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THERMAL DECOMPOSITION OF VANADIUM, MOLYBDENUM AND VANADIUM-MOLYBDENUM MIXED OXALATES AS THE PRECURSORS OF $V_2O_5-MoO_3$ CATALYSTS

E. Wenda

Department of Chemistry, Jagiellonian University,
30-060 Kraków, Karasia 3, Poland

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The processes accompanying the preparation of vanadia, molybdena and vanadia-molybdena catalysts by the thermal decomposition of appropriate simple or complex oxalates were studied using DTA and TG methods, IR spectroscopy and X-ray analysis. The complex oxalates of vanadium and molybdenum decompose into VO_2 and MoO_2, which are subsequently oxidized at 500° in air to V_2O_5 and MoO_3. The β-phase of ammonium vanadia-molybdena bronze in the samples containing both metals was thermally stable and did not decompose after 2 h of heating at 400°.

$V_2O_5-MoO_3$ catalysts are frequently used for the selective oxidation of aromatic hydrocarbons and accordingly have been the object of numerous physico-chemical studies. It has been demonstrated that the phase composition of the catalytically active mass (and hence its catalytic properties too) is fairly complicated and depends on both the method by which the fresh catalysts were prepared and the redox processes occurring when the catalyst remains in contact with the reagents of the catalytic reaction. The elucidation of all these effects necessitates a thorough study of the individual stages in the preparation of the catalysts. The synthesis of the industrial $V_2O_5-MoO_3$ catalyst by decomposition of the oxalates was recently the object of a patent [1]. However, there is a complete lack of physico-chemical data concerning this process in the literature. The aim of the present research was therefore to study the course of thermal decomposition of the products obtained by the calcination of vanadium and molybdenum oxalates.

To this end, thermogravimetry and differential thermal analysis were carried out on the samples obtained by evaporation of solutions of NH_4VO_3 or H_2MoO_4, and in a parallel series of experiments the physico-chemical properties of the final decomposition products (as calcined at 400°) were investigated.

Experimental

Vanadium and molybdenum pure and mixed oxalates were prepared as follows. Hot solutions of ammonium metavanadate (p.a., Reachim) and of molybdic acid (p.a., POCh, Poland) were prepared, to which the appropriate amounts of solid oxalic acid (pure, POCh, Poland), were added. The molar ratios of NH_4VO_3

and/or H_2MoO_4 to oxalic acid were chosen so as to include the concentration range indicated in the patent literature [1]. The solutions were evaporated on a water bath and the residues dried for 1 h at 110°. Subsequently the preparations were calcined for 1 at 360° and for 1 at 400°. The temperature of the latter period of calcination corresponds to the conditions under which industrial catalysts are employed. It should also be noted that the thermal curves of the samples indicated that all decomposition processes occurred below 400°.

Aqueous solutions of sample No. 1 (NH_4VO_3, as indicated in Table 1), sample No. 2 (as prepared according to [2]) and sample No. 6 (as prepared with a molar ratio of $H_2MoO_4 \cdot H_2O$ to $H_2C_2O_4 \cdot 2\,H_2O$ equal to 1 : 3) were dried and calcined as described above. They were applied as standards for interpretation of the experimental results.

Differential thermal analysis and thermogravimetry were carried out using a Mettler TA-2 Thermoanalyser. Al_2O_3 was used as reference material. The flow of air passing over the sample was 4 l/h. Two heating rates were applied in order

Table 1

Compositions and chemical and

Sample No.	Molar ratio of components			Chemical analysis, weight %			
	NH_4VO_3	$H_2MoO_4 \cdot H_2O$	$H_2C_2O_4 \cdot 2H_2O$	V (total)	Mo (total)	V^{4+}	Mo^{5+}
1	1	—	—	56.18	—	1.05	—
2		—	1 + 1 mol $(NH_4)_2C_2O_4$	not determined	—	61.42	—
3	1	—	1	55.68	—	36.79	—
4	1	—	0.5	54.93	—	13.92	—
5	1	—	0.34	57.64	—	3.09	—
6	—	1	3	—	not determined	—	not determined
7	—	1	1.3	—	63.33	—	3.71
8	1	0.27	0.34	37.37	20.88	12.65	—

to obtain either well-resolved heat effects (at 10°/min) or a distinct weight loss (at 5°/min).

The samples dried at 110° were heated from room temperature to 500°, while the samples calcined at 400° were heated from room temperature to 700°. The results of thermal analysis are given in Figs 1—6. The decomposition products were characterized by X-ray powder diffractometry using a DRON-2 X-ray diffractometer (CuK_α radiation). The interplanar distances of the products were compared with data from the Powder Diffraction File [3]. The IR spectra were obtained using the KBr pellet technique with a UR-10 Zeiss Spectrometer (Tables 2 and 3).

The vanadium and molybdenum concentrations in the final decomposition products were determined by means of a Perkin-Elmer Atomic Absorption Spectrophotometer. The concentrations of ions of lower valency were determined by permanganometric titration.

The results of chemical analysis are given in columns 5—8 of Table 1.

phase analyses of samples 1—8

Phase analysis		
Samples before calcination	Samples after calcination at 360°	Samples after calcination at 400°
NH_4VO_3 $(NH_4)_2V_6O_{13}$	V_2O_5 $(NH_4)_2V_6O_{13}$, V_3O_7	V_2O_5
$(NH_4)_3[VO_2(C_2O_4)_2] \cdot 2\ H_2O$ $(NH_4)_2[(VO)_2(C_2O_4)_3]$	not calcined at 360°	amorphous sample
amorphous sample	amorphous sample	V_2O_5, VO_2
$(NH_4)_3[VO_2(C_2O_4)_2] \cdot 2\ H_2O$ $(NH_4)_2V_6O_{16}$ NH_4VO_3	V_2O_5, V_3O_7, $VO_2 \cdot yH_2O$	V_2O_5, VO_2
$(NH_4)_3[VO_2(C_2O_4)_2] \cdot 2\ H_2O$ NH_4VO_3 $(NH_4)_2V_6O_{16}$ $VO_2 \cdot yH_2O$	V_2O_5, V_3O_7	V_2O_5
$Mo(C_2O_4)_3$	not calcined at 360°	MoO_3, MoO_2
$Mo(C_2O_4)_3$	MoO_3, MoO_2(trace)	MoO_3
NH_4VO_3, $Mo(C_2O_4)_3$ MoO_3	$(Mo_{0.3}V_{0.7})_2O_5$ $(NH_4)_{0.3}V_{1,7}Mo_{0.3}O_5$	$(Mo_{0.3}V_{0.7})_2O_5$ $(NH_4)_{0\text{-}3}V_{1.}M_7o_{0.3}O_5$

Table 2

Bands in IR spectra of samples $1_{(110°)}$—$8_{(110°)}$ before calcination at 400°

Bands, cm^{-1}							Character of bands [2, 5, 8]
$H_2C_2O_4 \cdot 2H_2O$	$1_{(110°)}$	$2_{(110°)}$	$3_{(110°)}$	$4_{(110°)}$ and $5_{(110°)}$	$6_{(110°)}$ and $7_{(110°)}$	$8_{(110°)}$	
3420—3580							ν(OH)
1720—1660		1730	1710	1710	1730	1710	$\nu_a(C=O)$
		1690	1670	1680	1680	1675	$\nu_a(C=O)$
				1640		1640	$\delta(H_2O)$
1615 1445					1440		ν(C—O), δ(OH)
	1410	1410	1400	1400	1400	1400	$\delta(NH_4^+)$
1345							
1250		1280	1280 1250	1270	1245	1270	ν(C—O)
1130							(C—OH)
	1010			1010			$\nu(V=O)$ in $(NH_4)_2V_6O_{16}$
	940	925 900	975 940 910	970 915	965 920	965 930	vibration of various metal—oxygen bonds
	895 850			890	850	890	δ(V—O) in NH_4VO_3
728		810	810	795 740	840 805	800	vibration of various metal—oxygen bonds
	685					710	V—O—V in NH_4VO_3
610—585	505	525	610	610	535	610	

Table 3

Bands in IR spectra of samples $1_{(400°)}$—$8_{(400°)}$ after calcination at 400°

Bands, cm^{-1}							Character of bands
$1_{(400°)}$	$2_{(400°)}$	$3_{(400°)}$—$4_{(400°)}$	$5_{(400°)}$	$6_{(400°)}$	$7_{(400°)}$	$8_{(400°)}$	
1620	one broad band	1620	1620	1640		1630	$\delta(H_2O)$
						1420	$\delta(NH_4^+)$
				1070			
						1038	band in IR spectrum of Ag—V—Mo bronze[12]
1022	950—1010	1020	1010			1010	$\nu(V=O)$
				995	1000	995	$\nu(Mo=O)$
830		825	940 810	880 820	980 890 879 830	855 830	vibration of various metal—oxygen bonds
600 475		475	530	630 515 485	650	635 535 460	

Results and discussion

Sample 1

Sample 1 was obtained by evaporation of an aqueous solution of ammonium metavanadate and drying the residue at 110°. The X-ray powder diffraction patterns of the non-calcined product indicated the presence of NH_4VO_3 as the main component, besides which lesser amounts of ammonium hexavanadate $(NH_4)_2V_6O_{16}$ [4] an intermediate of NH_4VO_3 decomposition, were present. The bands recorded in the IR spectrum correspond to those of NH_4VO_3 and also $(NH_4)_2V_6O_{16}$ (Table 2) [5].

The first distinct effect in the DTA curve (Fig. 2a) at 212°, is endothermic and is accompanied by the loss of 14.1 % of the initial sample weight. This corresponds well to the reaction

$$6\,NH_4VO_3 \rightarrow (NH_4)_2V_6O_{16} + 4\,NH_3 + 2\,H_2O \qquad (1)$$

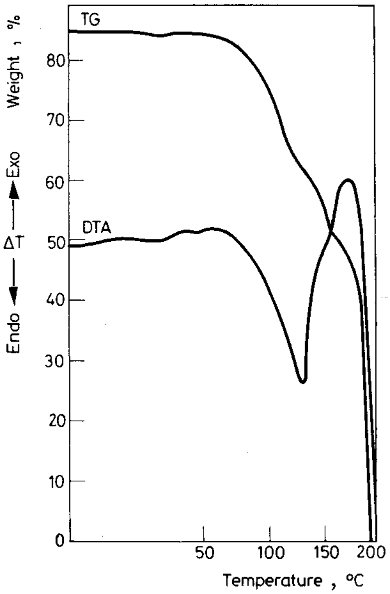

Fig. 1. DTA and TG curves of $H_2C_2O_4 \cdot 2\,H_2O$. Heating rate 10° min^{-1}

observed by Deschanvers and Nouet [6, 7] at 180° during their studies of the decomposition of ammonium metavanadate in air. The theoretical loss of weight calculated for this reaction is 14.8%. The fact that our value is somewhat lower can be explained by the contamination of the initial sample with $(NH_4)_2V_6O_{16}$, as already mentioned.

Within the temperature range 300—360° two endothermic effects are observed, at 314 and 331°, and an exothermic one at 355°. This indicates that the decomposition of $(NH_4)_2V_6O_{16}$ is a fairly complicated process. The exothermic effect appears when the decomposition is nearly complete, and is most probably due to oxidation of the reduced products of $(NH_4)_2V_6O_{16}$ decomposition. The presence of V_3O_7 in the samples calcined at 360° suggests that this lower oxide of vanadium, which is easily oxidized to V_2O_5, may be one of the products of $(NH_4)_2V_6O_{16}$ decomposition.

The total loss in weight corresponding to the reaction

$$(NH_4)_2V_6O_{16} \rightarrow 2\,NH_3 + H_2O + 3\,V_2O_5 \qquad (2)$$

amounts to 7.2% of the initial mass of the NH_4VO_3 sample. However, in our case it was somewhat larger, amounting to 8.6%, which indicates that the oxidation of the lower oxide (or oxides) of vanadium was not complete. It should be mentioned here the sample $1_{(400°)}$ calcined at 400° (that is under conditions where oxidation is much easier) still contained 1.05 wt.% of V^{4+}.

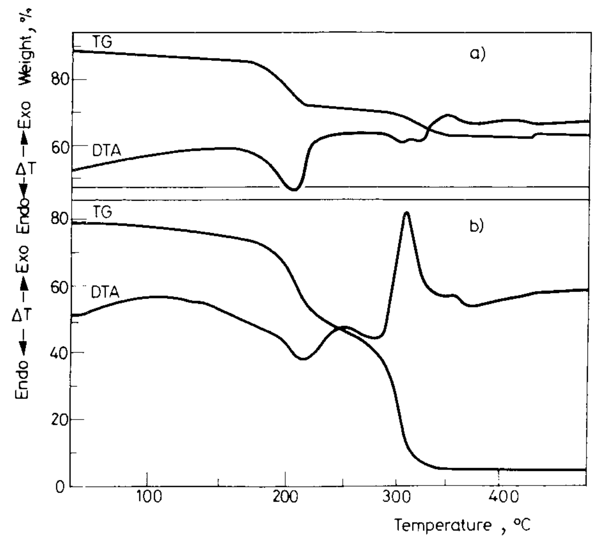

Fig. 2. DTA and TG curves of a) sample $1_{(110°)}$, b) sample $2_{(110°)}$. Heating rate 5° min^{-1}

Despite the reduction, this sample (as X-ray investigation showed) contained only the V_2O_5 phase. The IR spectrum (Table 3) too exhibited only the bands at 830 cm^{-1} and 1022 cm^{-1} characteristic of V_2O_5.

Sample 2

Sample 2 ($NH_4VO_3/H_2C_2O_4$ molar ratio 1 : 1) contained oxovanadium(V) dioxalate $(NH_4)_3[VO_2(C_2O_4)_2]$ (I) and oxodivanadium(IV) trioxalate $(NH_4)_2[(VO)_2(C_2O_4)_3]$ (II) as well as an unidentified phase or phases. The formation of (I) is due to the reaction

$$NH_4VO_3 + H_2C_2O_4 + (NH_4)_2C_2O_4 = (NH_4)_3[VO_2(C_2O_4)_2] + H_2O\,. \qquad (3)$$

The preparation was pale green, this colour being the result of the mixing of the yellow colour of (I) with the bluish-grey one of (II).

The IR spectrum of sample $2_{(110°)}$ corresponds very well to that obtained in [2] for (I) (Table 2).

The decomposition of sample $2_{(110°)}$ occurs in two stages (Fig. 2b). The first of these is accompanied by an endothermic effect at 214° and the other one by an exothermic effect at 312°. The loss of weight corresponding to the first stage amounts to 28.7% and can be attributed to the reaction

$$2\,(NH_4)_3[VO_2(C_2O_4)_2] = (NH_4)_2[(VO)_2(C_2O_4)_3] + 2\,CO_2 + 4\,NH_3 + 2\,H_2O \quad (4)$$

which in the case of pure ammonium dioxovanadium(V) dioxalate is accompanied by a decrease in weight amounting to 30.68%.

Since the composition of sample 2 after calcination at 400° (61.42 wt.% of V^{4+}) corresponds very well to that of the stoichiometric VO_2 phase (61.418% of V^{4+}), one can postulate that the second stage (exothermic) of sample decomposition is the formation of VO_2 according to the reaction

$$(NH_4)_2[(VO)_2(C_2O_4)_3] = 2\,VO_2 + 2\,NH_3 + H_2O + 3\,CO_2 + 3\,CO \quad (5)$$

The theoretical loss in weight accompanying this reaction is 42.82%, while in the present experiments it was 42.5%. This result shows that the assumption made in [2] that ammonium dioxovanadium(V) dioxalate decomposes into V_2O_5 is not exact.

From the thermogravimetric analysis the following composition of sample $2_{(110°)}$ was calculated.

(I)	ammonium dioxovanadium(V) dioxalate	91.3 wt.%
(II)	ammonium oxodivanadium(I) trioxalate	5.5 wt.%
	water	3.2 wt.%

Sample 3

The X-ray investigation of sample $3_{(110°)}$, with the highest content of oxalic acid, indicated that after drying at 110° the sample was röntgenographically amorphous. However, the bands characteristic of (I) and (II) were present in the IR spectrum of the sample (Table 2). The 940 cm^{-1} band attributed to the stretching vibration of the vanadium-oxygen bond in VO_2 could also be observed. DTA and TG curves of sample $3_{(110°)}$ are given in Fig. 3a. The endothermic effect at 113° is connected with the loss of water. The weight loss of 13.2% at 246° is due to the decomposition of (I) (reaction (4)). The endothermic effect corresponding to this reaction is more distinct in the thermal curves obtained at the higher heating rate (10°/min). The subsequent exothermic effects at 303° and 359° are connected with the decomposition of (II) to VO_2 (reaction (5)) and the partial oxidation of VO_2 to V_2O_5. From the losses in weight in the individual decomposition steps the composition of $3_{(110°)}$ was calculated:

43.0%	(I)
16.6%	(II)
30.4%	VO_2
10.0%	H_2O

On the basis of these data the overall process taking place during the evaporation of the original solution may be represented as

$$\begin{aligned} &12.6\,NH_4VO_3 + 12.6\,H_2C_2O_4 = 3\,(NH_4)_3[VO_2(C_2O_4)_2] + 8\,VO_2 + \\ &+ 0.8\,(NH_4)_2[(VO)_2(C_2O_4)_3] + N_2 + 16.6\,H_2O + 6\,CO_2 + 2.4\,CO\,. \end{aligned} \tag{6}$$

Vanadium dioxide originally present in the sample, as well as that obtained by the decomposition of compounds (I) and (II), is partially oxidized to V_2O_5 at 359°. The final composition of sample $3_{(400°)}$ obtained on the basis of X-ray and chemical analysis (Table 1) corresponds well to that calculated from the TG curve. Sample $3_{(400°)}$ consists of 59.9 wt.% VO_2 and 40.1 wt.% V_2O_5.

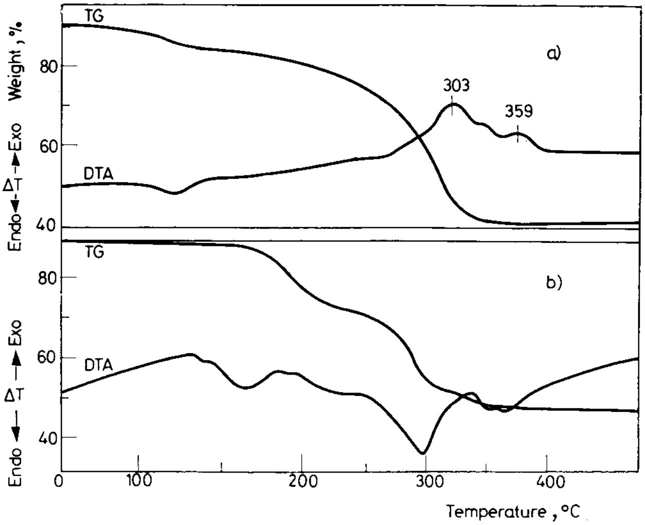

Fig. 3. DTA and TG curves of a) sample $3_{(110°)}$, b) sample $4_{(110°)}$. Heating rate 5° min^{-1}

Samples 4 and 5

The results of X-ray examination of samples $4_{(110°)}$ and $5_{(110°)}$ (Table 1) indicate that the X-ray diagram of sample $4_{(110°)}$ is less rich in diffraction lines. There is a small amount of NH_4VO_3 phase, while the strongest set of lines include some which are simultaneously characteristic of $(NH_4)_2V_6O_{16}$ and (I) phases. Comparison of the intensities of the lines suggests that both compounds are present. Sample $5_{(110°)}$ was composed of the following phases: NH_4VO_3, $(NH_4)_2V_6O_{16}$, (I) and $VO_2 \cdot H_2O$.

In the IR spectra of samples $4_{(110°)}$ and $5_{(110°)}$ (Table 2) the characteristic bands of (I), (II) and $(NH_4)_2V_6O_{16}$ are observed.

Therefore, during the evaporation of the original solutions the following reactions are most likely:

a) $$3\,NH_4VO_3 + 3\,H_2C_2O_4 = (NH_4)_3[VO_2(C_2O_4)_2] + \\ + 2\,VO_2 + 2\,CO_2 + 3\,H_2O \qquad (7)$$

b) decomposition of NH_4VO_3 remaining in excess of oxalic acid.

In the heating of samples $4_{(110^\circ)}$ and $5_{(110^\circ)}$ up to 400° complicated processes occur: the decomposition of ammonium metavanadate, the decomposition of (I) and the oxidation of the products.

The course of the decomposition as well as the final reduction degree of sample $4_{(110^\circ)}$ depended upon the heating rate.

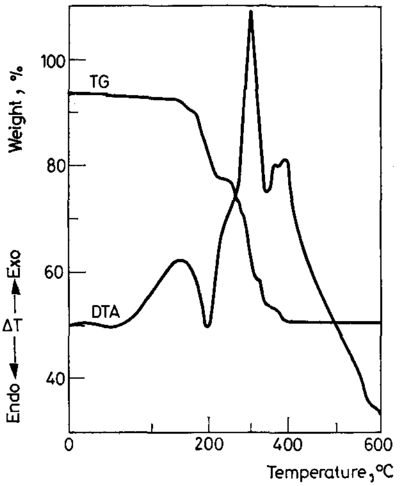

Fig. 4. DTA and TG curves of sample $4_{(110^*)}$. Heating rate 10° min^{-1}

In the DTA curve (heating rate 5°/min) two unidentified exothermic effects were observed (Fig. 3b). In the temperature range 180°—200° two exothermic effects are present; these are connected with mass loss due to reactions (1) and (4) similarly as in the case of sample $5_{(110^\circ)}$.

If sample $4_{(110^\circ)}$ is heated 10°/min, the large exothermic effect at 316° is present (Fig. 4), but on slower heating (5°/min) (Fig. 3b) a distinct endothermic effect also appears at 296°. In both cases the same loss of weight (19%) occurs. The large exothermic effect at 316° is attributed to the decomposition of (II) according to (2).

Most probably, during slower heating the products of decomposition of $(NH_4)_2[(VO)_2(C_2O_4)_3]$ and of NH_4VO_3 interact according to the reaction

$$(NH_4)_2V_6O_{16} + 2\,VO_2 \rightarrow 2\,NH_4V_4O_{10}\,. \qquad (8)$$

Deschanvers [6] has found that this reaction takes place in the course of heating NH_4VO_3 and VO_2 at 250° in a sealed tube. At 354° and 369° two endothermic effects can be distinguished (Fig. 4). They are probably connected with the decomposition of $NH_4V_4O_{10}$ obtained in reaction (8).

Sample $4_{(400°)}$ consists of V_2O_5 and VO_2. Figure 5a shows DTA and TG curves for sample $5_{(110°)}$. Up to 157° a 3 wt.% loss of water takes place. The endothermic effect at 210° corresponds to reactions (1) and (4) occurring in almost the same temperature range. The double effect in the DTG curve, with maxima at 201° and 210°, indicates the simultaneous courses of the two reactions.

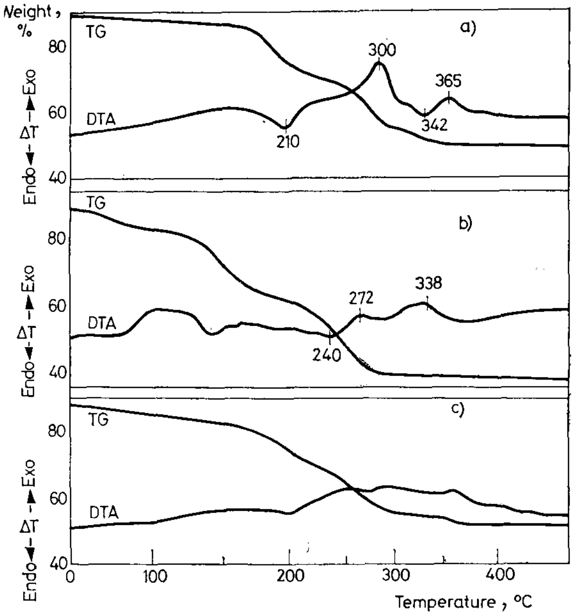

Fig. 5. DTA and TG curves of a) sample $6_{(110°)}$, b) sample $7_{(110°)}$, c) sample $8_{(110°)}$. Heating rate 5° min^{-1}

The decomposition of compound (II) according to reaction (5) gives rise to an exothermic effect at 300° similar to that for sample $2_{(110°)}$.

In the temperature range 320—380° endothermic and exothermic effects are observed that can be attributed to the decomposition of $(NH_4)_2V_6O_{16}$ and to the oxidation of the decomposition products.

It is not excluded that in the course of slow heating a certain amount of $NH_4V_4O_{10}$ is formed in sample $5_{(110°)}$ according to reaction (8). The endothermic effect of such process is masked in the DTA curve, however, by the much stronger exothermic effect of decomposition. On the basis of the weight losses in the individual stages of the processes of decomposition and reduction it was possible to determine the following approximate composition of sample $5_{(110°)}$:

36 wt.%	(I)
32 wt.%	NH_4VO_3
27 wt.%	$(NH_4)_2V_6O_{16}$
2 wt.%	$VO_2 \cdot H_2O$
3 wt.%	H_2O .

The DTA curves of samples $1_{(400^\circ)}$ and $3_{(400^\circ)}-5_{(400^\circ)}$ are identical in the temperature range 20–700°. Only a very broad exothermic effect at 300° without change of weight (except for sample $3_{(400^\circ)}$ and an endothermic one in the range 680–690° (V_2O_5 melting point) are observed.

Samples 6 and 7

Samples $6_{(110^\circ)}$ and $7_{(110^\circ)}$ after evaporating H_2MoO_4 with oxalic acid and drying represent a mixture of two or more oxalate compounds of molybdenum. The X-ray diffraction data show that $Mo(C_2O_4)_3$ is present. There are also numerous unidentified reflections, which probably arise from molybdenum oxalate coordination compounds of the same type as vanadium complexes (I) and (II) described earlier. Unfortunately there is a lack of X-ray diffraction data in the literature concerning the known molybdenum oxalate compounds. The presence of such compounds is confirmed by the IR band at 1730 cm^{-1}, indicating the strongly covalent character [2] of the bond between the metal and the oxalate group. If one assumes the above-mentioned compositions of the initial samples, the effects in the DTA curve (Fig. 5b) at 240, 272, and 338° and the connected losses of weight can be attributed to the reduction (240°), the decomposition of the molybdenum oxalate complex (272°) and oxidation of the products (338°). The DTA curves of samples $6_{(110^\circ)}$ and $7_{(110^\circ)}$ are very similar to each other, but that of sample $7_{(110^\circ)}$ is better resolved. After heating at 400°, sample $6_{(400^\circ)}$ consists of MoO_3 (orthorhombic) and MoO_2. Sample $7_{(400^\circ)}$ contains only a small quantity of MoO_2 (3.719 at.%).

Sample 8

Sample 8 was obtained by the simultaneous dissolution of NH_4VO_3 and $H_2MoO_4 \cdot H_2O$ in an aqueous solution of oxalic acid (see Table 1). The sample dried at 110° showed only a few X-ray reflections of low intensity: 5.91 Å, also appearing as a strong line in NH_4VO_3 diagrams; 8.47 Å, characteristic of $Mo(C_2O_4)_3$; 9.12 Å and 3.43 Å, corresponding to the most intensive reflections of MoO_3; and 7.22 Å also appearing in the X-ray diagrams of samples $6_{(110^\circ)}$ and $7_{(110^\circ)}$, probably due to molybdenum oxalate coordination compounds. The IR spectrum of sample $8_{(110^\circ)}$ (Table 2) shows bands similar to those in the spectra of samples $2_{(110^\circ)}-7_{(110^\circ)}$. The bands in the range 2000–1000 cm^{-1} are bands of the oxalate ion, while those in the range 1000–800 cm^{-1} are characteristic of both vanadium-oxygen and molybdenum-oxygen stretching vibrations. It is not unlikely that only molybdenum reacts with oxalic acid and NH_4VO_3 does not. Sample $8_{(110°)}$ is light-green, which may be due to the mixing of the yellow colour of NH_4VO_3 and the bluish-grey one of molybdenum oxalate compounds.

The above supposition is strongly supported by the shapes of the DTA and TG curves (Fig. 5c).

The endothermic effect at 201° connected with a 10.6 wt.% weight loss is the result of the first step of NH_4VO_3 decomposition (reaction (1)).

The recorded loss of weight corresponding to 71.6 wt.% of NH_4VO_3 is consistent with the quantity of NH_4VO_3 introduced into sample 8 (70.6 wt.% of the sample). This fact confirms the assumption that ammonium metavanadate does not react with oxalic acid in the presence of molybdic acid. The second step of NH_4VO_3 decomposition (at 354° and 362°) is accompanied by a loss of 1.75 wt.% of the sample, corresponding to 23.7% of the initial NH_4VO_3 instead of 70.6%. This means that the bulk of the intermediate compound of metavanadate decomposition, $(NH_4)_2V_6O_{16}$, reacts with molybdenum oxide to form ammonium-vanadium-molybdenum bronze, the presence of which is shown by the X-ray investigation. The latter compound is more stable and does not decompose below 600°, the highest temperature of our experiments.

Molybdenum dioxide is formed during the decomposition of the molybdenum oxalate complex. The data for samples 6 and 7 are the basis for this statement. This decomposition probably occurs at 267° (temperature of maximum rate of loss of weight), giving rise to a broad exothermic effect (220–350°). The endothermic effect at 272° is probably connected with the above-mentioned reaction of $(NH_4)_2V_6O_{16}$ and MoO_2, resulting in the formation of the bronze phase. The presence of the β-phase of the vanadia-molybdena bronze was found in sample $8_{(400°)}$ when the X-ray analysis data for this sample were compared with the data for $(Li_{0.3}V_{1.7}Mo_{0.3})_2O_5$ [9] and with the data for sodium and silver vanadia-molybdena bronzes [10].

The vanadia-molybdena bronzes of the same type are isostructural, irrespective of the nature of the univalent metal added. They show similar values of the interplanar distances (*d*). It is therefore possible to compare particular vanadium-sodium, vanadium-silver, etc. bronzes of the same structural type. In our case the ammonium ion replaces the unipositive metal cation. The weak band at 1420 cm^{-1} in the IR spectrum of sample $8_{(400°)}$ (Table 3) is evidence that the NH_4^+ ion is present. In this spectrum the 1030 cm^{-1} band attributed to the bronze phase [10] is present in the vicinity of the bands characteristic of the vanadium-oxygen and molybdenum-oxygen bonds. The solid solution of MoO_3 in V_2O_5 described by Kihlborg [11] as $(Mo_{0.3}V_{0.7})_2O_5$ is also present in sample $8_{(400°)}$. The solid solution is formed as a consequence of the heating of V_2O_5 (formed during NH_4VO_3 decomposition) and of MoO_3 present in the sample.

One broad exothermic effect at about 315° and two endothermic ones connected with melting are seen in the DTA curve of sample $8_{(400°)}$ (Fig. 6).

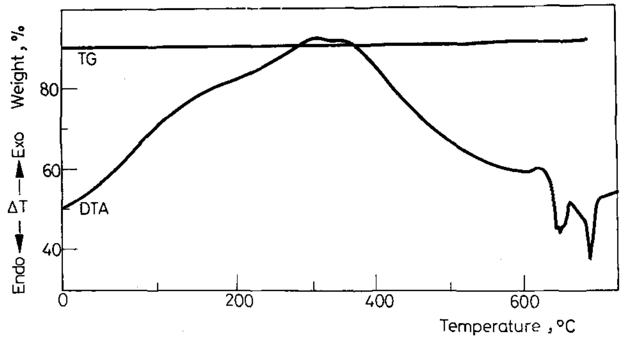

Fig. 6. DTA and TG curves of sample $8_{(400°)}$. Heating rate 5° min^{-1}

Conclusion

The thermal decompositions of the products obtained by the evaporation of aqueous solutions of NH_4VO_3 and H_2MoO_4 (or $NH_4VO_3 + H_2MoO_4$) with oxalic acid are complicated processes occurring through a number of intermediate stages. The presence of oxalic acid distinctly influences the properties of the final products. When NH_4VO_3 and H_2MoO_4 are treated with oxalic acid the dioxides of vanadium and molybdenum respectively, are obtained. The amounts of these dioxides depend on the amount of oxalic acid used. However, the predominant phase consists of the oxide in the highest oxidation state, independently of the thermal treatment of the preparations. Various types of vanadia-ammonia bronzes formed during heating up to 400° decompose with formation of the final product V_2O_5.

On the other hand, the presence of oxalic acid seems to enhance the formation of ammonia-vanadia-molybdena bronze when vanadia-molybdena preparations are calcined up to 400°. The bronze thus obtained is stable up to the melting temperature, unlike the above-mentiond ammonia-vanadia bronzes.

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Résumé — On a étudié par ATD et TG, spectroscopie IR et analyse aux rayons X, le processus de préparation par voie de décomposition thermique des oxalates appropriés simples ou complexes des catalyseurs de vanadium, molybdène et vanadium-molybdène. Les composés complexes d'oxalate de vanadium ou de molybdène se décomposent en VO_2 ou MoO_2, qui sont ensuite oxydés dans l'air à 200° en V_2O_5 et MoO_3. La phase β des bronzes d'ammonium—vanadium—molybdène est thermiquement stable dans les échantillons qui contiennent les deux métaux, et n'est pas décomposée après deux heures de chauffage à 400°.

Zusammenfassung — Der Begleitprozess bei der Präparation von Vanadium-, Molybdän- und Vanadium—Molybdän-Katalysatoren durch thermische Zersetzung geeigneter einfacher oder komplexer Oxalate wurde unter Anwendung von DTA- und TG-Methoden, IR-Spektroskopie und Röntgenanalyse untersucht. Die Oxalatkomplexverbindungen von Vanadium oder Molybdän werden zu VO_2 oder MoO_2 zersetzt, welche nachfolgend bei 500° in Luft zu V_2O_5 und MoO_3 oxidiert werden. In den Proben, welche beide Metalle enthielten, erwies sich die β-Phase der Ammonium—Vanadium—Molybdänbronze als thermisch stabil und wurde nach dem Erhitzen von 2 Stunden bei 400° nicht zersetzt.

Резюме — Используя ДТА, ТГ, ИК спектроскопию и рентгенографический анализ, были изучены процессы, протекающие при получении ванадия, молибдена и ванадий-молибденовых катализаторов при термическом разложении соответствующих простых и сложных оксалатов. Сложные оксалаты ванадия и молибдена разлагаются до VO_2 и MoO_2, которые затем при 500° окисляются в атмосфере воздуха до V_2O_5 и MoO_3. β-фаза аммониевой ванадий-молибденовой бронзы в образцах, содержащих оба металла, была термически стабильной и не разлагалась после нагревания в течении 2 часов при температуре 400°.