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THERMAL BEHAVIOR OF THE POLYOXOMETALATES DERIVED FROM $H_3PMo_{12}O_{40}$ AND $H_4PVMo_{11}O_{40}$
Influence of some monovalent cations

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Abstract

The aim of this study is to investigate the influence of some monovalent counter-ions (NH_4^+, K^+ and Cs^+) on thermal behavior of polyoxometalates derived from $H_3PMo_{12}O_{40}$ (HPM) and $H_4PVMo_{11}O_{40}$ (HPVM) by replacing the protons.

The IR and UV-VIS-DRS spectra of some acid and neutral NH_4^+, K^+, Cs^+ salts, which derived from HPM and HPVM, confirmed the preservation of Keggin units (KU) structure. The X-ray diffraction spectra clearly showed the presence of a cubic structure.

The non-isothermal decomposition of studied polyoxometalates proceeds by a series of processes:

- the loss of crystallization water;
- the loss of O_2 accompanying with a reduction of $V^{5+} \rightarrow V^{4+}$ and $Mo^{6+} \rightarrow Mo^{5+}$;
- the loss of constitution water started at 360°C for HPVM salts and 420°C for HPM salts; the decomposition of ammonium ion over 420°C with NH_3, N_2 and H_2O elimination and simultaneous processes of reduction ($V^{5+} \rightarrow V^{4+}$ and $Mo^{6+} \rightarrow Mo^{5+}$ or Mo^{4+}) associating with endothermic effects;
- reoxidation of Mo^{5+}, Mo^{4+} and V^{4+} with a strong exothermic effect;
- destruction of KU to the oxides: P_2O_5, MoO_3 and V_2O_5 and the crystallization of MoO_3.

Keywords: Keggin structure, monovalent counter-ions, non-isothermal decomposition, polyoxometalates

Introduction

Heteropolyacids and their salts include interesting properties which recommend them to be used for the design of new catalysts. Both acidic and redox properties of HPA could be adjust by a suitable selection of counter-ions and the constituent elements of heteropolyanions in the addition to a better define of their structure as conventional oxide catalysts [1, 2]. The most known heteropolyanions have a Keggin structure and in generally these are named Keggin units (KU).

Study of polyoxometalates as catalysts has been started with NH_4^+ and K^+ salts of $H_3PMo_{12}O_{40}$ (HPM) [3, 4], it has continued with mixed salts ammonium – potassium

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and ammonium – cesium of the same HPA [5–8], Cs salts of $H_4PVMo_{11}O_{40}$ (HPVM) [9, 10] and mixed salts (NH_4^+ and Cs^+) of HPVM [11]. In last years many studies are concerned on the influence of some counter-ions with variable valence (especially Cu^{2+} and Fe^{3+}) in variable quantities together with other counter-ions [12–14], and also as dopants [15, 16].

As the most important drawback to the design potential of these classes of catalysts is the weak thermal structural stability in reaction conditions (high temperature, reduction atmosphere), therefore many research teams have been studied the physical–chemical features in order to find out the reason of their low thermal stability [17].

The aim of our study is to investigate the influence of some monovalent counter-ions (NH_4^+, K^+ and Cs^+) on thermal behavior of polyoxometalates derived from HPM and HPVM by replacing the protons.

Experimental

The salts of HPVM were prepared by the reaction in aqueous solution of the parent acid to which the required stoichiometric quantity of counter-ion salts as nitrates was added. The resulting solutions were stirred at 80°C for two hours to ensure complete reaction. Then the solutions were filtered and the solids were dried at 80°C.

Thermogravimetric analysis was carried out with a Derivatograph system Paulik and Erdey type D (MOM Budapest). The measurements were conducted in air using platinum plates crucible. Heating rates were 2.5°C min^{-1} and the mass samples were 300 mg.

The IR spectra were recorded with a Biorad FTS 60A spectrometer (spectral range 4000-600 cm^{-1}, 256 scans, and resolution 2 cm^{-1}). A special stainless-steel IR cell, connected to a gas-flow system, was used for the 'in-situ' measurements up to 673 K. The argon-oxygen (80:20 ratio) flow through the cell was controlled using electronic flow controllers. For the study of the thermal behaviour of the samples, finely ground compounds were deposited as a film (as uniform as possible) on KBr pellets.

A Cary 4 spectrometer was used for 'in-situ' UV-VIS-DRS measurements on salt samples. Approximately 100 mg wafers were placed in a Praying Mantis chamber operating under continuous gas flow. All spectra were smoothed and the diffuse reflectance data were evaluated using the Kubelka-Munk equation. At first in each experiment the samples were outgassed for 30 min at room temperature at $\sim 2\cdot 10^{-5}$ Torr. The experiments for thermal behavior determination were carried out under argon-oxygen flow (by using a nitrogen flow was observed a slight reduction of the samples).

Powder X-ray diffraction data were obtained with a Dron 3 diffractometer using the Cu K_α radiation in the range $2\theta = 5\div 60°$. The experiments were done 'in situ' using a high-temperature camera with special gas inlets and a cooling system housing a stainless-steel sample holder. 'In situ' experiments were conducted in air, by holding the samples for 2 h at every temperature in order to allow the system to reach a stable thermal equilibrium.

Results and discussion

Molecular formulas of prepared HPM and HPVM salts were established by thermal analysis and quantitative analysis of K, Cs by flame atomic absorption spectroscopy; the efficiency of precipitation process of HPVM salts was calculated by UV-VIS analysis (there is a proportion between absorption band amplitude at 310 nm and the yield of $PVMo_{11}O_{40}^{4-}$).

First, thermal behavior of HPA salts was estimated from TG curves registered at heating rate of 2.5°C min^{-1} for samples of 300 mg, in platinum-plates crucibles, under air atmosphere. Thermal decomposition of HPA salts under non-isothermal conditions reveals four types of behaviors described by TG curves from Figs 1–4.

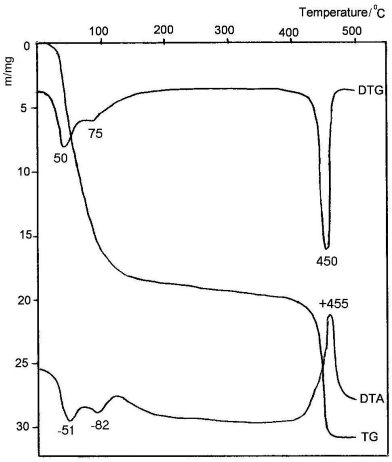

Fig. 1 TG curves of sample A0/$(NH_4)_3PMo_{12}O_{40}\cdot 7H_2O$

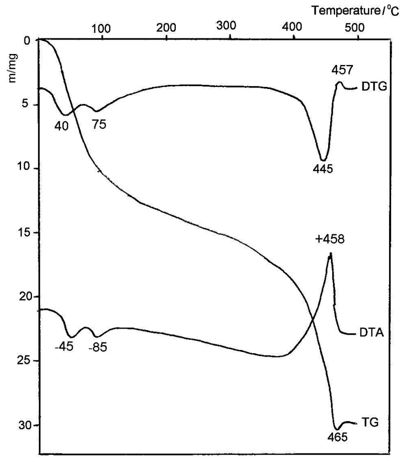

Fig. 2 TG curves of sample A1/$(NH_4)_3HPVMo_{11}O_{40}\cdot 6H_2O$

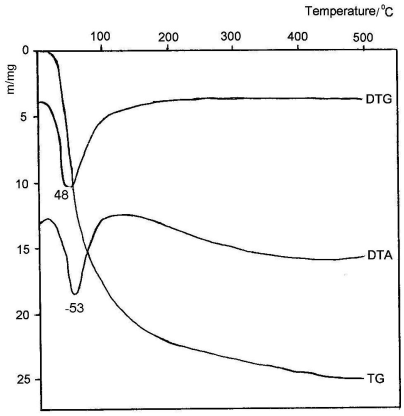

Fig. 3 TG curves of sample A7/ $Cs_3HPVMo_{11}O_{40}\cdot 7H_2O$

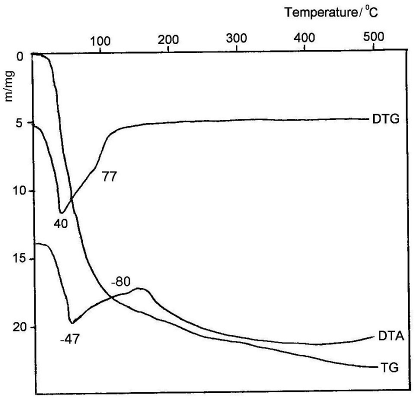

Fig. 4 TG curves of sample A9/$Cs_4PVMoO_{40}\cdot 9H_2O$

The results provided by TG curves under non-isothermal conditions combined with FT-IR, UV-VIS (DRS) and XRD ‘in situ’ investigations (experiments were carried out at temperatures established from thermal analyses) lead to the identification of physical and chemical processes of the salts thermal decomposition, according to Tables 1 and 2.

Acidic and neutral HPA salts contain lower quantities of crystallization water than parent acids because the protons which interconnected water molecules in $H_5O_2^+$ forms does not exist in neutral salts or exist in reduced number in acidic salts [18]. The loss of crystallization water proceeds in two steps, excepting Cs^+ and K^+ monoacidic salts of HPVM and Cs^+ neutral salt of HPM when water of crystallization is lost in one single step. For all HPA salts the upper temperature limit for the loss of crystallization water is around 170°C, however HPVM salts present a further mass loss in the temperature range considered to be a stable domain for anhydrous HPA salts.

Table 1. The processes and the characteristic temperatures of the TG curves at decomposition in non-isothermal conditions of ammonium, potassium and cesium salts of the HPM and HPVM (m = 300 mg, β = 2.5°C min^{-1}, Pt plates crucible, under air atmosphere)

Sample symbol/Molecular formula	Process/(–) decomposition product or (+) reactant	T range of DTG peaks/°C T_{peak}/°C	T_{peak} of DTA/°C (+) exo, (-) endo
A0/$(NH_4)_3PMO_{12}O_{40}\cdot 7H_2O$	Dehydration/–$4H_2O$	20–60/50	(-) 51
	Idem/–$3H_2O$	60–170/75	(-) 82
	Release O_2/–yO_2	170–420/-	–
	Decomposition*/–$1.5H_2O$;–$3NH_3$	420–460/450	–
	Reoxidation $Mo^{IV,V}$/+ zO_2	–	(+) 455
	KU degradation at oxides	–	–
A1/$(NH_4)_3HPVMo_{11}O_{40}\cdot 6H_2O$	Dehydration/– $2H_2O$	20–55/40	(-) 45
	Idem/– $3H_2O$	55–170/75	(-) 85
	Release H_2O and O_2/– xH_2O, yO_2	170–370	–
	Decomposition*/–$0.5H_2O$	370–420/-	–
	–$3NH_3$, –$1.5H_2O$	420–460/445	–
	Reoxidation V^{IV}, $Mo^{IV,V}$/+ zO_2	**/458	(+) 458
	KU degradation at oxides	–	–
A2/$(NH_4)_2KHPVMo_{11}O_{40}\cdot 4.5H_2O$	Dehydration/– $1.4H_2O$	20–55/40	(-) 45
	Idem/– $2.6H_2O$	55–170/75	(-) 85
	Release H_2O and O_2/–xH_2O, yO_2	170–370/-	–
	Decomposition*/–$0.5H_2O$	370–425/-	–
	–$2NH_3$,–$1H_2O$	425–460/445	–
	Reoxidation V^{IV}, $Mo^{IV,V}$/+ zO_2	** /457	(+) 457
	KU degradation at oxides	–	–

Table 1 Continued

Sample symbol/Molecular formula	Process/(–) decomposition product or (+) reactant	*T* range of DTG peaks/°C T_{peak}/°C	T_{peak} of DTA/°C (+) exo, (-) endo
A3/$(NH_4)_{1.5}CsH_{1.5}PVMo_{11}O_{40}\cdot 7H_2O$	Dehydration/– $3H_2O$	20–60/45	(-) 50
	Idem/– $4H_2O$	60–170/75	(-) 80
	Release H_2O and O_2/– xH_2O, yO_2,	170–350	–
	Decomposition*/$0.75H_2O$	360–415/-	–
	$–1.5NH_3$,$–0.75H_2O$	415–465/445	–
	Reoxidation V^{IV}, $Mo^{IV,V}$/+ zO_2	**/458	(+) 458
	KU degradation at oxides	–	–

*A part of NH_3 is chemisorbed and oxidized at N_2 with oxygen from the lattice, and a part from Mo^{VI} and V^{V} cations are reduced at $Mo^{IV,V}$, respectively V^{IV}.

**It can not be delimitated the beginning of the reoxidation process from the end of the decomposition and reduction processes.

Table 2. The processes and the characteristic temperatures of the TG curves at decomposition in non-isothermal conditions of potassium and cesium salts of the HPM and HPVM (m = 300 mg, a = 2.5°C min^{-1}, Pt plates crucible, under air atmosphere)

Sample symbol/Molecular formula	Process/(–) decomposition product or (+) reactant	T range of DTG peaks/°C T_{peak}/°C	T_{peak} of DTA/°C (+) exo, (-) endo
A6/$K_3HPVMo_{11}O_{40}\cdot 2H_2O$	Dehydration/–$2H_2O$	20–170/70	(-) 75
	Release H_2O and O_2/– xH_2O, yO_2,	170–375/-	–
	Partial decomposition/– $0.5H_2O$	375–500/-	–
	KU degradation at oxides	over 500	–
A7/$Cs_3HPVMo_{11}O_{40}\cdot 7H_2O$	Dehydration/– $7H_2O$	20–170/48	(-) 53
	Release H_2O and O_2/– xH_2O, yO_2,	170–390/-	–
	Partial decomposition/– $0.5H_2O$	420–500/-	–
	KU degradation at oxides	over 500	–
A8/$Cs_3PMo_{12}O_{40}\cdot 9H_2O$	Dehydration/– $9H_2O$	20–170/47	(-) 53
	Release H_2O and O_2/– xH_2O, yO_2,	170–500	–
	KU degradation at oxides	over 500	–
A9/$Cs_4PVMo_{11}O_{40}\cdot 9H_2O$	Dehydration/– $5H_2O$	20–60/40	(-) 47
	Dehydration/– $4H_2O$	60–170/77	(-) 80
	Release H_2O and O_2/– xH_2O, yO_2,	170–500	–
	KU degradation at oxides	over 500	—

This mass loss is associated with oxygen loss on the basis of UV-VIS(DRS) analysis which showed an evident decrease of reflectance over 170°C and an increase of Kubelka-Munk function at a constant wavelength of 620 nm. The explanation could be the formation of reduced species of $Mo^{6+}$and V^{5+} cations, probably Mo^{5+} and V^{5+} associated with an absorption band at 700 nm, as a result of electrons capture from O^{2-} [19].

Ilkenhans and coworkers had been found by GC-MS of gases from HPVM decomposition that oxygen and water were released, the last probably from hardly accessible pores [20].

Thermal decomposition of anhydrous HPA salts proceeds quite different depending on the counter-ions type and on the polyanions composition. Therefore, decomposition of acidic salts of HPVM (A1, A2, A3, A6, A7) started at 360–370°C by loosing the constitutional water which results from protons and lattice oxygen ions.

Decomposition of ammonium ion from A0 proceeds at 420°C with NH_3 and H_2O elimination followed by a partial reaction between NH_3 and O^{2-}. H_2O and N_2 are formed and Keggin structure of the polyanion are destructed according to following reaction:

$$2(NH_4)_3[PMo_{12}O_{40}]\rightarrow xN_2+(6-2x)NH_3+(3+3x)H_2O+P_2O_5+3MoO_{3-x}+21MoO_3$$

The thermal decomposition of vanadium salts proceeds after a similar reaction pathway with mention that V^{5+} ions were reduced to V^{4+} and they have been leaved the framework of KU when ammonium ion degradation begins. This mechanism of salts thermal decomposition was confirmed by ‘in situ’ UV-VIS (DRS) analysis: reduced species of Mo^{6+} and V^{5+} are present in larger quantities in the case of HPVM salts, especially at salts which contain ammonium counter-ion.

Our finding, that only a part of NH_3 is oxidized to N_2 result from the observation of mass loss registered during the decomposition process of ammonium HPVM salts, comes in contradiction with other studies which claim a complete NH_3 oxidation [6] or NH_3 oxidation does not take place [21].

Reoxidation process of Mo^{5+} ions in the case of ammonium HPM salts could not be observed as it take place at lower temperature than V^{4+} reoxidation and it is finished at the end of decomposition process.

At the end of decomposition process, corresponding oxides are resulted, but crystallization of MoO_3 are not observed unlike in the case of parent heteropolyacids [22], although for A1 salt, XRD measurements showed at 470°C a massive presence of MoO_3 in rhombic crystallographic form (Fig. 5). A7 salt has a remarkable thermal stability since at 470°C its Keggin structure is still preserved, as according to diffractometric analysis at this temperature only a single pattern assigned to MoO_3 is observed (Fig. 6). ‘In situ’ FT-IR analysis confirms the preservation of Keggin structure and a superior thermal stability of K and Cs acidic salts of HPVM in comparison with ammonium HPA salts. In the latter case, at 350°C a vibration band assigned to vanado-phosphates appeared (Fig. 7).

It could be mentioned that the complete disappearance of KU characteristic bands from IR spectra, at 400°C does not stand for a whole collapse (destruction) of Keggin structure as appeared in XRD spectra. Actually, with increasing temperature

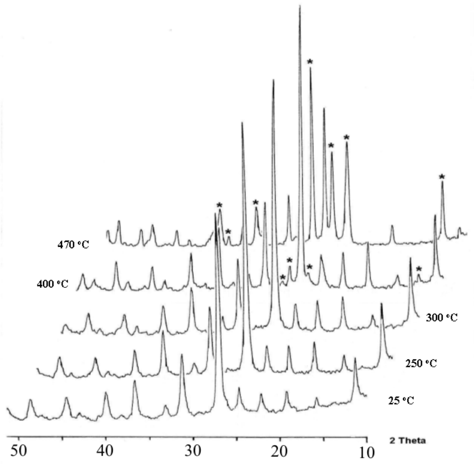

Fig. 5 Powder diffraction data of A3/$(NH_4)_{1,5}CsH_{1,5}[PVMo_{11}O_{40}]\cdot 7H_2O$ *vs.* temperature. Peaks corresponding to MoO_3 phase are marked

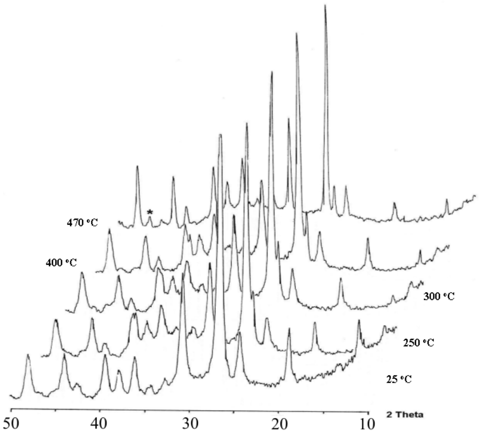

Fig. 6 Powder diffraction data of A7/$Cs_3H[PVMo_{11}O_{40}]\cdot 7H_2O$ *vs.* temperature. Peaks corresponding to MoO_3 phase are marked

a decrease of characteristic vibration bands amplitude of Keggin anions occurs since background increase as a result of electrons capture by Keggin units [19].

Conclusions

The IR and UV-VIS-DRS spectra of some acid and neutral NH_4^+, K^+, Cs^+ salts, which derived from $H_3PMo_{12}O_{40}$ (HPM) and $H_4PVMo_{11}O_{40}$ (HPVM), confirmed the preservation of Keggin units (KU) structure. The X-ray diffraction spectra clearly showed

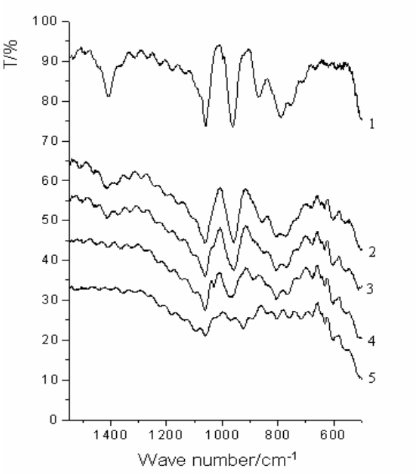

Fig. 7a The IR spectra of A1/$(NH_4)_3H[PVMo_{11}O_{40}]\cdot 7H_2O$(deposit on KBr support), at different temperatures: 1 – 20°C; 2 – 250°C; 3 – 300°C; 4 – 350°C; 5 – 400°C

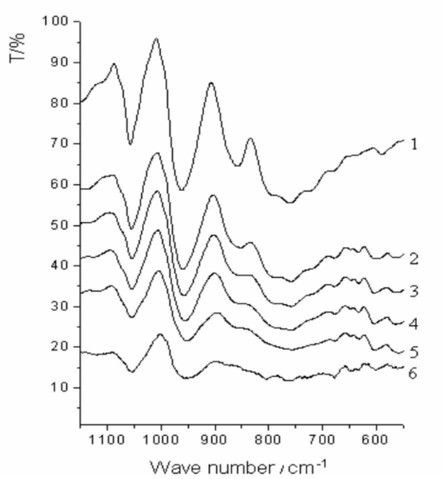

Fig. 7b The IR spectra of A7/$Cs_3H[PVMo_{11}O_{40}]\cdot 7H_2O$ (deposit on KBr support) at different temperatures: 1 – 20°C; 2 –200°C; 3 – 250°C; 4 – 300°C; 5 – 350°C; 6 –400°C

the presence of a cubic structure for salts unlike the corresponding heteropolyacid (HPA), which have a monoclinic structure at room temperature.

The thermal analysis carried out at heating rate of 2.5°C min^{-1}, in air atmosphere, pointed out different behavior as function of KU composition and counter-ion type:

- The loss of crystallization water proceeded in two steps between 20–170°C and is associated with the endothermic effects, as an exception for Cs_3HPVM when water of crystallization was loosing in one step;

- A slight mass loss was observed for HPM salts between 170÷420 C and respectively between 170÷360°C for HPVM salts. In the later case, the mass loss is more pronounced and according to UV-VIS-DRS is accompanying with a reduction of $V^{5+}\rightarrow V^{4+}$ and $Mo^{6+}\rightarrow Mo^{5+}$ respectively;
- The loss of constitution constitutional water started at 360±10°C for HPVM salts and with 420±5°C for HPM salts; decomposition of ammonium ion was observed at 420±5° with NH_3, N_2 and H_2O elimination and two simultaneous processes of reduction ($V^{5+}\rightarrow V^{4+}$ and $Mo^{6+}\rightarrow Mo^{5+}$or Mo^{4+}) associating with endothermic effects;
- Reoxidation of Mo^{5+} and V^{4+} was observed for HPVM salts because of a mass increase and an exothermal effect with maxima at 458°C; a total overlapping of reoxidation with constitution water loss and ammonium ion decomposition was occurred for HPM salts;
- Destruction of KU and the crystallization of the oxides: P_2O_5, MoO_3 and V_2O_5.

The constitutional water loss and the vanadium leaving from KU occurs simultaneously for HPVM acid salts, but however these processes could be delayed or partially blocked by counter-ion, especially in the presence of Cs^+ counter-ion. Cs_3HPVM have the best thermal stability and the decomposition to oxides began up to 470°C, unlike the ammonium salts for which MoO_3 phase was observed at 400°C in XRD patterns.

As a rule heteropolyacid salts have a better thermal stability as corresponding HPA and their cubic structure is preserved until the decomposition to corresponding oxides occurs.

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