

# ESR characterization of $V^{4+}$ as a counter-ion of the 12-molybdophosphate. Influence of thermal treatments

R. Bayer, C. Marchal, F.X. Liu, A. Tézé<sup>\*</sup>, G. Hervé

*Laboratoire d'Electrochimie et Chimie de Solides Inorganiques, EP CNRS 67, Université de Versailles, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France*

Received 6 July 1995; accepted 4 March 1996

## Abstract

Vanadyl cations were introduced as counter-ions of the 12-molybdophosphate Keggin anion and crystals of  $[VO(H_2O)_5]H[PMo_{12}O_{40}] \cdot 23H_2O$  were obtained. Dehydration under nitrogen of this hydrate occurs step by step which were studied by thermogravimetry and ESR characterization of vanadium after thermal treatment. Vanadyl exists as an aquo complex  $[VO(H_2O)_5]^{2+}$  up to 75°C. Between 75 and 210°C, loss of the water molecules leads to  $VO^{2+}$  becoming bound to the outer oxygen atoms of the molybdophosphate. All these transformations are readily reversible in the presence of water. At 320°C, a progressive decomposition of the Keggin structure occurs, characterized by a decrease of the intensity of the ESR signal of  $V^{4+}$  and the emergence of a signal of  $Mo^{5+}$ . This transformation is only partly reversible in the presence of water vapor.

*Keywords:* Polyoxometalates; Molybdophosphate; Vanadium; ESR

## 1. Introduction

Substitution of one to three vanadium for molybdenum atoms in  $H_3[PMo_{12}O_{40}]$  leads to  $H_{3+x}[PMo_{12-x}V_xO_{40}]$  species and strongly modifies its catalytic activity, especially for oxidation reactions [1–3]. Knowledge of the coordination of vanadium in the solid state was essentially obtained from ESR spectra which are very sensitive to modification of the  $V^{4+}$  local environment. ESR studies of tungsto- or molybdovanadic acids in solution [4] and in the solid state [5] are reported in the literature and modi-

fications of the spectra of bulk [6] and supported [7–9] samples during dehydration process occurring in a thermal treatment up to 773 K were interpreted by the successive loss of crystallization and constitutional water and finally the irreversible destruction of the heteropolyanionic structure, each state being characterized by one or more specific  $V^{4+}$  signals. A reversible water-dependent transformation between two types of  $V^{4+}$  was observed [10,11].

In all these studies, vanadium in the starting material is at the oxidation state five. Therefore,  $V^{4+}$  is in very small proportion and it was found that the intensity of the  $V^{4+}$  signal did not change significantly during thermal air or vacuum treatment [6]. It seems irrelevant to

<sup>\*</sup> Corresponding author.

found the discussion of the dehydration process and of the heteropolyanionic stability on results obtained from a minor element in the solid. Moreover, it has been recently shown [11,12] that important structural changes of the vanadomolybdic heteropolyacids occur during catalysis of the oxidative dehydrogenation of isobutyric acid: reduced ( $V^{4+}$ ) vanadium goes out of the Keggin structure and have to be considered, at the steady state, as a counter-ion of the 12-molybdophosphate anion [11]. This transformation appears to be general, irrespective of the nature of the substrate, and occurs also during a thermal treatment, at least partially, depending on the temperature and the extent of the treatment [13].

It was then important to take into account the presence of  $V^{4+}$  out of the Keggin structure in catalysts at the steady state. In this light, we investigated the ESR characterization of vanadium in heteropolyoxometallic materials in which  $V^{4+}$  is a counter-ion of Keggin type polyoxomolybdates and tungstates. In this paper, results obtained with the 12-molybdophosphate anion are reported.

## 2. Experimental

### 2.1. Preparations

The vanadyl hydrated acid salt  $[VO(H_2O)_5]H[PMo_{12}O_{40}] \cdot 23H_2O$  is obtained from the barium acid salt of the heteropolyacid  $H_3[PMo_{12}O_{40}]$ . A cationic exchange of vanadyl for barium is achieved using vanadyl sulfate.

Molybdophosphoric acid (10 g; 4.85 mmol) is dissolved in 10 ml of water. Solid barium hydroxide ( $Ba(OH)_2 \cdot 8H_2O$ ; 1.56 g; 4.85 mmol) is added to the stirred solution in several small quantities in order to avoid any increase of the pH of the solution, which would lead to a partial decomposition of the molybdophosphoric anion. Vanadyl sulfate pentahydrate (1.25 g; 4.85 mmol) is then quickly added and the vigorously stirred solution is kept at room tempera-

ture for half an hour. The barium sulfate precipitate is filtered off. The resultant solution is then kept at about 4°C. The slow low-temperature crystallization yields highly hydrated green crystals.

The purity of the compound was checked by  $^{31}P$  NMR spectroscopy (only one peak was obtained at  $-2.55$  ppm, taking 85%  $H_3PO_4$  as reference) and voltammetry in hydroorganic medium (water–dioxane v/v +  $HClO_4$  0.5 M), IR and elemental analysis. The amount of vanadyl cation is obtained by titration with  $Ce^{IV}$  in 0.1 M  $H_2SO_4$  solution.

Analysis: P%: 1.35 (calc. 1.35), Mo%: 52.32 (calc. 50.04), V%: 2.14 (calc. 2.21)

### 2.2. X ray diffraction

A X-ray diffraction study was performed on a single crystal of the hydrate  $[VO(H_2O)_5]H[PMo_{12}O_{40}] \cdot 23H_2O$  obtained from its solution at 4°C. A crystal was sealed in a Lindemann capillary tube. Crystals are cubic, space group  $Fd\bar{3}$  with  $a = 23.020$  (2) Å,  $V = 12199$ (13) Å<sup>3</sup> and  $Z = 8.2346$  reflections were collected on an Enraf Nonius CAD-4 diffractometer using graphite monochromated  $Mo K_{\alpha}$  radiation and  $\theta/2\theta$  scans (independent 903, with  $I > 3\sigma(I)680$ ).

### 2.3. Thermogravimetry and isotherms

Thermogravimetry (TG) was carried out under nitrogen flow (50 ml/min) with a Perkin Elmer electrobalance at a heating rate of 5°C/min up to a temperature of 460°C. Isotherms were also performed under nitrogen flow in order to determine the temperatures of thermal treatment leading to well defined hydration states of the solid. The selected temperature was reached at a heating rate of 5°C/min and was maintained during 15 h. For each isotherm, the temperature was chosen according to the TG results. The samples were powdered just prior to both TG or isotherm recording. About 16 mg

of finely ground powder was used for each experiment.

#### 2.4. Electron spin resonance

Crystals were powdered immediately before performing ESR measurement or thermal treatments. Thermal treatments were carried out dynamically under nitrogen flow (40 ml/min) in a glass fixed bed reactor at temperatures (75°C, 210°C and 320°C) selected from the isotherm experiments. Samples of ca. 400 mg were heated from room temperature to the selected temperature at a heating rate of 100°C/h and then kept at this temperature for 15 h. Eventually, the dehydrated samples were quickly cooled down to room temperature under nitrogen flow.

The ESR tube was directly connected to the inner gas tube of the reactor via a glass side arm in order to avoid hydration by ambient moisture during the transfer from the reactor. The ESR tubes containing a small amount of the dehydrated samples (50 mg) were finally sealed

under nitrogen flow. X-band ESR spectra were recorded on a Bruker ESR 300 spectrometer. The magnetic field was calibrated using Micro-Now NMR gaussmeter and NMR markers. All spectra were recorded at room temperature and 77 K. The time constant was the same for all spectra (5.12 ms). The microwave power was set to 10 mW except for the room temperature spectrum of the highly hydrated sample which was recorded using a microwave power of 1 mW. Precise values of the components of the  $g$  and  $A$  tensors were obtained from computer simulation.

### 3. Results

#### 3.1. X-ray diffraction

Attempts to resolve the structure of  $[\text{VO}(\text{H}_2\text{O})_5][\text{HPMo}_{12}\text{O}_{40}] \cdot 23\text{H}_2\text{O}$  by X-ray diffraction on a single crystal were done in order to try to understand anion–cation relation-

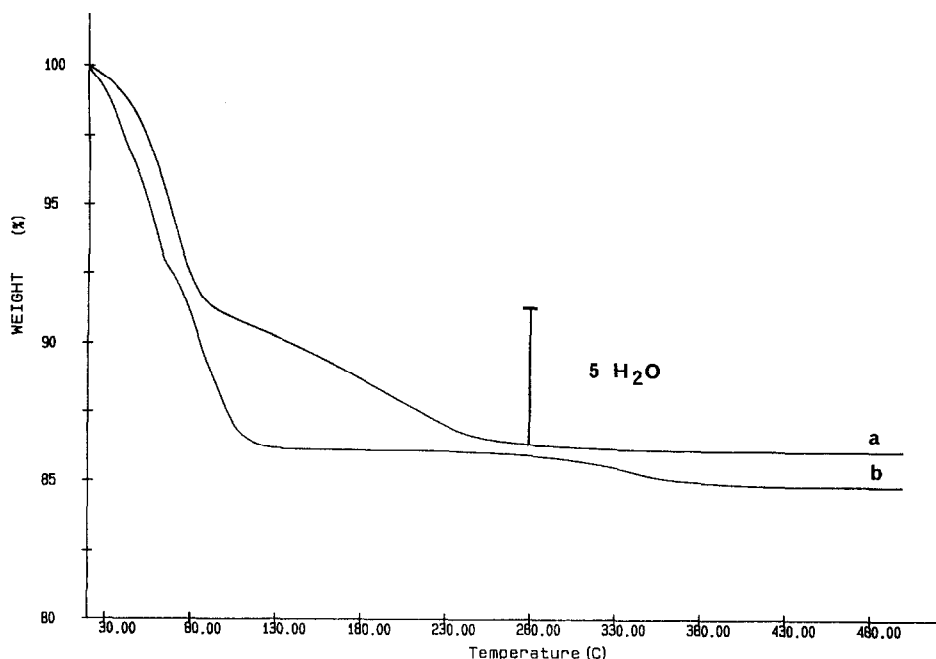


Fig. 1. TG curves of room temperature-stable hydrates: (a)  $\text{HVOPMo}_{12}\text{O}_{40}$ ; (b)  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ .

ships. Phosphorus, molybdenum atoms and their surrounding oxygen atoms of the unit cell were located by routine methods. All distances and bond angles were in the normal range usually found in previously reported Keggin structures [14]. Difficulties due to the high symmetry of the space group (cubic lattice, F3d) arise when vanadium counter-ions and oxygen atoms of water molecules had to be located. Difference Fourier map gave electronic densities but, because of the number of equivalent positions, these densities could be provided by fractional occupancies either of oxygen or vanadium atoms. Thus, the location of the vanadyl cations between the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  Keggin units cannot be determined.

### 3.2. Thermogravimetry

Heteropolyacids crystallize with a large number of water molecules depending on solution

acidity and temperature. At low temperature, highly hydrated crystals ( $28\text{--}30\text{H}_2\text{O}$ ) are usually obtained in which some water molecules are present as hydroxonium ions  $\text{H}_3\text{O}^+$  or  $\text{H}_5\text{O}_2^+$ . The  $23\text{H}_2\text{O}$  hydrate of the monovanadyl salt is not stable in air at room temperature: spontaneous loss of water leads to a  $8\text{H}_2\text{O}$  hydrate identified by thermogravimetry. Thermogravimetry gives lines of evidence for two types of water molecules in these solids, crystallization and constitution water. TG curves obtained with the acid and the vanadyl salt are reported for comparison (Fig. 1). In the case of the acid (Fig. 1b), loss of the crystallization water begins at room temperature and a plateau corresponding to the anhydrous acid is observed in the  $130\text{--}270^\circ\text{C}$  temperature range. Between  $270$  and  $400^\circ\text{C}$ , the water of constitution ( $1.5\text{H}_2\text{O}$ ) is lost. It is formed from the three protons bound to the polyanion  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  and polyanion oxygen atoms. In the case of

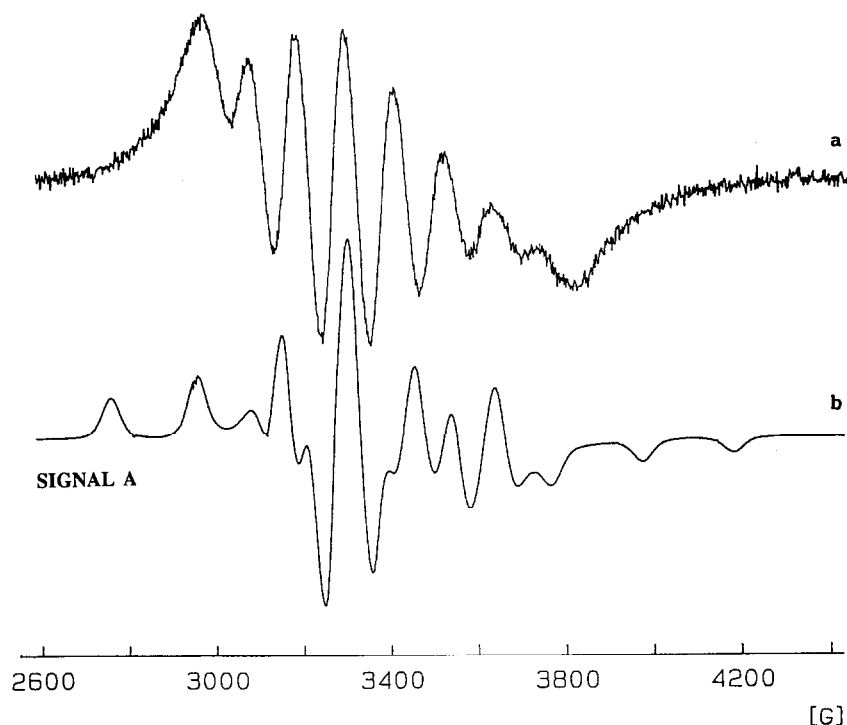


Fig. 2. ESR spectra ( $\nu = 9.4$  GHz) of the freshly powdered  $23\text{H}_2\text{O}$  hydrate recorded at (a) 293 K and (b) 77 K, signal A.

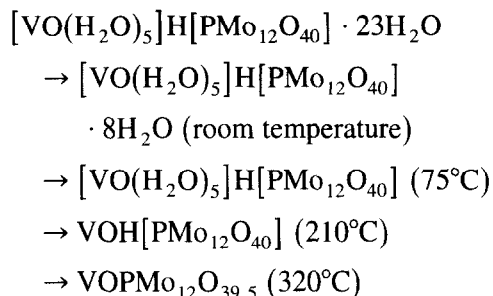
$[\text{VO}(\text{H}_2\text{O})_5]\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot 23\text{H}_2\text{O}$  (Fig. 1a), water molecule removal is realized in a three-step process. Below  $100^\circ\text{C}$ , the first type of crystallization water (about  $23\text{H}_2\text{O}$ ) is released, as observed with the phosphomolybdic acid. The second type of crystallization water loss (about  $5\text{H}_2\text{O}$ ) is achieved in the  $100\text{--}250^\circ\text{C}$  temperature range. A very poorly defined water loss occurring between  $250^\circ\text{C}$  and  $400^\circ\text{C}$  is attributed to the low content of water of constitution ( $0.5\text{H}_2\text{O}$ ).

The second kind of crystallization water of the vanadyl salt was never observed with heteropolyacids. Since the vanadyl cation is found as the  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  complex in aqueous solution, the water loss in the  $100\text{--}250^\circ\text{C}$  temperature range must be associated with the loss of the five water molecules coordinated to vanadium. This assignment is in agreement with the X-ray structure determination performed on a vanadyl salt of the 12-tungstosilicate anion [11].

### 3.3. Isotherms

One main disadvantage of thermograms is that they are not equilibrium curves. Because accurate temperatures corresponding to equilibrium states are required for thermal treatments of samples for ESR measurements, several isotherm experiments in the  $60\text{--}320^\circ\text{C}$  temperature range were carried out with  $[\text{VO}(\text{H}_2\text{O})_5]\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot 23\text{H}_2\text{O}$ . Several temperatures were selected in order to obtain

well defined hydration states of the solid, as summarized in the following scheme:



The formulation of the last compound corresponds to its formal composition without any reference to the exact structure of the solid.

### 3.4. ESR spectra of samples treated up to $210^\circ\text{C}$

The X-band ESR spectrum of the freshly powdered  $23\text{H}_2\text{O}$  hydrate strongly depends on the recording temperature,  $293\text{ K}$  (Fig. 2a) or  $77\text{ K}$  (Fig. 2b). The latter spectrum (signal denoted A) is characteristic of an unpaired 3d electron ( $S = 1/2$ ) interacting with the nuclear spin ( $I = 7/2$ ) of a  $\text{V}^{4+}$  ion. The spectrum exhibits eight broad parallel and perpendicular lines showing that the  $\text{V}^{4+}$  ion is in a tetragonal ligand field. The associated spin hamiltonian is then:

$$\begin{aligned} g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z \\ + A_{\perp} (S_x I_x + S_y I_y) \end{aligned}$$

where  $z$  corresponds to the main axis of the  $g$  and  $A$  tensors. The computer simulation gives the ESR parameters reported in Table 1. This

Table 1

ESR parameters of  $\text{V}^{4+}$  and  $\text{Mo}^{5+}$  signals observed after thermal treatment in  $\text{N}_2$  of the vanadyl molybdoophosphate as fitted by computer simulation

Compounds	$\text{V}^{4+}$					$\text{Mo}^{5+}$		
	$g_{\text{iso}}$	$g_{\parallel}$	$g_{\perp}$	$A_{\text{iso}}$ (G)	$A_{\parallel}$ (G)	$A$ (G)	$g_{\parallel}$	$g_{\perp}$
$\text{HVOPMo}_{12}\text{O}_{40}$								
$23\text{H}_2\text{O}$ hydrate signal A	1.970	1.932	1.978	113	202	77		
$75^\circ\text{C}$ signal C		1.926	1.978		205	84		
$210^\circ\text{C}$ signal D		1.930	1.961		165	44		
$320^\circ\text{C}$ signals D + E		1.930	1.961		165	44	1.855	1.958
$[\text{PMo}_{11}\text{VO}_{40}]^{5-}$		1.936	1.974		164	57		

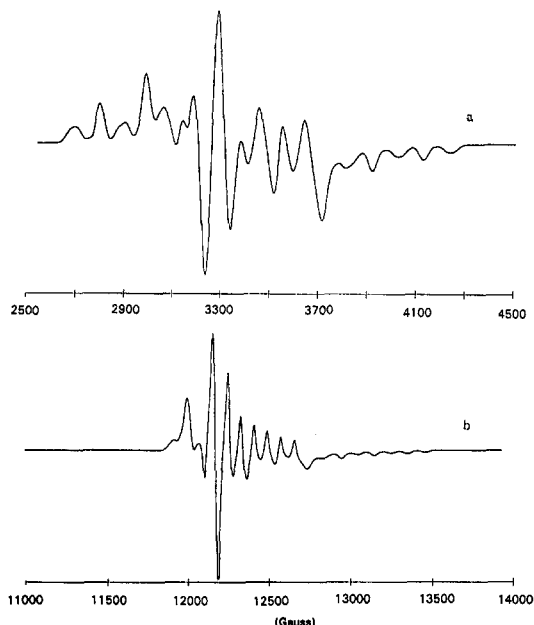


Fig. 3. ESR spectra of  $[\text{VO}(\text{H}_2\text{O})_5]\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$ : (a) X band ( $\nu = 9.4$  GHz); (b) Q band ( $\nu = 34$  GHz), signal B.

low temperature spectrum actually represents a frozen motion. Indeed, the isotropic eight line room-temperature spectrum shown in Fig. 2a

reflects the fast tumbling of the  $\text{V}^{4+}$  ions in the highly hydrated solid. The computed  $g_{\text{iso}} = 1.970$  and  $A_{\text{iso}} = 113$  G obtained from the isotropic spectrum are in satisfying agreement with the values estimated from  $g_{\text{iso}} = 1/3(g_{\parallel} + 2g_{\perp})$  and  $A_{\text{iso}} = 1/3(A_{\parallel} + 2A_{\perp})$  i.e.  $g_{\text{iso}} = 1.963$  and  $A_{\text{iso}} = 118$  G.

In natural air at room temperature, the hydrate  $[\text{VO}(\text{H}_2\text{O})_5]\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$  is obtained. The X-band spectrum (signal B), independent on temperature, is rather complex (Fig. 3a). Several hypotheses were considered in order to simulate this spectrum: in a first time, the best fit was obtained considering two distinct signals corresponding both to  $\text{V}^{4+}$  in a tetragonal environment. With this hypothesis, only the  $g_{\parallel}$  values differ for the two signals. In order to determine if the relative intensities of these two signals depend on the quantity of vanadyl species in the solid, salts containing variable amounts of vanadyl cation ranging from 0.3 to 1.3 per Keggin heteropolyanion were prepared. The same spectrum was obtained for all the samples irrespective of the V/heteropolyanion

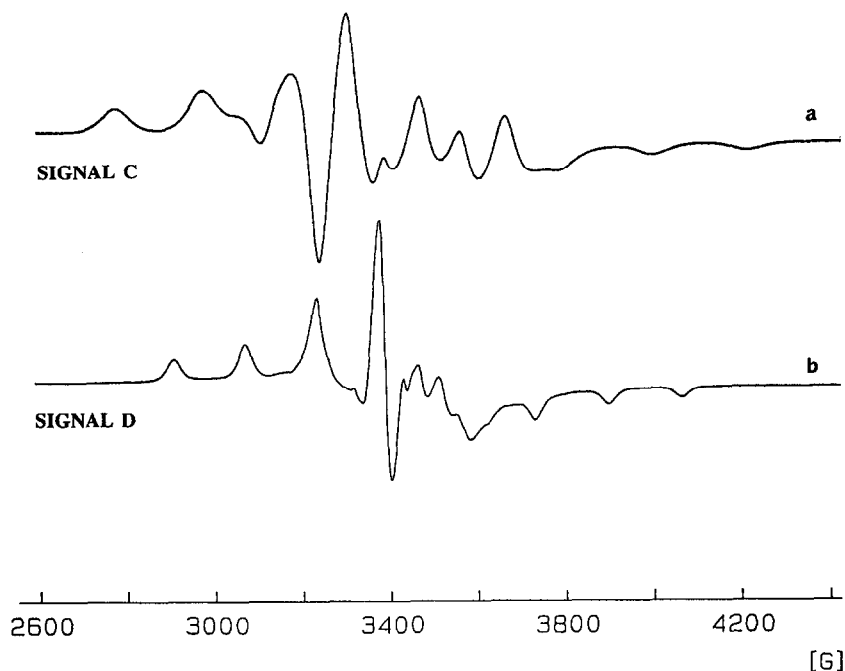


Fig. 4. ESR spectra ( $\nu = 9.4$  GHz) of (a)  $[\text{VO}(\text{H}_2\text{O})_5]\text{H}[\text{PMo}_{12}\text{O}_{40}]$ , signal C; (b)  $[\text{HVOPMo}_{12}\text{O}_{40}]$ , signal D.

ratio. The  $g_{\parallel}$  value of one of these signals was surprising (1.961, close to the  $g_{\perp}$  value, 1.978), therefore a Q-band spectrum was recorded (Fig. 3b). The resolution of the perpendicular components was increased but the parallel components showed the same pattern. Moreover, the two parallel signals were separated by 105 G both in Q and X-band spectra.

After thermal treatment at 75°C, only one temperature independent signal C (Fig. 4a), very similar to A at 77 K, was observed. The  $g$  and  $A$  values obtained from simulation of signal C (Table 1) are really close to those found with the highly hydrated initial solid. The dehydration process is reversible since the B signal was observed again after 24 h room temperature rehydration in natural air of the solid previously treated at 75°C.

A thermal treatment at 210°C lead to a new ESR signal denoted D (Fig. 4b). D is also temperature-independent and has a quite well resolved hyperfine structure for the parallel component but not for the perpendicular one. A very weak underlying broad line was observed in the spectrum. Simulation gave the  $g$  and  $A$  values reported in Table 1. After a treatment at 210°C under dry atmosphere followed by treatment in the presence of 4% of water at the same temperature, C is superimposed on signal D, but

has a low intensity. It was restored quantitatively when the treatment in the presence of water was performed at 75°C. Moreover, when the solid treated at 210°C was rehydrated at room temperature in natural air, the signal B was observed again. All the steps of the dehydration process are then reversible up to 210°C.

#### 4. ESR spectra of samples treated at 320°C

This temperature was chosen because it corresponds to the mean temperature conditions of industrial utilization of catalysts in oxidation reactions. Fig. 5 shows the spectra obtained after 17 h and 60 h of thermal treatment at 320°C under nitrogen flow. Two signals were observed, D and a new signal, denoted E without a visible hyperfine structure. Signal E can be simulated with the following  $g$  values in the approximation of an axial symmetry:  $g_{\parallel} = 1.855$  and  $g_{\perp} = 1.958$ . This signal has been previously observed after treatment of  $H_3[PMo_{12}O_{40}]$  at 400°C under nitrogen [15] and has been assigned to reduced molybdenum arising from the decomposition of the Keggin unit. The solid treated 60 h at 320°C is no longer fully soluble in water and the IR spectrum shows a significant broadening compared with the spectra ob-

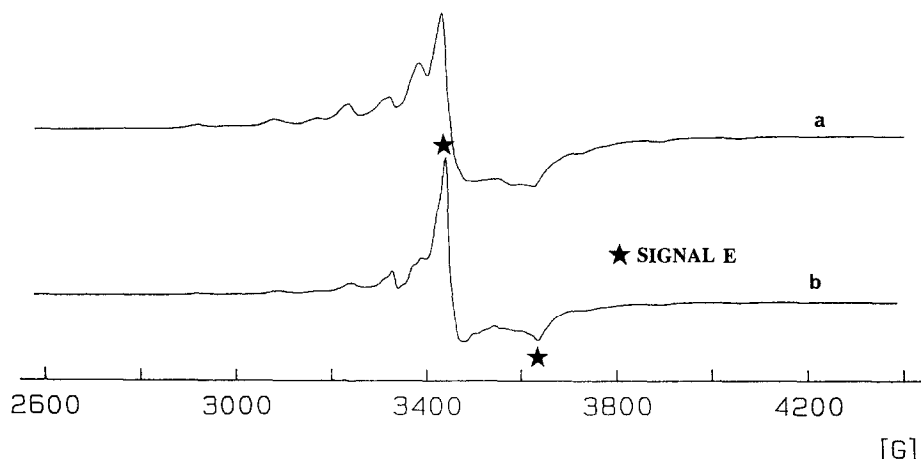


Fig. 5. ESR spectra ( $\nu = 9.4775$  GHz) of  $HVOPMo_{12}O_{40}$  after thermal treatment at 320°C under  $N_2$ , (a) 17 h; (b) 60 h.

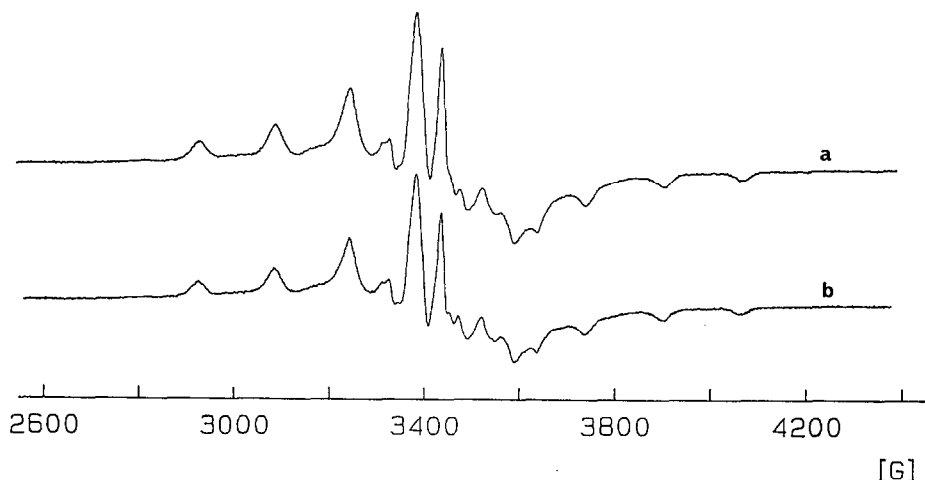


Fig. 6. ESR spectra ( $\nu = 9.775$  GHz) of  $\text{HVOPMo}_{12}\text{O}_{40}$  after thermal treatment at  $320^\circ\text{C}$  under  $\text{N}_2$  in the presence of 4% of water, (a) 17 h; (b) 60 h.

tained with samples treated between room temperature and  $210^\circ\text{C}$ , which well correspond to the Keggin structure. All these observations show that the vanadyl salt of the molybdophosphate is not stable at  $320^\circ\text{C}$  and suggest that insoluble bulk oxide phases are slowly formed at this temperature.

Since water is commonly added to the gas phase in catalytic oxidation reactions using heteropolyacids, the influence of water on the transformation of the vanadyl salt at  $320^\circ\text{C}$  was

studied. Fig. 6 shows the spectra obtained after 17 h and 60 h of treatment under  $\text{N}_2$  flow in the presence of 4% of water. Both signals D and E are visible, D is the most intense signal after 17 h but is less intense after 60 h. Therefore the question of whether water can reverse the transformation occurring at  $320^\circ\text{C}$  under dry nitrogen was studied. Samples were first treated for 60 h at  $320^\circ\text{C}$  in dry atmosphere, then water was added (4%) for a treatment at 320 or  $210^\circ\text{C}$ . The signal D was partly restored (Fig. 7) but the

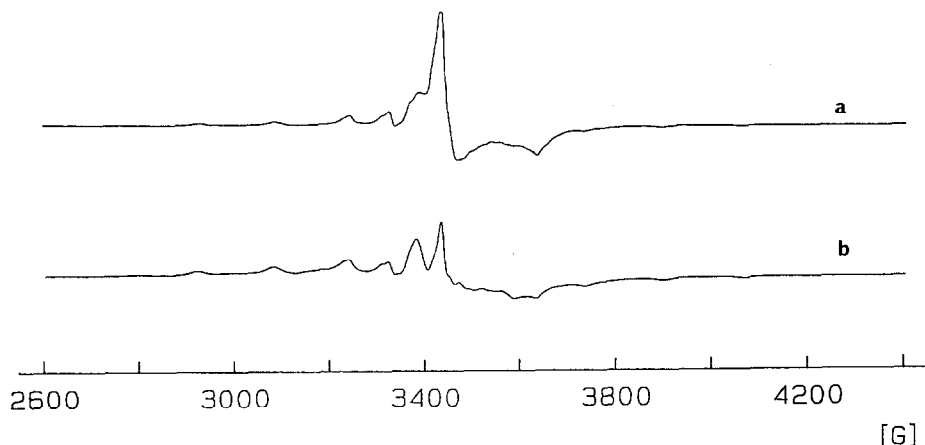


Fig. 7. ESR spectra ( $\nu = 9.775$  GHz) of  $\text{HVOPMo}_{12}\text{O}_{40}$  heated 60 h at  $320^\circ\text{C}$  under  $\text{N}_2$  and then treated in the presence of water 4%. (a)  $320^\circ\text{C}$ , 40 h; (b)  $210^\circ\text{C}$ , 30 h.



characteristic signal of  $\text{Mo}^{5+}$  remained, showing that the reversibility of the transformation was never complete, whatever the temperature and duration of the treatment with water vapor.

The vanadyl salt of the 12-molybdophosphate was also utilized as a catalyst for the oxydehydrogenation of IBA (17 h) and then transferred into an ESR tube without air exposure. When the reaction was performed in the presence of 4% of water, the ESR spectrum has been simulated by the superposition of the two  $\text{V}^{4+}$  signals C and D (the latter being the major component) and of the signal E characterizing  $\text{Mo}^{5+}$  but with a very low intensity. If the reaction was performed without water, the signal C disappeared and the relative intensity of the signal E increased. The relative intensity of the signal E observed after catalysis was always weaker than those observed after a thermal treatment either with or without water.

## 5. Discussion

In all the previous studies devoted to the characterization of vanadium in molybdic heteropolyanions, ESR spectra were recorded with solids containing initially the species  $\text{H}_{3+x}[\text{PMo}_{12-x}\text{V}_x\text{O}_{40}]$  in which the vanadium atoms are in the structure of the heteropolyanion. The ESR study of thermal evolution of vanadium containing heteropolyanions had to be reinvestigated for two main reasons: (1) in the solids studied, the paramagnetic probe  $\text{V}^{4+}$  was present in a very low proportion with respect to  $\text{V}^{5+}$  since the starting material was prepared with vanadium(V) and the  $\text{V}^{4+}$  proportion did not increase during the thermal treatment; (2) it was reported [11], and recently confirmed [12], that thermal treatment and use of vanadomolybdic heteropolyacids catalysts in IBA oxidation lead to a release of the vanadium atom from the polyanionic structure, without destruction of the Keggin unit since the heteropolyanion  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  is simultaneously rebuilt. This transformation has never been considered in all

the previous discussions of the ESR spectra of vanadomolybdic species in the solid state. Moreover, in the course of a catalytic oxidation reaction such as the oxidative dehydrogenation of isobutyric acid at  $320^\circ\text{C}$  or the oxidation of methanol at  $250^\circ\text{C}$ , this transformation is quantitative and all of the vanadium is in the  $\text{V}^{4+}$  state [11]. It is likely that this transformation occurs in all oxidation reactions and misleading conclusions may be drawn if it is ignored.

To characterize accurately the active solid at the steady state in oxidation reactions when the initial catalyst was  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ , the ESR study was performed on the well defined compound  $[\text{VO}(\text{H}_2\text{O})_5]\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot 23\text{H}_2\text{O}$  which has the same composition, except for the reduction state of the Keggin anion  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ , the polyanion being partly reduced in catalytic conditions [11]. All treatments were performed under nitrogen in order to keep all the vanadium atoms in the reduced state. Evolution of the values of ESR parameters with temperature is reported in Fig. 9. When the compound is fully hydrated, i.e. after crystallization from aqueous solutions at  $4^\circ\text{C}$ , the  $\text{V}^{4+}$  ESR signal A (Fig. 2) indicates, besides the expected strong localization of the odd electron on the vanadyl cation, that the molecular motion of the vanadyl is allowed at room temperature (Fig. 2a) as it would be in solution. This is clearly due to the large amount of water surrounding the  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  complex between the Keggin units. The correlation time calculated from simulation ( $3 \times 10^{-10}$  s) is about ten times those determined in aqueous solution.

The vanadyl molecular motion is quenched in the  $8\text{H}_2\text{O}$  hydrate obtained after partial dehydration at room temperature in natural air (Fig.

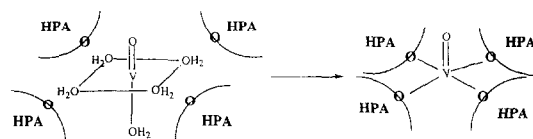


Fig. 8. Dehydration and change in the coordination mode of the vanadyl cation between  $75$  and  $210^\circ\text{C}$ .

3a). When further dehydration is achieved, the thermogravimetric curves and isotherms show that the loss of crystallization water and  $V^{4+}$  coordinated water molecules occur in two successive steps, before 75°C and in the temperature range 75–210°C respectively. After treatment at 75°C, the salt is anhydrous but the  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  complex is still present.

The similarity of signals A (at 77 K) and C strongly suggests that they correspond to  $V^{4+}$  included in the same first coordination sphere, i.e. to the  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  complex localized between Keggin units. We cannot assign at the present time the signal B observed with the intermediate 8  $\text{H}_2\text{O}$  hydrate obtained at room temperature (Fig. 3). This signal was observed with salts containing variable quantities of vanadyl and it was restored if the solids obtained at 75°C and 210°C are kept at room temperature in air of natural humidity. These observations suggest that, at room temperature, the vanadyl cations associated with the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  units are involved in aqua complexes as it has been observed in the structure of the salt  $[\text{Na}(\text{H}_2\text{O})_2]_2[\text{VO}(\text{H}_2\text{O})_5][\text{SiW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$  [11]. Without any information on the environment of  $V^{4+}$  by crystallographic methods, it is difficult to explain the spectra recorded either at 34 GHz or 9.7 GHz. The assumption that B is composed of two signals due to two independent  $V^{4+}$  cations cannot be held because the parallel signals would not be separated by 105 G both in X and Q-band spectra. All attempts to simulate these two spectra with two independent signals, for example with two different  $A_{\parallel}$  values, have failed. Another assumption was to consider pairs of  $V^{4+}$  cations, like those reported for binuclear species in vanadyl tartrate or citrate [16,17]. Their spectra present two parallel and two perpendicular components and a half field forbidden transition ( $\Delta M_S = 2$ ). In the case of the 8 $\text{H}_2\text{O}$  hydrate, only the parallel signal is split into two components but no half field signal was observed. Therefore, formation of a triplet state vanadyl complex here seems unlikely. Further studies

are needed to propose a satisfying explanation of this spectrum.

Between 75 and 210°C, the ESR signal is strongly modified, corresponding to the stripping of the vanadyl cation shown by the TG curves. The electron is once more localized on the  $V^{4+}$  ion in an tetragonal crystal field but decreasing of both  $A_{\parallel}$  (205 to 165 G) and  $A_{\perp}$  (84 to 44 G) shows that the electron delocalization is stronger than in  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ . Since the coordination sphere of  $V^{4+}$  must be reconstructed after water displacement, the new ligands are necessarily the outer oxygen atoms of heteropolyanions as schematically represented in Fig. 10. Heteropolyanions are then linked together by means of the vanadium atoms. Such a coordination of  $V^{4+}$  is in agreement with a higher delocalization of the electron through  $V^{4+}-\text{O}-\text{Mo}^{6+}$  bonds than in the isolated  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ . A similar situation exists when a vanadium atom is in a Keggin structure since it is then linked to four  $\text{Mo}^{6+}$  through  $V^{4+}-\text{O}-\text{Mo}^{6+}$  bonds. Actually, the ESR spectrum of the ammonium salt of  $[\text{PMo}_{11}\text{V}^{\text{IV}}\text{O}_{40}]^{5-}$  ( $g_{\parallel} = 1.936$ ,  $g_{\perp} = 1.974$ ,  $A_{\parallel} = 164$  G and  $A_{\perp} = 57$  G) is close to the signal D, that strongly supports the proposed coordination of vanadium. In contrast to the molecular structure of the initial material, the solid at 210°C can be viewed as an infinite covalent network in which anhydrous oxomolybdc Keggin units are linked by  $\text{VO}^{2+}$  groups. When dehydration was carried out between 75°C and 210°C, only C and D signals were observed, showing that there is no stable intermediate between  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  and heteropolyanion coordinated  $\text{VO}^{2+}$  cations. Since the transformation is reversible, it can be expected that these two vanadyl species are in equilibrium in the presence of water and that their relative amounts depend on the temperature and on the water vapor pressure of the gas phase.

The solid was treated under nitrogen atmosphere at 320°C since catalytic oxidation reactions are generally performed at temperatures ranging from 300 to 350°C. The appearance of

the  $\text{Mo}^{5+}$  signal E, different from the  $\text{Mo}^{5+}$  signal in a Keggin unit [18], corresponds to the destruction of the structure of the molybdophosphate [15]. The same  $\text{Mo}^{5+}$  signal has been observed when  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$  was submitted to a reducing atmosphere ( $\text{H}_2$ ) at a temperature above  $400^\circ\text{C}$  [7] and has been assigned to the reduction of molybdic species resulting from the decomposition of the Keggin unit. The almost complete disappearance of the  $\text{V}^{4+}$  signal after 60 h of treatment of the vanadyl salt shows that this decomposition has to be correlated with a major evolution of the vanadyl species. Formation of an oxide phase such as  $\text{V}_2\text{O}_4$  (undetectable by the ESR technique) or of precursors of this phase may be involved in this evolution.

The presence of water clearly slows and/or limits the evolution of the Keggin unit at  $320^\circ\text{C}$  since signal D can still be observed after 60 h under wet nitrogen (Fig. 7b). Perhaps most important is the observation that signal D is restored by a treatment under water vapor following a treatment under dry nitrogen atmosphere (Fig. 8). Therefore, water allows partial rebuilding of the Keggin units after almost total transformation of the solid. The absence of any powder X-ray diffraction diagram of the solid after any thermal treatment at  $320^\circ\text{C}$  shows that it is amorphous and does not contain crystallized oxides which are formed at higher temperatures. The possible rebuilding of the Keggin unit in the presence of water suggests that the solid resulting from the decomposition of the molybdophosphate at  $320^\circ\text{C}$  is constituted by poorly organized fragments of this structure containing the metallic cations at several oxidation states.

Water is used as an additive in the reaction mixture in order to stabilize the activity of the catalyst [19]. It has been proposed [12] that water did not stabilize the structure of the heteropolyanion by formation of a stable hydrate but could influence the catalytic cycle itself. The monovanadyl salt of the molybdophosphate can be considered as a suitable model of the most active phase [11,12]. Since ESR signals C

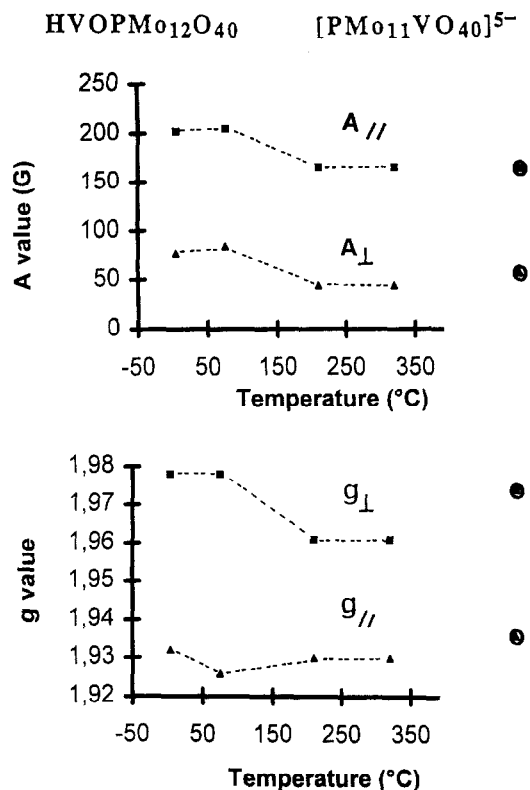


Fig. 9. Values of the ESR parameters according to the hydration of  $\text{HVOPMo}_{12}\text{O}_{40}$ . Values for  $(\text{NH}_4)_5\text{PMo}_{11}\text{V}^{\text{IV}}\text{O}_{40}$  are reported for comparison.

and D are observed after catalysis (without air and moisture exposure), it can be expected that rapid changes in the coordination sphere of  $\text{V}^{4+}$  could occur at  $320^\circ\text{C}$  in the presence of water, aquo complexes being in equilibrium with heteropolyanion bound species. Evolution of the structure of the solid, involving, for example, the formation of partially decomposed Keggin units and precursors of oxides such as  $\text{V}_2\text{O}_4$  and  $\text{MoO}_3$ , would be slowed down when the vanadium exists as  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$  and then decomposition of the Keggin unit would be more difficult.

## 6. Conclusion

The aim of this study was to obtain the 'fingerprints' of  $\text{V}^{4+}$  in heteropolymolybdic

solids since the knowledge of the vanadyl surroundings could be helpful for understanding of the catalytic reaction mechanism and, especially, of the role of vanadium. At temperatures lower than about 100°C, aquo complexes of VO<sup>2+</sup> are localized between the Keggin units but they are coordinated to the outer oxygen atoms of the molybdophosphate at temperatures higher than about 210°C. When the catalyst worked out for the oxydehydrogenation of isobutyric acid at 320°C in the presence of water the two types of vanadyl cations were identified. This is a possible explanation of the role of water in order to slow down the deactivation of the catalyst.

### Acknowledgements

The financial support of Atochem Company and CNRS is gratefully acknowledged. We thank Mr. B. Morin for help in recording the ESR spectra and the 'Laboratoire des Matériaux Inorganiques' (Université Paris 6) for providing calculation program of simulation.

### References

- [1] Y. Ono, in J.M. Thomas, K.I. Zamaraev (Eds.), *Perspectives in Catalysis*, Blackwell, London, 1992, p. 431.
- [2] N. Mizuno and M. Misono, *J. Mol. Catal.*, 86 (1994) 319.
- [3] R.J.J. Jansen, H.M. Van Veldhuizen, M.A. Schwegler and H. Van Bekkum, *Recl. Trav. Chim. Pays-Bas*, 113 (1994) 115.
- [4] J.J. Altenau, M.T. Pope, R.A. Prados and H. So, *Inorg. Chem.*, 14 (1975) 417.
- [5] M. Otake, Y. Komiya and T. Otaki, *J. Phys. Chem.*, 77 (1973) 2896.
- [6] R. Fricke, H.G. Jerschke and G. Öhlmann, *J. Chem. Soc., Faraday Trans. 1*, 82 (1986) 3479.
- [7] R. Fricke, H.G. Jerschke and G. Öhlmann, *J. Chem. Soc., Faraday Trans. 1*, 82 (1986) 3491.
- [8] E.M. Serwicka and C.P. Grey, *Colloids Surf.*, 45 (1990) 69.
- [9] Q. Shuhua, Z. Ruiyun and W. Yue, *Sci. Sin. B*, 31 (1988) 1025.
- [10] M. Fournier, C. Feumi-Jantou, C. Rabia, G. Hervé, M.J. Bartoli, P. Courtine, M. Kermarec, D. Olivier and M. Bettahar, *Proceedings of the First Franco-Maghreb Symposium*, (1990) 227.
- [11] E. Cadot, C. Marchal, M. Fournier, A. Tézé and G. Hervé, in M.T. Pope and A. Müller (Eds.), *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer, Dordrecht, 1994, p. 315.
- [12] Th. Ilkenhans, B. Herzog, Th. Braun and R. Schlögl, *J. Catal.*, 153 (1995) 275.
- [13] M. Fournier, C. Feumi-Jantou, C. Rabia, G. Hervé and S. Launay, *J. Mater. Chem.*, 2 (1992) 971.
- [14] M.T. Pope, *Hetero and Isopolymetalates*, Springer, Berlin, 1983.
- [15] R. Fricke and G. Öhlmann, *J. Chem. Soc., Faraday Trans.*, 82 (1986) 263.
- [16] R.H. Dunhill and T.D. Smith, *J. Chem. Soc. A*, (1968) 2189.
- [17] R.L. Belford, N.D. Chasteen, H. So and R.E. Tapscott, *J. Am. Chem. Soc.*, 91 (1969) 4675.
- [18] C. Sanchez, J. Livage, J.P. Launay, M. Fournier and Y. Jeannin, *J. Am. Chem. Soc.*, 104 (1982) 3194.
- [19] O. Watzemberger and G. Emig, *Stud. Surf. Sci. Catal.*, 72 (1992) 71.