^{17}O NMR determination of proton sites in solid heteropoly acid $H_3PW_{12}O_{40}$. ^{31}P, ^{29}Si and ^{17}O NMR, FT-IR and XRD study of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ supported on carbon

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^{17}O MAS NMR spectra for solid heteropoly acid (HPA) $H_3PW_{12}O_{40}$ are reported. Comparison of solid-state and solution ^{17}O resonances shows that in the solid dehydrated $H_3PW_{12}O_{40}$ terminal W=O oxygen atoms are the predominant protonation sites. $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ supported on chemically activated carbon have been studied by means of NMR, FT-IR and XRD. The carbon-supported HPA's retain their Keggin structure and form finely dispersed HPA species. No HPA crystal phase is developed even at an HPA loading as high as 45 wt%. ^{31}P, ^{29}Si and ^{17}O MAS NMR spectra for bulk and carbon-supported HPA's indicate interaction of the HPA Keggin units with the carbon surface, causing large line broadening in the NMR spectra.

Keywords: tungsten heteropoly acids; determination of proton sites; heteropoly acids supported on carbon; ^{31}P, ^{29}Si and ^{17}O MAS NMR; FT-IR; XRD

1. Introduction

Keggin-type heteropoly acids (HPA), $H_{8-x}XM_{12}O_{40}$ where $X = Si^{4+}$, P^{5+}, etc., x is its oxidation state and $M = Mo^{6+}$, W^{6+}, are widely used as acid catalysts due to their strong Brønsted acidity together with their special anion character [1,2]. Structural characterization of the HPA proton sites is an important step towards understanding the catalytic activity. Bond length–bond strength correlations [3] as

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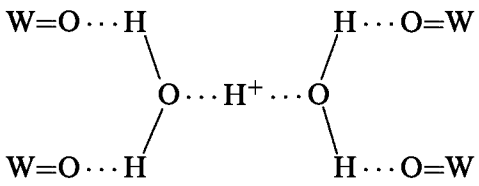
well as ^{17}O NMR data [4] indicate that in the free polyanions in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. In the free Keggin anion, edge-bridging M–O–M oxygens are assumed to be the predominant protonation sites [3] $H_3PW_{12}O_{40}$, the strongest HPA in the Keggin series, is completely deprotonated in aqueous solution and partially deprotonated in polar organic solvents [1]. In solid HPA's, the protons take part in the formation of the HPA crystal structure, linking the neighbouring heteropoly anions (HPAN). In this case the more accessible terminal oxygens can be protonated [5]. Thus, from single-crystal X-ray and neutron diffraction data [5], the proton sites in crystalline $H_3PW_{12}O_{40}\cdot 6H_2O$ are represented as diaquahydrogen ions, $H_5O_2^+$, each of which links four neighbouring HPAN's by forming hydrogen bonds with the terminal W=O oxygens (scheme 1).



Scheme 1.

There are, however, no experimental data on the proton locations in dehydrated bulk HPA's, although such HPA's are most widely used as catalysts [1]. Two options have been advanced. First, by analogy with HPA hydrates, protons in the dehydrated Keggin HPA's are assumed to be localized on the terminal M=O oxygens linking neighbouring HPAN's in the crystal cell. Alternatively, protonation of the bridging M–O–M oxygens has been suggested on the basis of IR band broadening upon dehydration of HPA [6]. 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 in solution [4]. We report here the ^{17}O magic angle spinning (MAS) NMR determination of the structure of proton sites in dehydrated crystalline $H_3PW_{12}O_{40}$, which is the most important acid catalyst in the HPA series [1].

HPA's supported on activated carbon are considered to be promising solid acid catalysts, in particular as fixed-bed catalysts for liquid-phase oxygenates synthesis, e.g. esterification, because of their high activity and extraordinary stability on the carbon surface [7,8]. The acid strength of supported $H_3PW_{12}O_{40}$ was found to decrease in the series of supports: $SiO_2 > \alpha\text{-}Al_2O_3 >$ carbon [9], indicating a significant interaction between HPA's and carbon support. However, the state of HPA's on the carbon surface has not yet been studied. We present here the results of our MAS NMR, Fourier transform infrared (FT-IR) and powder X-ray diffraction (XRD) investigation of the Keggin-type HPA's, $H_3PW_{12}O_{40}$ (PW) and $H_4SiW_{12}O_{40}$ (SiW), supported on a carbon.

2. Experimental

2.1. MATERIALS

PW and SiW crystalline hydrates were prepared from $Na_2WO_4 \cdot 2H_2O$ and NaH_2PO_4 or $Na_2SiO_3 \cdot 5H_2O$ [10] and recrystallized from water. According to ^{31}P and ^{29}Si NMR they contained >99 and 94 mol% Keggin HPA's, respectively. 3–5 at% ^{17}O enriched PW (PW-^{17}O) was prepared from ^{17}O enriched Na_2WO_4 in a similar way. The latter compound was prepared by heating $Na_2WO_4 \cdot 2H_2O$ with water containing 10 at% ^{17}O (from ICON, New Jersey, USA) in a sealed glass tube at 100°C for 7 days [11]. According to the ^{31}P MAS NMR, the ^{17}O enriched PW contained >99 mol% Keggin HPA.

As a support, "C-granular", an amorphous, chemically (H_3PO_4) activated carbon (C) (from Norit NV, Amersfoort, NL), was used because of its suitability for MAS NMR. This carbon had S_{BET} 1266 m^2/g, S_t 462 m^2/g, pore volume 0.61 cm^3/g, isoelectric point at pH 3.5 and oxygen content ca. 15 wt%. The adsorption of HPA's on various carbons, including C, was reported elsewhere [12]. Prior to use, C was finely powdered, washed with 0.1 mol ℓ^{-1} NaOH and water until pH 7, with 0.1 mol ℓ^{-1} HCl and again water until pH 7, dried at 100°C, and then heated at 200°C/0.4 mm Hg for 2 h. After such pretreatment no signal from H_3PO_4 was observed anymore in the ^{31}P MAS NMR spectrum of C.

C-supported HPA's were prepared by the impregnation of C (0.5–1.0 g) with HPA aqueous solution (5 ml, 0.01–0.1 g HPA/ml) by shaking overnight at room temperature, then dried at 100°C and heated at 200°C/0.4 mm Hg for 2 h prior to spectral measurements.

2.2. TECHNIQUES

2.2.1. 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. Special care was taken to protect solid samples from moisture.

161.903 MHz ^{31}P NMR spectra were taken with 4 μs (45° flip angle) pulses and a repetition time of 2 s. Spin rate 7.9 kHz. Several hundred pulse responses were collected before Fourier transform (FT) with 3 Hz exponential line broadening. 1% H_3PO_4 in D_2O was used as an external reference.

79.459 MHz ^{29}Si NMR spectra were taken with 4 μs (45° flip angle) pulses and a repetition time of 20 s. Spin rate 8 kHz. Several thousand pulse responses were collected before FT with 10 Hz line broadening. TMS in $CDCl_3$ was used as an external reference.

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. Spinrates between 3.7 and 6.8 kHz were used. $D_2{}^{17}O$ was used as an internal reference (liquids) or $H_2{}^{17}O$ as an external reference (solids).

2.2.2. Infrared spectroscopy

FT-IR spectra were recorded on a Bruker IFS 66 spectrometer in KBr over the range of 600–1300 cm^{-1} under atmospheric conditions without special precautions.

2.2.3. X-ray diffraction

XRD measurements were carried out on a Philips PW 1840 diffractometer using monochromatized Cu Kα radiation. Patterns were recorded over the range $2\theta = 20$–$40°$.

3. Results and discussion

3.1. ^{17}O NMR DETERMINATION OF PROTON SITES IN SOLID $H_3PW_{12}O_{40}$

The protonation sites in dehydrated solid PW have been determined by comparison of ^{17}O NMR spectra for ^{17}O enriched PW in the solid-state and in water (D_2O).

Representative spectra are shown in fig. 1. In the ^{17}O NMR spectrum of a 30 wt% PW-^{17}O (0.12 mol ℓ^{-1}, pH 0) solution in D_2O (fig. 1a) well-separated resonances for the terminal W=O (769 ppm from internal $D_2{}^{17}O$ and bridging W–O–W oxygens (two closely-spaced lines at 427 and 409 ppm for the edge- and corner-bridging W–O–W groups) are observed. This spectrum is fully consistent with those reported in the literature (line positions in ppm from external $H_2{}^{17}O$): 769, 431, 405 ([*n*-$Bu_4N]_3PW_{12}O_{40}$ in CH_3CN, 80°C) [13]; 767, 427, 408 ($H_3PW_{12}O_{40}^{3-}$ in H_2O, pH 1, 25°C) [3]. The resonance of the four inner P–O–W oxygens is not seen due to lack of enrichment at this site [13]. Such agreement of all the solution spectra indicates absence of protonation of the HPAN even in 30 wt% PW aqueous solution.

We have observed, for the first time, the ^{17}O MAS NMR spectrum of solid dehydrated PW (figs. 1b, 1c). As expected, this spectrum contains a number of spinning sidebands and is more complex than the solution spectrum. Varying the spinning rate [11] in the range of 3.7–6.8 kHz[#1] enabled us to determine all three center bands present at 708 ± 5 (W=O), 440 ± 3, 400 ± 3 ppm (W–O–W) from external $H_2{}^{17}O$. An estimate of the second-order quadrupolar shift [14] for the $(m = +\frac{1}{2}) \leftrightarrow (m = -\frac{1}{2})$ transition, using a fairly large value of 2 MHz for the nuclear quadrupolar coupling constant for ^{17}O bonded to tungsten [11,15], showed that the positions of the center bands will differ from the true isotropic chemical

[#1] At the moment we do not have the technical possibilities to spin at much higher rates.

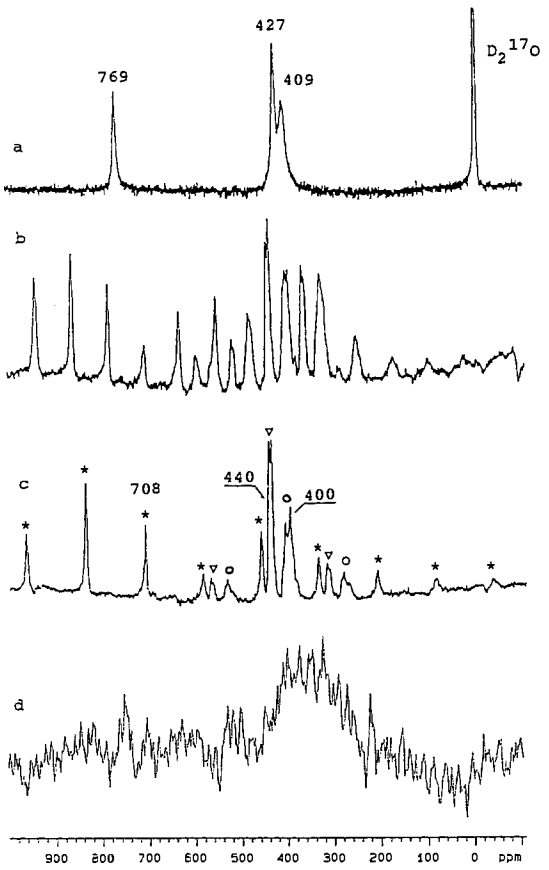


Fig. 1. ^{17}O NMR spectra of PW-^{17}O: (a) 0.12 mol ℓ^{-1} PW solution in D_2O, pH 0 (ref.: internal $D_2{}^{17}O$); MAS spectra (ref.: external $H_2{}^{17}O$); (b) solid PW pre-heated at 200°C/0.4 mm Hg for 2 h, 4.2 kHz spin rate; (c) same, 6.8 kHz spin rate, (*, ▽ and ○) spinning side band manifolds centered at 708, 440 and 400 ppm, respectively; (d) 35 wt% PW/C pre-heated at 200°C/0.4 mm Hg for 2 h, 4.4 kHz spin rate.

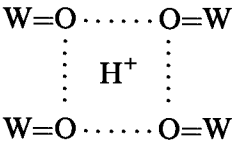
shifts by only a few ppm. Clearly, there is good agreement between the solid-state and solution spectra but there are also distinct and significant differences.

First, the resonances of the bridging oxygen atoms, which are singlets in the solution spectrum, show partially resolved 300–600 Hz splittings in the solid-state spectrum. This may be attributed either to a quadrupolar effect or to magnetic nonequivalence of chemically equivalent oxygens caused by a crystallographic site symmetry that is lower than the molecular symmetry [11,16]. The resonance centered at 708 ppm shows no such splittings; instead an extended manifold of spinning side bands is observed (figs. 1b, 1c), due to a chemical shift anisotropy of several hundred ppm [11]. Second, and most importantly, the resonance of the terminal W=O oxygen in the solid-state spectrum is shifted about −60 ppm compared to the solution spectrum, whereas the bridging W–O–W oxygen resonances have essentially the same chemical shifts in both spectra.

As mentioned above, in aqueous solution the $H_3PW_{12}O_{40}^{3-}$ anion is not protonated. In the solid PW, protons are localized on oxygen atoms in the HPAN upon dehydration of HPA [1]. The question is, which of the two types of surface oxygens present in the HPAN – the more accessible terminal W=O oxygen or the bridging W–O–W oxygen bearing a higher negative charge – is the protonation site in the solid dehydrated PW?

When an oxygen site is protonated, the metal–oxygen bonds to that oxygen are weakened, leading to an upfield shift of its ^{17}O resonance [4]. Thus the terminal oxygens, since their resonance undergoes a pronounced upfield shift, are the predominant protonation sites. Further evidence for the protonation of terminal W=O oxygens in solid dehydrated PW comes from the observation that, upon rehydration, the resonance of the terminal oxygen is shifted towards its position in solution. Thus in the spectrum of solid $PW \cdot 30H_2O$ it is found at 764 ppm. The extended manifold of spinning side bands for the signal centered at 708 ppm implies an important chemical shift anisotropy for this type of oxygen, which is also consistent with protonation of this site. Therefore, ^{17}O MAS NMR unambiguously identifies the terminal W=O oxygen, rather than the bridging W–O–W oxygen, as the dominant protonation site in the dehydrated crystalline PW.

The interpretation given above is essentially a static one. An equally plausible dynamic interpretation is that the HPA protons, as mobile species, are hopping around all peripheral oxygen atoms present in HPAN, but spending essentially all their time at the terminal oxygens.



Scheme 2.

The proton structure given in scheme 2 for the dehydrated PW is consistent with the data obtained and can be directly formed from that for PW hexahydrate (scheme 1). Stoichiometrically, each proton is shared by four terminal oxygens like in PW hexahydrate [6], since all the terminal oxygens in the PW crystal lattice are apparently equivalent. We suggest that the proton migrates between four equivalent positions, W=O...H^+...O=W, and thus links four HPAN's together, as does the $H_5O_2^+$ ion in scheme 1. It should be noted that for this structure to be formed, the HPA cell volume should decrease upon dehydration, which is indeed the case [17].

3.2. HETEROPOLY ACIDS SUPPORTED ON ACTIVATED CARBON

3.2.1. XRD study

XRD data show that C-supported HPA's are finely dispersed on the carbon surface (fig. 2). No patterns from HPA's are observed in the XRD of supported PW

and SiW. No detectable HPA crystal phase is developed even at an HPA loading as high as 45 wt%, which corresponds to 200 m^2 HPA monolayer per 1 g of C, assuming that the cross section of HPA (ϕ_{HPA} 12 Å) is equal to 100 $Å^2$. Therefore, the maximum area which may be occupied by HPA is much less than the surface area of C available in micro- and mesopores. Actually, in carbon micro- and mesopores, the formation of HPA crystals big enough to be observable by XRD, seems to be unfavourable. By contrast, when loading HPA's on silica (S_{BET} = 200–300 m^2/g), HPA crystallinity already appears at ca. 20 wt% HPA content [18,19].

3.2.2. FT-IR spectra

IR is a suitable method for the structural characterization of polyanions [20]. Our FT-IR data indicate that the Keggin structure is retained when loading PW

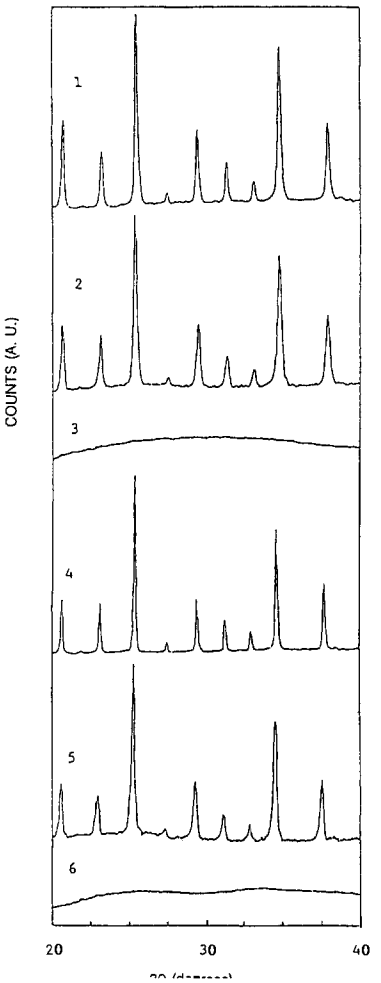


Fig. 2. XRD patterns: (1) PW, (2) PW + C 1 : 4 (wt) mixture, (3) 45 wt% PW/C, (4) SiW, (5) SiW + C 1 : 4 (wt) mixture, (6) 25 wt% SiW/C.

and SiW on carbon (fig. 3). This is clearly seen from the very good agreement of the spectral bands of pure and supported HPA's. However, at a lower level of loading, ca. 5 wt%, a partial decomposition of PW is observed (fig. 3). This is also confirmed by ^{31}P NMR (see below). In this case, the lack of stability of HPA is probably related to the state of the PW_{12} anion in aqueous solution. For the preparation of 5 wt% PW/C, one has to use a very diluted impregnating solution (1 wt% PW, pH ca. 2), in which the PW_{12} anion decomposes to form the lacunary PW_{11} anion [20]. This might be a reason for the decomposition of HPA in the 5 wt% PW/C catalyst.

3.2.3. MAS NMR spectra

NMR has been profitably used in the study of heteropolyanions in solutions for a long time [30]. More recently, solid-state NMR has been applied in studies of solid HPA's, both bulk and supported on SiO_2, Al_2O_3 and SiO_2–Al_2O_3 [21–24]. However, MAS NMR is of limited utility for carbon-supported catalysts due to the high conductivity of activated carbon. However, with the H_3PO_4-activated carbon

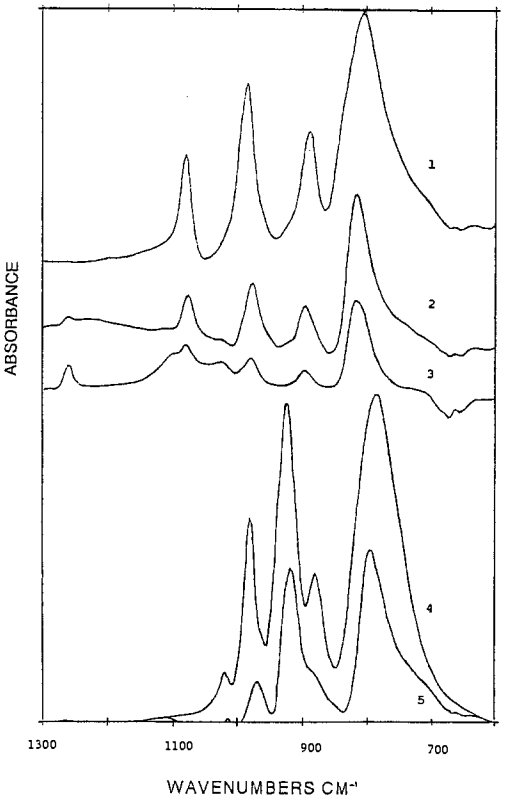


Fig. 3. FT-IR spectra (KBr): (1) PW, (2) 25 wt% PW/C, (3) 5 wt% PW/C, (4) SiW, (5) 25 wt% SiW/C.

C we have managed to prepare satisfactory samples, easily spinning at 4–5 kHz and with good spectral resolution.

The ^{31}P and ^{29}Si NMR spectra of bulk and C-supported PW and SiW are shown in figs. 4 and 5. The spectra of bulk HPA's are in agreement with reported data [21,23,25]. The ^{31}P spectrum consists of one isotropic line (−15.0 ppm, $\Delta\nu_{1/2}$ = 65 Hz). So does the ^{29}Si spectrum of bulk SiW (−83.3 ppm, $\Delta\nu_{1/2}$ = 72 Hz) (fig. 5).

The loading of HPA's on carbon has a profound effect on the NMR spectra of their central atoms. It generally causes a substantial line broadening and a more or less significant upfield shift. This indicates some kind of chemical interaction between HPA's and carbon. The same has been found for SiO_2-supported PW [23].

The ^{31}P spectrum of 5 wt% PW/C reveals the partial decomposition of PW (see above), a phosphate (0 ppm) and presumably a polyphosphate (15 ppm) being formed.

^{17}O MAS NMR spectra of bulk and C-supported PW are shown in fig. 1 (b, c and d). Loading HPA on carbon causes a large line broadening in the ^{17}O spectrum as well as in the ^{31}P and ^{29}Si spectra, which completely obscures the chemical shift dispersion. Any discussion of line shift or lack thereof is therefore senseless.

Thus ^{31}P, ^{29}Si and ^{17}O MAS NMR data clearly indicate the interaction of the HPA Keggin unit with the carbon support. However, its nature and mechanism still remain unknown. One can suggest that this interaction must be rather weak, since IR spectra do not change when loading HPA's on carbon (fig. 3). The interaction between mobile HPA protons and surface oxygen functions of the carbon is likely to play a prominent role in HPA binding, as a significant decrease of the acid

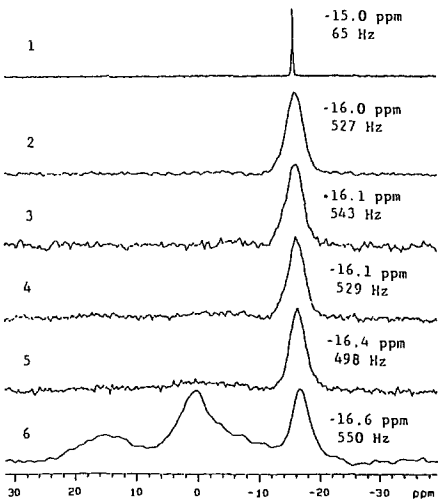


Fig. 4. ^{31}P MAS NMR spectra (ref.: external 1% H_3PO_4 in D_2O): (1) PW, (2) 45 wt% PW/C, (3) 35 wt% PW/C, (4) 25 wt% PW/C, (5) 15 wt% PW/C, (6) 5 wt% PW/C.

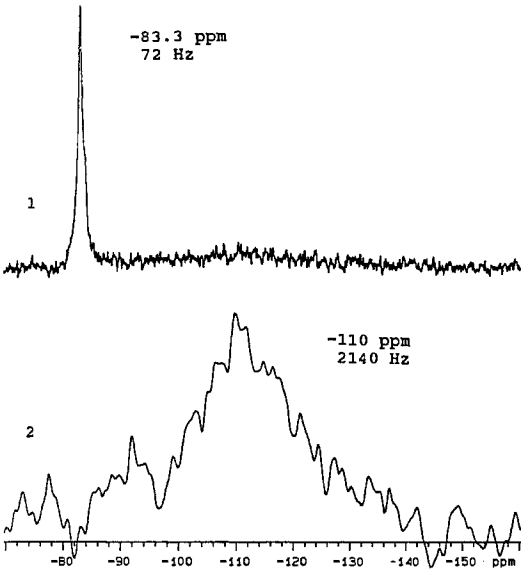


Fig. 5. ^{29}Si MAS NMR spectra (ref.: external 50% TMS in $CDCl_3$): (1) SiW, (2) 25 wt% SiW/C.

strength is observed when loading HPA on carbon [9]. Since C contains ca. 15 wt% of oxygen, one can suggest that such groups as OH, C=O, COOH, etc. are responsible for the HPA binding because of the strong affinity of HPA's for these groups.

4. Conclusion

Although HPA's are widely used as acid catalysts, their proton sites had not been fully characterised so far. We, for the first time, have observed ^{17}O NMR spectra for solid PW, which identify the terminal oxygen atoms as the predominant protonation sites in the dehydrated solid PW.

Carbon-supported PW and SiW, promising fixed-bed acid catalysts for liquid-phase reactions, have been characterised by ^{31}P, ^{29}Si and ^{17}O MAS NMR, FT-IR and XRD. It has been shown that C-supported PW and SiW retain their Keggin structure and form finely dispersed HPA species on the carbon surface. No HPA crystallinity has been observed even at an HPA loading as high as 45 wt%. Comparison of NMR spectra of bulk and C-supported HPA's shows that there is interaction between the HPA Keggin unit and carbon, causing a large line broadening in the NMR spectra. Oxygen containing surface groups of the carbon are assumed to play a major role here. The nature and mechanism of this interaction remain unknown.

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