



Characterization of the Catalytic Heteropoly Compounds using Solid-state NMR

Kim, Y, Ae* and Lee, W, Ho[†]

104-1, Munji-Dong, Analytical R&D Center
LG Chem., Res. Park, DaeJeon, 305-380, KOREA

[†]104-1, Munji-Dong, Chemical Process and Catalysis Research Institute
LG Chem., Res. Park, DaeJeon, 305-380, KOREA

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Abstract: Heteropoly compounds, $H_3PMo_{12}O_{40}$, $Cs_xH_{3-x}PMo_{12}O_{40}$, and vanadium containing heteropoly compound were characterized by Solid-state broad line 1H MAS NMR, ^{31}P MAS NMR, and High Speed MAS ^{51}V NMR spectroscopy of quadrupolar nuclei. The effects of calcination, dehydration, and the number of protons on the structure of heteropoly compounds were studied. The results of this study demonstrate that these Solid-state NMR techniques are very useful tools to study heteropoly compounds.

INTRODUCTION

The catalytic properties of heteropoly compounds have received wide attention over two decades owing to the versatility of these compounds as catalysts. Heteropolyanions are polymeric oxoanions formed by condensation of more than two different mononuclear oxoanions. Heteropoly catalysts can be applied in various ways.^{1,3} They are used as acid as well as oxidation catalysts. The structure of a heteropolyanion or polyoxoanion molecule itself is called a "primary structure"^{1,2,4} in

fig. 1(1). In solution, heteropolyanions are present in the unit of the primary structure, being coordinated with solvent molecules and/or protonated in fig. 1(2). Heteropoly compounds in the solid state are ionic crystals(or amorphous) consisting of large polyanions, cations, water of crystallization, and other molecules. This three dimensional arrangement is called the "secondary structure" in fig. 1(3). In addition to these structures, tertiary and higher-order structures influence the catalytic function in fig. 1(4).³

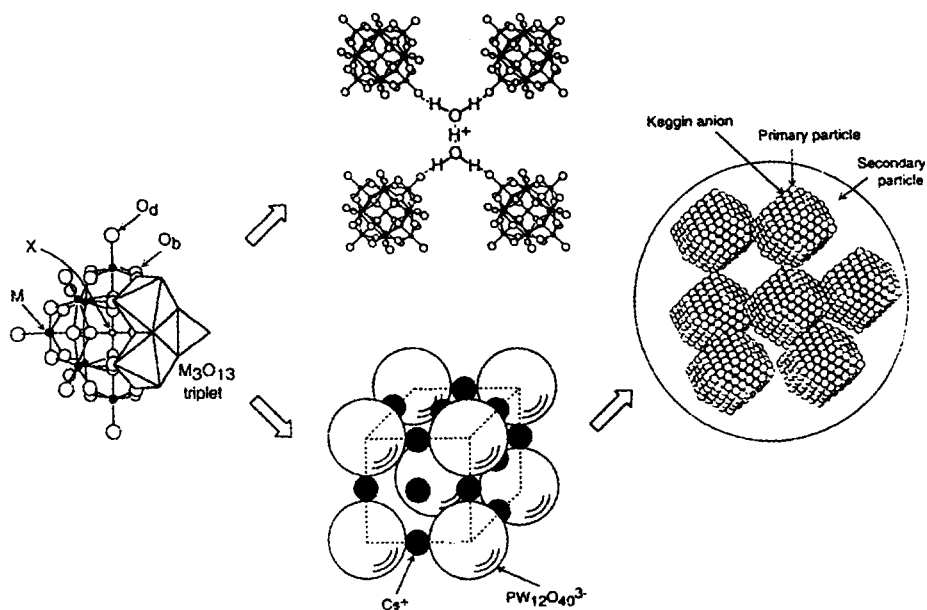


Fig. 1. Primary, secondary, and tertiary structures of heteropoly compounds. (1) Primary structure (Keggin structure, $\text{XM}_{12}\text{O}_{40}$); (2) secondary structure ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) \cdot 6 H_2O ; (3) secondary structure($\text{Cs}_3\text{PW}_{12}\text{O}_{40}$); (4) tertiary structure ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$), cubic structure as in (3).¹

In the present paper we reported new aspects of the characterization of various heteropoly compounds by Solid-state broad line ^1H , ^{31}P , ^{51}V Solid-state NMR. These techniques were used to study the effects of calcination, dehydration, and the number

of protons on the structure of heteropoly compounds.

The Vanadium-51 nucleus (natural abundance 99.76%) has a spin $I=7/2$, its electric quadrupole moment being $-4 \times 10^{-2} \times 10^{-24} \text{ cm}^2$; the relative intensity of ^{51}V NMR is 0.38 compared with an equal number of protons.⁵ Three different types of interactions influence the ^{51}V NMR spectra of solid diamagnetic samples. (1) the dipole interaction of the magnetic moments of other nuclei that broadens the lines.; (2) the quadrupole interaction of the ^{51}V nucleus with the electric field gradient that splits the lines and contributes to the shift of the central ($m_I = 1/2 \leftrightarrow m_I = -1/2$) line; and (3) the chemical shielding interaction that changes the position of the lines and makes them asymmetric. The lineshape might be rather complicated due to the simultaneous action of all types of interactions. ^{51}V is one of the heavy nuclei that have a wide range of the order of several hundreds of kilohertz to several megahertz due to the first order quadrupole interaction. Magnitude of chemical shift anisotropy is relatively large. High speed magic angle spinning (MAS) NMR technique of half integer quadrupolar nuclei is used among double rotation (DOR), dynamic angle spinning (DAS), (MAS) nutation NMR, and variable angle spinning (VAS) to study such nuclei.⁶

EXPERIMENTAL SECTION

Materials

12-Molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, Fluka 99.9+%) was commercially obtained. $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ ($x = 1-3$), were prepared as following. An aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (Aldrich, 99.8%) was prepared and then H_3PO_4 (Ducksan Chemical Co., 85wt. %) was added into the solution by drop wise with vigorous mixing (Solution A). An aqueous solution of CsNO_3 acidified with HNO_3 was

prepared (Solution B). Solution B was added into Solution A by drop wise with vigorous mixing to obtain the slurry. This slurry was evaporated to dried with stirring under heat. Then the resultant solid in the block state was dried in the oven at 120°C. The dried product was ground to 20 - 40 mesh and calcined in air at 400°C to obtain $Cs_xH_{3-x}PMo_{12}O_{40}$ by decomposing ammonium and nitrate ions originated from the starting materials.

Heteropoly compound containing V and Cu was prepared as following. A mixed aqueous solution of $(NH_4)_6 Mo_7O_{24}$ (Aldrich, 99.8%) and NH_4VO_3 , (Strem, 99%) were prepared by dissolving them in distilled water and then H_3PO_4 was added into the solution by drop wise with vigorous mixing (Solution A). A mixed aqueous solution of $CsNO_3$ and $Cu(NO_3)_2$ was prepared and acidified with HNO_3 (Solution B). Solution B was added into Solution A by drop wise with vigorous mixing to obtain the slurry. The same procedure as in the preparation of $Cs_xH_{3-x}PMo_{12}O_{40}$ was followed to obtain $Cs_{1.5}Cu_{0.3}PV_1Mo_{11}O_{40}$.

A commercial catalyst employed in the production of methacrolein to methacrylic acid industrially (referred as Catalyst A in fig. 4) was used for comparison.

NMR measurements

$^{51}V(I=7/2)$ spectra were measured at 78.4MHz on a Bruker DSX 300 MHz NMR Spectrometer with static magnetic field strengths of 7.05T, using a standard double bearing probe head. Samples were placed into 4mm zirconia rotor or silicone nitride rotor. Spectra were recorded using single pulse with/without dipolar decoupling under MAS with static and spinning samples (5 ~ 15KHz) and recorded under room temperature. Magic angle was adjusted using ^{79}Br resonance of KBr at first, and the ^{13}C and ^{51}V resonances were used to assure the accurate setting. 90

degree pulse length for aqueous NH_4VO_3 solution was set $12 \mu\text{s}$ and the pulse duration used for the recorded spectra was $3 \mu\text{s}$ and the repetition time was 1.0s. Echo sequences are used for static samples. The chemical shifts are referenced to neat VOCl_3 and NH_4VO_3 aqueous solution (-574ppm from VOCl_3). Each spectrum was recorded with the spectral width of maximum 1MHz.

$^{31}\text{P}(I=1/2)$ NMR measurements were performed at 121.5MHz on a Bruker DSX 300 MHz NMR Spectrometer with static magnetic field strengths of 7.05T, using a standard double air bearing probe head. Samples were placed into 7 mm zirconia rotor. Spectra were recorded using (CP)MASDD with 5~7 KHz spinning rate and recorded under room temperature. Chemical shift reference is $\text{NH}_4\text{H}_2\text{PO}_4$ powder and the 90 degree pulse is $3 \mu\text{s}$.

RESULTS AND DISCUSSIONS

Solid state ^{51}V NMR of V_2O_5 and NH_4VO_3

Fig. 2. (1) shows Solid-state ^{51}V static spectrum of V_2O_5 which has a line shape ruled by the first-order quadrupole interaction and chemical shift anisotropy. Fig. 2. (2) is the off-MAS spectrum which shows the signals only from the central transition. Satellite transitions are broadened by the first-order quadrupole interaction. Therefore, chemical shift interaction and second-order quadrupole interaction are measured. The chemical shift interaction is responsible for the spinning side band (SSB) intensity and the second-order quadrupole interaction for the fine structure of each SSB. The second order quadrupole effects are inversely proportional to ν_0 . Thus at a sufficiently high ν_0 ($\geq 7\text{T}$), the second order quadrupole effects are suppressed and can be neglected, while the effects of the chemical shielding

anisotropy became more pronounced and can be measured more precisely.⁵ From the off-MAS spectrum, we can measure chemical shift anisotropy and quadrupole interaction. O. B. Lapina *et al.*⁷ obtained chemical shift parameters of V_2O_5 from analysis of the simulated spectra at 101.25MHz. The second order quadrupole effect on the lineshape was ignored in this high field. The obtained parameters were $\sigma_{11} = \sigma_{22} = -310\text{ppm}$, $\sigma_{33} = -1270\text{ppm}$, $\sigma_{\text{iso}} = -610\text{ppm}$, $\delta\sigma = 960\text{ppm}$, $\eta = 0.04$ ^{1,2,3}, and the quadrupole coupling constant was 0.8MHz.

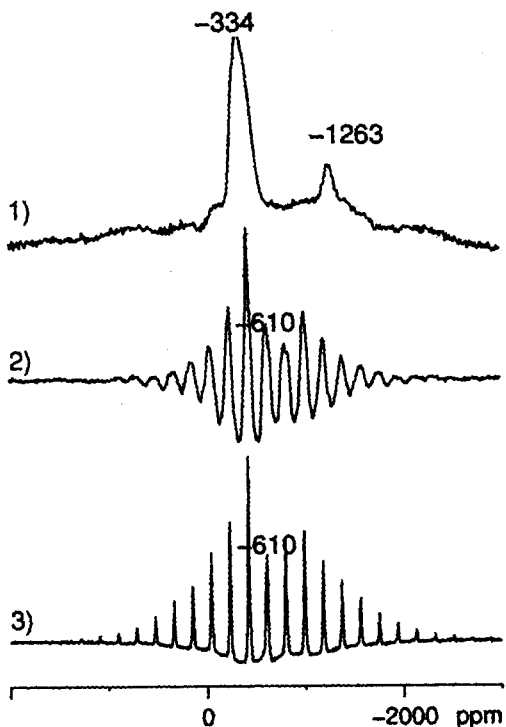


Fig. 2. ^{51}V Solid-state NMR spectra of V_2O_5 at 78.4MHz with 15KHz spinning rate (1) static, (2) off-MAS, (3) MAS spectra

Our experimental values are $\sigma_{11} = \sigma_{22} = -334\text{ppm}$, $\sigma_{33} = -1263\text{ppm}$ from the static and off MAS spectra, while $\sigma_{\text{iso}} = -610\text{ppm}$ from the variable spinning speed experiments(not shown in this study), are in good agreement.

Fig. 3. (1) shows the off-MAS spectrum of ammonium metavanadate, NH_4VO_3 while Fig. 3. (2) shows its MAS spectrum. A large number of SSBs spread over a frequency range wider than 800KHz. Each SSB has a symmetric lineshape without a fine structure. The off-MAS spectrum does not show any fine structure of symmetric SSB line shape either. Thus, the second order quadrupole effect can be ignored. Experimental values are of $\delta_{\text{iso}} = -573\text{ppm}$ from the off MAS and MAS spectrum, $\Delta\delta_{\text{anis}} = -370\text{ppm}$ from the off MAS spectra. S. Hayashi *et al.* obtained parameters from the SSB intensities of the simulated off-MAS spectrum, $\delta_{\text{iso}} = -572.5 \pm 0.5\text{ppm}$, $\Delta\delta_{\text{anis}} = -365 \pm 20\text{ppm}$, $\eta = 0.70 \pm 0.06$. These values are in good agreement with our experimental results.

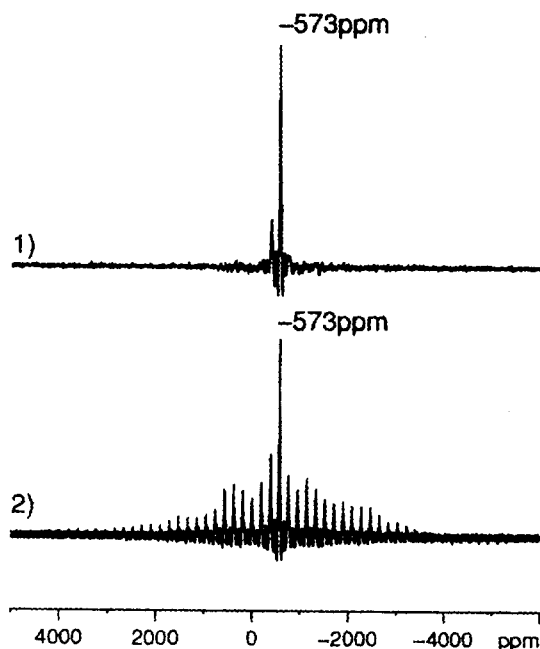


Fig. 3. ^{51}V Solid-state NMR spectra of ammonium metavanadate at 78.4MHz with 15KHz spinning rate. (1) off-MAS spectra, (2) MAS spectra

Solid-state ^{51}V NMR of heteropoly compound catalysts

Fig. 4 shows High Speed Solid-state ^{51}V MAS NMR spectra for three catalysts, Catalyst A and $\text{Cs}_{1.5}\text{Cu}_{0.3}\text{PV}_1\text{Mo}_{11}\text{O}_{40}$ prepared in this study before and after calcination (see *Materials* section). Catalyst A is known to have a Keggin structure with one molybdenum ion substituted by vanadium ion. However, the composition is not known in detail while it is believed to have similar compositions as one prepared in this study. All catalysts were evacuated at 200°C before measurement to remove water.

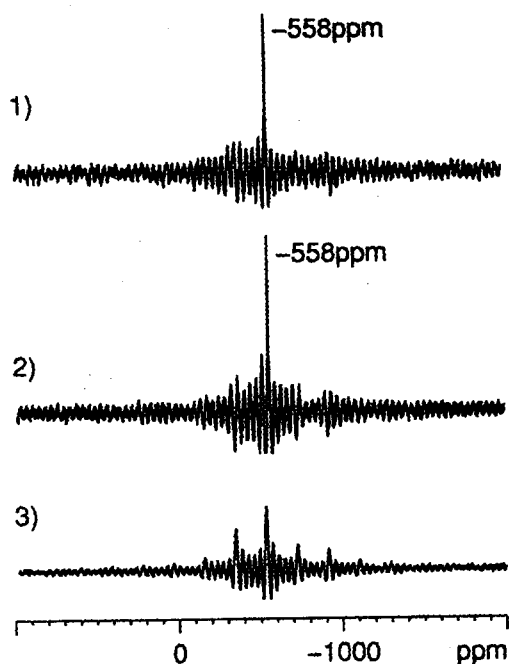


Fig. 4. ^{51}V Solid-state NMR spectra of heteropoly compounds of catalyzing methacrolein to methacrylic acid at 78.4MHz with 15KHz spinning rate. (1) catalyst A (commercial), (2) catalyst B ($\text{Cs}_{1.5}\text{Cu}_{0.3}\text{PV}_1\text{Mo}_{11}\text{O}_{40}$) before calcination, (3) catalyst B ($\text{Cs}_{1.5}\text{Cu}_{0.3}\text{PV}_1\text{Mo}_{11}\text{O}_{40}$) after calcination

Fig. 4(1) shows a sharp resonance at -558 ppm indicating that a single vanadium species is present in the structure of Catalyst A. This result is in a good agreement with the fact that this catalyst have a Keggin structure with one molybdenum ion substituted by vanadium ion. A large number of SSBs spread over a wide frequency range is due to V_2O_5 , suggesting that some of vanadium ions in Catalyst A are not present in the Keggin structure.

Fig. 4(2) for $Cs_{1.5}Cu_{0.3}PV_1Mo_{11}O_{40}$ before calcination also shows sharp single resonance at -558 ppm indicating that one vanadium species is present instead of molybdenum in the Keggin structure after preparation of the catalyst. However, the sharp resonance at -558 ppm disappears after calcination at 400°C in fig4.(3). Only a large number of SSBs spread over a wide range due to V_2O_5 are observed.

This result suggests that the Keggin structure is completely destroyed after the calcining $Cs_{1.5}Cu_{0.3}PV_1Mo_{11}O_{40}$ prepared in this study. The catalyst activity was much less than that of Catalyst A. The results from this study demonstrate that Solid-state ^{51}V NMR is a powerful tool to identify the structure of hetropoly compounds containing vanadium.

Broad line Solid-state 1H NMR spectroscopy on $H_3PMo_{12}O_{40} \cdot xH_2O$

Fig. 5 shows the solid-state 1H NMR spectra for $H_3PMo_{12}O_{40} \cdot xH_2O$ obtained at room temperature with different states of dehydration. Fig. 5(1) for $H_3PMo_{12}O_{40} \cdot xH_2O$ prior to dehydration pretreatment, shows a sharp 1H resonance indicating that protons are in an uniform state and highly mobile. This chemical shift may be attributed to the clusters of hydrated water in Fig. 1(2). As the water content decreases, however, spectrum becomes broader and shifts to 6.52ppm indicating that protons become less mobile and attached to the most basic bridging oxygen atoms.¹ Proton chemical shifts are referenced to tetrakis(trimethylsilyl)silane (TKS, 0.27ppm)⁹.

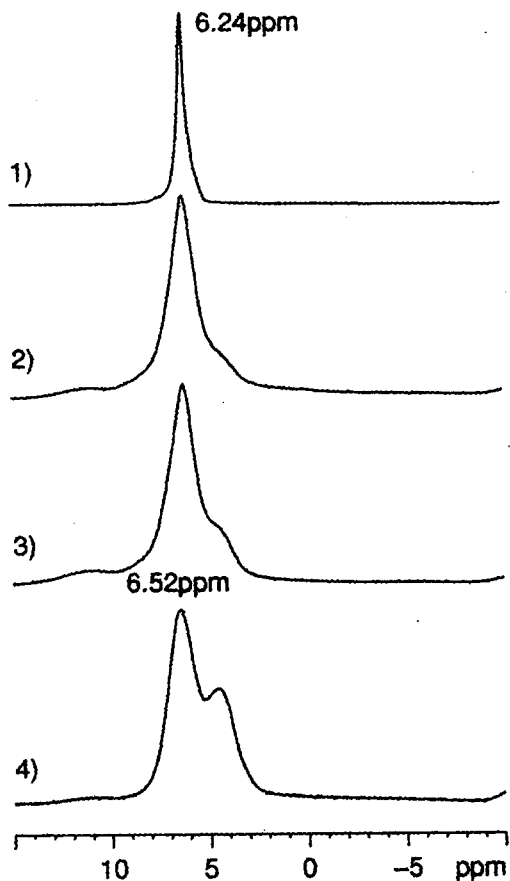


Fig. 5. Broad line Solid-state ^1H NMR spectra of heteropoly compounds, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ at 300.13MHz with 5KHz spinning rate. (1) $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$, (2) after overnight drying at 85 °C, (3) after 1.5hrs drying at 200 °C, (3) after 6hrs drying at 360 °C

Solid-state ^{31}P NMR Spectroscopy on $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ and $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$

The ^{31}P chemical shift provides import information relating to the structure, composition and electronic states of heteropoly compounds. Fig. 6 shows that the ^{31}P NMR chemical shift of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ is greatly dependent upon water content.

The chemical shift changes from -4.5 ppm to -2.5 ppm as the water content decreases. The resonance at -4.5 ppm may be attributed to protonated water $\text{H}(\text{H}_2\text{O})_2^+$ connected with the heteropolyanion by hydrogen-bonding at terminal oxygens. The resonance at -2.5 ppm in Fig. 6(4) is assigned to protons directly attached to oxygen atoms of the polyanion.¹

Solid-state ^{31}P NMR spectra were obtained for $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ to get an information on protons distributed throughout the bulk of the material and thus on their structure. Special care was necessary to protect the sample from the moisture during the measurement. Fig. 7(1) for $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ shows a resonance at -5.5 ppm. This means that the heteropoly anionic compound, $\text{PMo}_{12}\text{O}_{40}^{3-}$, does not have any proton. Fig. 7(2) for $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$ also shows a single resonance at -5.5 ppm, which is very similar to that for $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$. However, in the case of $\text{Cs}_{1.5}\text{H}_{1.5}\text{PMo}_{12}\text{O}_{40}$, an additional resonance is observed at -4.5 ppm, -3.5 ppm, -2.5 ppm after deconvolution. The resonance at -4.5 ppm may be attributed to one proton directly attached to the polyanion and the resonances at -3.5 ppm and -2.5 ppm may be assigned to two and three protons attached to the Keggin structure, respectively. Therefore, solid-state ^{31}P chemical shift is determined by the number of the protons attached to the polyanion, and the four peaks correspond to the Keggin anions having 0, 1, 2, and 3 protons, respectively.

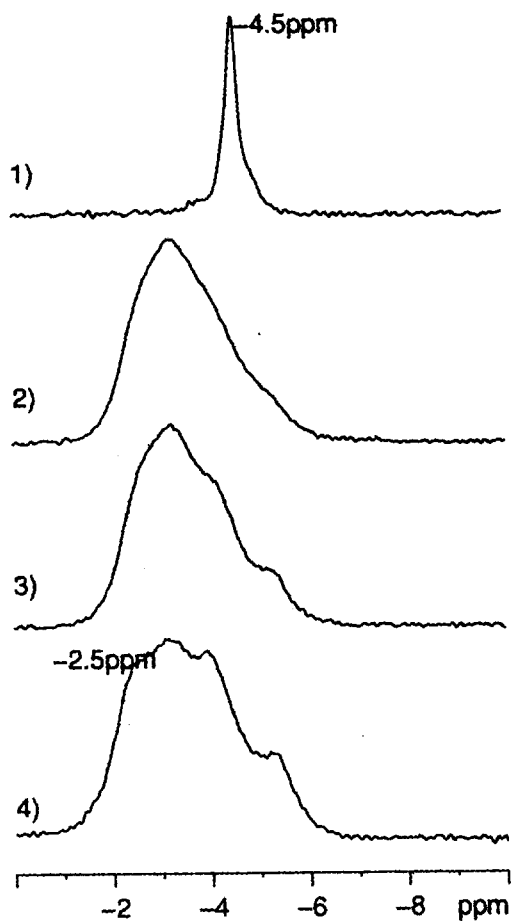


Fig. 6. Solid-state ^{31}P NMR spectra of heteropoly compounds, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ at 121.5MHz with 5KHz spinning rate.

(1) $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, (2) after overnight drying at 85 °C, (3) after 1.5hrs drying at 200 °C, (4) after 6hrs drying at 360 °C

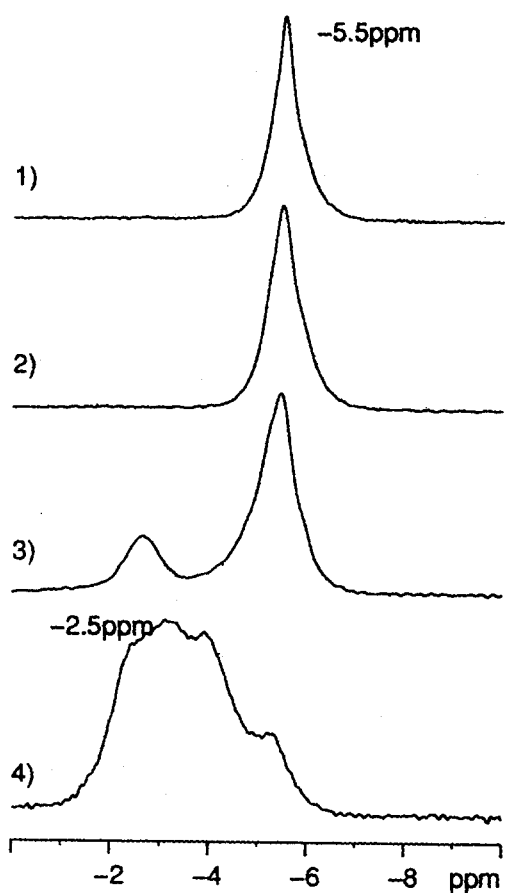


Fig. 7. Solid-state ^{31}P NMR spectra of heteropoly compounds at 121.5MHz with 5KHz spinning rate. (1) $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$, (2) $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$, (3) $\text{Cs}_{1.5}\text{H}_{1.5}\text{PMo}_{12}\text{O}_{40}$, (4) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ after 6hrs drying at 360 °C

CONCLUSION

Several heteropoly compounds were examined using solid-state broad line ^1H MAS NMR, ^{31}P MAS NMR, and High Speed ^{51}V MAS NMR spectroscopy of quadrupolar nuclei. The results from this study demonstrated that these solid-state NMR techniques are very useful to figure out the structures, compositions, hydration

states and phases of the heteropoly compounds.

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