



*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

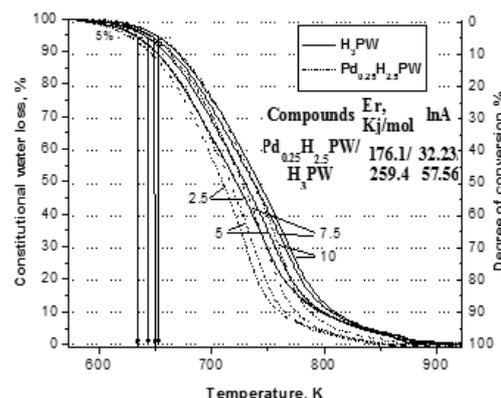
THERMAL DECOMPOSITION OF Pd DOPED 12-TUNGSTOPHOSPHORIC ACID AND SOME OF ITS CESIUM SALTS

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The $H_3PW_{12}O_{40} \cdot xH_2O$ and its acid salts with Cs are known acidic catalysts. The thermal decomposition of Pd doped $H_3PW_{12}O_{40}$ and its acid salts with Cs occurs by the constitutional water release over 573 K. The thermal decomposition process could be explained based on the microstructure model for cesium acidic salts as agglomerates with a core consisting of $Cs_3PW_{12}O_{40}$ crystallites covered of acid layers, but in this case the layers of acid contain PdHPW also. No important differences were observed between composition, structure and thermal behaviour of the two series of Pd doped compounds obtained by changing the order of reactants adding. The apparent activation energy of constitutional water loss was determined using the Standard Test Method for Decomposition Kinetics by Thermogravimetry-E 1641-04. The Pd doping causes a significant decrease of apparent activation energy, especially for acid salts with lower Cs content because it supports the release of constitutional water.



INTRODUCTION

The tungstophosphoric acid, $H_3PW_{12}O_{40} \cdot xH_2O$ (H_3PW) and its Cs acidic salts are ones of the most known heteropoly compounds-HPCs with application in catalysis.¹⁻¹⁰ Their catalytic activity is due to the high Bronsted acidity these compounds being included among super acids.^{1,3} Therefore, their thermal stability is a very important property because the Bronsted acidity could be lost or diminished drastically at high reaction temperatures and as consequence the catalytic activity could decrease also.^{2,11,12} The thermal decomposition of H_3PW and its acidic

salts which occurred as a result of the constitutional water release (the water formed of the protons and the oxygen from the $[PW_{12}O_{40}]^{3-}$ named Keggin Unit) leads to their deactivation.² The other type of deactivation as result of strong adsorbed species on catalysts during operation was trying to be avoided by Pt or Pd doped catalysts as was mentioned in the literature.^{2,13,14}

Many HPCs have been studied in detail in purpose to design catalysts with controlled catalytic activity and some models of their microstructure were proposed.^{3,11,14-17} The microstructure of HPCs with Mo or W is a controversial one, but the theory advanced by Okuhara et al.¹⁴ who describe the $Cs_xH_{3-x}PW_{12}O_{40}$

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($Cs_xH_{3-x}PW$) as crystallites with a core of Cs_3PW embedded of H_3PW layers gains supporters.^{8,16}

The study of the thermal decomposition of Pd doped H_3PW and its cesium acid salts, especially the study of kinetics for constitutional water loss, can offer valuable information on composition, structure and their thermal stability.¹⁷ In order to compare the thermal stability for different compounds it is necessary to have reliable values of activation energy. The method used for kinetic parameters calculation has to be a suitable one, also the work conditions and conversion function.¹⁸ The Standard Test Method for Decomposition Kinetics by Thermogravimetry-ASTM E 1641-04, based on Flinn-Wall isoconversional method, satisfies the demand of high confidence for kinetic parameters and these can be used to calculate thermal endurance and to estimate lifetime of the compounds at a certain temperature.¹⁹

For the mentioned reasons, in this work was studied the thermal decomposition of tungstophosphoric acid and some of its cesium acidic salts comparatively with the same Pd doped HPCs.

EXPERIMENTAL

Cesium salts of tungstophosphoric acid $H_3[PW_{12}O_{40}] \cdot xH_2O$ (H_3PW) were prepared by precipitation from an 0.1 M aqueous solution of the parent acid (Merck, p.a., $13H_2O$) adding drop by drop the required stoichiometric quantity of Cesium nitrate as aqueous solution under stirring. Finally, the solid samples corresponding to the general formula $Cs_xH_{3-x}PW \cdot y H_2O$, where $x = 1; 2; 2.25$ and 2.5 , were obtained.

The $Cs_xH_{3-x}PW \cdot y H_2O$ salts doped with 0.25 at Pd/KU were prepared in two manners. In the first procedure (named S1), a stoichiometric amount of $Pd(NO_3)_2$ as aqueous solution 0.1 M was added into the $H_3PW_{12}O_{40} \cdot 13H_2O$ aqueous solution of 0.1 M and after, the required stoichiometric quantity of Cesium nitrate (aqueous solution) was poured drop by drop under stirring. In the second procedure (named S2), the stoichiometric amount of $Pd(NO_3)_2$ solution was poured in the suspension obtained after the required stoichiometric quantity of Cesium nitrate as aqueous solution was added to the 0.1 M solution of tungstophosphoric acid. The pH was kept under 1.5 during all syntheses. The suspensions of precipitate were heated at 333-343 K under stirring until a paste was obtained. Finally, the samples were heated at 523 K in air for nitrate anion total decomposition.

The $H_3PW_{12}O_{40} \cdot 6H_2O$ doped with 0.25 at Pd/KU was obtained by heating at 333-343 K under stirring the solution of $Pd(NO_3)_2$ and $H_3PW \cdot 13H_2O$ in the proper ratio until paste was obtained. After, the samples were heated at 523 K in air for nitrate anion total decomposition.

The thermal analyses were carried out on a thermoanalyzer system Mettler TGA/SDTA 851/LF/1100. The measurements were conducted in dynamic atmosphere of air (50ml/min), using the alumina plates crucibles of 150 μ l and the mass samples were about 30 mg. The heating rates were of

2.5, 5, 7.5 and 10 K/ min in the range of temperature 298-923 K with an isothermal step at 573 K for 1 hour.

The FTIR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm^{-1} range, 256 scans, and resolution 2 cm^{-1}) using KBr pellets for the all prepared heteropoly compounds at room temperature. Also, the FTIR spectra of the heteropoly compounds which were heated to 523 K and 873 K, 2 hour, under air atmosphere, were recorded.

Powder X-ray diffraction data were obtained with X'Pert PRO MPD PANalytical diffractometer with the following measurement parameters: Theta/Theta PW3050/60 Goniometer, PixCEL detector, zero background sample holder (Si), Ni-filtered CuK α radiation, 45 kV/30 mA, continuous scanning, step size 0.0130 [2 θ] in the 2θ range 5-60° for the heated samples at 523 K and 873 K, 1 hour, under air atmosphere.

RESULTS AND DISCUSSION

The thermal decomposition of the Pd doped $H_3PW \cdot xH_2O$ and its acid Cs salts takes place between 298 K and about 873 K, similarly with $H_3PW \cdot xH_2O$ and its acid Cs salts as was earlier reported.¹⁷ Thus, generally, three steps of mass loss accompanied by endothermic effects were observed (see Fig. 1a,b). The first one from 298 to about 383 K corresponds to the loss of the physical adsorbed water (bigger for the salts with higher content of Cs and with high specific surface area) and the water molecules weaker bonded. The second step from about 383 K to 573 K corresponds to the loss of water molecule from $H_5O_2^+$ and the third step (over 573 K) is the constitutional water loss (the water formed of the protons and the oxygen of the $[PW_{12}O_{40}]^{3-}$). The second step can be observed just as a shoulder on the DTG curve for the acid salts containing $0.25Pd^{2+}$ and $2.5Cs^+/KU$ and the third step which corresponds to constitutional water release consists of a slight loss observed over 573 K, what signifies a small amount of H^+ in this HPC (about $0.25H^+/KU$). On the other hand, the first step corresponding to the physical adsorbed water, probable water from pores, is more evidenced in this last case accordingly with the literature data that mentions the highest porosity and specific surface area for this acidic salts (Fig. 1a,b).^{14,16} The KUs which have lost their constitutional water are destroyed with formation of corresponding oxides. The WO_3 , in the highest amount between oxides, crystallized between 850 and 870 K with exothermic effect on DTA curves, which decreases from $Pd_{0.25}H_{2.5}PW \cdot 6H_2O$ to $Pd_{0.25}Cs_2H_{0.5}PW \cdot 5H_2O$ and no exothermic peak can be observed on the DTA curve for $Pd_{0.25}Cs_{2.5}H_{0.25}PW \cdot 6H_2O$ in the before mentioned range of temperature.

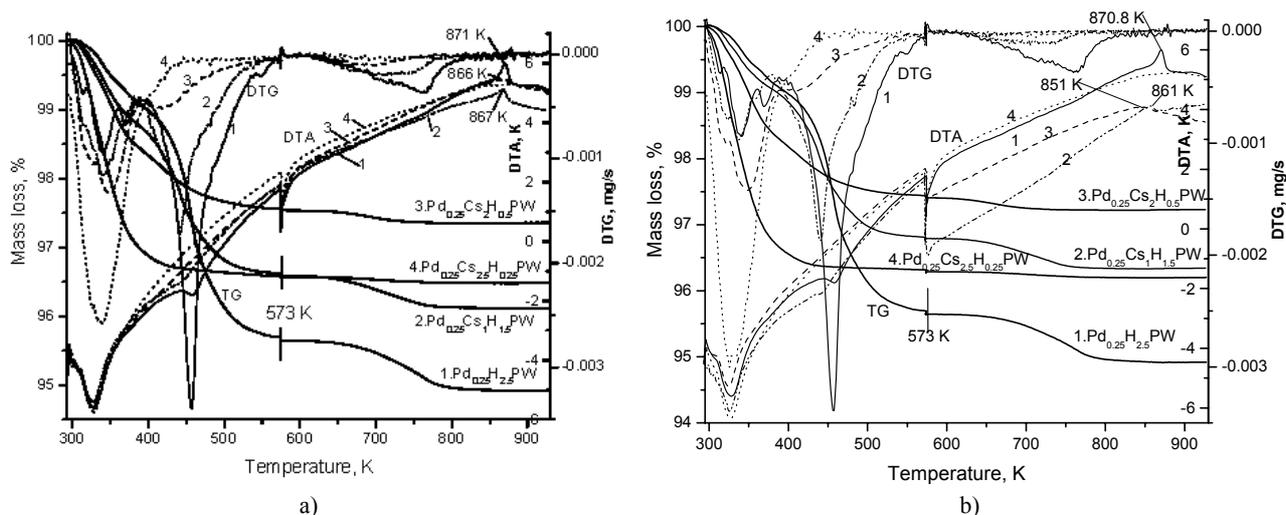


Fig. 1 – The thermal decomposition curves of the Pd_{0.25}Cs_xH_{2.5-x}PW 5-7H₂O, S1(a), S2(b) at the heating rates of 10 K/min.

Table 1

The content of water molecules and protons per Keggin Unit-KU of Pd doped HPCs determined by the thermal analysis

Compounds-theoretical formula	Physical adsorbed water	Crystallization water	H ⁺ /KU
Pd _{0.25} H _{2.5} PW	1.4-1.5	5.7-5.8	2.44-2.48
Pd _{0.25} CsH _{1.5} PW-S1/S2	1.0-1.5/1.0-1.5	3-3.1/3-3.2	1.48-1.54/1.47-1.57
Pd _{0.25} Cs ₂ H _{0.5} PW-S1/S2	3.0-3.2/3.0-3.1	1-1.3/0.9-1.2	0.57-0.61/0.42-0.61
Pd _{0.25} Cs _{2.25} H _{0.25} PW-S1/S2	3.4-4.2/3.3-3.4	0.6-0.8/0.7-1.0	0.29-0.38/0.38-0.48
Pd _{0.25} Cs _{2.5} PW-S1/S2	5.0-6.0/5.0-5.5	0.4-0.6/0.5-0.7	0.20-0.32/0.27-0.35

The thermal decomposition behaviour of the heteropoly compounds-S1 and S2 prepared by the change of the order of reactants adding is very close comparing to the corresponding thermal curves from Fig.1a and b. This means a similar composition, structure and texture could be supposed for every S1-S2 couple of heteropoly compounds.

The content of physisorbed water, crystallization water and number of protons/KU were calculated from TG curves for heating rate of 2.5, 5, 7.5 and 10.. The results are summarized in Table 1.

The Keggin structure known as primary structure is evidenced by characteristic IR bands for the main vibration bonds of Keggin Unit:

ν_{as} P-O_i-W, 1080-1081; ν_{as} W-O_t, 976-995; ν_{as} W-O_c-W, 890-900; ν_{as} W-O_e-W, 805-810 cm⁻¹,²⁰

respectively, ν_{as} (P-O_i-W) 1079; ν_{as} (W-O_t) 975; ν_{as} (W-O_c-W) 887; ν_{as} (W-O_e-W) 795 cm⁻¹ in H₃PW and ν_{as} (P-O_i-W) 1080; ν_{as} (W-O_t) 985; ν_{as} (W-O_c-W) 890; ν_{as} (W-O_e-W) 804 cm⁻¹ in C_{2.7}H_{0.3}PW.²¹ Weaker absorptions band due to δ (P-O-P) and ν_s (W-O-W) appeared at 596 and 525 cm⁻¹, respectively.²¹

A large band 3000-3400 cm⁻¹ with a shoulder is observed and it was assigned to crystallization water-hydrogen bonded and to hydrogen-bond vibrations (hydrogen-bonds formed between neighbouring KUs). The shoulder at 3355 cm⁻¹ was assigned to ν (OH) of protonated water.^{21,22} The other two bands in relation to water molecules vibration, the 1710-1720 cm⁻¹ and the 1615 cm⁻¹, were assigned to δ vibrations of protonated water

(hydroxonium ions, H_3O^+ or H_5O_2^+), respectively to δ vibrations of nonprotonated water molecules.^{22,23} The FT-IR spectra shows the presence of the specific absorption bands for KUs in the Pd doped H_3PW and its Cs salts, as can be observed from Fig. 2a. All characteristic bands of the KU are still observed for samples heated at 523 K, even the bands assigned to water and hydroxonium ions. This means that the samples take water in short time from atmosphere during the procedures of samples shaping as KBr pellets. No significant differences between the FT-IR spectra for H_3PW and its Cs salts, respectively the same heteropoly compounds doped with Pd were observed. Also, all Pd doped Cs salts-S1,S2 gives similar FT-IR spectra as can be observed from

Fig. 2 a, b, therefore it could be concluded that Pd does not modify significantly the primary structure even if the order of reactants adding was changed.

The FT-IR spectra of samples heated at 873 K show the complete disappearance of specific KU absorption bands for H_3PW and Pd doped H_3PW and an increase of intensity for these bands with higher Cs/KU ratio (see Fig. 3 a,b).

The more so as, if the $\text{Pd}_{0.25}\text{CsH}_{1.5}\text{PW}_{12}\text{O}_{40}$, $\text{Pd}_{0.25}\text{Cs}_2\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Pd}_{0.25}\text{Cs}_2\text{H}_{0.25}\text{PW}_{12}\text{O}_{40}$ are true acidic salts, their decomposition have to give lacunary Keggin structure, which have to be observed in FTIR spectra by P-O band splitting as result of lower symmetry for central atom (P) by one oxygen removal,²⁴ but such change was not observed in the spectra.

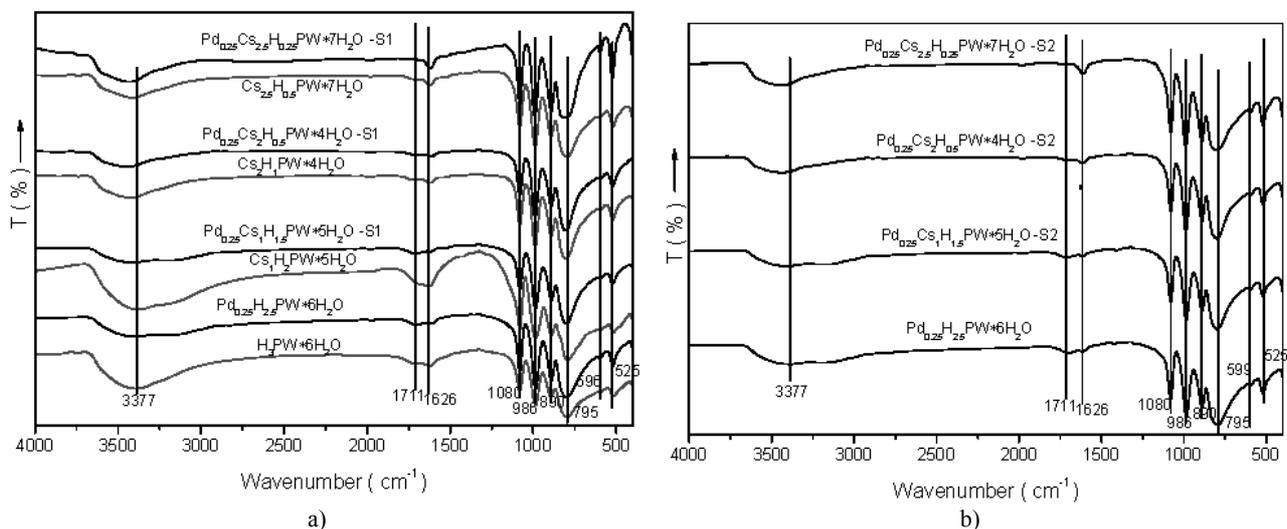


Fig. 2 – FTIR spectra of: a) H_3PW , CsH_2PW , Cs_2HPW , $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$ and Pd doped heteropoly compounds-S1; b) Pd doped heteropoly compounds-S2.

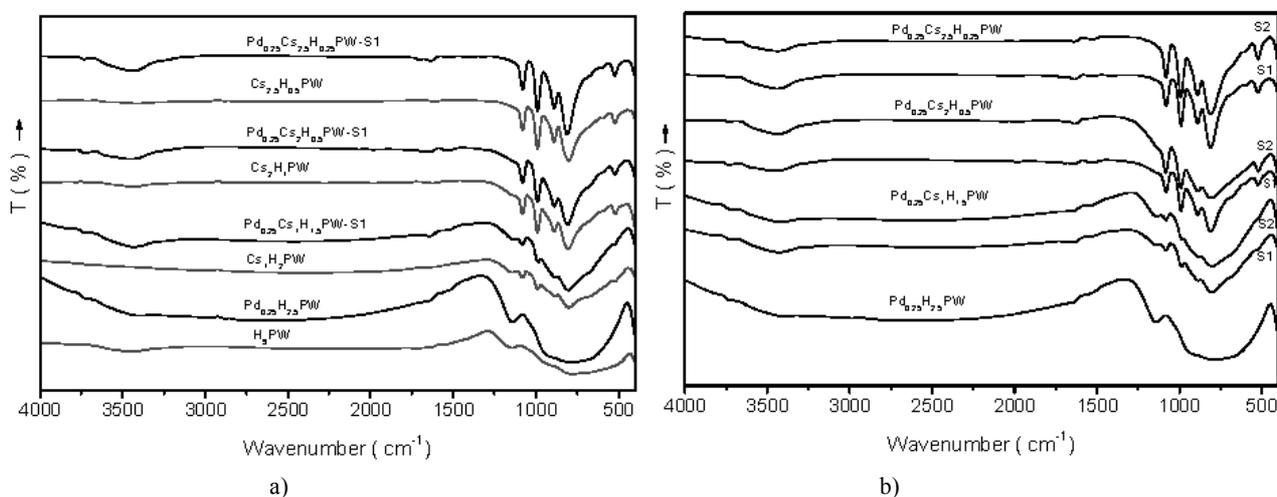


Fig. 3 – FTIR spectra of the samples after calcination at 873 K, 1h, in air atmosphere: a) H_3PW , CsH_2PW , Cs_2HPW , $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$ and Pd doped heteropoly compounds-S1; b) Pd doped heteropoly compounds-S2.

The Pd doped $H_3PW \cdot 6H_2O$ and their Cs acidic salts show X-ray diffraction spectra close to the $H_3PW \cdot 6H_2O$ and its Cs acidic salts as can be seen in Fig. 4 a,b. All HPCs containing Cs show larger widths of diffraction maxima and a shifting to higher angles at the same time with Cs content increases. However, the diffraction maxima from smaller angles of 2θ -10.3 and 14.6 are reduced drastically for HPC containing Pd. Therefore Cs^+ and Pd^{2+} exercise a significant influence over the secondary structure only, because IR characteristic bands remain unchanged practically. The

identification of HPCs based on their specific crystalline structure from X-ray diffraction spectra was carried out using the apparatus' database.

The X-ray diffraction spectra of synthesized compounds exhibit all the reflections corresponding to cubic crystalline structure, similar with other literature data.^{7,8,12,15-17,25-27} but only the diffraction maxima for $H_3PW \cdot 6H_2O$ and Cs_3PW which have crystal structure of cubic $Pn3m$ symmetry²⁵ were found by comparing the X-ray diffraction spectra from Fig. 4a,b with those from Fig. 5.

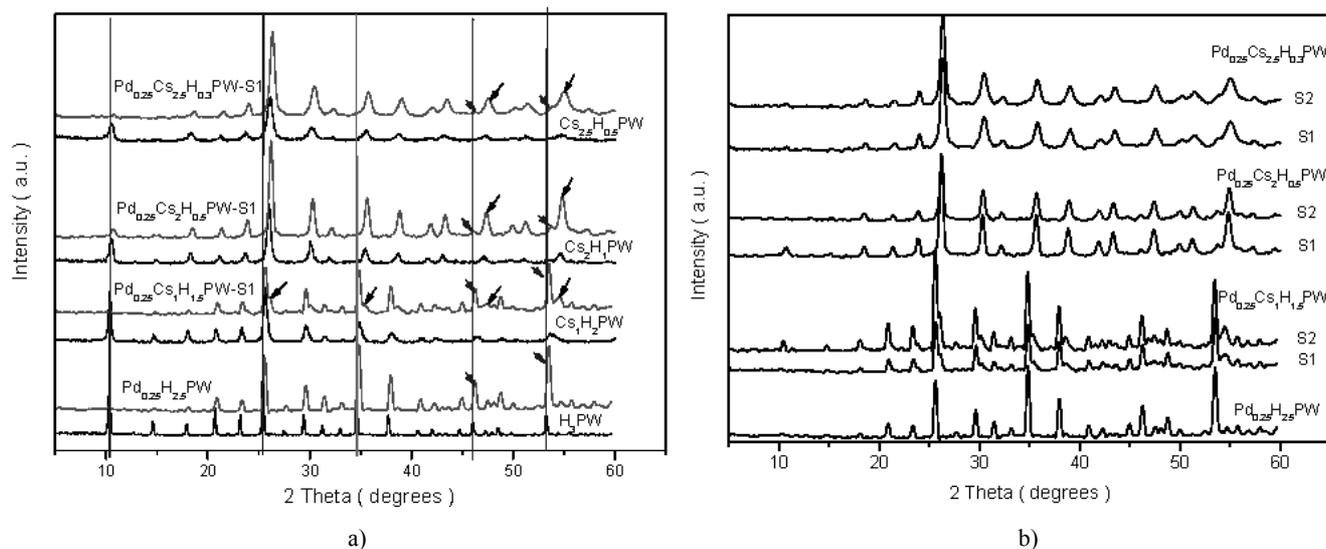


Fig. 4 – X-ray diffraction patterns of: a) H_3PW , CsH_2PW , Cs_2HPW , $Cs_{2.5}H_{0.5}PW$ and Pd doped heteropoly compounds-S1, b) $Pd_{0.25}H_{2.5}PW$, $Pd_{0.25}CsH_{1.5}PW$ -S1/S2, $Pd_{0.25}Cs_2H_{0.5}PW$ -S1/S2 and $Pd_{0.25}Cs_{2.5}H_{0.25}PW$ -S1/S2 at room temperature.

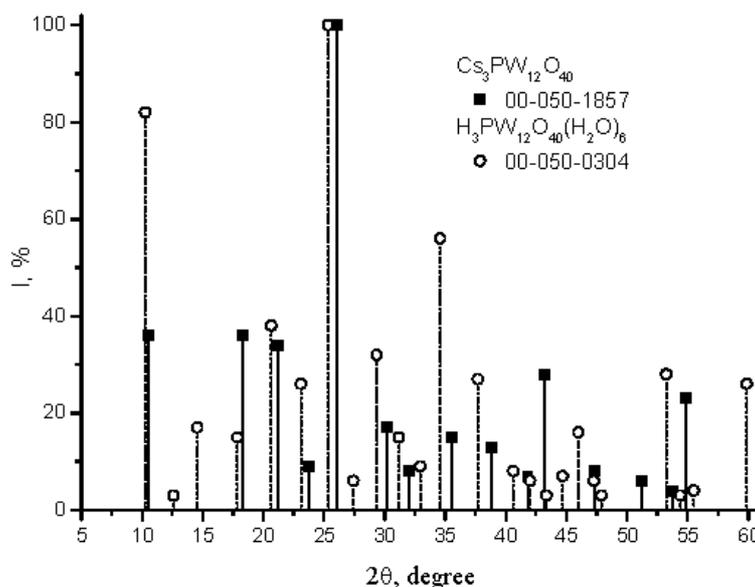


Fig. 5 – X-ray diffraction lines for the main planes of reflections from $H_3PW \cdot 6H_2O$ and Cs_3PW according to files 00-050-304, respectively 00-050-1857 files (from the diffractometer's database).

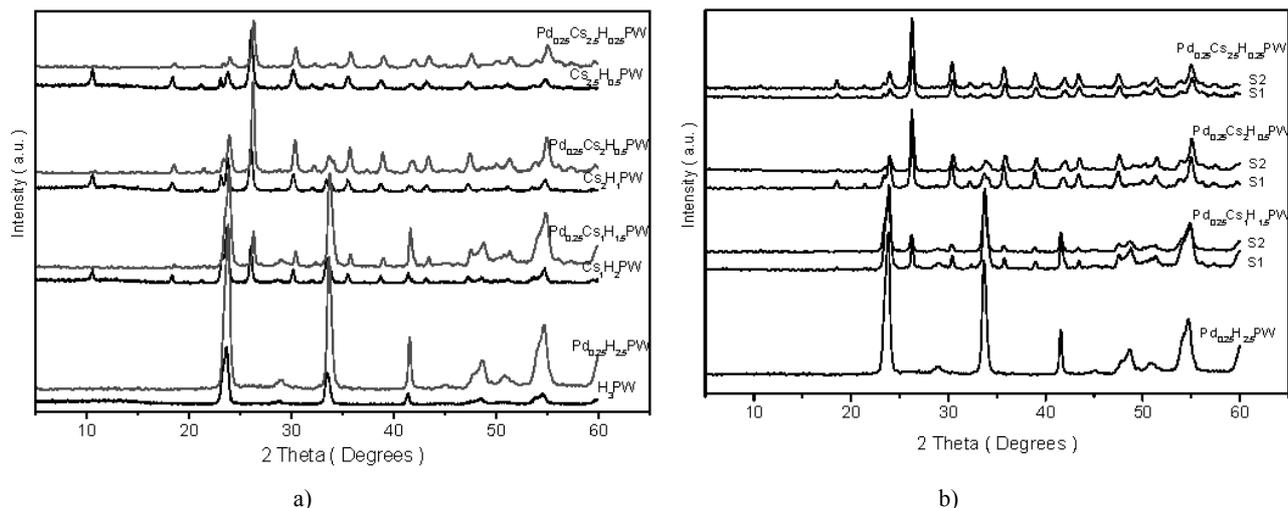


Fig. 6 – X-ray diffraction patterns of: a) H_3PW , CsH_2PW , Cs_2HPW , $Cs_{2.5}H_{0.5}PW$ and Pd doped heteropoly compounds-S1, b) $Pd_{0.25}H_{2.5}PW$, $Pd_{0.25}CsH_{1.5}PW$ -S1/S2, $Pd_{0.25}Cs_2H_{0.5}PW$ -S1/S2 and $Pd_{0.25}Cs_{2.5}H_{0.25}PW$ -S1/S2 after calcination at 873 K, 1h, in air atmosphere.

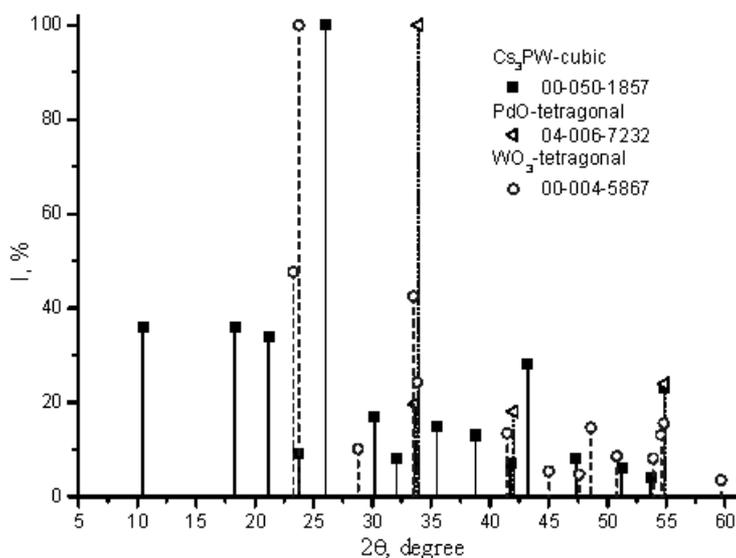


Fig. 7 – X-ray diffraction lines for the main planes of reflections from Cs_3PW , WO_3 and PdO according to 00-050-1857, 00-004-5867 and 04-006-7232 files (from the diffractometer's database).

The X-ray diffractograms of samples heated at 873 K are showed in (Fig. 6 a,b). For identification of existent phases, these spectra have been compared with the most likely files of HPCs and oxides using the apparatus' database and literature data. The main lines of the X-ray files found in the spectra of Fig. 6 a,b are showed in Fig. 7. The results confirm the TG-DTA analyses and the IR investigations: the H_3PW was decomposed totally to corresponding oxides and the WO_3 was crystallized. The H_3PW heated at 873 K gives a spectrum (Fig. 6a), similar with the spectrum corresponding to tetragonal WO_3 .^{26,27}

The tetragonal WO_3 is present in the spectra of acidic salts as a result of partial decomposition, as its main characteristic line (100) can be observed

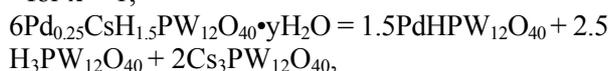
in these spectra with decreasing intensities with respect to Cs content increases. Also, the main reflections lines of the Cs_3PW were observed, but their intensity increase for higher Cs content. In the same time the H_3PW 's diffraction lines decrease as intensity.

WO_3 and PdO , both crystallized in tetragonal form, give close reflection lines, so PdO presence can be proved only by comparison of the ratio between intensity for the same 2 lines of undoped HPCs with corresponding Pd doped HPCs. In this purpose, the reflection lines at $2\theta = 23.754$ ($I_{110}=100$) and $2\theta=33.506$ ($I_{111}=42.5$) for WO_3 were chosen because PdO shows the line $I_{101}(100)$ at $2\theta=33.855$. Thus, a higher ratio I_{111}/I_{110} from spectra corresponding to heated samples at 873 K

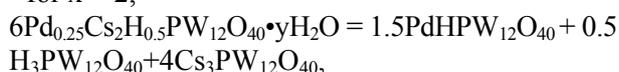
(if HPC forms containing Pd were decomposed) is expected. The values for I_{111}/I_{110} (WO_3) summarized in Table 2 have confirmed this supposition because all values for Pd doped HPCs are significantly bigger.

The acidic salts with Cs consists of a Cs_3PW core covered with H_3PW layers as it has been proposed and proved in the literature.¹⁴⁻¹⁶ Thus, the Pd doped acid salts of Cs can be written down also as mixture of H_3PW , PdHPW and Cs_3PW based on this model and the thermal analyses, IR and X-ray diffraction data:

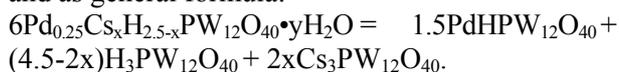
- for $x = 1$,



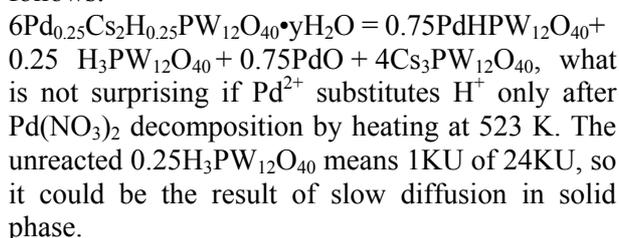
- for $x = 2$,



and as general formula:



For $x = 2.5$, the thermal analysis gives only 0.25 H^+/KU , so its composition could be write as follows:



The main decomposition processes of the $\text{H}_3\text{PW}\cdot 6\text{H}_2\text{O}$ and the acidic salts, $\text{Pd}_{0.25}\text{Cs}_x\text{H}_{2.5-x}\text{PW}_{12}\text{O}_{40}\cdot y\text{H}_2\text{O}$ based on the thermal analyses, IR and X-ray diffraction data are:

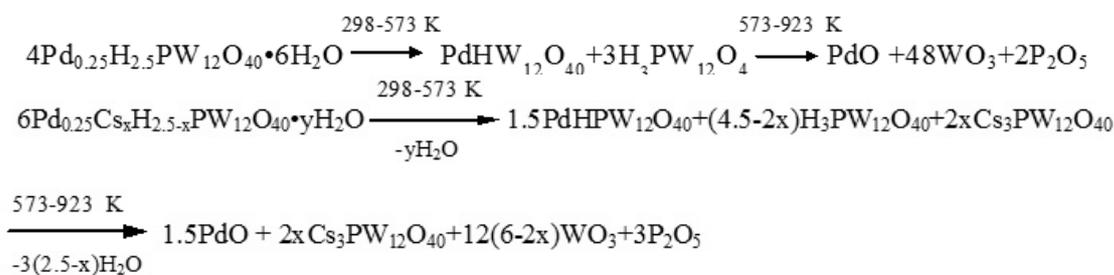


Fig. 8 – The scheme for the thermal decompositions of the $\text{Pd}_{0.25}\text{H}_{2.5}\text{PW}\cdot 6\text{H}_2\text{O}$ and $\text{Pd}_{0.25}\text{Cs}_x\text{H}_{2.5-x}\text{PW}\cdot y\text{H}_2\text{O}$.

Table 2

The I_{111}/I_{110} for tetragonal WO_3 of X-ray diffraction spectra of heated HPCs at 873 K

		Cs/KU	0	1	2	2.5
I_{111}/I_{110} (WO_3)	Undoped HPCs		0.60	0.51	0.40	0.40
	Pd doped HPCs		0.83	0.85	0.52	0.47

The thermal stability of HPCs was compared by means of kinetic parameters for constitutional water loss. In this purpose the Standard Test Method for Decomposition Kinetics by Thermogravimetry was used.¹⁹ Method assumes for decomposition the first-order kinetics and an independent E_a value of reaction order in the early stages of decomposition. The range of conversions between 5% and 10 % decomposition is recommended for calculations. This method takes into consideration the observation about Doyle's

approximation for $x \equiv \frac{E}{RT} < 20$ that leads to errors higher than 10%¹⁸ and solved it by iterative calculation of E_a . The apparent activation energy-

E_a and pre-exponential coefficient-A have been calculated from TG curves (Fig. 1a,b), the segments from 573 K to 923 K. The first step was plotting of $\log(\text{heating rate}-\beta)$ vs the inverse of absolute temperatures at constant conversions- α (for the range of constant conversion values from 5% to 95%, with the interval of 5%), as can be seen in Fig. 9. Using the least-squares method was fitted a straight line to these data and the slope was determined as can be seen in Fig. 10.

Generally, the thermal decomposition of Pd doped HPCs occurs at lower temperature than corresponding undoped HPCs as it ensues from TG curve showed in Fig. 9 and Fig. 11.

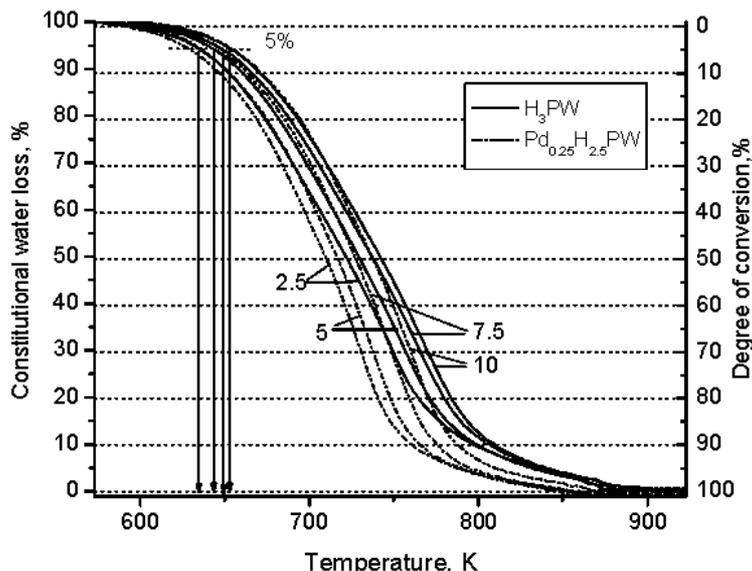


Fig. 9 – The constitutional water loss curves at 2.5, 5, 7.5 and 10 K/min for H_3PW and $Pd_{0.25}H_{2.5}PW$.

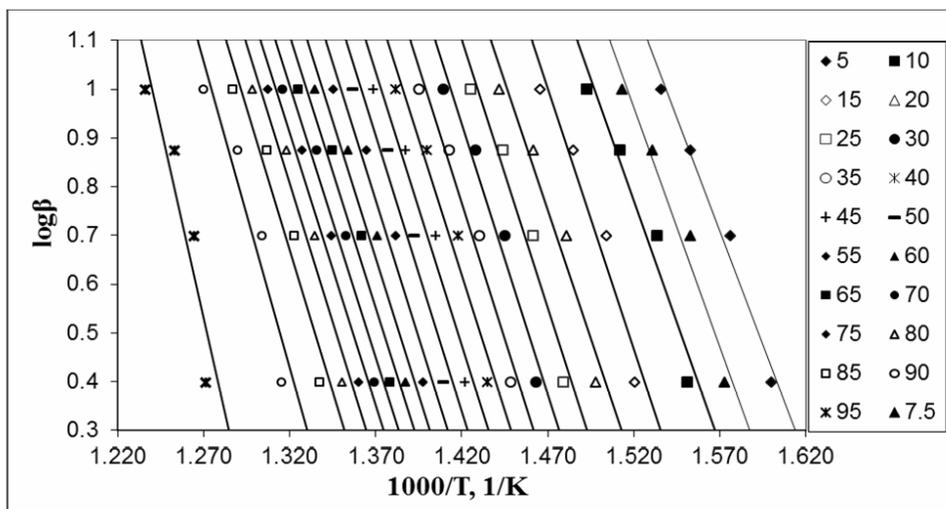


Fig. 10 – The Arrhenius plot of $\log(\text{heating rate}-\beta)$ function of inverse temperature ($1/T$) of constant conversion data for $Pd_{0.25}H_{2.5}PW$.

The procedure of kinetic parameters calculation accordingly with ASTM E 1641-04 was described in detail earlier.¹⁷ The results of these calculations are showed in the Table 3.

The apparent activation energy varies with not more than $\pm 10\%$ between 10% and 80% degree of conversion for the $Pd_{0.25}H_{2.5}PW$, $Pd_{0.25}Cs_1H_{1.5}PW$ and $Pd_{0.25}Cs_2H_{0.5}PW$, respectively with $\pm 11\%$ and $\pm 28\%$ for the $Pd_{0.25}Cs_{2.25}H_{0.4}PW$ and $Pd_{0.25}Cs_{2.5}H_{0.25}PW$ between the same limits. In the last two cases it can be assumed that the influence of diffusion on constitutional water release is concerned, if Pd^{2+} concentration is the same in the H_3PW layers for the studied heteropoly compounds.

The pairs of values E_a - $\ln A$ were plotted for to identify a possible kinetic compensation effect (KCE), as can be seen in Fig. 12. The KCE

supposes a linear relationship between Arrhenius parameters $\ln A$ and E for a family of related processes. On the other hand, it was shown that the kinetic compensation effect mathematically results from the exponential form of the rate constant. Thus, a change of activation energy is compensated by the same change in temperature or in the logarithm of the pre-exponential factor.²⁸ In consequence, the distributions of E_a - $\ln A$ points and their deviations from each line on the compensation plots provide a measure of the consistency of the results, thus the identifying of incorrect computational procedure, inadequate method or work condition and/or assumption could be achieved. On the contrary, other authors sustain that an observed kinetic compensation effect (KCE) can be a result of differences in the sample

or experimental conditions, an indication of complex reaction controls, or, a computational artifact.²⁹ More reasonable assumption that an observed compensation effect on the same set of

data using different method of calculation demonstrates the incorrect setup the experiment was stated.³⁰

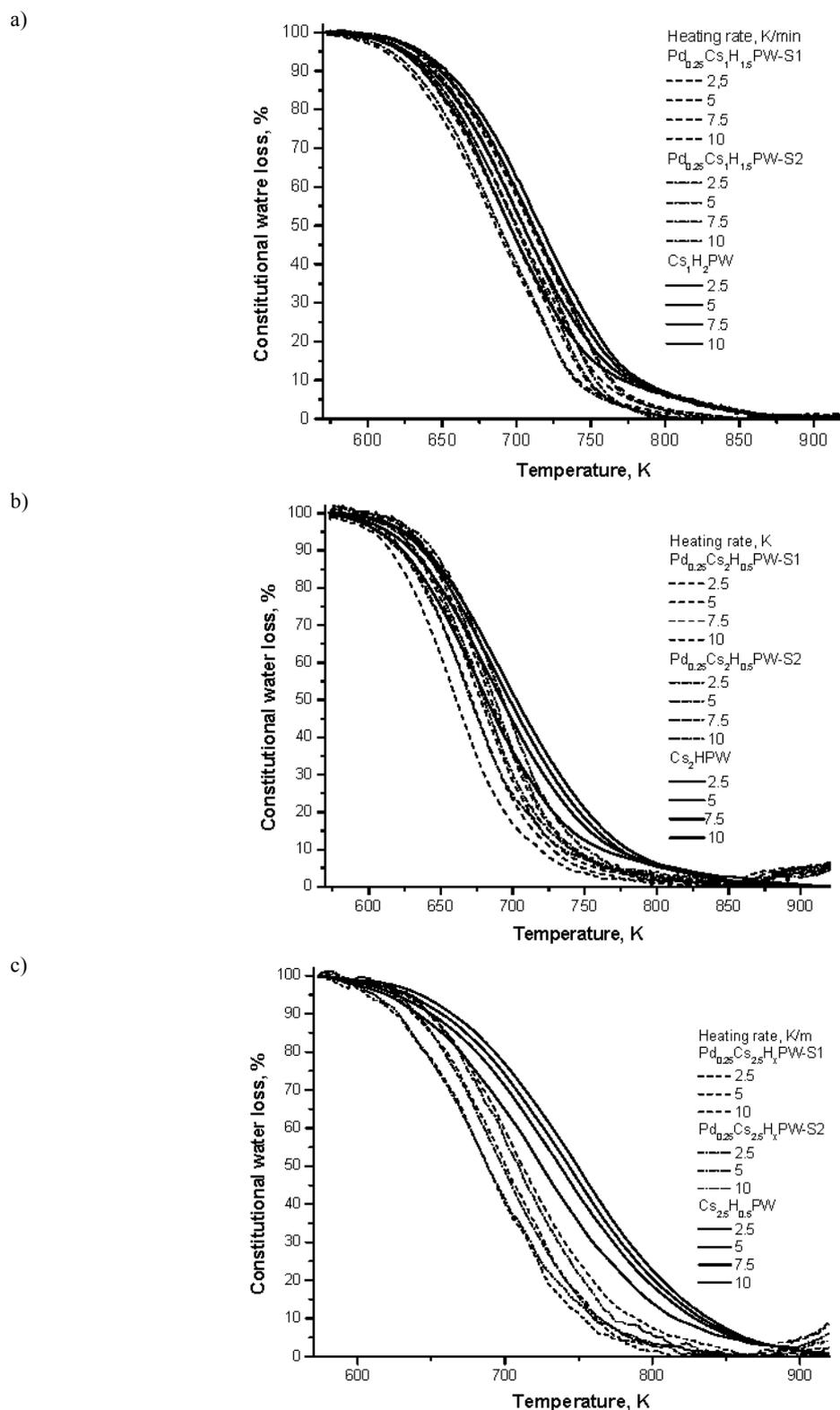
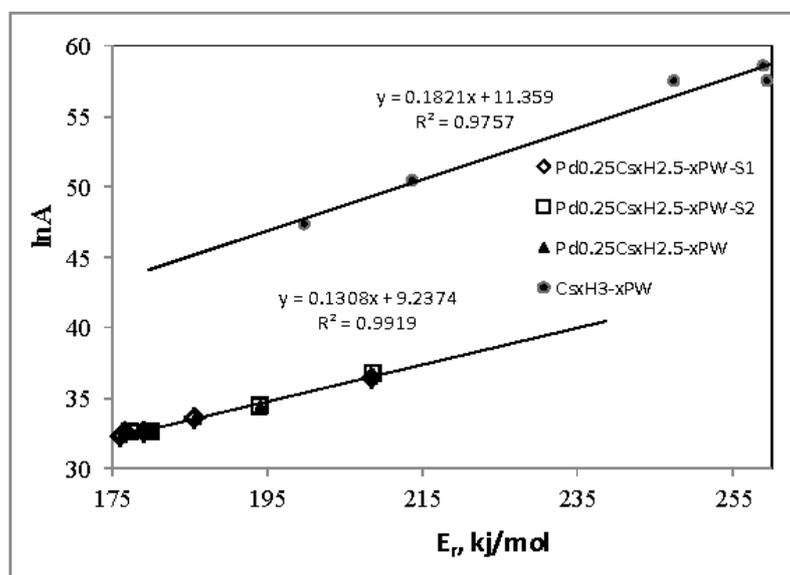


Fig. 11 – TG curves of constitutional water loss at heating rate of 2.5, 5, 7.5 and 10 K/min for: a) $\text{Cs}_1\text{H}_2\text{PW}$ and $\text{Pd}_{0.25}\text{Cs}_1\text{H}_{1.5}\text{PW-S1, S2}$; b) $\text{Cs}_2\text{H}_1\text{PW}$ and $\text{Pd}_{0.25}\text{Cs}_2\text{H}_{0.5}\text{PW-S1, S2}$; c) $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$ and $\text{Pd}_{0.25}\text{Cs}_{2.5}\text{H}_{0.25}\text{PW-S1, S2}$.

Table 3

The values of activation energy- E_r and $\ln A$ for pure HPCs and Pd doped HPCs

Compounds	S1		S2	
	E_r , Kj/mol	$\ln A$	E_r , Kj/mol	$\ln(A, \text{min}^{-1})$
$\text{Pd}_{0.25}\text{H}_{2.5}\text{PW}/$ H_3PW	176.1/ 259.4	32.23/ 57.56	-	-
$\text{Pd}_{0.25}\text{Cs}_1\text{H}_{1.5}\text{PW}/$ $\text{Cs}_2\text{H}_2\text{PW}$	208.5/ 259.0	36.42/ 58.61	208.2/ -	36.71/ -
$\text{Pd}_{0.25}\text{Cs}_2\text{H}_{0.5}\text{PW}/$ $\text{Cs}_2\text{H}_2\text{PW}$	176.8/ 247.5	32.56/ 57.55	174.3/ -	32.56/ -
$\text{Pd}_{0.25}\text{Cs}_{2.25}\text{H}_{0.4}\text{PW}/$ $\text{Cs}_{2.25}\text{H}_{0.75}\text{PW}$	179.1/ 213.7	32.55/ 50.45	180.0/ -	34.43/ -
$\text{Pd}_{0.25}\text{Cs}_{2.5}\text{H}_{0.25}\text{PW}/$ $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}$	185.6/ 199.7	33.59/ 47.36	194.1/ -	34.43/ -

Fig. 12 – The plotting of $\ln A$ vs E_r for to point out the KCE.

The KCE plots from Fig. 12 show clearly KCEs inside of both families of our related compounds, undoped HPCs and Pd doped HPCs, because the $R^2=0.9757$ for undoped HPCs and $R^2=0.9919$ for Pd doped HPCs point out a linear relation between kinetic parameters.

The E_r values for the H_3PW and CsH_2PW from Table 3 are very close because the CsH_2PW 's microstructure consists of mixture with ratio=2:1 between the H_3PW and the Cs_3PW , with a core of Cs_3PW crystallites covered of H_3PW molecules as outer layers,¹⁶ but with similar secondary structure for the H_3PW of mixture and the H_3PW in bulk as it appears from their X-ray diffraction spectra. Cs content over 2/KU generates a significant

decreasing of E_a . The Pd doping causes a drastic decrease of E_a , especially for HPCs with lower Cs content because it supports the release of constitutional water by replacing of proton. The close E_a values for Pd doped HPCs, S1 and S2, are in agreement with TG, IR and X-ray diffraction data which point out their similar composition and structure.

The microstructure model for Cs acid salts consists of a Cs_3PW crystallites core covered of H_3PW molecules as outer layers explain the thermal behavior for both families of studied HPCs with the remark that the layers of H_3PW contain also PdHPW for Pd doped acidic salts with Cs. The XRD data pointed out the existence of a high

number of H₃PW crystallites in the CsH₂PW case and consequently the same activation energy as the H₃PW in bulk, a lower number of H₃PW crystallites in the Cs₂HPW case and a very low number of H₃PW crystallites in the Cs_{2.5}H_{0.5}PW with the consequences of lower activation energy, especially for the last situation. The same assertions are valid for Pd doped acid salts with Cs.

CONCLUSIONS

The thermal decomposition of Pd_{0.25}H_{2.5}PW and its acidic Cs salts doped with Pd occurs as result of the constitutional water release (the water formed of the protons and the oxygen from the [PW₁₂O₄₀]³⁻) over 573 K. Their thermal decomposition process could be explain based on the microstructure model proposed for cesium acidic salts of H₃PW as agglomerates with a core consists of Cs₃PW crystallites embedded of H₃PW layers, but in this case the layers of H₃PW contain PdHPW also.

No important differences were observed between composition, structure and thermal behaviour of the two series of compounds obtained by change the order of reactants adding. This is a proof for PdHPW presence in the layers of H₃PW which cover the Cs₃PW crystallites in both cases.

The Pd doping causes a drastic decrease of E_a, especially for HPCs with lower Cs content because it supports the release of constitutional water by replacing of proton. The close values of kinetic parameters corresponding to Pd doped HPC with the same composition, but which were prepared by changing the order of reactants adding, demonstrates their similitude and the proper conduct of thermal analyses experiments.

The activation energy values calculated in respect of Standard Test Method for Decomposition Kinetics by Thermogravimetry are reliable and it can be used to calculate thermal endurance and to estimate the lifetime of the compounds at a certain temperature.

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