

Stability of the phospho-molybdc Dawson-type ion $P_2Mo_{18}O_{62}^{6-}$ in aqueous media

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The stability of the ammonium phospho-molybdc Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ in aqueous solution has been studied. The polyanion $P_2Mo_{18}O_{62}^{6-}$ decomposes into the lacunar Keggin-type anion $H_xPMo_{11}O_{39}^{(7-x)-}$, $H_xMo_5P_2O_{23}^{(6-x)-}$, phosphate and oxomolybdate species, regardless of the concentration and acid–base conditions.

Introduction

Dawson-type heteropolyoxometalate compounds $P_2M_{18}O_{62}^{6-}$ ($M = W, Mo$) have received increasing attention in the catalytic field due to the combination of redox and acid properties in the same structure. Many research efforts have been devoted to the synthesis/characterization, stability and catalytic analysis of phospho-tungstic Dawson-type compounds. Comuzzi *et al.*¹ have studied the thermal stability of a Wells–Dawson potassium salt $K_6P_2W_{18}O_{62} \cdot 10H_2O$. This compound showed a structural rearrangement around 577 °C, resulting in a new material composed of a mixture of K_3PO_4 , $K_3PW_{12}O_{40}$ and a surface amorphous phase of unknown composition generated by decomposition of the Keggin phase. Briand *et al.*² extended those studies on a vanadium-substituted Dawson salt α_2 -1- $K_7P_2VW_{17}O_{61} \cdot 18H_2O$. This compound recrystallizes as a potassium–tungsten Keggin salt and P_2O_5 – WO_3 –(K_2O) upon calcination above 400 °C. Vanadium that was initially part of the tungsten framework is expelled out of the structure and covers the surface of the new phases.

Molybdenum-based Dawson-type compounds $P_2Mo_{18}O_{62}^{6-}$ have recently been considered as suitable catalytic materials; nevertheless, the information available on these materials is still rather scarce. The industrial application of phospho-molybdc Dawson compounds in the catalytic oxidation of alkanes to unsaturated carboxylic acids was patented by Wijesekera *et al.*³

For the oxidative dehydrogenation of isobutyraldehyde, Hu *et al.*⁴ have studied the thermal stability and reactivity of a series of phospho-molybdc Dawson-type salts with varying counter-cations [$P_2Mo_{18}O_{62}X_6$, with $X = K^+, Rb^+, NH_4^+, Cs^+$ and $(CH_3)_4N^+$]. Spectroscopic analysis demonstrated that these materials undergo a solid state rearrangement at ca. 260 °C producing the Keggin-type ion $PMo_{12}O_{40}^{3-}$.

The instability at mild temperatures and scarcity of specific surface area for Dawson-type compounds restricts the application of those compounds in many heterogeneous catalytic processes. However, the spreading of the heteropoly-oxoanions on a metal oxide *via* an impregnation process would overcome these disadvantages. The knowledge of the stability of the anion in aqueous media at different pH and temperature conditions is a key in the development of heteropoly-compounds supported on oxides suitable for catalytic applications. Raman studies of monolayer molybdenum- and vanadium-supported catalysts under ambient conditions (hydrated surface) have established that the

structure of the surface species is controlled by the net surface pH at the point of zero charge of a particular oxide support.^{5,6} In fact, oxide supports such as Al_2O_3 , SiO_2 , TiO_2 , *etc.*, in the presence of water (moisture), impart a specific pH that controls the structure of the supported phase.

The condensation–hydrolysis equilibria in solutions of the heteropoly-anions in aqueous and organic media have been thoroughly studied.^{7–9} The Keggin structure $X^n+M_{12}O_{40}^{(8-n)-}$ progressively loses MO species when the pH of the solution is raised. The pH at which the structure is unstable is a function of the heteropoly-anion composition and the nature of the heteroatom.

Solutions of phospho-tungstic Dawson-type heteropoly-anions $X_2W_{18}O_{62}^{6-}$ are stable up to ca. pH 6. Above this pH, the anions are hydrolyzed into a mixture of lacunary species.

Petersson *et al.*¹⁰ studied the speciation of molybdate and phosphate mixtures of varying concentrations and acidities. These studies established the composition of several molybdophosphate species and the formation of the 18-molybdophosphate $P_2Mo_{18}O_{62}^{6-}$ anion. The existence of the anion was observed at high Mo : P (>9) concentrations and pH < 3.

The present work screens the stability of the aqueous soluble ammonium phospho-molybdc Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ over a wide range of concentrations and acid–base conditions (pH). The aim of this research is to obtain fundamental information to assist in the synthesis and surface characterization of $P_2Mo_{18}O_{62}^{6-}$ supported on metal oxides.

Experimental

Synthesis of the ammonium phospho-molybdc Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$

The Dawson-type salt $(NH_4)_6P_2Mo_{18}O_{62} \cdot 12H_2O$ was synthesized according to the technique described by Hu.¹¹ A mixture of 20 g of $Na_2MoO_4 \cdot 2H_2O$ (J. T. Baker ACS, 100%), 3.0 ml of concentrated PO_4H_3 (Merck, 85%) and 16.5 ml of concentrated HCl (Merck, 37%) in 50.0 ml of distilled water was kept boiling for 8 h. Then the mixture was cooled down to room temperature and 20 g of solid NH_4Cl (J. T. Baker ACS, 100%) were added. The precipitation of a green solid was observed immediately after the addition of ammonium chloride. This precursor and the supernatant solution were kept at 5 °C overnight in order to enhance the precipitation. The solid was

filtered on a Buchner funnel and redissolved in the minimum amount of distilled water. This solution was filtered to separate undissolved impurities, and 10 g of solid NH_4Cl (J. T. Baker ACS, 100%) were added to re-precipitate the salt. Again, the precursor and the supernatant solution were kept at 5°C overnight. Finally, the salt was filtered, washed with ethanol (3×10.0 ml, Merck, 99.5%) and anhydrous diethyl ether (3×10.0 ml, Merck, 99.5%), and dried at room temperature under vacuum. This product, called P_2Mo_{18} throughout the paper, is highly soluble in water, light green and is composed of fine powdered crystals. The salt possesses 12 water molecules per molecule of the Dawson $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ unit according to thermal gravimetric analysis (data not shown).

Synthesis of the sodium phospho-molybdic Keggin-type salt $\text{Na}_2\text{HPMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$

This salt was synthesized according to the technique reported by Rocchiccioli-Deltcheff *et al.*¹² Concentrated PO_4H_3 (2.0 ml, Merck, 85%) and concentrated HClO_4 (101.0 ml, Merck, 70%) were added to 150.0 ml of a 2.8 M aqueous solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (J. T. Baker ACS, 100%) at room temperature. A yellow solid precipitated from the solution within minutes. The product was filtered and dried under vacuum at room temperature and re-crystallized from a mixture of 14.0 ml $\text{Et}_2\text{O}/71.0$ ml H_2O .

The purity of the Keggin structure was determined by infrared spectroscopy. This compound is called PMO_{12} throughout the paper.

Synthesis of the sodium phospho-molybdic salt $\text{Na}_6\text{P}_2\text{Mo}_5\text{O}_{23} \cdot 14\text{H}_2\text{O}$

This salt was synthesized according to the technique reported by Hedman.¹³ A mixture of 5.0 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (J. T. Baker ACS, 100%), 1.1 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Carlo Erba ACS, 99%), 2.0 ml of concentrated HClO_4 (Merck, 70%) and 10.0 ml of distilled water was kept at room temperature for slow evaporation of the solvent. Colourless crystals of the salt precipitated from the solution within 10 days.

The X-ray diffraction spectrum is in agreement with the signals calculated with the Rietveld method for $\text{Na}_6\text{P}_2\text{Mo}_5\text{O}_{23} \cdot 14\text{H}_2\text{O}$ (orthorhombic, space group $P2_12_12_1$, $a = 15.8304 \text{ \AA}$, $b = 19.876 \text{ \AA}$ and $c = 10.6828 \text{ \AA}$), which ensures the purity of the product. The compound is called P_2Mo_5 throughout the paper.

Additional materials

Commercial $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (J. T. Baker ACS, 81.4%) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (J. T. Baker ACS, 100%) were used to obtain infrared reference spectra.

Spectroscopic characterization

^{31}P NMR spectroscopy. Liquid NMR spectra were obtained with a Bruker AM 500 spectrograph under ambient conditions. The equipment operates at a frequency of 202.459 MHz with 5–10 μs pulses. The analysis involved 8–800 pulse responses with a resolution of 0.25 Hz per point.

^{31}P MAS-NMR analysis was performed with Bruker MSL 300 equipment operating at 121.496 MHz. A sample holder of 5 mm diameter and 17 mm height was used. The spin rate was 2.1 kHz and several hundreds of pulse responses were collected. The reference used was external 85% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$ for liquid and solid NMR analyses.

Infrared analysis (FTIR). Infrared analysis was performed with FTIR Bruker IFS 66 equipment under ambient conditions.

Solid samples were diluted with KBr and pressed into thin wafers. The solutions of the Dawson salt at different pH values were analysed by placing a drop of the liquid between KBr plates.

X-Ray diffraction. X-Ray diffraction spectra were obtained with Philips PW1390 equipment ($\text{CuK}\alpha$ source and Ni filter) with an automated sampling system. The analysis was performed under the following conditions: voltage, 40 kV; current, 20 mA; goniometer speed, 2°min^{-1} ; slit, $1^\circ/0.1^\circ/1^\circ$; and sampling rate, 0.02° .

Laser Raman spectroscopy. Spectra were obtained under ambient conditions with an Ar^+ ion laser (Spectra Physics Model 2020-50, excitation line 514.5 nm) delivering 15–40 mW of incident radiation. The powdered solid (*ca.* 100–200 mg) was pressed into a thin wafer about 1 mm thick which was then mounted onto a spinning sample holder and rotated at 2000 rpm to avoid local heating effects. The scattered radiation from the sample was directed into a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research OMA III optical multichanneled analyzer (Model 1463) equipped with an intensified photodiode array detector cooled to 243 K. The spectral resolution and reproducibility were 2 cm^{-1} .

Stability experiments

Experiments to assess the stability of the Dawson ion under different acid–base conditions were performed in the range 0.0–9.0 pH units with a concentration of 20 mM of the salt. The acidity of the solutions was adjusted with standard buffer solutions¹⁴ (with the exception of the solution at pH = 0.0 that was prepared with concentrated HCl). Additionally, a set of solutions whose acidity was adjusted with HNO_3 or NH_4OH was prepared in order to determine the influence of the buffer solutions on the stability of the heteropoly-anion.

Results and discussion

Spectroscopic characterization of the $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 12\text{H}_2\text{O}$ salt. Stability in aqueous solution

Fig. 1 shows the infrared, Raman and X-ray diffraction spectra of the P_2Mo_{18} salt in powder form. The characteristic infrared vibrations of molybdenum–oxygen bonds appear in the $600\text{--}1000 \text{ cm}^{-1}$ range, the P–O stretching band at 1075 cm^{-1} and NH_4^+ at 1400 cm^{-1} .^{4,15} The Raman spectra of the Dawson heteropoly-oxoanion possess two major signals at 979 and 715 cm^{-1} in agreement with the literature.¹⁶

The following main signals (ordered according to increasing intensity) and average intensities (in brackets) were identified in the X-ray diffraction spectra: 9.2° (100), 25.2° (57), 24.7° (45), 24.2° (43), 18.4° (43), 26.9° (40), 8.0° (40), 14.6° (34), 12.8° (33) and 7.1° (33).

The observation that the X-ray diffraction and the infrared spectra do not possess signals of Keggin-type heteropoly-compounds, P_2Mo_5 and MoO_3 , and that the P_2Mo_{18} salt is completely soluble in aqueous media [the $(\text{NH}_4)_3\text{PMO}_{12}\text{O}_{40}$ salt, which can be produced during the synthesis of $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$, is not soluble] are evidence of the purity of the starting material. Moreover, ^{31}P MAS-NMR showed a single signal at -3.215 ppm in agreement with the literature for the pure $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 12\text{H}_2\text{O}$ salt^{3,4} (spectra not shown).

The maximum concentration of the Dawson-type salt in aqueous medium is reached at 430 mM, which corresponds to a solubility of $1.3 \times 10^3 \text{ g l}^{-1}$ at room temperature (*ca.* 25°C). However, the spontaneous precipitation of $(\text{NH}_4)_3\text{PMO}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ was observed after 24 h at concentrations above 100 mM. The Keggin-type salt was identified

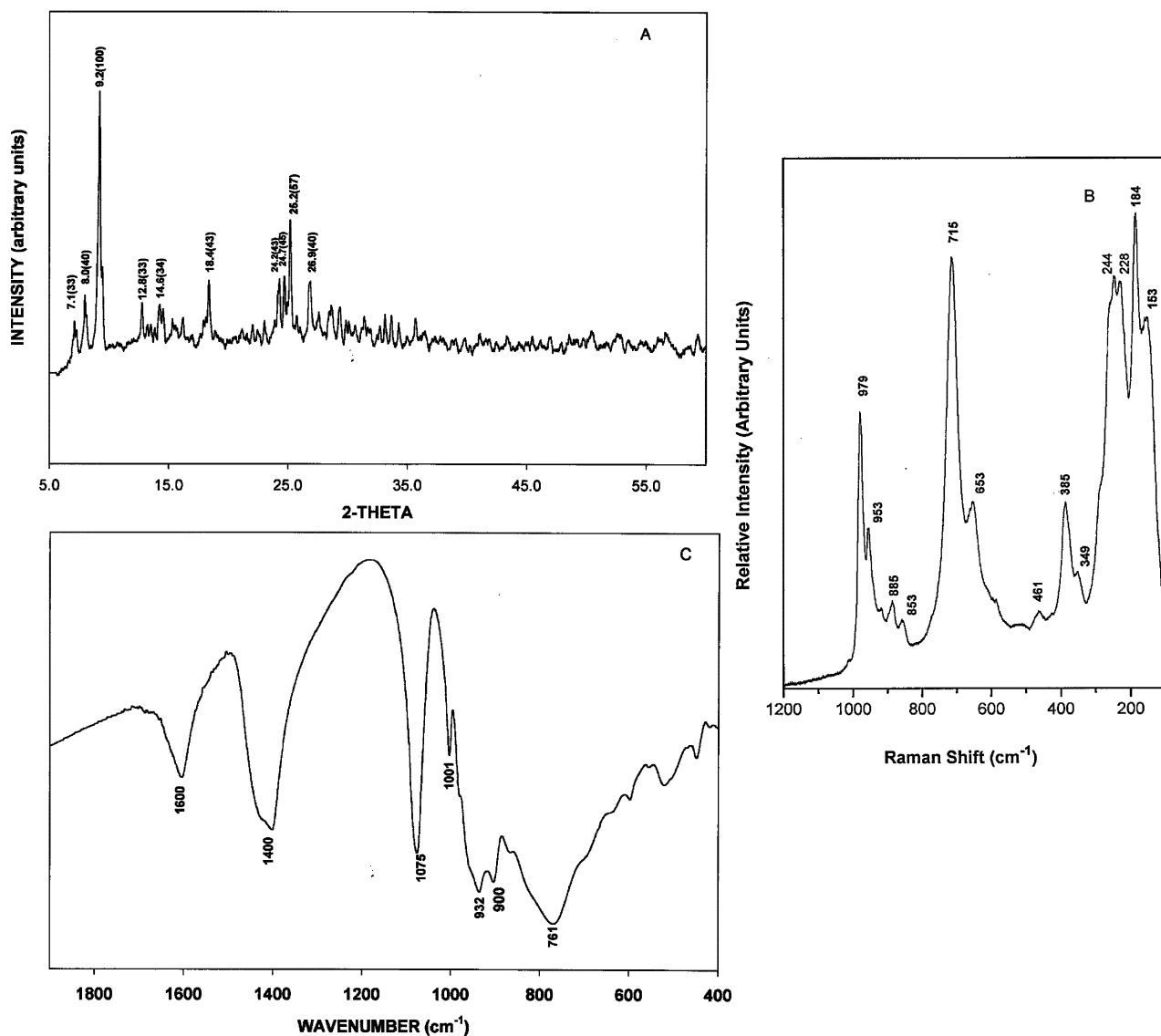


Fig. 1 (A) X-Ray diffraction, (B) Raman and (C) infrared spectra of the pure $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 12\text{H}_2\text{O}$ salt in powder form.

through infrared and the X-ray diffraction spectroscopy^{12,17} (data not shown). The decomposition of the $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ anion is attributed to the acidity produced by the ammonium salt at high concentration (pH *ca.* 2). This issue is further discussed in the next section.

Aqueous solutions of the P_2Mo_{18} salt at various concentrations were analysed by ^{31}P NMR spectroscopy in order to study the stability of the Dawson anion. Fig. 2 shows the signals of phosphorus-containing species of aqueous solutions with 20–200 mM of the P_2Mo_{18} salt. The most intense signal observed at -0.25 ppm corresponds to the lacunar Keggin-type anion $\text{H}_x\text{PMo}_{11}\text{O}_{39}^{(7-x)-}$ according to the spectroscopic studies of the speciation of $\text{H}^+ - \text{MoO}_4^{2-} - \text{HPO}_4^{2-}$ mixtures reported by Pettersson *et al.*^{10,18} Minor amounts of the species $\text{H}_x\text{Mo}_5\text{P}_2\text{O}_{23}^{(6-x)-}$ (2.40 ppm) and monomeric orthophosphate species H_2PO_4^- (0.91 ppm) and HPO_4^{2-} (4.11 ppm) are also observed. The signal at 1.15 ppm could not be identified.

The efforts to study the stability of the heteropoly-anion in organic media were in vain due to the insolubility of the P_2Mo_{18} salt in 1,4-dioxane, chloroform and carbon tetrachloride.

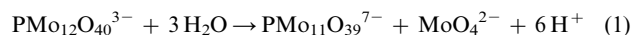
Influence of the acidity–basicity on the stability of the $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ anion

Fig. 3 shows ^{31}P NMR analysis of a series of aqueous solutions of the P_2Mo_{18} salt (20 mM) under a wide range of acid–base

conditions ($0.0 \leq \text{pH units} \leq 9.0$). Two signals are detected at high acidity (pH = 0.0 and 1.0) that correspond to $\text{H}_x\text{Mo}_5\text{P}_2\text{O}_{23}^{(6-x)-}$ and the lacunar Keggin-type anion $\text{H}_x\text{PMo}_{11}\text{O}_{39}^{(7-x)-}$. A signal of low intensity that may be attributed to the H_2PO_4^- species is also observed at pH = 1.0.

The lacunar Keggin-type anion $\text{H}_x\text{PMo}_{11}\text{O}_{39}^{(7-x)-}$ along with the HPO_4^{2-} species are the major species at pH conditions of 2.0 and above; however, minor contributions of the $\text{H}_x\text{Mo}_5\text{P}_2\text{O}_{23}^{(6-x)-}$, H_2PO_4^- and lacunar phospho-molybdic B species (0.60 ppm) are also observed in these spectra¹⁰ (see Fig. 3, pH = 2, 4, 6, 9).

The solutions at $0.0 \leq \text{pH} \leq 2.0$ underwent spontaneous precipitation of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ immediately after their preparation. It is known that the Keggin-type anion $\text{PMo}_{12}\text{O}_{40}^{3-}$ degrades to the lacunar $\text{PMo}_{11}\text{O}_{39}^{7-}$ species according to reaction (1),^{19,20}



Therefore the high concentration of protons favours the presence of the non-degraded $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion and NH_4^+ species that react to produce the non-soluble $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ salt.

Further analysis of the stability of the Dawson-type anion at different acid–base conditions was performed by infrared spectroscopy. The Keggin-type salt PMo_{12} , the pentamolybdo-diphosphate salt P_2Mo_5 and commercial $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and

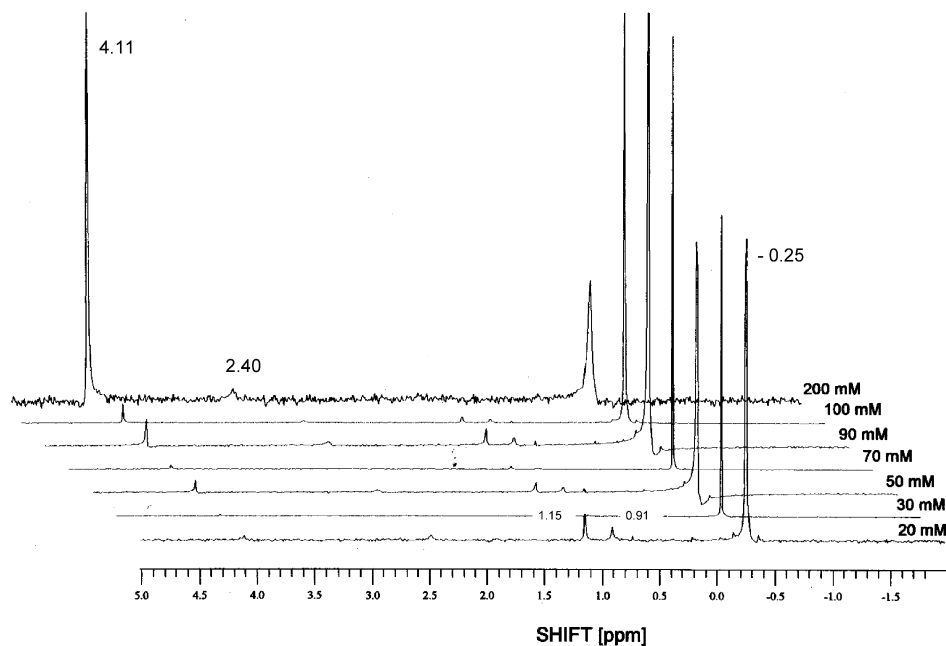


Fig. 2 ^{31}P NMR spectra of aqueous solutions of the $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ salt at different concentrations.

Na_2MoO_4 were analysed by infrared spectroscopy and used as reference compounds in order to identify the species involved in the decomposition of the Dawson anion. The characteristic infrared signals of these compounds, along with $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ from literature references,²¹ are summarised in Table 1.

The Keggin-type salt PMo_{12} and the pentamolybdodiphosphate salt P_2Mo_5 were analysed in powder form and aqueous media. The PMo_{12} salt possesses the characteristic bands of the $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion.¹² The signal at 1065 cm^{-1} corresponds to the P–O bond; 960 cm^{-1} to Mo=O; 869 and 776 cm^{-1} to Mo–O–Mo; and 596 cm^{-1} to O–P–O bonds. Although the $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion degrades to $\text{PMo}_{11}\text{O}_{39}^{7-}$ species in aqueous media, no differences are observed in the infrared spectra of these species. However, the P_2Mo_5 salt in aqueous solution shows a shift of the bands corresponding to the P–O bond (1114 , 1111 and 1089 cm^{-1}) to lower wavenumbers (1111 and 1057 cm^{-1}).

The infrared spectra of 20 mM aqueous solutions of the

P_2Mo_{18} salt at various acid–base conditions are shown in Fig. 4 A and B. The spectral regions characteristic of the PO_4 tetrahedron bond stretching (1200 – 1000 cm^{-1}) and the symmetric and asymmetric stretching of the different kinds of Mo–O bonds (950 – 800 cm^{-1}) give further evidence of the speciation of the Dawson-type anion in aqueous solution.¹²

The presence of $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ species at $\text{pH} > 2.0$ is confirmed with the bands in the range 1110 – 1076 cm^{-1} . The asymmetric stretching of the P–O bond of the lacunar Keggin-type species $\text{H}_x\text{PMo}_{11}\text{O}_{39}^{(7-x)-}$ is observed in the 1050 – 1063 cm^{-1} region in almost the entire set of acid–base conditions, in agreement with the results obtained *via* ^{31}P NMR spectroscopy. The shifting of this vibration could be attributed to the protonation of the molecule or the reduction of molybdenum atoms. The contribution of the vibrations of $\text{H}_x\text{Mo}_3\text{P}_2\text{O}_{23}^{(6-x)-}$ species in the same range cannot be discarded; however, the amount of this species is scarce at $\text{pH} > 2.0$.

Infrared analysis provided evidence of the decomposition of

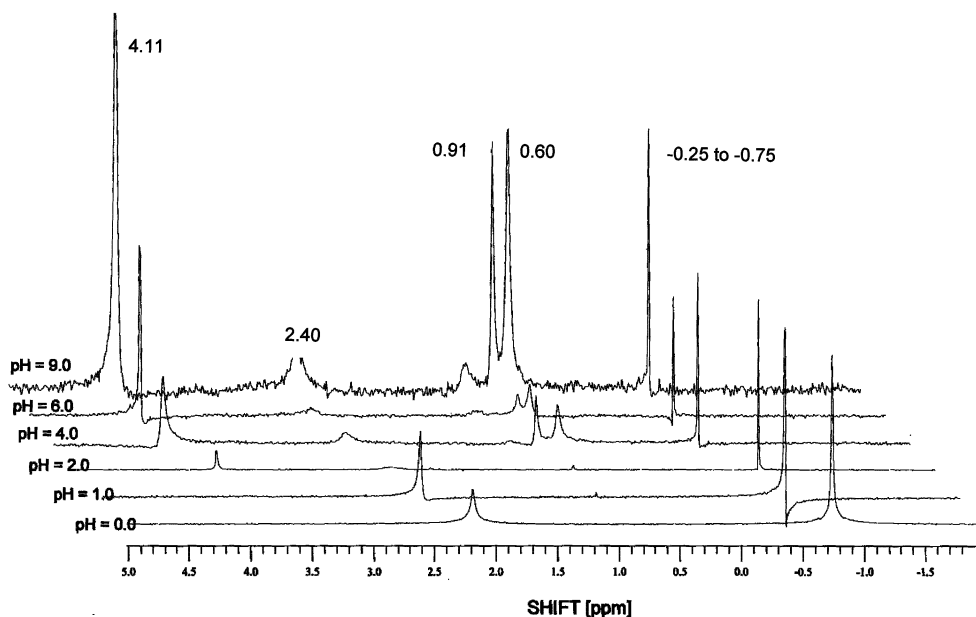


Fig. 3 ^{31}P NMR spectra of 20 mM aqueous solutions of the $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ salt at different acid–base conditions.

Table 1 Summary of characteristic infrared signals of reference compounds

Species	Infrared band/cm ⁻¹ (intensity ^b)
(NH ₄) ₂ HPO ₄ ^a	1215 (w)
	1070 (s, b)
	1023 (w)
	950 (m)
	892 (m)
NH ₄ H ₂ PO ₄ ^a	1289 (s)
	1090 (s)
	810 (m)
Na ₂ HPMo ₁₂ O ₄₀ (solid)	1063 (s)
H _x PMo ₁₁ O ₃₉ ^{(7-x)-} (aqueous)	1038 (sh)
	962 (s)
Na ₆ P ₂ Mo ₅ O ₂₃ (solid)	868 (s)
	1144 (s)
	1111 (s)
	1089 (s)
	1000 (w)
	941 (w)
	906 (s)
	627 (s)
Na ₆ P ₂ Mo ₅ O ₂₃ (aqueous)	1113 (m, b)
	1057 (m, b)
	996 (w)
	906 (m)
Mo ₇ O ₂₄ ⁶⁻	917 (s)
	882 (vs)
	837 (s)
	639 (s)
	575 (s)
MoO ₄ ²⁻	905 (m)
	859 (s)
	823 (s)
	636 (m)
	545 (m)

^aData from ref. 21. ^bvs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad.

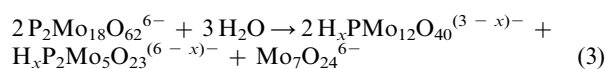
the Dawson-type anion in oxomolybdate species. The signals at 913 and 887–892 cm⁻¹ indicate the presence of Mo₇O₂₄⁶⁻ species up to pH = 4.0. However, the characteristic signals of molybdate species MoO₄²⁻ are observed at 910 and 837 cm⁻¹ at pH = 9.0. This observation is in agreement with the degradation of the heptamolybdate to the molybdate species that typically occurs at pH 6.0 and above.^{19,22}



The same results described above were obtained when the acidity–basicity was adjusted with NH₄OH or HNO₃ solutions. This result ensures that the stability of the Dawson salt is not influenced by species involved in the buffer solutions.

Conclusions

Spectroscopic analysis has given insights into the stability of the P₂Mo₁₈O₆₂⁶⁻ anion in solution. The phospho-molybdc Dawson-type anion decomposes completely regardless of the concentration or the acidity–basicity of the aqueous medium. The following reaction describes the decomposition of the anion:



The phospho-molybdc Dawson-type anion degrades to the Keggin-type anion H_xPMo₁₂O₄₀^{(3-x)-}, pentamolybdodiphosphate H_xP₂Mo₅O₂₃^{(6-x)-} and heptamolybdate Mo₇O₂₄⁶⁻ or molybdate MoO₄²⁻ species depending upon the acidity [see

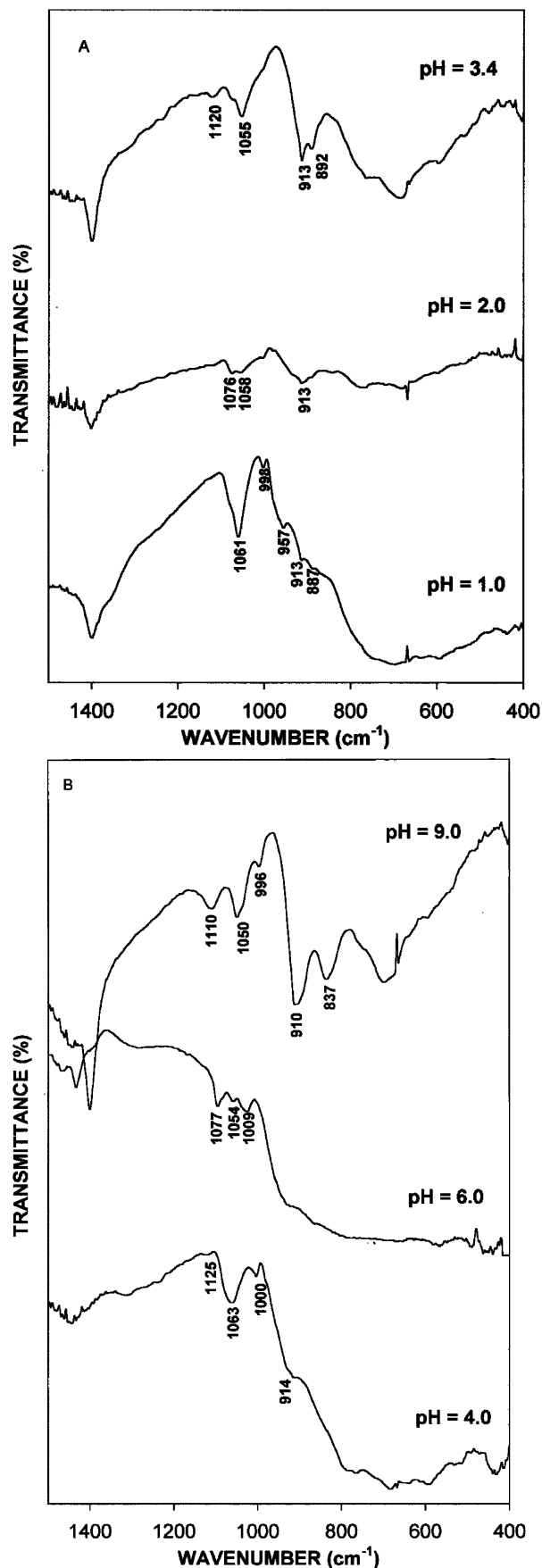
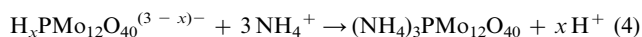


Fig. 4 Infrared spectra of 20 mM aqueous solutions of the (NH₄)₆P₂Mo₁₈O₆₂ salt at various acid–base conditions: (A) pH = 1.0, 2.0 and 3.4; (B) pH = 4.0, 6.0 and 9.0.

reaction (2)]. The Keggin-type anion degrades to the lacunar species H_xPMo₁₁O₃₉^{(7-x)-} and molybdate species in aqueous medium [see reaction (1)] or precipitates to the ammonium

phospho-molybdic salt $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ at high acidity values ($\text{pH} \leq 2$):



The pentamolybdodiphosphate anion $\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$ decomposes at $\text{pH} \geq 6$ according to the observation of Cheng and Luthra²³ and Pettersson:²⁴



This equilibrium is in agreement with the predominance of phosphate species and almost total disappearance of the pentamolybdodiphosphate species observed in the spectroscopic analysis at $\text{pH} > 2$.

The present investigation provides evidence that accounts for the results reported in the literature about the surface structure of supported heteropoly-anion catalysts. Many investigations have studied the synthesis of supported catalysts through the wetness impregnation with ammonium heptamolybdate and phosphoric acid mixtures.^{16,25} However, the spectroscopic analysis showed the *in situ* generation of Keggin, Dawson and pentamolybdodiphosphate species in these impregnation solutions; no Dawson-type species were observed on the surface of the impregnated materials. This observation is in agreement with the instability of the heteropoly-anion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ demonstrated in the present investigation.

Nevertheless, studies reported on phospho-molybdic Dawson-type salts synthesized in water–1,4-dioxane media indicate that the organic species stabilises the structure of the heteropoly-anion.⁴ The influence of the acidity–basicity and the temperature upon the stability of these compounds has yet to be studied for these structures to be suitable as precursors in the synthesis of supported catalysts.

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