Assignment of the 27Al and 31P NMR Spectra of the Aluminophosphate Molecular Sieve VPI-5

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Using correlations between structural data and quadrupole coupling constants and isotropic chemical shifts in tandem with the results of 2D-heteronuclear correlation spectroscopy an alternative assignment is proposed for the 27Al and 31P NMR resonances to the three crystallographically distinct Al and P sites in the aluminophosphate molecular sieve VPI-5.

The aluminophosphate molecular sieve VPI-5 has attracted considerable interest owing to its unique structure with very large 18-membered rings which form one-dimensional channels of 12 Å diameter. The crystal structure of hydrated VPI-5 (space group $P6_3$)[1] reveals the presence of three crystallographically inequivalent Al and P sites in the aluminophosphate framework (see Fig. 1), two of them located at the connection of six- and four-membered rings [4/6 sites Al(2), P(2) and Al(3), P(3)] and the third in fused four-membered rings [4/4 site Al(1), P(1)]. While Al(2) and Al(3) are tetrahedrally coordinated to four framework oxygens, Al(1) is octahedrally coordinated to four framework oxygens and to two water molecules. In agreement with this structure, the 31P MAS (magic angle spinning) NMR spectrum of hydrated VPI-5 consists of three resonances of equal intensity at δ −23.7 (P^A), −27.5 (P^B) and −33.2 (P^C),[2] and three resonances could also be resolved in the 27Al DOR (double rotation) NMR spectra measured at 4.7 and 9.4 T with (quadrupolar corrected) isotropic chemical shifts of δ 43.6 (Al^A), 41.6 (Al^B) and −10.4 (Al^C).[3] The overall features of the NMR spectra are thus well understood, but the detailed assignment of the distinct resonances to the specific crystallographic P and Al sites is still problematic. However, the reliable interpretation of the 27Al and 31P NMR spectra is a prerequisite for the NMR investigation of structural transformations of VPI-5 e.g. by de- and re-hydration.[2,4–6]

Table 1 summarizes different assignments of the 31P and 27Al NMR lines proposed in the literature. Very recently, van Eck and Veeman[9] have shown that the correct interpretation of the 31P NMR spectrum can be proved by 2D-heteronuclear 27Al–31P correlation spectroscopy, provided the assignment of the 27Al NMR lines to the distinct Al sites is known. Since owing to its chemical shift line Al^C can unambiguously be attributed to the octahedral Al(1) site it follows from the 2D correlation spectrum that the 31P peak P^C must be assigned to
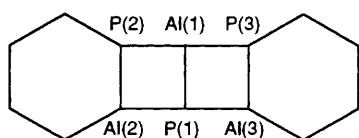

Fig. 1 Schematic drawing of a part of the VPI-5 structure showing the labelling of the crystallographically distinct P and Al sites. Oxygen atoms are not shown for clarity.

P(1).[9] The two 27Al peaks Al^A and Al^B have been attributed to Al(2) and Al(3), respectively, by Grobet et al.[3] If this interpretation is correct, an assignment of the 31P lines P^A to site P(2) and P^B to site P(3) would follow from the 2D correlation spectrum. However, for the reasons outlined below the assignment of line Al^A and Al^B of Grobet et al. may be incorrect and should be interchanged, i.e. line Al^A belongs to Al(3) and line Al^B to Al(2), with the corresponding consequences for the interpretation of the 31P NMR lines derived from the 2D correlation spectrum.

Our main argument for the alternative assignment of the two tetrahedral 27Al peaks is based on the relation between the strength of the quadrupole interaction of the 27Al nucleus and the local distortion of the AlO_4 tetrahedron. Increasing deviation of the AlO_4 coordination from tetrahedral symmetry results in a higher electric-field gradient and, therefore, in a stronger quadrupole interaction of the Al nucleus. The quadrupole interaction is characterized by the quadrupole coupling constant (QCC) and the asymmetry parameter of the electric-field gradient η, while the AlO_4 distortion may be described quantitatively by a shear strain parameter $|\Psi| = \Sigma_i |\tan(\theta_i - \theta_0)|$ where the sum runs over the six O–Al–O angles θ_i, and θ_0 is their ideal value (109.5°).[10] This local distortion parameter is a more appropriate measure

Table 1 Assignments of the 31P and 27Al NMR spectra of hydrated VPI-5 given in the literature and in this work

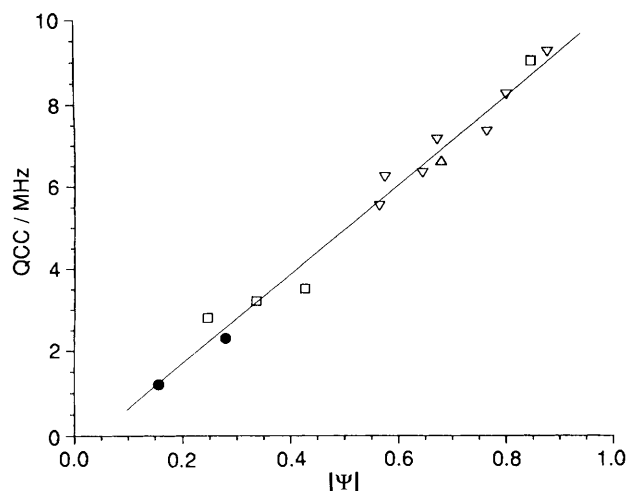|	δ(31P)		
Ref.	−23.7 (P^A)	−27.5 (P^B)	−33.2 (P^C)
4, 5	P(1)		P(2), P(3)
6, 9		P(2), P(3)	P(1)
7, 8	P(2)	P(3)	P(1)
This work	P(3)	P(2)	P(1)
	δ(27Al)		
	+43.6 (Al^A)	+41.6 (Al^B)	−10.4 (Al^C)
3	Al(2)	Al(3)	Al(1)
9		Al(2), Al(3)	Al(1)
This work	Al(3)	Al(2)	Al(1)

Fig. 2 Plot of QCCs of ^{27}Al *vs.* shear strain parameters $|\Psi|$ of the AlO$_4$ tetrahedra in aluminate sodalites[11] (∇, $\triangle$), the feldspars albite, microcline and anorthite[10] ($\square$), and VPI-5 ($\bullet$)

for the change of the field gradient at the ^{27}Al nucleus in the AlO$_4$ environment than the disperison of the four Al–O–P bond angles around the Al site used in the assignment by Grobet *et al.*[3] Indeed, Fig. 2 shows that a linear correlation exists between $|\Psi|$ and QCC of tetrahedral AlO$_4$ sites of framework aluminosilicates (exemplified by the feldspars anorthite, albite and microcline)[10] and aluminate sodalites.[11] QCCs of the two Al sites of VPI-5 have been calculated from the experimental shift values δ_1 and δ_2 determined by Grobet *et al.*[3] from the ^{27}Al DOR NMR spectra of VPI-5 registered at different resonance frequencies ν_{L1} and ν_{L2} according to eqn. (1) (derived from the expressions given in ref. 11) where $K = 6.10^3/\nu_L^2$. No direct information on η can be derived from the

$$QCC\,(1 + \eta^2/3)^{1/2} = [(\delta_1 - \delta_2)/(K_2 - K_1)]^{1/2} \qquad (1)$$

data, but taking into account that η may vary between 0 and 1, QCC between 2.3 and 2.0 MHz are obtained for resonance Al^A and between 1.2 and 1.0 MHz for resonance Al^B. However, from the crystal structure data of VPI-5[1] follows $|\Psi|$ = 0.157 for site A(2) and $|\Psi|$ = 0.280 for site Al(3). Clearly, according to the correlation between $|\Psi|$ and QCC shown in Fig. 2, the ^{27}Al NMR resonance Al^A has to be assigned to site Al(3) and Al^B to site A(2), in contrast to the result of Grobet

et al. On the basis of our assignment of the tetrahedral Al resonances it follows immediately from the ^{27}Al–^{31}P 2D correlation spectrum[9] that the ^{31}P resonance P^B must be attributed to site P(2) and resonance P^A to site P(3).

The interpretation of the ^{27}Al and ^{31}P NMR spectra given above is further corroborated by the well known relation between the mean T–O–T (T = Si, Al, P) bond angles and the isotropic chemical shifts of tetrahedral framework sites derived from theoretical considerations[12] and experimentally confirmed for a series of aluminophosphates by Müller *et al.*[13] According to this relation the isotropic chemical shift is expected to decrease with increasing mean T–O–T angle. The increase of the mean Al–O–P angles from 143.8° for Al(3) to 151.8° for Al(2) and of the mean P–O–Al angles from 145.5° for P(3) to 146.1° for P(2) to 154.5° for P(1)[1] and the corresponding decrease of the attributed chemical shifts (see Table 1) is in line with this expectation.

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