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Reducibility and thermal behaviour of some Anderson phases

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Abstract

The thermal behaviour of the $(NH_4)_3[M(III)Mo_6O_{24}H_6] \cdot 7H_2O$, Anderson phases, where M is Al, Co, Fe has been analysed in N_2, N_2/O_2 and N_2/H_2 atmospheres using TG–DTA, TPR, and XRD techniques. Additional measurements were made by IR, EPR and Mössbauer spectroscopies, and also by scanning electron microscopy. Similar studies were carried out on ammonium heptamolybdate for comparative purposes.

Molybdenum oxide and metallic molybdate are the solid products of the thermal treatment in N_2 and N_2/O_2 atmospheres. While $M_2(MoO_4)_3$ is observed when M is Al and Fe, the β-$CoMoO_4$ binary oxide is stabilized under both experimental conditions. The intermediate $[(NH_4)_2O]_{0.8}MoO_3(H_2O)_{0.3}$ phase is only observed when working in static air atmosphere at a very low heating rate.

The temperature-programmed reduction (TPR) study permits the analysis of the different reduction steps of the Mo(VI) and M(III) is Fe, Co components. Mo_4O_{11}, MoO_2, Mo and $MMoO_4$ (M is Co, Fe) are also observed. The formation of an Al–Mo reduced oxidic phase (related to MoO_2) can be inferred for the Al compound.

INTRODUCTION

Molybdenum chemistry is very interesting because of its role in industrial catalytic oxidation and hydrodesulphurization (HDS) processes [1].

It is well known that bimetallic catalysts, such as CoO/MoO_3 on an alumina support, are more reactive in HDS than MoO_3 alone. However, nowadays, heteropoly compounds are widely used as heterogeneous and homogeneous catalysts [1–3]. Hence, the synthesis and characterization of this type of material are important areas of research [4–6].

The Anderson-type heteropolyanions of general formula $[XMo_6O_{24}H_6]^{n-}$ are characterized by the presence of a heteroatom X in a central octahedral cavity of the crown by edge-sharing six MoO_6 octahedra [7, 8].

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The aim of this study was to measure in detail the thermal stability and reducibility of some $(NH_4)_3[M(III)Mo_6O_{24}H_6] \cdot 7H_2O$ (M(III) is Fe, Co, Al) Anderson phases in order to obtain a more complete description of their characteristics [9, 10]. The highly sensitive temperature-programmed reduction (TPR) technique was employed to determine the stability of these compounds in an H_2 atmosphere for their potential use in HDS processes.

EXPERIMENTAL

The $(NH_4)_3[MMo_6O_{24}H_6] \cdot 7H_2O$ phases were obtained by solution reaction according to the method described previously [8]. The purity of the samples was checked by XRD using a Philips PW-1714 diffractometer (Cu Kα radiation, Ni-filtered), and by IR spectroscopy using a Perkin-Elmer 580-B spectrophotometer (KBr pellet technique).

Thermogravimetric and DTA measurements were carried out on a Rigaku thermoanalyser (type YLDG/CN 8002 L2), using a chromel–alumel thermoelement and working in static air and flowing N_2 (0.4 $l\,min^{-1}$). The heating rate was $10°C\,min^{-1}$ and α-Al_2O_3 was used as the DTA standard. The temperature was raised to 500°C.

Additional thermal studies were carried out in a furnace, using conditions similar to those of the TG–DTA measurements. These experiments provided a characterization of the intermediates and pyrolysis residues.

The reduction studies were carried out using the temperature-programmed reduction technique (TPR) and the reactor was fed with 10% H_2 reducing agent in N_2 (100 $cm\,m^{-1}$), from 20 to 1000°C. The heating rate was $5°C\,min^{-1}$. The H_2 consumed was detected by a thermal conductivity cell.

Samples were also observed by scanning electron microscopy (Philips-505 electron microscope with an EDAX-9100 microsound and energy dispersive detector).

The Mössbauer spectra of the Fe-phase were obtained using a $^{57}Co/Rh$ source of approx. 10 mCi activity. The isomer shift was relative to α-Fe.

Finally, the EPR spectra of the Al-phase were registered at room temperature on a Bruker 200-D (X band) spectrometer.

RESULTS AND DISCUSSION

Thermal treatment in N_2/O_2 atmosphere

The thermal behaviour in oxidant or inert atmospheres of some heteropolymolybdates with Anderson structure was analysed by La Ginestra and co-workers several years ago [11–14], but study of the $(NH_4)_3[M(III)Mo_6O_{24}H_6] \cdot 7H_2O$ phases was not included. However, the

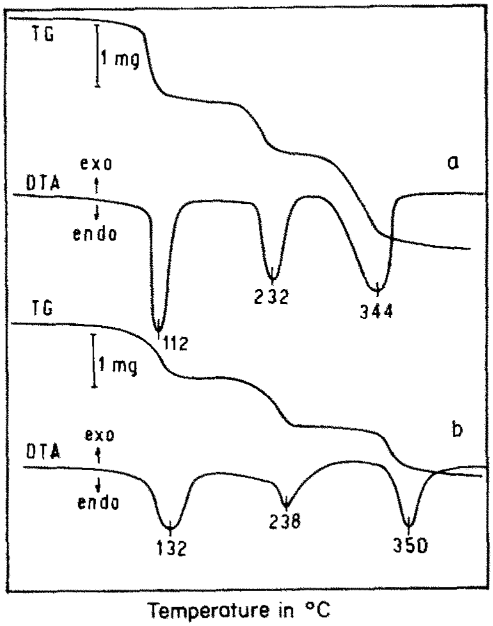

Fig. 1. TG and DTA plots of: (a) ammonium heptamolybdate; and (b) $(NH_4)_3$-$[CoMo_6O_{24}H_6] \cdot 7H_2O$ Anderson-phase.

thermal treatment of the phase containing Ga(III) has recently been published [15].

Figure 1 shows the TG and DTA plots of the $(NH_4)_3[CoMo_6O_{24}H_6] \cdot 7H_2O$ Anderson phase; the ammonium heptamolybdate curves are also provided for comparative purposes. All the phases analysed have similar patterns which, basically, are characterized by three endothermic peaks. Table 1 gives the temperature of each thermal effect. The first, which corresponds to the loss of the hydration water, is a reversible process and the anhydrous phase readily recovers the seven molecules of water [9]. This loss does not affect the structural characteristics of the heteropolyanion, as confirmed by IR spectroscopy [9]. Moreover, the morphology

TABLE 1

Temperature of the main endothermic DTA peaks (°C) for the Co, Fe and Al Anderson phases, and for ammonium heptamolybdate (AHM)

Sample	Step			Sample	Step		
	1	2	3		1	2	3
Co-phase	132	238	350	Al-phase	175	255	395
Fe-phase	181	205	365	AHM	112	232	344

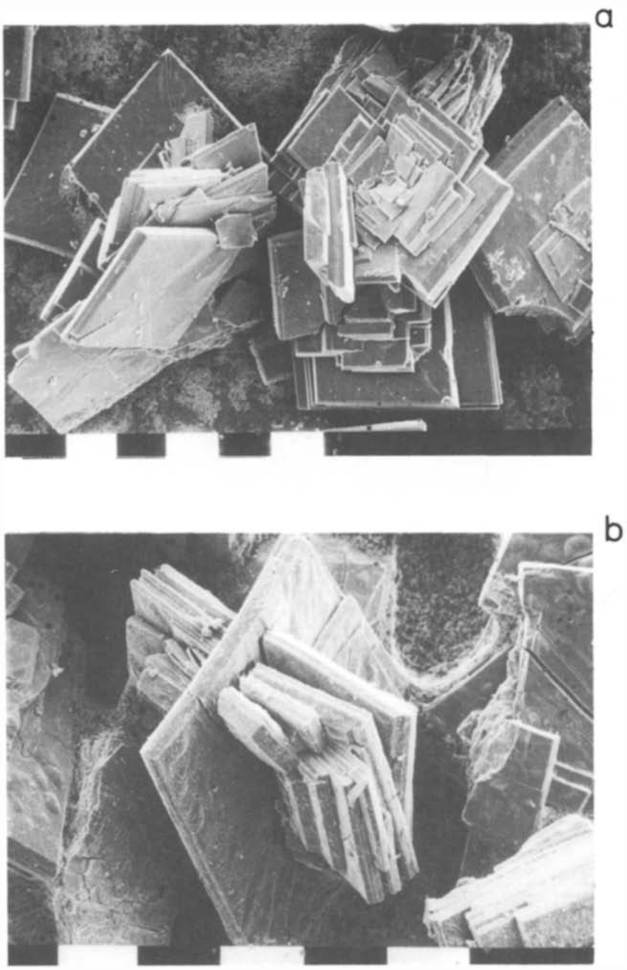

Fig. 2. SEM micrographs of $(NH_4)_3[CoMo_6O_{24}H_6] \cdot 7H_2O$ phase during thermal treatment in N_2/O_2 atmosphere (original magnification, ×200; scale bar, 100 μm): (a) before any treatment; (b) dehydrated phase.

of the crystals was not altered by the treatment, as seen by microscopical analysis. Figure 2(a) and (b) shows the scanning electron micrographs of the original and the anhydrous Co-phases.

The second endothermic peak corresponds to the loss of NH_3. However, a different decomposition scheme can be inferred if the experimental conditions are changed. Slow heating in static air results in the formation and isolation of the $[(NH_4)_2O]_xMoO_3(H_2O)_y$ phase ($x = 0.075$–0.085 and $y = 0.32$–0.42) [16]. This process involves a partial release of NH_3 with an additional loss of water (from the intermolecular H atoms). The third endothermic effect is associated with the removal of the three remaining water molecules, leading to formation of MoO_3, according to the DTA–TG measurements.

With regard to the heteroatom, the formation of the corresponding molybdates can be suggested. However, a reduction process must be taken into account in the Co-phase. The presence of $NH_3(g)$ can reduce Mo(VI) to Mo(V) [17] producing N_2 and H_2O, whereas the reduction of Co(III) to Co(II) may be a consequence of the destruction of the Anderson phase, which stabilizes the Co(III), as well as by the action of $NH_3(g)$. The β-$CoMoO_4$ monoclinic phase [18, 19] (ASTM 21-868) is detected by XRD after heating at 500°C; below this temperature, the phases are amorphous to this technique. The formation of β-$CoMoO_4$ has also been corroborated by photoacoustic spectroscopy [20, 21].

The Mo(VI) species, however, is partially reduced to Mo(V), as shown by EPR spectroscopy. It is known that the EPR spectra of Mo(V) exhibit a variety of line shapes which depend on the nature of the sample and its treatment. However, g values of between 1.8 and 2 are characteristic of this species [22]. The EPR spectrum of a sample of $(NH_4)_3[AlMo_6O_{24}H_6]\cdot 7H_2O$ heated at 450°C in static air atmosphere shows a weak signal with a g value of 1.933, attributed to the reduced Mo.

Hence the following decomposition scheme can be suggested for $(NH_4)_3[CoMo_6O_{24}H_6]\cdot 7H_2O$

$$\begin{array}{l}
(NH_4)_3[CoMo_6O_{24}H_6]\cdot 7H_2O \xrightarrow{N_2} CoMoO_4 + 5MoO_{(3-x)} + 0.167N_2(g) + \\
\qquad\qquad\qquad\qquad\qquad 2.666NH_3(g) + (12+5x)H_2O(g) \\
\quad \downarrow \text{static air} \\
[(NH_4)_2O]_{0.08}MoO_3(H_2O)_{0.3} + CoMoO_4 \\
\qquad\quad \downarrow \\
\qquad ``MoO_{(3-x)}"
\end{array}$$

where $x < 0.01$, according to the intensity of the signal.

It was impossible to detect similar behaviour for the Fe- and Al-phases. The difference is attributed to the stability of the Fe(III) and Al(III) oxidation states. The formation of $M_2(MoO_4)_3$ compounds is difficult to observe by XRD but the iron compound was clearly detected at 500°C by Mössbauer spectroscopy. Similarly the formation of $Al_2(MoO_4)_3$ phase is to be expected.

The Mössbauer spectrum of the Fe Anderson phase heated at 500°C shows a unique, well-defined absorption line, with a δ (isomer shift) value of 0.41 mm seg^{-1}, in agreement with the literature data for $Fe_2(MoO_4)_3$ [22, 23] and characteristic of high-spin ferric ions.

Experimental and theoretical weight loss values of 20.8% and 21.14%, 22.0% and 22.06%, and 21.40% and 21.53%, respectively, for the Co, Al and Fe Anderson phases are independent of the experimental conditions.

For the $(NH_4)_3[MMo_6O_{24}H_6]\cdot 7H_2O$ phase with M being Al or Fe, the

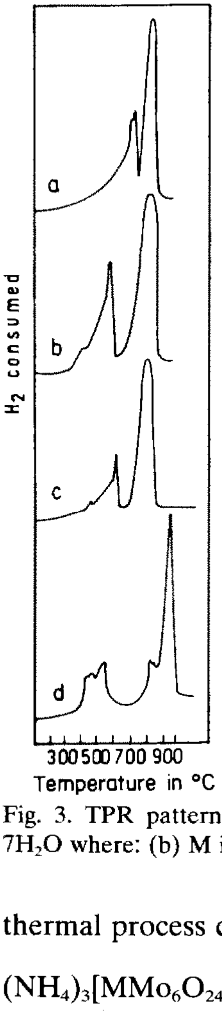

Fig. 3. TPR patterns of: (a) ammonium heptamolybdate; and of $(NH_4)_3[MMo_6O_{24}H_6] \cdot 7H_2O$ where: (b) M is Co; (c) M is Fe: (d) M is Al.

thermal process can be outlined according to the scheme

$$(NH_4)_3[MMo_6O_{24}H_6] \cdot 7H_2O \xrightarrow{N_2} 0.5M_2(MoO_4)_3 + 4.5MoO_{3-x} + 0.015N_2(g) + 2.970NH_3(g) + (11.5 + 4x)H_2O(g)$$

where $x < 0.01$ is suggested.

Thermal treatment in H_2/N_2 reducing atmosphere (TPR)

Temperature-programmed reduction (TPR) is one of the most important techniques used in the field of catalysis to characterize oxidic systems.

Figure 3 shows the TPR patterns of the $(NH_4)_3[MMo_6H_6O_{24}] \cdot 7H_2O$ Anderson phases, where M is Co (Fig. 3(b)), Fe (Fig. 3(c)) and Al (Fig. 3(d)). It also includes the pattern of ammonium heptamolybdate (Fig. 3(a)), for comparison. All the patterns have two characteristic regions. The first shows a series of weak bands close to an intense band, all assigned to the reduction of Mo(VI) → Mo(V) → Mo(IV), of Co(III) → Co(II), and of Fe(III) → Fe(II). It is apparent that the Al(III)-phase shows a slightly

TABLE 2

Temperatures (°C) of the main phases of the reduction steps in the TPR treatment of the Co, Fe and Al Anderson phases and of ammonium heptamolybdate (AHM)

Sample	Mo_4O_{11}	$M^{II}MoO_4$	MoO_2	Mo^0
Co-phase	430	500	610	848
Fe-phase	457	500	630	845
Al-phase	470	–	586	990
AHM	500	–	730	850

different behaviour due to the stability of the trivalent ion. The second region, between 830 and 1000°C, presents a strong band attributed to the final reduction to metallic Mo.

Table 2 shows the temperature of the TPR signals for each compound of the series, as well as the major phase present in each step, according to the XRD and IR analyses. Figure 4 shows the SEM micrographs for each step of the reduction. Figure 4(a) shows the crystals obtained by TPR treatment of the Co-phase up to 300°C, before the formation of Mo_4O_{11}. The presence of the $(NH_4)_{0.15} \cdot MoO_3 \cdot 5H_2O$ phase can be identified by XRD. Figure 4(b) corresponds to the Mo_4O_{11} phase. Figure 4(c) shows the formation of metallic Mo. The morphology of the original crystals remains practically unaltered up to 600°C.

The reduction of Mo(VI) oxide to form MoO_2 has long been considered as a one-step reaction, but Burch in 1972 [24] suggested that Mo_4O_{11} is formed as an intermediate in the process. Later, other studies confirmed this, proving that the process can be described as a consecutive autocatalytic reaction in which the $Mo(V) \rightarrow Mo(IV)$ step is catalysed by traces of MoO_2 [24, 25]. The overall process can be described by the "shrinking core model" [26]. Likewise, traces of dispersed metals, usually present in the lower oxides, may also activate the reducing agent: small quantities of Co^0 were found on reduced Co(III) molybdate [27]. Moreover, the reduction of Co_3O_4 shows the formation of traces of Co^0 at relatively low temperatures ($\approx$400°C) [28]. In this context, it is interesting to note that there is a relationship between the reducibility of metal oxides in an H_2 stream and their bond strength [29]. The Co-oxide shows a lower bonding energy and activation energy for the reduction process than the Fe-oxide. Consequently, the promoting effect of these metals may affect the Mo(VI) reduction in the Anderson phases in a different way.

In fact, the higher reducibility of the Co-phase is consistent with the lower temperature of heteromolybdate breaking to form Mo_4O_{11}. However, these heteropolymolybdates are, in general, reduced at lower temperatures than polymolybdates such as ammonium heptamolybdate, as can be observed in Fig. 3 and Table 2.

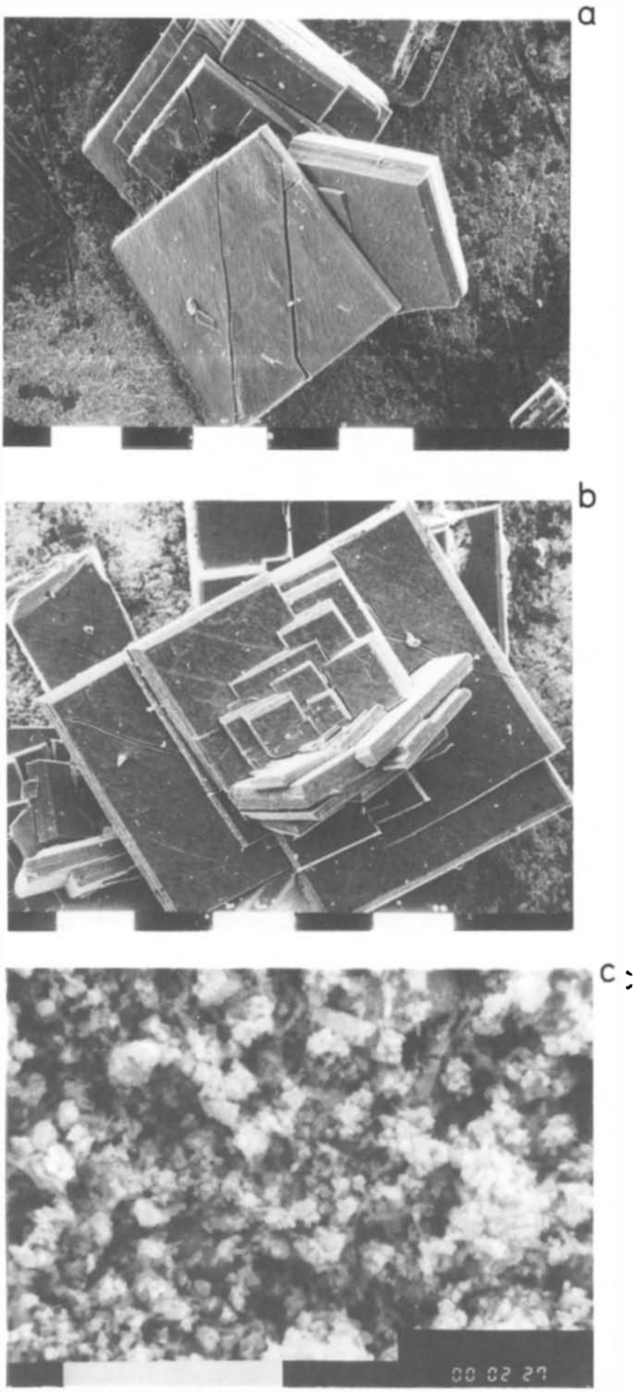

Fig. 4. Scanning electron micrographs of $(NH_4)_3[CoMo_6O_{24}H_6] \cdot 7H_2O$ phase during the TPR treatment (original magnification, ×200; scale bar, 100 μm): (a) up to 300°C; (b) up to 500°C; (c) up to 1000°C.

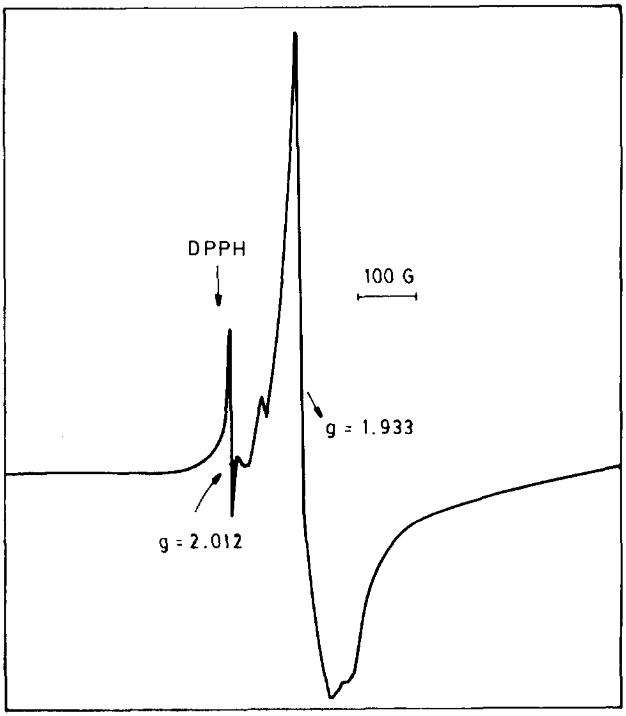

Fig. 5. EPR spectrum of $(NH_4)_3[AlMo_6O_{24}H_6] \cdot 7H_2O$ heated at 450°C in static air.

The reduction to Mo(V) is evident from EPR spectroscopy. The EPR spectrum reproduced in Fig. 5 corresponds to a sample of $(NH_4)_3[AlMo_6O_{24}H_6] \cdot 7H_2O$ heated up to 450°C. It shows an intense signal at $g = 1.934$ characteristic of this species [21]. In addition to this signal, a single line at $g = 2.012$ is observed. Similar EPR patterns have been found for some other oxides subjected to a reducing treatment [30, 31]. The last signal can be attributed to F-centres as well as to the presence of radicals [30]. The thermal processes of some Keggin heteropolymolybdates, accompanied by a partial reduction to Mo(V), have recently been analysed by EPR spectroscopy [32]. In these studies, the destruction of the anionic structure is sometimes apparent from the presence of oxygen radicals.

With respect to the heteroatom, the formation of $CoMoO_4$ and $FeMoO_4$ in the region of 400°C can be revealed by XRD analysis, although the identifying patterns of these compounds are not clear, due to their low levels relative to Mo-oxides and to their poor crystallinity. Mössbauer spectroscopy corroborates this assumption. The spectrum of the Fe-phase heated to 500°C reveals the presence of β-$FeMoO_4$. The quadrupole splitting and isomer shift for the two doublets at 2.50–1.10 mm s^{-1} and 0.9–1.0 mm s^{-1}, respectively, are characteristic of the high-spin ferrous ions in the β-$FeMoO_4$ phase [23, 33].

The reduction process involves the steps

$$(NH_4)_3[MMo_6O_{24}H_6]\cdot 7H_2O \xrightarrow{200\text{–}300^\circ C} (NH_4)_{0.15}\cdot MoO_3\cdot 5H_2O \xrightarrow{300\text{–}400^\circ C}$$

$$Mo_4O_{11} + MMoO_4 \xrightarrow{400\text{–}500^\circ C} MoO_2 + MMoO_4 \xrightarrow{800\text{–}900^\circ C} Mo^0 + M^0$$

where M is Fe, Co.

It is interesting to note that the lowest temperature for the formation of Mo(IV) is observed for the Al-phase. Simultaneously, the "MoO_2" cell volume becomes larger (by approx. 8‰) than that of MoO_2 (ASTM 5-452).

The stability of the M(III) trivalent ion plays an important role in this reduction process. A tentative explanation of this behaviour can be proposed by considering a similar phenomenon in the titanium oxide "reduced rutile" system. It can be assumed that the non-stoichiometry is accommodated by CS planes and also by "additional" trivalent atoms (and not by a deficit in the O-array) [34–36]. Likewise, the stability of the "$(Mo,Al)O_2$" phase can also be inferred from the increase in the temperature of reduction to metallic Mo, which is approximately 150°C higher than that observed for the similar phases of Fe and Co, where stoichiometric MoO_2 (ASTM 5-452) is formed. The presence of α-Al_2O_3 can also be suggested at 1000°C.

Finally, the formation of molybdenum nitride (ASTM 23-1256) is possible above 1000°C in the pyrolysis of the Fe and Co phases, depending on the experimental conditions.

CONCLUSIONS

In the thermal treatment of $(NH_4)_3[MMo_6O_{24}H_6]\cdot 7H_2O$ in oxidant and inert atmospheres, the heteroatom is stabilized as $M_2(MoO_4)_3$ when M is Al or Fe, while the Co-phase forms $CoMoO_4$. In addition, all Anderson phases give $MoO_{(3-x)}$ as a final product.

The $[(NH_4)_2O]_xMoO_3(H_2O)_y$ phase is only observed as an intermediate with thermal treatment in static air.

The TPR process reveals that the presence of the heteroatom decreases the stability of the polyanion. The following sequence for the heteropolyanion stability was established: $Co < Fe < Al$.

The heteroatom is observed as $MMoO_4$ at 500°C when M is Co or Fe, while the formation of a non-stoichiometric "$(Mo,Al)O_2$" phase, related to the "reduced-rutile" systems is suggested for the Anderson phase containing Al.

While the temperature of the $MoO_2 \rightarrow Mo$ reduction is similar for the Co- and Fe-phases, as well as for the HMA ($\approx$850°C), indicating the presence of a stoichiometric MoO_2 oxide, the incorporation of Al in this lattice decreases its reducibility.

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