Synthesis of molybdenum oxides by the sol–gel method

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Abstract

Molybdenum oxides were synthesized by the sol–gel method, from a precursor prepared with $MoOCl_4$ and nPrOH. The precursor was hydrolyzed, using different catalysts. The process was studied by infrared spectroscopy (IR) and diffuse reflectance. It was found that the hydrolysis produced new species. The catalysts which were used did not significantly modify the spectroscopic properties of the products. A thermal treatment transformed the initial oxides into MoO_3 at 600 °C, and upon heating at 900 °C transformed them into Mo_8O_{23}.

Introduction

Molybdenum is one of the essential elements in biological systems, such as nitrogen fixing bacteria. It is characterized by presenting, besides many oxidation states, an extensive variety of stereochemistries; in fact, it can be said that molybdenum is one of the most complicated of the transition elements.

Mo(VI) structural chemistry is dominated by the presence of oxo groups bonded to Mo. These oxygen atoms utilize σ and π bonds to produce a strong multiple bond Mo–O. Mo(VI) forms tetrahedral oxoanions MoO_4^{2-} that polymerize by acidification; this causes the formation of very complex isopolyanions. The principal characteristic of isopolymolybdates is that they can be considered as aggregates of MoO_6 octahedrons and, in a simplified way, their formation can be considered in terms of component blocks of 'MoO_3' [1]

The MoO_4^{2-} ion contains four terminal oxo groups as the dominant form in Mo(VI) solutions above pH = 7. It has a *Td* structure. Tetrahedral coordination is characteristic of Mo species that are isolated from basic solutions. As the pH decreases, the coordination number increases from four to six and the octahedral Mo(VI) predominates.

The experimental study consisted in making $MoOCl_4$ react with nPrOH in order to obtain an alkoxide. The resulting product was used as a precursor to synthesize molybdenum oxides via the sol–gel process.

$$MoOCl_4 + pHO\text{-}Pr^n \longrightarrow MoOCl_{4-p}(OPr^n)_p + pHCl \quad (1)$$

The alkoxide obtained was hydrolyzed and treated with different catalysts. These reactions produce the hydrolysis and condensation phenomenon which are components of the so-called sol–gel process.

$$MOOCl_{4-p}(OPr^n)_p + (q+r)H_2O \xrightarrow{\text{catalyst}} MoOCl_{4-p-q}(OPr^n)_{p-r}(OH)_{q+r} + qHCl + rPr^nOH \quad (2)$$

$$MoOCl_{4-p-q}(OPr^n)_{p-r}(OH)_{q+r} \xrightarrow[100\ °C]{} \underset{\text{xerogel}}{(MoO_2Cl_2)_2} + H_2O + HO\text{-}Pr^n \quad (3)$$

The existence of xerogel of eqn. (3) was proven by means of thermal gravimetrical analysis (TGA) as well as by chemical analysis, as will be mentioned in 'Results and discussion'.

Xerogel was thermally treated. The proposed reactions for these steps are:

$$(MoO_2Cl_2)_2 \xrightarrow[600\ °C]{} MoO_3 \xrightarrow[900\ °C]{} Mo_8O_{23} \quad (4)$$

Every product was studied by spectroscopic techniques.

Experimental

Synthesis of the alkoxide

A total of 3.938×10^{-3} mol of $MoOCl_4$ (Pfaltz & Bauer) was dissolved in 0.267 mol of nPrOH, dried

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and recently distilled in N_2 atmosphere. The solution, which was transparent and of a very intense green color, was refluxed at 90 °C for 24 h (solution 1P). Later, a dark blue solid was obtained after evaporation of the excess solvent at reduced pressure.

Hydrolysis and variation of pH

Solution 1P was hydrolyzed with $nH_2O/nMo = 300$ (solution 1P*). Also prepared were solutions consisting of solution 1P* and 2.5×10^{-3} mol of: (a) NH_4OH, (b) HCl, (c) acetic acid, in order to obtain different samples. Reflux was continued for 24 h.

Each of the products obtained – solids of dark blue color – was divided into three parts and subjected to thermal treatment at 300, 600 and 900 °C for 72 h.

Samples were analyzed by UV–Vis spectroscopy in a liquid phase using a Varian UV–Vis DMS-80 spectrophotometer and as a solid in Varian Cary 17D equipment. IR spectra were recorded in the liquid phase with Nujol and in the solid state as KBr pellets. This analysis was made in a Nicolet MX-1 spectrophotometer with Fourier transformation, which reaches an accuracy level of 0.02 cm^{-1}. TGA and differential thermal analysis (DTA) were achieved in a Nitrogen atmosphere between 25 °C and 1000 °C with Shimadzu DT-30 equipment.

Special care was taken in the preparation of the samples analyzed by IR spectroscopy. The pellets were first prepared in a nitrogen atmosphere and stored in a dessicator and then analyzed. All the analyses were realized immediately after the samples were prepared.

Results and discussion

Production of MoO_3 by molybdates in an acidic medium by chemical or electrochemical reactions, leads to different complexes of Mo(V) as intermediates. The nature of the species obtained by this process depends critically on concentration, pH and on anions present in the system. The most important species is possibly the emerald green ion $[MoOCl_5]^{2-}$ that can be isolated forming salts with diverse cations. $[MoOCl_5]^{2-}$ has been widely studied, both in solution and in crystals; its electronic spectrum has been interpreted in terms of the existence of a marked tetragonal distortion in comparison with the regular octahedral symmetry [2]. When $[MoOCl_5]^{2-}$ solutions are less than 10 M in HCl, an intensification of color is produced. This phenomena is due to the formation of oxo bridges.

Anal. of the xerogels: Mo, 48.63; Cl, 35.28. Calc. for $(MoO_2Cl_2)_2$: Mo, 48.25; Cl, 35.66%.

Liquid UV–Vis spectroscopy

Spectra were obtained in the 800–400 nm region. Four spectra were recorded: (a) before reflux, (b) reflux for 1 h, (c) reflux for 4 h, (d) reflux for 24 h.

In the electronic spectra of the hexamolybdates, inter-valence charge transfer bands (IVCT) and d–d for Mo(V) appear. The two different bonds – edge and corner – between the MoO_6 octahedrons produce two different types of IVCT transitions.

Electronic transitions between MoO_6 octahedrons that share edges are known as 'intragroup' while those which occur between corners are named 'extragroup'. The absorption bands in the near infrared have been attributed to intragroup and extragroup IVCT transitions by Fruchart *et al.* [3]. They assigned extragroup transitions to the region 10 000–13 000 cm^{-1}.

Table 1 exhibits the UV–Vis spectrum results of the alkoxide in the liquid phase. Two bands are observed: the first one is located at 13 700 cm^{-1} and has been assigned to transition $^2B_2 \rightarrow {}^2E$. The second band appears at 22 472 cm^{-1} and has been assigned to the $^2B_2 \rightarrow {}^2B_1$ transition, both of Mo(V) [4, 5]. It is considered that the predominant species in the diluted solutions employed in the UV–Vis study is $[Mo_6O_{19}]^{3-}$, solutions of which are brown in color. The electronic transitions of this species are so intense that they obscure the bands corresponding to the simultaneously formed alkoxides.

Diffuse spectroscopy

The loss of an alkyl group in an alkoxide complex tends to confirm the greater stability expected from a complete double M=O bond, as compared with a bond of partial π character for oxygen in M–O–R [6].

In Table 1, the diffuse spectroscopy results of the compound $MoOCl_2(OPr^n)_2$ [7] is observed as obtained by evaporation at reduced pressure. Inasmuch as the compound contains Mo(VI), which is a d^0 ion, the spectrum should contain only bands of charge transfer; nevertheless, bands are observed in the visible region. The weak band at 11 364 cm^{-1} cor-

TABLE 1. UV–Vis and diffuse spectroscopy results of the alkoxide $MoOCl_2(OPr^n)_2$

	Assignment	Wavenumber (cm^{-1})
UV–Vis spectroscopy	$^2B_2 \rightarrow {}^2B_1$	22472
	$^2B_2 \rightarrow {}^2E$	13700
Diffuse spectroscopy	$^2B_2 \rightarrow {}^2B_1$	20833
	$^2B_2 \rightarrow {}^2B_1$	14815
	$^2B_2 \rightarrow {}^2E$	11364

responds to transition $^2B_2 \rightarrow {}^2E$ which involves the π orbitals of the molybdenil oxygen [5, 8]. The second peak, located at 14 815 cm^{-1} is assigned to transition $^2B_2 \rightarrow {}^2B_1$, although it is also attributable to species Mo(V) formed by solvolytic dissociation, since a band in this region is characteristic of the presence of Mo(V)=O [5, 9]. The band appearing at a longer wavelength, 20 833 cm^{-1}, corresponds to transition $^2B_2 \rightarrow {}^2B_1$ [10].

The bands appearing in the spectrum obtained after the hydrolysis of $MoOCl_2(OPr^n)_2$ are observed at 9217, 10 204 and 11 364 cm^{-1} corresponding to a transfer of interligand electrons, since OH ions attract some of the electronic density once the inductive effect of the $nPrO^-$ radicals has disappeared. The band at 14 815 cm^{-1} also appears again, as in the case of the alkoxide. The last band appears at 20 000 cm^{-1}; that is, it is displaced to a slightly lower energy with respect to the alkoxide (20 833 cm^{-1}). This can be explained if one supposes that an electronic transition exists between the units Mo(V) and Mo(VI) which are present in the dimer. This case is comparable to that proposed by Sánchez *et al.* for tungsten polyanions [11].

Diffuse spectroscopy results corresponding to: (a) hydrolyzed alkoxide, (b) hydrolyzed and catalyzed with NH_4OH, (c) catalyzed with HCl, and (d) catalyzed with acetic acid are observed. Certain similarities can be seen between the spectra in the region of greater energy, where three bands appear at 11 240, 14 815 and 20 000 cm^{-1}, that were assigned before; there are, nevertheless, several differences in the region of minor energy.

Characteristic electronic spectra of reduced polymolybdates present bands in the visible and near-infrared regions. These are of two types: d–d bands for a Mo(V) center in a location approximately C_{4v} and intervalence charge transfer (IVCT) transitions between Mo(V) and Mo(VI) through an oxo bridge. Intensities and the position of O–Mo are not greatly affected by the reduction.

Hexamolybdates possess only MoO_6 octahedrons which share edges. Consequently, only an IVCT transition type is expected. This is the so-called 'intragroup' transition. In this case, the transitions are of the d–d type, from the base state $^2B_2$.

In the hydrolyzed alkoxide spectrum, the first band is presented clearly at 9217 cm^{-1} as can be seen in Table 2, although imperceptible in the other samples. It is assigned to IVCT transitions. This is the most intense band and the large size can be attributed to a strong base-state delocalization of the valence electron. A second band at 10 204 cm^{-1} appears only in the hydrolyzed alkoxide, so it can be attributed to the metal–ligand electronic transition between Mo and nOPr; not all the propoxy groups of the dimer are entirely substituted in the absence of a catalyst. A very weak band is observed in the hydrolyzed alkoxide spectrum, appearing as a shoulder at 11 364 cm^{-1}; it is also weakly present in the alkoxide catalyzed with NH_4OH and in the sample catalyzed with HCl; in both cases at a lower energy region, 11 236 cm^{-1}, and it corresponds to the transition $^2B_2 \rightarrow {}^2E$ of Mo(V) [12, 13]. This band is almost imperceptible in the spectrum obtained of the sample catalyzed with acetic acid.

TABLE 2. Diffuse spectroscopy results

Sample	Assignment	Wavenumber (cm^{-1})
Hydrolyzed alkoxide	$^2B_2 \rightarrow {}^2B_1$	14815, 20000
	$^2B_2 \rightarrow {}^2E$	11240, 11364
	Ligand–metal transition	10204
	IVCT	9217
Catalyzed with NH_4OH	$^2B_2 \rightarrow {}^2B_1$	14815, 20000
	$^2B_2 \rightarrow {}^2E$	11236
Catalyzed with HCl	$^2B_2 \rightarrow {}^2B_1$	14815, 20000
	$^2B_2 \rightarrow {}^2E$	11236
Catalyzed with CH_3COOH	$^2B_2 \rightarrow {}^2B_1$	14815, 20000
	$^2B_2 \rightarrow {}^2E$	11240

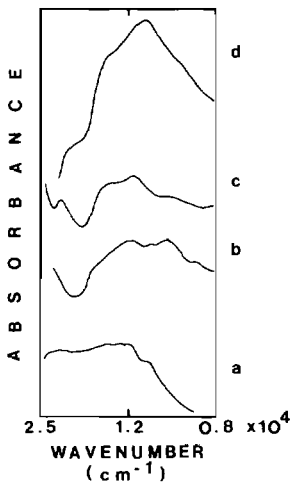

Fig. 1. Diffuse spectroscopy of Mo oxides obtained using HCl as a catalyst at: (a) 25, (b) 300, (c) 600, (d) 900 °C; all for a 72-h period.

Diffuse reflectance of thermally treated oxides

Spectra were obtained from the oxides produced by thermal treatment of the samples at 300, 600 and 900 °C for 72 h.

In Fig. 1 the diffuse reflectance spectra for molybdenum oxide prepared using HCl as catalyst are shown. Spectra for the other samples exhibit identical bands.

Figure 1(b) presents the spectrum of the sample heated to 300 °C. A shoulder is observed at 15 625 cm^{-1} and is better defined than in Fig. 1(a). It corresponds to a Mo(V) → Mo(VI) IVCT transition. This band has also been found in substituted isoelectronic heteropolymolybdates with reduced blues of bands assigned to V(IV) → Mo(VI) [14]. The well-defined band at 12 346 cm^{-1} can be assigned to $^2B_2 \rightarrow {}^2E$ and to an IVCT transition [9]. A weak band is found at 11 494 cm^{-1} but is not conspicuous because it is placed in between two bands of greater intensity. It is an extra-group IVCT band [15], that appears slightly displaced towards a higher energy region in comparison with Fig. 1(a). A new band is also observed at 10 363 cm^{-1} and is attributed to transition $^2B_2 \rightarrow {}^2E$ of a d–d band in a Mo(V) ion.

Figure 1(c) shows the spectrum at 600 °C in which four bands are observed: one at 20 408 cm^{-1}, assigned to $^2B_2 \rightarrow {}^2B_1$; another at 13 514 cm^{-1}, which appeared in Fig. 1(a); a third band at 12 500 cm^{-1} (assigned in former spectra) and a fourth band at 10 363 cm^{-1}. The spectrum of this compound corresponds to MoO_3. It is a microcrystalline solid pale yellow in color.

In Fig. 1(d) the spectrum of the sample treated at 900 °C can be seen. In it, five bands appear: at 19 048 ($^2B_2 \rightarrow {}^2B_1$), 14 286 and 11 765 cm^{-1} (IVCT intragroup bands); 10 929 and 9390 cm^{-1} (IVCT extragroup bands) [16]. The compound obtained at this temperature was analyzed by X-ray diffraction in a Philips PW-1140-00-62 diffractometer and was identified as Mo_8O_{23}.

IR spectroscopy of liquids

Spectra were obtained of liquid samples of refluxed solutions, analyzed by dilution with Nujol and plates of NaCl in a Nicolet MX-1 spectrophotometer in the 4000–300 cm^{-1} range.

Alkoxide IR

Bands appear as follows: a band at 3500 cm^{-1} assigned to O–H stretching [17, 18]; two bands at 1456 and 1232 cm^{-1} corresponding to C–H bending [19]. Bands at 1100 and 1058 cm^{-1} can be assigned to a CH_3 vibration [20, 21]. The band corresponding to the $Mo{=}O_t$ vibration appears in the spectra well defined at 972 cm^{-1} [22–24]. It is important to note the presence of bands at 849 and 726 cm^{-1}, corresponding to Mo–O–Mo vibrations [25–28], which support the assumption that the sample contains many oligomers. As the amount of oligomeric species increases, a reduction in the intensity of the bands is produced, probably due to the non-homogeneity of the analyzed samples. The color of the final product is a very intensive green.

IR of the hydrolyzed alkoxide

Upon addition of water, the color of the solution turned immediately from green to a very dark blue. This indicates the presence of Mo(VI) and Mo(V) in the solution. This change of color is due to the substitution of nOPr radicals by OH ions, which causes formation of new bonds with Mo. Reducibility of polymolybdates to blues of mixed valence has been studied by Pope [29] and by Nomiya and Makoto [30].

For the hydrolyzed sample, the same bands are observed as in the former sample; it is important, however, to note the displacement of a band initially found at 3364 cm^{-1} and now in a higher energy region, at 3378 cm^{-1} [17, 18], which is due to the formation of new O–H bonds, more stable and bonded to the Mo atom.

IR of the solids

All samples obtained are powders dark blue in color at 25 °C. The quantity of water was larger than the stoichiometric quantity necessary for complete hydrolysis of the alkoxides.

In Fig. 2 the spectra of samples prepared at 25 °C are shown. In all of them, bands are observed at 3400 and 3205 cm^{-1} due to stretching and bending modes of hydroxyl groups of water molecules existing in the gels [17, 18]. In samples catalyzed with NH_4OH and catalyzed with acetic acid, the 3205 cm^{-1} band appears as a shoulder. There are a pair of very sharp and intense bands at 1398 and 1384 cm^{-1} in all the spectra, which correspond to a symmetrical deformation band of the C–H group [19]. The existence of these groups can be attributed to the production

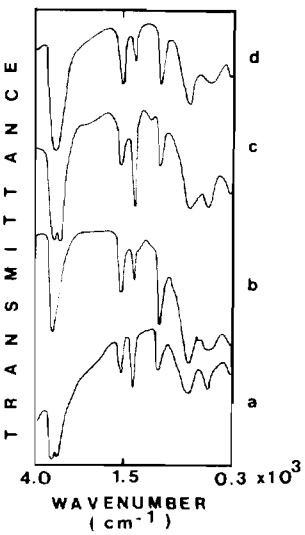

Fig. 2. IR spectra of the solid samples: (a) hydrolyzed $MoOCl_2(OPr^n)_2$, (b) catalyzed with NH_4OH, (c) catalyzed with HCl, (d) catalyzed with acetic acid.

of nPrOH during alkoxide hydrolysis. There is also a sharp and intense band at 979 cm^{-1}, indicative of the present of Mo=O bonds [22–24]. At 719 cm^{-1} there is a wide but well defined band assigned to the Mo–O bond; at a lower wavenumber (639 and 567 cm^{-1}) are two wide low-intensity bands, corresponding to the Mo–O–Mo bonds [25–28]. In the lower energy region very sharp bands appear at approximately 300 cm^{-1}. These bands can be assigned to Mo–Cl terminal bonds [31, 32].

Change in pH has no appreciable effect on the formation of the final compound since both position and intensity of the bands remain almost invariable. Based on the chemical analysis, IR spectroscopy, the TGA results, the assignation of Mo=O, M–O–Mo, and Mo–Cl bands, the existence of the dimer $(MoO_2Cl_2)_2$ is proposed.

IR study of samples with thermal treatment

All of the samples treated at 300 °C present a pale yellowish-green color. Figure 3 shows the IR spectra of the NH_4OH-hydrolyzed sample. The spectra of this sample is representative of the other samples.

At 300 °C there is an appreciable reduction in the intensity of bands in the 3500–1620 cm^{-1} region, assigned to the O–H bonds of water and of nPrOH, which indicates that these molecules are being eliminated from the compound's network. This same reduction is observed in the C–H deformation bands. The band at 979 cm^{-1} slightly diminishes in intensity and is displaced to 986 cm^{-1}, which indicates the π character of the Mo=O bond. The pair of 740 and 719 cm^{-1} bands are also displaced toward 841 and 813 cm^{-1}.

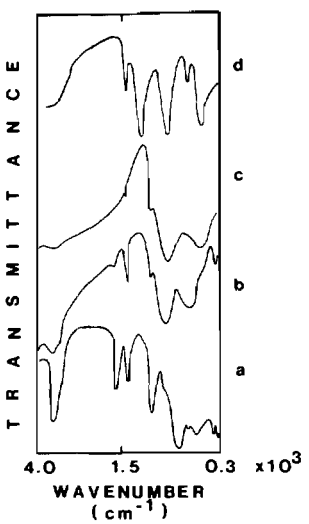

Fig. 3. IR spectra of the hydrolyzed sample with NH_4OH with different thermal treatment: (a) without heating, (b) 300, (c) 600, (d) 900 °C all for a 72-h period.

Likewise, the 639 and 567 cm^{-1} bands intensify and appear at 675 and 632 cm^{-1}. This means that the strength of the Mo–O–Mo bonds increases. No changes occur in the Mo–Cl bands.

At 600 °C the bands of H_2O completely disappear, as do the C–H bands. The Mo=O band is displaced to 1000 cm^{-1} although it now appears very small because of the great intensity of the Mo–O band which has been placed at 820 cm^{-1}. At this temperature, the Mo–Cl bands disappear. All these bands coincide exactly with those of MoO_3. The spectrum of the sample heated at 900 °C shows the formation of the compound Mo_8O_{23}. In order to determine if the formation of this new molybdenum oxide occurs in a short time, samples were heated at 900 °C for a one hour period. The spectra obtained present several differences, attributed to the presence of the radicals of catalysts used, which cause the compound structures to evolve in a different pathway. None of the spectra obtained coincides with the one of the sample heated for 72 h at 900 °C. These results indicate that in order to form the new structure it is necessary to heat for a longer period.

Conclusions

The dimer $(MoO_2Cl_2)_2$ was obtained via the sol–gel method, from the molybdenum alkoxides $MoOCl_{4-p}(OPr^n)_p$. The catalysts used in the hydrolysis of the alkoxides did not significantly modify the spectroscopic properties of the final solids. The slight differences that appeared were detected through IR and UV–Vis spectroscopy. The thermal treatment of the samples showed that at 600 °C MoO_3 is formed, and that, at 900 °C Mo_8O_{23} is obtained.

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