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RAPID COMMUNICATION

Unexpected structural/motional mode of water intercalated into an α-crystalline zirconium phosphate deduced by ^{31}P and ^{2}H Solid-State MAS NMR Spectra

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Abstract: In developing the approach to understanding dynamics of intercalates in layered materials, crystalline layered zirconium phosphate $Zr(HPO_4)_2 \cdot 0.35D_2O$ has been prepared and characterized by the ^{1}H, ^{31}P and ^{2}H solid-state MAS NMR spectra, including ^{31}P and ^{2}H T_1 measurements. At temperatures > 253 K, the intercalated water shows two spectrally-distinguished deuterons unprecedentedly with different DQCC's and ^{2}H T_1 times, one of which is hydrogen bonded. The collected data allowed to identify an unexpected bonding/dynamic mode of water molecules, which experience fast rotation around the hydrogen bond, formed with a zirconium-coordinated oxygen. The low-temperature ^{2}H MAS NMR experiments have demonstrated the presence of additional hydrogen bond P–(H)O···DO, population of which grows on cooling to 195 K corresponding to the doubly hydrogen-bonded immobile water molecule.

KEYWORDS

Zirconium phosphates, structural elucidation, NMR, relaxation, dynamics

1. INTRODUCTION

Zirconium phosphate materials,[1–3] due to their layered structure, are widely used in ion-exchanges, catalysis, drug delivery, nuclear waste treatment, and proton conduction.[7] A crystalline α-zirconium phosphate $Zr(HPO_4)_2 \cdot H_2O$ (**1**)[8,9] is the most typical representative of these materials, where the stacking of the layers (which are 7.6 Å apart from each other) creates a cavity of 2.61 Å (Figure 1), occupied by a water molecule.[10] According to ab initio calculations, detailing the structure of **1**, oxygen and proton of water molecules and proton and oxygen in phosphate groups form hydrogen bonds (the insert of Figure 1),[11] leading to a situation, in which motions of the water can be limited to show the physically-distinguishable protons. However, up to now, these calculations are not confirmed experimentally and thus, the bonding / motional mode of the water in **1** still remains unclear. Potentially, only the ^2H MAS NMR experiments,[12,13] particularly the measurements of deuterium quadrupole coupling constants (DQCC) can provide reliable information in this context, which are very sensitive to the molecular mobility, decreasing in the presence of motions.[14,15]

Here Figure 1

Herein we report the ^1H, ^{31}P and ^2H solid-state MAS NMR study of the crystalline layered zirconium phosphate, $Zr(HPO_4)_2 \cdot 0.35D_2O$ (**1-D_2O**), which shows an unexpected structural/motional mode of the water.

2. RESULTS AND DISCUSSION

According to the PXRD pattern shown in Figure S1, **1-D_2O** is a layered, and highly-ordered crystalline material with the interlayer distance of 7.6 Å.[7,8] The $^{31}P\{^1H\}$ MAS NMR spectrum of

1-D_2O manifests two resonances at δ of -21.4 ppm and -23.1 ppm (Figure 2). Since the chemical shift difference of these signals is small, their accurate assignment clearly plays a principal role.

Here Figure 2

As seen in Figure 2, the intensity of the low-field resonance reduces when the water is removed from **1-D_2O** (compound **1-*dried***) after two drying stages controlled by ^{2}H MAS NMR (see below). Then the phosphorus low-field resonance grows again after treatment of **1-*dried*** with D_2O. Therefore, this resonance can be assigned to HPO_4 groups, neighboring with water molecules.[7] In turn, the resonance at -23.1 ppm belongs to water-free HPO_4 groups. It is also important that the ^{1}H MAS NMR spectrum of compound **1-D_2O**, manifesting a single resonance of HPO_4 groups at δ(iso) of 6.8 ppm, remains practically unchanged after the drying and thus, compound **1-*dried*** can be formulated as $Zr(HPO_4)_2$. Finally, deconvolution of the phosphorus resonances in the $^{31}P\{^1H\}$ MAS NMR spectrum of compound **1-D_2O** (Figure 2 top) results in their integral ratio giving formula $Zr(HPO_4)_2 \cdot 0.35D_2O$ in account for a maximal content of one water molecule in the structural $Zr(HPO_4)_2$ fragment (compound **1**). A simple calculation for this formula gives a water mass loss of 2.4%. The latter is in satisfactory agreement with the TGA curve (Figure S2), illustrating a small mass loss (1.5%) in the first step from 25 °C to 250 °C.

Variations in ^{31}P chemical shift for the hydrated and anhydrous zirconium phosphate intercalates have been interpreted earlier in terms of hydrogen bonds, formed by the interlayer phosphate group, where a *donor* hydrogen bond leads to displacement Δδ(iso) of ~ 3 ppm, while Δδ(iso) of ~ -2 ppm corresponds to an acceptor hydrogen bond.[16] Following this rule, the low-

field resonance of HPO_4 groups at δ of -21.4 ppm could be attributed to hydrogen bond P–OH···OD_2[11] (Figure 1). Upon formation of such a bond, rates of rotations around the P–O axis in the structurally-different HPO_4 groups of compound **1-D_2O**, which cause phosphorus NMR relaxation by the *dipolar proton-phosphorus* mechanism,[17] will have to differ. However, both phosphorus resonances of **1-D_2O** (-21.4 ppm and -23.1 ppm) show at 295 K almost equal ^{31}P T_1 times of 1.9 and 2.0 $\times 10^2$ s, which run counter to the formation of the acceptor hydrogen bond (*vide infra*).

The state of the intercalated water in compound **1-D_2O** was characterized by the ^2H solid-echo MAS NMR spectra recorded at different spinning rates (from 4 to 12 kHz) and temperatures. The spectrum at 295 K in Figure 3 is well resolved to show the deuterium quadrupole pattern, corresponding to a limited molecular mobility of the water. In general, observation of a limited

Here Figure 3

mobility at room temperature is not typical of water molecules in solids. As we assume, this behavior is connected with the unusual bonding mode of the water in **1-D_2O**.

The most important feature of the room-temperature ^2H MAS NMR spectrum in Figure 3 is the *emergence of two deuterium resonances with δ_{iso} of 8.5 and 3.7 ppm, the ratio of the integral intensities of which is determined to be 1 to 1* accounting for all of the sidebands. According to the spinning sideband analysis, exampled in Figure S3, the DQCC's of these resonances, averaged in the room-temperature experiments carried out at varying spinning rates are quite different: 202 ± 5 kHz versus 107 ± 5 kHz (Table 1), illustrating, thus, different mobility of the corresponding

deuterons. This is in full agreement with the ^{2}H T_1 times of 0.17 and 0.015 s that are different for these resonances at 295 K. Two possible interpretations could account for this phenomenon. First: both resonances belong to the same molecule D_2O, containing two spectroscopically-distinguishable deuterons, one of which is hydrogen-bonded (δ_{iso} = 8.5 ppm). Second: the resonances characterize two states of water molecules, which move differently and only one of the molecules is hydrogen-bonded. The latter evidently implies an energy difference of these molecules. Then, the equal populations of these energy-different molecular states in the frameworks of the second hypothesis is rather surprising. Moreover, when D_2O is removed by a consequent drying of a **1-D_2O** sample, the intensities of both ^{2}H resonances reduce, while maintaining, however, their 1 to 1 ratio (Figure S4). In addition, temperature does not affect this 1 to 1 ratio as shown by the ^{2}H MAS NMR spectra of **1-D_2O** recorded on cooling from 325 to 253 K (Figure S5). All of these factors are consistent with the one-molecule water model with two spectroscopically-distinguished deuterons, where one of the deuterons, forming a strong hydrogen bond, is binding to the zirconium-coordinated oxygen (Zr–*O*–P–OH) as shown in Scheme 1.

Here Scheme 1

Namely this coordination will not affect mobility of the HPO_4 groups. Finally, the low-field position of the hydrogen-bonded deuteron (δ_{iso} = 8.5 ppm) is not unusual because similar shifts have been reported earlier for crystalline hydrates and ice.[18]

Dynamics of water in solids or semi-solids is not simple, changing from fast isotropic (liquid-like) motions in porous materials[14,19] or phospholipids[20,21] to flipping motions even at

room temperature in deuterated hydrated salts.[22] In the literature, 180°-jumps in zirconium phosphates,[23] jumps with tetrahedral symmetry or a six-site exchange between different orientations of the water molecules in ice have also been suggested.[24-27] It is remarkable that the molecular reorientations often occur on the NMR (T_2) time scale. In contrast, all the deuterium resonances of water in the ^{2}H MAS NMR spectrum of **1-D_2O** remain sharp between 325 K and 253 K (Figures 3 and S5). Thus, if the water molecules in **1-D_2O** are mobile, their reorientations must be fast on the ^{2}H NMR time scale. Table 1 lists the DQCC values, characterizing the resonances in the ^{2}H MAS NMR spectra of **1-D_2O** obtained between 325 and 253 K at a spinning rate of 8 kHz. As seen, the DQCC's,

TABLE 1. The DQCC values (± 5 kHz) and asymmetry parameters η calculated for the resonances with δ_{iso} of 8.5 ppm (1) and δ_{iso} of 3.7 ppm (2) in the ^{2}H MAS NMR spectra of **1-D_2O**.

T (K)	DQCC(1)	η(1)	DQCC(2)	η(2)
325	200	0.0	111	0.67
295	202	0.075	107	0.70
253	207	0.0	120	0.67

calculated for resonance at δ_{iso} of 8.5 ppm in Table 1 are always significantly larger than those for the deuterons at δ_{iso} of 3.7 ppm. The large DQCC's are close to the values reported for frozen water in pores of silica (215 kHz at 173 K),[19] crystalline hydrates (240 kHz at 143 K),[22] and ice (192 kHz[24] or 213 - 226 kHz[27]), while the smaller DQCC's are well compared to 121 kHz

obtained for *mobile* water molecules in crystalline hydrates at room temperature.[22] Thus, the high-field deuterons in **1-D_2O** are more mobile, leading to the effectively increased η parameter in Table 1. Note that such an η effect, caused by the molecular mobility has been noted earlier.[22] As we believe, all the above factors satisfy fast rotations of the intercalated water around the axis along the linear hydrogen bond in Scheme 1. Here the DQCC's of the hydrogen-bonded deuterons with the principal components of electric field gradients, situated along the motional axis will not be affected by the rotation ($\theta = 0^o$) in contrast to those of the high-field deuterons, where the principal components form the angle θ equal to -105° for the water. Note also that the different ^2H T_1 times measured for these deuterons corroborate well with this model. This motional DQCC effect can be estimated semi-quantitatively by applying equation (**1**) valid for fast rotations, where $\Delta\nu$ is the observed quadrupolar splitting ($\Delta\nu = 3/4\ DQCC_{obs}$), $DQCC_{static}$ is the quadrupolar

$$\Delta\nu = ¾\ DQCC_{static}\ (kHz)(3\cos^2\theta - 1)/2 \qquad (1)$$

coupling constant in the absence of motions and θ is the angle, formed by the main electric field gradient and the rotational axis.[28] Taking $DQCC_{static}$ as 207 kHz (Table 1, 253 K) and angle θ of 105°, the equation gives $DQCC_{obs}$ of 83 kHz. Comparison with the experimental values of 107-120 kHz shows that the model reproduces only the expected tendency. In reality, the situation can be more complex if, for example, the hydrogen bond is not linear but bent. In this context, a temperature effect on the ^2H MAS NMR spectra of compound **1-D_2O**, clearly visible below 253 K, is of great interest. As seen in Figure 4, on cooling the character of the quadrupolar pattern changes to show a slight increase in DQCC's and the high-field resonance moves towards a low

magnetic field. This evolution leads to a single broadened low-field resonance, observed at 195 K, which is characterized by δ_{iso} of ~ 8 ppm and the DQCC of 207 kHz. This phenomenon can be interpreted by the presence of a weak hydrogen bond P–(H)O···DO in Scheme 1: At high temperatures, population of this water state is small. On cooling, however, the population grows, leading to the doubly hydrogen-bonded immobile water molecule with the large DQCC value. Finally, the preparation of compound **1-D_2O** by treatment of **1** with D_2O could lead to *D*PO_4 groups appearing due to a potential *deuterium*-proton exchange between the acidic *H*PO_4 protons[7] and D_2O. The ^2H solid-echo MAS NMR spectra presented in the present study do not show DPO_4 signals. Nevertheless, this problem requires a comprehensive study which is currently in progress.

In summary, the ^1H, ^2H, and ^{31}P solid-state MAS NMR data collected for the crystalline layered zirconium phosphate material **1-D_2O** have resulted in an unprecedented observation of the intercalated water with two spectrally-distinguished deuterons, which show different DQCC's and ^2H T_1 times. The data obtained were interpreted by fast reorientations of water molecules around the O···D–O axis of the hydrogen bond, formed with a zirconium-coordinated oxygen.

3. EPERIMENTAL.

3.1. Synthetic methodology

Compound **1-D_2O** was prepared from compound **1** treated with D_2O. Details for the synthesis and treatment can be seen in the supporting information.

3.2. Techniques / Instrumentation.

The X-ray diffraction pattern of **1-D_2O** (Figure S1) was obtained with a Bruker-AXS D8 short arm diffractometer equipped with a multiwire lynx eye detector using Cu (Kα, λ=1.542Å). It was operated at a potential of 40 kV and a current of 40 mA. TGA (Figure S2) was carried out on a Mettler Toledo TGA/DSC 1 instrument. A sample was heated from room temperature to 800 °C at a heating rate of 5 °C min^{-1} under air.

$^{31}P\{^1H\}$, ^1H and ^2H MAS NMR spectra were obtained with a Bruker Avance-400 spectrometer (400 MHz for ^1H nuclei) equipped with a standard a 4-mm MAS NMR probe head. A standard 4 mm zirconium oxide rotors have been applied. The ^1H, ^2H, and ^{31}P chemical shifts are referenced to external TMS, CD_3OD (referred to TMS), and $(NH_4)_2HPO_4$, respectively. ^2H and ^{31}P T_1 relaxation times were determined by inversion−recovery (180°−τ−90°) experiments with the well calibrated *rf* pulses and relaxation (recycle) delays adjusted to provide full nuclear relaxation in each cycle. The obtained experimental curves "signal intensity versus τ time" have been treated with a standard nonlinear fitting computer program based on the Levenberg−Marquardt algorithm. ^2H MAS NMR spectra were recorded with a regular solid-echo pulse sequence with 90^0 *rf* pulse of 3.5 μs generally with numbers of scans of 3550 – 6500. The variable-temperature NMR experiments have been performed with a standard temperature unite of the spectrometer. DQCC calculations were carried out by a sideband analysis with a standard Bruker program package.

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