WATER CLUSTERS AND LINDE TYPE-A ALUMINOPHOSPHATE: INTERPLAY BETWEEN STRUCTURAL ORDER AND DISORDER

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ABSTRACT

In this study a hydrophilic microporous $AlPO_4$-LTA, which is crystalline when dry [1], but heavily disordered when hydrated, will be presented. More precisely we first describe an experimental approach to gain deeper understanding of atomistic disorder in such a complex material. Based on the sufficient experimental insight, we then used computer simulations to explore the theoretical aspect behind the mentioned material. Finally, we propose a structural model of the disordered hydrated $AlPO_4$-LTA for the first time, which is consistent with both theory and experiments.

Key words: disorder, PDF, NMR, molecular dynamics, microporous $AlPO_4$-LTA.

INTRODUCTION

Heat storage and reallocation is increasingly important in modern society. Hydrophilic porous solids play a crucial role in this context, possessing properties that make them potentially useful in technological solutions. One such material is microporous LTA aluminophosphate, which achieves heat storage through a process of water sorption. More precisely, the material stores energy in its dry state and releases it during hydration.

To guide the development of materials effectively, a deep understanding of the water adsorption process at the atomic level is necessary, requiring an accurate description of the atomic structure. For crystalline materials this is usually not an issue, since crystallography offers essential information about the average atomic structure needed to explain the macroscopic properties. On the other hand solids can build structures where conventional crystallographic tools fall short. Examples include amorphous solids, disordered crystals, nanoparticles, solids with various types of defects, materials with adsorbed molecules, crystals with short-range structural fluctuations, etc. In such cases crystallography struggles to determine atomic structures at the nanoscale, termed as "the nanostructure problem" [2]. Among these structurally pestilent solids we often find various porous materials because of their complex atomic structures. Their typically large unit cell dimensions, containing several hundred atoms, makes computer simulations and experimental data fits immensely challenging or even impossible.

The whole ordeal seems even dimmer when considering that often different types of materials need different strategies to uncover their atomic nanostructure, consequently making a general strategy impossible. However, comparing investigated systems with similar known structures can provide valuable insights. In our study a well ordered microporous $AlPO_4$-34 [3] was used to help elucidate some of the limitations of the unknown structure of hydrated $AlPO_4$-LTA. In the latter case water adsorption into its pores makes the otherwise crystalline framework in its dry state highly disordered, while preserving chemical bonding between Al, P and O atoms [1]. In this study we present new insights, employing solid-state nuclear magnetic resonance (NMR), X-ray and neutron pair distribution function (PDF) analysis and computer simulations.

EXPERIMENTAL

For the synthesis of microporous AlPO$_4$-LTA the procedure described by A. Krajnc et al. [1] was followed. As a last step a careful activation process, calcination, of the material was performed within laboratory X-ray diffractometer. The calcination evolution was monitored *in-situ* up to 900 °C and back down to room temperature.

The hydration process of the samples was performed by using three types of water vapour chambers, separately and depending on the experiment we used H$_2$O, ^{2}H$_2$O and H$_2$^{17}O. Hydration took place in a desiccator, where a saturated NaCl salt solution maintained controlled air at 75 % relative humidity. Prior to hydration, the samples were dried in vacuum oven at 100 °C for 3 h.

Solid-state NMR experiments were performed on a 600 MHz Varian NMR spectrometer equipped with a 1.6 mm Varian HXY MAS probe. Larmor frequencies for ^{2}H and ^{17}O were 92.01 MHz and 81.25 MHz, respectively. Magic angle spinning (MAS) frequency were 10 kHz and 20 kHz, for ^{2}H and ^{17}O, respectively. For ^{2}H and ^{17}O measurements, ^{2}H and ^{17}O single excitation pulses of 2.5 μs and 0.8 μs were used, respectively. In ^{2}H MAS NMR measurements number of scans was 400 and repetition delay was 1.0 s. In ^{17}O MAS NMR measurements 100000 scans were co-added with a repetition delay of 30 ms between scans. The frequency axes of both ^{2}H and ^{17}O spectra were referenced to tetramethylsilane.

Experimental PDFs were obtained by high-energy X-ray scattering at a synchrotron source (beamline I15-I – XPDF, Diamond Light Source, Oxfordshire, United Kingdom). We used X-rays with energy of 76 keV, which corresponds to a wavelength of 0.161669 Å. The measurements were carried out using a 2D detector, the time of individual measurements was 20 minutes and ramping time to target temperature equaled 10 minutes. During the measurement, each sample was in a glass capillary that was open on one side and sealed with glass wool, which allowed water to escape from the material at a higher temperature. The capillary was rotated during the experiment in the transmission geometry to prevent any preferential orientation contributions of particles to the 2D scattering pattern.

To obtain a complementary set of PDFs, we performed neutron scattering experiments, the source of which was a nuclear reactor (beamline D4 – Disordered Materials, Institut Laue-Langevin, Grenoble, France). In the case of neutron scattering, the samples were hydrated with heavy water, i.e. deuterated water (contains ^{2}H isotope of hydrogen) and thereby achieved approximately 80-90 % isotopic enrichment of adsorbed water, which was confirmed by measuring ^{1}H MAS NMR spectra. The neutrons had a wavelength of 0.49857 Å, which was determined from measuring a diffractogram of the Ni standard. We used a 1D detector with an angular resolution of 0.125° and measured the scattering in steps of 0.125° up to a maximum angle of 140°. Each measurement lasted approximately 39 h. First, the pre-hydrated sample was measured. Subsequently, it was dried in a vacuum chamber at a temperature of 200 °C for 3 hours, cooled to room temperature, and then the dry sample was measured. An additional 24 h of measurement time was allocated for background measurement. During the measurement, each sample was contained in a vanadium cylinder.

Due to the unknown structure and number of water molecules in hydrated AlPO$_4$-LTA, we used a similar system, AlPO$_4$-34, to optimize the initial calculation parameters used in computer simulations. AlPO$_4$-34 is chemically, structurally and functionally similar to AlPO$_4$-LTA, the main difference being in the structural topology and symmetry in the hydrated state. We know the exact structure of hydrated framework in the mentioned reference system [3]. We started by using the software tool VASP (Vienna Ab initio Simulation Package) [4-6]. Based on accurate calculations from first-principles and available experimental data, we first

optimized the empirical force-field parameters on the AlPO$_4$-34 example. We later used these in classical molecular dynamics simulations to capture the relevant physics of the water binding process in AlPO$_4$-LTA, for which we used the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software (available on 23.06 .2022) [7].

RESULTS AND DISCUSSION

We conducted a multitude of experiments, each serving distinct purpose. Some experiments yielded rich information crucial for guiding subsequent computer simulations, while others served to validate our data interpretations. With 1D solid-state NMR experiments we mainly observed ^{1}H, ^{2}H (Figure 1, left) and ^{17}O nuclei. Using various isotopes we were able to detect multiple contributions of water environments within pores, which was not previously possible. Notably, the adsorbed water molecules are heavily disordered and exhibit different dynamics.

To find out how far does the positional correlation of water clusters extends, i.e. probing structural order, we measured neutron PDF of dry and hydrated AlPO$_4$-LTA. Using neutrons as a probe we gain significant sensitivity to deuterons contained in heavy water, which is adsorbed within pores. We observed short range order coming from water clusters, extending only to about 8 Å, which is interestingly very similar to bulk liquid water.
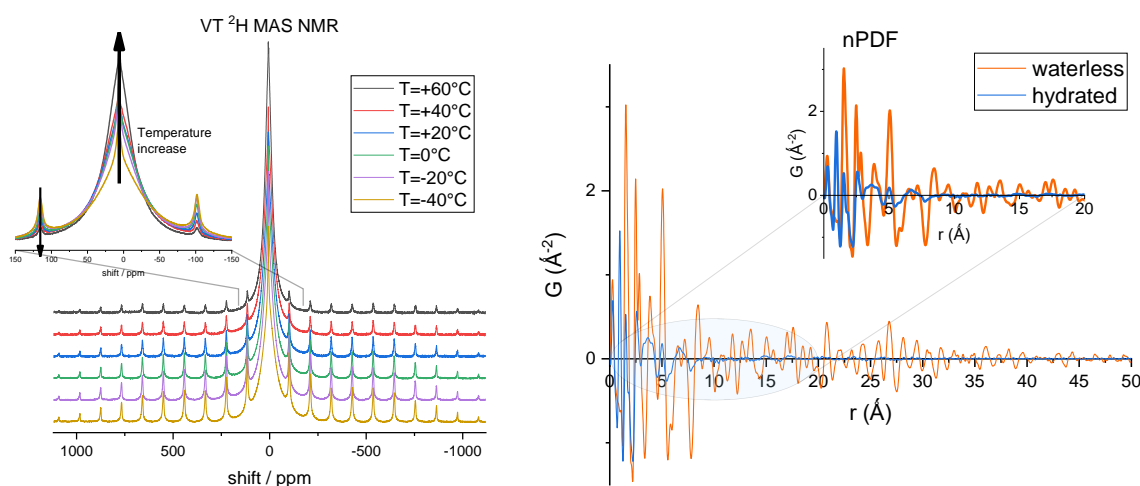

Figure 1. Variable temperature ^{2}H MAS NMR spectra of hydrated (left) and neutron pair distribution functions (right) of hydrated and dehydrated AlPO$_4$-LTA, utilizing heavy water in both experiments.

The information obtained from both previous and new studies was used as a starting base for virtual experiments. With first-principle calculations we optimized local interactions, most notably those between framework aluminium and water oxygens. To achieve this, a known structure of hydrated AlPO$_4$-34 was used as a training model. The optimized parameters were then used in molecular dynamics experiments for hydrated AlPO$_4$-LTA. We tested different sizes of supercells needed to capture disorder and various amounts of water that can be bedded within the materials pores. From this we successfully reproduced the experimentally obtained X-ray structure functions, S(Q), and used them to estimate the number of water molecules present in fully hydrated AlPO$_4$-LTA, by comparing them to the experimental X-ray structure function [8]. The choice to use synchrotron X-ray S(Q) as a reference experimental function for testing the theory was deliberate. This method encompasses scattering from all framework atoms and also water oxygens, providing all important atom pair distances, while also capturing information about the extent of structural order. This stands in contrast to neutron scattering, where the signal from water molecules

strongly dominates that from the framework, limiting the ability to discern structural details. At the end we concluded that a supercell model with dimensions of 2x2x2, as shown in Figure 2, was sufficient to capture vital experimental insights.
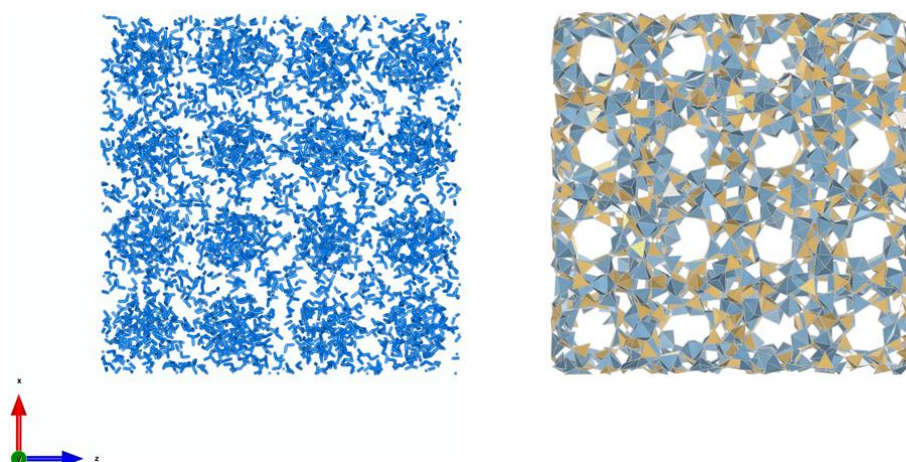

Figure 2. Separate structural models of highly disordered water clusters (left) and deformed supercell framework AlPO$_4$-LTA that confines them (right). Model comprises 2688 water molecules and 4608 framework atoms.

CONCLUSION

Through the utilization of advanced characterization techniques such as solid-state NMR, X-ray and neutron PDF, and revisiting the insights from the previous study, we have acquired enough experimental knowledge to delve into the atomic-scale structural disorder of hydrated AlPO$_4$-LTA. This experimental data served as a base for our theoretical study. More precisely, we used a combination of first-principle calculations and molecular dynamics, and for the very first time, succeeded in constructing an atomistic structural model, capturing both ordered and disordered motifs in hydrated microporous AlPO$_4$-LTA.

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