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Solid State NMR and IR Studies of Phosphomolybdenum and Phosphotungsten Heteropoly Acids Supported on SiO_2, γ-Al_2O_3, and SiO_2–Al_2O_3

It is well known that dodecamolybdophosphoric (HPMo) and dodecatungstophosphoric (HPW) acid and their salts exhibit catalytic multifunctionality arising from their combined acid and redox properties (*1–5*). Recently Kasztelan and Moffat (*6*) have reported that heteropolyoxometalates (HPM) supported on SiO_2 show similar properties to those of unsupported catalysts. A silica-supported HPM is more efficient than silica-supported vanadium pentoxide in the partial oxidation of methane. The versatility of these systems is related to their unusual physicochemical properties and their structure. For instance, phosphomolybdic acid $H_3PMo_{12}O_{40} \cdot nH_2O$ exhibits high proton conductivity. The phosphomolybdate anion ($PMo_{12}O_{40}^{3-}$) and phosphotungstate anion ($PW_{12}O_{40}^{3-}$) consist of 12 edge-shared molybdenum (VI) MoO_6 octahedra surrounding a PO_4 tetrahedron (Keggin primary structure). The Keggin structures can form relatively stable secondary structures with water molecules filling the interconnected space between the Keggin units. Each Keggin structure exhibits a characteristic IR spectrum in the range 1100–600 cm^{-1} (*7*). Molybdenum and tungsten atoms are displaced outward from the center of the MoO_6 octahedra; consequently these polyanions are extremely acidic. The concentration of mobile protons in hydrogen-bonded water between the anions in the secondary structure is high. At room temperature these protons conduct as in a liquid phase.

Due to the variable nature of the secondary structure, various molecules like water and alcohol penetrate into and emerge from the bulk changing the distance between the anions. Certain reactions such as the dehydration of alcohols proceed in the bulk. This behavior (pseudo-liquid phase) affords heteropoly compounds a high catalytic activity and unique selectivity (*1*). Studies on the diffusion of hydrogen ions have been carried out by ^1H NMR and ^{31}P NMR (*8–10*), but there are very few reports on catalysis by heterogeneously supported heteropoly acids. However, it has been reported that heteropoly acids exhibit high catalytic activity when supported on silica gel or carbon (*11*). It was also found that Al_2O_3 is not suitable as a support because it probably decomposes the heteropoly acid primary structure (Keggin unit). Fricke *et al.* (*12*) have found that SiO_2 has a less drastic destabilizing effect, while Moffat and Kasztelan (*13*) have concluded that the Keggin structure of phosphotungstic acid dispersed on silica is surviving even after calcination at 843 K. In this contribution we show that the combined use of ^{13}C MAS NMR and IR can give information on the interaction of HPMo and HPW with the surface of silica, alumina, and silica–alumina and consequently elucidate their role in stabilizing or destabilizing the primary (Keggin) structure of the supported heteropoly acids. The effects of the thermal treatments in the 273–473 K interval are also investigated.

The supported catalysts (wt% HPMo or HPW) were prepared by impregnation either in aqueous or in acetone media and the slurries were dried at 360 K for several hours. SiO_2 (000-1.5 E: 210 $m^2\,g^{-1}$), γ-Al_2O_3 (CK-300: 200 $m^2\,g^{-1}$), and SiO_2–Al_2O_3 (100-3P, LA: 330 $m^2\,g^{-1}$) were kindly supplied by

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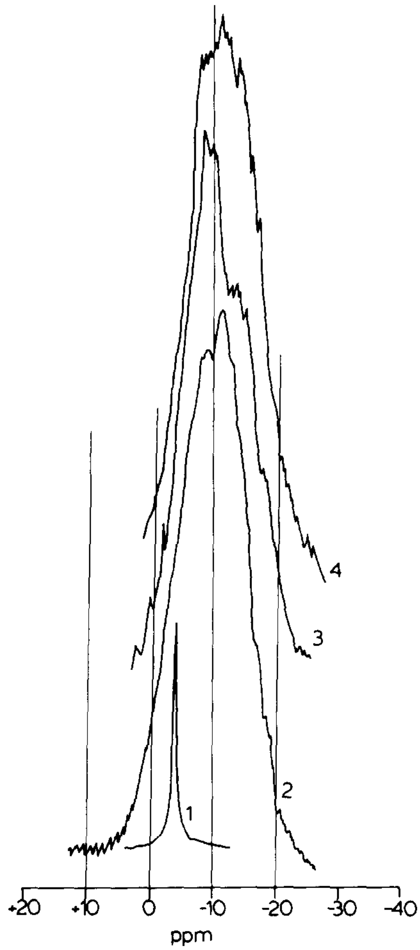

FIG. 1. Magic angle spinning NMR spectra of phosphomolybdic acid supported on (1) SiO_2 (14%), (2) γ-Al_2O_3 (14 wt%), (3) SiO_2–Al_2O_3 (14 wt%), and (4) SiO_2–Al_2O_3 (28 wt%).

AKZO Kemie. The silica–alumina sample contained 13.5 wt% γ-Al_2O_3 in the mixture.

CP/MAS spectra were obtained using a JEOL GX 270 NMR spectrometer at ambient temperature (298 K) operating at 109.25 MHz for ^{31}P. The ^1H 90° pulse length was set to 6 s and the Hartmann–Hann match was optimized consequently by maximizing the signal of PPh_3 under CP conditions. Samples were packed in Delrin rotors and spun at speeds between 3.0 and 4.0 kHz at the magic angle. A sweep width of 20 kHz with a total acquisition time of 66 ms and pulse repetition time of 1.0 s was used. Free induction decays were collected between 100 and 1000 and transformed with an experimental line broadening of 10 Hz. Chemical shift data were referenced to 85% H_3PO_4.

IR spectra were obtained with a Perkin–Elmer 580B instrument equipped with a data station. The sample was suspended in analytical grade isopropyl alcohol and a thin coating of this mixture was made on a sodium chloride window. The solvent was then evaporated at room temperature before recording the IR spectra. The window carrying the thin layer of the sample was heated at various temperatures up to 473 K.

Figures 1 and 2 report the ^{31}P NMR spectra of phosphomolybdic acid and phosphotungstic acid supported on silica, alumina, and silica–alumina, respectively.

The linewidth of the NMR signal of phosphomolybdic acid on silica nearly coincides with that of pure phosphomolybdic acid (Table 1) while the signal on alumina and silica–alumina is much broader. The line broadening observed in the alumina-containing systems obviously depends on the unaveraged dipolar interaction between the ^{31}P and the ^{27}Al nuclei. Since ^{27}Al is a quadrupolar nucleus, dipolar interaction will not be averaged to zero by magic

TABLE 1

^{31}P NMR Spectra of Phosphomolybdic Acid (HPMo)

	Chemical shift (ppm)	Linewidth (Hz)
Parent compound HPMo	−3.7	70
Parent compound supported on SiO_2 (14 wt%)	−3.8	75
Parent compound supported on SiO_2–Al_2O_3		
(14 wt%)	−9.5/−12.5	1240[a]
(28 wt%)	−9.5/−12.5	1245[a]
Parent compound supported on γ-Al_2O_3 (14 wt%)	−9.5/−12	1365[a]

[a] The linewidth is referred to the overall peak.

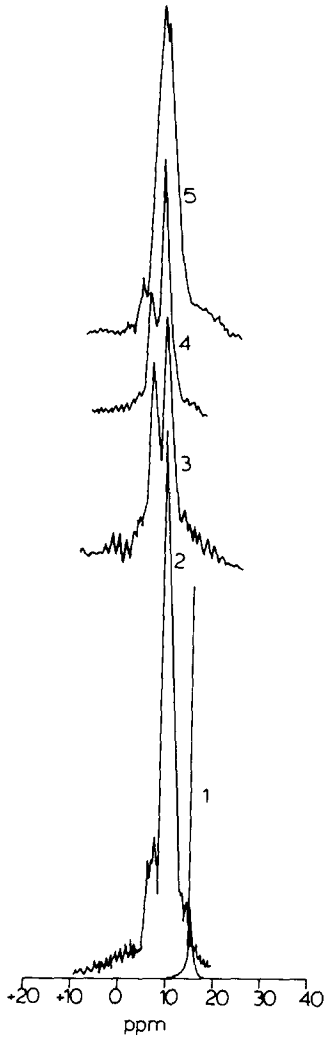

FIG. 2. Magic angle spinning NMR spectra of phosphotungstic acid supported on (1) SiO_2 (36 wt%), (2) γ-Al_2O_3 (18 wt%), (3) SiO_2–Al_2O_3 (28 wt%), (4) SiO_2–Al_2O_3 (36 wt%), and (5) SiO_2–Al_2O_3 (36 wt%) heated at 473 K for 2 hr.

angle spinning. However, this physical effect cannot be the only one responsible for the observed broadening, because it cannot explain the large difference in the linewidth between the phosphomolybdic acid and the phosphotungstic acid supported on the same γ-Al_2O_3-containing systems. On this basis the exceedingly large linewidth (Table 1) observed for phosphomolybdic acid on γ-Al_2O_3-containing systems suggests that some other factor such as strong chemical interaction or even decomposition must be responsible.

From this observation it is inferred that the catalyst primary structure is only weakly perturbed on silica whereas on alumina and silica–alumina it is more heavily modified or even partially destroyed.

This same phenomenon is not observed for phosphotungstic acid supported on alumina and silica–alumina (Table 2). This indicates that the interaction between the phosphotungstic acid and the γ-Al_2O_3-containing supports is much smaller and that the primary structure is almost preserved. Only after being heated to 473 K is some further broadening observed, which suggests an initial interaction and (possibly) decomposition of the Keggin unit. These results show that the lower catalytic activity of phosphotungstic acid supported on Al_2O_3 (with respect to SiO_2) (*11*) can be explained in terms of destruction of the Keggin unit slowly occurring at the reaction temperature.

In the NMR spectra of phosphomolybdic

TABLE 2

^{31}P NMR Spectra of Phosphotungstic Acid (HPW)

	Chemical shift (ppm)	Linewidth (Hz)
Parent compound HPW	−15.3	40
Parent compound after heating at 473 K for 2 hr	−14.6	86
Parent compound supported on SiO_2 (36 wt%)	−15.1	52
Parent compound supported on SiO_2–Al_2O_3		
(28 wt%)	−7.5/−10.2	218/241
(36 wt%)	−7.6/−10.4	219/243
36% after heating at 473 K for 2 hr	−8.5/−10.4	470[a]
Parent compound supported on γ-Al_2O_3		
(18 wt%)	−12	262
(36 wt%)	−12	262

[a] The linewidth is referred to the overall peak.

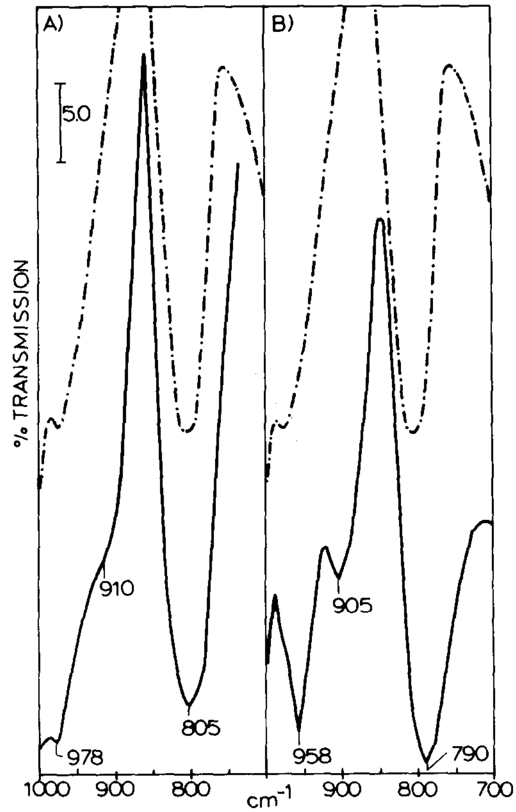

FIG. 3. (A) IR spectra of phosphotungstic acid supported on SiO_2 (18 wt%). The broken line is due to pure SiO_2 and the full line is due to the phosphotungstate anion supported on SiO_2. (B) IR spectra of phosphomolybdic acid supported on SiO_2 (14 wt%). The broken line indicates the spectrum of pure SiO_2 and the full line is due to the phosphomolybdate anion supported on SiO_2.

acid supported on γ-Al_2O_3-containing catalysts, two components with different chemical shifts are observed whose relative abundance is influenced by the concentration and the nature of the support (Table 1). They are probably associated with two different surface decomposition products of the Keggin units. Also in the case of phosphotungstic acid, the NMR signal appears to be the superimposition of two components (Table 2) whose relative concentration is influenced by loading. These components are associated with different interaction states of the Keggin unit with the surface, but we shall not attempt to treat this point in any detail in this Note.

The weak interaction of the Keggin unit with the silica support is also confirmed by *in situ* IR studies. In Fig. 3A and 3B, the IR spectra of SiO_2, HPW/SiO_2, and HPMo/SiO_2 are compared. Many bands are observed on the latter which are absent on the SiO_2 support (Table 3). These bands can be attributed to the supported heteropoly acid primary structure. The existence of a heteropoly acid band at 978 cm^{-1} (Fig. 3A) is also clearly demonstrated by the difference spectra. Comparison with the literature data on pure HPMo and HPW (*7*) (Table 3) shows a good correspondence even though a systematic shift of +25 cm^{-1} is observed for the highest Me–O–Me stretching mode (suggesting that some support-induced perturbation is taking place). We can therefore conclude that the primary structure (Keggin unit) is substantially preserved. Moreover, as the IR spectra do not change by calcining at temperatures lower than 473 K, it can be inferred that the Keggin structure is thermally stable in the range 273–473 K. These conclusions coincide with those of Moffat and Kasztelan (*13*); these authors in fact claim thermal stability up to 873 K.

IR spectroscopy is not useful in concluding the state of the heteropoly acids supported on γ-Al_2O_3 and SiO_2–Al_2O_3 because they are not transparent to the IR radiation

TABLE 3

Infrared Spectroscopic Data for Phosphotungstic Acid (HPW) and Phosphomolybdic Acid (HPMo)

	HPW[a] (cm^{-1})	HPW/SiO_2 (cm^{-1})	HPMo[a] (cm^{-1})	HPMo/SiO_2 (cm^{-1})
P–O	1080	*c*	1070	*c*
Me–O_{as}	985	978	965	958
Me–O–M[b]	887	910 (sh)	870	905
Me–O–M[b]	807	805	790	790

[a] Values from Ref. (7).

[b] Antisymmetric modes associated with bridged Me–O–Me located in external position.

[c] Not visible because of the presence of a strong IR mode of the SiO_2 support.

in the range 1000–700 cm^{-1}. For these solids only NMR measurements are useful.

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