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Structure and NMR assignment in $AlPO_4$-15: A combined study by diffraction, MAS NMR and first-principles calculations

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ABSTRACT

A multi-technique investigation involving X-ray diffraction, solid-state NMR and first-principle calculations was carried out on the aluminophosphate material $AlPO_4$-15. A synchrotron X-ray single-crystal diffraction study was carried out on the same sample as that used in solid-state NMR studies. The model from the single crystal study, together with a model from a literature high resolution study of the same material, was used as starting points for the first-principles calculations of the NMR parameters. This enabled the ^{31}P and ^{27}Al NMR spectra to be unambiguously assigned and all the NMR parameters calculated agreed well with the experimental spectra even without relaxing the X-ray derived structural models.

1. Introduction

The variable pore size and shape of zeolites and zeotypes provide a range of potential uses as ion-exchange materials, catalysts and sorbents. The first framework oxides synthesized without the silicon found in zeolites were the open-framework aluminophosphates (AlPOs) [1], usually denoted $AlPO_4$-*n* for the various structure types. In order to avoid the formation of dense phases, hydrothermal synthesis of AlPOs typically requires an organic amine base (termed a structure directing agent (SDA) or template), enabling the production of open frameworks. Many of these remain stable after calcination, producing neutral, porous frameworks composed of AlO_4 and PO_4 tetrahedra [2–5]. In some ways AlPOs are more flexible in terms of their structural chemistry than corresponding silica based zeolites. As-synthesized materials may contain Al in a variety of coordination environments, including Al^{IV}, Al^{V} and Al^{VI}, (where the superscript denotes the number of coordinated atoms), with moieties such as hydroxides, water and fluoride also typically coordinated [6]. For example, SSZ-51, an AlPO with the SFO zeolite framework type, contains five-coordinate aluminium in its as-made (templated) form, only tetrahedrally-coordinated Al in its calcined and dehydrated state, but once hydrated has a mixture of four, five and six-coordinate Al [7].

The applications of porous materials such as AlPOs are intimately connected with their structural architecture. Obtaining high quality structural data is, therefore, extremely important for determining how these materials function. As AlPOs are generally highly crystalline solids, X-ray diffraction is the main technique by which such information is obtained. Such structure determinations can be broadly split into two types; high resolution studies that focus on atomic position and charge density evaluation, and 'normal' resolution structures that are commonly utilized to obtain the atomic positions. Whilst it is expected that the high resolution structures will be the most accurate, these are rare for complex materials such as zeolites and other porous solids. However, recent work by Poulsen [8,9] and Clausen [10] has shown that it is possible to obtain accurate charge density information for porous solids such as metal organic frameworks, which has some exciting implications given their important applications in gas storage and catalysis [11,12]. One of the first, if not the only, aluminophosphate material for which a high resolution structure has been obtained is $AlPO_4$-15 [13], an aluminophosphate material which contains only Al^{VI} octahedral units along with PO_4 tetrahedra in the framework, with the NH_4^+ SDA cation found in the relatively small pores [14].

Along with diffraction, solid-state nuclear magnetic resonance (NMR) spectroscopy is also an important tool for studying structure

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and ordering in zeotype frameworks [15]. The basic constituents of many frameworks are NMR-active nuclei (e.g., ^{29}Si, ^{27}Al, and ^{17}O for zeolites and ^{31}P, ^{27}Al, and ^{17}O for aluminophosphates). In addition, mineralisers, charge-balancing cations and many structure directing agents also contain NMR-active species. NMR has been used to both determine and confirm structure and space groups in frameworks, to study disorder, to identify through-bond connectivities, to detect Brønsted acid sites and to investigate exchange kinetics and dehydration [15–20]. Furthermore, NMR is an excellent probe of dynamics in microporous frameworks, through either wideline experiments [21] or, more recently, through high resolution MAS NMR [22]. In addition to experimental approaches, there has been growing interest in the calculation of NMR parameters in the solid state owing, at least in part, to the recent introduction of first-principle approaches which exploit the inherent periodicity of many solids. In particular, the gauge including projector augmented wave (GIPAW) [23] formalism, implemented within CASTEP [24,25], a planewave, pseudopotential code, has been shown to provide accurate shielding and quadrupolar tensors for a variety of nuclei in a range of materials, including porous frameworks, [26,27] aiding spectral assignment and interpretation. This is of particular importance for quadrupolar ($I > 1/2$) nuclei, such as ^{27}Al ($I = 5/2$), where the second-order quadrupolar broadening observed under MAS hinders the extraction of information. Typically, more complex high-resolution experiments need to be performed (e.g., multiple-quantum (MQ) MAS [28] or satellite-transition (ST) MAS) [29,30] which, although an aid to resolution, do result in diminished sensitivity. Calculations also enable the relationship of NMR parameters to the local structural environment (e.g., their dependence on bond lengths or angles) to be investigated in an easy and flexible manner.

A crucial pre-requisite for first-principles calculations is an accurate initial crystal structure. The quality of structures obtained from diffraction vary depending upon the type of approach (e.g., X-ray or neutron) and the type of sample (e.g., powder or single crystal) utilized. In particular, the positions of lighter atoms, such as hydrogen, can be difficult to determine accurately using X-ray techniques but errors in these positions often have very large effects on calculated NMR parameters. Furthermore, the recent observation of microsecond timescale dynamics (associated with the template and water molecules in the pores of as-synthesized framework materials) using ^{27}Al STMAS NMR is a further complicating factor [22]. Indeed, recent work has demonstrated that there was very poor agreement between calculated and experimental ^{27}Al and ^{31}P NMR parameters in AlPO$_4$-14 (in both calcined and templated forms), unless some optimization of the X-ray derived atomic positions was performed prior to the NMR calculation [31]. Although the modifications to the structure were reasonably small, and only minor differences observed between simulated diffraction patterns and those reported from experiment, the differences observed in the NMR parameters were considerable, demonstrating the sensitivity of NMR to small changes in the local environment.

In this work we utilize a multi-technique approach to study the microporous framework AlPO$_4$-15, synthesized using the NH_4^+ cation as a structure directing agent. Previous ^{27}Al MAS NMR spectra [32] (78.2 MHz) appear confusing, containing a broad composite resonance around −10 ppm (a shift typical of six-coordinate Al), and no resolution of the two distinct Al^{VI} species expected. An unexplained signal with an unusual shift (approximately −100 ppm) was also observed. The present work, therefore, has a number of aims; (i) to employ high resolution ^{27}Al NMR experiments to attempt to resolve and identify the distinct Al species in AlPO$_4$-15, (ii) to unambiguously assign the resonances in both ^{27}Al and ^{31}P NMR spectra with the aid of first-principles calculations, and (iii) to test the quality of different X-ray diffraction structures as starting points for first-principle calculations by comparing a model obtained using a high resolution charge density X-ray approach with synchrotron X-ray data obtained from a very small crystal.

2. Methods

2.1. Synthesis

Aluminium sulfate hexadecahydrate (4 g, Aldrich) was dissolved in deionised water (50 ml) and ammonia (12.5 ml, Fisher). The solution was filtered and the resulting slurry dispersed in water (30 ml) and stirred. Once the solid had dissolved, ethanol (10 g BDH), phosphoric acid (1.4 g, 85% in H_2O, Aldrich) and tripropylamine (1.5 g, Aldrich) were added dropwise and mixed thoroughly. The solution was decanted to a Teflon lined autoclave and placed in a preheated oven for 4 days at 180 °C. After the crystallization period the autoclave was allowed to cool to room temperature overnight. The product was filtered, washed with water and dried. This material was used (as synthesized) for both synchrotron diffraction and solid-state NMR experiments.

2.2. Diffraction

The crystals prepared as described above were too small for data to be collected using an in-house X-ray source and so were studied using the high flux station 9.8 [33,34] at the Synchrotron Radiation Source (SRS), Daresbury, UK at low temperature (150 K) using an Oxford Cryosystems Cobra$^+$. A Bruker–Nonius APEXII CCD area detector and D8 diffractometer using X-rays of wavelength 0.71073 Å. The structure was solved using direct methods (SHELXS-97) [35] and refined against F^2 using the least squares package (SHELXL-97). The hydrogen atoms were added geometrically and refined as riding on the atom to which they were attached, and all the non-hydrogen atoms were refined anisotropically. Further information on the structure is available in the Supporting Information.

2.3. NMR spectroscopy

Experiments were performed using a either a Varian Infinity Plus 500 MHz or a Bruker Avance 400 spectrometer, equipped with widebore 11.7 and 9.4 T magnets, with Larmor frequencies of 130.3 and 104.3 MHz (^{27}Al), and 162.0 and 202.5 MHz (^{31}P). Powdered samples were packed in conventional 4-mm or 2.5-mm ZrO_2 rotors and rotated at rates between 10 and 30 kHz. Typical recycle intervals were 500 ms (^{27}Al) and 60 s (^{31}P). Chemical shifts are shown relative to 1 M $Al(NO_3)_3$ (aq) for ^{27}Al and 85% H_3PO_4 for ^{31}P. For ^{27}Al MAS spectra were recorded using a spin-echo pulse sequence selective for the central transition. Triple-quantum MAS experiments were performed using a split-t_1 shifted-echo pulse sequence [36], with typical radiofrequency field strengths of 130 kHz for multiple-quantum excitation and conversion and 10 kHz for the central-transition selective inversion pulse. The scale of the isotropic δ_1 axis is plotted according to the conventions described in Ref. [37].

2.4. Calculations

Calculations were carried out using the CASTEP [24,25] density functional theory (DFT) code, which employs the gauge including projector augmented wave (GIPAW) [23] algorithm, to reconstruct the all-electron wave function in a magnetic field. The generalized gradient approximation (GGA) PBE [38] functional was used and