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THERMAL REACTIVITY OF MAGNESIUM HEXAVANADATES

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The thermal reactivities of $MgV_6O_{16}.9H_2O$, $Mg(HV_6O_{16})_2.17H_2O$ and their anhydrous forms were studied within the temperature range 20-1000°C. Both hydrates are thermally unstable. After dehydration, they decompose to V_2O_5 and $Mg(VO_3)_2$. The mixture of decomposition products of $MgV_6O_{16}.9H_2O$ is stable. After decomposition of the second compound, additional reactions take place above 750°C.

The hydrates of hexavanadates with bivalent cations belong to that type of polyvanadates whose structure is stabilized by crystal water. They are thermally unstable. After the loss of the final water, they decompose to other vanadates and V_2O_5 [1-6].

The present paper deals with the dehydration and thermal decomposition of $MgV_6O_{16}.9H_2O$ and $Mg(HV_6O_{16})_2.17H_2O$, which were studied by DTA, X-ray phase analysis and IR spectroscopy in order to describe the thermal reactivities of the anhydrous substances.

Experimental

$MgV_6O_{16}.9H_2O$ and $Mg(HV_6O_{16})_2.17H_2O$ were prepared from the $Mg(VO_3)_2$-HNO_3-H_2O reaction system. Their compositions were verified by chemical analysis, X-ray diffraction patterns and IR spectroscopy [7].

The thermal analysis were performed on a Q-1500 derivatograph (MOM, Budapest). Conditions: air atmosphere, heating rate 10 deg min^{-1}, sample mass 200 mg,Pt crucible, Al_2O_3 as reference material. In order to explain the processes connected with endo and exo effects,the dynamic heating was

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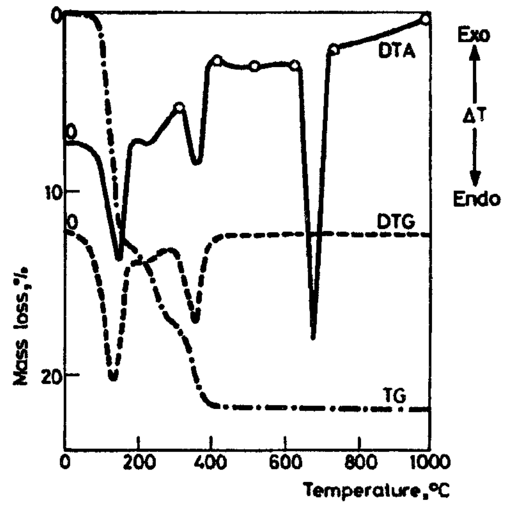

Fig. 1 Thermoanalytical curves of MgV_6O_{16} . $9H_2O$; o – interuption of heating

interrupted at chosen temperatures (according to the DTA curve). The products obtained were cooled to room temperature and identified by X-ray phase analysis and IR spectroscopy. X-ray powder diffraction patterns were taken on a Philips PW 1050 diffractograph, equipped with a copper anticathode and nickel filter. The infrared spectra were taken on a SPECORD M-80 instrument (C.Zeiss, Jena, GDR), with the Nujol null technique.

Results and discussion

Thermal decomposition of $MgV_6O_{16}.9H_2O$

Thermal decomposition of $MgV_6O_{16}.9H_2O$ are given in Fig. 1. In according with [8], the dehydration was found to be a three-step process. The total relative mass loss up to 405° is Δm = 21.6% (Δm(theor.) = 21.65%).The mass losses Δm = 12.5, 17.0 and 21.6% up to 190, 300 and 405° correspond to the release of totals of 5, 7 and 9 moles of water in the various steps. The substance obtained after the second step of dehydration at 322° is amorphous. However, as follows from the IR spectra (Fig. 2 b), the water content is high enough to preserve the parent structure of the anion. Only after total dehydration is the compound decomposed. The formation of new phases is indicated in the DTA curve by a small exothermic maximum at 405°. X-ray phase analysis and the IR spectra of the products obtained at 420, 520 and 640° (Table 1, Fig. 2 c) show that the products of decomposition are V_2O_5 and $Mg(VO_3)_2$ (brannerite type) [9,10].The mixture has the same composition if the starting compound is decomposed isothermally at 400°.

The eutectic mixture of V_2O_5 and $Mg(VO_3)_2$ melts in the temperature range 640-730° (endothermic peak with minimum at 675°). Cooling of the melts obtained on heating the mixture up to 740 or 1000°, respectively, yielded the same compounds as those identified in the mixture before melting (Table 1, Fig. 2).This is interesting fact, because $Mg(VO_3)_2$ itself is thermally unstable [12] and decomposes above 800° to V_2O_5 and $Mg_2V_2O_7$.

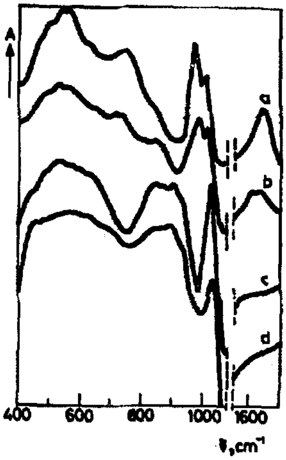

Fig. 2 IR spectra of MgV_6O_{16} . $9H_2O$ (a) and products of its thermal decomposition at various temperatures: 322°C (b), 640 and 740°C (c), 1000°C (d)

Thermal decomposition of $Mg(HV_6O_{16})_2.17H_2O$

It is evident from the thermoanalytical curves (Fig. 3) that the dehydration of $Mg(HV_6O_{16})_2.17H_2O$ in the temperature range 60-400° proceeds in three-steps. The total relative mass loss is Δm = 22.0% (Δm(theor.) = 22.24%).In the individual steps (up to 190, 320 and 405°), the mass losses are Δm = 16.4, 20.5, and 22.0%, and correspond to the total release of 13, 17 and 18 moles of water. The parent structure of the anion is still maintained after the release of the 17 moles of water (320°). The IR spectrum of the partially dehydrated material and that of the original compound are identical (Fig. 4 a). The X-ray powder diffraction pattern is almost the same as that of the original compound. Only the intense diffraction at the lowest Θ value is divided into several diffractions with lower intensities. If we accept the opinion [3] that compounds of the composition $M^{II}(HV_6O_{16})_2.xH_2O$ have a layer structure, then, after the release the of a definite amount of water, only inappreciable changes appear between the layers, while the V-O bond lengths and the structure of the layer remain unchanged. As soon as the last mole of water is released, the structure of the original compound breaks down. The characteristic exothermic maximum at 365° in the curve indicates the formation of new phases. After interruption of the heating at either 420° or 640°, the products of decomposition were V_2O_5 and $Mg(VO_3)_2$ of brannerite type.

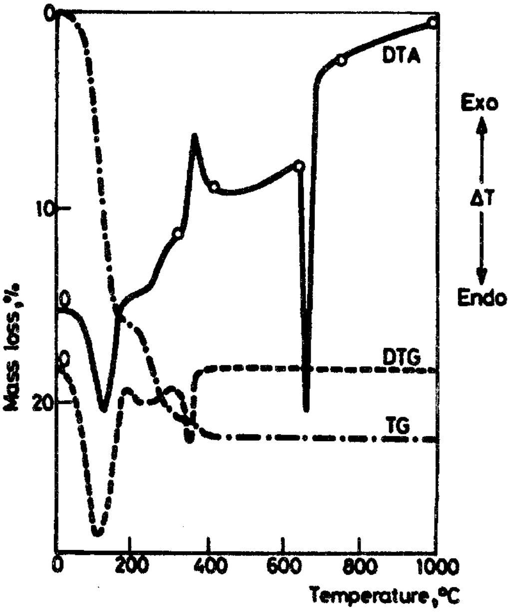

Fig. 3 Thermoanalytical curves of $Mg(HV_6O_{16}.)$. $17H_2O$ (o – interruption of heating)

Table 1 Interplanar distances (nm) in products of thermal decomposition of MgV_6O_{16} . $9H_2O$ at 640, 740 and 1000°C

d, nm	$I_{rel.}$		d, nm	$I_{rel.}$	
0.624	5	M	0.2214	x	M
0.575	6	V	0.2171	22	M V
0.435	100	V M	0.2137	7	M V
0.406	18	V	0.2105	x	M
0.348	3	V	0.2080	3	M
0.339	7	V	0.2032	x	V
0.322	2	M	0.1989	2	V
0.314	12	M	0.1918	8	V M
0.305	16	M	0.1888	9	V M
0.288	22	V	0.1852	3	V
0.275	3	V	0.1831	x	M
0.272	3	M	0.1776	2	V
0.2675	x	V	0.1752	5	V M
0.2606	3	V	0.1739	2	V
0.2481	7	V	0.1679	x	M
0.2399	x	V	0.1645	2	V M
0.2306	2	M	0.1600	5	M

V = V_2O_5 [9]; M = $Mg(VO_3)_2$ [10]; x = less than 2

The melting of the eutectic mixture is an endothermic process proceeding in the temperature range 635-750° (with minimum at 670°). V_2O_5 and $Mg(VO_3)_2$ of brannerite type crystallized out from the cooled melt obtained by heating the mixture to 750° (Table 2, Fig. 4). This mixture consists of the same components as the mixture obtained after the decomposition of MgV_6O_{16} . $9H_2O$, but the molar ratio of the components is different. The mixture contain s 2.5 times more V_2O_5 in this case. This is probably the reason for the additional reactions in the temperature range 750-1000°.Only the presence of V_2O_5 can be identified in the IR spectrum of the product obtained after cooling of the melt heated to 1000° (Fig. 4c). X-ray phase analysis demonstrated the presence of a small quantity of $Mg_2V_2O_7$ (Table 2).There is a slight mass decrease (Δm = 0.25%) in the TG curve in the temperature range 750-1000°, which can be connected with the release of oxygen. The product is brown (V_2O_5 is orange, while $Mg_2V_2O_7$ is ochre).

Table 2 Interplanar distances (nm) in products of decomposition of $Mg(HV_6O_{16})_2 . 9H_2O$

640-750°C			1000°C		
d,nmI	Irel.		d,nm	Irel.	
0.623	2	M	0.574	3	V
0.573	4	V	0.435	100	V
0.435	100	V M	0.423	2	D
			0.413	2	D
0.407	11	V	0.407	8	V
			0.392	x	D
0.346	x	V	0.371	x	D
0.339	4	V	0.347	x	V
0.322	x	M	0.340	2	V
			0.330	x	D
0.313	2	M	0.319	4	D
0.305	5	M	0.306	x	D
0.288	10	V	0.302	x	D
0.275	3	V	0.288	10	V
0.272	x	M	0.276	2	V
0.2680	x	V			
0.2605	2	V	0.2679	x	V D
0.2395	x	V	0.2607	x	V D
0.2309	x	M	0.2401	x	V
0.2178	23	V M	0.2219	x	D
0.2139	6	V M	0.2182	98	V D
0.2103	x	M	0.2140	6	V D
0.2083	x	M			
0.2037	x	V	0.2034	x	V
0.1987	x	V	0.1991	x	V D
0.1916	3	V M	0.1919	3	V D
0.1892	3	V M	0.1894	4	V D
0.1859	2	V	0.1858	x	V
0.1836	x	M			
0.1779	2	V	0.1780	x	V
0.1752	x	V M	0.1775	2	V
0.1740	x	V	0.1735	x	V D
0.1681	x	M			
0.1646	x	V M	0.1648	x	V
0.1631	x	V	0.1634	x	V
0.1604	x	V M	0.1598	x	V D

V = V_2O_5 [9]; M = $Mg(VO_3)_2$ [10]; D = $Mg_2V_2O_7$ [11]; x = less than 2

This indicates the presence of a further component in the mixture, probably a vanadium-oxygen bronze of magnesium. The composition of this bronze has not been identified to date.

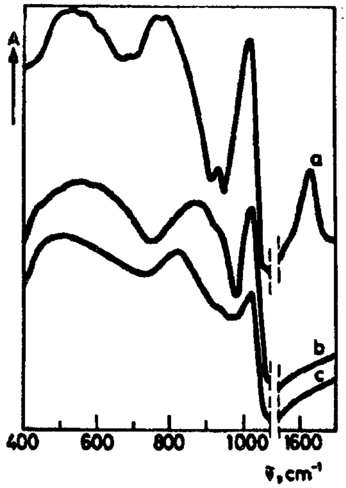

Fig. 4 IR spectra of $Mg(HV_6O_{12})_2 \,.\, 17H_2O$ (a) and products of its thermal decomposition at various temperatures: 640 and 750°C (b), 1000°C (c)

The results show that magnesium hexavanadates are thermally unstable. Their dehydration starts at 60° The anhydrous substances are decomposed V_2O_5 and $Mg(VO_3)_2$ at 400 and 405° respectively:

$$MgV_6O_{16}.9H_2O \xrightarrow[-9H_2O]{400^\circ} 2V_2O_5 + Mg(VO_3)_2$$

$$Mg(HV_6O_{16})_2.17H_2O \xrightarrow[-18\,H_2O]{405^\circ} 5V_2O_5 + Mg(VO_3)_2$$

The stability of mixture of decomposition products depends on their molar ratio.

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Zusammenfassung - Innerhalb des Temperaturbereiches 20-1000° wurde die thermische Reaktivität von $MgV_6O_{16}.9H_2O$, $Mg(HV_6O_{16})_2.17H_2O$ sowie deren wasserfreier Formen untersucht. Beide Verbindungen sind wärmaunbeständig. Nach der Dehydratation zerfallen sie in V_2O_5 und $Mg(VO_3)_2$. Das Gemisch der Zersetzungsprodukte von $MgV_6O_{16}.9H_2O$ is beständig. Nach der Zersetzung der zweiten Verbindung treten oberhalb 750° weitere Reaktionen auf.