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Thermal features and behaviour of protonated diethylenetriamine isopolyvanadates

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Abstract

Thermal decomposition of 3-aza-1,5-pentamethylenediammonium metavanadate(V), $(H_2C_4H_{13}N_3)(VO_3)_2$, and bis(diethylenetriammonium) decavanadate(V) tetrahydrate, $(H_3C_4H_{13}N_3)_2[V_{10}O_{28}] \cdot 4H_2O$ (hereafter abbreviated as DIENVA1 and DIENVA10, respectively) has been studied by thermogravimetry (TG and DTG) and differential thermal analysis (DTA) under argon–oxygen and argon atmospheres. Thermoanalytical data show that the decomposition processes are different for both compounds and the surrounding atmosphere influences the thermal processes as well as the final products. In argon–oxygen atmosphere, the compounds undergo decomposition during several endothermic and exothermic steps to give vanadium(V) oxide. In the oxidative thermal decomposition of DIENVA10, a mixture of mixed-valance vanadium oxides, V_3O_7 and V_6O_{13}, has been identified. The experiments in an inert atmosphere lead to vanadium(IV) and vanadium(III) oxides. The essential thermal features of the protonated diethylenetriamine isopolyvanadates are reviewed and discussed.

INTRODUCTION

Polyoxometalate chemistry has been progressing at a brisk pace in recent years, because of the participation of these compounds in important industrial processes [1]. Polyvanadates with nitrogen organic cations, are used as precursors for preparation of vanadium oxides, which play an important role in catalysis. These oxides, which are normally prepared by means of thermal decomposition of precursors previously deposited on the catalyst carriers, may be useful to support other metals, to improve the efficiency of oxidative processes catalyzed by other metal oxides, and to catalyse oxidative processes involving organic reactions [2–5].

Isopolyvanadates with protonated cations are also excellent model systems for investigating several fundamental problems in important

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catalytic processes (oxidation of SO_2, Stretford Process, etc.) which imply the presence of species which contain V(IV) centres [6, 7]. Thermal decompositions of organoammonium polyoxovanadates suggest that the organic cation gets oxidized by the vanadium–oxygen core and reduced vanadium species are formed.

In this context, and during the course of our general research programme on thermal behaviour of organoammonium polyoxometalates [8–10], we decided to study the thermal properties and thermochemistry of protonated diethylenetriamine isopolyvanadates. In this paper the essential thermal features of the compounds 3-aza-1,5-pentamethylenediammonium metavanadate(V), $(H_2C_4H_{13}N_3)(VO_3)_2$ (DIENVA1) and bis(diethylenetriammonium) decavanadate(V) tetrahydrate, $(H_3C_4H_{13}N_3)_2[V_{10}O_{28}] \cdot 4H_2O$ (DIENVA10) are reported.

EXPERIMENTAL

Vanadium pentoxide and alkylamine bases were purchased from Merck and were used without further purification. The synthesis and chemical characterization of the compound as well as the crystal structure of DIENVA1 are described in a previous paper [11].

Thermal studies were carried out under argon–oxygen (4:1) and argon atmospheres. Thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) were performed on a Setaram TAG 24 S 16 simultaneous thermal analyser at a heating rate of 5 deg min^{-1}. All thermal decompositions were recorded in a dynamic atmosphere with a flow rate of 50 $cm^3 min^{-1}$. An amount of sample (6–20 mg) was exactly weighted in the platinum crucible. The thermally inert reference was 15 mg of α-Al_2O_3 previously calcinated at 1300°C for 5 h.

RESULTS AND DISCUSSION

Table 1 lists steps, initial and final temperature, partial and total mass loss, endothermic or exothermic condition and maximum peak for each step in the thermal decomposition of the compounds in an argon–oxygen and argon atmospheres. In both atmospheres, the thermogravimetric curves indicate that the decompositions are not simple, and stable intermediate products are not found during the processes owing to the fact that most of the stages are almost overlapped. Attempts to correlate the results with theoretical mass losses were not successful, except for the final solid products which were identified by X-ray powder diffraction methods.

Figure 1 displays the TG, DTG and DTA curves for DIENVA1 in both atmospheres. This compound is anhydrous and stable up to approximately 170°C. After this temperature a first abrupt mass loss takes place corresponding to an endothermic peak in the DTA curve in the oxidative

TABLE 1

Thermal analysis data for DIENVA1 and DIENVA10 in argon–oxygen and argon atmospheres.

Ar + O_2					Ar				
Step	T_i (°C)	T_f (°C)	T_m[a] (°C)	Δm[b] (%)	Step	T_i (°C)	T_f (°C)	T_m[a] (°C)	Δm[b] (%)
DIENVA1									
1	170	220	200(−)	9.29	1	170	220	200(−)	8.92
2[c]	220	310		6.79	2	220	270	245(−)	3.40
3[c]	310	350		4.88	3	270	410	335(−)	19.88
4	350	400	390(+)	7.57	4[c]	410	650		13.00
5	400	480	430(+)	10.69					(45.20)
				(39.22)					
DIENVA10									
1	60	120	95(−)	4.48	1	60	115	100(−)	4.24
2[c]	120	165		1.24	2	120	170	140(−)	1.58
3	165	220	190(−)	6.79	3	170	225	210(−)	7.22
4[c]	220	340		5.31	4	225	650		21.38
5	340	430	420(+)	11.44					(34.42)
6	430	480		−1.74					
				(27.52)					

[a] Endothermic (−) or exothermic (+) process. [b] Total mass losses are shown in parentheses. [c] Progressive mass loss without clear peaks in DTG and/or DTA curves.

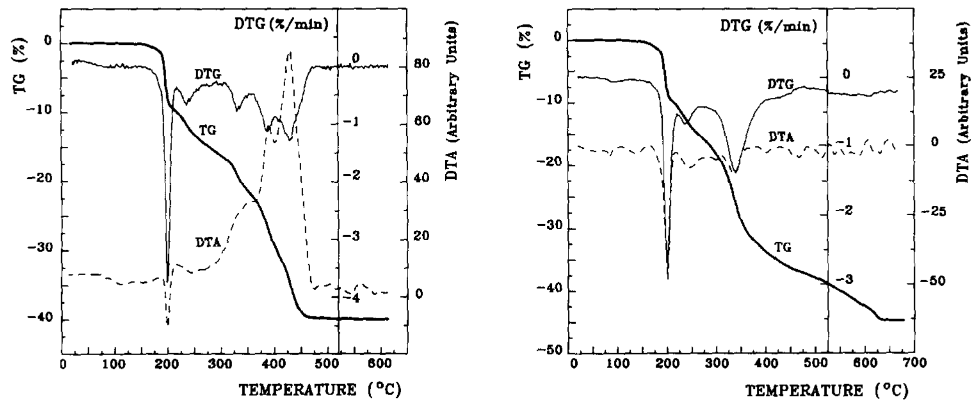

Fig. 1. TG, DTG DTA curves for the thermal decomposition of DIENVA1 in argon–oxygen (left) and argon (right) atmospheres.

atmosphere. This first decomposition step is followed by a progressive mass loss with poorly resolved peaks in the DTG curve and no clear peaks in the DTA curve. After several exothermic processes, the thermal decomposition finishes above 480°C. The X-ray powder diffractogram shows that the final residue is vanadium(V) oxide. In the inert atmosphere, the thermal decomposition starts with an endothermic process similar to that found in the oxidative atmosphere, which is attributed to oxidation, at least partially, of the organic cation by the metalate–oxygen core [5]. This decomposition step is followed by several endothermic processes and a progressive mass loss with poorly resolved peaks in the DTG curve, corresponding to the pyrolysis of the organic cation and the reduction of V_2O_5. At 650°C the final solid residue was identified as V_2O_4. No V_2O_5 or any other vanadium oxide were detected.

Some authors have suggested that the catalytic decomposition of NH_3 on the surface of V_2O_5 causes some degree of reduction of the oxide [12–14] or that it is possible that a product formed during the thermal decomposition of the organic base could produce some reduction of the metal or react with it to give metal oxocarbides or metal carbides [9]. In our case, elemental analyses of final black product give no indication of carbon presented in the composition.

Figure 2 shows the thermal decompositions for DIENVA10, which is tetrahydrated. Three of the water molecules are lost during a first strong endothermic process

$$(H_3C_4H_{13}N_3)_2[V_{10}O_{28}]\cdot 4H_2O(s) \xrightarrow{[O]/[Ar],\Delta} (H_3C_4H_{13}N_3)_2[V_{10}O_{28}]\cdot H_2O(s) + 3H_2O(g) \qquad (1)$$

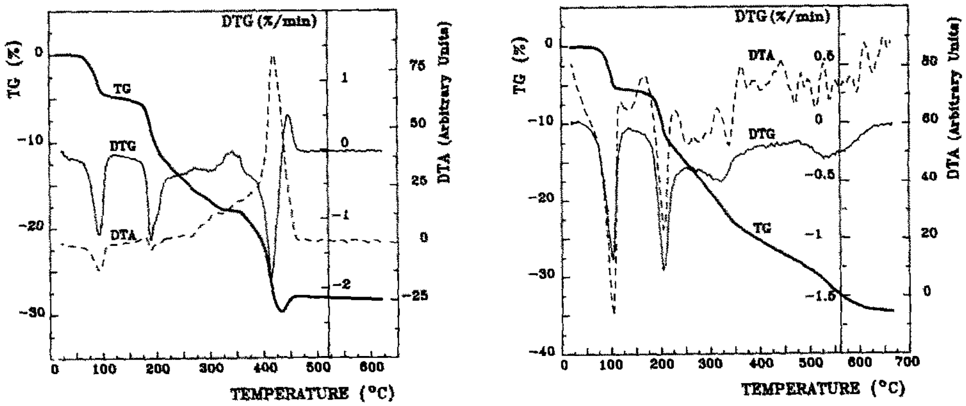

Fig. 2. Thermal decomposition of DIENVA10 in argon–oxygen (left) and argon (right) atmospheres.

and the fourth one is released in a later endothermic process

$$(H_3C_4H_{13}N_3)_2[V_{10}O_{28}]\cdot H_2O(s) \xrightarrow{[O]/[Ar],\Delta} (H_3C_4H_{13}N_3)_2[V_{10}O_{28}](s) + H_2O(g) \quad (2)$$

The temperature range of the dehydration steps is similar in both atmospheres. The dehydration steps are followed by an endothermic process which does not depend on the surrounding atmosphere as found for DIENVA1. In the oxidative atmosphere, several exothermic processes take place up to 430°C which lead to a higher mass loss than that expected for V_2O_5. The elemental analyses give no indication of carbon, nitrogen or hydrogen in the residue composition at this stage of the reaction. The X-ray powder diffraction pattern of this residue indicates the presence of a mixture of V_3O_7 and V_6O_{13}

$$(H_3C_4H_{13}N_3)_2[V_{10}O_{28}](s) \xrightarrow{[O],\Delta} V_3O_7(s) + V_6O_{13}(s) + NO_x(g) + CO_2(g) + H_2O(g) \quad (3)$$

Then an increase of mass takes place due to the oxidation of vanadium oxides which yields V_2O_5 above 480°C

$$V_3O_7(s) + V_6O_{13}(s) \xrightarrow{[O],\Delta} V_2O_5(s) \quad (4)$$

In the thermal decomposition of *n*-alkylammonium decavanadates [10] there is no detectable increase in mass during the thermal decomposition. A possible explanation for this behaviour can be ascribed to the different number of amine groups of the aliphatic base. In the mononitrogen aliphatic base decavanadates the oxidation of organic base and the reduced vanadium oxides formed by the catalytic decomposition of the NH_3 are simultaneous processes. Nevertheless, the diethylenetriamine base has a higher reduction powder due to the three amine groups, so that the presence of oxygen cannot produce the simultaneous oxidation of the cation and the reduced vanadium oxides and there are high amounts of these oxides after the total decomposition of the protonated organic base.

In the inert atmosphere, the reduction process is stronger than in argon–oxygen atmosphere

$$(H_3C_4H_{13}N_3)_2[V_{10}O_{28}](s) \xrightarrow{[Ar],\Delta} V_2O_4(s) + V_2O_3(s) + NO_x(g) + CO_2(g) + H_2O(g) \quad (5)$$

and the final residue at 650°C has mainly been identified as vanadium(IV) oxide, V_2O_4. The X-ray powder diffractogram also shows the presence of vanadium(III) oxide, V_2O_3.

CONCLUDING REMARKS

Thermal decomposition of the isopolyvanadates described in this paper are complex and numerous intermediate steps take place before final products are formed. The thermoanalytical results indicate that the decomposition processes as well as the final products are influenced by the atmosphere involved and the starting material. Whereas a thermal decomposition under an excess of oxygen leads to V_2O_5 as final solid stable product, in an inert atmosphere the organoammonium cation reduces, direct or indirectly, the vanadium atoms of the polyanion reaching vanadium(IV) oxide for DIENVA1 and a mixture of vanadium(IV) and vanadium(III) oxides for DIENVA10. During the oxidative thermal decomposition of decavanadate salt a mixture of mixed-valance vanadium oxides, V_3O_7 and V_6O_{13}, has been identified, and an unexpected increase in mass is observed which corresponds to the oxidation to V_2O_5.

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