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THERMAL REACTIVITY OF SODIUM MANGANESE DECAVANADATES

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The hydrates of sodium manganese decavanadates are thermally unstable: $Na_4MnV_{10}O_{28} \cdot 19H_2O$ decomposes on dehydration to give $Mn(VO_3)_2$, $NaVO_3$ and NaV_3O_8, while $Na_2Mn_2V_{10}O_{28} \cdot 20H_2O$ decomposes to $Mn(VO_3)_2$, $NaVO_3$, NaV_3O_8 and NaV_6O_{15}. At a lower $n(Na) : n(V)$ molar ratio in the starting compound, a product containing a bronze with a higher vanadium(IV) content is formed. The mixtures of products are stable in the temperature ranges 500–1000°C, and 610–1000°C, respectively.

Introduction

The structure of the hydrates of decavanadates is stabilized by crystal water. The parent structure decomposes on hydration. The course of thermal decomposition of a decavanadate depends on the bonding properties of the cation. It has been found that on thermal decomposition of the hydrates of decavanadates of bivalent cations, the corresponding metavanadate and vanadium pentoxide are formed [1]. The products of thermal decomposition of the manganese decavanadate are $Mn(VO_3)_2$ and V_2O_5 [2]. $NaVO_3$ and vanadium bronze, NaV_3O_8, were found to be formed on decomposition of the hydrate of sodium decavanadate [1, 3]. The nature of the compounds formed on thermal decomposition of the crystallohydrates of sodium manganese decavanadates is not known so far.

The present paper deals with the dehydration and thermal decomposition of $Na_4MnV_{10}O_{28} \cdot 19H_2O$ and $Na_2Mn_2V_{10}O_{28} \cdot 20H_2O$, and with the thermal reactivity of the compounds formed on dehydration.

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Experimental

$Na_4MnV_{10}O_{28}\cdot 19H_2O$ and $Na_2Mn_2V_{10}O_{28}\cdot 20H_2O$ were prepared by the reaction of $NaVO_3$, $Mn(ClO_4)_2$ and $HClO_4$, according to [4]. Their purity was verified by chemical analysis, via their X-ray diffraction patterns and by IR spectroscopy.

The thermal analysis was performed on a Q-1500 derivatograph (MOM, Budapest), under the following conditions: temperature interval 20–1000°C, air atmosphere, heating rate 10 deg·min^{-1}, sample weight 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 interrupted at chosen temperatures. The products obtained were cooled to room temperature and identified by X-ray phase analysis and IR spectroscopy. The 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 Perkin-Elmer 180 spectrophotometer, using the Nujol mull technique.

Results and discussion

Thermal decomposition of $Na_4MnV_{10}O_{28}\cdot 19H_2O$

The thermoanalytical curves (Fig. 1) show that the dehydration is a one-step process (70–250°C). The total mass loss up to 500°C [Δm(exp.)] is

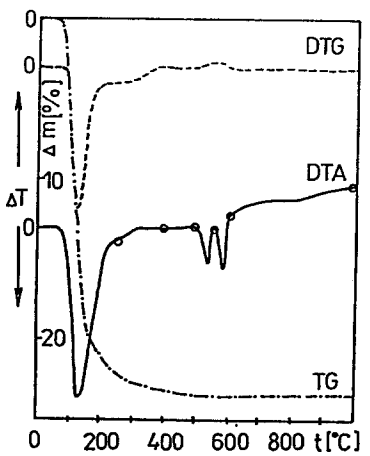

Fig. 1 Thermoanalytical curves of $Na_4MnV_{10}O_{28}\cdot 19H_2O$; o – interruption of heating

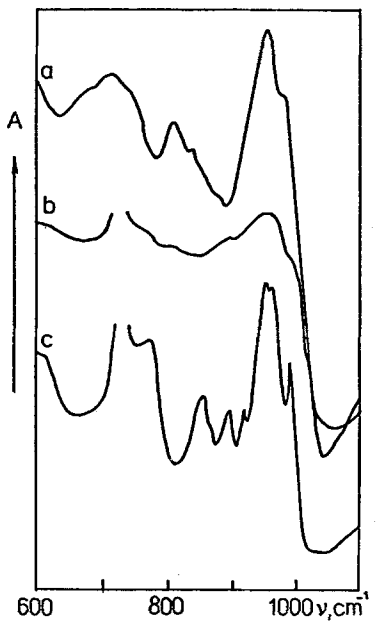

Fig. 2 IR spectra of $Na_4MnV_{10}O_{28}\cdot 19H_2O$ (*a*), and products of its thermal decomposition at: 250°C (*b*); 545 and 1000°C (*c*)

23.50% [Δm(calc.) = 23.66%]. The endo 'shoulder' observed in the range 250–395° is connected with the formation of new phases. Although the IR spectra of the product obtained at 250°C (Fig. 2b) exhibits some changes, the product is X-ray amorphous. The formation of new phases was observed in the temperature range 395–500°C too. The X-ray phase analysis and the IR spectra of the product obtained at 500°C indicate that $Mn(VO_3)_2$, $NaVO_3$ and vanadium-oxygen bronze, NaV_3O_8, are formed as decomposition products.

The mixture of compounds melts in the temperature range 500–600°C (two endothermic peaks, with minima at 535 and 580°C). The cooling of the melt obtained on heating the mixture up to 545, 600 and 1000°C, respectively, yielded the same compounds as those identified before melting (500°C) (Table 1, Fig. 2c).

Thermal decomposition of $Na_2Mn_2V_{10}O_{28}\cdot 20H_2O$

The dehydration of $Na_2Mn_2V_{10}O_{28}\cdot 20H_2O$ (Fig. 3) in the temperature range 70–230°C was found to be a two-step process. The mass loss corresponds to the release of 10 moles of water in each step. The mass loss (up to

Table 1 Interplanar distances (nm) in products of thermal decomposition of $Na_4MnV_{10}O_{28} \cdot 19H_2O$ at 500, 545 and 1000°C

d, nm	$I_{rel.}$		d, nm	$I_{rel.}$	
0.697	100	B N	0.244	5	B M
0.619	x	M	0.232	13	N B M
0.575	2	B	0.224	18	B
0.533	x	B	0.220	2	M
0.492	4	N	0.215	2	M
0.468	x	N	0.213	2	N
0.456	2	B	0.209	3	M N
0.441	7	B M	0.196	5	B N
0.427	2	M	0.192	2	M
0.386	8	B	0.190	3	M
0.367	2	B N	0.185	x	N
0.349	12	B	0.183	2	B
0.345	6	N	0.182	3	B N
0.338	4	B	0.180	9	B
0.325	13	N M	0.176	4	B M
0.320	26	B	0.175	3	N B
0.314	13	M N	0.172	6	N B
0.309	14	M	0.168	x	M
0.302	28	B M	0.165	4	B N M
0.285	x	N	0.1595	3	M
0.276	3	N	0.1587	4	B
0.272	6	M	0.1578	3	B M N
0.265	5	N B	0.1576	x	B

N = $NaVO_3$ [5]
M = $Mn(VO_3)_2$ [4]
B = NaV_3O_8 [5]
x = less than 2

120°C) is Δm = 12.73% and the total relative mass loss up to 230°C is Δm(found) = 25.33% [Δm(calc.) = 24.45%]. The substance obtained after the second step at 215°C is amorphous. The structure of the starting compound decomposes after the release of the final moles of water. The exothermic maximum at 258°C in the DTA curve indicates the formation of new phases. The products obtained after the exothermic process was completed (at 270 and 320°C) are amorphous. In the temperature range 230–570°C, a further small mass loss (1.34%) was observed, which is con-

nected with reduction and the formation of vanadium-oxygen bronzes of sodium. The X-ray phase analysis (Table 2) and the IR spectrum (Fig. 4) of the substance obtained at 550° show that $Mn(VO_3)_2$, $NaVO_3$, and vanadium bronzes, NaV_3O_8 and NaV_6O_{15}, are formed.

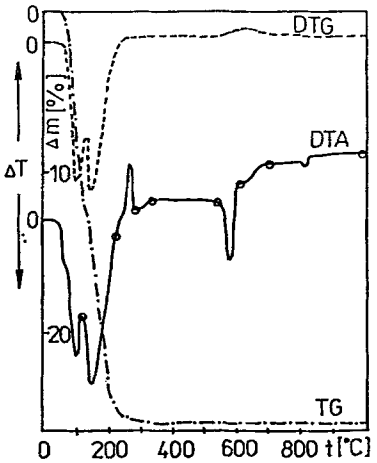

Fig. 3 Thermoanalytical curves of $Na_2Mn_2V_{10}O_{28}\cdot 20H_2O$; o – interruption of heating

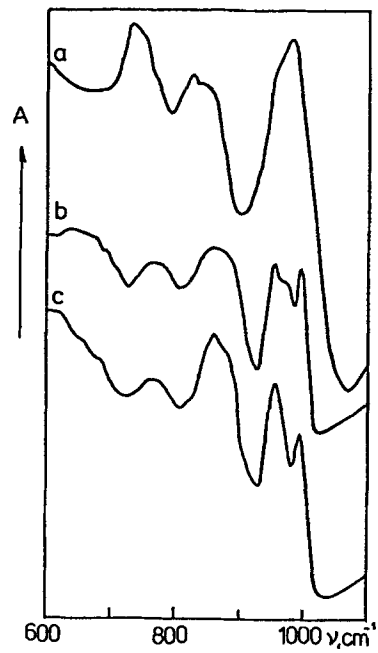

Fig. 4 IR spectra of $Na_2Mn_2V_{10}O_{28}\cdot 20H_2O$ (*a*) and products of its thermal decomposition at various temperatures: 550°C (*b*), 610 and 1000°C (*c*)

Table 2 Interplanar distances (nm) in products of thermal decomposition of $Na_2Mn_2V_{10}O_{28} \cdot 20H_2O$ at:

610, 700 and 1000°C			550°C		
d, nm	$I_{rel.}$		*d*, nm	$I_{rel.}$	
0.949	x	B	0.938	8	B
0.720	45	V	0.720	19	V
0.697	100	B N	0.689	82	B N
0.619	x	M	0.619	8	M
0.583	x	B V	0.577	7	B
0.562	x	V	0.558	4	V
0.531	x	B	0.531	7	B
0.501	x	N V	0.502	4	N
0.479	3	N V	0.473	8	N
0.440	4	M B	0.440	20	M
0.427	17	M	0.429	9	M
0.384	4	B V	0.385	16	B
0.362	5	N B V	0.362	6	N B
0.347	8	N B V	0.347	22	B V
			0.344	19	N
0.337	5	B V	0.336	19	B V
0.326	14	M N	0.326	66	N M
0.320	12	B V	0.319	82	B V
0.316	20	M N	0.316	100	M N
0.305	49	V M	0.308	54	V M
0.303	70	B M	0.303	95	M
			0.300	52	B
0.291	9	B V	0.291	16	B V
0.284	x	N			
0.280	x	N			
0.273	13	M V	0.273	59	M V
0.265	x	B N	0.264	9	B N
0.256	2	V	0.256	8	V
0.251	2	V	0.250	3	V
0.243	2	M V	0.244	10	M V
0.242	4	B V	0.241	4	B
0.232	17	N B M	0.232	42	N B M
0.226	13	B V	0.226	28	B V
0.221	7	M	0.221	11	M
0.217	22	V	0.217	7	V
0.215	22	M N	0.215	8	M

Table 2 (continued)

610, 700 and 1000°C			550°C		
d, nm	$I_{rel.}$		*d*, nm	$I_{rel.}$	
			0.213	10	N
0.208	4	M N	0.207	20	M N
0.200	2	V	0.200	11	V
0.196	4	B N	0.196	12	N B
0.192	4	M V	0.192	13	V M
0.190	4	M	0.190	16	M
0.186	2	M V	0.188	15	N V
0.1823	x	B			
0.1817	4	B N	0.1816	5	B
0.1800	5	B V	0.1799	30	B
0.1762	8	B M N V	0.1765	32	B M N V
			0.1743	6	B
0.1716	3	B N	0.1717	11	N B
0.1682	2	M	0.1685	6	M V
0.1669	x	V			
0.1644	6	B M N V	0.1646	17	B V
0.1597	3	B M			
0.1590	2	V			
0.1580	x	B M N			
0.1555	x	B			
0.1543	9	B M V	0.1543	29	B M V

N = $NaVO_3$ [5]
M = $Mn(VO_3)_2$ [4]
B = NaV_3O_8 [5]
V = NaV_6O_{15} [5]
x = less then 2

In the temperature interval 550°–610°C, an endothermic peak with minimum at 578°C was observed, followed by a small peak between 610° and 700°C, corresponding to melting of the mixture. On cooling of the melt obtained by heating to 610°, 700° or 1000°C, the same components crystallized out as those present in the mixture before melting (550°C). Although we identified the same substances, the IR spectra of the products formed at 550° and 610°C differed. In this region, a further small mass loss was observed, which indicates oxygen release, probably according to the equation:

$$5NaV_3O_8 \xrightarrow{-1/2\,O_2} 2\,NaV_6O_{15} + 3NaVO_3$$

The small endothermic peak in the range 800°–815°C probably corresponds to the melting of $Mn(VO_3)_2$ in the mixture.

The results show that hydrates of sodium manganese decavanadates are thermally unstable. Their dehydration starts at 70°C. The anhydrous substances are decomposed. The formation of new compounds, completed at 500° and 610°C, respectively, can be described by the equation:

$$Na_4MnV_{10}O_{28} \cdot 19H_2O \xrightarrow[-19\,H_2O]{} Mn(VO_3)_2 + 2NaVO_3 + 2NaV_3O_8$$

$$Na_2Mn_2V_{10}O_{28} \cdot 20H_2O \xrightarrow[-20\,H_2O]{1/2\,O_2} 2\,Mn(VO_3)_2 + 3/5\,NaVO_3 + NaV_3O_8 + 2/5\,NaV_6O_{15}$$

Manganese and sodium metavanadates and vanadium bronzes are formed by thermal decomposition. At a lower $n(Na) : n(V)$ molar ratio in the starting compound, a product containing a bronze with a higher vanadium(IV) content ($NaV^{IV}V_5^{V}O_{15}$) is formed The mixtures of products are stable in the temperature ranges 500°–1000° and 610°–1000°, respectively.

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Zusammenfassung — Hydrate von Natrium-magnesiumdekavanadat sind thermisch instabil. $Na_4MnV_{10}O_{28} \cdot 19H_2O$ zersetzt sich durch Dehydratierung in $Mn(VO_3)_2$, $NaVO_3$ und NaV_3O_8 und $Na_2Mn_2V_{10}O_{28} \cdot 20H_2O$ in $Mn(VO_3)_2$, $NaVO_3$, NaV_3O_8 und NaV_6O_{15}. Bei einem niedrigerem n(Na):n(V) molarem Verhältnis der Ausgangsverbindungen wird ein Produkt geformt, welches eine Bronze mit einem höherem Vanadium(IV)-gehalt enthält. Das Produktegemisch ist im Temperaturbereich 500°-1000°C bzw. 610°-1000°C thermisch stabil.