Inorg. Chem. **2005**, *44*, 6695–6703

Inorganic Chemistry
Article

New Evidence on the Structure of Potassium Salts of 12-Tungstophosphoric Acid, $K_xH_{3-x}PW_{12}O_{40}$

Jerzy Haber,*,† Leszek Matachowski,† Dariusz Mucha,† Jerzy Stoch,† and Priit Sarv‡

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-239 Kraków, ul. Niezapominajek 8, Poland, and National Institute of Chemical Physics and Biophysics, Estonian Academy of Sciences, Tallinn, Estonia

Received March 7, 2005

Physicochemical properties and compositions of $K_xH_{3-x}PW_{12}O_{40}$ salts, where $2 \leq x \leq 3$, have been investigated. It has been found that freshly prepared $K_2HPW_{12}O_{40}$ salt (drying at 313 K) contains particles of heteropolyacid and particles of the neutral potassium salt, the sample being in 78.6% amorphous. On aging at room temperature, the heteropolyacid spreads to form a surface layer covering the neutral potassium salt particles $K_3PW_{12}O_{40}$. Heat treatment of $K_xH_{3-x}PW_{12}O_{40}$ salts, where $2 \leq x < 3$, from 313 K to higher temperatures induces the transformation of the heteropolyacid-covering K_3 core into a well-dispersed, amorphous surface layer. On further heating of the acidic potassium salts, the surface layer decomposes between 855 and 915 K with the formation of a PW_8O_{26}-type bronze as a new phase, the $K_3PW_{12}O_{40}$ salt remaining unchanged. The latter starts to decompose at 1093 K, and in the case of all samples, the process is completed at about 1183 K. Rietveld structure refinement, XPS, and ^{31}P NMR measurements of acidic potassium salts indicate that the core of these salts is always formed by the $K_3PW_{12}O_{40}$ salt, which is covered by a heteropolyacid. Comparison of lattice parameters of the K_3 salt and HPW leads to the conclusion that the layer is composed of partially or completely dehydrated heteropolyacid molecules. The coverage of the core by HPW in the K_2 sample was estimated to be equal to one monolayer.

Introduction

Heteropolyacids (HPA's) and their acidic salts with the Keggin structure are well-known as effective catalysts in hydrocarbons oxidation[1,2] and hydration of olefins.[3] Although the heteropolyacid is a useful solid catalyst, the amount of acid sites on the surface is small because of the low surface area (about 5 m^2/g). However, its catalytic activity can be improved by increasing the HPA dispersion, which can be achieved by two methods: (a) the impregnation of the HPA on porous supports; (b) the partial neutralization of the HPA with different cations (e.g. K^+, Cs^+, NH_4^+) to form porous insoluble salts. The analysis of nitrogen adsorption−desorption isotherms has shown that substitution of large monovalent cations for one or more of the protons generates microporous structures and relatively high surface areas.[4−8] The creation of a microporous structure characterized by high surface area results in the increase of the catalytic activity of these salts.[9,10]

While structures of heteropolyacids and their neutral salts are generally known, two structural models have been proposed in the literature to represent the acidic salts of alkali metals.[11] In the first model it is assumed that an acidic salt of alkali metal consists of a surface monomolecular layer of heteropolyacid which is dispersed on the particles of its neutral salts and can be stabilized at the surface of these particles in the form of an epitaxial layer, isostructural

---

* To whom correspondence should be addressed. E-mail: nchaber@cyf-kr.edu.pl.
† Polish Academy of Sciences, Kraków, Poland.
‡ Estonian Academy of Sciences.

[1] Okuhara, T.; Mizuno, N.; Misono, M. T. Catalytic Chemistry of Heteropoly Compounds. In *Advances in Catalysis*; Academic Press: New York, 1996; Vol. 41, p 113.
[2] Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171.
[3] Izumi, Y. *Catal. Today* **1997**, *33*, 371.
[4] McMonagle, J. B.; Moffat, J. B. *J. Colloid Interface Sci.* **1984**, *101*, 479.
[5] Taylor, D. B.; McMonagle, J. B.; Moffat, J. B. *J. Colloid Interface Sci.* **1985**, *108*, 278.
[6] McGarvay, G. B.; Moffat, J. B. *J. Colloid Interface Sci.* **1988**, *125*, 51.
[7] McGarvay, G. B.; Moffat, J. B. *J. Catal.* **1991**, *130*, 483.
[8] Gao, S.; Rhodes, C.; Moffat, J. B. *Catal. Lett.* **1998**, *55*, 183.
[9] Parent, M. A.; Moffat, J. B. *Catal. Lett.* **1997**, *48*, 135.
[10] Essayem, N.; Kieger, S.; Coudurier, G.; Vedrine, J. C. *Stud. Surf. Sci. Catal.* **1996**, *101A*, 591.
[11] Langpape, M.; Millet, J. M. M.; Ozkan, U. S.; Boudeulle, M. *J. Catal.* **1999**, *181*, 80.

10.1021/ic050350s CCC: $30.25

with the support. It has been shown that thin coats of $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 0-3$) formed at the surface of the potassium salt $K_3PMo_{12}O_{40}$ of high surface area of 70 m^2/g as the support display modified chemical and catalytic properties and enhanced thermal stability.[12-14] Black et al.[15] described the epitaxial growth of the $H_3PMo_{12}O_{40}$ layer on the surface of the crystallites taking place in the series of catalysts $K_xH_{3-x}PMo_{12}O_{40}$ ($2 < x < 3$) during calcinations at 673 K. The presence of an epitaxial layer in the $K_{2.5}H_{0.5}PMo_{12}O_{40}$ salt established by the XRD method did not affect the diffraction pattern of the $K_3PMo_{12}O_{40}$ matrix, indicating that the surface layer of that salt is isostructural with the support and formed by an epitaxial deposition.

In the second model the formation of the solid solution upon heating is postulated.[16] The existence of the solid solution in the case of the K^+, NH_4^+, and Cs^+ salts of tungstophosphoric acid, where $2 \leq x < 3$, was observed by Corma et al.[17] for the thermally treated samples. Authors postulated that in the case of this range of e.g. cesium contents the resulting solids form a mixture of the $Cs_2HPW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ salts. Thermal treatment at 573 K would accelerate the diffusion of K^+, NH_4^+, or Cs^+ and H^+ ions transforming the initial mixture of crystalline salts into more homogeneous acidic salts.

In the early studies performed for the series of $K_xH_{3-x}PW_{12}O_{40}$ salts (where $x = 1, 1.5, 2, 2.5, 3$), it was found that the $K_2HPW_{12}O_{40}$ salt precipitated as a most stable phase.[18] The diffraction patterns and thermal analysis of $KH_2PW_{12}O_{40}$ and $K_{1.5}H_{1.5}PW_{12}O_{40}$ salts revealed the presence of biphasic mixtures of unreacted heteropolyacid and its potassium salt. The unreacted heteropolyacid could be washed away by treating the precipitate with water. No heteropolyacid could be washed away when the molar composition K:H = 2:1 was reached. It was concluded that for the content of potassium ions changing in the range $0 < x < 2$ the mixture of the $K_2HPW_{12}O_{40}$ and unreacted heteropolyacid, soluble in water, is formed, according to the following reaction pathway:

$$2H_3PW_{12}O_{40} + xK_2CO_3 = xK_2HPW_{12}O_{40} + (2 - x)H_3PW_{12}O_{40} + xH_2CO_3 \quad (1)$$

The question why it is $K_2HPW_{12}O_{40}$ which precipitates in these conditions remained however open.

This paper addresses two fundamental questions which emerge from the results obtained to date:

(i) What is the structure of the acidic salts of potassium dodecatungstophosphate of composition $K_xH_{3-x}PW_{12}O_{40}$ (where x varies in the range $2 \leq x < 3$)? Are these compounds solid solutions of the heteropolyacid in the respective heteropolysalt or heterogeneous systems composed of the particles of neutral heteropolysalt with the layer of heteropolyacid deposited at their surface?

(ii) What is the origin of the texture of these compounds generating the microporosity of high surface area?

Experimental Section

Materials. Potassium dodecatungstophosphates (K_2, $K_{2.5}$, and K_3) were obtained as precipitates by adding the stoichiometric quantities of potassium carbonate (POCh) to an aqueous solution of dodecatungstophosphoric acid (Merck). The resultant salts were dried in the oven at 313 or 363 K.

Nitrogen Physisorption Measurements. BET surface areas of the samples were calculated from nitrogen adsorption−desorption isotherms at 77 K in Autosorb-1 Quantachrome equipment. The samples were degassed, prior to the measurements, under vacuum at 473 K for 2 h.

X-ray Diffraction. X-ray diffraction patterns were collected using the Siemens D5005 diffractometer (Cu Kα radiation, 40 kV, 40 mA) equipped with a diffraction beam graphite monochromator. All high-temperature measurements were performed using additionally an XRK900 (Anton Paar) reaction chamber. The patterns were collected in the range of 2θ, step, and time/step as follows.

(1) Measurements at ambient temperature: 16−100°, 0.02°, and 12 s/step. (2) Measurements of K_2 salt at 473 and 673 K: 8−100°, 0.02°, and 2 s/step. Silicon (pa 325 mesh, Aldrich) was added to samples to determine the amorphous phase content. (3) Measurements at 363, 773, 923, 1093, and 1183 K: 20−27°, 0.04°, and 2 s/step.

Scanning Electron Microscopy. Samples of K_2 salt were placed on stubs with adhesive carbon tabs and covered with thin layer of carbon using an SCD 050 sputter (Bal-Tech). The images of crystals were examined by means of a JSM-5800 scanning electron microscope (JEOL) coupled with a Link ISIS 300 energy-dispersive X-ray spectrometer, Oxford Instruments Ltd. (Si(Li) detector, and ATW-atmospheric thin window, resolution 131 eV for Mn Kα at 10 000 counts. The images were observed at magnification in the range 350−2000 times.

Transmission Electron Microscopy. The samples of K_2 salt were deposited from a suspension in ethanol on a Cu grid with a carbon film. The images were obtained with TEM transmission electron microscopy (Philips CM 20) at magnification of 88 000.

XPS Measurements. The XPS spectra were obtained with the ESCA-3 VG Scientific spectrometer using the Al $K\alpha_{1,\,2}$ X-ray source ($h\nu = 1486.6$ eV, 13 kV, 8−10 mA). W 4f, C 1s, and O 1s bands were recorded with electron emission angle 45° at a pressure below 2×10^{-8} Torr. Handling of spectra consisted of Shirley's background subtraction, $K_{3,4}$ satellite removal, and fitting with Gauss−Lorentz peaks. The binding energies were referenced to the C 1s line assumed to correspond to the binding energy of 284.8 eV.

^{31}P MAS NMR Measurements. The ^{31}P MAS NMR spectra were obtained at room temperature on a Brucker AM 500 NMR spectrometer at 202.4 MHz using a custom-built MAS probehead. Samples were spun at approximately 15 kHz. ^{31}P NMR spectra were acquired with 90° (3.5 μs) pulse and 120 s delays. Each spectrum is an accumulation of 8 scans.

Thermal Analysis. Thermal analysis was carried out in static air, in a Paulik, Paulik, and Erdey DTA-TG thermal analyzer. Samples of about 500 mg were heated with the rate of 10 K/min up to 1073 K.

---

(12) Bruckman, K.; Haber, J.; Lalik, E.; Serwicka, E. M. *Catal. Lett.* **1988**, *35*, 1.

(13) Bruckman, K.; Haber, J.; Serwicka, E. M. *Faraday Discuss. Chem. Soc.* **1989**, *87*, 1.

(14) Serwicka, E. M.; Bruckman, K.; Haber, J.; Paukshis, E. A.; Yurchenko, E. N. *Appl. Catal.* **1991**, *73*, 153.

(15) Black, J. B.; Clayden, N. J.; Gai, P. L.; Scott, J. D.; Serwicka E. M.; Goodenough, J. B. *J. Catal.* **1987**, *106*, 1.

(16) Misono, M. *Chem. Commun.* **2001**, 1141.

(17) Corma, A.; Martinez, A.; Martinez, C. *J. Catal.* **1996**, *164*, 422.

(18) Haber, J.; Pamin, K.; Matachowski, L.; Napruszewska, B.; Połtowicz, J. *J. Catal.* **2002**, *207*, 296.

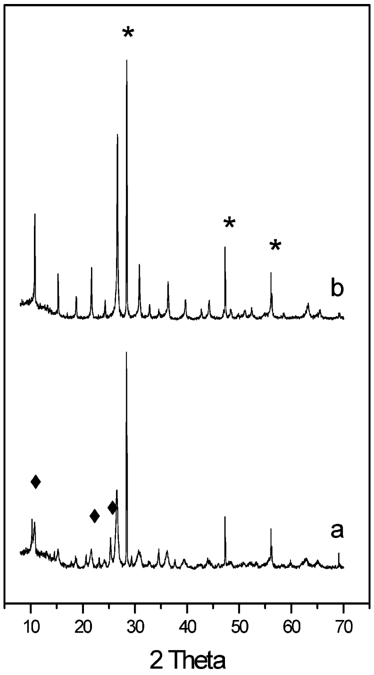

Figure 1. Powder X-ray diffraction patterns with silicon (∗) as an internal standard of the (a) freshly prepared K_2 salt (♦, diffraction patterns originating from HPW) and (b) aged K_2 salt.

Rietveld Refinement. Structural analyses were performed by the full-matrix Rietveld method using TOPAS R (AXS Brucker) software.[19] The fundamental approach for peak profile description was used.[20] The following parameters of analyzed phases (all atoms except hydrogen) and of the internal standard were refined: scale factors; cell parameters; partial coordinates; site occupancy factors (SOF) for potassium cation; isotropic thermal parameters *B*, which were constrained to be not smaller than 0.5.

Results and Discussion

The diffraction patterns of a freshly prepared K_2 salt dried at 313 K and registered after adding silicon as an internal standard indicate that the material is composed of 78.6% amorphous phase and two crystalline phases: 17.2% neutral K_3 salt and 4.2% heteropolyacid (Figure 1). Its surface area amounted to 79.2 m^2/g. It should be mentioned that because of pretreatment of the sample at 473 K for 2 h prior to BET measurement the value of the surface area is probably overestimated.

After the sample was aging for 23 days at room temperature, the content of amorphous phase decreased to 73.2% and only the X-ray pattern of one crystalline phase of $K_3PW_{12}O_{40}$ in the amount of 26.8% was visible, whereas the crystalline phase of HPW disappeared. Apparently, during the time of aging at room temperature the latter spreads over the surface of crystallites of K_3 salt in form of a monolayer. The fact that it does not affect the diffraction pattern of K_3 indicates that a surface layer of HPW has been formed on K_3 matrix. This resulted in the increase of surface area to 100.6 m^2/g. The bulk HPW formed after precipitation hinders the access of gases to the K_3 cores. This effect disappears after spreading, and the value of surface area as measured by the BET method increases. After a longer time of aging, the BET surface area becomes stabilized. It may be noted that potassium salts of HPW described in the literature were characterized by surface areas (e.g. for the $K_{2.5}$ salt) varying from 60 [17] to 150 m^2/g.[21] A hypothesis may be thus advanced that the time of aging at room temperature is one of the important parameters determining the structure and texture of acidic potassium salts of HPW.

Figure 2 presents the scanning (A) and transmission (B) electron micrographs of the K_2 salt, dried at 313 K. The SEM picture shows that the preparation is composed of almost ideally spherical particles of 2.0−2.5 μm in diameter. The TEM analysis revealed that the spherical particles are aggregates of very small primary particles or crystallites, immersed in amorphous material, which generates the microporosity and explains the high surface area.

To corroborate the influence of time of aging, we carried out the XPS measurements for freshly prepared K_2 salt (dried at 313 K) and for the same sample after 2, 7, and 23 days and also after 1 year of aging at room temperature. For comparison binding energies of W 4f electrons for HPW and freshly prepared K_3 salt are also given. The XPS spectra are presented in Figure 3, and binding energies of W 4f, P 2p, and K 2p bands are collected in Table 1. In the case of HPW, freshly prepared K_2 salt, and this salt after 2 days of aging two bands of W 4f electrons are visible at about 34.1 and 35.4−35.8 eV, whereas in the case of the K_3 salt only one band at 36.0 eV appears. This band may be interpreted as due to the presence of W^{6+} ions (35.4−36.0 eV) whereas that at 34.1 eV is due to the presence of reduced tungsten ions. This would indicate that the K_3 salt is resistant to reduction whereas HPW undergoes reduction probably in the course of the experiment in the high vacuum of the ESCA spectrometer. We may, thus, conclude that in the freshly prepared sample as well as the one after 2 days of aging free bulk HPW is present while in samples after 7, 23 days, and 1 year of aging the HPW spread over the surface of the K_3 core forming an epitaxial surface layer resistant to reduction. This conclusion is also supported by the changes of the intensity ratio of K/W bands, which is equal to 0.28 for freshly prepared K_2 salt and decreases to 0.22 after 1 year of aging due to coverage of the surface of K_3 core by heteropolyacid. Thus, the transformation of the bulk HPW, formed during the precipitation of K_2 salt, into a surface layer deposited on the K_3 core takes place between 2 and 7 days of aging at room temperature.

Further information on the real structure of the K_2 salt after 23 days of aging was obtained from ^{31}P NMR measurements. Spectra of HPW and K_2 and K_3 salts measured after this time of aging are presented in Figure 4. ^{31}P NMR spectra of HPW and K_3 show a homogeneous environment of P atoms while in the case of the K_2 salt two different surroundings of the P atom are observed. The characteristic chemical displacements of HPW and K_3 salt occur at −15.6 and −15.1 ppm, respectively (Figure 4c,a).

---

(19) Cheary, R. W.; Coelho, A. A. *J. Appl. Crystallogr.* **1992**, *25*, 109.
(20) Coelho, A. A. *J. Appl. Crystallogr.* **2000**, *33*, 899.
(21) Garaud, P. Y.; Stewart, I. H.; Derouane-Abd Hamid, S. B.; Essayem, N.; Derouane, E. G.; Vedrine, J. C. *Catal. Today* **2000**, *63*, 223.

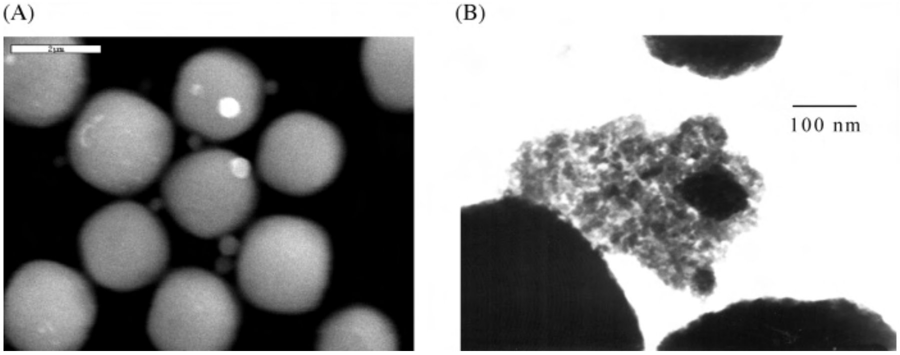

Figure 2. (A) Scanning and (B) transmission electron micrographs of aged K_2 salt.

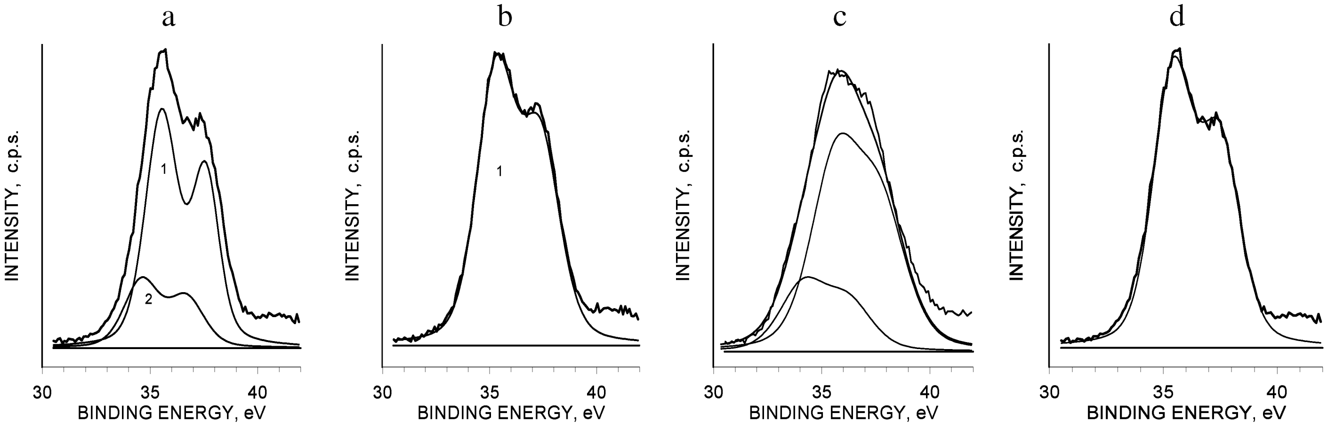

Figure 3. XPS spectra of (a) freshly prepared K_2 salt, (b) K_2 salt after 23 days of aging at room temperature, (c) tungstophosphoric acid, and (d) K_3 salt.

Table 1. Binding Energies of W 4f, P 2p, and K 2p Electrons for Freshly Prepared K_2 Salt Changing with Time of Aging at Room Temperature

	binding energy (eV)				
sample	W 4f electrons		P 2p electrons	K 2p electrons	K/W intensity ratio
freshly prepared K_2 salt	34.2	35.8	134.6	293.1	0.28
K_2 salt after 2 days of aging	34.1	35.4	134.0	293.1	0.23
K_2 salt after 23 days of aging	-	35.6	134.2	293.1	0.22
K_2 salt after 1 year of aging	-	35.4	133.5	293.5	0.22
K_3 salt		36.0	134.5	293.5	0.35
$H_3PW_{12}O_{40}$	34.1	35.6	134.0		

In the spectrum of the K_2 salt (Figure 4b) two separate lines are visible. The line at −15.0 ppm corresponds to the neutral potassium salt in which each Keggin unit of the K_3 core is surrounded by six potassium atoms located in the first coordination sphere and by eight Keggin anions in the second. This small displacement for K_2 sample indicates that the core in this sample still has a K_3 structure. The second line at −15.2 ppm is assigned to the surface layer of tungstophosphoric acid. In this case Keggin units are surrounded by no more than 1 potassium cation and 5−6 protons which are in the first coordination sphere and 4 Keggin anions in the second. These differences of environments in comparison to pure HPW are manifested in the change of chemical displacement from −15.6 to −15.2 ppm. The ratio of the relative intensities of the HPW to K_3 signals attains about 1:2 and corresponds to the ratio of the amounts of protons and potassium ions in the K_2 sample.

Thus, the formation of surface layer after 23 days of aging was fully confirmed by XRD, XPS, and ^{31}P NMR methods. It was also corroborated by the increase of surface area measured for the K_2 salt after 1 month of aging.

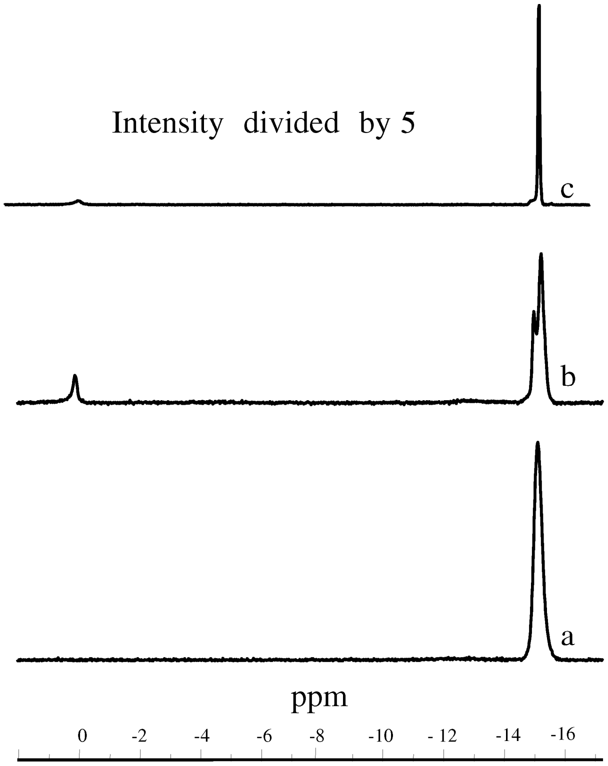

Figure 4. ^{31}P MAS NMR spectra of the (a) K_3 salt, (b) aged K_2 salt, and (c) HPW.

Differences in the structures of the K_2, $K_{2.5}$, and K_3 compounds are reflected in their thermal properties as

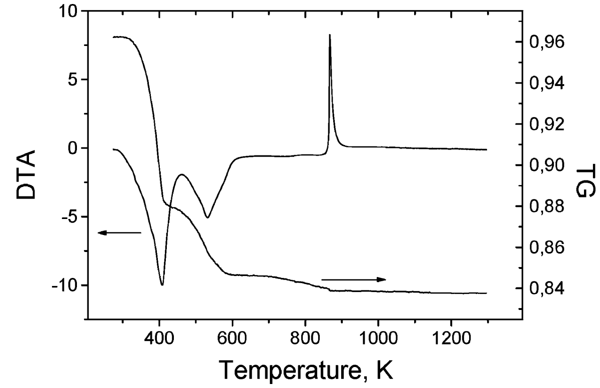

Figure 5. DTA-TG profiles of HPW.

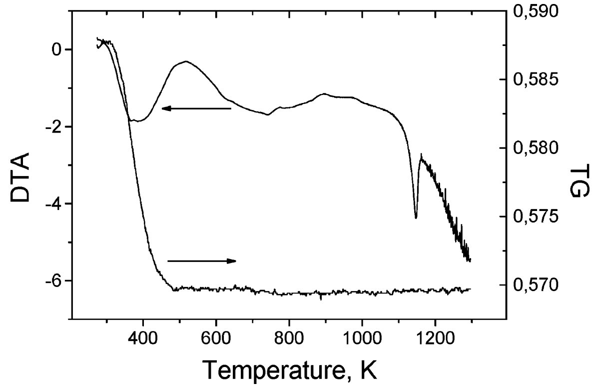

Figure 6. DTA-TG profiles of the K_2 salt.

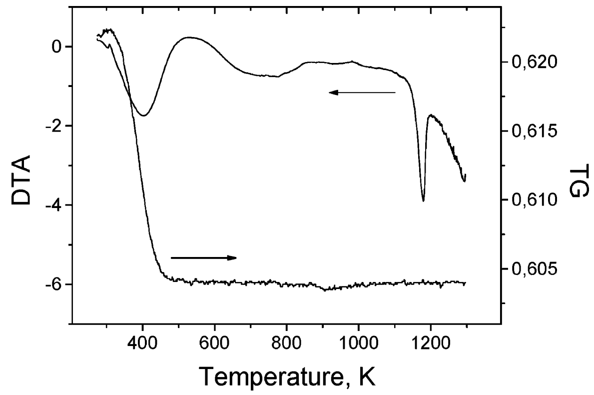

Figure 7. DTA-TG profiles of the $K_{2.5}$ salt.

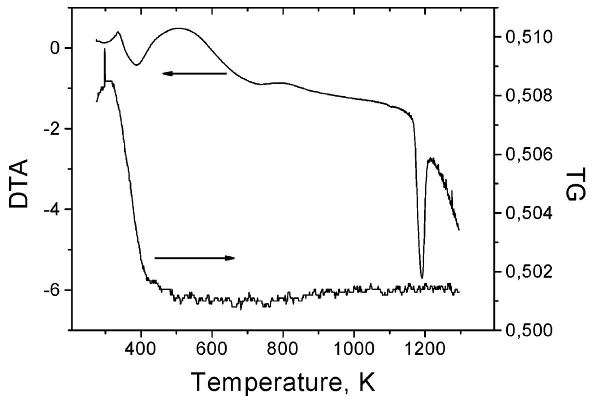

Figure 8. DTA-TG profiles of the K_3 salt.

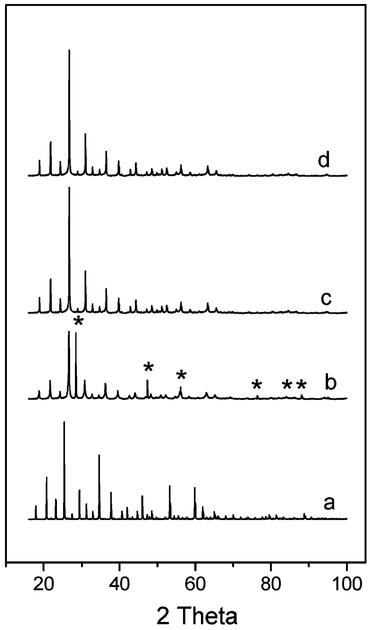

Figure 9. Powder X-ray diffraction patterns of (a) HPW, (b) K_2 salt with silicon ($*$) as an internal standard, (c) $K_{2.5}$ salt, and (d) K_3 salt.

revealed by DTA-TG analyses. For comparison pure tungstophosphoric acid was also examined. Figures 5−8 show the DTA and TG profiles of the HPW, K_2, $K_{2.5}$, and K_3 samples, respectively.

The curve of HPW exhibits two strong endothermic effects at 396 and 537 K. The first one is connected with the loss of crystallization water, and the other originates from the loss of water hydrating protons. The weight loss visible in the range from 705 to 855 K corresponds to the removal of 1.5 water molecules/1 Keggin anion, and it is associated with the loss of constitutional water. The very strong exothermic effect observed at 868 K results from the decomposition of the Keggin anion and crystallization of the new phase.

The DTA traces of the K_2, $K_{2.5}$, and K_3 samples demonstrate only a small thermal effect at 390 K, responsible for the loss of the crystallization water, but no loss of water hydrating protons can be discerned. In the K_2 and $K_{2.5}$ salts a broad and small exothermic effect originating from decomposition of HPW appears at about 890 K. On comparison with the decomposition temperature of HPW (about 868 K) we can conclude that HPW surface layer is stabilized on the K_3 support, in both the K_2 and $K_{2.5}$ salts. Pure K_3 salt shows in the DTA experiment no exothermic effect originating from the decomposition of HPW. However, the phase transformations of the acidic and neutral potassium salts can be observed as an endothermic peak which is connected with process of decomposition of the salt. The K_3 salt starts to decompose and melt at 1170 K. The decomposition temperature of the K_3 core slightly decreases in the $K_{2.5}$ and K_2 samples to 1120 and 1090 K, respectively. Thus, DTA-TG experiments confirm the conclusion that in the K_2 and $K_{2.5}$ salts tungstophosphoric acid exists on the surface of the K_3 core in the form of a dehydrated phase which is stabilized by the support.

The diffraction patterns of K_2, $K_{2.5}$, and K_3 freshly prepared samples dried at 363 K (Figure 9) revealed the existence of only one crystalline phase scattering X-rays, and in all patterns the visible phase is the K_3 salt. This indicates that in all samples crystallites of the K_3 salt are present.

However, we have shown earlier on the basis of XRD, XPS, and ^{31}P NMR measurements that in the freshly prepared K_2 samples (dried at 313 K) two crystalline phases exist: K_3 and HPW. After aging of the sample for a longer time, the crystalline HPW phase disappeared due to spreading over the surface of K_3 crystallites. The fact that in the case of samples dried at 363 K the XRD spectrum of e.g. the K_2 salt shows the presence of only one K_3 phase indicates that a higher temperature of drying accelerates the process of spreading and forming a surface layer of HPW.

Although partial coordinates of atoms in the epitaxial layer can duplicate the structure of the core only approximately, the values of unit cell parameters have to be equal in both the support and the epitaxial layer. According to Bruckman et al.[13] the surface layer deposited on the neutral salt can be visualized as a hexahydrate of the respective acid. In the case of our samples it seems not to be a realistic assumption. Comparison of the unit cell parameters of the $K_3PW_{12}O_{40}$ salt ($a = 11.5893$ Å) and $H_3PW_{12}O_{40}\cdot 6H_2O$ ($a = 12.17062$ Å) at room temperature shows that the formation of an epitaxial layer of hexahydrated tungstophosphoric acid on a K_3 core would induce strong strains in that surface layer. However, the lattice parameter of $H_3PW_{12}O_{40}\cdot 3H_2O$ ($a = 11.76$ Å, at 673 K)[22] is more similar to the one observed in the K_3 salt. This suggests that dehydrated HPW should be able to form a surface layer, close to an epitaxial, with less strains than the hydrated heteropolyacid. For this reason one can expect that the surface layer deposited on the K_3 support is formed by at least partially dehydrated HPW. Such a dehydrated heteropolyacid is not stable as a separate phase and can exist only because it is stabilized by deposition on the surface of the support.[13] This phenomenon can be a reason for the formation of a surface acid layer derived from partially hydrated HPW, isostructural with the cubic lattice of the K_3 support. Namely, stabilization is most effective if lattice parameters of the surface layer are adjusted to lattice parameters of the support.

An interesting question may be asked why in the case of K_2 and $K_{2.5}$ samples the HPW surface layers on K_3 core are formed instead of solid solutions of $K_2HPW_{12}O_{40}$ and $K_{2.5}H_{0.5}PW_{12}O_{40}$, respectively**.** The formation of a solid solution should be preferred because of the large contribution of mixing entropy of this system as compared to the case of surface layer−core system. The difference between mixing entropy of solid solution and surface layer−core system can be compensated by the large entropy of surface amorphous phase of HPW-covering K_3 core which causes an increase of the total entropy of the surface layer−core system. It is also well-known that the higher is the temperature, the more significant becomes the entropy effect. Moreover, the formation of a solid solution would cause strains in places in which a hydrated proton would be situated. The effect for potassium salts seems to be more remarkable than for $Cs_{2.5}$ salt which, as showed by Misono,[16] is transformed from an epitaxial layer−core system to a solid solution at temperature below 473 K. Moreover, the lattice parameter of the Cs_3 salt is within the range of the lattice parameter of HPW with different amounts of water, so formation of a solid solution $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ does not cause such a large strains as in acidic potassium salts.

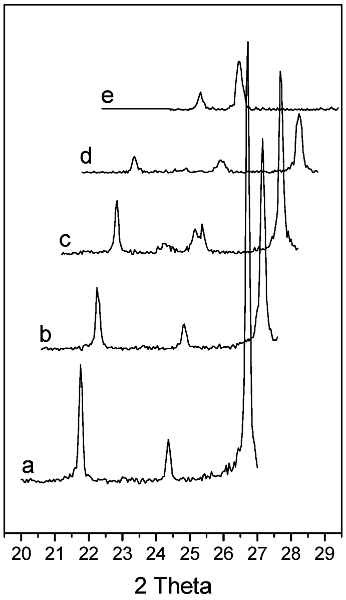

Figure 10. Powder X-ray diffraction patterns of the K_2 salt measured at (a) 363 K, (b) 773 K, (c) 923 K, (d) 1093 K, and (e) 1183 K.

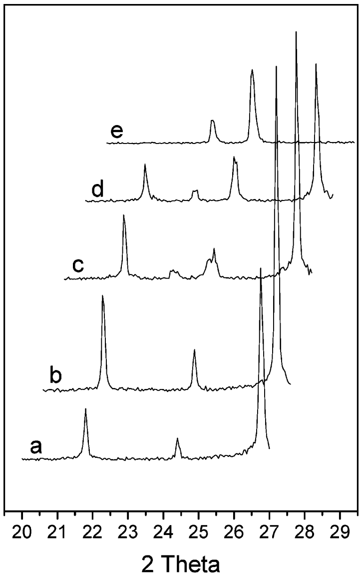

Figure 11. Powder X-ray diffraction patterns of the $K_{2.5}$ salt measured at (a) 363 K, (b) 773 K, (c) 923 K, (d) 1093 K, and (e) 1183 K.

To establish the state of crystalline phase at higher temperatures, in situ XRD patterns for all potassium salts were collected in the temperature range changing from 773 to 1183 K (Figures 10−12). For comparison the XRD pattern at 363 K is also shown.

Measurements of the K_2 and $K_{2.5}$ salts (Figures 10and 11) reveal the presence of only one phase—that of the neutral salt K_3—up to at least 773 K. When the temperature reaches 923 K, the formation of small quantities of a new phase,

---

[22] Marosi, L.; Platero, E. E.; Cifre, J.; Arean, C. O. *J. Mater. Chem.* **2000**, *10*, 1949.

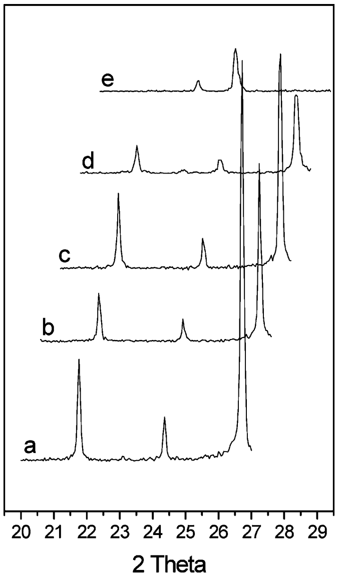

Figure 12. Powder X-ray diffraction patterns of the K_3 salt measured at (a) 363 K, (b) 773 K, (c) 923 K, (d) 1093 K, and (e) 1183 K.

observed as an additional peak at 23.0°, starts without the change of the K_3 phase. Formation of this new phase, apparently the product of the decomposition of the surface layer of heteropolyacid, is visible at slightly higher temperature than that observed in DTA spectra probably due to the effect of different systems of heating and temperature measurement. Moreover, formation of phosphates is not detected but a growth of a PW_8O_{26}-type bronze as a new phase is very likely. This compound could have still the structure of WO_3 with the P_2O_5 molecules located among WO_6 octahedra.

In the case of the K_3 salt (Figure 12) its decomposition starts at 1093 K and the process is completed at about 1183 K, which is visible as a disappearing peak at 26.5°.[23] This indicates that the formation of a new phase starts in the K_2 and $K_{2.5}$ samples at the temperature about 170 K lower than in the K_3 salt, but the process is completed at 1183 K for all three samples. This observation indicates that between 773 and 923 K the process of decomposition of HPW deposited on the surface of K_3 core takes place. If it were a solid solution, the decomposition would require diffusion of protons to the surface, the decomposition of the heteropolyacid formed at the surface, and diffusion of potassium ions inward into the bulk of the salt. Such a complicated transformation seems to be highly improbable.

XRD measurements with silicon as an internal standard revealed that the content of amorphous phase in the K_2 salt decreases with the temperature of annealing:

temp of annealing (K)	313 (fresh)	313 (aged)	363	473	673
content of amorphous phase (%)	78.6	73.2	74.3	66	63

It may be seen that even after annealing at 673 K a large proportion of the sample remains amorphous, both the K_3 salt and HPW. It should be borne in mind that in the case of the crystalline K_3 core covered by a surface layer of HPW it is obvious that interactions between protons and Keggin units are not the same as between Keggin anions and potassium countercations. This difference results in formation of disorder in the surface layer which, in fact, becomes not epitaxial. It means that partial coordinates of atoms of this layer are not exactly the same as the partial coordinates of atoms of the core. Interactions in the core and in the surface layer are to some extent counteracting. Due to these small deviations, the amorphous surface layer is not detected by the XRD technique.

The amount of amorphous phase does not influence the Rietveld refinement. Thus, the full-matrix Rietveld refinements with the XRD data for the heteropolyacid and its potassium salts were performed to determine the content of potassium ions in salts structures. The structure of the tungstophosphoric acid hexahydrate was chosen as the initial model for the potassium salts structures.[24] Therefore, for the $K_xH_{3-x}PW_{12}O_{40}$ (where $x = 2, 2.5, 3$), protons originally placed in the 6d positions of the $H_3PW_{12}O_{40}\cdot 6H_2O$ structure were exchanged by potassium cations. Because water molecules were omitted, the initial cell parameters for potassium salts were assumed to be 11.59 Å. For each salt, the site occupancy factor (SOF) was also calculated, but for the K_2 and $K_{2.5}$ samples the calculations of SOF were performed using the same value of *B* factor for potassium atom as was previously calculated for the K_3 sample because of the strong correlation of *B* and SOF factors. During the refinements all isotropic factors of *B* thermal oscillations were restrained to be not less than 0.5. The structural parameters, atomic fractional coordinates, and site occupancy factors for HPW and its potassium salts are collected in Tables 2 and 3.

Comparison of the lattice parameters, atomic fractional coordinates, and site occupancy factors of the K_2, $K_{2.5}$, and K_3 salts indicates that the structures practically do not change when the content of potassium decreases. The Rietveld refinement allows us to make the following observations: First, we did not observe any HPW phase in the acidic potassium salts. Apparently, only one crystalline phase remains after drying the preparations at 363 K. Second, the amorphous phase content in the K_2 sample diminishes from 78.6% (at 313 K) to 74.3% (at 363 K). Such a large value means that all crystallographic information which we obtained originates from only 25.7% of the sample. It can be assumed that in the $K_{2.5}$ sample the amorphous phase content is very similar. Third, the lattice parameter *a* of each potassium salt (Table 2) is close to 11.6 Å and is significantly different from the lattice parameter of hexahydrate HPW ($a = 12.17$ Å) but relatively close to that of the trihydrate HPW structure ($a = 11.76$ Å). This confirms the observation that in potassium salts the cations are not hydrated by water molecules. Fourth, calculated microstrains of HPW and K_3 salt are small, but for the K_2 and $K_{2.5}$ samples they increase by at least 1 order of magnitude. The microstrains represent variable displacements of atoms from their sites in the

---

(23) Mioè, U. B.; Dimitrijevic, R. Z.; Davidoviè, M.; Nedic, Z. P.; Mitrovic, M. M.; Colomban, Ph. *J. Mater. Sci.* **1994**, *29*, 3705.

(24) Brown, G. M.; Noe-Spirlet, M. R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1977**, *B33*, 1038.

Table 2. Structural Parameters for Rietveld Refinement of HPW and Its Potassium Salts

	phase name			
param	$H_3PW_{12}O_{40}\cdot6H_2O$	$K_2HPW_{12}O_{40}$	$K_{2.5}H_{0.5}PW_{12}O_{40}$	$K_3PW_{12}O_{40}$
R_{wp}	20.10	15.75	17.66	19.43
GOF	1.85	1.71	2.01	2.19
R_{Bragg}	7.565	3.524	5.31	5.082
space group (No.)	*Pn*3*m* (224)	*Pn*3*m* (224)	*Pn*3*m* (224)	*Pn*3*m* (224)
cell mass (au)	5946.311	5967(7)	5965(7)	5993(7)
cell vol (Å^3)	1802.76(3)	1573.4(3)	1552(1)	1556.2(2)
microstrains	0.02(1)	0.88(3)	0.20(1)	0.04(1)
cryst density (g/ cm^3)	5.4772(1)	6.31(1)	6.38(1)	6.39(1)
lattice param *a* (Å)	12.1706(1)	11.631(1)	11.577(2)	11.5883(4)

Table 3. Atomic Fractional Coordinates, Isotropic Thermal Parameters (Å^2), and Site Occupancy Factors

atom	Wycoff posn	param	$H_3PW_{12}O_{40}\cdot6H_2O$	$K_2HPW_{12}O_{40}$	$K_{2.5}H_{0.5}PW_{12}O_{40}$	$K_3PW_{12}O_{40}$
W	24k	x	0.7581(2)	0.7534(6)	0.7557(4)	0.7572(3)
		$y = z$	0.9562(1)	0.9670(2)	0.9676(2)	0.9675(2)
		B_{iso}	1.10(6)	0.90(8)	2.44(8)	1.87(6)
P	2a	$x = y = z$	0.75	0.75	0.75	0.75
		B_{iso}	2.6(10)	0.5(12)	0.5(10)	0.5(9)
O1	8e	$x = y = z$	0.819(2)	0.828(2)	0.824(2)	0.825(2)
		B_{iso}	3.2(15)	0.5(17)	0.9(16)	2.4(17)
O2	24k	$x = y$	0.660(1)	0.622(3)	0.627(3)	0.626(2)
		z	0.499(2)	0.482(4)	0.490(3)	0.488(3)
		B_{iso}	0.5(7)	0.5(13)	0.5(11)	0.9(9)
O3	24k	$x = y$	0.869(2)	0.848(2)	0.852(2)	0.853(2)
		z	0.039(2)	0.034(4)	0.033(3)	0.036(3)
		B_{iso}	0.5(7)	0.5(14)	0.5(11)	0.5(9)
O4	24k	$x = y$	0.724(3)	0.764(7)	0.729(4)	0.736(4)
		$y = z$	0.062(2)	0.074(2)	0.065(2)	0.070(2)
		B_{iso}	3.1(8)	0.5(10)	2.2(10)	0.9(8)
other		type	O(water)	K	K	K
		x	0.75	0.75	0.75	0.75
		y	0.121(4)	0.25	0.25	0.25
		z	0.25	0.25	0.25	0.25
		B_{iso}	12(3)	6.886	6.886	6.886
		SOF	0.5	0.91(3)	0.90(3)	1.02(3)

Table 4. Macroscopic Parameters of HPW and Its Potassium Salts Grains

	sample			
param	$H_3PW_{12}O_{40}\cdot6H_2O$	$K_2HPW_{12}O_{40}$	$K_{2.5}H_{0.5}PW_{12}O_{40}$	$K_3PW_{12}O_{40}$
s_{BET}(freshly prepared) (m^2/g)	5	79.2	98.7	114.3
s_{BET}(aged) (m^2/g)		100.6	105.8	
s_{calcd}(freshly prepared) (m^2/g)		77.2	95.9	
coverage of (100) plane		1.21	0.47	
coverage of (110) plane		0.85	0.34	
crystallite size (Å)	7000	1310	2380	3420

idealized crystal structure caused by any lattice imperfection (dislocations, vacancies, interstitials, substitutionals, and similar defects), but we suppose that in our case microstrains may be caused by substitution of some potassium cations by protons in the highly disordered subsurface region.

The site occupancy factors for potassium cations in K_2 and $K_{2.5}$ samples are almost the same and are equal to 0.91 and 0.90, respectively. One should, however, bear in mind that a strong correlation exists for potassium SOF and *B* factors of all refined atoms and that a large amount of amorphous phase, of which at least a part forms a surface layer with the structure similar to that of the core, exists in our samples, which influences the quality of refinement. Thus, the values of SOF should be looked upon with certain care. The conclusions should be confronted with those drawn on the basis of lattice parameters. As we can see, the lattice parameters of the K_3 and $K_{2.5}$ salts are almost the same. This suggests that in both structures the phase we observe is the K_3 salt, which in the $K_{2.5}$ sample forms a K_3 core covered by an amorphous phase of HPW. However, in the K_2 salt we found that the lattice parameter is slightly longer than that in the K_3 and $K_{2.5}$ samples, so in this case we cannot exclude that some amount of protons can be incorporated into the structure of the K_3 core, at least in the highly defected subsurface region.

The surface area and crystallite size of heteropoly compounds are collected in Table 4. Surface area was measured by the BET method, and crystallite size was calculated automatically by means of TOPAS software using the Sherrer equation. For calculations the broadening of the Lorenz curve was used, showing the linear dependence of the crystallite size from cation contents.

The BET surface areas of potassium salts increase almost linearly as the metal contents increases from 2 to 3. If the dissipated phase in the K_2 sample is the K_3 core, its size as well as the size of the crystallites will diminish proportionally to the decrease of potassium content in the samples. This can be explained by taking into account that concentration of potassium cations in the solution is responsible for crystallite sizes of the cores. The crystalline cores of the K_2, $K_{2.5}$, and K_3 samples have the diameters in the range 130−340 nm and are embedded in the amorphous aggregates of the diameter 2−2.5 μm.

At this point a question may be raised as to how thick is the surface layer of heteropolyacid covering the K_3 cores. Taking into account the size of BET surface area of the K_3 salt which was found to be equal to 114.3 m^2/g and assuming that two crystal planes (100) and (110) are exposed at the surface of the K_3 salt to the same extent, the amount of Keggin anions needed to form a monolayer can be calculated using the following data:

For the plane (100), a (unit cell parameter of the K_3 salt calculated from XRD measurement) = 1.159 nm.

$S = a^2$ (surface area of plane (100) of the unit cell) = 1.341×10^{-18} m^2, on which 1 Keggin anion is exposed.

The BET surface area of the K_3 salt = 114.3 m^2/g. Thus, 1 g of K_3 salt exposes at the surface 114.3 m^2/g: 1.341×10^{-18} $m^2 = 8.52 \times 10^{19}$ Keggin anions, or 1 mol of K_3 salt exposes at the surface $8.51 \times 10^{19} \times 2994.35 = 2.55 \times 10^{23}$ Keggin anions. Note that 1 mol of HPW contains 6.02×10^{23} Keggin anions. Assuming that the K_2 salt is a biphasic mixture of the K_3 salt and unreacted heteropolyacid HPW, the mixture has the molar ratio 2**:**1. Thus, in $K_2HPW_{12}O_{40}$, 6.02×10^{23} Keggin anions of the heteropolyacid are deposited at the surface of K_3 core exposing 5.10×10^{23} Keggin anions which permits the estimation of the surface coverage to be $\Theta = 1.18$.

In the case when crystal plane (110) is exposed, two Keggin anions are present in one unit the cell. The calculation gives the coverage $\Theta = 0.83$.

Table 4 summarizes the coverages of the surface of neutral potassium salt particles by heteropolyacid. It is seen that in the K_2 sample the K_3 core can be covered by approximately 1 monolayer of HPW, assuming equal exposition of (100) and (110) planes. The coverage of the K_3 core by heteropolyacid in the $K_{2.5}$ sample is lower than 1 monolayer.

On the basis of the BET measurements of the neutral K_3 salt (Table 4), the calculations of the surface area s_{calc} for the fresh acidic potassium salts were performed as follows: One particle of neutral salt with a surface area s_{ss} is covered by HPW molecules. Assuming that this surface is covered by the bulk of HPW whose surface area is of the order of about 1−5 m^2/g, so the contribution of HPW molecules to the total surface area of the freshly prepared acidic potassium salts can be neglected. However, the mass of the covered particle increases by the mass of HPW molecules. The surface area of the acidic salts can be calculated from the following equation:

$$s_{\mathrm{calc}} = s_{\mathrm{ns}} \frac{n_{\mathrm{c}} M_{\mathrm{ns}}}{n_{\mathrm{c}} M_{\mathrm{ns}} + (1 - n_{\mathrm{c}}) M_{\mathrm{HPW}}}$$

where s_{ns} is surface area of neutral potassium salt, n_{c} is the stoichiometric factor of potassium cation, M_{ns} is the molar mass of neutral potassium salt, and M_{HPW} is the molar mass of dehydrated tungstophosphoric acid.

The results (Table 4) indicate a very close agreement between surface areas of the K_2 and $K_{2.5}$ salts measured by the BET method and calculated using the above equation. Both the values of s_{calc} are within the experimental error equal to the values measured by the BET method. The above calculations also confirm our earlier observations that freshly prepared K_2 and $K_{2.5}$ samples exist as a K_3 core covered by heteropolyacid bulk which spreads over the surface of K_3 through the next several days.

Conclusions

Our recent findings lead us to the conclusion that in the course of precipitation and drying (at 313 K) of $K_2HPW_{12}O_{40}$ salt the heteropolyacid is deposited in the bulk form on the $K_3PW_{12}O_{40}$ core. The exposure of this salt to air at room temperature results in the formation of a surface monolayer of heteropolyacid on its neutral potassium salt. The process is completed after 23 days of aging. Heat treatment of $K_xH_{3-x}PW_{12}O_{40}$ salts, where $2 \leq x < 3$, from 313 K to higher temperatures induces the transformation of heteropolyacid covering the K_3 core into a well-dispersed, amorphous surface layer. On further heating of the acidic potassium salts the surface layer decomposes between 855 and 915 K with the formation of a PW_8O_{26}-type bronze as a new phase, the $K_3PW_{12}O_{40}$ salt remaining unchanged. The latter starts to decompose at 1093 K, and in the case of all samples, the process is completed at about 1183 K.

Rietveld structure refinement, XPS, and ^{31}P NMR measurements of acidic potassium salts indicate that the core of these salts is always formed by the $K_3PW_{12}O_{40}$ salt. The core is covered by heteropolyacid. Comparison of lattice parameters of the K_3 salt and HPW leads to the conclusion that the layer is composed of partially or completely dehydrated heteropolyacid molecules. The coverage of the core by HPW in the K_2 sample was estimated to be equal to one monolayer.

Acknowledgment. The authors are grateful to M. Mikołajczyk and Z. Czuła for XPS and BET measurements and K. Pamin for sample preparation.

IC050350S