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Oxygen coordination of aluminum cations in dehydrated $AlPW_{12}O_{40}$ investigated by solid-state NMR spectroscopy

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ABSTRACT

Dehydrated aluminumdodecatungstophosphate ($AlPW_{12}O_{40}$) was investigated by ^{27}Al MAS NMR spectroscopy in magnetic fields of 9.4 and 17.6 T. Two kinds of octahedrally coordinated (δ_{27Al} = 1–2 ppm, C_Q = 2.4–2.5 MHz, and δ_{27Al} = 4–6 ppm, C_Q = 6.0–6.5 MHz), two kinds of penta-coordinated (δ_{27Al} = 24–30 ppm, C_Q = 7.0–7.3 MHz, and δ_{27Al} = 44 ppm, C_Q = 7.5–8.7 MHz), and a small amount of tetrahedrally coordinated aluminum cations (δ_{27Al} = 65 ppm, C_Q = 8.2–8.5 MHz) were found. Comparison with ^1H MAS NMR spectroscopic studies indicates that the dehydroxylation of aluminum OH groups (δ_{1H} = 4.2 ppm and 5.6 ppm) at temperatures of 473 and 573 K is accompanied by a partially irreversible change of the oxygen coordination of aluminum cations.

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1. Introduction

Heteropoly acids and their salts are often applied in aqueous solution or as solid catalysts with a 'pseudo-liquid phase' [1,2]. The chemical behavior of these materials at low temperatures is closely related to coordinated molecules, such as water, alcohols, and ethers, which move into the three-dimensional bulk phase and expand the distance between the Keggin units acting as structural units. The crystal structure of the hexahydrate of $H_3PW_{12}O_{40}{\cdot}6H_2O$ consists of $PW_{12}O_{40}^{3-}$ polyanions, which are packed in a cubic structure, and the acidic protons (H^+) compensating the negative framework charges are present in form of $H_5O_2^+$ cations [3]. In the anhydrous $H_3PW_{12}O_{40}$, without water molecules acting as spacers between the Keggin units, the acidic protons exist in an isolated manner and give rise to a ^1H MAS NMR signal at the chemical shift of ca. 9.1 ppm [4].

Recently, the hydroxyl coverage of aluminumdodecatungstophosphate ($AlPW_{12}O_{40}$) obtained by an aluminum exchange of $H_3PW_{12}O_{40}$ in aqueous solution was investigated by solid-state NMR spectroscopy upon dehydration at 373–673 K [5]. Interestingly, the increase of the dehydration temperature from 473 to 573 K led to a significant broadening of XRD reflexes of $AlPW_{12}O_{40}$ and a slight shift of the reflex positions to larger angle values corresponding to a weak shrinking of the unit cell parameters, while the characteristic reflex intensities of the Keggin structure remained stable (see Fig. 1 of Ref. [5]). In addition, a strong dehydroxylation of the acidic protons (H^+) occurred from 0.300 mmol g^{-1} at 473 K to 0.025 mmol g^{-1} at 573 K. The hydroxyl groups of dehydrated $AlPW_{12}O_{40}$ are formed by the following processes [1,5]:

$$[Al(H_2O)_n]^{3+} \rightarrow [Al(OH)_2]^+ + 2H^+ - (n-2)H_2O \quad (1)$$

$$[Al(H_2O)_n]^{3+} \rightarrow [AlOH]^{2+} + 1H^+ - (n-1)H_2O \quad (2)$$

which correspond to a dissociation of water molecules in the electrostatic field of the aluminum cations and the formation of acidic protons (H^+) and aluminum hydroxyl groups (AlOH), respectively. In the reverse case, also an interconnection should exist between the dehydroxylation of AlOH and H^+ compounds.

In order to clarify the effect of dehydroxylation of $AlPW_{12}O_{40}$ on the oxygen coordination of aluminum cations in this material, the hydroxyl coverage and coordination of aluminum cations in $AlPW_{12}O_{40}$ upon dehydration at 473 and 573 K are investigated by ^1H and ^{27}Al MAS NMR spectroscopy in the present work.

2. Experimental part

The preparation of aluminumdodecatungstophosphate ($AlPW_{12}O_{40}$) was performed as described in Ref. [5]: The parent dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$) was commercially obtained from POCH S.A., Poland. $AlPW_{12}O_{40}$ was obtained by the addition of a stoichiometric amount of aqueous solution of $Al(NO_3)_3{\cdot}9H_2O$ to the aqueous solution of $H_3PW_{12}O_{40}$ at room temperature for 1 h. This mixture was dried at 323 K. About 250 mg of material were thermally treated with the following temperature program in a 5 mm glass tube connected to a vacuum line. The temperature was raised with 0.5 K min^{-1} from room temperature

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to the final temperatures of 473 and 573 K and evacuated at a pressure of $p < 10^{-2}$ mbar for 6 h. Subsequently, the samples were sealed in glass tubes. Before the solid-state NMR experiments, the dehydrated materials were filled into gas-tight 4 mm or 2.5 mm rotors in a glove box purged with dry nitrogen gas. Rehydration of some dehydrated samples was carried out for 48 h in a desiccator over a saturated solution of $Ca(NO_3)_2$.

The solid-state NMR experiments were performed on Bruker MSL 400 and Bruker Avance 750 spectrometers at resonance frequencies of 400.3 MHz (9.4 T) for ^{1}H nuclei and 104.3 MHz (9.4 T) or 195.5 MHz (17.6 T) for ^{27}Al nuclei. For ^{1}H MAS NMR spectroscopy, the flip angle of $\pi/2$ and the repetition time of 10 s were used. ^{27}Al MAS NMR spectra were recorded upon a single-pulse $\pi/12$ excitation with the pulse duration of 0.61 μs (9.4 T) and 0.34 μs (17.6 T) and the repetition time of 2 s. For the ^{1}H and ^{27}Al MAS NMR studies, 4 mm and 2.5 mm Bruker rotors were used with sample spinning rates of 10 and 25 kHz, respectively. To record the ^{27}Al MAS NMR spectra in magnetic fields of 9.4 T and 17.6 T, the induction decays of 160.000 and 40.000 scans were accumulated, respectively.

The concentration of hydroxyl groups of the dehydrated $AlPW_{12}O_{40}$ was determined by comparing the ^{1}H MAS NMR intensities with that of an external standard consisting of zeolite Na,H–Y, which was obtained by exchange of 35% of the sodium cations by ammonium ions and calcination at 673 K. In the case of ^{27}Al MAS NMR spectroscopy, the total intensity was related to the aluminum concentration determined by optical emission spectroscopy with inductively coupled plasma (ICP/OES). The chemical shift values were referenced to tetramethylsilane for ^{1}H and a 0.1 M aqueous solution of $Al(NO_3)_3$ for ^{27}Al MAS NMR spectroscopy.

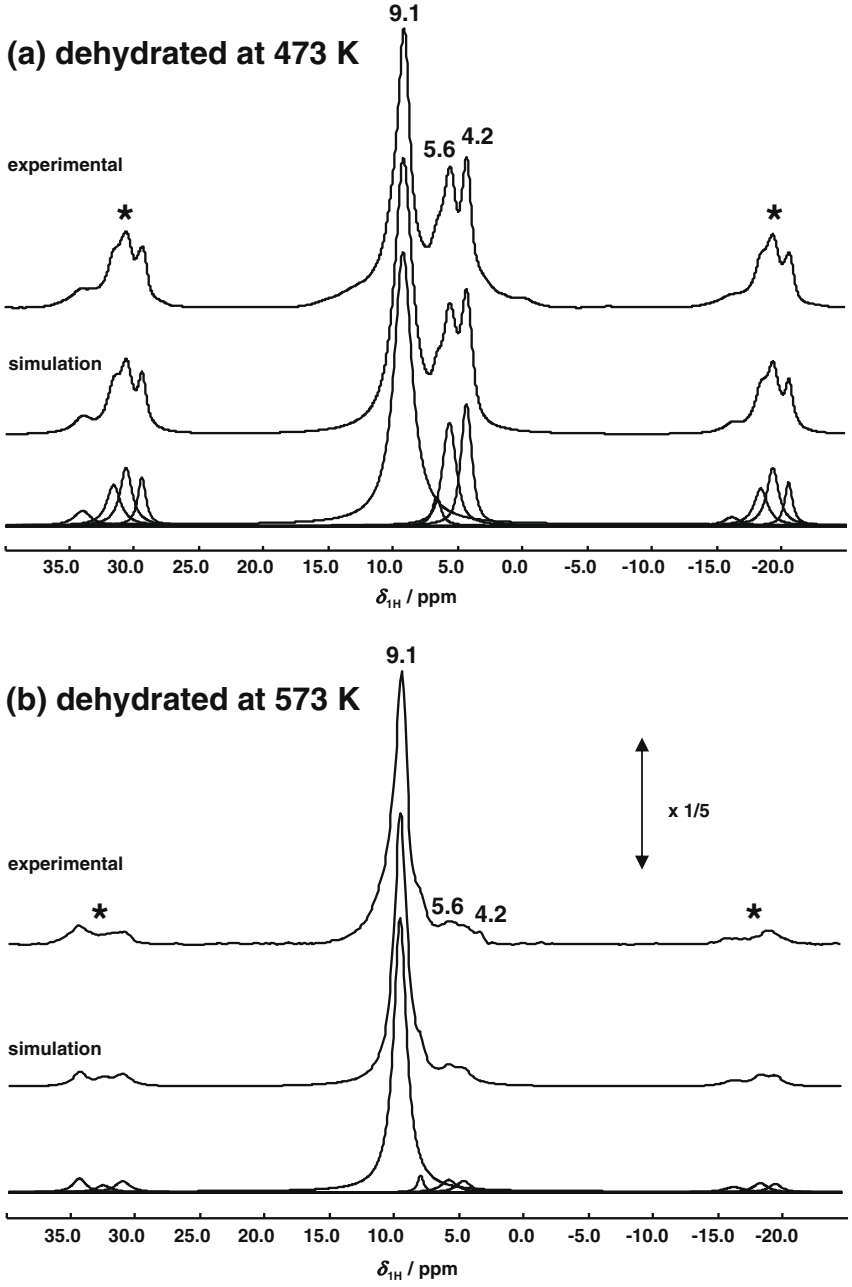

Fig. 1. ^{1}H MAS NMR spectra of $AlPW_{12}O_{40}$ recorded upon dehydration at 473 K (a) and 573 K (b).

Table 1
Chemical shifts δ_{1H}, assignments, and concentration of the hydroxyl groups occurring in the ^{1}H MAS NMR spectra of $AlPW_{12}O_{40}$ recorded upon dehydration at 473 and 573 K (see Fig. 1).

Dehydration temperature (K)	Signal/δ_{1H} (ppm)	OH groups	OH concentration (mmol g^{-1})[a]
473	4.2	$[AlOH]^{2+}$	0.110
	5.6	$[Al(OH)_2]^+$	0.270
	9.1	Acidic H^+	0.300
573	4.2	$[AlOH]^{2+}$	0
	5.6	$[Al(OH)_2]^+$	0.006
	9.1	Acidic H^+	0.025

[a] Determined in comparison with external intensity standard (experimental accuracy: ±10%).

The data were processed with the Bruker software WINNMR and WINFIT in order to separate the MAS NMR signals and to obtain a quantitative evaluation of signal intensities.

3. Results and discussion

3.1. Quantitative ^{1}H MAS NMR studies of $AlPW_{12}O_{40}$ dehydrated at 473 and 573 K

Dehydration of aluminumdodecatungstophosphate ($AlPW_{12}O_{40}$) at temperatures higher than 473 K leads to a significant decrease of the coverage with acidic protons (H^+), as it was demonstrated by the intensity behavior of the ^{1}H MAS NMR signal at δ_{1H} = 9.1 ppm in our previous work [5]. Therefore, the quantitative comparison of the hydroxyl coverage and aluminum coordination

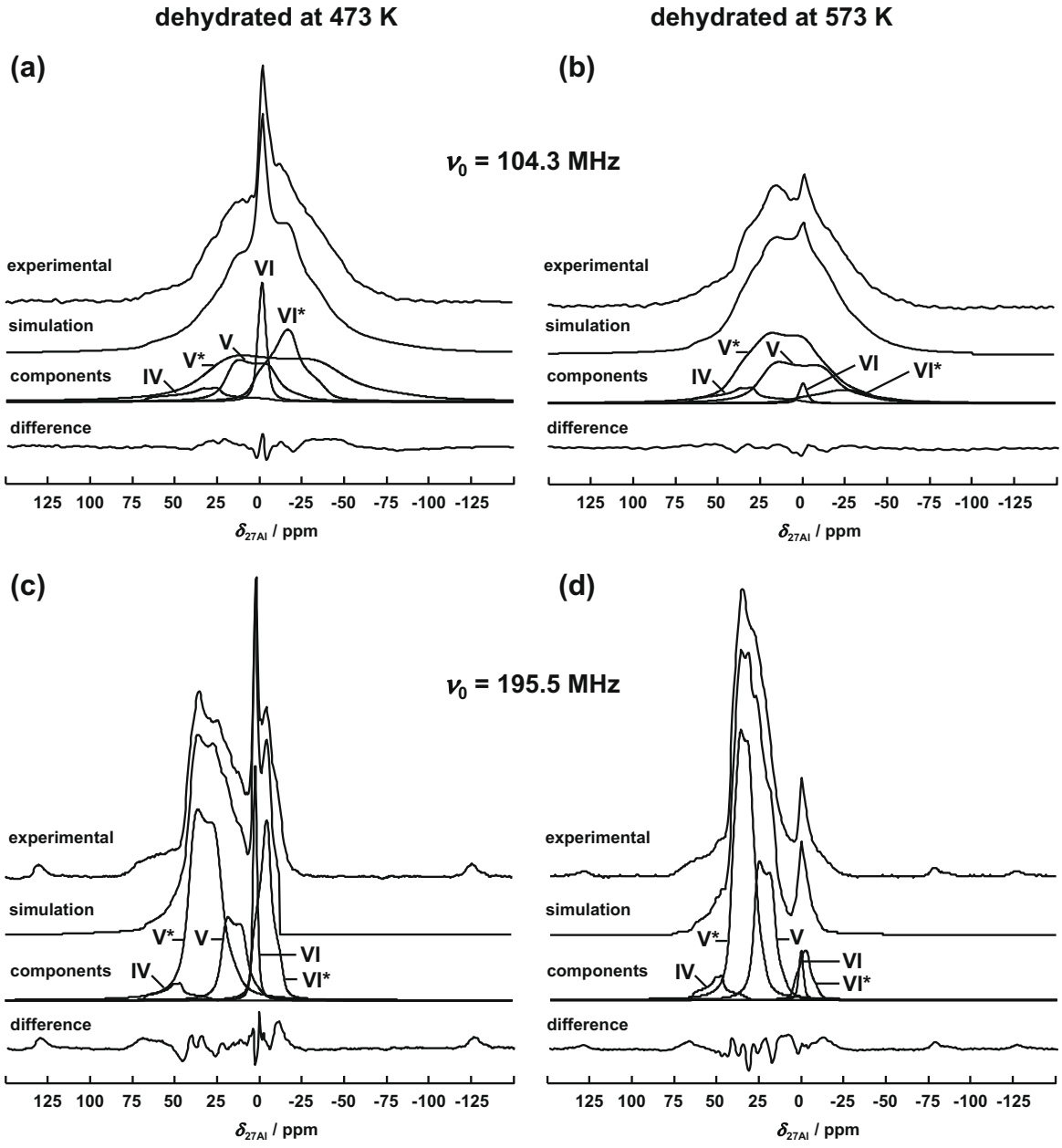

Fig. 2. ^{27}Al MAS NMR spectra of $AlPW_{12}O_{40}$ recorded upon dehydration at 473 K (a and c) and 573 K (b and d) in magnetic fields of B_0 = 9.4 T (a and b: ν_0 = 104.3 MHz) and B_0 = 17.6 T (c and d: ν_0 = 195.5 MHz). The figures show from top to bottom the experimentally recorded spectra, the simulated spectra, the components used for the simulation, and the difference between the experimental and simulated spectra.

in dehydrated $AlPW_{12}O_{40}$ was performed in the present study with samples dehydrated at 473 and 573 K. The corresponding ^1H MAS NMR spectra and their simulation are shown in Fig. 1. In addition to the signal of acidic protons at 9.1 ppm, there are two signals at 4.2 and 5.6 ppm, which can be attributed to $[AlOH]^{2+}$ and $[Al(OH)_2]^+$ groups, respectively. The assignment of these signals was supported by adsorption of deuterated pyridine (C_5ND_5) as a probe molecule leading to a low-field shift of the signal at 9.1 ppm, but not of the signals at 4.2 and 5.6 ppm. Furthermore, $^1H\{^{27}Al\}$-TRAPDOR MAS NMR experiments utilizing the dipolar coupling between ^1H nuclei with spin $I = 1/2$ and quadrupolar ^{27}Al nuclei having a nuclear spin of $S = 5/2$ were performed [5]. The difference spectrum of the $^1H\{^{27}Al\}$-TRAPDOR MAS NMR experiment consisted exclusively of the signals at 4.2 and 5.6 ppm with strong spinning sidebands indicating dominating heteronuclear dipolar interactions (H–Al). The larger residual MAS NMR line width of the signal at 5.6 ppm in comparison with the broadening of the signal at 4.2 was explained by the residual dipolar H–H interactions in the local structure of the $Al(OH)_2$ groups with two hydroxyl protons [5].

Generally, the ^1H MAS NMR signals of unperturbed metal OH groups, such as AlOH groups at the outer surface of Al_2O_3 particles, occur at chemical shifts of ca. 0 ppm [6,7]. In the case of internal AlOH groups interacting via hydrogen bondings with neighboring oxygen atoms, chemical shifts of the ^1H MAS NMR signals of 2.6–4.5 ppm were observed [6–8]. Therefore, also the resonance positions of the ^1H MAS NMR signals occurring at 4.2 and 5.6 ppm in the spectra of dehydrated $AlPW_{12}O_{40}$ (Fig. 1) are a hint for the presence of hydrogen bonds of the corresponding $[AlOH]^{2+}$ and $[Al(OH)_2]^+$ groups, respectively, with neighboring oxygen species.

Table 1 gives a survey on the quantitative evaluation of the ^1H MAS NMR spectra in Fig. 1. According to these data, raising the dehydration temperature from 473 to 573 K is accompanied by a decrease of the concentration of acidic protons (9.1 ppm) by 0.275 mmol g^{-1} and of hydroxyl groups at aluminum cations (4.2 and 5.6 ppm) of 0.374 mmol g^{-1}. This simultaneous decrease of both types of hydroxyl groups can be explained by the reversed process of hydroxyl formation [5], i.e. by the following reactions:

$$[Al(OH)_2]^+ + 2H^+ \rightarrow Al^{3+} + 2H_2O \quad (3)$$

$$[AlOH]^{2+} + 1H^+ \rightarrow Al^{3+} + 1H_2O \quad (4)$$

The observation that more hydroxyl groups at aluminum cations are dehydroxylated than acidic protons could be an indication that also some $[Al–O–Al]^{4+}$ species are formed upon increase of temperature.

Table 2
Isotropic chemical shifts δ_{27Al}, assignments, quadrupole coupling constants C_Q, asymmetry parameter η_Q, symmetric broadenings *EM*, and concentration of aluminum cations occurring in the ^{27}Al MAS NMR spectra of $AlPW_{12}O_{40}$ recorded upon dehydration at 473 and 573 K at $B_0 = 9.4$ and 17.6 T.

Dehydration temperature (K)	Signal/ δ_{27Al} (ppm)	Aluminum coordination	C_Q (MHz)	η_Q	*EM* (Hz)	Aluminum concentration (mmol g^{-1})[a]
473	2	VI	2.4	1	100	0.030
	4	VI*	6.0	0.8	30	0.074
	24	V	7.0	0.2	40	0.056
	44	V*	8.7	0.2	45	0.169
	65	IV	8.5	0.8	10	0.015
573	2	VI	2.5	1	100	0.008
	6	VI*	6.5	0.7	30	0.027
	30	V	7.3	0.2	40	0.102
	44	V*	7.5	0.4	35	0.192
	65	IV	8.2	0.8	10	0.015

[a] Aluminum concentration determined via chemical analysis (0.344 mmol Al per gram $AlPW_{12}O_{40}$) and relative MAS NMR intensities (experimental accuracy: ±10%).

3.2. ^{27}Al MAS NMR investigations of dehydrated $AlPW_{12}O_{40}$ at 9.4 and 17.6 T

For identifying and quantifying the various signals of aluminum cations in dehydrated $AlPW_{12}O_{40}$, ^{27}Al MAS NMR spectra were recorded in magnetic fields differing by a factor of ca. 2. ^{27}Al MQMAS NMR spectroscopy, applied in a number of recent studies focusing on the local structure of aluminum in solids [9–11], was not successful due to the small concentration of ^{27}Al nuclei and various signals with similar quadrupolar parameters in the present case. However, the characteristic singularities in the one-dimensional

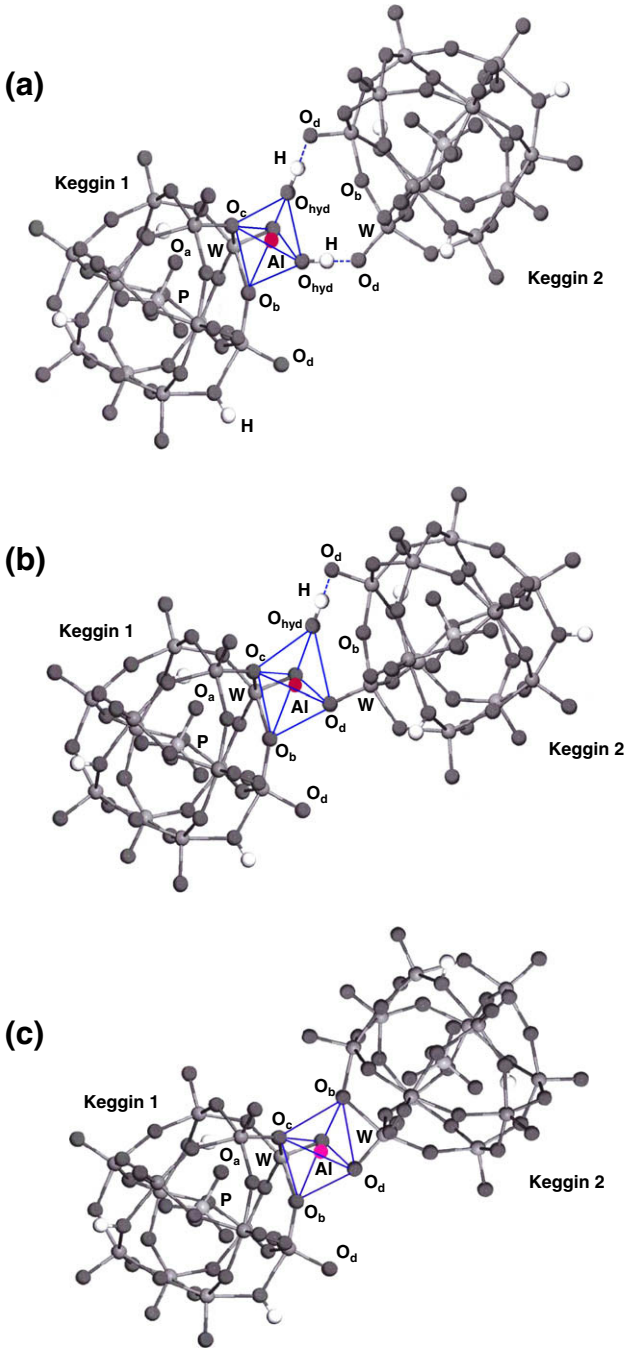

Fig. 3. Suggested local structures of penta-coordinated aluminum cations with two aluminum hydroxyl groups ($AlO_{hyd}H$) involved in hydrogen bondings to two terminating oxygen atoms O_d of Keggin unit 2 (a), with one aluminum hydroxyl group ($AlO_{hyd}H$) involved in hydrogen bonding to one terminating oxygen atom O_d of Keggin unit 2 (b), and upon dehydroxylation of all aluminum hydroxyl groups (c).

^{27}Al MAS NMR spectra of dehydrated $AlPW_{12}O_{40}$ recorded at 9.4 and 17.6 T allowed to describe both sets of spectra by six signals as demonstrated in Fig. 2. The strategy of performing these simulations consisted in finding the smallest set of signals necessary for the description of all singularities. Although the resolution of the spectra recorded at 9.4 T is low, these spectra were very useful to exclude quadrupole parameters leading to second-order shifts lying outside of the experimentally observed spectral range.

In Table 2, the ^{27}Al MAS NMR signals and their spectroscopic parameters used for the simulations shown in Fig. 2, bottom, are listed. According to the isotropic chemical shifts, δ_{27Al}, of these signals, two types of octahedrally coordinated (signals VI and VI*), two types of penta-coordinated (signals V and V*), and one type of tetrahedrally coordinated (signal IV) aluminum cations exist in dehydrated $AlPW_{12}O_{40}$ (cf. Refs. [12–18]). The signals marked by an asterisk are involved in slightly stronger quadrupolar interactions corresponding to larger quadrupole coupling constants C_Q in comparison with the second type of aluminum species of same oxygen coordination type. Larger C_Q values indicate a more inhomogeneous charge distribution in the local structure of the resonating quadrupolar ^{27}Al nuclei. In the present case, the larger C_Q values are due to slightly strained AlO_6 (signal VI*) and AlO_5 (signal V*) compounds. Interestingly, both signals V and V* are characterized by small asymmetry parameters η in the range of 0.2–0.4 indicating a local structure with rotational symmetry, i.e. similar x- and y-components of the electric field gradient, if z denotes the direction of the maximum gradient at the position of the aluminum nucleus.

Comparing the concentration of aluminum OH groups in Table 1, last column, with the concentration of aluminum cations with different oxygen coordination in Table 2, last column, no relationships between these values are obvious. On the other hand, the increase of the dehydration temperature from 473 to 573 K is accompanied by a decrease of the concentration of octahedrally coordinated aluminum cations (signals VI and VI*) by 0.07 mmol g^{-1} and a corresponding increase of the number of penta-coordinated aluminum species (signals V and V*). These penta-coordinated aluminum cations have a high local symmetry as indicated by the low asymmetry parameter η. Within the experimental accuracy of the method, the concentration of tetrahedrally coordinated aluminum species did not change upon dehydration of $AlPW_{12}O_{40}$ at 473 and 573 K and is very small indeed (0.015 mmol g^{-1}). The preferred oxygen coordination of aluminum atoms in $AlPW_{12}O_{40}$ at the dehydration temperatures under study, therefore, is the fivefold oxygen coordination.

In comparison with the concentration of aluminum OH groups ($[AlOH]^{2+}$, $[Al(OH)_2]^+$), which dehydroxylate between 473 and 573 K (0.374 mmol g^{-1}, see Section 3.1), the concentration of aluminum species changing their oxygen coordination number in the same temperature range (0.07 mmol g^{-1}) is significantly lower. Hence, progressing dehydroxylation of aluminum OH groups in $AlPW_{12}O_{40}$ must be accompanied by a stronger coordination of these aluminum species to the oxygen atoms of Keggin units, thus replacing their previous coordination to hydroxyl oxygen atoms. This replacement of the coordinating oxygen atoms of hydroxyl groups by the Keggin oxygen atoms leads to a slight change in the local symmetry of the coordinating aluminum atoms (see C_Q and η values) and therefore is consistent with and explains the weak broadening and shift of the XRD reflexes (cf. Section 1).

Based on the data summarized in Tables 1 and 2 it can be stated that most of the aluminum cations in dehydrated $AlPW_{12}O_{40}$ exist in a fivefold coordination with high local symmetry, i.e. low asymmetry parameter η. After thermal treatment at 473 K, a significant content of these aluminum cations coordinate to hydroxyl groups and do not change their oxygen coordination number upon dehydroxylation at 573 K. This finding is a hint for the presence of a significant number of aluminum species in trigonal bipyramids, similar to AlO_5 found in andalusite [9,19]. As suggested models, Fig. 3a–c shows arrangements of aluminum cations in trigonal bipyramids linking two Keggin units 1 and 2 (for structures of $PW_{12}O_{40}$ units, see Refs. [15,16]). In these models, the aluminum cations are coordinated to oxygen atoms O_b, O_c, and O_d of Keggin unit 1 and two hydroxyl oxygen atoms of $AlO_{hyd}H$ groups (a), one hydroxyl oxygen atom and one oxygen atom O_d of Keggin unit 2 (b), and oxygen atoms O_b and O_d of Keggin unit 2 (c). The hydrogen bondings of the hydroxyl protons of $AlO_{hyd}H$ groups to oxygen atoms of Keggin unit 2 in models (a) and (b) explain the significant low-field shift of the ^{1}H MAS NMR signals caused by the aluminum hydroxyl groups at 4.2 and 5.6 ppm.

3.3. ^{27}Al MAS NMR investigations of as-exchanged and rehydrated $AlPW_{12}O_{40}$

For studying the reversibility of dehydration and rehydration of $AlPW_{12}O_{40}$, ^{27}Al MAS NMR investigations of the as-exchanged material (Fig. 4a) and the materials rehydrated upon dehydration at 473 K (not shown) and 573 K (Fig. 4b) were performed. The spectra in Fig. 4 consist of the signals VI and VI* of octahedrally coordinated aluminum species characterized by isotropic chemical

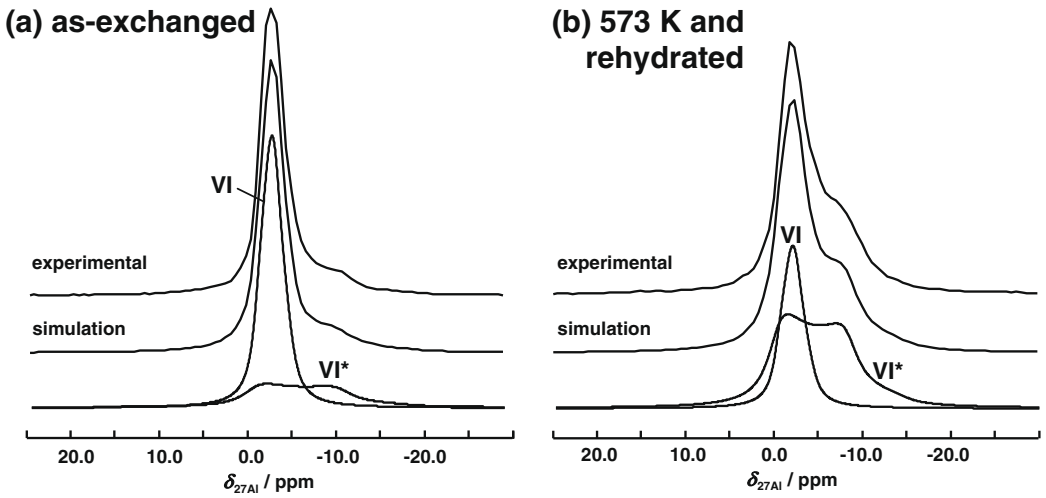

Fig. 4. ^{27}Al MAS NMR spectra of as-exchanged $AlPW_{12}O_{40}$ (a) and the material rehydrated after dehydration at 573 K (b). The spectra were recorded in a magnetic field of B_0 = 9.4 T (ν_0 = 104.3 MHz).

shifts of δ_{27Al} = 0 and 2 ppm and quadrupole coupling constants of $C_Q \leqslant 1.6$ MHz and 3.5 MHz, respectively. Therefore, it can be assumed that all aluminum species in the dehydrated $AlPW_{12}O_{40}$ are accessible for water molecules and coordinate to these adsorbate molecules until reaching an octahedral coordination. Signal VI is comparable with the ^{27}Al MAS NMR spectroscopic behavior of hexa-aqua complexes [20]. The larger C_Q value of signal VI*, on the other hand, indicates a lower symmetry in the local structure of the corresponding AlO_6 units in comparison with the aluminum species causing signal VI. This is a hint for the coordination of these aluminum species (signal VI*) with oxygen atoms of water molecules as well as Keggin units.

Interestingly, in the spectrum of the as-exchanged $AlPW_{12}O_{40}$, the signal VI* has a relative intensity of 24%, while the materials obtained upon dehydration at 473 and 573 K and subsequent rehydration give signals IV* with relative intensities of 64–66%. According to the discussion in Section 3.2, the dehydroxylation of aluminum OH groups upon dehydration of $AlPW_{12}O_{40}$ at 473 and 573 K leads to an increasing coordination of the aluminum cations to the oxygen atoms of Keggin units. Therefore, the larger intensity contents of signal VI* in the ^{27}Al MAS NMR spectra of rehydrated materials may indicate that the increasing coordination of aluminum cations to the Keggin oxygen atoms is a partially irreversible process. Rehydration of the dehydrated $AlPW_{12}O_{40}$ sample does not lead to a full replacement of the Keggin oxygen atoms by water molecules in the local coordination sphere of aluminum cations.

4. Conclusions

^1H and ^{27}Al solid-state NMR spectroscopy was successfully applied for studying the interconnection of dehydroxylation and coordination change of aluminum cations in aluminumdodecatungstophosphate ($AlPW_{12}O_{40}$). In agreement with earlier investigations [5], the strongest dehydroxylation of aluminum OH groups in this material was found to occur in the temperature range of 473–573 K. This dehydroxylation process is accompanied by only a moderate coordination change of aluminum cations since most of these metal ions remain in their fivefold oxygen coordination. However, changes in the spectroscopic parameters of the corresponding ^{27}Al MAS NMR signals indicate changes in the local structure of the penta-coordinated aluminum cations during the dehydroxylation process. These changes in the local structure of aluminum cations are explained by a replacement of the coordination to oxygen atoms of aluminum hydroxyl groups by coordination to the Keggin oxygen atoms without changing the total oxygen coordination number, in comparison to the situation before and after thermal treatment and dehydroxylation.

Different ^{27}Al MAS NMR spectra of the as-exchanged $AlPW_{12}O_{40}$ and samples obtained after the rehydration of dehydrated materials indicate that the above-mentioned coordination change of aluminum cations is not fully reversible. A significant content of aluminum cations coordinating exclusively to the Keggin oxygen atoms due to the dehydroxylation process at 573 K do not form the hexa-aqua complexes upon rehydration of the previously dehydrated $AlPW_{12}O_{40}$ material.

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