Thermochimica Acta, 223 (1993) 167–175
Elsevier Science Publishers B.V., Amsterdam

Synthesis of oxides, oxocarbides and carbides of molybdenum by thermal decomposition of diethylenetriamine oxomolybdenum compounds

Pascual Román *, Antonio Luque and Ana Aranzabe

Departamento de Química Inorgánica, Universidad del País Vasco, Apartado 644, 48080 Bilbao (Spain)

(Received 11 December 1992; accepted 18 January 1993)

Abstract

Thermal decompositions of four diethylenetriamine oxomolybdenum compounds, the oxocomplex diethylenetriaminetrioxomolybdenum(VI), $[MoO_3(dien)]$ (DIENMO1), two polymorphs of bis(diethylenetriammonium) heptamolybdate(VI) tetrahydrate, $(H_3dien)_2[Mo_7O_{24}] \cdot 4H_2O$ (DIENMO7-I) and (DIENMO7-II), and the bis(3-aza-1,5-pentamethylenediammonium) octamolybdate(VI) hexahydrate, $(H_2dien)_2[Mo_8O_{26}] \cdot 6H_2O$ (DIENMO8), have been studied using TG, DTA and DTG techniques under an argon atmosphere from room temperature to 600°C. Whereas the themal decompositions of the three polyoxomolybdate salts DIEMNO7-I, DIENMO7-II, and DIENMO8 lead to a mixture of MoO_2 and Mo_2C, the final residue from the oxycomplex is a mixture of Mo_2C and the mixed valence molybdenum(V, VI) oxide Mo_4O_{11}. The results show that the molybdenum oxide/molybdenum carbide ratio depends on the starting material. An increase in the formation of molybdenum oxide is observed as the ratio Mo/C increases. The ulterior oxidation of the final mixtures yields Mo_4O_{11} and MoOC as intermediate solid products, and MoO_3 as the final product above 535°C. The final solid residues in an argon atmosphere and the intermediate products in the oxidative atmosphere were analysed by elemental analysis and X-ray powder diffractometry.

INTRODUCTION

Interest in polyoxomolybdates has increased dramatically in recent years because they are excellent model systems for the investigation of interactions between organic substrates and catalytic metal oxide surfaces in a great number of industrial processes [1] and because of their successful applications in the catalytical and biomedical fields [2, 3]. Thermal decompositions of organoammonium polyoxomolybdates, previously deposited on the catalyst carriers, have been used for the preparation of molybdenum oxides. These molybdenum oxides and the mechanism of

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* Corresponding author.

0040-6031/93/$06.00

their reduction have been extensively studied due to both their importance in the production of metallic molybdenum and the role of MoO_3 as an essential component of many industrial catalysts for the selective oxidation of olefins [4] and the hydrodesulphurization of oil [5]. Recent studies on the thermochemical reactivity of organoammonium polyoxometalates [6–8] suggest that the onset temperatures of their thermal decomposition, the corresponding reaction mechanism, and the final solid products are strongly influenced by the atmospheric conditions, as well as by the chemical and structural features of the starting compounds. It is known that their thermal decompositions under inert atmosphere produce not only low oxidation-state molybdenum oxides but also molybdenum carbides, oxocarbides and molybdenum mixed-oxides as final products [6–8]. The carbides, mainly tungsten and molybdenum carbides, could be potential substitutes for noble metals (Pt, Pd) in many hydrocarbon-reforming reactions [9]. Conventional metal carbide powders are manufactured by reacting the corresponding oxide with carbon under reduction conditions followed by grinding. In many cases, this method requires a very high reaction temperature and vacuum conditions. Nevertheless, the synthesis and fabrication of advanced ceramics obtained by pyrolysis of chemically designed precursors offers several advantages, for example, lower processing temperatures and controlled pyrolysis conditions, and it could lead to the formation of material such as oxocarbides, carbides and oxides that may develop novel properties.

In this context, and as part of our investigation into the thermal behaviour of organoammonium polyoxometalates, we decided to study the thermal decomposition of the oxocomplex diethylenetriaminetrioxomolybdenum(VI), $[MoO_3(dien)]$ (DIENMO1) and three polyoxomolybdates of protonated diethylenetriamine: two polymorphs of bis(diethylenetriammonium) heptamolybdate(VI) tetrahydrate, $(H_3dien)_2[Mo_7O_{24}] \cdot 4H_2O$ (DIENMO7-I) and (DIENMO7-II), and the bis(3-aza-1,5-pentamethylenediammonium) octamolybdate(VI) hexahydrate, $(H_2dien)_2[Mo_8O_{26}] \cdot 6H_2O$ (DIENMO8). The purpose of this work is to reveal the influence of the surrounding atmopshere on the thermal decomposition, as well as to obtain various molybdenum oxides and molybdenum carbides, which represent important materials in the field of heterogeneous catalysis [1, 2, 9]. In a previous paper, we have described the syntheses, chemical characterization and thermal behaviour in argon–oxygen atmosphere of these compounds [10]. The crystal structures of DIENMO7-I [10], DIENMO7-II [11] and DIENMO1 [12] have also been previously reported. In an oxidative atmosphere, all the compounds undergo decomposition upon heating, leading to MoO_3 above 500°C; however, because the compounds decompose in a great number of stages and the pathways are not simple, no other molybdenum oxides or other intermediate products could be isolated.

EXPERIMENTAL

Compounds were heated under an argon atmosphere from room temperature to 600°C. After cooling the thermobalance down to 100°C, the final products obtained under an inert atmosphere were reheated to 600°C in an oxygen–argon atmosphere (1:4 v/v). The TG, DTA and DTG were performed on a Setaram TAG 24 S 16 simultaneous thermal analyser at a heating rate of 5°C min^{-1}. All thermal analysis runs were recorded in a dynamic atmosphere with a flow rate of 40 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. An exact amount of sample (15–20 mg) was weighed in the platinum crucible; the thermal inert reference was 20 mg of α-Al_2O_3, previously calcinated at 1300°C for 6 h. The intermediate and final products were examined by X-ray powder diffraction. The data were recorded at room temperature with a Philips PW 1710 equipped with a graphite monochromator, using Cu Kα radiation. Diffraction patterns were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards.

RESULTS AND DISCUSSION

Table 1 lists the decomposition steps, the initial and final temperatures (°C), the partial and total weight losses, and the enthalpy (endothermic or exothermic) and peak maximum for each step in the thermal decomposition of the compounds in argon atmosphere. In Table 1, the percentage values of the final stable mixtures were calculated from the experimental total weight loss at 600°C, assuming that only the compounds identified in the X-ray powder diffractogram are present.

The thermal decompositions of the four compounds are quite different from those studied under an oxygen atmosphere. The thermogravimetric curves indicate that the decompositions are not simple, and stable intermediate products were not found because most of the stages were not resolved. Attempts to correlate the results with theoretical weight losses were not successful, except for the final solid products which were identified by X-ray powder diffraction methods.

The thermal analysis of DIENMO1 (Fig. 1) shows that the compound is anhydrous and stable up to approximately 230°C when the first abrupt weight loss takes place, corresponding to an endothermic peak centred at 290°C in the DTA curve. This first decomposition step is followed by an endothermic process in the temperature range 310–435°C, and a progressive weight loss with poorly resolved peaks in the DTG curves and no clear peaks in the DTA curves. Finally, an exothermic step takes place between 535 and 600°C and the total weight loss is different to that expected for molybdenum trioxide. The final black residue, whose elemental analysis revealed the presence of high amounts of carbon, has been identified by

TABLE 1

Steps, initial and final temperature (°C), partial and total weight losses, and enthalpy and peak maximum for each step in the thermal decomposition of the compounds DIENMO1, DIENMO7-I, DIENMO7-II, and DIENMO8 in an argon atmosphere

Step	T_i	T_f	T_m	ΔH	$\%\Delta m$	$\Sigma\ \%\Delta m$
DIENMO1						
1	230	310	290	Endo	19.30	
2	310	435	385	Endo	13.62	
3 [a]	435	535				
4	535	600	590	Exo	16.05	55.95
Mo_4O_{11} (23.4%) + Mo_2C (76.6%) [b]						
DIENMO7-I						
1	110	175	160	Endo	5.25	
2	175	265	233	Endo	6.80	
3 [a]	265	465				
	465	600				35.50
MoO_2 (85.5%) + Mo_2C (14.5%) [b]						
DIENMO7-II						
1	130	200	170	Endo	5.55	
2	200	275	230	Endo	5.40	
3 [a]	265	470				
	470	600				35.30
MoO_2 (87.1%) + Mo_2C (12.9%) [b]						
DIENMO8						
1	80	220	215	Endo	7.11	
2	220	320	260	Endo	6.87	
3 [a]	320	470				
	470	600				32.80
MoO_2 (94.6%) + Mo_2C (5.4%) [b]						

[a] Progressive weight loss without clear peaks in the DTG and DTA curves. [b] Stable final products at 600°C.

X-ray powder diffraction patterns as a mixture of the mixed-valence molybdenum(V, VI) oxide Mo_4O_{11} (ASTM 5-337) and Mo_2C (ASTM 11-680) in a ratio of 1/3. No MoO_3 or other molybdenum oxide could be detected. The Mo_4O_{11} oxide is an intermediate product of the reduction of MoO_3 to MoO_2 [13]. It is possible that a product formed during the thermal decomposition of the organic base could cause some reduction of the oxide of molybdenum or it could even react with it to give molybdenum oxocarbides or molybdenum carbides.

The main features of the thermal decomposition for the three polymolybdate compounds are quite similar. The two hydrated heptamolybdate compounds, DIENMO7-I (Fig. 2) and DIENMO7-II (Fig. 3) have four

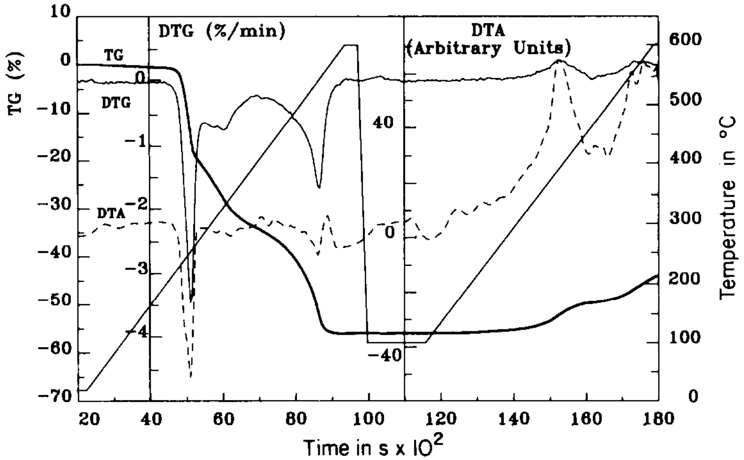

Fig. 1. TG, DTG and DTA curves for the thermal decomposition of the compound DIENMO1.

water molecules which are lost during a first endothermic process in the temperature range 110–200°C. The compound DIENMO8 shows a low thermal stability and the six water molecules are lost between 80 and 220°C (Fig. 4). The DTG peaks of the dehydration steps are not symmetrical and the DTA curve peaks are broad, indicating that the water molecules are not isoenergetically bound and are lost by different overlapping steps. This agrees with the X-ray structural studies which show that the four water molecules in the heptamolybdate salts are differently located in the crystal lattice. A comparison of the dehydration step in argon atmosphere with that in the oxidative atmosphere shows some analogies. The stability of the

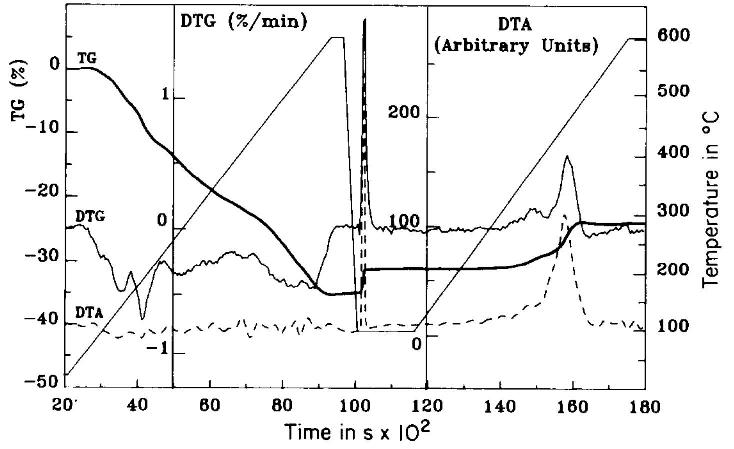

Fig. 2. TG, DTG and DTA curves for the thermal decomposition of the compound DIENMO7-I.

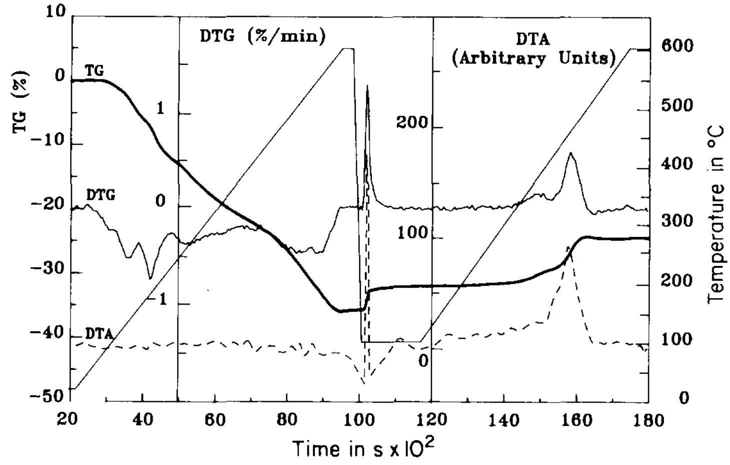

Fig. 3. TG, DTG and DTA curves for the thermal decomposition of the compound DIENMO7-II.

hydrated polyoxomolybdates is similar in both atmospheres [10], but the total dehydration process in inert atmosphere takes place over a wider temperature range. The temperature limits for the dehydration steps show some dependence on the compound density in both atmospheres. In an argon atmosphere, the dehydration step of the densest polymorph (DIENMO7-II, $D_0 = 2.74(1)$ g cm^{-3}) is shifted higher by 20°C than that of the other polymorph (DIENMO7-I, $D_0 = 2.68(1)$ g cm^{-3}). A similar thermal behaviour has been shown by analogous alkylammonium heptamolybdates in which a gradual shift towards higher temperature values is observed in the denser crystal structures. This tendency can be explained on the basis of the strong hydrogen contacts of the water molecules in the

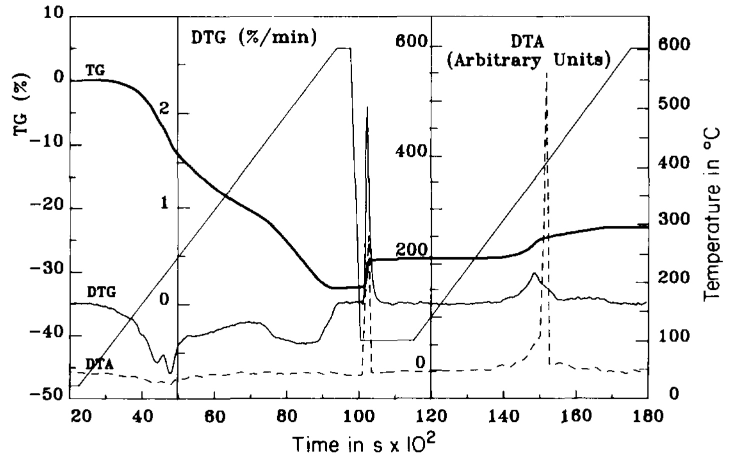

Fig. 4. TG, DTG and DTA curves for the thermal decomposition of the compound DIENMO8.

crystal lattices of the polyoxometalates. An increase in density of the compounds produces a more compact crystal packing and leads to stronger hydrogen contacts. The DIENMO7-I and DIENMO7-II compounds are, to our knowledge, the heptamolybdate salts which have the highest density of all organoammonium heptamolybdates described in the literature, and show a high thermal stability.

The dehydration processes imply a lowering in the stability of the crystal structure, because the anhydrous compounds are not stable and the decompositions follow immediately after the dehydration step with one endothermic peak. This is a typical behaviour of polyoxometalates with structures stabilized by crystal water, the release of which is accompanied by the crystal structure decomposition and a strong endothermic peak in the DTA curve which does not depend on the atmosphere. The endothermic peak may be attributed, at least partially, to the oxidation of the organic cation by the metalate–oxygen core [14] which is accompanied by the release of polyanion oxygens [15]. This redox step is followed by a progressive weight loss without peaks in the DTG and DTA curves and an endothermic stage, attributable to the pyrolysis of the organoammonium cations and the formation of the inorganic degradation residues. Elemental analyses of the final black residues indicated the presence of carbon in their compositions. X-ray powder diffraction data revealed the presence of the monoclinic MoO_2 (ASTM 5-0452) and Mo_2C. In contrast with the oxocomplex, in the polyoxomolybdates the amount of molybdenum oxide is higher than that of molybdenum carbide, because their Mo/base ratio is greater.

After cooling the thermobalance down to 100°C and introducing a flow of argon–oxygen, the final residues were reheated to 600°C. Table 2 shows the results provided by this oxidative process. The calculated total weight loss in each oxidative step was obtained from the percentage of the final mixture in Table 1. For DIENMO1, the residue is stable and no increase in mass takes place until 240°C where an exothermic mass gain is observed, corresponding to the oxidation of Mo_2C to MoOC (ASTM 17-104). This result is confirmed by the mass gain obtained in the thermogravimetry curve (exp. 7.43%, calc. 7.28%). Between 385 and 535°C, another increase in mass takes place due to the total oxidation of Mo_4O_{11} and MoOC to MoO_3. X-ray powder diffraction data of the final stable product above 535°C indicate only peaks belonging to MoO_3.

For polyoxomolydates salts, immediately after introducing the argon–oxygen mixture there is an abrupt increase in mass over a short temperature range. This increase is related to the occurrence of a strong exothermic peak in the DTA curve due to the oxidation of the molybdenum(IV) oxide to the molybdenum(V, VI) mixed oxide Mo_4O_{11}, which releases a high amount of energy. X-ray powder diffraction data of the stable products show only peaks belonging to the mixture Mo_4O_{11}/Mo_2C. This mixture is

TABLE 2

Thermoanalytical data for the oxidation processes of the residues from the thermal decomposition of the compounds DIENMO1, DIENMO7-I, DIENMO7-II, and DIENMO8

T_i–T_f	Products	$\%\Delta m_{exp}$	$\Sigma\ \%\Delta m_{exp}$	$\Sigma\ \%\Delta m_{cal}$
DIENMO1				
100 [a]	$Mo_4O_{11} + Mo_2C$			
100–240	No oxidation: $Mo_4O_{11} + Mo_2C$			
240–385	$Mo_4O_{11} + MoOC$	−7.43	48.52	48.67
385–535	MoO_3	−5.83	42.69	41.75
DIENMO7-I				
100 [a]	$MoO_2 + Mo_2C$			
100–100	$Mo_4O_{11} + Mo_2C$	−4.30	31.20	30.40
280–380	$Mo_4O_{11} + MoOC$	−3.05	28.15	28.37
380–480	MoO_3	−4.80	23.35	24.81
DIENMO7-II				
100 [a]	$MoO_2 + Mo_2C$			
100–100	$Mo_4O_{11} + Mo_2C$	−4.20	31.10	30.00
280–380	$Mo_4O_{11} + MoOC$	−3.15	27.95	28.22
380–480	MoO_3	−4.60	23.35	24.81
DIENMO8				
100 [a]	$MoO_2 + Mo_2C$			
100–100	$Mo_4O_{11} + Mo_2C$	−4.16	28.64	26.85
240–385	$Mo_4O_{11} + MoOC$	−3.43	25.21	25.05
385–535	MoO_3	−1.33	23.88	23.38

[a] Final mixtures from the thermal decompositions of the oxomolybdenum compounds in an argon atmosphere at 600°C.

stable up to 240 or 280°C and its further oxidation steps are similar to those described for DIENMO1, yielding MoO_3 as the final product.

CONCLUDING REMARKS

The thermoanalytical results indicate that the thermal decomposition of the diethylenetriamine oxomolybdenum compounds, as well as the final products, is strongly influenced by the atmosphere present and the starting compounds. Whereas the thermal decompositions under an excess of oxygen lead to MoO_3 as the final solid stable product, in an inert atmosphere the unprotonated or protonated organoamine base reduces, direct or indirectly, the molybdenum atoms of the compound yielding mixtures of MoO_2/Mo_2C for the polyoxomolybdate salts and Mo_4O_{11}/Mo_2C for the molybdenum oxocomplex. The ratio of molybdenum oxide/molybdenum carbide in the final products is strongly influenced by the ratio of Mo/B (where B is organic base) in the starting material. An increase in the formation of molybdenum oxide is observed as the ratio of Mo/B is increased. The reoxidation of these residue mixtures yields Mo_4O_{11} and MoOC as intermediate solid products and MoO_3 as the final product above 535°C.

ACKNOWLEDGEMENT

We thank UPV/EHU (Grant No. 169.310-T180/91) for financial support.

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