Thermochimica Acta, 143 (1989) 325–332
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PREPARATION AND THERMAL REACTIVITY OF MAGNESIUM METAVANADATES

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(Received 20 September 1988)

ABSTRACT

Metavanadates of the composition $Mg(VO_3)_2 \cdot 6\text{–}8H_2O$ were prepared from aqueous–alcoholic and aqueous–acetonic media. By their gradual dehydration, the hydrates with four and two molecules of crystal water as well as two modifications of anhydrous $Mg(VO_3)_2$ were obtained. The high temperature modification of magnesium metavanadate decomposes at 775 °C to V_2O_5 and $Mg_2V_2O_7$, and the oxide immediately melts. Magnesium divanadate undergoes a polymorphic change at 930 °C.

INTRODUCTION

The compositions of the metavanadates of $Mg(VO_3)_2 \cdot nH_2O$, where $n = 5.5$, 6 or 7, are considered in refs. 1 and 2, which do not, however, contain any descriptions of the preparation of the given compounds. The authors [2] refer to paper [3] which deals with the preparation of calcium metavanadate, but the application of the method described there to the preparation of magnesium metavanadate is not successful without some modification. In addition, refs. 1 and 2 lack any data which would enable the identification of magnesium metavanadates or make clear some of their properties.

The present paper deals with the experimental conditions for the preparation of differently hydrated magnesium metavanadates, their thermal stability, and the nature of the decomposition of the anhydrous salt. All the prepared compounds were characterized by IR spectroscopy and X-ray powder diffraction patterns.

EXPERIMENTAL

Synthesis of $Mg(VO)_3)_2 \cdot nH_2O$

Small portions of a thoroughly homogenized mixture of equimolar amounts of MgO and V_2O_5 were added to water heated to 90 °C. The volume of water should be large enough to yield a 0.08 mol dm^{-3} concentration of vanadium in the reaction solution. After the mixture has dissolved, the reaction solution must be stirred for 30 minutes. The preparation of the differently hydrated magnesium metavanadates is significantly influenced by the pH value of the solution cooled at room temperature, as well as by the type of precipitant used. If the pH value is less than the values given below, solid MgO must be added to the solution, which is heated again and the process of stirring repeated. The best pH values for preparation of $Mg(VO_3)_2 \cdot 6H_2O$ are in the range 7.5–8.1 and a volume of ethanol twice that of the reaction solution is needed. When preparing $Mg(VO_3)_2 \cdot 7H_2O$, acetone in the volume ratio 1 : 1 must be added to a solution having a pH value between 7.3 and 7.6. The narrowest range of pH, 8.85–8.90, was found to be suitable for the precipitation of $Mg(VO_3)_2 \cdot 8H_2O$ from a solution containing twice the volume of acetone. Solutions in which a very soft haze is formed after addition of the precipitant were put into a refrigerator for at least 24 hours. The very soft crystals obtained were washed on a filter with a sufficient amount of the precipitant and were freely dried at room temperature.

$Mg(VO_3)_2 \cdot 6H_2O$ is a colourless, stick-shaped substance, $M = 330.29$ g mol^{-1}. Calculated: 7.36% Mg, 30.85% V, 32.73% H_2O. Found: 7.37% Mg, 30.63% V, 33.25% H_2O.

$Mg(VO_3)_2 \cdot 7H_2O$ is a creamy yellow substance with an irregular crystal shape, $M = 348.30$ g mol^{-1}. Calculated: 6.92% Mg, 29.25% V, 36.20% H_2O. Found: 7.07% Mg, 29.50% V, 36.50% H_2O.

$Mg(VO_3)_2 \cdot 8H_2O$ crystallizes in long colourless needles, $M = 366.32$ g mol^{-1}. Calculated: 6.63% Mg, 27.81% V, 39.34% H_2O. Found: 6.52% Mg, 27.76% V, 39.20% H_2O.

Methods and instrumentation

The magnesium content was determined complexometrically [4]. Vanadium(V) was determined volumetrically by titrating with iron(II) sulphate using diphenylamine as indicator [5]. The amount of water of crystallization was estimated by drying the substance at 400 °C as well as by thermogravimetry. The presence of carbon in the samples was checked using the automatic CHN/O analyser made by Carlo Erba, model 1104. The results were negative.

The thermal analysis of the compounds was performed on a Q 1500 D derivatograph (MOM Budapest), sample weight 100 mg, heating rate 10 °C min^{-1}. The products, obtained by interrupted DTA, by drying over silica gel and by isothermal heating at definite temperatures (see Table 1) to constant weight in a crucible furnace, were cooled to room temperature and identified by IR spectroscopy and X-ray phase analysis.

TABLE 1

Isothermal preparation of magnesium metavanadates

Reactant	Experimental conditions	Product
$Mg(VO_3)_2 \cdot 8H_2O$	Room temperature	$Mg(VO_3)_2 \cdot 6H_2O$
	100 °C	$Mg(VO_3)_2 \cdot 2H_2O$
$Mg(VO_3)_2 \cdot 7H_2O$	40 °C, silica gel	$Mg(VO_3)_2 \cdot 4H_2O$
	100 °C	$Mg(VO_3)_2 \cdot 2H_2O$
$Mg(VO_3)_2 \cdot 6H_2O$	100 °C	$Mg(VO_3)_2 \cdot 2H_2O$
$Mg(VO_3)_2 \cdot 2H_2O$	350 °C	α-$Mg(VO_3)_2$
α-$Mg(VO_3)_2$	500 °C	β-$Mg(VO_3)_2$

The IR spectra were taken on a Perkin–Elmer type 567 instrument using the nujol technique.

The X-ray diffraction patterns were taken on a Philips PW 1050 diffractograph equipped with a copper anticathode and a nickel filter.

RESULTS AND DISCUSSION

The hydrated magnesium metavanadates are extremely soluble compounds. This makes their isolation from aqueous solution very difficult. The procedure by which the vanadium concentration is increased by evaporation of the solvent excess, combined with subsequently by cooling the solution at 2–5 °C is considered to be entirely unsuccessful. The problem of attaining a suitable vanadium concentration is present even when a precipitant is used. When precipitants are added to the solutions whose vanadium concentration is higher than in those mentioned above, the haze first formed disappears after a short standing time and a very viscous yellow liquid appears at the bottom of the beaker.

The crystallohydrates prepared are the highest hydrated forms of vanadates of the $M^{II}(VO_3)_2 \cdot nH_2O$ composition.

The composition of the investigated compounds was determined on the basis of chemical analysis. However, the molar ratio Mg : V = 1 : 2 was not sufficient proof of their incorporation into the group of hydrated metavanadates. The crucial point in the determination of the formulae of these compounds was the presence of anhydrous magnesium metavanadate of known structure [6]. Thus, if the prepared compounds belong to the group of variously hydrated magnesium metavanadates, then $Mg(VO_3)_2$ must be the end product of their dehydration. The results of the differential thermal analysis satisfied this condition.

In Fig. 1, it can be seen that the higher the content of water of crystallization, the lower the thermal stability of the compound. The hexahydrate begins to release its water of crystallization at 80 °C, the

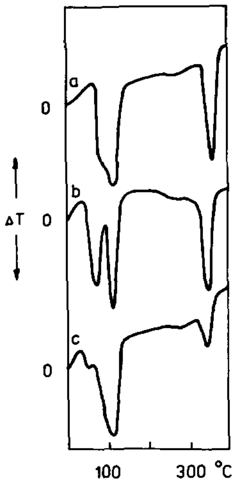

Fig. 1. DTA curves. (a) $Mg(VO_3)_2 \cdot 6H_2O$, (b) $Mg(VO_3)_2 \cdot 7H_2O$, (c) $Mg(VO_3)_2 \cdot 8H_2O$.

heptahydrate at 50 °C and the octahydrate at just 40 °C. The different contents of water of crystallization and the nature of its bonding in the structure of the investigated compounds, also influence the first dehydration phase, up to approximately 150 °C.

The endothermic process in $Mg(VO_3)_2 \cdot 6H_2O$ occurs between 80 and 150 °C (Fig. 2) and is connected with the release of 4 molecules of water (calculated for one formula unit) and with the simultaneous formation of

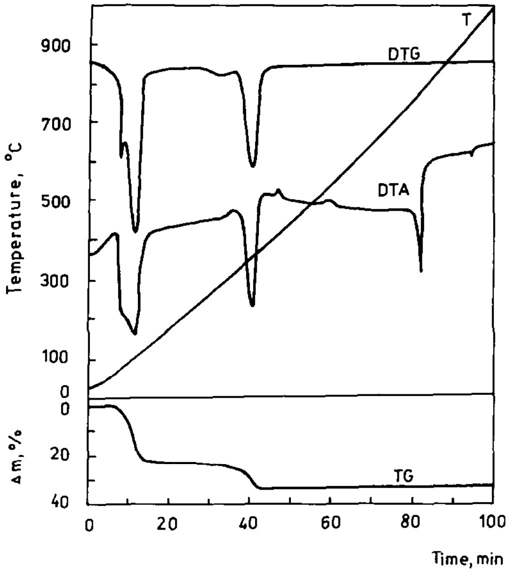

Fig. 2. DTA, TG and DTG curves of $Mg(VO_3)_2 \cdot 6H_2O$.

TABLE 2

X-Ray phase analysis results

d_{hkl} (nm)	I_{rel}	Assignment	d_{hkl} (nm)	I_{rel}	Assignment	d_{hkl} (nm)	I_{rel}	Assignment
0.620	20	M	0.303	100	D+M	0.208	12	M
0.571	14	O	0.286	27	O	0.198	4	O
0.509	10	D	0.275	6	O	0.191	10	O+M
0.504	8	D	0.271	20	M	0.189	7	M
0.434	75	O	0.267	4	D	0.183	4	M
0.429	70	D+M	0.260	14	O	0.179	4	M
0.406	20	O	0.258	9	D	0.177	4	O
0.389	7	D	0.252	10	D	0.175	8	O
0.369	6	D	0.249	5	D	0.174	12	O+M
0.347	4	O	0.239	4	O	0.167	4	M
0.338	14	O	0.230	11	M	0.164	10	O+M
0.328	6	D	0.218	26	O+M	0.160	5	M
0.322	13	M	0.217	25	M	0.157	4	O
0.315	35	D	0.214	9	O	0.156	4	O
0.313	47	M	0.209	9	O+M	0.154	10	O+M

M, β-$Mg(VO_3)_2$; O, V_2O_5; D, $Mg_2V_2O_7$.

crystalline $Mg(VO_3)_2 \cdot 2H_2O$. The hydrate formed is stable for approximately a further 100 degrees; its dehydration begins slowly at 250 °C and reaches its highest rate within the range 320–370 °C. A weight loss corresponding to release of almost 50% of the water results in only insignificant changes in the IR spectrum and in the X-ray diffraction pattern, compared with those of the dihydrate. These facts indicate that $Mg(VO_3)_2 \cdot 2H_2O$ has a very stable structural arrangement; its structure is destroyed in the temperature interval 320–370 °C, after the release of more than 50% of the water. The exothermic process with a maximum at 405 °C indicates the formation of α-$Mg(VO_3)_2$. Its change to the β modification with a known structure [6] is connected with the second, not very pronounced, exothermic effect (maximum at 550 °C). Increasing the temperature of the sample further leads to two endothermic effects (minima at 775 and 930 °C). When DTA was interrupted at 770 °C, β-$Mg(VO_3)_2$ was found to be still stable. The products obtained by the interruption of dynamic heating at 800 and 1000 °C and cooled to room temperature have the same composition, according to X-ray phase analysis (Table 2).

On the basis of these results, both processes can be explained as follows. The polarizing properties of the magnesium cation increase with temperature so much that above 770 °C magnesium metavanadate decomposes, magnesium divanadate and vanadium pentoxide result and the latter compound immediately melts. The polymorphic change of β-$Mg_2V_2O_7$ to γ-$Mg_2V_2O_7$ [7] connected with the last endothermic process is obviously a reversible one. The presence of β-$Mg(VO_3)_2$ in the products (see Table 2) is evidently connected with the subsequent reaction between magnesium divanadate and vanadium pentoxide in the course of their cooling. We found that the amount of β-$Mg(VO_3)_2$ present was dependent on the rate of cooling of the products, as well as on the size of the reaction surface.

The processes taking place during the heating of $Mg(VO_3)_2 \cdot 7H_2O$ differ from those discussed above only in the formation of $Mg(VO_3)_2 \cdot 4H_2O$ which precedes the formation of dihydrate in the interval 50–110 °C (Fig. 1b). The formation of the tetrahydrate is also indicated on the TG curve, on which an expressionless break appears at 110 °C. Tetrahydrate is thermally unstable and changes to dihydrate at moderately increased temperatures.

The release of crystal water from the structure of $Mg(VO_3)_2 \cdot 8H_2O$ is characterized by a TG curve analogous with that of the hexahydrate, although the DTA curve (Fig. 1c) shows a small endothermic minimum within the temperature range 40–80 °C. When interrupting the DTA, the hydrate found was the same as that discussed in the case of the hexahydrate.

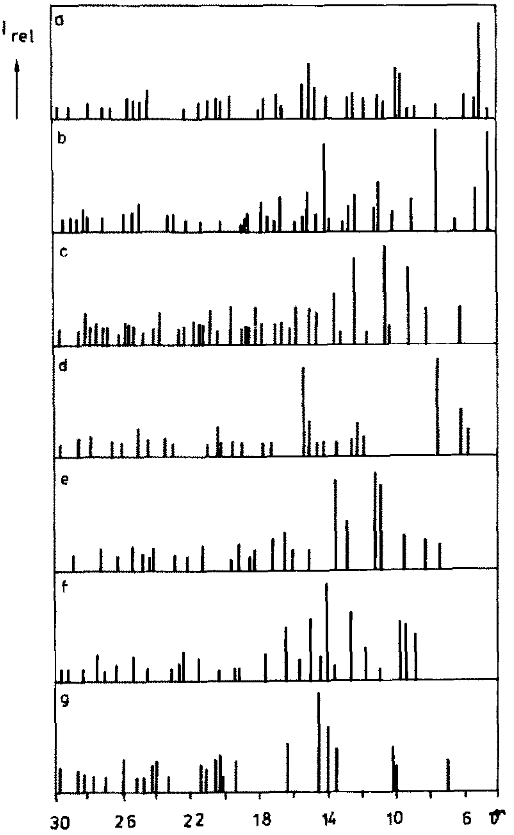

Fig. 3. X-ray powder diffraction patterns. (a) $Mg(VO_3)_2 \cdot 8H_2O$, (b) $Mg(VO_3)_2 \cdot 7H_2O$, (c) $Mg(VO_3)_2 \cdot 6H_2O$, (d) $Mg(VO_3)_2 \cdot 4H_2O$, (e) $Mg(VO_3)_2 \cdot 2H_2O$, (f) α-$Mg(VO_3)_2$, (g) β-$Mg(VO_3)_2$.

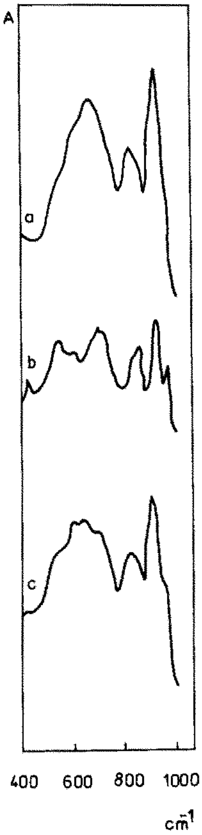

Fig. 4. IR spectra. (a) $Mg(VO_3)_2 \cdot 8H_2O$, (b) $Mg(VO_3)_2 \cdot 7H_2O$, (c) $Mg(VO_3)_2 \cdot 6H_2O$.

However, we found that the octahydrate changed very slowly (within 4 months) to hexahydrate at room temperature.

All the above discussed lower hydrates arising during DTA, as well as the α and β modifications of $Mg(VO_3)_2$, were also prepared by isothermal heating under the conditions given in Table 1.

The X-ray diffraction patterns and the IR spectra of magnesium metavanadates are shown in Figs. 3, 4 and 5.

The IR spectra of the octa- and hexahydrate indicate a considerable similarity in the V–O chain of both hydrates. This finding and the abovementioned slow change of octa- to hexahydrate enable us to assume that water molecules in $Mg(VO_3)_2 \cdot 8H_2O$ are very weakly bound and their release from the structure does not cause a significant rearrangement of the remaining atoms.

The structural analogy between α- and β-$Mg(VO_3)_2$ is also apparent (Fig. 5c, d). It seems probable that in both modifications there are only small differences in the coordination polyhedron of the vanadium atom.

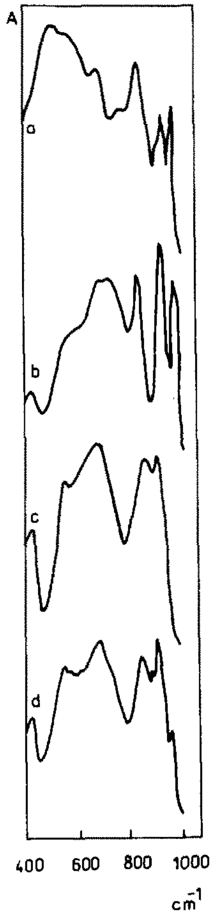

Fig. 5. IR spectra. (a) $Mg(VO_3)_2\cdot 4H_2O$, (b) $Mg(VO_3)_2\cdot 2H_2O$, (c) α-$Mg(VO_3)_2$, (d) β-$Mg(VO_3)_2$.

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