allow locating the hydrogen positions, revealing the behaviour of the H-bond as a function of temperature, and will help to better define the ordering of the water near the pore wall. The results will contribute to a better understanding of the H-bonded water confined in hydrophilic nanopores as well as to the understanding of the conditions for its possible crystallization.

Beamtime report – proposal number: 6-07-10 – D4

Ordering of water confined in hydrophilic nanopores – low temperature investigation

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Abstract. Pair-Distribution Function (PDF) analysis from neutron diffraction patterns of $AlPO_4$-54•$x$$H_2O$, in the range of T=10-300 K, were carried out using a cryofurnace at atmospheric pressure conditions in a powder sample on the D4 instrument. $AlPO_4$-54•$x$$H_2O$ exhibits 1-D pores along the **c** direction, which are among *the largest pores known for zeolites* with a diameter of 12.7 Å in which H_2O molecules form a disordered H-bonded network at ambient pressure and temperature. This is thus an ideal system to probe water confined in a hydrophilic nano-pore. The dependence on temperature of water ordering in the pore has been previously studied by single-crystal X-ray diffraction (XRD), which obviously could not detect hydrogen. The PDF experiment allowed locating the hydrogen positions, revealing the behaviour of the H-bond as a function of temperature, and together with new molecular dynamics (MD) simulations will help to better define the ordering of the nanoconfined water upon cooling.

Introduction, previous work and objectives. Some studies have shown that, for temperatures below the bulk freezing point, water confined in hydrophobic nanopores crystallizes [1-4]. Such phenomenon is supported by studies which show the formation of ice nanotubes in carbon nanotubes [4]. A different scenario was reported concerning the freezing of water in hydrophilic nanopores (D=1.2 nm). It was observed that while the pore surface induces orientational order of water in contact with it, water inside the pore does not crystallize at temperatures down to 173K [5]. However, full crystallization at the surface is considerably suppressed as the number of hydrogen bonds (HB) formed is insufficient, while crystallization in the pore center is hindered as the curvature prevents the formation of a network of tetrahedrally coordinated molecules, reported as rigid (i.e., glassy) structure. Experimental single-crystal XRD and molecular dynamics simulations (MD) structures studies of water in the $AlPO_4$-54*$x$$H_2O$ at the T=173-300 K range have confirmed that water ordering (ice-like orientational order) and site occupancies are more marked as T decreases, especially for molecules in the vicinity of the pore surface. New experiments realised by our group probed water dynamics in the same hydrophilic nanopores down to 10 K, by incoherent inelastic neutron scattering (IINS), quasi-elastic neutron scattering (QENS), Far- and Mid-infrared (IR) spectroscopy as a function of temperatures. These new studies suggest an increase within lowering the temperature of the number of HB of the water nanoconfined together with a strengthening of the interaction, most likely near the pore surface. This is indicative of a different ordering taking place at low temperature in the water network compared to the previous study [4]. However, new direct structural information was needed to elucidate this hypothesis.

Experimental protocol. Pair-Distribution Function (PDF) analysis from neutron diffraction patterns of $AlPO_4$-54•$x$$H_2O$, in the range of T=10-300 K, were carried out using a cryofurnace at atmospheric pressure conditions in a powder sample on the D4 instrument. 332 mg of $AlPO_4$-54•$x$$H_2O$ were load into a cylindrical vanadium can (5x20 mm sample diameter and high, respectively). D4 is a two-axis diffractometer, equipped with nine 1-D position-sensitive microstrip detectors pressurized with 3He gas to 15 bar for efficient detection. The diffraction patterns were measured over a large Q-range, 0.5 Å wavelength (327 meV), Q_{range}=0.5-23.5 $Å^{-1}$, with flux on sample is on the order of $5.0 \cdot 10^7$ $n.cm^{-2}.s^{-1}$. Making use of a Cu220 monochromator, the beam collimation is made by 2x2-slit horizontal, vertical diaphragm at 30 cm upstream of sample, plus additional vertical slits at 5 cm upstream of sample. More information concerning D4 instrument can be found elsewhere [6]. Experiments were carried out on dehydrated and hydrogenated samples at 4 temperatures points (T=10, 100, 173 and 300 K). The spectra were accumulated over 1.5 h for T=100, 173 and 300 K, and over 13.5 h for T=10 K.

Results. Fig. 1 show the pair distribution functions $D(r)$ of $AlPO_4$-54•$x$$H_2O$ at T=10, 100, 173 and 300 K, and its dehydrated phase ($AlPO_4$-54) at T=10 K. Both hydrated and dehydrated phase were normalised to the total mass illuminated by the beam. Assignment of the peaks can be obtained by comparison with single-crystal XRD data from previous studies [5]. The distances above 4 Å are somewhat more difficult to assign, due the overlap of several features, here we present only the lower region (< 4 Å). At 1.51 Å, 1.76 Å, 2.5 Å and 2.8 Å typical framework intratetrahedral distances from P–O, Al–O, O–O (PO_4 tetrahedra) and O–O (AlO_4 tetrahedra), respectively, are found. The intertetrahedral Al–P distance across the bridging angle is observed at 3.11 Å. Above 3.4 Å several intra- and intertetrahedral distances are observed and overlapped, such as O–O, P–O and Al–O. The peak at 2.14 Å is attributed to distances Al–H from the 6-fold Al. At 1.82 Å and 2.8 Å the hydrogen bond (HB) and O–O distances from the pore water, respectively, are observed. The peak at 1.18 Å is attributed to adsorbed N [7] from the cryostat atmosphere at the zeolite surface. The *D*(*r*) of $AlPO_4$-54•xH_2O shows the distances evolution from the $AlPO_4$ structure as temperature decreases. Here we will focus on changes concerning the nanoconfined water. Upon cooling, is observed an increase on the number of the O bonded via H-bonds with a typical distance of 2.8 Å (Fig. 1), representative of an increase in the ordering for the nanoconfined water. For the sake of clarity, we subtracted the *D*(*r*) of $AlPO_4$-54•xH_2O at *T*=10, 100, 173 and 300 K from its dehydrated phase at *T*=10 K, the result is showed at Fig. 2. From the PDF *D*(*r*) difference showed at Fig.2, decreasing the temperature, the HB (at around 1.82 Å) is observed to shift towards lower values, which is coherent to the strengthening of the H-bond network. In $AlPO_4$-54•xH_2O structure, one-third of the aluminium cations are octahedrally coordinated due to the presence of two H_2O molecules in their coordination sphere, one of which strong hydrogen bonds with the free water in the pore and, while, at 300 K, no hydrogen bonds are formed with the second coordinated water [8]. The strong shift observed at around 2.14 Å, Figs. 1 and 2, points out at changes on the water molecules bonded to the 6-folded Al.

New MD simulations of nanoconfined water should be performed in order to obtain a better interpretation of these results.

These preliminary results are in agreement with current results from our group on water confined in $AlPO_4$-54•xH_2O nanopores on IINS and QENS measurements using the IN1-Lagrange and IN16b instruments (proposal number: 6-02-563), respectively, and with synchrotron Far- and Mid-IR spectroscopy under low temperatures (Synchrotron SOLEIL – proposal 20160566).

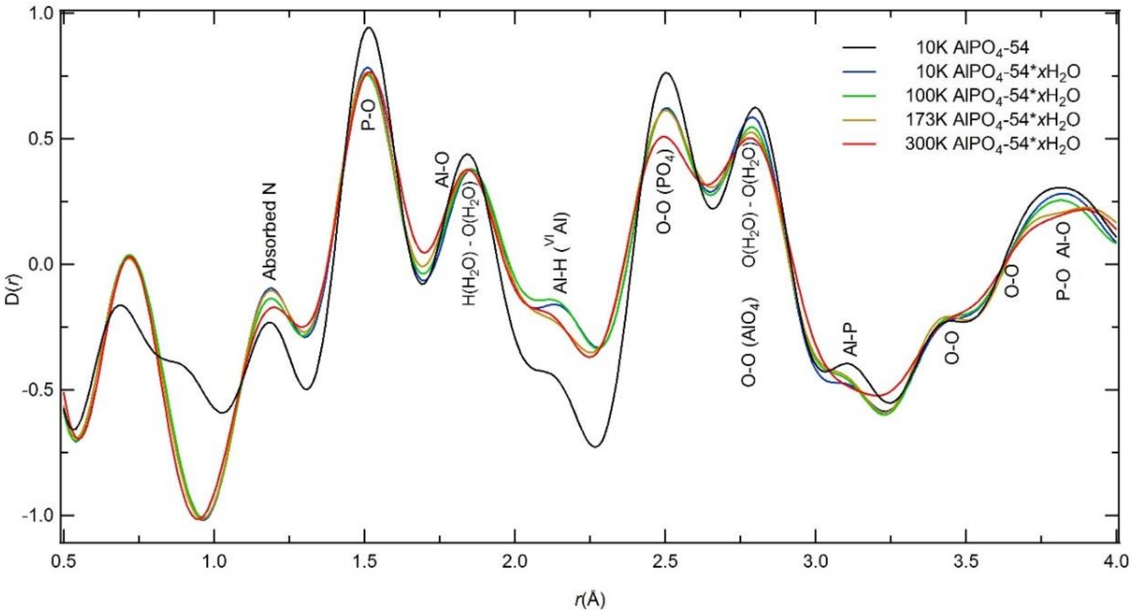

Figure 1: Pair distribution functions *D*(*r*) of $AlPO_4$-54•xH_2O at *T*=300, 173, 100 and 10 K, and for $AlPO_4$-54 at *T*=10 K.

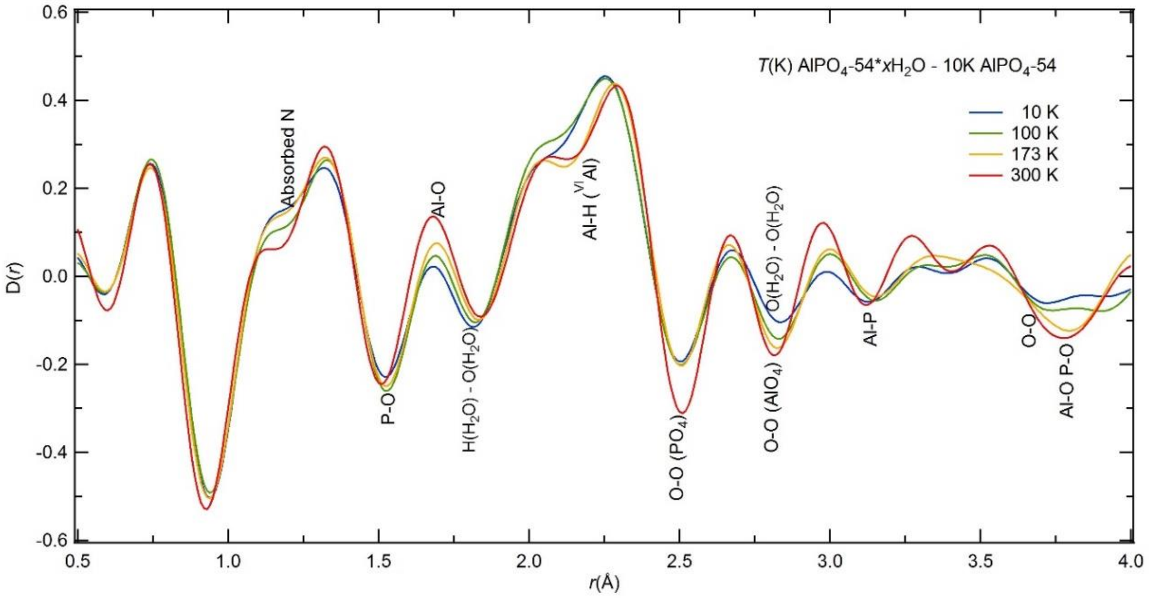

Figure 2: Pair distribution functions $D(r)$ difference of $AlPO_4$-54•xH_2O at T=300, 173, 100 and 10 K from its dehydrated form ($AlPO_4$-54) at T=10 K.

References.

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