THERMAL BEHAVIOUR STUDIES ON SOME HETEROTRINUCLEARPOLYACIDS

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Abstract

An improved method for the synthesis of four heterotrinuclearpolyacids of the type: $H_x[EM_y'M_z''O_{40}]$ nH_2O (E=P, Si; M'=Mo, W; M''=V, W) was elaborated. The studied compounds were characterized by elemental analysis, IR spectra and thermal behaviour over 20–800°C temperature range.
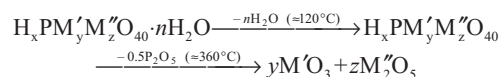
Introduction

The polyoxometalates and their components: molybdenum, tungsten and vanadium oxides are used as catalysts in various processes (e.g. hydrogenation, polymerization, izomerization of hydrocarbons and ether products) [1–4].

Several metal-substituted heteropolyoxometalates have been the subject of electrochemical studies in order to investigate their electrochemical [5, 6] or analytical [7–9] behaviour.

In this work the following heteropolyacids with 12 metal centers: $H_5[PMo_{10}V_2O_{40}]\cdot7H_2O$ **1**, $H_5[PW_{10}V_2O_{40}]\cdot12H_2O$ **2**, $H_6[SiMo_{10}V_2O_{40}]\cdot25H_2O$ **3** and $H_3[PMo_6W_6O_{40}]\cdot22H_2O$ **4** were obtained and characterized (Table1).

The thermal behaviour of these compounds was studied by means of derivatographic measurements.

The studied thermal decomposition of heterotrinuclearpolyacids (Scheme 1) could be an advantageous alternative method for the synthesis (~360°C) of a mixture of two and three oxides, respectively, presumably presenting catalytic properties.

$$H_xPM_y'M_z''O_{40}\cdot nH_2O \xrightarrow{-nH_2O\ (\approx120°C)} H_xPM_y'M_z''O_{40}$$
$$\xrightarrow{-0.5P_2O_5\ (\approx360°C)} yM'O_3 + zM_2''O_5$$

where: $M'O_3$=WO_3 and MoO_3, respectively.

Scheme 1

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Experimental

The heteropolyacids $\underline{1} \div \underline{4}$ presented in Table 1 were obtained by a modified version of the Kokorin's methods [10–13].

Table 1 Some physical and elemental analytical data of the studied heteropolyacids

	Compound	η%	Appearance	Analysis/%		
					calcd	found
$\underline{1}$	$H_5[Pmo_{10}V_2O_{40}]\cdot 7H_2O$	85	dark red octahedra	Mo	51.49	51.32
				V	5.46	5.27
				P	1.66	1.43
				H_2O (constitution)	2.43	2.31
				H_2O (crystallization)	6.80	6.65
$\underline{2}$	$H_5[PW_{10}V_2O_{40}]\cdot 12H_2O$	81	brick-red octahedra	W	64.91	64.50
				V	3.60	3.52
				P	1.09	0.86
				H_2O (constitution)	1.59	1.85
				H_2O (crystallization)	7.63	7.40
$\underline{3}$	$H_6[SiMo_{10}V_2O_{40}]\cdot 25H_2O$	76	red square prisms	Mo	43.90	43.55
				V	4.66	4.10
				Si	1.28	1.46
				H_2O (constitution)	2.47	2.65
				H_2O (crystallization)	20.60	20.99
$\underline{4}$	$H_3[PMo_6W_6O_{40}]\cdot 22H_2O$	82	orange needles	W	50.40	50.02
				Mo	17.04	17.45
				P	0.92	0.88
				H_2O (constitution)	0.80	0.99
				H_2O (crystallization)	11.73	11.97

The new method using the following molar ratios between the reagents: 0.01 mole aqueous solution of $NaH_2PO_4\cdot 2H_2O$ were treated with an aqueous solution of a mixture of: 0.06 mole $NaVO_3\cdot 2H_2O$ and 0.10 mole $Na_2MoO_4\cdot 2H_2O$ respectively 0.1 mole $Na_2WO_4\cdot 2H_2O$ for $\underline{1}$ and $\underline{2}$, respectively; and 0.02 mole Na_2SiO_3+0.03 mole $NaVO_3\cdot 2H_2O$+0.10 mole $Na_2MoO_4\cdot 2H_2O$ for $\underline{3}$; 0.06 mole $Na_2MoO_4\cdot 2H_2O$ and 0.06 mole $Na_2WO_4\cdot 2H_2O$ for $\underline{4}$. For all the compounds, the obtained hot solutions pH was adjusted to the value of 1.5 using H_2SO_4 1 M and then 2 h boiled. The free $H_x[EM'_yM''_zO_{40}]nH_2O$ with colours ranging from orange to dark red were obtained from the solution by double ether extraction and recrystallized at room temperature in darkness, with considerable yield, between 76 and 85% (Table 1).

The metal contents (Mo, W, V) of the samples were determined by atomic emission spectrometry with flame on a Baird Spectrovac 2000 (The Netherlands); the phosphorus and silicium content was determined by methods given in literature [14] and [15], respectively and H_2O content was calculated from the TG curves. The infrared spectra were recorded in KBr pellets with an UR-20-Spectrophotometer. The thermal behaviour was studied with an OD-103 MOM. Derivatograph (Budapest), sample mass: 200±1÷2 mg; the sensitivity of the balance 50 mg; heating rate: $10°C\ min^{-1}$; reference material: Al_2O_3; atmosphere: static air.

Results and discussions

In the modified synthesis method suggested in the present paper the output increases from 50 to 85% comparatively to the classical method [10] due to two new factors optimizing the synthesis reaction of 1÷4 compounds, namely the reagents ratios and a value of the media pH-s stabilized at 1.5. Some chemical physical properties of the synthesized compounds are listed in Table 1. The heteropolycompounds 1÷4 are highly soluble in water, insoluble in apolar organic solvents (ether, $CHCl_3$, CCl_4, benzene) and soluble in some polar organic solvents (DMFA, DMSO). The heterocompounds decompose in aqueous medium at pH>5.

IR spectra

At room temperature the IR spectra of the compounds 1÷4 present absorption bands in the 680–1700 cm^{-1} region of the spectrum. Two absorption peaks assigned to the Mo–O; Mo–O–Mo and W–O; W–O–W valence vibrations appear at 960 and 1060 cm^{-1}, respectively and other two peaks at 680 and 800 cm^{-1} assigned to the V–O valence vibrations [16–18] appear in the IR spectra of compounds 1, 2 and 3. The bands from 1400 and 1630 cm^{-1} were assigned to the crystallization water molecules, in agreement with X-ray diffraction effectuated on diheteropolyacids [19]. The mentioned studies showed the involvement of these water molecules in hydrogen bonds between the molecules placed inside the heteropolyacid molecule or between the molecules themselves.

In the IR spectrum of the $H_3[PMo_6W_6O_{40}]·22H_2O$ triheteropolyacid, the peaks corresponding to Mo^{6+}–O and W^{6+}–O are shifted at 980 and 1080 cm^{-1}, respectively and those assigned to the crystallization water molecules appear at 1400 and 1630 cm^{-1}. New references [20] report that structurally, the trinuclear heteropolycompounds present positional α-Keggin isomers.

Thermal analysis

All the studied compounds show similar thermal behaviour. Figure 1 shows one representative TG, DTG and DTA curves recorded for $H_3[PMo_6W_6O_{40}]·22H_2O$.
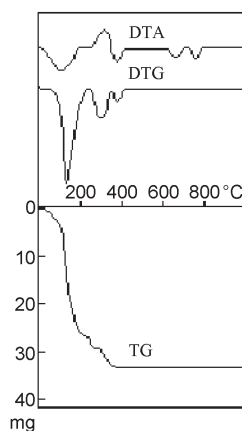
Fig. 1 TG, DTG and DTA curves of $H_3[PMo_6W_6O_{40}]\cdot 22H_2O$

The main processes and their characterization are given in Table 2.

Table 2 Thermal data of the heteropolyacids with three heteroatoms (noted 1÷4)

	Temperature range/°C	DTA peak/°C		TG data/%		Assignment
		endo	exo	calcd	found	
1	20–400	115	–	6.80	6.65	$7H_2O$
	400–800	–	307	2.43	2.31	$2.5H_2O$
		360	–	3.81	3.45	$0.5P_2O_5$
		600	–	–	–	
		726	–	–	–	V_2O_5 and MoO_3
2	20–400	118	–	7.63	7.40	$12H_2O$
		–	309	1.59	1.85	$2.5H_2O$
		360	–	2.50	2.12	$0.5P_2O_5$
	400–800	480	–	–	–	
		600	–	–	–	V_2O_5 and WO_3
		715	–	–	–	
3	20–400	124	–	20.60	20.99	$25H_2O$
		–	313	2.47	2.65	$3H_2O$
	400–800	600	–	–	–	
		722	–	–	–	V_2O_5 and MoO_3
4	20–400	120	–	11.73	11.97	$22H_2O$
		–	328	0.80	0.99	$1.5H_2O$
		360	–	2.10	2.48	$0.5P_2O_5$
	400–800	488	–	–	–	
		735	–	–	–	WO_3 and MoO_3

The dehydration is a two-step process. The loss of the crystallization water (also named *lattice water*) occurs at ~120°C. This determines an increase of the lattice cohesion by the formation of hydrogen bonds, both with the constitution water and with

the terminal oxygen atoms [19], confirmed by the t_{max} value of the reaction, which decreases as $t_1 < t_2 < t_4 < t_3$, in agreement with the increase of the number of the crystallization water molecules.

The second step in the dehydration is an endothermic process and it involves the loss of the constitution water (also named *structure water*). This loss significantly influences the geometry of the molecule, leading to a new structural rearrangement of the polyanionic complex for the compounds $\underline{1} \div \underline{4}$, at $\approx 300°C$.

In the DTG curve of the compounds $\underline{1}$, $\underline{2}$ and $\underline{4}$ the peak at 360°C was assigned to a mass loss corresponding both to 0.5 mole P_2O_5 (in good agreement with the sublimation temperature of P_2O_5) and to the obtained residue which corresponds to the stoichiometric ratio of the metal oxides.

The endothermic reactions from 480, 600 and 725°C in the DTA curves correspond to the crystalline phase transformations of the oxides: at ~480°C WO_3 changes its geometry from tetragonal to rhombic, at 600°C one can observe the melting of V_2O_5 and in the 720–740°C temperature range, the tetragonal MoO_3 becomes rhombic and the rhombic WO_3 becomes powder [21].

Conclusions

The crystalline phase formed at 360°C is a mixture of metal oxides in stoichiometric ratios: $\underline{1}$ $10MoO_3 + V_2O_5$; $\underline{2}$ $10WO_3 + V_2O_5$; $\underline{3}$ $10MoO_3 + V_2O_5 + SiO_2$ and $\underline{4}$ $6MoO_3 + 6WO_3$, results obtained by comparing the obtained and the calculated calcination residue. These results allow us to propose an alternative method for the synthesis of a mixture of two and three oxides, respectively, with a known composition, a method which consists of the calcination of the compounds $\underline{1} \div \underline{4}$, at $\approx 360°C$.

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