# Anderson phases as precursors of nickel–molybdenum–tungsten oxides

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Mixed Ni–Mo–W oxides have been prepared by decomposition at 873 K of Anderson-type $[NiMo_{6-x}W_xO_{24}H_6](NH_4)_4 \cdot 5H_2O$ ($x=0$, 2, 3, 4, 6) heteropolyoxometallates. Thermal analysis of the precursors, X-ray diffraction and Raman spectroscopy on the mixed oxides were performed. X-Ray powder patterns, collected at the end of the thermal treatment, revealed that the final products are $NiMoO_4$ and $MoO_3$ for the $x=0$ composition, whereas for tungsten-containing materials the final products are $Mo_{1-x}W_xO_3$ solid solutions, $NiWO_4$ and $WO_3$, depending on the Mo/W atomic ratio. Raman spectra have confirmed the XRPD analysis, revealing the presence of a stable $WO_3$-type phase at high molybdenum contents and a high structural stability of $Mo_{1-x}W_xO_3$ solid solutions.

Heteropolyoxometallates are polymeric species formed by the condensation of more than two oxoanions. Anderson-type heteropolyanions, with the general formula $[XM_6O_{24}H_6]^{n-}$, have received great interest because of their potential applications.[1] The mixed molybdotungstonickelates were first described by Matijevic *et al.*[2] The compounds (in which M is molybdenum or tungsten and X is a transition-metal atom such as cobalt or nickel) can be used as catalysts directly as bulk materials,[3–5] or deposited on different supports.[6] Moreover, they form readily, under mild thermal treatment, highly dispersed bi- or tri-metallic oxides ($XO/MoO_3$, $XO/WO_3$, $XO/Mo_{1-x}W_xO_3$), metal molybdates or tungstates ($XMoO_4$, $XWO_4$), which are well known catalysts (supported or unsupported on alumina) for industrial oxidation and hydrodesulfurization (HDS) processes.[7]

Structurally, the $[XM_6O_{24}H_6]^{n-}$ anion is made up of a compact package of six $MoO_6$ octahedra which surround one $XO_6$ polyedron in a planar hexagonal configuration.[8] There are three types of M—O bonds: M—O terminal bonds, M—O(H)—X and M—O—M bridge bonds. A monovalent cation ($NH^{4+}$, $Na^+$, *etc.*) is coordinated by oxygen atoms from the heteropolyanion and some hydration water molecules. Anderson phases are able to lose the hydration water without the destruction of the heteropolyanion structure.

The aim of this work is to complete a previous study on the preparation and characterization of molybdotungstonickelate Anderson-type compounds[9] examining, by X-ray diffraction and Raman spectroscopy, the structural properties of nickel–molybdenum–tungsten oxides obtained after thermal decomposition of the Anderson phases. In particular, our interest is directed towards the $Mo_{1-x}W_xO_3$ solid solutions which are formed when the Mo–W Anderson phases decompose. The $Mo_{1-x}W_xO_3$ system has been widely studied,[10,11] and is characteristic because both end members reveal octahedral environments of the metals but different octahedral networks.

## Experimental

$[NiMo_{6-x}W_xO_{24}H_6](NH_4)_4 \cdot 5H_2O$ ($x=0$, 2, 3, 4, 6) were prepared by dropwise addition of nickel sulfate into boiling solutions containing appropriate amounts of $(NH_4)_4Mo_7O_{24} \cdot 4H_2O$ and $Na_2WO_4 \cdot 2H_2O$. Details of the sample characterizations performed by X-ray powder diffraction (XRPD), diffuse reflectance spectroscopy (DRS), magnetic susceptibility and X-ray photoelectron spectroscopy (XPS) are given in ref. 9.

Thermal analysis was performed under air with a Stanton Redcroft STA 781 simultaneous TG–DTG–DTA apparatus (Pt crucibles, Pt–Pt/Rh thermocouples). The heating rate was 5 K $min^{-1}$ from 293 to 873 K for all the samples.

XRPD patterns were obtained for the powders obtained at the end of the thermal treatment by a Philips Debye-Scherrer camera (114.6 mm i.d.) with the asymmetric Straumanis film mounting method. Phase analysis was carried out with Cu-K$\alpha$ (nickel-filtered) radiation. Reflections in the region $2\theta=10$–$60^\circ$ were read by means of a Norelco measuring device with an accuracy of $\pm 0.005$ cm.

Raman spectra were collected at room temperature by a Spex-Ramalog 1403 double monochromator spectrometer,

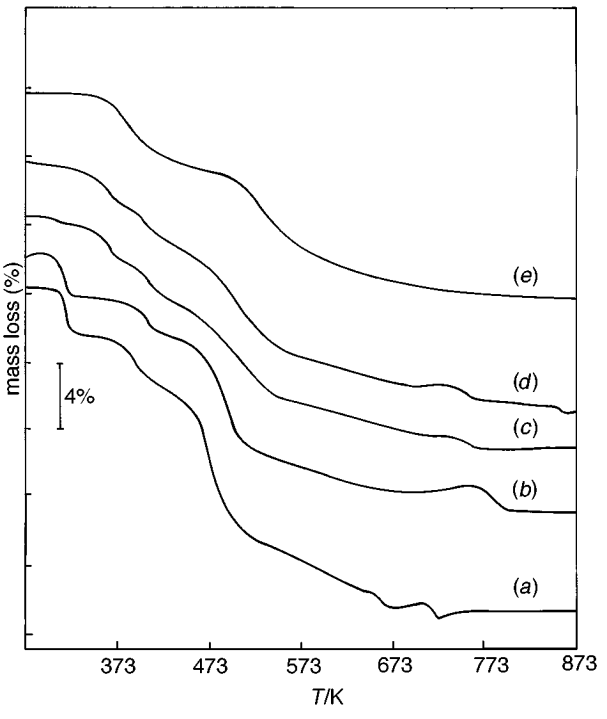


**Fig. 1** Thermogravimetry patterns of $[NiMo_{6-x}W_xO_{24}H_6](NH_4)_4 \cdot 5H_2O$ Anderson phases. (*a*) $x=0$; (*b*) $x=2$; (*c*) $x=3$; (*d*) $x=4$; (*e*) $x=6$.

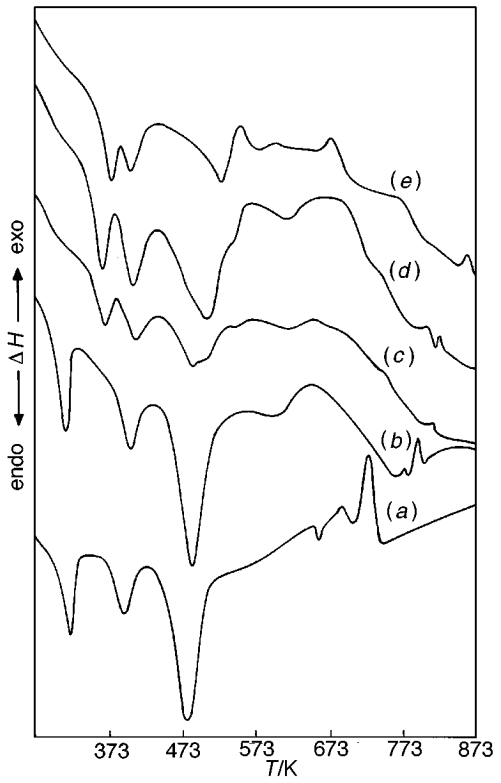


**Fig. 2** Differential thermal analysis patterns of $[NiMo_{6-x}W_xO_{24}H_6](NH_4)_4 \cdot 5H_2O$ Anderson phases. (*a*) $x=0$; (*b*) $x=2$; (*c*) $x=3$; (*d*) $x=4$; (*e*) $x=6$.

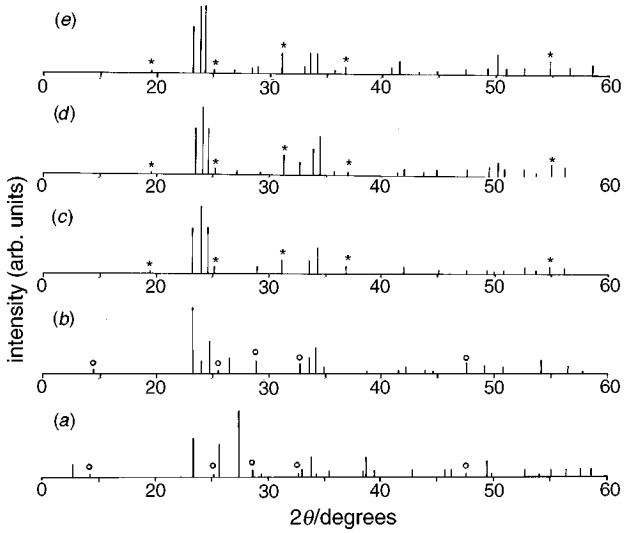


**Fig. 3** X-Ray powder diffraction patterns of Anderson phases after thermal treatment at 873 K. (*a*) $x=0$; (*b*) $x=2$; (*c*) $x=3$; (*d*) $x=4$; (*e*) $x=6$. ○, $NiMoO_4$; ×, $NiWO_4$.

equipped with a SCAMP data processor. The 514.4 nm line of an Ar ion laser was used for excitation.

## Results and Discussion

The thermal analyses performed on the $[NiMo_{6-x}W_xO_{24}H_6](NH_4)_4 \cdot 5H_2O$ ($x=0$, 2, 3, 4, 6) materials confirm the results given by La Ginestra *et al.*, who showed that the decomposition of $[XMo_6O_{24}H_6](NH_4)_4 \cdot 5H_2O$ materials (X = Mn, Co, Ni, Cu, Zn) occurs in many steps.[12]

Fig. 1 shows the thermogravimetry patterns of all the samples. The mass decrease observed for the molybdenum-containing sample [Fig. 1(*a*)] below 443 K is due to the loss of water of hydration, those between 443 and 723 to the elimination of both constitutional water (from the six OH groups bound to nickel) and ammonia. With increasing tungsten content [Fig. 1(*b*)–(*e*)] the different mass loss steps become smoother and shifted to higher temperatures. The latter observation is more visible in the DTA patterns reported in Fig. 2, where a delay of about 50 K with respect to the molybdenum compound ($x=0$) is detected for the tungsten sample ($x=6$) in the endothermic peak around 500 K and which corresponds to the loss of both constitutional water and ammonia. Since the three constitutional water molecules must be considered as fundamental in preserving the Anderson-type structure of the samples, the delay in their elimination gives evidence of the higher structural stability of tungsten-containing heteropolyanions with respect to the molybdenum ones.

The two exothermic peaks with maxima at 693 and 723 K in the molybdenum-containing sample ($x=0$) relative to the formation of $NiMoO_4$ and $MoO_3$ are also shifted to higher temperatures with increasing tungsten content, indicating a greater structural stability of tungsten-containing oxides, namely Mo–W mixed oxides and $NiWO_4$.

The XRPD patterns, collected on the samples obtained at the end of the thermal analysis, are shown in Fig. 3 where the $2\theta$ values and intensities of the observed reflections are reported. The X-ray lines for the nickel molybdate and tungstate minority phases are indicated.

Phase analysis of the $x=0$ compound reveals almost exclusively the presence of orthorhombic $MoO_3$[13*a*] and a small amount of $NiMoO_4$.[13*b*] Patterns of the $x=2$, 3 and 4 compounds show no trace of $MoO_3$ and reveal the presence of $Mo_{1-x}W_xO_3$ solid-solution phases, namely those reported in the literature as $Mo_{0.6}W_{0.4}O_3$ ($\theta$ phase, orthorhombic symmetry)[13*c*] and as $Mo_{0.47}W_{0.53}O_3$ ($\xi$ phase, monoclinic symmetry).[13*d*] In addition, the pattern of the $x=2$ compound still reveals the presence of $NiMoO_4$, while in the $x=3$ and 4 samples $NiWO_4$[13*f*] is formed. Finally, in the $x=6$ compound the triclinic form of $WO_3$[13*e*] and $NiWO_4$ are the phases present. As reported previously,[10] it may then be derived that a decrease of symmetry (from orthorhombic to triclinic) occurs also in our Mo–W mixed oxide samples with increasing tungsten content. The absence of the $MoO_3$ phase also at high Mo/W atomic ratio (sample with $x=4$) also reveals that in the mixed Mo–W oxide system it is molybdenum that prefers to enter the $WO_3$ structure rather than tungsten in the $MoO_3$ lattice.

Regarding Raman spectroscopy it may be recalled that, in the condensed phases we have investigated, $Mo^{VI}$ and $W^{VI}$ are in octahedral coordination.[14] Thus they show patterns more complex than those observed for the same species in simple oxide systems, as those obtained by thermal treatment of the original Anderson phase. In fact, for tetrahedral or octahedral symmetry the internal modes associated to the W—O or Mo—O stretchings are located in characteristic regions of the spectra.[15–17] So, for molybdate ion these Raman lines are located in the 800–870 $cm^{-1}$ region while some lines observed at higher wavenumbers (at about 950 $cm^{-1}$) can be assigned to Mo—O terminal bonds.[18]

Fig. 4 shows Raman spectra of all the samples heated to 873 K. The $x=0$ sample [Fig. 4(*a*)] reveals the typical spectrum of $MoO_3$ with the three most intense lines at 665, 819 and 994 $cm^{-1}$.[10] Some additional weak bands at 881, 898, 916, 937 and 959 $cm^{-1}$ are attributed to tetrahedral $MoO_4$ species of $NiMoO_4$.[19]

On the other hand, the $x=6$ sample [Fig. 4(*e*)] shows the typical Raman spectrum of $WO_3$ with the strongest lines at 715 and 807 $cm^{-1}$.[10] Some additional weak bands corresponding to $NiWO_4$ can be observed in the region around 900 $cm^{-1}$.[19]

The Raman spectrum of the most dilute tungsten mixed oxide [$x=2$, Fig. 4(*b*)] compared to that of the $x=0$ sample,

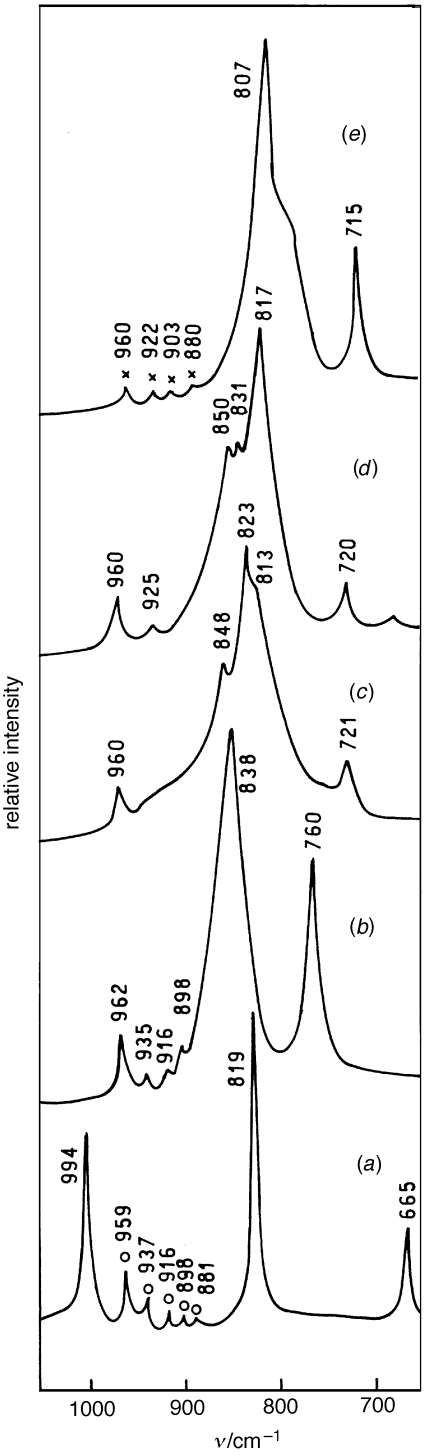


**Fig. 4** Raman spectra of Anderson phases after thermal treatment at 873 K. (*a*) $x=0$; (*b*) $x=2$; (*c*) $x=3$; (*d*) $x=4$; (*e*) $x=6$. ○, $NiMoO_4$; ×, $NiWO_4$.

shows a shift towards higher frequency for the strongest line (from 819 to 838 $cm^{-1}$) as well as the disappearance of the lines at 665 and 994 $cm^{-1}$. This is related to the formation of the $Mo_{1-x}W_xO_3$ solid solution which presents a $WO_3$-type structure, also at high molybdenum content.

With increasing tungsten content [samples with $x=3$, 4, Fig. 4(*c*), (*d*)] the spectra resemble more and more that of the $WO_3$ phase [$x=6$, Fig. 4(*e*)]. However, the most intense Raman line at *ca.* 800 $cm^{-1}$ is broad and split. This is probably due to a decrease of symmetry caused by the presence of more than one type of atom in the lattice.

In the spectrum of the $x=2$ sample [Fig. 4(*b*)] the weak lines due to $NiMoO_4$ are still clearly visible, whereas only for the sample with $x=6$ [Fig. 4(*e*)] can the weak bands corresponding to $NiWO_4$ be observed in the region around 900 $cm^{-1}$.

## Conclusions

XRPD and Raman analyses on the mixed oxides obtained by thermal decomposition at 873 K of $[NiMo_{6-x}W_xO_{24}H_6](NH_4)_4\cdot 5H_2O$ ($x=0$, 2, 3, 4, 6), Anderson-type heteropolymetallates have revealed that: (i) the products are $NiMoO_4$ and $MoO_3$ for the $x=0$ compound, whereas for tungsten-containing materials the final products are $Mo_{1-x}W_xO_3$ solid solutions, $NiWO_4$ and $WO_3$, depending on the Mo/W content; (ii) the presence of a stable $WO_3$-type phase, also at high molybdenum content, indicates that $Mo^{VI}$ ions enter the $WO_3$ lattice preferably rather than $W^{VI}$ into the $MoO_3$ one.

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