Journal of Thermal Analysis, Vol. 36 (1990) 1113-1121

THERMAL PROPERTIES OF HYDRATED LANTHANUM AND YTTRIUM POLYVANADATES

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(Received October 16, 1989)

The study of thermal properties of $La(HV_6O_{16})_3.19.5H_2O$ and $Y(HV_6O_{16})_3.22H_2O$ showed, that the dehydration of both compounds is discontinuous. After release of last water amount, the parent structure is destabilized and products of thermal decomposition, V_2O_5 and corresponding orthovanadates, start to be formed.

The decomposition of $La(HV_6O_{16})_3.19.5H_2O$ results in formation of V_2O_5 and $LaVO_4$, the temperatures of crystallization of which differ. The decomposition products of yttrium salt crystallize simultaneously. All compounds formed melt at 685°C. By crystallization of the melt, the mixtures V_2O_5-$LaVO_4$ and V_2O_5-YVO_4, respectively, are formed which are stable up to 1000°C.

The hydrated hexavanadates of some mono- and divalent cations [1-4] are thermally unstable compounds. In dependence on the present cation they decompose at higher temperatures and different types of polyvanadates, V_2O_5 or vanadium-oxygen bronzes are formed. Therefore, it was interesting to study from this view point the thermal stability of the analogical compounds with trivalent lanthanum and yttrium cations.

Experimental

The polyvanadates, $La(HV_6O_{16})_3.19.5H_2O$ and $Y(HV_6O_{16})_3.22H_2O$, were prepared according to [5] and identified by chemical analysis and IR spectra.

Vanadium(V) and vanadium(IV) were estimated by titration with $FeSO_4$ and $KMnO_4$, respectively [6], lanthanum and yttrium were titrated by complexone III using xylenole orange as indicator [5]

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The IR spectra in Nujol mulls were registered on Specord M 80 spectrophotometer. The powder diffraction patterns were obtained on Philips PW 1050 diffractometer.

The DTA measurements were performed on derivatograf Q 1500 D (MOM Budapest) conditions: air atmosphere, sample weight 200 mg, heating rate 10 deg/min, Pt crucible, Al_2O_3 as internal standard, temperature interval 20 - 1000°.

The analysis of individual exo- and endothermic processes was based on interruption of thermal analysis at chosen temperatures, cooling of the products to room temperature and their identification by qualitative X-ray phase analysis and IR spectroscopy.

Results and discussion

The DTA and DTG thermoanalytical curves of $La(HV_6O_{16})_3.19.5H_2O$ (Fig. 1) indicate a three-step process of water release.The first and second step of dehydration finished at 290°, are not separated markedly. The third mass loss (1.23%), finished at 375°, corresponds to release of approximately 1.5 moles of water. The mass loss corresponding to 21 molecules water is: 17.16% calculated and 17.10% found.

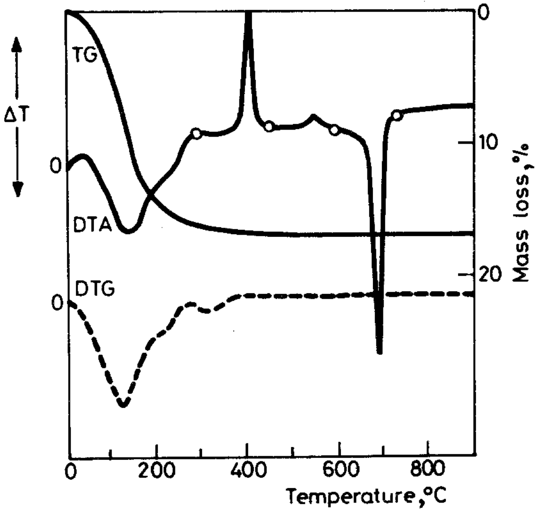

Fig. 1 Thermoanalytical curves of $La(HV_6O_{16})_3.19.5H_2O$

The IR spectra (Fig. 2) and powder diffraction patterns of the product obtained by interruption of heating at 290° and of starting compound are almost identical (the calculated interplanar distances are given in Table 1).

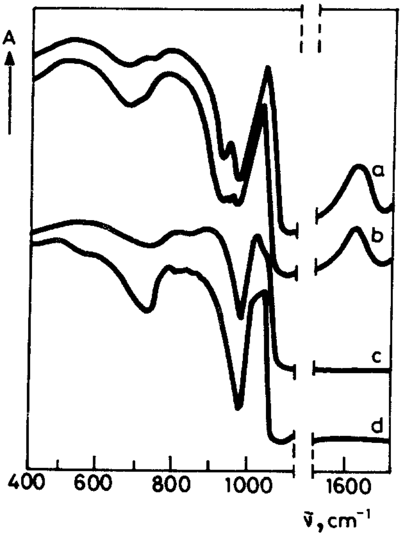

Fig. 2 Infrared spectra of $La(HV_6O_{16})_3.19.5H_2O$ a) and products of thermal analysis obtained at 290°C b), 445°C c), 590°-1000°C d)

During the last step of weight loss the parent structure is destabilized and the products of thermal decomposition start to be formed. When the dehydration is finished, a marked exothermic effect having maximum at 400° appears on the DTA curve (Fig. 1). The following less intensive exothermic process has a maximum at 550°. To explain these processes, the heating was interrupted at 445° and 590°. The product obtained at 445° contains V_2O_5, whereas at 590° it is formed a mixture containing V_2O_5, $LaVO_4$ and small amount of an unidentified admixture, whose presence is manifested in diffraction pattern by one weak diffraction (d_{nm} = 0.371). The low vanadium (IV) content indicates the presence of another component in the product. As follows from these data, the exothermic effect with maximum at 400° corresponds to crystallization of V_2O_5 and the exothermic effect at 550° predominantly to crystallization of $LaVO_4$ and eventually, to a redox process.

The melting of sample is manifested on the DTA curve by strong slightly asymmetric endothermic peak with maximum at 685°. The interruption of heating at 730° and cooling of the melt resulted in formation of mixture con-

Table 1 Interplanar distances in the products of thermal decomposition of $La(HV_6O_{16})_3 . 19.5 H_2O$

Starting $^+$ compound		290°C		440°C			590°C			730 – 1000°C		
d_{nm}	I_{rel}	d_{nm}	I_{rel}	d_{nm}	I_{rel}	ass.	d_{nm}	I_{rel}	ass.	d_{nm}	I_{rel}	ass.
1.290	100	1.260	100	0.570	12	V	0.572	23	V	0.572	15	V
0.426	8	0.423	18	–			0.543	5	O	0.544	6	O
0.344	28	0.346	35	–			0.482	8	O	0.482	8	O
0.296	17	0.301	18	0.437	100	V	0.436	83	V,O	0.434	100	V,O
0.256	19	0.256	17	0.409	23	V	0.407	32	V	0.408	52	V
0.1916	13	0.1914	13	–			0.371	9	X	–		
0.1799	20	0.1801	21	–			0.363	12	O	0.363	11	O
0.1520	10	0.1520	10	0.339	85	V	0.338	100	V,O	0.338	41	V,O
				–			0.320	29	O	0.321	18	O
				–			0.308	5	O	0.308	8	O
				–			0.296	23	O	0.297	14	O
				0.283	54	V	0.284	65	V	0.283	56	V
				0.276	30	V	0.276	37	V,O	0.276	17	V,O
				0.268	12	V	0.268	13	V	0.268	9	V

O – $LaVO_4$ [10], *V* – V_2O_5 [9], $^+$ – $La(HV_6O_{16})_3 . 19.5 H_2O$ [5], *X* – non identified admixture

Table 1 continued

Starting $^+$ compound		290°C		440°C			590°C			730-1000°C		
d_{nm}	I_{rel}	d_{nm}	I_{rel}	d_{nm}	I_{rel}	ass.	d_{nm}	I_{rel}	ass.	d_{nm}	I_{rel}	ass.
				–			0.261	33	V	0.261	14	V
				0.259	23	V	0.254	8	O	0.255	4	O
				–			0.249	7	O	0.249	5	O
				–			0.240	3	V	0.240	3	V
				–			0.235	5	O	0.234	3	O
				–			0.2260	9	O	0.2269	3	O
				–			0.2228	6	O	0.2221	7	O
				0.2190	24	V	0.2181	16	V,O	0.2177	90	V,O
				–			0.2150	6	V	0.2141	26	V
				–			0.2010	11	O	0.2014	7	O
				0.1989	11	V	0.1990	19	V	0.1993	9	V
				–			0.1949	11	O	0.1948	6	O
				0.1909	15	V	0.1910	30	V	0.1919	17	V
				–			–			0.1895	17	V
				0.1863	17	V	0.1858	16	V	0.1858	12	V
				–			0.1830	8	O	0.1831	6	O

O – $LaVO_4$ [10], *V* – V_2O_5 [9], $^+$ – $La(HV_6O_{16})_3 \cdot 19.5\ H_2O$ [5]

taining V_2O_5 and $LaVO_4$ (Table 1, Fig. 2). The mentioned unidentified admixture decomposed in course of melting. Further increase of temperature up to 1000° has no influence on the qualitative composition of the product.

It must be mentioned that authors [7] have studied the dehydration of $La_2(V_{12}O_{31})_3.37H_2O$ having the same La/V mass amount ratio as the polyvanadate described in this paper. They found the dehydration to be a two-step process, however, they did not deal with its thermal decomposition from the view point of identification of the decomposition products, as well as with its thermal stability.

The thermoanalytical curves of $Y(HV_6O_{16})_3.22H_2O$ (Fig. 3) show, that the dehydration, finished at 395°, is not continuous. The total mass loss is 19.20%, calculated for 23.5 moles of water is 19.24%.

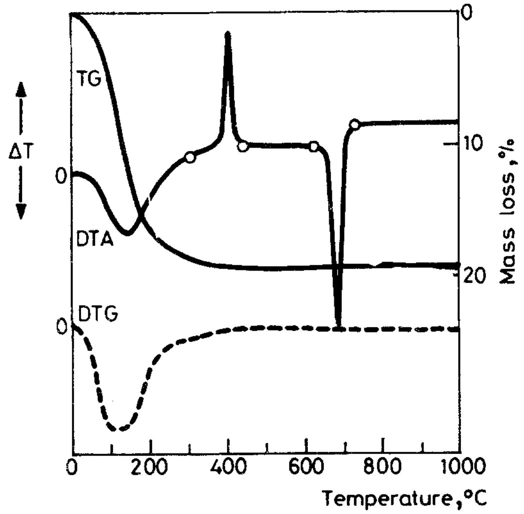

Fig. 3 Thermoanalytical curves of $Y(HV_6O_{16})_3.22H_2O$

The thermal decomposition was interrupted at 300° when the dehydration is still not completed (Fig. 3). The IR spectrum of the product formed is similar to that of parent compound. A shift of two diffractions at smaller angles (d_{nm} = 1.312 and d_{nm} = 0.293) was observed in powder diffraction patterns, a fact which can indicate a layer structure of the polyvanadate anion. Based on the spectral and diffraction properties (Fig. 4, Table 2) we suppose that interlayer distances are diminished in course of dehydration while the parent composition of the anionic layer remains unchanged. Immediately after endothermic processes connected with dehydration, an exothermic maximum at 400° appears on the DTA curve. Identification of the product obtained by interruption of heating at 430° showed that this maximum is connected with formation of new types of compounds, V_2O_5 and YVO_4. The mixture formed is stable up to 620°. The further temperature increase causes a simultaneous melting of both components which is on the DTA curve accompanied by a strong endothermic effect with maximum at 685°. The crystallization of the melt gave V_2O_5 and YVO_4 again.

The courses of thermal decomposition of both compounds, when compared, allow to make following conclusion. The release of last amount of water causes a decomposition of parent compounds and products of thermal decomposition start to be formed according to the scheme:

$$2M^{III}(HV_6O_{16})_3.xH_2O \xrightarrow[-3H_2O]{heating} 17V_2O_5 + 2M^{III}VO_4 + xH_2O$$

In the yttrium salt the exothermic maximum at 400° corresponds to simultaneous formation of both products of decomposition, while in case of

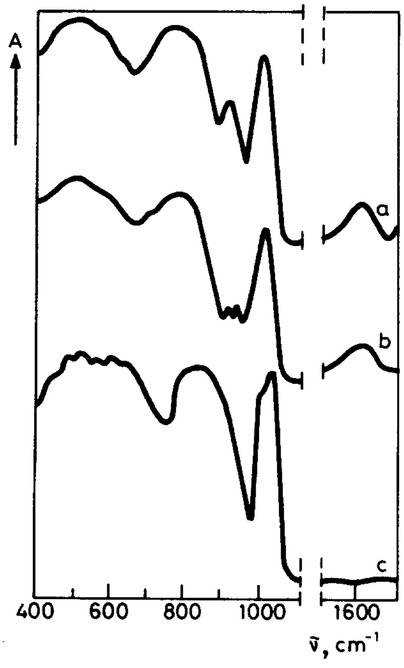

Fig. 4 Infrared spectra of $Y(HV_6O_{16})_3.22H_2O$ a) and products of its thermal analysis obtained at 300°C b), 430-1000°C c)

lanthanum only to crystallization of vanadium pentoxide. The crystallization of $LaVO_4$ is accompanied by further exothermic effect with maximum at 550°.

Table 2 Interplanar distances in the product of thermal decomposition of $Y(HV_6O_{16})_3225H_2O$

Starting compound $^+$		300°C		430 – 1000°C		
d_{nm}	I_{rel}	d_{nm}	I_{rel}	d_{nm}	I_{rel}	ass.
1.312	100	1.282	100	0.577	34	V
0.440	13	0.438	20	0.439	90	V
0.345	26	0.342	34	0.407	30	V
0.293	13	0.286	15	0.356	32	O
0.256	17	0.256	17	0.340	100	V
0.1917	18	0.1914	20	0.287	59	V
0.1798	25	0.1800	27	0.276	31	V
0.1519	13	0.1519	13	0.270	20	V,O
				0.261	33	V
				0.2510	7	O
				0.2408	4	V
				0.2220	5	O
				0.2169	5	V
				0.2136	7	V
				0.1993	15	O
				0.1910	28	V
				0.1893	3	V
				0.1869	7	V
				0.1831	15	O
				0.1779	30	V
				0.1756	10	V
				0.1649	13	V
				0.1593	5	V
				0.1575	12	V

O – YVO4 [8], *V* – V2O5 [9], + – Y(HV6O16)3225H2O [5]

Both mixtures formed, with vanadium pentoxide as essential component, melt at the same temperature, 685°.

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Zusammenfassung — Die Untersuchung der thermischen Eigenschaften von $La(HV_6O_{16})_3 19.55H_2O$ und $Y(HV_6O_{16})_3 22.5H_2O$ ergab, daß die Dehydratation beider Verbindungen diskontinuierlich verläuft. Nach Abgabe des letzten Wassers wird die ursprüngliche Struktur destabilisiert und die Bildung thermischer Zersetzungsprodukte wie V_2O_5 und der entsprechenden Orthovanadate setzt ein.

Die Zersetzung von $La(HV_6O_{16})_3 19.55H_2O$ endet mit der Bildung von V_2O_5 und $LaVO_4$, deren Kristallisierungstemperatur abweicht. Die Zersetzungsprodukte des Yttriumsalzes kristallisieren simultan. Alle Verbindungen bildeten bei 685°C eine Schmelze. Beim Kristallisieren der Schmelze wurden die Gemische V_2O_5-$LaVO_4$ bzw. V_2O_5-YVO_4 gebildet, die bis zu 1000°C stabil sind.