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Short Communication

THERMAL BEHAVIOUR OF TRANSITION- AND TETRAVALENT-METAL OXIDES AND PHOSPHOROUS OXIDE COMPOSITES

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The mixed zirconium, titanium, hafnium and first-row transition metal oxides (containing phosphorous oxide) were prepared using ion exchange method followed by calcinations at 1020 K during 12 h. The resulted mixed oxides were identified by XRPD method and studied their thermal behaviour by TG-DTA analysis. As a result of thermal analysis there were found one exothermic (with a peak at about 950 K), and one endothermic (with a peak at about 1300 K) processes, both without mass loss. The observation was valid for all investigated samples.

The analysis of XRPD patterns of the investigated samples showed well-defined crystal phases characteristic of each oxide. The XRPD analysis also verified the phase transition of tetravalent metal oxides from orthorhombic to tetragonal, observed by DTA analysis.

Keywords: *hafnium, oxides, thermal analyses, titanium, transition metals, X-ray analyses, zirconium*

Introduction

The phosphates of tetravalent metals (as Zr, Ti and Sn) have been known on the end of 19th century and their basic behaviours were investigated in a wide scale till now. Later on the hafnium phosphate was synthesised and investigated in more detail by various authors [1–4]. The real interest on them arose since 1950s, in connection with their good resistance against ionising radiation. Their structural behaviour and also their possible use in radio-analytical practice were published in monographs [5, 6], respectively. Because of the possible use in catalytic processes the mentioned phosphates were prepared in form containing first-row transition metals [7–13].These materials in oxide form also can be used in catalytic reactions. From this reason would be necessary to have more knowledge about their thermal behaviour. In the literature we found valuable data about the individual oxides of tetravalent-, and transition metals [14–17] and also similar data concerned to phosphorous pentoxide [18].

The results concerned the thermal behaviour and structure of composite containing some mixed tetravalent- and first-row transition metal oxides and phosphorous pentoxide are shown in this article.

Experimental

Synthesis

All chemicals were analytical grade.

The phosphates of Zr, Ti and Hf were prepared via the fluoro-complex, as first proposed by Alberti and Torracca [19]. The transition metal containing forms of the mentioned phosphates were synthesized by ion exchange method, described earlier [20]. The mixed oxide obtained by calcifying the mentioned materials during 12 h at 1020 K.

Methods

Analytical

The metal and phosphorous content of various samples were determined by spectrophotometer, at given conditions, described in book edited by Sandell [21]. The samples were controlled by elemental (carbon) analysis to determine the possible acetic acid content.

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Thermal analysis

The measurements were carried out using Mettler TA1-HT type computer controlled thermobalance simultaneously provided DTA and TG data. The heating rate was chosen 5 K min^{-1} in temperature range of 850–1500 K. The reference material was dehydrated Al_2O_3, the ambience was air, the Pt crucible was used. The found data were evaluated by adequate computer software.

Identification

The samples were identified by XRPD analysis. The study was performed with Bragg–Brentano geometry, using powder samples, with DRON-2 computer controlled diffractometer (at 45 kV, 35 mA) with the β filtered CoK_α radiation (λ=1.7890 Å) at 298 K. The goniometer speed was chosen 1/4° min^{-1} in the range of 2Θ=3–110°. The diffraction patterns were evaluated using 'EXRAY' peak searching software [22] and then compared with the given JCPDS cards. Based on the measured and calculated data of diffraction patterns the cell parameters were determined and modelled the structure using Powder Cell 2.3 software [23]. During the evaluation of the diffraction patterns an effect of texture on the line intensity was taken into consideration.

Results and discussion

The elemental analysis of samples gave carbon content under the detection limit. It means that the initially present acetic acid was completely evaporated during the preparation process.

According to the chemical analytical data the following compositions are proposed for the investigated samples:

$[ZrO_2\cdot 0.30CoO\cdot P_2O_5]$; $[TiO_2\cdot 0.58CoO\cdot P_2O_5]$; $[HfO_2\cdot 0.35CoO\cdot P_2O_5]$;
$[ZrO_2\cdot 0.46NiO\cdot P_2O_5]$; $[TiO_2\cdot 0.69NiO\cdot P_2O_5]$; $[HfO_2\cdot 0.42NiO\cdot P_2O_5]$;
$[ZrO_2\cdot 0.49MnO\cdot P_2O_5]$; $[TiO_2\cdot 0.77MnO\cdot P_2O_5]$; $[HfO_2\cdot 0.61MnO\cdot P_2O_5]$;
$[ZrO_2\cdot 0.54CuO\cdot P_2O_5]$; $[TiO_2\cdot 0.78CuO\cdot P_2O_5]$; $[HfO_2\cdot 0.50CuO\cdot P_2O_5]$;
$[ZrO_2\cdot 0.55ZnO\cdot P_2O_5]$; $[TiO_2\cdot 0.77ZnO\cdot P_2O_5]$; $[HfO_2\cdot 0.55ZnO\cdot P_2O_5]$;

At the same conditions of preparation, the titanium containing samples have significantly more transition metal ions than those containing zirconium or hafnium. The latter samples have practically the same transition metal contents.

The samples were identified by XRPD method, then an appropriate analysis, attempts were made to determine the crystal structure of the investigated mixed oxides. As an example, the fragments of XRDP pattern concerning manganese containing hafnium dioxide is shown on the Fig. 1. The titanium and hafnium oxide samples showed similar behaviour.

The diffraction patterns were evaluated, refined and compared with the suitable JCPDS cards No. 73-0431, 77-1542, 78-0424, 78-0643, 83-0602, 83-0808, 83-0810 and 84-1750, respectively. The best fittings were found for the orthorhombic structure in case of tetravalent metal oxides treated at

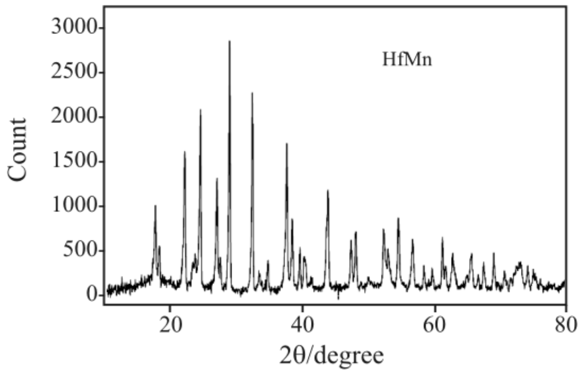

Fig. 1 A fragment of XRPD pattern of manganese containing hafnium dioxide

Table 1 Unit cell parameters of tetravalent metal oxides

	ZrO_2		TiO_2		HfO_2	
	Ortho-rhombic at 800 K	Tetragonal at 1050 K	Ortho-rhombic at 950 K	Tetragonal at 1100 K	Ortho-rhombic at 830 K	Tetragonal at 1050 K
a/Å	5.473(3)	3.623(3)	4.532(3)	4.587(4)	10.018(3)	5.140(4)
b/Å	6.342(1)	–	5.502(5)	–	5.228(2)	–
c/Å	3.250(1)	5.206(6)	4.906(8)	2.954(3)	5.060(2)	5.251(3)
Volume/$Å^3$	112.81	68.92	122.37	62.15	264.99	138.70
Rel. mass	985.75		639.19		1383.91	
X-ray density/g cm^{-3}	14.510		8.674		10.552	
Mass abs. coef/cm^2 g^{-1}	109.04		191.78		226.79	
Atoms in unit cell	24		24		24	
Atoms in symmetry/unit	3		3		3	

Table 2 Unit cell parameters of phosphorous pentoxide

	monoclinic	orthorhombic
a/Å	9.808(2)	9.198(8)
b/Å	9.975(4)	4.831(4)
c/Å	6.841(2)	7.168(7)
β/°	96.83(1)	–
Volume/Å^3	664.58	318.45
Rel. mass of cell	567.78	1011.66
X-ray density/g cm^{-3}	1.419	5.275
Mass abs. coeff./cm^2 g^{-1}	59.65	53.03
Atoms in unit cell	28	52
Atoms in asymmetric units	7	7

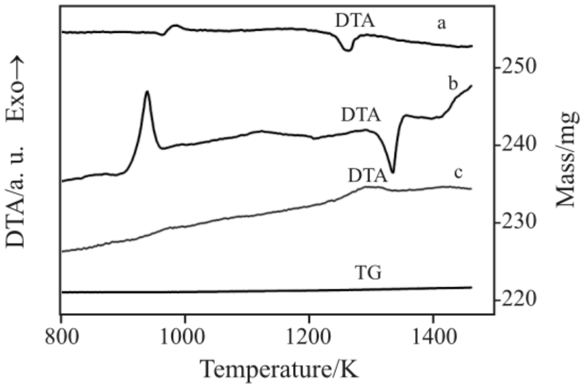

Fig. 2 DTA-TG pattern of manganese containing samples; a – zirconium dioxide, b – titanium dioxide, c – hafnium dioxide

850 K, and for the tetragonal form when the same oxides were treated at 1050 K. As a result of evaluation of the different XRDP patterns, belonging to the different samples, the type and the unit cell parameters of their crystal structure were calculated. The results are summarised in Tables 1–3.

The detailed analysis of diffraction patterns showed a uniform behaviour of samples containing both various first-row divalent-transition metals and various tetravalent-metals; on the other hand their distribution (based on peak analysis) inside the samples shows good correlation with the data of chemical analysis. Based on the data of evaluation, became clear, that the composite is a multi-phase system from crystallographic point of view, because the individual oxides save their crystal structure under the thermal treatment. The XRPD patterns belonging to various temperatures (990, 1100 K) showed a phase transition of tetravalent metal oxides, from orthorhombic to tetragonal. The observed phase transformation characterizes the exothermic process found by DTA measurements.

Similar phenomenon was found in case of mixed vanadium-chromium oxide too [24, 25]. To be known exactly the nature of the found, temperature dependent phase transformation must be taken further detailed investigations. Such investigations are now in progress.

The results of thermal analysis are summarised in Table 4 and as an example the DTA-TG pattern of manganese containing samples are shown on Fig. 2.

The DTA was carried out on the thermally treated, calcified samples. On them were found, for all investigated samples, an exothermic process in temperature range of 900–1130 K, with peak near at 1000 K. Looking at the results in detail, in the case of zirconium and titanium containing samples the character of the exothermic process practically identical for all transition metal oxides. In case of hafnium oxide containing samples, the starting temperature of exothermic process is successively decreased (about 40 K) from cobalt containing sample to direction of zinc containing one. Beside the mentioned process two slow, protracted endothermic ones, in temperature range of 1100–1450 K, were also found. It must be mentioned that the processes are much weaker than those for zirconium and titanium samples. In case of zirconium, and titanium containing materials the mentioned processes found to be equal.

All found processes existed without mass loss as evident from TG curves.

Table 3 Unit cell parameters of transition metal oxides

	CoO	NiO	MnO	CuO	ZnO
	cubic	cubic	cubic	cubic	cubic
A/Å	4.2620(2)	4.1761(3)	4.4421(3)	4.2452(5)	4.28(4)
Volume of cell/Å^3	77.42	72.83	87.65	76.49	78.40
Rel. mass of cell	3596.77	3586.06	3405.00	3818.18	3905.74
X-ray density/g cm^{-3}	77.147	81.768	64.506	82.872	82.66
Mass abs. coeff./cm^2 g^{-1}	262.84	38.33	223.31	44.55	50.73
Atoms in unit cell	96	96	96	96	96
Atoms in asymmetric unit	2	2	2	2	2

Table 4 Thermal analytical data

	Co(II)		Ni(II)		Mn(II)		Cu(II)		Zn(II)	
	endo	exo	endo	exo	endo	exo	endo	exo	endo	exo
ZrP	1125–1215 1305–1395	909–995	1160–1290 1310–1380	910–960	1140–1310 1315–1372	908–980	1260–1315 1336–1385	908–990	1190–1240 1240–1315	975–1030
TiP	1135–1275 1390–1450	910–1005	1170–1190 1190–1465	990–1045 1045–1090	1130–1305 1305–1345	910–970	1260–1310 1310–1385	890–950	1160–1210 1310–1370	915–985
HfP	1300–1410	1010–1130	1210–1290 1315–1390	990–1035	1215–1300 1325–1400	970–995	1240–1310 1310–1380	980–1110	1235–1310 1310–1395	970–1025

The exothermic processes were identified as phase transition of tetravalent-metal oxide from orthorhombic to tetragonal, while the endothermic ones, as phase transition of phosphorous pentoxide from monoclinic to orthorhombic.

The results in general, make clear that the given thermal treatment does not result homogeneous mono-phase crystal structure, but originate a composite having multi-phase crystal one.

Conclusions

Based on the above described results, the following conclusions can be done:

- Using the described method there can be prepared mixed oxides, containing various first-row divalent-transition-metals, various tetravalent-metals and phosphorous;
- The composite found to be multi-phase crystalline system. The individual metal and phosphorous oxides save their original structure;
- By the XRPD pattern analyses were determined the crystalline structure of individual oxides. Beside this, was identified the phase transition of tetravalent-metal oxide from monoclinic to orthorhombic take place in temperature range of 800–1050 K,
- The endothermic process going at temperature ranges of 1110–1450 K, covers the phase transition (from monoclinic to orthorhombic) of phosphorous pentoxide.

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