

Synthesis of Polyoxovanadates from Aqueous Solutions

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

Polyoxovanadates have been synthesized from aqueous solutions of V^V in the presence of inorganic Na^+ and organic $[N(CH_3)_4]^+$ cations. Decavanadate crystals are precipitated at room temperature around pH 7, whereas layered compounds $Na[V_3O_8] \cdot H_2O$ and $N(CH_3)_4[V_4O_{10}]$ are formed at the same pH under hydrothermal conditions. *In situ* ^{51}V NMR experiments show that upon heating solute decavanadate species are progressively transformed into cyclic metavanadates $[V_4O_{12}]^{4-}$. A chemical mechanism is suggested for the formation of these layered vanadium oxides. It involves the ring-opening polymerization of cyclic metavanadates arising from co-ordination expansion favored by protonation or vanadium reduction.

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INTRODUCTION

Many new polyoxovanadates have been synthesized during the past decade via hydrothermal methods (1–3). They exhibit a large variety of structures, ranging from chain metavanadates $[VO_3^-]_n$ to layered oxides $N(CH_3)_4[V_4O_{10}]$ and compact polyanions $[V_{10}O_{28}]^{6-}$ (4–6). Hollow clusters encapsulating anionic or neutral species such as $(TMA)_6[V_{15}O_{36}Cl] \cdot 4H_2O$ or $(Cs)_9[H_4V_{18}O_{42}I] \cdot 12H_2O$ have also been reported (7). Chemical syntheses via “chimie douce” methods favor the formation of open structures such as layered vanadium oxides that could exhibit improved properties as cathodic materials for advanced lithium batteries. pH plays a critical role in the formation of vanadium oxides from aqueous solutions. The coordination of V^V decreases as pH increases. It turns from $[VO_5]$ square pyramids or trigonal bipyramids to $[VO_4]$ tetrahedra above pH 7. Therefore, room temperature and hydrothermal syntheses have been performed in the pH range from 6 to 8 where V^V coordination turns from five to four (1, 8).

The structures and properties of these new polyoxovanadates have been extensively described but the chemical

mechanisms leading to the formation of such solids from solutions remain largely unknown. The relationship between the reaction conditions and the nature of molecular clusters is still far from understood (9, 10). Therefore, this paper presents a discussion of the relationships between the nature of molecular precursors in solution and the structure of crystalline polyoxovanadates.

EXPERIMENTAL

Chemical Syntheses of Compounds I and II

A V_2O_5 powder (1 g) was dissolved in an aqueous solution of NaOH (1 M, 5 mL) or TMAOH (10%, 5 mL). The V_2O_5 /base molar ratio is close to 1. Dissolution was rather slow and the suspension was stirred for about 2 days at room temperature. Vanadium pentoxide in excess was then removed by filtration and the resulting clear orange solution (pH \approx 7) was slowly evaporated at room temperature for 1 week giving rise to orange crystals of compounds **I** (with NaOH) and **II** (with TMAOH).

Hydrothermal Syntheses of Compounds III and IV

As previously, V_2O_5 (1 g) was mixed with aqueous solutions of NaOH (1 M, 5 mL) or TMAOH (10%, 5 mL). These mixtures were then heated for 48 h at 200°C in a Parr Teflon-lined digestion bomb under autogeneous pressure. A red pasty material was formed in the presence of NaOH (compound **III**) whereas black shiny flat crystals (compound **IV**) precipitated in the presence of TMAOH. In both cases a yellow supernatant solution (pH 7.5) was obtained.

Characterization

The structure of crystalline compounds was determined by X-ray diffraction. For compounds **I** to **IV**, X-ray diffraction powder patterns were recorded in the 2θ range from 2 to 50° on a Philips PW 1830 diffractometer ($CuK\alpha_1$ radiation, $\lambda = 1.5406 \text{ \AA}$). For compounds **II** and **IV**, measurements were also collected at room temperature on single crystals on a CAD4 diffractometer using $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and a graphite monochromator.

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ESR spectra were recorded on an X-band Bruker spectrometer ($\nu = 9.47$ GHz) equipped with a heating device.

^{51}V NMR solution spectra were recorded on a Bruker AC 300 (or MSL 400) spectrometer operating at 78 MHz (or 105.25 MHz), using a 90° pulse width of 11 μs , and a relaxation delay of 1 s. Neat VOCl_3 was used as an external reference for chemical shifts ($\delta = 0$ ppm). The temperature dependence of NMR spectra was studied with decavanadate solutions heated in sealed NMR glass tubes.

Thermogravimetric analyses were carried out under an oxygen flux of $5\text{ cm}^3/\text{min}$ at a heating rate of $5^\circ\text{C}/\text{min}$ using a Netsch STA 409 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Characterization of Crystalline Compounds

Compound I. Orange crystals corresponding to compound **I** are grown from aqueous solutions at room temperature. The X-ray diffraction pattern of this compound is identical to that of the previously reported decavanadate compound $\text{Na}_6[\text{V}_{10}\text{O}_{28}] \cdot 18\text{H}_2\text{O}$ (Fig. 1a) (11). The well-known decavanadate anion is a highly condensed polyanion made of 10 VO_6 octahedra sharing corners and edges. All vanadium atoms have distorted octahedral geometry and taking into account the ideal symmetry of the decavanadate anion D_{2h} , three types of VO_6 octahedra can be distinguished.

Two weight losses around 100°C and 175°C are observed by thermal analysis (Fig. 2a). They correspond to the departure of about 19 water molecules per decavanadate, in agreement with the water content reported from the single-crystal X-ray diffraction study (11). No further weight loss is observed beyond 200°C and a mixture of NaVO_3 and NaV_3O_8 is obtained upon heating at 500°C as shown by X-ray diffraction.

Compound II. Orange crystals are grown from an aqueous solution of V_2O_5 in TMAOH. The molecular structure of compound **II** was resolved by single-crystal X-ray diffraction showing that it corresponds to a tetramethyl ammonium decavanadate $(\text{TMA})_4[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$. The structure of this compound was found to be identical to the one recently reported (12). As a consequence, the main X-ray data are reported in Table 1.

The thermal analysis of compound **II** exhibits four successive weight losses around 100°C , 190°C , 320°C , and 395°C (Fig. 2b). The first two, associated with endothermic DTA peaks, should be due to the departure of water molecules. The last two, above 300°C , correspond to exothermic processes arising from the combustion of organic groups. A slight weight increase is observed above 400°C in air.

X-ray diffraction patterns recorded on powders heated at different temperatures show that decavanadate clusters (compound **II**) (Fig. 3a) are transformed into the crystalline

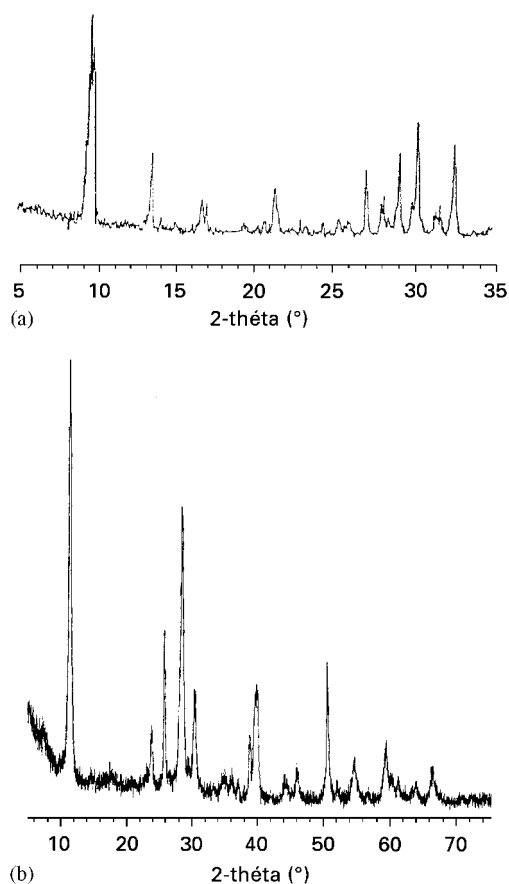


FIG. 1. X-ray diffraction patterns of (a) compound **I** and (b) compound **III**.

layered compound $(\text{TMA})[\text{V}_4\text{O}_{10}]$ around 300°C (Fig. 3b). A mixture of nonstoichiometric vanadium oxides is then formed at higher temperature. They are oxidized in air above 400°C to give orthorhombic V_2O_5 . The color of compound **II** turns from orange to black above 200°C , suggesting that some V^{5+} are reduced by organic groups upon heating. ESR spectra recorded at different temperatures show that a signal actually appears and grows above

TABLE 1
X-Ray Data for the Structures of Compounds **II** and **IV**

Formula	$(\text{TMA})_4[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$	$(\text{TMA})[\text{V}_4\text{O}_{10}]$
a (\AA)	12.626(3)	17.116(2)
b (\AA)	12.639(4)	6.6425(9)
c (\AA)	15.733(2)	11.739(1)
α ($^\circ$)	68.07(2)	90
β ($^\circ$)	83.09(2)	90
γ ($^\circ$)	78.71(2)	90
V (\AA^3)	2281.1(9)	1334.6
Z	2	4
Space group	$P - 1$	$Cmc2_1$

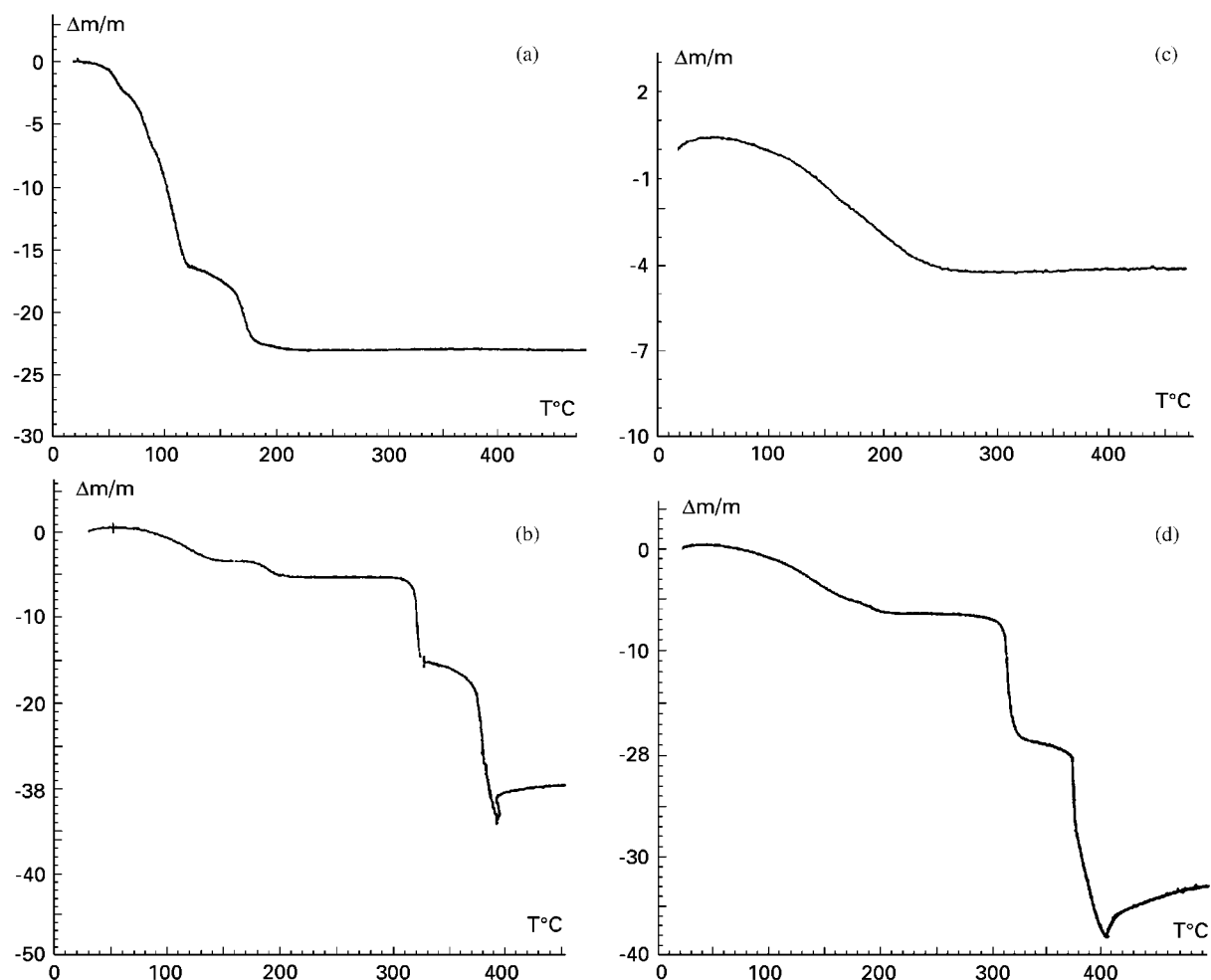


FIG. 2. TGA curves of compounds I–IV under O_2 gas flow. (a): I; (b): II; (c): III; (d): IV.

200°C. It is made of a single band, without hyperfine structure, centered around $g = 1.97$, a value typical of V^{4+} ($3d^1$) ions. The intensity of the ESR signal increases as a function of temperature, showing that more vanadium is reduced upon heating (Fig. 4). Above 400°C, the signal decreases again due to the oxidation of vanadium oxides in air.

Compound III. A red pasty solid is obtained after the hydrothermal treatment of an aqueous solution of V_2O_5 in NaOH. The X-ray diffraction pattern recorded on the precipitate dried at room temperature (compound III) is identical to that reported for $NaV_3O_8 \cdot nH_2O$ (Fig. 1b) (13). A continuous weight loss ($\sim 5\%$) is observed by thermal analysis upon heating up to 250°C (Fig. 2c). It corresponds to the departure of about one water molecule per formula unit. The crystalline NaV_3O_8 “high-temperature” (NaV_3O_8 HT) phase is then observed by X-ray diffraction (13–15). Its structure has not yet been resolved but it was shown to be isostructural with LiV_3O_8 (16). It is made of $[V_3O_8]^-$ layers built up of distorted $[VO_6]$ octahedra and distorted $[VO_5]$

trigonal bipyramids sharing corners and edges (Fig. 5a) (16). The structure of the hydrated phase $NaV_3O_8 \cdot nH_2O$ should be close to that with Na^+ ions and water molecules lying between the vanadium oxide layers.

Compound IV. Black flat crystals are precipitated via the hydrothermal treatment of an aqueous solution of V_2O_5 in TMAOH. The X-ray structure of compound IV was resolved by single-crystal X-ray diffraction and found to be identical to the $TMA[V_4O_{10}]$ compound already described by Whittingham *et al.* (4). The main X-ray data of compound IV are reported in Table 1. Compound IV is made up of double chains of edge-sharing $[VO_5]$ tetragonal pyramids with TMA^+ cations distributed between the $[V_4O_{10}]^-$ layers (Fig. 5b). The neutrality of this compound suggests that one of four vanadium has been reduced to V^{4+} .

Three weight losses are observed with compound IV, followed by a slight increase in weight above 400°C (Fig. 2d). The TGA curve is similar to that obtained for

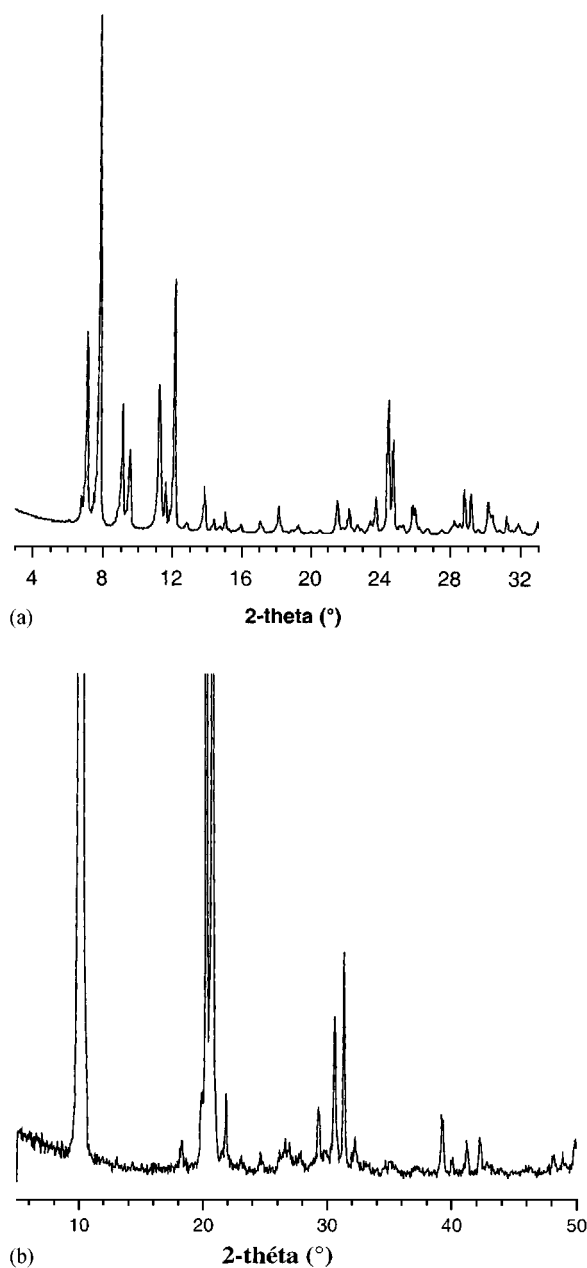


FIG. 3. X-ray diffraction patterns of compound **II** heated at two different temperatures: (a) 20°C, (b) 300°C.

compound **II** above 300°C. It corresponds to the departure of organic groups followed by the oxidation of reduced vanadium oxides into V_2O_5 .

Characterization of the Supernatant Decavanadates Solutions

The ^{51}V NMR spectra of the orange solutions obtained at room temperature in the presence of NaOH and TMAOH are quite close. The spectrum for the orange

solution in TMAOH is presented in Fig. 6a. At a pH close to 7 and at room temperature, both spectra exhibit three peaks at $\delta = -427$, -502 , and -518 ppm due to the decavanadate polyanion $[H_nV_{10}O_{28}]^{(6-n)-}$ that contains three different vanadium sites in the ratio 2:4:4 (17). Two smaller peaks at $\delta = -581$ and -591 ppm can be assigned to the cyclic metavanadates, $[V_4O_{12}]^{4-}$ and $[V_5O_{15}]^{5-}$, respectively (17, 18). Decavanadates are by far the main species. Integration of NMR peaks shows that they correspond to 95% (with NaOH) and 93% (with TMAOH) of the whole V^V .

After hydrothermal synthesis, the ^{51}V NMR spectra of the supernatant solutions obtained with NaOH (compound **III**) and TMAOH (compound **IV**) are rather different. Only two peaks corresponding to metavanadate species ($\delta = -576$ and -585 ppm) are seen in the presence of NaOH, with very small signals corresponding to traces of decavanadates. Both decavanadates ($\delta = -423$, -498 , and -513 ppm) and metavanadates ($\delta = -582$ and -592 ppm) are clearly seen in the presence of TMAOH. Surface measurements of these NMR peaks show that 44% of the vanadium is present as decavanadate species and 56% as metavanadates (30.5 and 25.5 for the tetramer and pentamer, respectively).

Temperature Dependence of the ^{51}V NMR Spectra of Decavanadate Solutions

These experiments have been performed with the supernatant orange solution obtained in the presence of TMAOH (pH ≈ 7) from which crystals of compound **II** were grown. ^{51}V NMR spectra are recorded on solutions

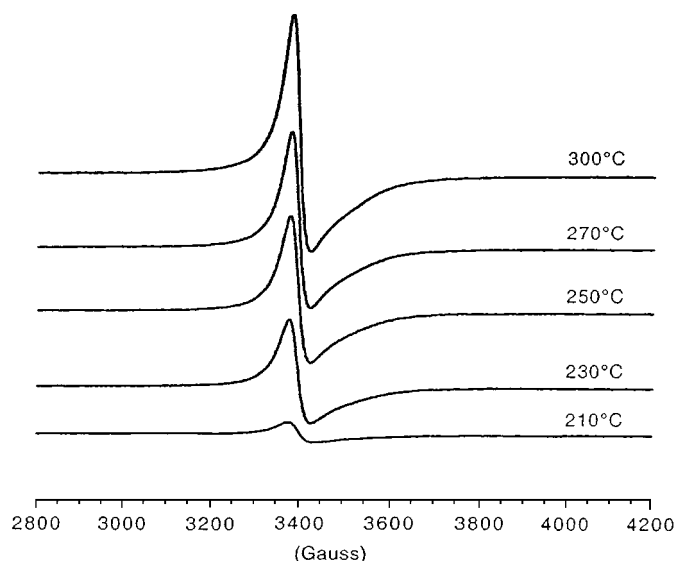


FIG. 4. ESR spectra of compound **II**, $(TMA)_4[H_2V_{10}O_{28}] \cdot 4H_2O$, recorded at different temperatures.

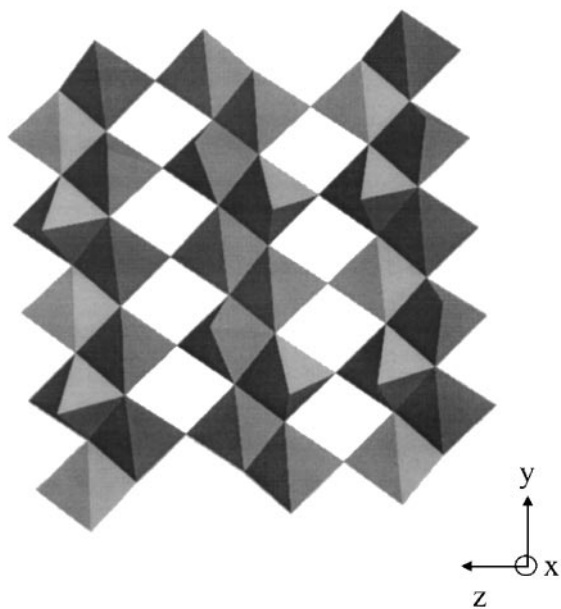
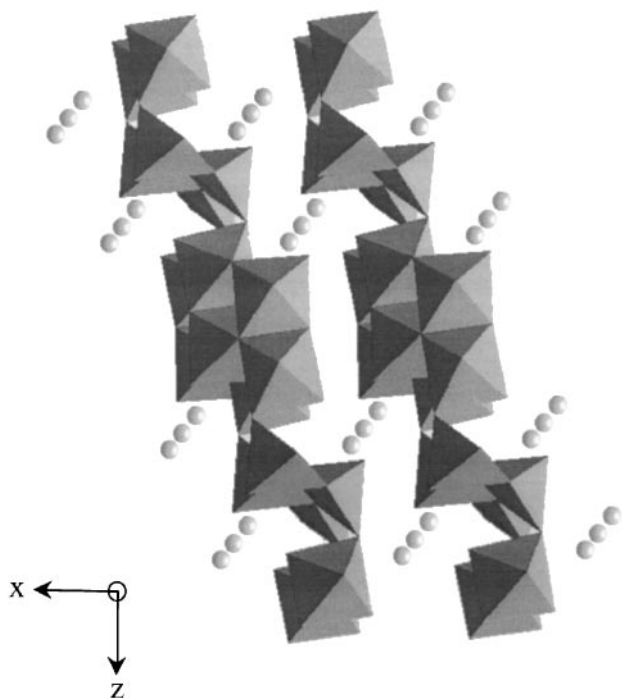


FIG. 5. (a) Projection of the structure of LiV_3O_8 along $[010]$ showing the stacking of $[\text{V}_3\text{O}_8]^-$ inorganic layers between which the Li^+ cations are inserted (16). (b) Projection of the structure of $\text{N}(\text{CH}_3)_4[\text{V}_4\text{O}_{10}]$ along $[100]$ (4).

heated in sealed tubes at different temperatures from room temperature to 200°C (Fig. 6).

The small peak corresponding to the cyclic $[\text{V}_5\text{O}_{15}]^{5-}$ species disappears rapidly around 40°C . The relative intensity of the three decavanadate peaks decreases compared to

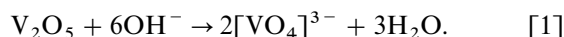
the peak corresponding to the cyclic metavanadate $[\text{V}_4\text{O}_{12}]^{4-}$ (Fig. 6). The molecular ratio [decavanadate]/[metavanadate] decreases progressively from 91/9 at room temperature to 76/24 at 100°C . At a given temperature, it also decreases as a function of the heating time. Upon heating at 200°C for example, the ratio decreases from 24/76 after 0.5 h to 3/97 after 3 h. It has to be pointed out that this decavanadate–metavanadate transformation is partially reversible. A ratio of 82/18 is again observed when a solution heated to 150°C for 12 h is cooled to room temperature.

The overall intensity of ^{51}V NMR peaks decreases with the temperature as some black solid phase forms above 150°C while the solution turns green.

DISCUSSION

At room temperature, the molecular structure of V^{V} species mainly depends on the pH of the aqueous solution and several isopolyvanadates have been clearly characterized by ^{51}V NMR spectroscopy (17, 18).

The dissolution of V_2O_5 at high pH leads to the formation of orthovanadate species as follows:



The pH of the aqueous solution decreases as dissolution goes on, leading to the formation of protonated vanadate ions $[\text{H}_n\text{VO}_4]^{(3-n)-}$. Below pH 12, condensation may occur

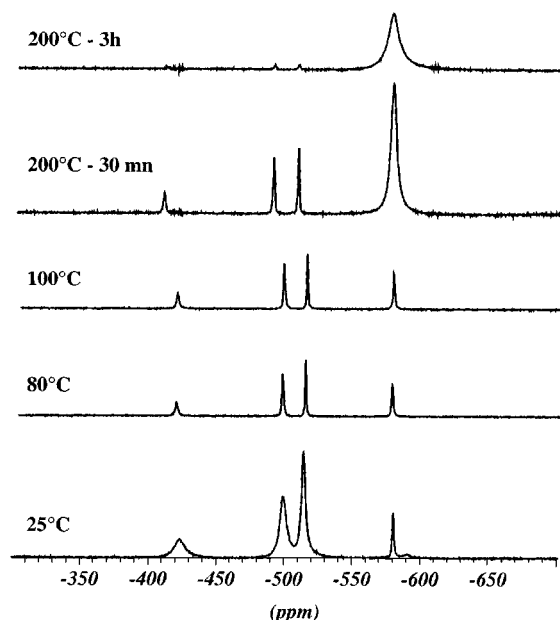


FIG. 6. ^{51}V NMR spectra of decavanadate solutions heated at different temperatures (a) $T = 25^\circ\text{C}$, (b) $T = 80^\circ\text{C}$, (c) $T = 100^\circ\text{C}$, (d) $T = 200^\circ\text{C}$ during 30 min, (e) 200°C during 3 h (Larmor frequency = 78 MHz; number of scans, NS = 400 for (a), (b), (c); Larmor frequency = 105.25 MHz; NS = 44 for (d) and (e)).

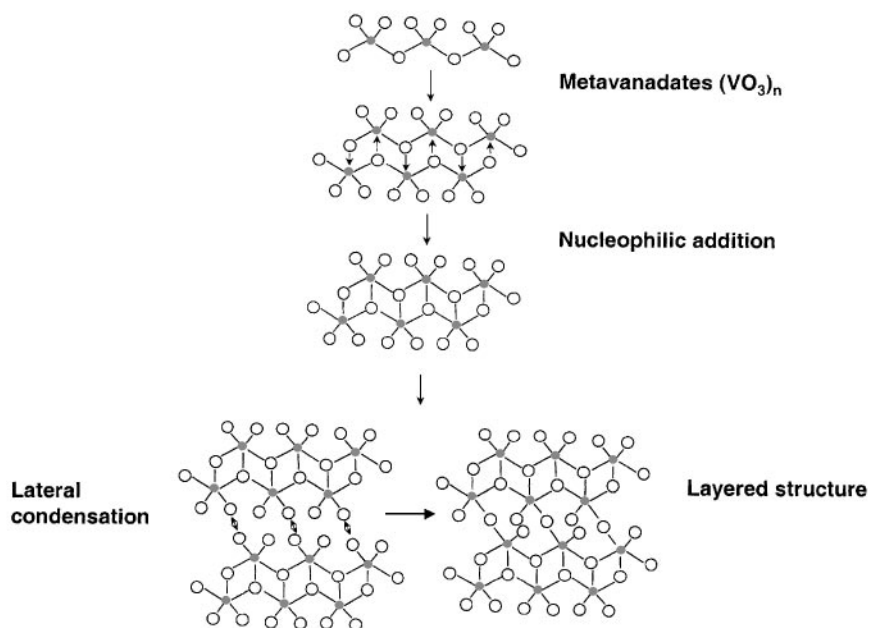
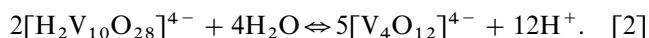


FIG. 7. Suggested mechanism for the formation of $[\text{V}_4\text{O}_{10}]^-$ layers from chain metavanadates.

via the oxolation of two V–OH groups. Pyrovanadates $[\text{V}_2\text{O}_7]^{4-}$, metavanadates $[\text{V}_4\text{O}_{12}]^{4-}$, and decavanadates $[\text{V}_{10}\text{O}_{28}]^{6-}$ are formed as the pH decreases. The first two species are formed of corner-sharing tetrahedra whereas decavanadates are made of 10 densely packed $[\text{VO}_6]$ octahedra sharing corners and edges.

The final pH of the aqueous solutions depends on the relative amount of V_2O_5 and base. In our case, for $\text{V}_2\text{O}_5/\text{base} = 1$, it ranges between 6 and 7, so that decavanadates are the main solute species. Therefore, sodium or tetramethyl ammonium decavanadates are precipitated from such solutions at room temperature. There is a straightforward correlation between V^{V} molecular species in the solution and in the solid state.

This is no longer the case under hydrothermal conditions. The nature of solute V^{V} species varies with temperature, which becomes a major parameter. Therefore, *in situ* ^{51}V NMR experiments have to be performed in order to study the molecular structure of V^{V} precursors. There is no obvious structural relationship between the decavanadate polyanions observed in the supernatant solutions at room temperature after hydrothermal treatment and the layered polyoxovanadates precipitated from these solutions. In the pH range 5–9, both decavanadate and metavanadate species are in equilibrium in aqueous solutions:



In situ ^{51}V NMR experiments show that the equilibrium between decavanadate and metavanadate species is progressively displaced toward the formation of cyclic meta-

vanadates $[\text{V}_4\text{O}_{12}]^{4-}$ when the temperature increases (Fig. 6). At 200°C , under the hydrothermal conditions used in this paper, only metavanadates are observed by ^{51}V NMR. It may then be assumed that these metavanadates behave as molecular precursors for the layered oxides, $\text{Na}[\text{V}_3\text{O}_8] \cdot \text{H}_2\text{O}$ and $(\text{TMA})[\text{V}_4\text{O}_{10}]$. Crystallization from metavanadate aqueous solutions is always accompanied by polymerization of the anion (19) and it may be assumed that layered polyoxovanadates should be formed via the ring-opening polymerization (ROP) of cyclic metavanadates $[\text{V}_4\text{O}_{12}]^{4-}$.

Actually metavanadates are based on corner-sharing $[\text{VO}_4]$ tetrahedra and room-temperature precipitation currently leads to the formation of chain compounds made of corner-sharing $[\text{VO}_4]$ tetrahedra as in KVO_3 or edge-sharing $[\text{VO}_5]$ trigonal bipyramids as in $\text{KVO}_3 \cdot \text{H}_2\text{O}$ (20). Hydrothermal conditions may favor the coordination expansion of vanadium V^{V} from four to five or even six. Protons are formed when decavanadate species are transformed into metavanadates (Eq. [2]). The “measured” pH of the solution decreases upon heating and protonation is known to lead to coordination expansion in this pH range.

The formation of layered vanadium oxides from aqueous solutions of vanadates may then be described as follows. The ring-opening of cyclic metavanadates leads to the formation of chains made of corner-sharing tetrahedra. Protonation and reduction (in the case of TMA compounds) favor coordination expansion via the nucleophilic addition of $[\text{VO}_4]$ tetrahedra, giving rise to double chains of edge-sharing $[\text{VO}_5]$ square pyramids. These double chains may be further linked together via corners to form $[\text{V}_2\text{O}_5]$ -

like layers. Such a condensation process may occur via oxolation between protonated V–OH bonds along the vanadate chains. Without protonation only chain compounds are formed. A possible mechanism for the formation of layered $(\text{TMA})[\text{V}_4\text{O}_{10}]$ from chain metavanadates is suggested in Fig. 7. Only V^{V} compounds are formed under hydrothermal conditions in the presence NaOH whereas mixed valence polyoxovanadates are formed with TMAOH. Some vanadium reduction then occurs via the decomposition of organic compounds upon heating.

Reduction should also play a major role during the solid-state transformation of tetramethyl ammonium decavanadate $(\text{TMA})_4[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ into the layered $\text{TMA}[\text{V}_4\text{O}_{10}]$ oxide. Such a transformation was already described by Riou *et al.* in the case of the decavanadate $(\text{NC}_7\text{H}_{14})_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ (6). Such a transformation is not observed with the sodium decavanadate that directly leads to the stable oxide phases NaVO_3 and NaV_3O_8 . The transformation of compact decavanadate clusters into layered vanadium oxide seems to occur only in the presence of organic cations. ESR experiments show that the transformation does not occur until some V^{5+} cations are reduced to V^{4+} . This reduction, due to the partial decomposition of organic species, favors condensation and coordination expansion. Indeed V^{4+} ions being larger than V^{5+} do not adopt tetrahedral coordination.

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