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^{17}O MAS NMR study of 12-molybdophosphoric acid

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^{17}O MAS NMR spectra for ^{17}O enriched solid heteropoly acid $H_3PMo_{12}O_{40}$ are reported. The oxygen exchange between solid $H_3PMo_{12}{}^{17}O_{40}$ and $H_2{}^{16}O$ vapor at 200–250°C is shown to be accompanied by fast mixing of terminal Mo=O and bridging Mo–O–Mo oxygens in the Keggin unit. The oxygen exchange in $H_3PMo_{12}{}^{17}O_{40}$ is much faster than in $H_3PW_{12}{}^{17}O_{40}$ in solution as well as in the gas phase.

Keywords: heteropoly acid; $H_3PMo_{12}O_{40}$; ^{17}O MAS NMR; oxygen exchange

1. Introduction

Keggin-type heteropoly acids (HPAs), $H_{8-x}XM_{12}O_{40}$ where X is the central atom (P^{5+}, Si^{4+}, etc.), x its oxidation state and M the metal ion (Mo^{6+}, W^{6+}, etc.), are increasingly used as acid and oxidative catalysts [1–5]. Structural characterization of HPAs is an important step towards understanding the catalytic activity. One of the most powerful tools for this purpose is multinuclear NMR [6]. In the last decade, solid-state NMR has been profitably applied to the characterization of HPAs and catalysts based thereon [7–14]. Recently it was demonstrated [15–17] that ^{17}O MAS NMR can discriminate between different types of oxygen atoms in solid tungsten HPAs $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ – terminal M=O, bridging M–O–M (edge- and corner-bridging) and internal X–O–M oxygens (fig. 1) – almost as efficiently as solution NMR. Hence direct evidence for the predominant protonation of the terminal oxygens in the solid tungsten HPAs was obtained [15–17].

In this work, ^{17}O MAS NMR is used, for the first time, to characterize a solid molybdenum HPA, $H_3PMo_{12}O_{40}$ (PMo), an oxidative catalyst, utilized in for example the oxidation of methacrolein to methacrylic acid [1,2]. More specifically, we have tried to obtain more evidence on the reactivity of different types of oxygen atoms in the Keggin unit, which is relevant to heterogeneously catalyzed oxidation (for a review, see ref. [1]). In this sense, we have studied the oxygen exchange between solid $H_3PMo_{12}{}^{17}O_{40}$ (PMo-^{17}O) and $H_2{}^{16}O$ vapor by ^{17}O MAS NMR.

2. Experimental

^{17}O MAS and solution NMR spectra were taken at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe or Magic-angle Supersonic-spinning Solids NMR Probe with 5 mm silicon nitride rotor, as described elsewhere [15–17].

2 atom% ^{17}O enriched PMo was prepared by oxygen exchange [19] between $H_3PMo_{12}O_{40}$ (Janssen Chimica) and $H_2{}^{17}O$ (ICON, 10 atom% ^{17}O) in aqueous solution

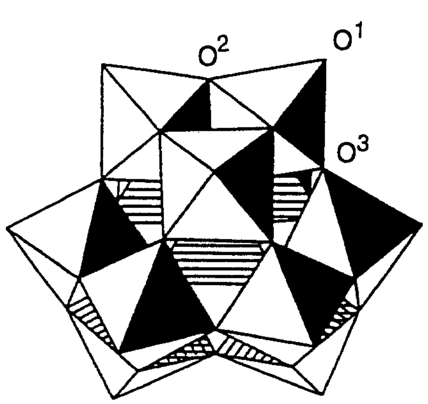

Fig. 1. The Keggin structure of the α-$XM_{12}O_{40}^{x-8}$ anion [18]: terminal (O^1), edge-bridging (O^2) and corner-bridging (O^3) oxygen atoms; internal oxygen atoms are not shown.

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at room temperature and a PMo concentration of 30 wt%. The exchange of the 36 outer oxygens was complete within 1 h; no exchange of the four internal oxygens was observed. Terminal and bridging oxygens appear to be exchanged at comparable rates [19]. As found by ^{31}P NMR, the PMo-^{17}O solution contained 80 mol% PMo_{12} together with $H_6PMo_9O_{34}^{3-}$ and a little $P_2Mo_{18}O_{62}^{6-}$ species which are known to exist in equilibrium with PMo_{12} in aqueous solution [20]. The pure crystalline PMo-^{17}O was obtained by extracting the acidified (HCl) solution with diethyl ether followed by evaporation and drying in a vacuum desiccator over P_2O_5 at ambient temperature. The product had a greenish color, indicating the presence of traces of Mo^{5+} in the sample. Addition of Br_2 to the aqueous PMo-^{17}O solution had little effect on the color of the final solid product.

3 atom% ^{17}O enriched $H_3PW_{12}O_{40}$ (PW-^{17}O) was prepared as described earlier [15,16].

The oxygen exchange between solid PMo-^{17}O or PW-^{17}O and $H_2{}^{16}O$ vapor was carried out at 150–300°C and atmospheric pressure by passing a N_2 flow (20 ml min^{-1}), containing water vapor (20 Torr), through the HPA bed (0.2 g) placed into a glass tube. Upon heating (> 150°C), the greenish PMo turned yellow. The oxygen exchange was followed by ^{17}O MAS NMR.

3. Results and discussion

^{17}O NMR spectra for PMo-^{17}O are shown in fig. 2. In the spectrum of an equilibrated 30 wt% (0.2 M, pH 0) PMo-^{17}O aqueous solution containing 2 mol% $H_2{}^{17}O$ (fig. 2a) well-separated resonances for the terminal Mo=O (941 ppm from internal $H_2{}^{17}O$) and bridging Mo–O–Mo oxygens (two lines at 566 and 549 ppm, for the edge- and corner-bridging Mo–O–Mo groups) are observed. This spectrum is fully consistent with that reported elsewhere [19,21]. Resonance of inner P–O–Mo oxygens, expected at 78 ppm [21], is not seen due to lack of enrichment at this place [19].

Fig. 2b, for the first time, shows an ^{17}O MAS NMR spectrum of solid PMo-^{17}O (as-synthesized sample after drying in a vacuum desiccator, residual water content less than one H_2O molecule per Keggin unit). The spectrum contains a number of spinning sidebands, similar to that of solid PW-^{17}O (fig. 3a) [15,16]. By varying the spinning frequency in the range of 3.7–7.1 kHz the positions of all three centre bands present were determined: 971 (Mo=O) and 577, 569 ppm (two closely-spaced, poorly resolved Mo–O–Mo lines) from external $H_2{}^{17}O$. This is in fair agreement with the solution spectrum (fig. 2a). As estimated in the case of PW-^{17}O [15,16], the second-order quadrupolar effect may cause the positions of the centre bands to differ from the true isotropic chemical shifts by only a few ppm.

But there are significant differences between the solid-state spectra of PMo-^{17}O and PW-^{17}O (cf. figs. 2b and 3a). In the case of PMo, lines are much broader and therefore the resolution is poorer than for PW. Although in both cases the lines for bridging oxygens M–O–M in the solid-state and solution spectra have approximately the same positions, the lines for terminal M=O oxygens in the solid-state spectra exhibit different shifts compared to the corresponding solution spectra. For solid

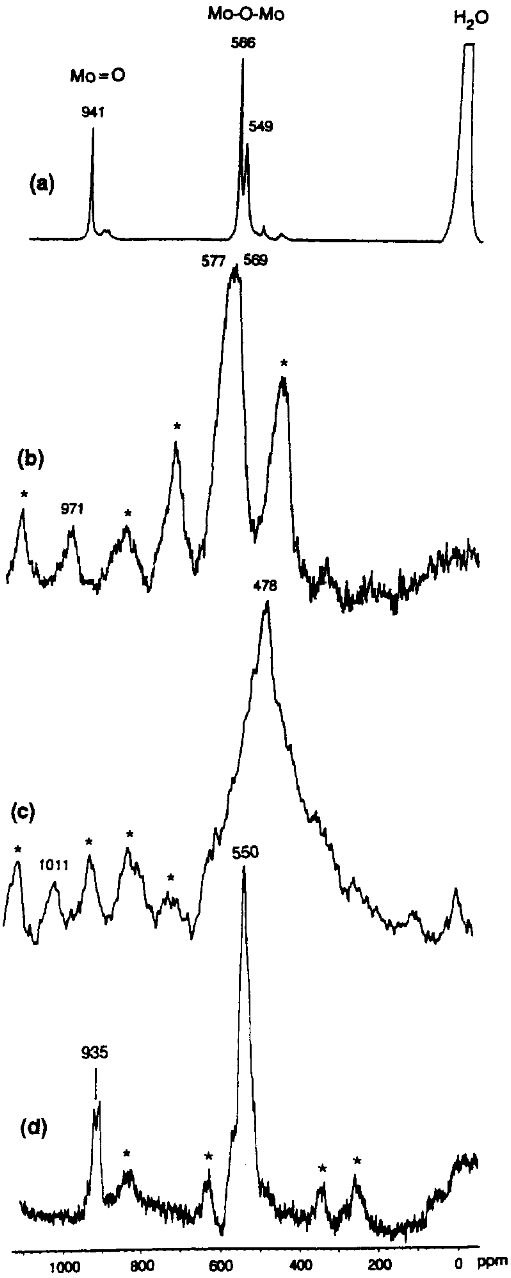


Fig. 2. ^{17}O NMR spectra of PMo-^{17}O: (a) an equilibrated 0.2 M aqueous solution containing 2 mol% $H_2{}^{17}O$ (ref.: internal $H_2{}^{17}O$); (b) and (c) MAS spectra of solid HPA (ref.: external $H_2{}^{17}O$; positions of centre bands are indicated; spinning sidebands are asterisked); (b) solid PMo-^{17}O dried in a vacuum desiccator (7.1 kHz spin rate); (c) solid PMo-^{17}O pre-heated at 150°C/1 mm Hg for 1 h (5.0 kHz spin rate); (d) solid PMo-^{17}O after pre-heating at 150°C/1 mm Hg for 1 h followed by rehydration in air at ambient temperature for 2 days (15.5 kHz spin rate).

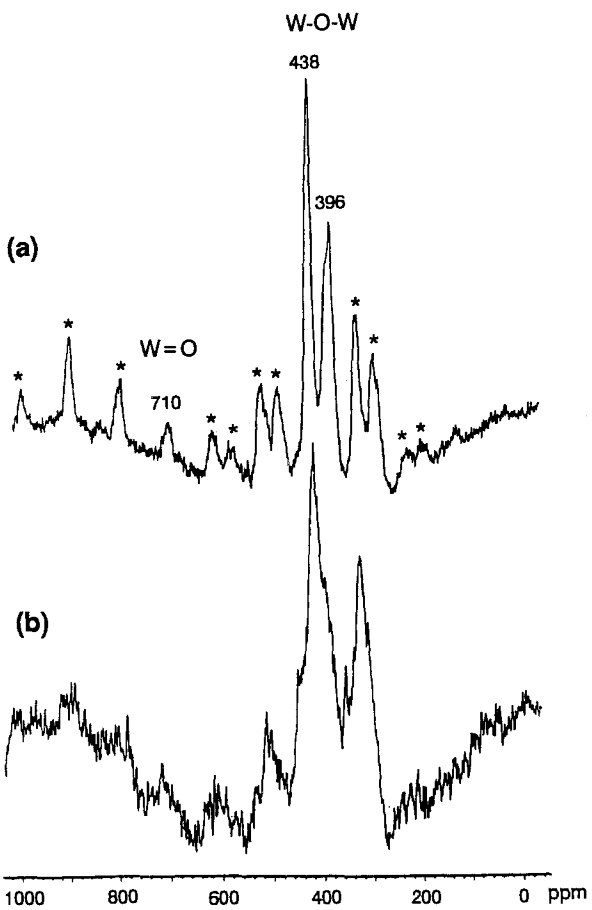


Fig. 3. ^{17}O MAS NMR spectra of solid PW-^{17}O (ref.: external $H_2{}^{17}O$; 5.2 kHz spin rate): (a) solid HPA dried in a vacuum desiccator (positions of centre bands are indicated [15,16]; spinning sidebands are asterisked); (b) solid HPA pre-heated at 300°C for 2 h.

PW, the W=O line is shifted 60 ppm upfield from that in the solution spectrum due to the protonation of the terminal oxygens [15,16]. For solid PMo, the Mo=O line is observed 30 ppm downfield compared to the solution spectrum (figs. 2a and 2b). Moreover, after pre-heating PMo at 150°C/1 mm Hg for 1 h, which is known [1,22,23] to change the crystal (secondary) structure of HPA, its ^{17}O MAS spectrum exhibited a strong shift of the Mo=O and Mo–O–Mo centre bands in opposite directions: the former went downfield (1011 ppm) and the latter upfield (478 ppm) (fig. 2c). (In fig. 2c the Mo–O–Mo line at 478 ppm is broader than that in fig. 2b because the spinning frequency (5.0 kHz) is less than the line width (6.0 kHz) in the static spectrum; the sample did not spin faster.) Rehydration of this sample in air at ambient temperature for 2 days to adopt about 12 water molecules per Keggin unit greatly narrowed spectral lines (fig. 2d). Their positions now become very close to those in the solution spectrum (fig. 2a). However, two Mo–O–Mo lines for the edge- and corner-bridging oxygens still remain unresolved, showing one peak at 550 ppm. The Mo=O line at 935 ppm exhibits a small splitting, which may be attributed to a crystal disorder. Presumably, the shift and broadening in the PMo-^{17}O spectrum are caused by traces of the paramagnetic Mo^{5+} present in the sample. It should be noted that Mo^{5+} is present in solid PMo even after calcination at 350°C in air, as shown by ESR [24]. The effect of Mo^{5+} on the ^{17}O spectra is difficult to analyze in detail because too many factors are involved. Among them, changing the crystal structure as well as the proton and electron mobilities upon thermal treatment of PMo are probably the most important.

Fig. 3a shows the ^{17}O MAS spectrum of PW-^{17}O (dried in a vacuum desiccator), which is in excellent agreement with that reported previously [15,16]. Preheating the PW sample at 300°C for 2 h caused some line-broadening (cf. figs. 3a and 3b), but in contrast to PMo, no shift was observed. It should be noted that this effect is reversible: exposing the PW sample to air for 2 days at room temperature totally restored the initial spectrum (fig. 3a). Likewise, exposure to air or saturated water vapor greatly narrowed lines of ^{31}P MAS spectra for PMo, PW and $H_6P_2W_{18}O_{62}$ [11]. Such an effect on solid-state NMR spectra of metal oxide systems, e.g. zeolites, is also well-known [25].

The significant paramagnetic shift and the broadening in the PMo ^{17}O solid-state spectra make it impossible to examine the proton location in solid PMo by ^{17}O NMR, as has been done for the truly diamagnetic PW and SiW [15–17].

Having discriminated the terminal and the bridging oxygens in the PMo Keggin unit, ^{17}O MAS NMR can, in principle, be helpful in distinguishing their reactivities. This problem has been discussed [26–28] in connection with vapor-phase oxidation of organic compounds, e.g. methacrolein and methanol, catalyzed by Keggin-type heteropolymolybdates (for a review, see ref. [1]). Such reactions are usually carried out above 300°C in the presence of steam. A redox mechanism is suggested, involving oxidation of the substrate by HPA, possibly acting as an oxygen donor, followed by reoxidation of the reduced form of HPA by O_2. However, oxygen transfer from water molecules into the substrate is not excluded either. On top of that, a fast oxygen exchange between water vapor and solid PMo takes place at 200–250°C [23], which makes it difficult to prove the source of oxygen atom entering the substrate.

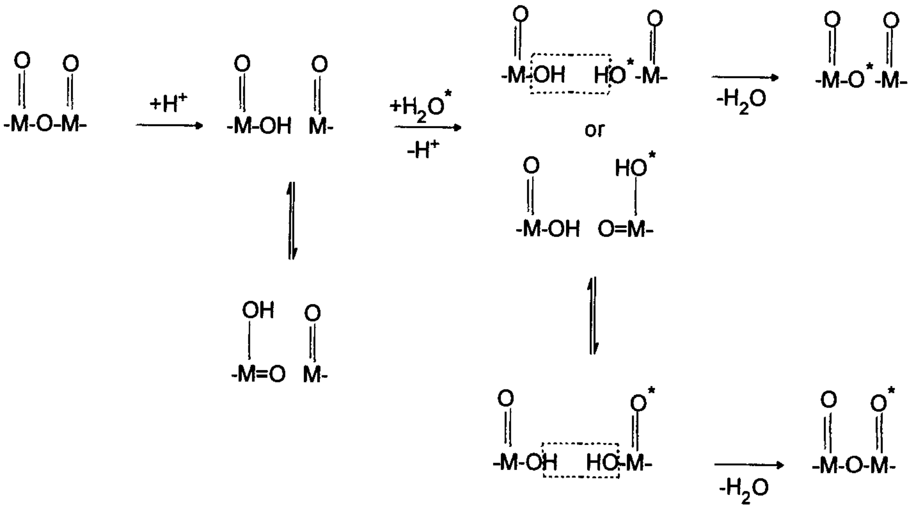
To obtain more information regarding this problem, we have studied the oxygen exchange between solid

Table 1

Oxygen exchange between ^{17}O-enriched solid HPAs and $H_2{}^{16}O$ vapor (20 Torr) at atmospheric pressure

HPA	T (°C)	Time (h)	Exchange (%)[a]
PMo-^{17}O	200	1	$\leqslant 5$
PMo-^{17}O	250	1	20
PMo-^{17}O	250	5	60
PW-^{17}O	300	2	0

[a] Percentage of outer oxygen atoms exchanged (ca. 20% accuracy).



Scheme 1.

PMo-^{17}O and $H_2{}^{16}O$ vapor by ^{17}O MAS NMR. Earlier, Misono et al. [23] studied the ^{16}O/^{18}O-exchange in this system by IR spectroscopy. However, IR failed to discriminate unambiguously between the behavior of different oxygen atoms in the Keggin unit, as mentioned elsewhere [1]. Moreover it is important that ^{17}O NMR, in contrast to IR, allows to directly measure the oxygen isotope content in HPA.

Our results are shown in table 1. Below 200°C, practically no oxygen exchange in PMo was observed. Upon increasing the temperature to 250°C, the exchange proceeded readily, in agreement with literature [23]. In contrast, no exchange was found in PW, even at 300°C. It is noteworthy that Keggin heteropolyphosphates easily exchange their outer oxygens with H_2O in aqueous solution, but not internal ones, as found by ^{17}O NMR [19,29]. The oxygen exchange rate in solution decreases in the order: PMo$\gg$PW, as it does in the gas phase (table 1).

Importantly, no change in ^{17}O MAS spectra of PMo was observed in the course of the ^{17}O-exchange. Regardless of the degree of ^{17}O-exchange, the appearance of the spectra and the ratio of intensities of the terminal and bridging oxygens remained constant in the temperature range of 150–250°C. This clearly shows that oxygen exchange, even at the initial stage of ca. 20% conversion, is accompanied by fast mixing of the terminal and bridging oxygen atoms in the Keggin unit. We have no evidence of such mixing happening in the absence of water in the system. This seems unlikely in the temperature region studied.

A mechanism for the oxygen exchange between water and solid PMo, explaining the mixing, is represented in scheme 1, where $M = Mo^{6+}$. It includes the breaking of an oxygen bridge initiated by protonation to form a pentacoordinated Mo^{6+}, probably adopting a distorted trigonal bipyramid coordination structure. The latter is attacked by a H_2O molecule to give an octahedrally coordinated Mo^{6+}, containing the entering HO group in the equatorial or the axial position with approximately equal probabilities. Finally, the release of an H_2O molecule restores the PMo structure, with either the terminal or the bridging oxygen atom being exchanged.

In conclusion, the oxygen exchange between PMo and water accompanied by the fast mixing of the terminal and bridging oxygen atoms in the PMo Keggin unit makes the two types of oxygens hardly discriminable under conventional conditions of heterogeneously catalyzed gas-phase oxidation of organic compounds ($\geqslant$300°C in the presence of steam).

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