Structural modifications of Cu(II) 12-tungstophosphoric acid salt studied by IR and Raman spectroscopy*

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In this paper local processes and structural phase transformations of the copper salt of 12-tungstophosphoric acid are investigated. The structural phase transformations were followed through bands, characteristic for the host lattice, in the IR and Raman spectra. The results of these investigations, as well as those of XRPD analysis and impedance measurements as a function of temperature show that some local processes provoke the change in the secondary structure of the Keggin anions.

Keywords: IR spectra, Raman spectra, heteropoly compounds, proton conductors, phase transformations.

INTRODUCTION

The high degree of hydration of heteropolyacids (HPA) and their salts (n = 29 – 15 water molecules) determines the high statistic disorder of the different proton species and a developed network of hydrogen bonds which enable fast proton transport.1–4 As a result of this, these compounds are superionic proton conductors at room temperature [σ = (100–1)x10–5 S/cm]. Recently, there has been many investigations dealing with proton species (H3O+, H2O, H2O, OH− and H+) as charge carriers, their dynamic equilibrium and the nature and strength of hydrogen bonds. From the literature data,1–6 it is evident that the number and nature of different proton species depend very much on the state of hydration of the compounds, which in turn depends on the temperature and relative humidity of the surrounding. However, there is little information about the structure of the host lattice. On the basis of XRD results of Keggin for WPA·29H2O,7 Brown, Noe-Spirlet, Busing and Levy for the most stable WPA hydrate hexahydrate;8 and 21-hydrate WPA determined by Noe-Spirlet and Busing9 and our data,6 it is evident that the

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primary crystal structure of HPC is very dependent on the degree of hydration. Information about structural changes of the host lattice, i.e., Keggin's anions, induced by different proton entities and the dynamic equilibrium between them do not exist. The secondary structure is variable due to the interaction of the host lattice with various molecules and ions, such as water, proton species and counter-ions. As a result of this, it is of great interest to establish the nature of the secondary structure and its influence on the mechanism and values of the conductivity.

In our earlier papers, the splitting of some fundamental bands in the IR and Raman spectra was reported. The splitting depends very much on temperature and it is a spectroscopic criterion for different non-equivalent groups and/or the appearance of a new phase. The splitting is most pronounced for the $v_1 (PO_4)$ band in both the IR and Raman spectra. The reason for such behavior could be found in different local processes.

Our in situ studies of the hexahydrate of WPA by X-ray powder diffraction and Raman spectroscopy have shown the existence of a non-convergent, reversible transition in the 40–100 °C temperature range, produced by the partial reduction and oxidation of tungsten, well known as an element with mixed valence (V and VI). It could be expected that this effect should be much more pronounced in the case of salts with two ions with mixed valence, such as copper and tungsten in the CuHWPA salt. For this reason we have performed in situ IR and Raman investigations of the copper salt of WPA (CuHWPA), as well as XRPD and impedance measurements as a function of temperature with the aim of solving the problem of local structure and phase structural transformation.

EXPERIMENTAL

Thermogravimetric (TGA) and differential thermal analysis (DTA) were performed using Perkin Elmer-4 thermal analyser. Measurements of the thermal transformation were made in a nitrogen atmosphere, with a flow rate of 50 ml min$^{-1}$. The scanning rates were 3 and 10 K min$^{-1}$.

X-Ray powder diffraction (XRPD) patterns were obtained on a Phillips PW-1710 automated diffractometer, with a copper tube operated at 40 kV and 35 mA. Diffraction data were collected in the 2θ range from 4° to 70°, counting for 0.25 s at each 0.02° 2θ step. All the XRPD experiments on the samples, previously heated at a characteristic temperature chosen from the DTA curve, were performed at room temperature.

IR spectra were recorded in the range of 4000–350 cm$^{-1}$ at room temperature using a Perkin Elmer 983G spectrophotometer. Spectra at high temperature were recorded in situ with a recording step of 10 °C, in a variable temperature cell, model VLT-2, RIIC, London.

Raman spectra were scanned with a Raman microscope Microdil 28 Dilor using an argon ion laser, wavelength $\lambda = 514.53$ nm. The laser power was 0.4 mW. The crystal was exposed to the laser beam for 3 min and the spectra were scanned every 10 s. The exposure times of the crystal to laser beam correspond to the increase of temperature.

Impedance measurements were made for frequencies from 5 Hz to 500 kHz using a HP4190 A vector impedance meter in the temperature interval from 20 to 70 °C. Values of the DC conductivity $\sigma(\omega=0)$ were determined from the intersections of the semicircular arcs with the $z'$ axes in the complex impedance plane ($z'' = f(z')$).
RESULTS AND DISCUSSION

From the DTA and TGA data, Fig. 1, it is evident that the CuHWPA salt is a crystalhydrate with 25 water molecules which it looses in several steps:

\[
\text{CuHWPA-25} \xrightarrow{25-55} \text{CuHWPA-9} \xrightarrow{65-87} \text{CuHWPA-5} \xrightarrow{125-141} \text{CuHWPA-3} \xrightarrow{180-205 \, ^\circ C} \text{CuHWPA-0}
\]

The CuHWPA salt is completely dehydrated at 205 \(^\circ C\) and free protons stabilize the Keggin's anions\(^6\) as confirmed by inelastic incoherent neutron scattering measurements (IINS)\(^5,12\). These measurements showed the existence of free protons (H\(^+\)) - free "proton gas" in the solid structure of heteropoly compounds\(^6,7\). In the temperature interval from 205 to 500 \(^\circ C\), this salt looses 0.5 water molecules which is characteristic for WPA itself and all other alkaline and earth-alkaline salts.\(^6,12,13\) The exothermic peak at 571 \(^\circ C\) corresponds to the process of solid-solid recrystallization and the formation of copper and phosphorus doped bronzes.\(^12\)

![Graph](Image)

Fig. 1. DTA and TGA curves of the copper salt CuHWPA. The numbers on the figure indicate the temperatures of the phase transitions: 1–59, 2–87, 3–141, 4–205, 5–571 \(^\circ C\). Inserted figure is DTA curve obtained by scanning rate of 3 \(^\circ C\)/min.

The results of X-ray powder diffractions (XRD) are summarized in Fig. 2. It is obvious from the observed XRD patterns that the basic Keggin's ion configuration remains preserved in the temperature range from 25 to 190 \(^\circ C\). However, dehydration of the unstable initial CuWPA–25 (curve a) starts between 25 and 55 \(^\circ C\). This process is very fast and in this temperature interval practically all the CuHWPA–25 hydrate is transformed to the CuHWPA–9 hydrate (curve b). Between 65 and 87 \(^\circ C\) (curve b–c), the discussed dehydration is completed and the stable cubic CuHWPA–5 phase is formed (curve c). With prolonged calcination up to 190 \(^\circ C\) (curve d–f) this phase remains unchanged, which is consistent with the thermal measurements.
DTA and TGA data, as well as XRPD show that this salt is stable in the temperature interval from 87 to 141 °C, but the IR spectra scanned in this temperature interval, Fig. 3, and the Raman spectra, Fig. 4, show that the \( v_1(\text{PO}_4) \) band at about 1000 cm\(^{-1}\) is split into three bands at 994, 981 and 968 in the IR and at 1010, 995 and 975 cm\(^{-1}\) in the Raman spectra, respectively, the intensities of which change with temperature, being more pronounced in the Raman spectra. These bands, evident in both spectra, change their intensities in a way which indicates a structural phase transition, Fig. 5 a and b. These changes could be correlated with the change of secondary structure, while the primary structure of Keggin anions is preserved. The intensities as a function of temperature show discontinuities at about 60, 87 and 140 °C. The bands at 994 in the IR, and 1010 cm\(^{-1}\) in the Raman spectra decrease with temperature, i.e., with the exposure time of the sample to the laser beam. The band at 1010 cm\(^{-1}\) in the Raman spectra disappears and the band at about 995 cm\(^{-1}\) becomes the most intense band in this region. After 120 s of exposure of the sample to the laser beam the sample becomes stable. No changes in the spectra characteristics for the formation of bronzes\(^6\) are evident in the IR and Raman spectra. This means that the structure of the Keggin anions is preserved after calcination. However, the spectral data show that the Keggin anions are exposed to great strain provoked by different local processes: non-equivalent \( \text{PO}_4 \) groups formed in interaction of protons with the \( \text{PO}_4 \) group - HPO\(_4\)^{2-}; interaction of protons with terminal oxygen atoms and the formation of OH groups, interaction of water molecules with oxygen atoms\(^5,6,10\) and local oxidation-reduction processes.\(^11\) All the above-mentioned processes in HPC can be explained by the reaction of dissociation/association:
Fig. 3. IR spectra of the copper salt CuHWPA at different temperatures.

Fig. 4. Some micro-Raman spectra of the copper salt CuHWPA scanned for 3 min, with the step of 10 s.
Fig. 5. Bands intensities: a) in the IR spectra versus the temperature; b) in the micro-Raman spectra

\[ \text{H}_5\text{O}_2^+ \Leftrightarrow \text{H}_2\text{O}^+ + \text{H}_2\text{O} \Leftrightarrow \text{H}^+ + 2\text{H}_2\text{O} \]

Any of a given species can react with the elements of the Keggin anions and induce the changes in the structural geometry of the Keggin anions, a charge redistribution with reflections on the Keggin anions and the connections between them. The
consequence is that the P–O$_{a}$ bonds decrease and the distance between the Keggin anions increase with increasing temperature. This change in the bonding character produces changes in the charge distribution within the Keggin anions and the partial reduction of W$_{6}^{6+}$ to W$_{5}^{5+}$ and Cu$_{2+}$ to Cu$^{1+}$. These processes occur very easily and are reversible because tungsten and copper are elements with mixed valence. The oxidation-reduction process may also be followed by the change of the color of Cu(II)WPA sample during the process of calcination in the interval of hydration stability of the sample. At the beginning of the calcination the sample was blue and during the calcination the sample's color gradually change to light green. After the cooling the sample had the same blue color as at the beginning of the experiment.

This reduction can be provoked by covalent bonding of OH groups:

$$4\text{OH}^{-} + 2\text{W}^{6+} \Leftrightarrow 2\text{H}_{2}\text{O} + \text{O}_{2} + 2\text{W}^{5+} + 2\text{e}^{-}$$

Two electrons are sufficient to reduce not only the tungsten but also the copper. On the basis of the above mentioned considerations, it could be expected that the contribution of electron conductivity to the total conductivity will be more pronounced.

In such cases, when molecules or groups, such as the Keggin anions, are exposed to large strain, the fundamental T$_{d}$ symmetry of the PO$_{4}$ group is disturbed. The corresponding v$_{1}$ vibration becomes active in the IR spectra and in some cases A$_{g}$ (about 1000 cm$^{-1}$) and B$_{u}$ (about 995 cm$^{-1}$) bands are activated. So both bands belong to the v$_{1}$ (PO$_{4}$) vibration. The third band at about 968 in the IR and at 975 cm$^{-1}$ in the Raman spectra is assigned to v(W=O).
From the temperature dependence of the conductivity, (Arrhenius diagram), shown in Fig. 6, at temperatures above 60°C, a deviation of \(\ln(\sigma T)\) from the straight line with decreasing values of \(1/T\) is evident. This fact is in accordance with the phase transition registered by the IR and Raman spectra at the same temperature and so confirms the spectral data.

We have also found a discontinuity on the static permittivity versus temperature plot. This is another fact in favour of the assumption of a phase transition at a temperature around 60°C.

The salt CuHWPA is a proton conductor. The conductivity was measured for two crystallohydrates, \(n = 17\) and \(n = 15\), and values of \(\sigma = 1.95 \times 10^{-6}\) and \(\sigma = 2.27 \times 10^{-7}\) S/cm, respectively, were found. These values refer to the temperature of 25°C.

The activation energies, calculated from the Arrhenius plot, for both specimens are the same, \(E_a = 0.54\) eV. Such an independence of the activation energy on hydration, for lower hydrates, was obtained earlier for the sodium salts of WPA,\(^{14}\) and attributed to the same mechanism of proton conduction in heteropoly compounds; individual proton jumps.

CONCLUSIONS

From the spectral data it is evident that a change in the dynamic equilibrium of the proton species \(\text{H}^+\), \(\text{OH}\) and hydrated proton entities is closely connected to the structural modifications of the Keggin anions and the partial reduction of \(\text{W}^{6+}\) to \(\text{W}^{5+}\) and \(\text{Cu}^{2+}\) to \(\text{Cu}^+\). The Keggin anions are geometrically stable over the whole investigated temperature interval, as evidenced by XRPD data, but the distances between the oxygen atoms of the PO₄ and WO₆ groups, as well as between the Keggin anions are changed. Two processes have occurred: a contraction of the bonds within the Keggin anion and an expansion of those between the Keggin anions.

Non-convergent, reversible phase transitions were confirmed by IR and Raman spectroscopy, as well as by the conductive properties of CuHWPA. The cause of these modifications is the partial reduction of the Keggin anion elements.

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ИЗВОД

И РАМАНСКА ИСПИТИВАЊА СТРУКТУРНИХ МОДИФИКАЦИЈИ БАКАРНЕ СОЛИ 12-ВОЛФРАМФОФОРНЕ КИСЕЛИНЕ

УБАВКА Б. МИОЧ, МАРИЈА ТОДОРОВИЋ, СНЕЖАНА УСКОКОВИЋ-МАРКОВИЋ, ЗОРАН НЕДИЋ, ВОИСЛАВ СТАМЕНКОВИЋ и ТАМАРА ЧАКОВСКИ

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У овом раду испитивани су локални процеси и структурне фазне трансформације соли бакара 12-волфрамфофорне киселине. Структурне фазне трансформације праћене су према трајању карактеристичних за кристалну решетку у графичким и раманским спектрима. Резултати ових испитивања као и они добијени јединствено структурном анализом и из имедијалних мера, односно проводњивост у функцији температуре, показују да је фазна трансформација везана за промене локалне структуре, тј. секундарне структуре Кегинових ангиона.

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REFERENCES