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# Proton sites in Keggin heteropoly acids from $^{17}$O NMR

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The structure of the bulk proton sites in dehydrated solid Keggin-type heteropoly acids (HPA) $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ was determined by $^{17}$O NMR. The terminal W=O oxygen atoms in Keggin heteropolyanions were found to be the predominant protonation sites. The protonation of HPAs in solution is also discussed on the basis of $^{17}$O NMR data.

**Keywords:** tungsten heteropoly acids; determination of proton sites; $^{17}$O MAS and solution NMR

## 1. Introduction

Catalysis by heteropoly acids (HPAs), both fundamental and applied, is a field of growing importance, attracting increasing attention worldwide [1–6]. It is primarily their very high Brønsted acidity and special structural properties that render HPAs promising catalysts. Among a wide variety of HPAs those belonging to the so-called Keggin series are of the utmost importance for catalysis. They include quite rigid heteropolyanions (HPANs) of the form $XM_{12}O_{40}^{x-8}$, where X is the central atom ($Si^{4+}$, $P^{5+}$, etc.), $x$ is its oxidation state, and M is the metal ion ($Mo^{6+}$, $W^{6+}$, etc.). These HPANs adopt a well-known Keggin structure, with a central tetrahedron ($XO_4$) surrounded by twelve edge-sharing metal–oxygen octahedra ($MO_6$) (fig. 1) [7]. In the crystal form of HPA, e.g. $H_3PW_{12}O_{40}\cdot 6H_2O$, Keggin HPANs are hydrogen-bonded to each other by hydrated protons [8]. Unlike the rigid anionic zeolite framework, the Keggin anions retain their mobility even in dehydrated HPA crystals. Such structural flexibility of solid HPA should be taken into account when using HPA as a heterogeneous catalyst ("pseudo-liquid phase") [4].

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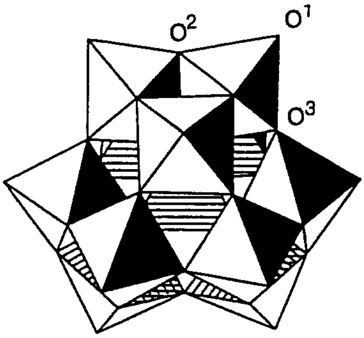

Fig. 1. The Keggin structure of the $\alpha$-$XM_{12}O_{40}^{x-8}$ anion [7]: terminal ($O^1$), edge-bridging ($O^2$) and corner-bridging ($O^3$) oxygen atoms.

Structural characterization of the HPA proton sites is an important step towards understanding the catalytic activity. The proton structure of HPAs has been discussed elsewhere [1,4,9]. Keggin HPANs have three types of outer oxygen atoms as potential protonation centers: terminal oxygens M=O and two types of bridging oxygens M–O–M, edge-sharing and corner-sharing (fig. 1). Bond length–bond strength correlations [10] as well as $^{17}O$ NMR data [11] indicate that in the free polyanions (e.g. $V_{10}O_{28}^{6-}$) in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. In the free Keggin anion, edge-bridging M–O–M oxygens are assumed to be the predominant protonation sites [10], although that has not yet been proven experimentally. $H_3PW_{12}O_{40}$, the strongest HPA in the Keggin series, is completely deprotonated in aqueous solution and partially deprotonated in polar organic solvents [9]. In solid HPAs, the protons take part in the formation of the HPA crystal structure, linking the neighboring heteropoly anions (HPAN). In this case the more accessible terminal oxygens can be protonated [8]. Thus, from single-crystal X-ray and neutron diffraction data [8], the bulk proton sites in crystalline hexahydrate $H_3PW_{12}O_{40}\cdot 6H_2O$ are represented as diaquahydrogen ions, $H_5O_2^+$, each of which links four neighboring HPANs by forming hydrogen bonds with the terminal W=O oxygens (fig. 2a).

There are, however, little data on the proton structure of bulk dehydrated HPA although they are widely used as acid catalysts. Protonation of the bridging M–O–M oxygens in dehydrated HPAs was suggested on the basis of IR band broadening upon dehydration of HPA [12]. However, IR studies have failed to establish unambiguously the protonation sites in polyanions. As demonstrated elsewhere, $^{17}O$ NMR is a sensitive probe for the determination of protonation sites in polyanions [11]. Recently we have shown [13], by $^{17}O$ NMR, that in the dehydrated $H_3PW_{12}O_{40}$ the protons are predominantly localized on the terminal oxygens. The structure of bulk proton sites has been represented as in fig. 2b, where the proton migrates between four equivalent positions, $W{=}O\cdots H^+\cdots O{=}W$, and

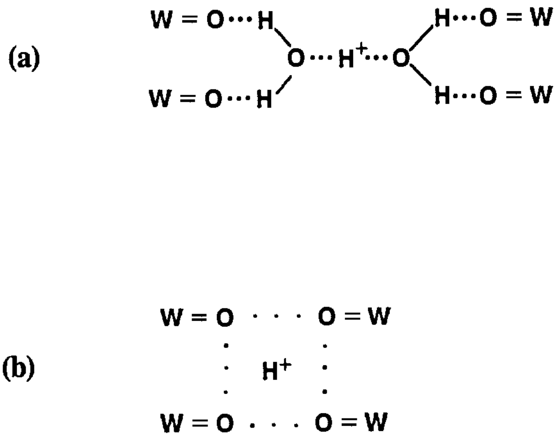

Fig. 2. Proton sites in solid heteropoly acids: (a) $H_3PW_{12}O_{40}$ hexahydrate [8]; (b) dehydrated $H_3PW_{12}O_{40}$ [13].

thus links four HPANs together, as does the $H_5O_2^+$ ion in $H_3PW_{12}O_{40}$ hexahydrate (fig. 2a). It is assumed that this structure is directly formed from the proton structure of the $H_3PW_{12}O_{40}$ hydrate upon dehydration.

The objective of this work is to continue the study of the proton structure of Keggin tungsten HPAs in the solid state and solution by $^{17}O$ NMR. We report here $^{17}O$ NMR MAS spectra for dehydrated solid $H_4SiW_{12}O_{40}$ and an insoluble neutral salt, $Cs_3PW_{12}O_{40}$. The latter is supposed to be a close structural analog to $H_3PW_{12}O_{40}\cdot 6H_2O$ (fig. 2a), where the $H_5O_2^+$ ion is substituted by $Cs^+$ [8]. $Cs_{3-n}H_nPW_{12}O_{40}$ is increasingly used as solid acid catalyst [2,4]. The data obtained provide further evidence that in dehydrated Keggin HPAs the protons are predominantly localized on the terminal W=O oxygens. The protonation of HPAs in solution is also discussed.

## 2. Experimental

### 2.1. MATERIALS

Aqueous solutions of 2–3 at% $^{17}O$ enriched $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were prepared using procedures described elsewhere [14]. Solid HPAs were isolated from acidified (HCl) solutions by extraction with diethyl ether. $^{17}O$ enriched $Cs_3PW_{12}O_{40}$ (a water-insoluble salt) was prepared from $H_3PW_{12}{}^{17}O_{40}$ with a stoichiometric amount of $Cs_2CO_3$ in aqueous solution [15]. According to $^{31}P$ NMR, $H_3PW_{12}{}^{17}O_{40}$ and $Cs_3PW_{12}{}^{17}O_{40}$ contained >99 and 90 mol% Keggin heteropoly compounds, respectively. From $^{17}O$ NMR, $H_4SiW_{12}{}^{17}O_{40}$ contained 95 mol% Keggin HPA. Prior to $^{17}O$ NMR measurements, samples were heated at 200°C/0.4 mmHg for 2 h to completely remove water.

### 2.2. NMR SPECTROSCOPY

NMR spectra were measured at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe [13]. Special care was taken to protect solid samples from moisture. 54.241 MHz $^{17}O$ NMR spectra were taken with 2 μs (10° flip angle) pulses for liquids and 2 μs (20° flip angle) for solids. Repetition time was 0.1 s and several thousand pulse responses were collected in both cases. Exponential multiplication with 10 Hz (liquids) or 50 Hz (solids) line broadening was applied prior to FT. $D_2{}^{17}O$ was used as an internal reference (liquids) or $H_2{}^{17}O$ as an external reference (solids). The positions of the centre bands in the MAS spectra were determined by varying the spinning frequency in the range of 4.2–7.1 kHz. An estimate of the second-order quadrupolar shift showed that the positions of the center bands will differ from the true isotropic chemical shifts by only a few ppm [13].

## 3. Results

First, we have reproduced our results for $H_3PW_{12}O_{40}$. A new $^{17}O$ enriched sample of $H_3PW_{12}O_{40}$ was prepared and characterized by $^{17}O$ NMR in solution (0.12 M in $D_2O$) and in the solid state. The spectra now obtained were fully consistent with those reported earlier [13].

Fig. 3a shows the $^{17}O$ NMR spectrum of $H_3PW_{12}O_{40}$ in HOAc–$H_2O$ 94 : 6 v/v solution, which is similar to that in $H_2O$ (table 1). There are the well-known signals from terminal W=O oxygens (761 ppm) and bridging W–O–W oxygens (two types, 428 and 405 ppm), as well as the signals from HOAc and $H_2O$. The resonances from the four internal P–O–W oxygens are missing because of lack of $^{17}O$ enrichment at this site. These resonances may be expected in the range of 30–80 ppm [14].

Fig. 3b shows the $^{17}O$ MAS NMR spectrum for solid $Cs_3PW_{12}O_{40}$. As expected, this spectrum contains a number of spinning sidebands, similar to that of $H_3PW_{12}O_{40}$ [13]. Lines are somewhat broader than for $H_3PW_{12}O_{40}$, but the resolution is good enough to analyze the spectrum. Varying the spinning frequency enabled us to determine the chemical shifts of all centre bands present: 767 (W=O), 429, 386 ppm (W–O–W) from external $H_2{}^{17}O$. As seen from table 1, the spectrum for $Cs_3PW_{12}O_{40}$ is similar to the solution spectra of either $H_3PW_{12}O_{40}$ in $H_2O$, where HPA is deprotonated [9], or $(Bu^n_4N)_3PW_{12}O_{40}$ in MeCN. On the other hand, there is a large difference in resonances of the terminal W=O oxygens in the solid-state spectra of $Cs_3PW_{12}O_{40}$ (767 ppm) and $H_3PW_{12}O_{40}$ (708 ppm) [13].

The solution $^{17}O$ NMR spectrum of $H_4SiW_{12}O_{40}$ in $H_2O$ is shown in fig. 4a. The spectrum agrees well with that reported elsewhere (table 1). It is almost the same as that of $H_3PW_{12}O_{40}$ in aqueous solution. But in contrast to $H_3PW_{12}O_{40}$, the line from internal Si–O–W oxygens (28 ppm) is seen in the spectrum of

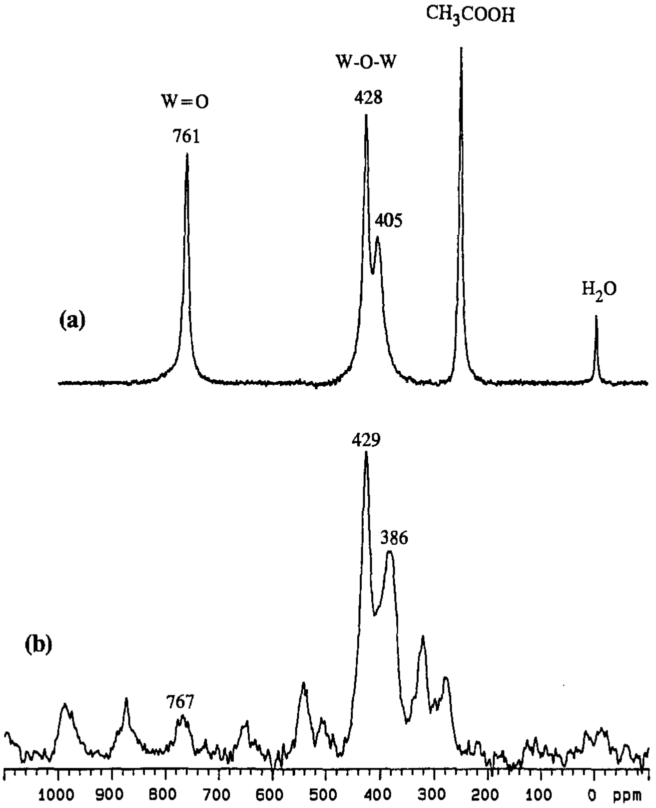

Fig. 3. $^{17}O$ NMR spectra: (a) 0.05 M solution of $H_3PW_{12}{}^{17}O_{40}$ in $CH_3COOH$–$H_2O$ 94 : 6 v/v (ref.: internal $H_2{}^{17}O$); (b) MAS spectrum of solid $Cs_3PW_{12}{}^{17}O_{40}$ preheated at 200°C/0.4 mmHg for 2 h, 7.1 kHz spin rate (ref.: external $H_2{}^{17}O$; positions of center bands are indicated).

$H_4SiW_{12}O_{40}$. This is probably due to the fast $^{16}O/^{17}O$ exchange in the silicate anion, occurring during the HPA preparation.

Fig. 4b shows the $^{17}O$ spectrum of solid $H_4SiW_{12}O_{40}$. The positions of center bands were determined to be: 720 (W=O, 413, 406 (W–O–W) and 18 ppm (Si–O–W). As with $H_4PW_{12}O_{40}$ [13], in the solid-state spectrum of $H_4SiW_{12}O_{40}$, the line of the W=O oxygen is shifted 47 ppm upfield compared to the solution spectrum, whereas the W–O–W oxygen resonances (two closely-spaced lines) have the same chemical shifts within ±9 ppm in both spectra. The line of the inner Si–O–W oxygen resonance, which is a singlet in the solution spectrum, exhibits a partially resolved 700 Hz splitting in the solid-state spectrum. This splitting may be attributed either to a quadrupolar effect or to magnetic non-equivalence of chemically equivalent oxygens caused by the crystallographic site symmetry [17,18]. Similar splittings have been found in the solid-state spectrum of $H_3PW_{12}O_{40}$ for the W–O–W bands [13].

Table 1
$^{17}O$ NMR data for heteropolycompounds

| HPA | Conditions | Chemical shift, ppm [a] | | |
|---|---|---|---|---|
| | | W=O | W–O–W | X–O–W |
| $H_3PW_{12}O_{40}$ | 0.12 M solution in $D_2O$ | 769 | 427, 409 [13] | |
| $H_3PW_{12}O_{40}$ | 0.05 M in HOAc–$H_2O$ 94 : 6 v/v | 761 | 428, 405 | |
| $H_3PW_{12}O_{40}$ | aqueous solution | 766 | 428, 406 [16] | |
| $(Bu^n_4N)_3PW_{12}O_{40}$ | 0.05 M solution in MeCN, 80°C | 769 | 431, 405 [11] | |
| $H_3PW_{12}O_{40}$ | saturated aqueous solution | 767 | 427, 408 [10] | |
| $H_3PW_{12}O_{40}$ | solid state [b] | 708 | 440, 400 [13] | |
| $Cs_3PW_{12}O_{40}$ | solid state [b] | 767 | 429, 386 | |
| $H_4SiW_{12}O_{40}$ | 0.04 M aqueous solution | 767 | 422, 408 | 28 |
| $H_4SiW_{12}O_{40}$ | 0.31 M aqueous solution | 763 | 417, 404 | 25 [16] |
| $(Bu^n_4N)_4SiW_{12}O_{40}$ | 0.03 M solution in MeCN, 90°C | 761 | 427, 405 | 27 [11] |
| $H_4SiW_{12}O_{40}$ | solid state [b] | 720 | 413, 406 | 18 [c] |

[a] Chemical shifts are given from $H^{17}O$. Unless otherwise stated, spectra were recorded at room temperature. Resonance of inner P–O–W oxygen is not seen due to lack of enrichment at this site.
[b] Pre-heated at 200°C/0.4 mmHg for 2 h.
[c] Center of doublet (see fig. 4).

## 4. Discussion

### 4.1. PROTON SITES IN DEHYDRATED SOLID HPA

The application of $^{17}O$ NMR for the determination of protonation sites in polyanions has been described earlier [11]. When an oxygen site in a polyanion is protonated, the metal–oxygen bonds to that oxygen are weakened, leading to an upfield shift of its $^{17}O$ resonance. The remaining metal–oxygen bonds are strengthened in order to maintain approximately constant total bond order at the metal atom. This can lead to the downfield shift of resonances of the neighboring oxygens.

Bulk proton sites in solid Keggin HPAs can be characterized by comparing their solid-state and solution $^{17}O$ NMR spectra [13]. All representative data, both ours and those taken from the literature, for tungsten HPAs $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ as well as for their salts are listed in table 1. In aqueous solution, these HPAs are completely deprotonated [9]. (It is relevant to note that $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ anions remain deprotonated even after accepting 2 and 3 extra electrons, respectively, upon their polarographic reduction in aqueous solution at pH 1 [19].) This is in full agreement with the $^{17}O$ NMR data (table 1). Thus, the solution spectra of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (in $H_2O$) and their neutral $Bu^n_4N^+$ salts (in MeCN) are nearly the same. So are the spectra of $H_3PW_{12}O_{40}$ in $H_2O$ and $D_2O$,

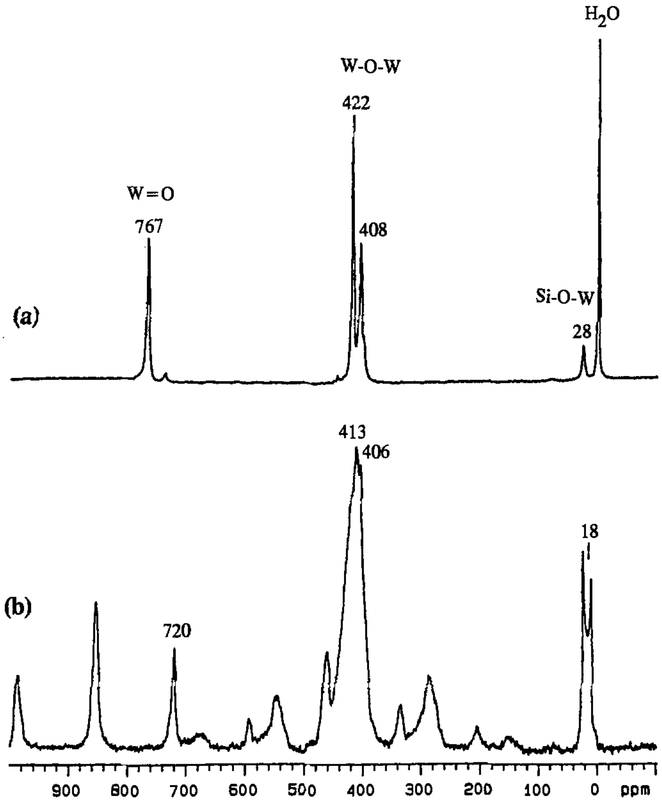

Fig. 4. $^{17}O$ NMR spectra of $H_4SiW_{12}{}^{17}O_{40}$: (a) 0.04 M solution in $H_2O$ (ref.: internal $H_2{}^{17}O$); (b) MAS spectrum of solid $H_4SiW_{12}O_{40}$ pre-heated at 200°C/0.4 mm Hg for 2 h, 7.1 kHz spin rate (ref.: external $H_2{}^{17}O$; positions of central bands are indicated).

hence the replacement of $H^+$ for $D^+$ does not affect the spectra, as expected for the deprotonated HPA.

Given the HPA solutions as a reference, let us consider the spectra of dehydrated solid HPAs. The solid-state spectrum of $H_3PW_{12}O_{40}$ has been discussed earlier [13]. In this spectrum, the line of the terminal W=O oxygen (708 ppm) is shifted 60 ppm upfield compared to the solution spectrum, whereas the bridging W–O–W oxygen resonances have the same chemical shifts in both spectra (table 1). Thus, it has been concluded [13] that the terminal W=O oxygens are the ones that are predominantly protonated in the dehydrated $H_3PW_{12}O_{40}$.

The same result has been obtained in this work for solid $H_4SiW_{12}O_{40}$ (fig. 4, table 1): the W=O line (720 ppm) is shifted 47 ppm upfield compared to the solution spectrum, while the W–O–W lines have almost the same positions in both spectra. Therefore, one can conclude that in the dehydrated solid $H_4SiW_{12}O_{40}$, as in $H_3PW_{12}O_{40}$, the predominant protonation sites are the terminal W=O oxygens. The extended manifold of spinning sidebands for the signal of W=O oxygens in the solid-state spectra of $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ implies an important chemical shift anisotropy for this type of oxygen, which is also consistent with the protonation of this site. Small shifts of the lines for the W–O–W and Si–O–W oxygens in the spectra of solid HPAs compared to the solution spectra can be explained by the change of bond strengths at these oxygen sites due to the protonation of the W=O oxygen [11].

Protonation of the W=O oxygens in Keggin HPAs is strongly supported by the $^{17}O$ NMR data for solid $Cs_3PW_{12}O_{40}$. This salt can be considered to be a structural analog to the dehydrated $H_3PW_{12}O_{40}$. In $Cs_3PW_{12}O_{40}$, each $Cs^+$ ion is suggested to have four equivalent terminal oxygens as the closest neighbors [8]. Therefore, if the terminal oxygens in solid Keggin HPAs are protonated, the W=O line in the $^{17}O$ MAS NMR spectrum of solid $Cs_3PW_{12}O_{40}$ must be similar to that in the solution spectra of the $PW_{12}O_{40}^{3-}$ anion. This is indeed the case (fig. 2, table 1).

### 4.2. ON THE PROTONATION OF HPA IN SOLUTION

While in aqueous solution tungsten HPAs are completely deprotonated, in less polar organic solvents they are only partially dissociated [9]. For example, in HOAc, from conductivity data [9], their dissociation is very weak, $pK_1 \approx 5$. The question arises what is the state of protons in the non-dissociated HPA molecules in such solvents as HOAc? To answer this question, we have obtained the $^{17}O$ NMR spectrum of 0.05 M $H_3PW_{12}O_{40}$ in HOAc–$H_2O$ 94 : 6 v/v (fig. 3a). (Some water (3.3 M) was added to increase the solubility of HPA which otherwise is very low.) This spectrum is evidently the same as that of HPA in aqueous solution (table 1). This is indicative that in both solvents the heteropolyanion is not protonated. Hence one can suggest that in HOAc and, possibly, in other less polar solvents, HPA exists as an ion aggregate, in which the solvated protons (i.e. localized on the solvent molecule) are bound to the HPAN as a whole rather than to certain basic centers in HPAN, as suggested from conductivity data [9]. It should be noted that under such conditions water may play an important role, promoting the HPA ionization, for at least traces of water are always necessary to dissolve HPAs in organic solvents [20].

## 5. Conclusion

In the present and preceding [13] papers we have studied, by means of $^{17}O$ NMR, the proton structure of the two strongest Keggin HPAs, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, which are also the most important acid catalysts in the HPA series. In aqueous solutions, these HPAs are completely deprotonated and even in a less polar solvent such as HOAc they are ionized and may exist as ion aggregates, where the protons are localized on the solvent molecules rather than on heteropolyanions. The $^{17}O$ MAS NMR spectra of dehydrated solid $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ enabled us to determine unambiguously the structure of their bulk proton sites in the solid state. By comparing chemical shift values for the solid-state and solution $^{17}O$ NMR spectra, we have found that in dehydrated solid HPAs the predominant protonation sites are the terminal W=O oxygens. The structure of proton sites in dehydrated HPAs can be represented as shown in fig. 2b [13]. Such acid sites probably dominate in "pseudo-liquid phase" conversions of polar molecules, which were discussed in detail elsewhere [4]. As to the surface proton sites, these may be both the protons localized on the terminal W=O oxygens and the protons localized on the edge-bridging W–O–W oxygens in the surface HPANs. The latter must be particularly important in supported HPA catalysts, e.g. HPA/$SiO_2$ as discussed earlier [9].

## References

[1] I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311; see also J.M. Thomas, Sci. Amer. 266 (1992) 85.
[2] Y. Izumi, K. Urabe and M. Onaka, *Zeolite, Clay and Heteropoly Acid in Organic Reactions* (Kodansha/VCH, Tokyo/Weinheim, 1992) p. 99.
[3] Y. Ono, in: *Perspectives in Catalysis*, eds. J.M. Thomas and K.I. Zamaraev (Blackwell, London, 1992) p. 431.
[4] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269; 30 (1988) 339.
[5] M. Misono and N. Nojiri, Appl. Catal. 64 (1990) 1.
[6] R.J.J. Jansen, H. van Veldhuizen and H. van Bekkum, Rec. Trav. Chim. Pays-Bas 113 (1994) 115.
[7] J.F. Keggin, Proc. Roy. Soc. A 144 (1934) 75.
[8] G.M. Brown, M.-R. Noe-Spirlet, W.R. Bushing and H.A. Levy, Acta Cryst. B 33 (1977) 1038.
[9] I.V. Kozhevnikov, Russ. Chem. Rev. 56 (1987) 811.
[10] L.P. Kazanskii, M.A. Fedotov and V.I. Spitsyn, Dokl. Akad. Nauk SSSR 233 (1977) 152; 234 (1977) 1376.
[11] W.G. Klemperer and W. Shum, J. Am. Chem. Soc. 99 (1977) 3544; 100 (1978) 4891.
[12] K.Y. Lee, N. Mizuno, T. Okuhara and M. Misono, Bull. Chem. Soc. Japan 62 (1989) 1731.
[13] I.V. Kozhevnikov, A. Sinnema, R.J.J. Jansen and H. van Bekkum, Mendeleev Commun. (1994) 92; Catal. Lett. 27 (1994) 187.
[14] M. Filowitz, R.K.C. Ho, W.G. Klemperer and W. Shum, Inorg. Chem. 18 (1979) 93.
[15] S. Tatematsu, T. Hibi, T. Okuhara and M. Misono, Chem. Lett. (1984) 865.
[16] K. Piepgrass, J.N. Barrows and M.T. Pope, J. Chem. Soc. Chem. Commun. (1989) 10.
[17] S. Schramm and E. Oldfield, J. Am. Chem. Soc. 106 (1984) 2502.
[18] C.A. Fyfe, *Solid State NMR for Chemists* (CFC Press, Guelph, 1983) pp. 284ff, 347, 352.
[19] M.T. Pope and E. Papaconstantinou, Inorg. Chem. 6 (1967) 1147.
[20] M.T. Pope, *Heteropoly and Isopoly Oxometalates* (Springer, Berlin, 1983).