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Molybdenum-Doped V–P–O System

I. Preparation and Characterization

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Attempts to prepare and to characterize new catalysts belonging to the (V–P–Mo–O) system selective in the mild oxidation of butane or butene to maleic anhydride lead to the conclusion that molybdenum can be substituted up to 7% in $VOPO_4$ phases. Thermal analysis of the hydrated precursor, XRD, ESR spectroscopies, UV–visible and IR spectroscopies of both hydrated and anhydrous solid phases obtained show that the solid solutions isostructural with $VOPO_4 \cdot 2H_2O$ and α_I-$VOPO_4$, respectively, can be formulated:

$$[(VO)^{3+}_{0.93}(VO)^{2+}_{0.07}\,(PO_4)^{3-}_{0.93}(MoO_4)^{2-}_{0.07} \cdot nH_2O]\ (n = 1 \text{ to } 2)$$

and

$$[(VO)^{3+}_{0.93}(VO)^{2+}_{0.07}\,(PO_4)^{3-}_{0.93}(MoO_4)^{2-}_{0.07}].$$

Introduction

Vanadium–phosphorus oxides are known as catalysts for the mild oxidation of butene and butane to maleic anhydride (*1–8*). Extensive work has been done on the preparative chemistry and showed that the valency of vanadium is important with regards to selectivity: the mean state of vanadium must be (4+) in the oxidation of butane and (4+, 5+) in the oxidation of butene (*4–7*). We have recently justified these results by showing the presence of γ-$(VO)_2P_2O_7$ at the steady state obtained by a topotactic decomposition of the precursor $VOHPO_4 \cdot 0.5H_2O$ (oxidation of butane) (*8, 9*), while other preparations yielding mixed phases $VOPO_4/(VO)_2P_2O_7$ are preferable for the oxidation of butene (*1*).

In the (V–Mo–O) system, V^{4+} is formed in the solid solution $(Mo_xV_{1-x})_2O_5$ (*10*) in which ESR and magnetic susceptibility measurements indicate the presence of V^{4+}–O–Mo^{6+} pairs (*11*); this phase is selective in the oxidation of benzene to maleic anhydride (*12*) whereas the $VOMoO_4$,V^{4+} compound, which is isostructural with α_{II}-$VOPO_4$ (*13*), is not catalytically active.

As shown in the case of Co^{2+} or Zn^{2+} introduced in V–P–O catalysts (*14, 15*), the presence of V^{4+} cannot be systematically correlated with an increase of selectivity; however, the addition of a few molybdenum atoms has been shown effective for the performance of $VOPO_4$ in the oxidation of butene (*16*).

Since no study of the V–P–Mo–O system exists in the literature, we have tried to make some definite compounds by means of various methods of preparation, but we

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have succeeded only in the synthesis of V–P–O phases doped with a low molybdenum content following this presented preparation. These other methods consist of (i) studying the binary systems of $VOPO_4$–$MoOPO_4$, $VOPO_4$–$VOMoO_4$, and $VOMoO_4$–$MoOPO_4$, taking into account the isotypic structure of $MoOPO_4$, $VOPO_4$, and $VOMoO_4$ phases, but these phases did not appear to form even limited solid solutions; (ii) mixing directly molybdenum, vanadium, and phosphorus oxides in a liquid acid medium, followed by an evaporation; or (iii) synthesizing by thermal decomposition of pounded mixtures of oxalated and/or ammonium salts (for example, the mixture of $NH_4[(VO)_2C_2O_4(HPO_4)_2] \cdot 5H_2O + V_2O_5 + NH_4(MoOC_2O_4)$ in stoichiometric atomic ratios of V : P : Mo). In this paper we shall emphasize the chemical preparation of the new compounds obtained, as well as their structure, which influences their reactivity in terms of their catalytic properties (*17*).

Preparation

The starting material V_2MoO_8 was prepared from V_2O_5 and MoO_3 (Merck, reagent grade) by (i) dissolution in excess hydrochloric acid followed by evaporation of the solution, drying and calcination of the residue at 580°C under O_2 for 8 hr (*18*), or (ii) heating of stoichiometrically mixed powdered solids in a quartz crucible, sealed under vacuum, at 600°C for 1 hr (*19*).

The compound P_1 was prepared as follows: 4.02 g of V_2MoO_8 was added to an aqueous solution containing 5.75 ml of 85% H_3PO_4 and this mixture was stirred under reflux for 20 hr. The color of the solution turned to reddish brown after dissolution of V_2MoO_8 (6 hr). After concentration of the solution to 20 ml under 730 Torr (obtained with a vacuum water pump), the resulting green precipitate was filtered off under 30 Torr and dried at 100°C in an oven for exactly 6 hr, thus leaving it in the air for a short time before the final product P_1 is obtained. The calcination of P_1 in a platinum crucible, performed in a furnace at 500°C under nitrogen flow for 5 hr, yields the anhydrous compound P_2.

For a better understanding of this paper, it is necessary to define the compounds obtained. The *P_1 compound* is the final product of this preparation. It is a hydrate containing approximately one water molecule of crystallization. This P_1 compound is subject to hydration when left in air for a long time, the (x) number of water molecules is between 1 and 2, and may become close to 2. This sample is called *hydrated P_1*. When this hydrated P_1 is slightly heated, (x) decreases to 1, and after leaving the sample in air, (x) goes up to between 1 and 2. This sample is called *rehydrated P_1*. Whereas P_2 is an *anhydrous compound* obtained from calcination of P_1, P_2 is not sensitive to rehydration.

Results

1. Chemical Analysis

Chemical analyses were done by means of atomic spectrophotometry (Perkin–Elmer 560) and X-ray fluorescence (Tracor Northen TN 2000). X-Ray emission spectroscopy was performed using a Cameca microscope.

Atomic absorptiometry revealed the presence of Mo, P, V, checked by X-ray emission spectroscopy, and X-ray fluorescence indicated that the atomic ratio Mo/V is less than 10%: several runs reproducibly indicated that Mo/V equals 0.07 in P_1 and P_2.

2. Structural Analysis

2.1. X-Ray diffraction. The XRD patterns of P_1 and P_2 have been obtained and indexed in the tetragonal system on the ba-

TABLE I

Indexation of the X-Ray Pattern of the Hydrated Compound P_1

I/I_0	hkl	d_{calcd} (Å)	$2\theta_{calcd}$	$2\theta_{obs}$	d_{obs} (Å)
100	001	6.850	15.00	15.00 ± 0.05	6.852
42	002	3.425	30.28	30.28 ± 0.05	3.422
93	200	3.105	33.48	33.50 ± 0.05	3.101
38	201	2.828	36.88	36.80 ± 0.05	2.823
35	031	1.981	53.66	53.50 ± 0.05	1.987
54	130	1.963	54.20	54.20 ± 0.05	1.963
40	032	1.771	66.66	66.70 ± 0.05	1.770
35	040	1.552	70.46	70.40 ± 0.05	1.550

Diffractometer, Co$K\alpha$ radiation
$a = 6.210$ Å, $c = 6.850$ Å, $P_{4/n} - D^7_{4h}$.

TABLE II

Indexation of the X-Ray Pattern of the Anhydrous Compound P_2

I/I_0	d_{obs} (Å)	hkl	d_{calcd} (Å)
st	4.172	001	4.170
w	3.105	200	3.103
vst	3.025	111	3.023
w	1.976	012	1.976
vw	1.964	130	1.962
vw	1.854	301	1.853
vw	1.552	400	1.552

$a = 6.207$ Å, $c = 4.170$ Å
Seeman–Bohlin chamber, Cu$K\alpha$ radiation.
Relative intensity: w = weak, m = medium, st = strong, v = very.

sis of a structural isotopy with the hydrates of $VOPO_4$ (*16, 20, 21*) and anhydrous α_I-$VOPO_4$, respectively, (*22, 23*) (Tables I and II). The cell parameters found by the least-squares method are the following:

$$P_1\text{: } a = 6.210 \text{ Å},\ c = 6.85 \text{ Å}$$

$$P_2\text{: } a = 6.207 \text{ Å},\ c = 4.17 \text{ Å}.$$

The XRD patterns were obtained on Seeman–Bohlin chambers (Cu$K\alpha$ radiation) and on CGR Guinier camera and diffractometer (Co$K\alpha$ radiation).

2.2. Infrared and UV–visible spectra. Infrared spectra (4000–250 cm^{-1}) were recorded on a Perkin–Elmer 451 spectrometer using the KBr disk technique. The IR spectra of P_1 reveal the presence of crystal water whose main bands due to O–H stretching and bending appear near 3400–1620 cm^{-1}, respectively, and resemble the spectra of $VOPO_4 \cdot 2H_2O$ (Fig. 1). When a KBr disk containing $VOPO_4 \cdot 2H_2O$ is

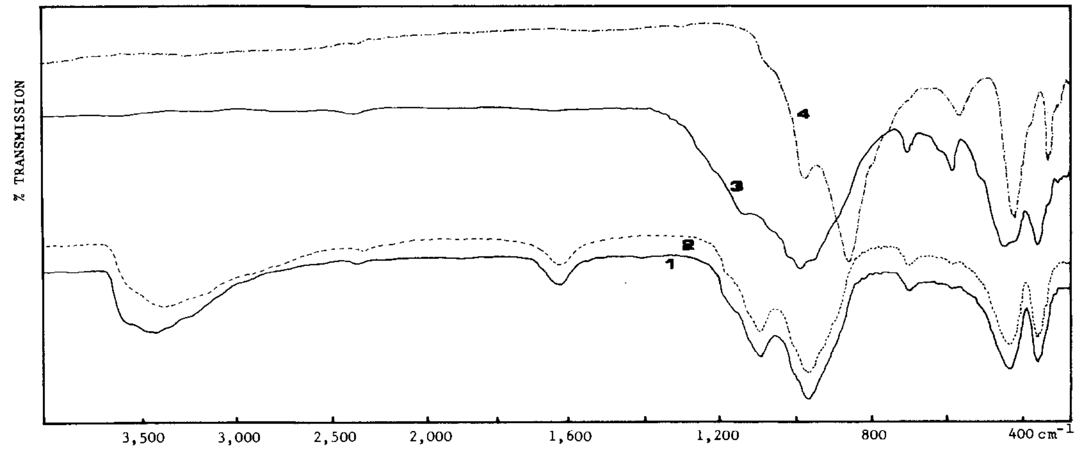

Fig. 1. Comparison of IR spectra of (1) hydrated P_1, (2) $VOPO_4 \cdot 2H_2O$, (3) P_2, (4) $VOMoO_4$.

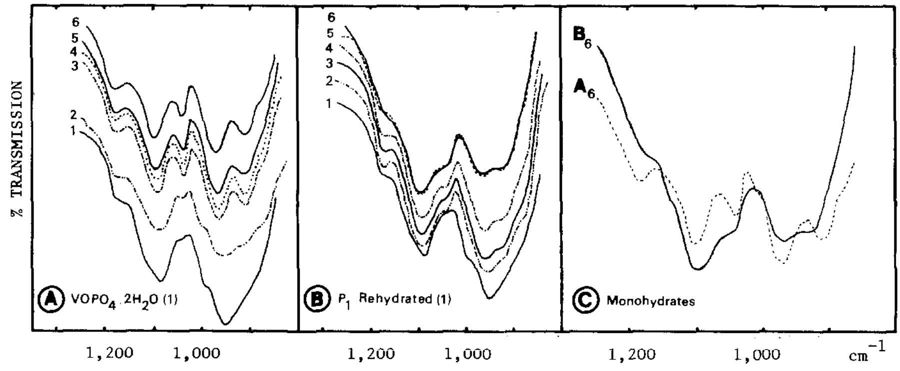

FIG. 2. Variation of IR spectra in terms of dehydration of $VOPO_4 \cdot 2H_2O$ (A) and rehydrated P_I (B), both leading to monohydrates when the KBr disk was heated to (1) 20°C, (2) 125°C for 15 min, (3) 30 min, (4) 3 hr, (5) 20 hr, or (6) 30 hr. (C) explicitly shows the similarity between $VOPO_4 \cdot H_2O$ and P_I spectra.

heated at 125°C in an oven for various periods (from 15 min to 30 hr), its spectrum is modified and becomes close to the monohydrate P_I spectra corresponding to B(5) and B(6) in Fig. 2. Few differences are noticed between anhydrous α_I-$VOPO_4$ and P_2 (Fig. 3).

Ultraviolet–visible diffuse reflectance spectra of solid samples were obtained on a Beckman DK2A spectrophotometer from 5000 to 50,000 cm^{-1} using MgO as the standard. Diffuse-reflectance spectra of P_I and P_2 in UV-visible range have been performed in order to detect vanadyl $(VO)^{2+}$ or Mo^{5+} species. It is very well known that absorption bands are expected in the crystal field range for such d^1 compounds which are due to d–d transitions, whereas only charge transfer bands occur for V^{5+} or Mo^{6+} (d^0) (Fig. 4).

3. Thermal Analysis

Thermogravimetric (TGA) and differential thermal analysis (DTA) were performed, respectively, on a Setaram MTB 10-8 microbalance and semimicroanalyzer M5 at various heating rates under nitrogen flow. According to DTA the water molecules of rehydrated P_I are lost in two steps at 74 and 165°C under N_2 at the rate of

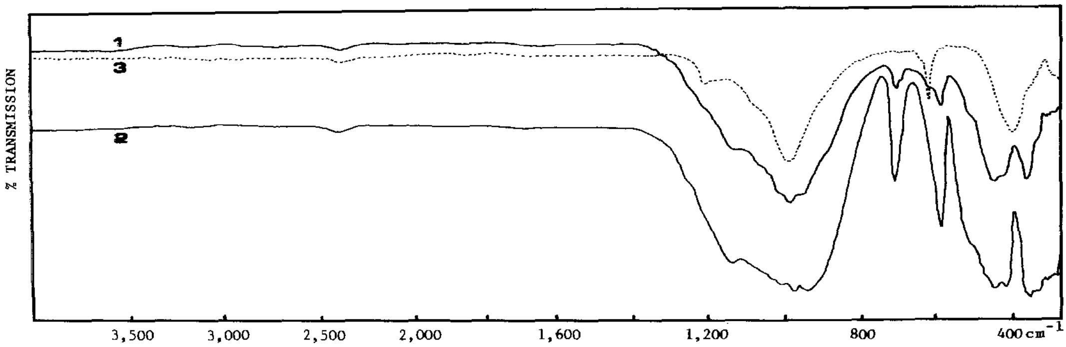

FIG. 3. Comparison of IR spectra of (1) P_2, (2) α_I-$VOPO_4$, and (3) α_{II}-$VOPO_4$, dehydrated in all three cases.

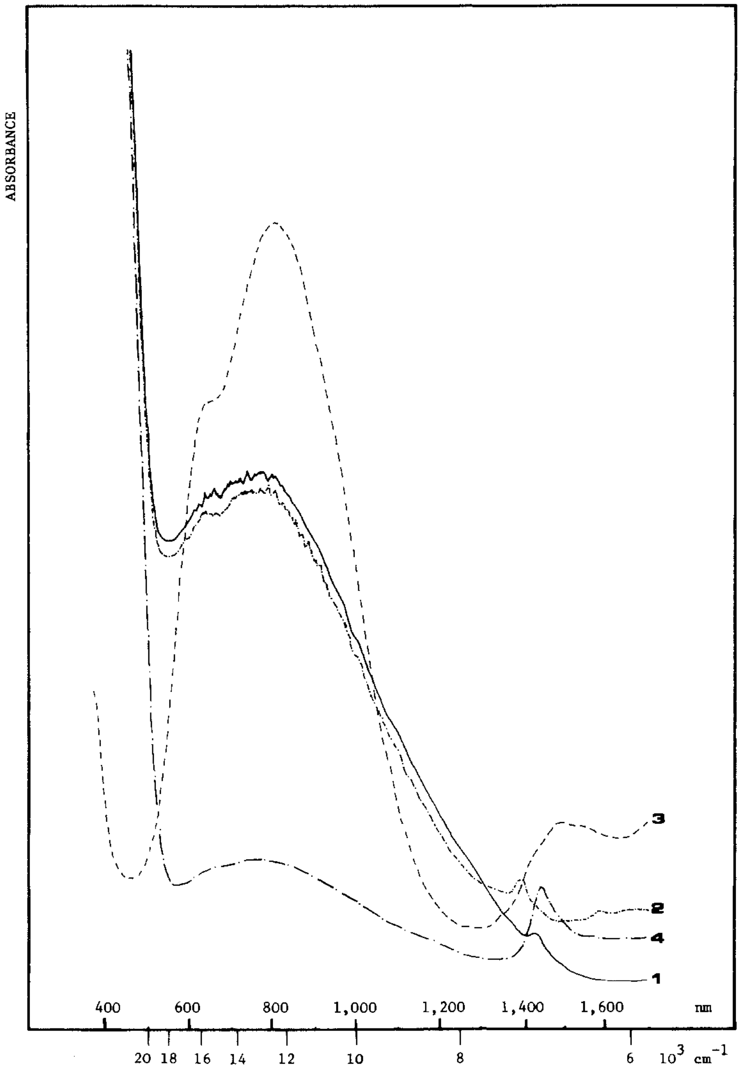

FIG. 4. UV-visible spectra of (1) P_I, (2) P_2, (3) $VOHPO_4 \cdot 0.5H_2O$ (V^{4+} content), (4) $VOPO_4 \cdot 2H_2O$ (V^{5+} content, with a few having a quantity of V^{4+} due to H_2O interaction).

600°C · hr^{-1}. TGA indicates that in fact the dehydration is not completely finished until 300°C (17.7% weight loss) which corresponds to the third endothermic peak at 293°C in DTA experiments (Fig. 5). At higher temperatures under nitrogen, phases analogous to α_{II}-$VOPO_4$, γ-$VOPO_4$, and $(VO)_2P_2O_7$ are obtained, as will be explained in a forthcoming paper.

4. Electron Resonance Spectroscopy (ESR)

V^{4+} ions, with d^1 configuration, are paramagnetic and can be detected by ESR study. The electron resonance spectrum of V^{4+} shows a strong hyperfine contribution due to the $I = 7/2$ spin of the vanadium nucleus. Figure 6 presents the ESR spectra of P_1 recorded at room temperature. It can be described by the axial symmetry spin Hamiltonian:

$$H = g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\|} S_z I_z + A_{\perp}(S_x I_x + S_y I_y)$$

where β: Bohr magneton
S: effective spin
H: magnetic field
$g_{\|}$, $g_{\perp}$: main magnitudes of g-tensor
$A_{\|}$, $A_{\perp}$: main magnitudes of the coupling constant A.

The ESR parameters characterizing the paramagnetic centers are

$$g_{\|} = 1.935,\ A_{\|} = 198\ \text{G},$$
$$g_{\perp} = 1.985,\ A_{\perp} = 76\ \text{G}.$$

The ESR spectra were obtained on Varian E 09 at room temperature.

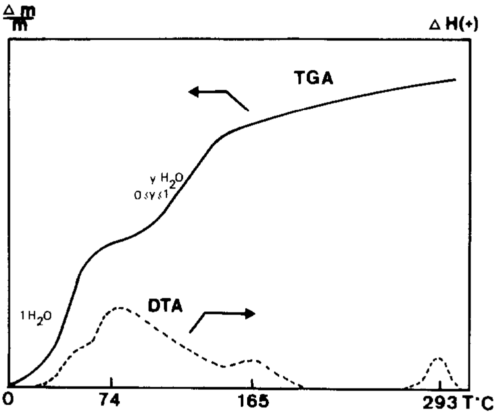

FIG. 5. TGA curve, in concordance with DTA endothermic peaks, of the hydrated P_I showing the number of water molecules of crystallization released in each step in terms of temperature variation. The presence of these two steps indicates the different types of interactions exhibited by the water molecules: one strongly linked on V^{5+} (higher temperature) and another held by weak hydrogen-bonding to another water molecules (lower temperature).

Discussion

1. Chemical Composition of P_1 and P_2

P_1 compound contains approximately one water molecule and is slowly hydrated in air to become a dihydrate which crystallizes as $VOPO_4 \cdot 2H_2O$. Very carefully controlled conditions of partial pressure of H_2O are needed to synthesize P_1 owing to the use of a water vacuum pump.

According to the experimental results, P_1 and P_2 can be understood as solid solutions of molybdenum up to 7 atom% in the V–P–O system: this value seems to correspond to a limit in the system since its chemical preparation consists of the dissolution of the starting material V_2MoO_8 (Mo/V = 50 atom%), whereas the green precipitate obtained contains only Mo/V = 7 atom%. The ingestion of molybdenum in a lattice of α_I-$VOPO_4$ is proved by the difference of chemical reactivity of P_2 and α_I-$VOPO_4$ (*24*); on the other hand, X-ray emission spectroscopy still shows the presence of Mo after a high thermal treatment of P_2 at 700°C (*24*). The composition of $V_{1.08}P_{0.92}O_5$ obtained by Jordan and Calvo (*25*), which is isostructural with α_{II}-$VOPO_4$ (*26*), shows that the substitution of phosphorus seems to realize up to 7 or 8 atom% of solubility in the $VOPO_4$ structure.

The question arising now is, which atom, V or P, is substituted for by the small quantity of 0.07 atom of Mo. The presence of

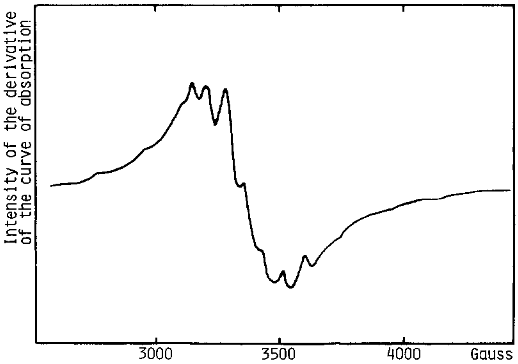

FIG. 6. ESR spectrum of P_I.

Mo^{6+}, which is required for the electrical neutrality is assumed. According to (*27*), the Mo^{6+} is thermodynamically easier to obtain if the molybdenum atom forms MoO_4^{2-}, MoO_3, (or MoF_6). On the other hand, in the case of the anion MoO_4^{2-}, the Mo^{6+} is stabilized in a *tetrahedron* as in several salts such as Ca^{2+} $(MoO_4)^{2-}$, $Co^{2+}(MoO_4)^{2-}$, and as the oxisalt $(VO)^{2+}$ $(MoO_4)^{2-}$. This indicates that the MO is stabilized in a tetrahedral site like P in PO_4^{3-}, unless it forms MoO_3, which is volatile at 600°C. As has been mentioned previously, the Mo is still detected beyond 700°C so the tetrahedral anion PO_4^{3-} is certainly substituted for by 0.07 $(MoO_4)^{2-}$.

2. *Reflectance Spectroscopy*

Vanadyl-containing compounds are known to present well-defined absorption bands between 8000 and 32,000 cm^{-1} (*28*). Due to the C_{4v} distortion of the octahedral field around vanadium in VO^{2+}, two bands at least are expected corresponding to $^2E \leftarrow {}^2B_2$ (11,000–14,700 cm^{-1}) and $^2B_1 \leftarrow {}^2B_2$ (14,800–20,400 cm^{-1}) transitions; a third one between 21,000 and 31,300 cm^{-1} due to $^2A_1 \leftarrow {}^2B_2$ transition is frequently obscured by the tail of charge transfer bands. The existence of VO^{2+} species is detected by the presence of one band with a shoulder which is due to the overlapping of the two first bands. Such a band has been effectively observed in P_1 and P_2 spectra (Fig. 4).

3. *Infrared Spectroscopy*

The P_1 and P_2 spectra can be compared with $VOPO_4 \cdot 2H_2O$ and α_I-$VOPO_4$, P_1 and $VOPO_4 \cdot 2H_2O$ spectra are very similar (Fig. 1), as P_2 is to α_I-$VOPO_4$ spectra (Fig. 3). The two main points gathered from this comparison could be interpreted as follows. First, the symmetry is the same in each pair, and second, the bands assigned to the vibration of water molecules enhance the fact that P_1 is a hydrate. With the intention of getting more information, the comparison of the P_2 spectrum with α_{II}-$VOPO_4$ and $VOMoO_4$ spectra has been done; the α_{II}-$VOPO_4$ and P_2 spectra are significantly different indicating that no confusion exists between the P_2 spectrum and that of α_I-$VOPO_4$ (Fig. 3). On the other hand, the spectrum of $VOMoO_4$ does not permit a better identification of the small quantity of $(MoO_4)^{2-}$ tetrahedra in P_2 (and P_1) (Fig. 1). Certain relevant data such as the vibration frequencies of PO_4, V=O, and V—O are given in Table III.

4. *Crystal Structure*

XRD and IR spectroscopies show that rehydrated monohydrate P_1 and anhydrous P_2 are, respectively, isostructural with $VOPO_4 \cdot 2H_2O$ and α_I-$VOPO_4$.

The same value "*a*" ~ 6.2 Å obtained for the cell parameter of P_1 and P_2 and pure $VOPO_4$ indicates that the introduction of molybdenum in $VOPO_4$, anhydrous or hydrated, does not induce a disorder inside the layers, that is to say that the difference of size between molybdates and phosphates tetrahedron (*29*) cannot be correlated to the modification of "c" parameter.

On the contrary, the variation of "*c*" in hydrated compounds (7.4 Å in $VOPO_4 \cdot 2H_2O$; 6.5 Å in $VOPO_4 \cdot 1H_2O$; 6.85 Å in hydrated P_1) and anhydrous compounds (4.11 Å in α_I-$VOPO_4$; 4.17 Å in P_2) accounts for the presence of V^{4+}: the decrease of "*c*" parameter in the hydrated P_1 (6.85 Å instead of 7.40 Å) implicates a perturbation in the layer charge balance involving a decrease of the number of water molecules intercalated. Figures 5 and 7 show the different kinds of interaction exhibited by the water molecules. The presence of V^{4+} affects the Lewis base interaction between water molecules and the layer (Figs. 7a and b). In the anhydrous compound α-$VOPO_4$, layers are joined together by the interaction of the oxygen doublets of the upper vanadyl

TABLE III

ASSIGNMENT OF IR BANDS IN V–P–O AND V–P–Mo–O COMPOUNDS ($\bar{\nu}$, cm^{-1})

$VOPO_4 \cdot 2H_2O$	Rehydrated P_I	α_I-$VOPO_4$	P_2	α_{II}-$VOPO_4$	Assignment
1165	1182 (sh)	1140	1135	1210	(ν_3)
1087	1085	—	1080	1080 (sh)	ν_{as} PO_4
1032	—	1010	1010	—	
950	955	970	975	985	νV=O
900	915 (sh)	935	942	—	(ν_1)
—	870 (sh)	—	870 (sh)	—	ν_s PO_4
685	682	690	690	622 (sh)	(ν_4)
565 (sh)	570 (sh)	567	602	600	δ_{as} PO_4
—	—	—	570	—	
—	—	487	490	—	(ν_2)
—	—	422	425	—	δ_s PO_4
420	428 (sh)	—	—	—	+
405 (sh)	410	395	400	380	ν V—O
320	335	340	—	—	
—	—	330	—	—	

Note: (sh) = shoulder, O–H: $VOPO_4 \cdot 2H_2O$: 3550, 3320 cm^{-1}; P_I: 3550, 3410 cm^{-1}. δO–H: $VOPO_4 \cdot 2H_2O$: 1635, 1620 cm^{-1}; P_I: 1620 cm^{-1}.

(V=O) with the V^{5+} (Fig. 7c), like a Lewis acid–base interaction. So, the presence of V^{4+} in P_2 may perturb this bonding by its elongation (Fig. 7d).

5. *Electron Resonance Spectroscopy*

The hyperfine structure with an axial symmetry of the ESR spectrum of P_I indicates that the unpaired electron remains localized mainly on a single vanadium site during the time scanning. Values of the hyperfine coupling constant $A_\parallel$ and $A_\perp$, and g-parameter value of the P_I compound are close to the ESR parameter values of hydrated V^{4+}: $[VO(H_2O)_5^{2+}]$ (*30*); i.e., the site symmetry of V^{4+} in P_I is approximately C_{4v} (Table IV; Fig. 6).

Studies on the ESR lineshape evolution of V_2O_5 in terms of the V^{4+} concentration show a distinct hyperfine structure at lower concentration (about 1–2 atom% of V^{4+}); the hyperfine structure tends to disappear with the increase of V^{4+} concentration, narrowing the resonance line (*31*). Consequently, the ESR lineshape suggests an important relative concentration of V^{4+} in P_I.

The absence of signal characteristics of the ESR spectrum of Mo^{5+} paramagnetic centers may suggest that the oxidation state of the molybdenum is 6+.

Conclusion

The structural results in this paper demonstrate that molybdenum can be substituted for phosphorus up to 7 atom% in vanadyl phosphate phases as molybdate MoO_4^{2-}. To ensure the electrical neutrality, V^{4+}, is formed. This assumption is also sup-

TABLE IV

ANISOTROPIC ESR PARAMETERS

	$g_\parallel$	$g_\perp$	$A_\parallel$ (G)	$A_\perp$ (G)	Ref.
$VO^{2+}(H_2O)_5$	1.931	1.978	205.4	76.5	(*30*)
P_I	1.935	1.985	198.0	76.0	—

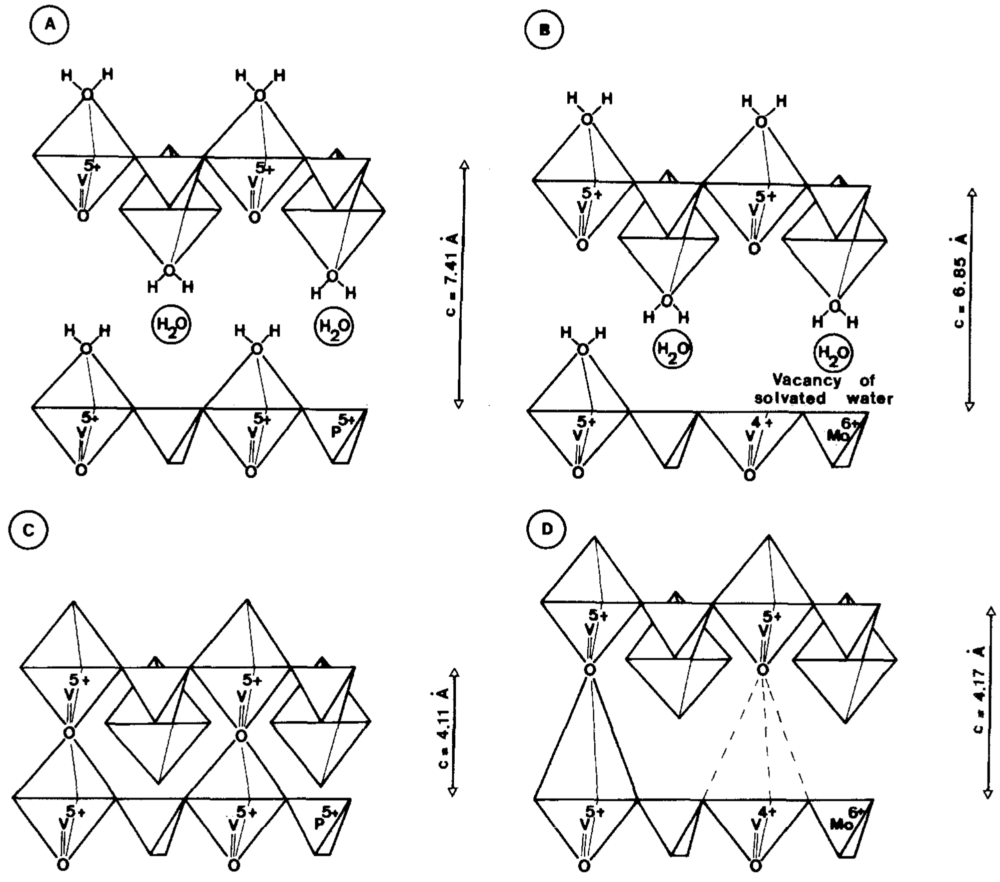

FIG. 7. The presence of the supplementary electron in V^{4+} decreases the interactions R'—V^{5+} · · · $|\overline{O}<^{R}_{R}$ Hence, a water molecule strongly linked on V^{5+} in $VOPO_4 \cdot 2H_2O$ (A) may be absent in hydrated P_I (B) involving the decrease of "c" parameter. The relaxation of bonding of layers in α_I-$VOPO_4$ (C) is observed in P_2 (D).

ported by thermal analysis of the decomposition which yields reproducibly P_2 from P_I with a weight loss corresponding to the formula $[VO(MoO_4)_{0.07}(PO_4)_{0.93} \cdot H_2O]$. On the other hand, it can be concluded that the formula of this anhydrous compound P_2 can be written as a solid solution $[(VO)^{3+}_{0.93}(VO)^{2+}_{0.07}(PO_4)^{3-}_{0.93}(MoO_4)^{2-}_{0.07}]$ which is isostructural with α_I-$VOPO_4$.

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